

Preferred Analyses and Sample Preparation for Surface Geochemical Sediment Samples in Petroleum Exploration*

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Abstract

A range of options is available for shallow core sample acquisition, preservation and analyses. In acquisition, it has been shown that gravity coring provides samples of equal quality to piston coring, at greater safety and lower cost; while the best preservation is freezing to -80°C, since bactericides do not always penetrate clay samples and will contaminate at least the solvent extracts. The advantages of analysing occluded and adsorbed gases instead of just headspace gas have also been shown. Regarding analyses of liquid hydrocarbons, the two most critical choices involve i) the bulk assessment of the total extract, and ii) the GC-MS analyses of the extract, and these techniques are the focus of this work.

Bulk analysis of the extract usually involves performing both gas chromatography (GC) and total scanning fluorescence (TSF). The GC method shows in chromatogram form, directly and unequivocally, the compounds present in the sample and show if biodegradation has occurred. This analysis is indisputably necessary to perform, not only due to its ability to show at a glance the type of hydrocarbons present, but also, when the extraction is performed quantitatively, to give the amounts of thermogenic hydrocarbons as opposed to those from recent organic matter. TSF is rather an 'indirect' method, targeting the aromatic compounds, and relying on the fluorescing properties of these under different wavelengths. By comparison with reference samples containing known types of hydrocarbons the emission data are qualitatively interpreted. It is shown here, however, that the TSF results do not consistently agree with the GC analyses, which are considered as the benchmark. The disagreement locally can be quite marked; e.g., TSF indicating thermogenic hydrocarbons in barren samples and vice versa. The value of performing TSF is then strongly questioned, especially as GC must in any case be performed on all samples.

GC-MS of the extract, to investigate biomarker, and aromatic compounds for source, and maturity parameters, can be performed by analysis of the whole extract, or of the saturated and aromatic fractions after liquid chromatography (e.g., MPLC) separation. The latter was previously considered the more reliable technique. However with development of high resolution MS, data of at least equal quality can be gained from the whole extract alone.

This simplifies sample preparation besides lowering analysis costs. Examples are given of the preferential use of high resolution GC-MS showing this method to be the most effective.

Introduction

Offshore surface geochemistry has been used in exploration for oil and gas since the mid-1930s (Horwitz, 1939). In the early days it was normal to take samples in a geographical grid, while in latter years it has been more normal to select the sample locations from 3D or 2D seismic. Also, if the seismic is old, or if it is not easy to pin-point the location where a potential leak is found at the surface, it is common to use multi-beam bathymetry and/or sub-bottom profiling. Since there is no discussion regarding this today, it will not be considered further. However, there is significant discussion regarding sampling methods, methods of preservation and which analysis to use regarding offshore surface geochemistry, and these are the main subjects of this paper.

Regarding sampling, three main types of coring systems have been used for the collection of shallow cores for surface geochemistry in the years since the first surveys. If the upper part of the seafloor is coarse sand or gravel, the only technique that will give good cores is a vibro-corer. Since there is basically no dispute regarding this in the industry, this will not be discussed further. However, if the seafloor consists of soft clayey sediment, two other coring techniques, 'gravity coring' and 'piston coring,' have been used.

Gravity coring in different forms and with different lengths of core barrel has been used since the 1930's by several organisations (Horwitz, 1939; Gewirtz et al., 1983; Faber and Stahl, 1984; Schiener et al., 1985; Emmel et al., 1985; Bjorøy and Løberg 1993; Bjorøy et al., 1999; Bjorøy and Ferriday, 2003). From the late 1970s/early 1980s some organisations reported that they used piston coring which has also been used routinely by some organisations since then (Brooks et al., 1986; Kennicutt et al., 1987; Cameron and White, 1999). So what is the difference between these two coring methods and which coring method should be preferred?

Gravity coring is the most simple and fastest method for coring since it basically uses what amounts to a weight with a core barrel attached. Inside the corer head there is a no-return valve which will help stopping the core from sliding out from the liner. In this article, by gravity coring is meant that a steel wire is attached to the top of the weight and the corer is lowered at a controlled rate to the sea floor by using a winch. The corer is normally stopped at 30 – 50 m above the sea floor to bring the corer within the target area, before the corer is lowered at top speed on the corer winch so that the core barrel penetrates the sea floor before it is brought back onboard. The winch used is normally of a fast electro-hydraulic type. Studies undertaken during the 1970s, aimed at determining the best speed of entry to get the longest cores showed this to be 1.5 to 2.0 m/sec (George Maisey 1996). With a lower speed a poorer penetration was registered, while a faster speed resulted in a good penetration but with a shorter core; i.e., the sediment did not move into the core barrel equivalent with the penetration. After the sediment had moved a certain amount into the core barrel the corer continued penetrating the sediment as a solid lance. Similar results were experienced by us during older surveys offshore Mid-Norway and in the Barents Sea. When studying the reports and papers from the organisations that have been using a 'piston coring device', it is clear that they are referring to a Kullenberg corer (Kullenberg, 1947), with a collapsible piston inside the liner in the core barrel. A Kullenberg corer device works in such a way that a weight triggers a locking mechanism holding the corer fastened as it hits the bottom. The corer will then drop a certain distance, which can be regulated by controlling the length of the wire holding the triggering weight. The core barrel will penetrate the sediment, which will then push the piston towards the top of the liner. The corer can then be brought onboard and the sample(s) for analysis can be collected from the liner. Since the organisations that have been using the Kullenberg coring device have called this 'piston coring,' there has grown up a belief in the industry, partly due

to lack of knowledge regarding different corers and partly due to the lack of using proper terminology in reports and publications, that “piston coring” entails that a Kullenberg system is used.

However, in correct terminology, piston coring means simply that a collapsible piston is used inside the liner of the core barrel. This piston will let the water move through when the sediment enters the liner. When the core barrel is lifted out of the sediment the collapsible piston closes and a vacuum is generated between the core and the piston, helping to retain the sediment within the core barrel. A ‘piston corer’ therefore can be either a gravity corer with a collapsible piston inside the core liner, or a Kullenberg corer with a collapsible piston inside the core liner. It just means that a collapsible piston is used in the liner. It has nothing to do with the corer device that is used; i.e., a simple gravity corer or the more cumbersome Kullenberg system. When the term ‘piston corer’ is used in this article, we are referring to a Kullenberg device.

Since the mid-1980s there has been significant discussion in the industry regarding which preservation method is most effective in the conservation of the samples. It is important that the samples are preserved properly; i.e., so that the hydrocarbons found in the samples, when analysed, are the same as those that were present in the samples when they were collected. A number of different preservation methods have been reported in the literature; i.e., canning of samples after bactericide have been added (Kvenvolden et al., 1981), canning and freezing the samples after adding bactericide (Brooks et al., 1986; Kennicutt et al., 1987; Cameron and White, 1999), canning and freezing the samples to -80°C without adding bactericide (Emmel et al., 1985; Bjorøy and Løberg, 1993; Bjorøy et al., 1999; Bjorøy and Ferriday, 2003), wrapping the samples in aluminium foil and immersing it in liquid nitrogen (Faber and Stahl, 1983, 1984). We will therefore evaluate the different types of preservation of samples; i.e., which preservation methods will stop any bacteriological degradation of surface geochemical samples.

Up to the late 1970s it was mainly analysis of gases that was used regarding offshore surface geochemical surveys. However, with the development of better equipment for analysis of small quantities of liquid hydrocarbons, extraction of surface geochemical samples with GC and fluorescence analysis of the extract was introduced, (Engdahl, 1981; Brooks et al., 1983; Gevirtz, 1983; Vargo et al., 1990; Bjorøy and Ferriday, 2002). During the latter years there has been some discussion regarding the usefulness of the different analyses, both regarding the gases and liquid hydrocarbons. In this paper we will therefore examine the different types of analyses and evaluate which analyses that are most useful regarding surface geochemical studies.

Analytical Procedures

The samples were taken out of the freezers and left at room temperature overnight before the day of analysis. For each sample three gas-fractions were analysed by GC; i.e., headspace gas, occluded (interstitial) gas and adsorbed gas. The carbon isotope compositions of a number of these were also analysed by GC-IRMS. Selected samples were also extracted with hexane and the liquid hydrocarbons analysed by gas chromatography. The procedures are briefly as follows:

Headspace Gas Analysis

The analysis is performed using a Varian 3400 gas chromatograph with a 50-m PLOT fused silica $\text{Al}_2\text{O}_3/\text{KCL}$ column, loop injector and flame ionization detector. Helium is used as carrier gas and the column is run from 70°C to 200°C , at a rate of $12^{\circ}\text{C}/\text{min}$. Final hold time is 13 min. Two cm^3

of headspace gas are removed from each sample can for chromatographic analysis of the C₁ to C₆ range of hydrocarbons.

Occluded (Interstitial) Gas Analysis

A 50 g (wet weight) aliquot of total sediment was ball-milled in a sealed container fitted with a septum from which the released interstitial gas was withdrawn for analysis by gas chromatography. The interstitial gas was analysed on a Varian 3400 gas chromatograph fitted with a 50-m PLOT Fused Silica column with 0.32 mm internal diameter coated with 5 µm Al₂O₃/KCl film (Chrompack inc.). The temperature program on the column has an initial temperature of 70°C, 12° C/min heating rate up to 200°C held for 5 min. The detectors are standard FIDs. Correlation and quantification are achieved by use of external standards.

Adsorbed (Acid released) Gas Analysis

This analysis was carried out on a 100 g aliquot (wet weight) of the <63 µm sediment fraction. The gas was released by acid treatment with orthophosphoric acid at 70° C. The resulting gas was passed through concentrated potassium-hydroxide solution, to remove carbon dioxide, and analysed by gas chromatography. The adsorbed gas was analysed on a Varian 3400 gas chromatograph fitted with a 50 m Plot Fused Silica column with 0.32 mm internal diameter and 5 µm Al₂O₃/KCl film thickness (Chrompack inc.). The temperature program on the column has an initial temperature of 50°C, a heating rate of 8°C/min up to 200°C held for 15 min. The detectors are standard FIDs. Correlation and quantification is achieved by use of external standards.

Gas Carbon Isotope Analysis

A 3 ml aliquot of the gas was analysed for the concentration of δ¹³C isotope composition of C₁-C₄ relative to PDB (Pee Dee Belemnite) on a Hewlett Packard 5890A gas chromatograph coupled to a VG Isochrom II Mass Spectrometer. The gas chromatograph was fitted with a 25-m PLOT Fused Silica column with an internal diameter of 0.32 mm coated with 10 µm Poraplot Q film. The temperature program of the column has an internal temperature of -40°C (cooled down by liquid nitrogen) held isothermally for 2 minutes, heated at a rate of 8° C/min to -10°C, and further heated at a rate of 15°C/min up to 200°C with a final hold-time of 5 min.

Liquid Extraction

The < 63 µm sediment fraction of the sediment was air dried, in an effort to minimise the loss of volatile compounds. The samples used for comparison of using hexane or dichloromethane as solvent were split and extracted for 3 hours at 90°C either with hexane or dichloromethane as solvent, using a Soxtec extraction system. Activated copper was used to remove elemental sulphur from the solution. The extract was then rotavapored and air-dried to near dryness. For the rest of the samples only hexane was used as solvent.

EOM Gas Chromatographic Analysis

The Gas Chromatographic analysis of the extracted liquid hydrocarbons was performed on a Dani 8500 Gas Chromatograph. A 25 m OV-1 Fused Silica column with 0.25 mm internal diameter was used. The temperature program on the column has an initial temperature of 50°C (hold time 1 min), a heating rate of 10°C/min up to 310°C held for 15 min. The detectors are standard FIDs. Correlation is achieved by use of external standards, while the quantification is achieved by squalane as internal standard. Chromatographic data is processed using the Multichrom data acquisition and processing system.

Total Scanning Fluorescence (TSF)

The same extracts used for gas chromatographic analysis are diluted by extra pure hexane (fluorescence quality) to appropriate volume and then scanned by TSF using 200 and 500 nm wavelengths. Fluorescence spectra, including maximum fluorescence intensity, and single wavelength measurements are carried out on a Perkin Elmer LS-50B spectrophotometer.

Gas Chromatography - Mass Spectrometry (GC-MS)

The GC-MS analyses of the extracts are performed on an Autospec Ultima system interfaced to a Hewlett Packard 5890 gas chromatograph. The GC is fitted with a fused silica SE54 capillary column (40 m x 0.22 mm i.d.) directly into the ion source. Helium (12 psi) is used as carrier gas and the injections are performed in splitless mode. The GC oven is programmed from 45°C to 310°C at 5°C/min where the column is held isothermally for 15 min. The mass spectrometer is operated in electron impact (EI) mode at 70 eV electron energy, a trap current of 500 uA and a source temperature of 220°C. The instrument resolution used is 3000 (10% value).

The data system used is a VG OPUS system. The samples are analysed in multiple ion detection mode (MID) at a scan cycle time of approximately 1.1 sec. Calculation of peak ratios is performed from peak heights in the appropriate mass fragmentograms.

Terpanes

The most commonly used fragment ions for detection of terpanes are m/z 163 for detection of 25,28,30 trisnormoretane or 25,28,30 trisnorhopane, m/z 177 for detection of demethylated hopanes or moretanes, m/z 191 for detection of tricyclic, tetracyclic, and pentacyclic terpanes and m/z 205 for methylated hopanes or moretanes. The molecular ions m/z 370 and 384 are also recorded for identification of C₂₇ and C₂₈ triterpanes, respectively.

Steranes

The most commonly used fragment ions for detection of steranes are m/z 149 to distinguish between 5 α and 5 β steranes, m/z 189 and 259 for detection of rearranged steranes, m/z 217 for detection of rearranged and normal steranes and m/z 218 for detection of 5 α (H)14 β (H) 17 β (H) steranes.

The m/z 231 fragment ion is used to detect possible aromatic contamination of the saturated fraction. It is also used for detection of methyl steranes.

Aromatics

Alkyl-substituted Benzenes

The m/z 106 fragment ion is often used to detect the alkyl-substituted benzenes. It is especially useful for the detection of di-substituted benzenes. m/z 134 can also be used for the detection of C₄-alkylbenzenes, but benzothiophene will also give a signal with this fragment ion.

Naphthalenes

Methyl naphthalenes are normally detected by the m/z 142 fragment ion, while C₂-naphthalenes are detected by m/z 156 and C₃-naphthalenes by m/z 170.

Benzothiophenes and Dibenzothiophenes

Benzothiophene can be detected, as mentioned above, by m/z 134. The m/z 198 and m/z 212 fragment ions are used for methyl-substituted dibenzothiophenes and dimethyl-substituted dibenzothiophenes, respectively.

Phenanthrenes

Phenanthrene is detected using the m/z 178 fragment ion. Anthracene will, if present, also give a signal in the m/z 178 fragment ion. Methyl-substituted phenanthrenes give signals in the m/z 192 fragment ion, while the m/z 206 fragment ion shows the dimethyl-substituted phenanthrenes and the m/z 220 fragment ion shows the C₃ substituted phenanthrenes.

Aromatic Steranes

Monoaromatic steranes are detected using the m/z 253 fragment ion, while the triaromatic steranes are detected using the m/z 231 fragment ion.

Results and Discussion

Sampling Using Different Types of Corers

To test if there were any differences regarding the quality of the cores collected using either gravity corer or piston corer, samples from 10 locations were collected, each within a target area with a radius of 25m. Both the gravity corer and the piston corer were fitted with a 6m core barrel. The gravity coring was first undertaken. When this was completed a piston corer was fitted and the same locations sampled again.

The main difference in using piston coring (Kullenberg type) and gravity coring was in the time used in the collection of the samples, as shown in [Table 1](#). This shows more than twice the time using a piston corer compared with that using a gravity corer. For the other sampling parameters, there are hardly any differences. This shows that the only difference in collection of surface geochemical samples using either gravity coring or piston coring would be in the cost, where the piston coring would be more than twice the cost compared to using gravity coring. There will be no difference in the penetration of the corer or the length of recovered core.

For both types of samples; i.e., from the cores collected by piston corer and by gravity corer, samples were collected from the liners every ½ meter down the core; i.e., from 0.5m, 1.0m, 1.5m, etc. from the top of the sediment, by cutting the liner with the core inside using a hand saw, and the sediment put into a can after any pieces of the liner were removed, flushed with nitrogen, sealed and frozen to –80°C to preserve the hydrocarbons from being destroyed by bacteria. Headspace gas, occluded (interstitial gas), adsorbed gas, TOC/TC of the < 63 µm sediment fraction of the sediment, and solvent extraction / GC analyses of the extracts were undertaken on all the samples.

Based on the results from these analyses it is clear that none of the cores contained macro-seeps; i.e., no large amounts of seeped hydrocarbons in the samples. Most of the samples did not contain any seeped hydrocarbons, while two of the ten samples were found to contain micro-seeps; i.e., with small, but distinctive amounts of seeped hydrocarbons. The details from these analyses were presented as a poster at the 2008 AAPG Annual Convention (Bjørøy and Ferriday, 2008). They showed that there were no differences for any of the analyses; i.e., both for gases and liquid hydrocarbons between the samples collected with piston corer or gravity corer. When comparing the data for the samples collected with the piston corer with those collected with the gravity corer, only minor differences are registered for the two suites of samples. With the samples being frozen to –80°C until a few hours before the analysis, and from results of other surface geochemical studies where the samples have been frozen to –80°C (Emmel et al., 1985; Bjørøy and Løberg, 1993; Bjørøy et al., 1999; Bjørøy and Ferriday, 2003), it was not expected to find any significant amount of gas in the headspace, neither in the samples with no seepage nor in the samples with micro-seepage. None of the analysed samples was found to contain any other gases than methane. There are only small differences regarding the abundance of methane in the headspace gas between the samples taken with gravity corer and piston corer for both the samples with no seepage and the samples containing micro-seepage of hydrocarbons. More

gaseous hydrocarbons were found, both for occluded gas and adsorbed gas, compared with what was found for headspace gas in both samples with no seepage and samples with micro-seepage. For these analyses all the samples were found to contain not only methane but also ethane, propane iso-butane and n-butane. Variations, such as these between headspace gas, occluded gas and adsorbed gas, have been reported for other areas where the samples have been frozen to –80°C, (Emmel et al., 1985; Bjørøy and Løberg, 1993; Bjørøy et al., 1999; Bjørøy and Ferriday, 2003). For all the different gases only minor differences are found between the samples taken with gravity corer and those taken with a piston corer for the same depths.

During the solvent extraction an internal standard (squalane) was added so that the abundance of the different compounds could be calculated. To do this each of the extracts was analysed by high resolution gas chromatography and the abundance of the different compounds calculated. For both types of samples; i.e., samples which were found to contain no seeped hydrocarbons and samples which are found to contain hydrocarbons from micro-seepage, there are only minor differences in the amounts of extracts, regarding both the EOM (total extractable organic matter) and the n-alkanes, between the samples which are collected with a gravity corer and those collected with a piston corer.

The best way to determine whether or not samples contain seeped liquid hydrocarbons is to study the high resolution chromatograms of the solvent extracts. The chromatograms will also show clearly if there are any differences in the extracts of samples collected with gravity or piston corer. The gas chromatograms show very clearly that there are no seeped liquid hydrocarbons present in the samples which were determined to contain no seeped hydrocarbons based on the gas data, and also that the gas chromatograms are similar for both the samples collected with a gravity corer and those collected with a piston corer, (Bjørøy and Ferriday, 2008). A similar situation is found for the gas chromatograms of the samples where the gas analyses indicated micro-seeps. Thermogenic hydrocarbons are clearly mixed with hydrocarbons from recent organic matter (ROM), and there are only minor differences between the gas chromatograms of the extracts of the samples that are collected with piston corer and those collected with a gravity corer (Bjørøy and Ferriday, 2008). The gas chromatographic data for the samples collected from the anoxic part of the cores are similar to those reported from other areas regarding samples with no seepage and samples with micro-seepage, when the samples have been frozen at -80°C , (Emmel et al., 1985; Bjørøy and Løberg, 1993; Bjørøy et al., 1999; Bjørøy and Ferriday, 2003). When there is only micro-seepage, as in these samples, natural bacteria in the sediment are normally in such low concentration that the liquid hydrocarbons have not been affected, as is seen also for the samples described here.

It is therefore clear that there are no differences, either in the abundance of hydrocarbons or the type of hydrocarbons, if the samples are collected with a piston corer or a gravity corer. There is no difference in the quality of the samples or the results from the analyses. The only difference is in the cost of collecting the samples since piston coring, using the Kullenberg type of piston corer, takes more than twice the time in collecting the samples (Table 1).

Evaluation of Preservation Methods

Various preservation methods have been reported in the literature, such as freezing the samples in liquid nitrogen, canning and freezing to -80°C , canning, adding bactericide, shaking vigorously and freezing to -18 to -25°C , canning and freezing to -18 to -25°C and canning, adding bactericide, shaking vigorously and kept at ambient temperature. It is well known that bacteria will consume hydrocarbons and generate methane with $\delta^{13}\text{C}$ values of -80‰ or less.

The most common way to detect if there is any biogenic activity in a sample; i.e., that there are bacterially generated hydrocarbons in a surface geochemical sample, is to undertake carbon isotope analysis of the $\text{C}_1\text{--C}_4$ hydrocarbons in the sample. General guidelines in the literature (Kvenvolden and Field, 1981; Faber and Stahl, 1983) suggest that oil associated gases have $\delta^{13}\text{C}$ values for methane between -40 and -50‰ , while $\delta^{13}\text{C}$ values $< -50\text{‰}$ are associated with biogenic gases and $\delta^{13}\text{C}$ values of $> -40\text{‰}$ suggest either the gas originating from a source with a gas window maturity or from kerogen type III; i.e., from coaly material. Schoell (1983) suggests the range of oil-associated gases to be between -40 and -55‰ PDB, while the range between -55 and -60‰ is associated with mixed thermogenic and biogenic gases and values $< -60\text{‰}$ associated with biogenic gases.

Bjørøy and Ferriday (2008) reported testing 100 samples collected from the Barents Sea, with each sample being split into four and preserved; i.e., canning and freezing to -80°C , canning, adding bactericide, shaking vigorously and freezing to -18 to -25°C , canning and freezing to -18 to -25°C

and canning, adding bactericide, shaking vigorously and kept at ambient temperature. All the samples collected were analysed by GC-IRMS where the carbon isotope composition of methane, ethane and propane were measured when peak heights allowed. Significant variations are found in the carbon isotope values for the different samples, due to analysing different fractions of the gases; i.e., headspace gas, occluded gas and adsorbed gas, or due to the type of preservation. The headspace analyses show only values for methane. For all the other components the peak magnitudes were insufficient to get any measurements. For the occluded and adsorbed gas analyses, however, the carbon isotope values for both ethane and propane were measured.

These showed that there was very little difference in the isotope values between the different fractions; i.e., different preservation methods, if the samples did not contain seeped hydrocarbons; while for samples that contained micro seeps, significant variations were found for all gases; i.e., headspace gas, occluded gas and adsorbed gas. The headspace gas shows methane carbon isotope values of approximately -70‰ for the sample which was preserved at ambient temperature using bactericide and for both the samples, which were frozen at -18°C , regardless of bactericide being used or not. This would indicate that the sample contains biogenic gas. However, when compared with the sample which was preserved at -80°C and which has an isotope ratio of -72‰ , it is clear that the sample contains mainly thermogenic gas (Figure 1a).

The same is seen for the occluded gas where the samples are ‘preserved’ using a bactericide and kept at ambient temperature, or kept at -18°C with or without the use of a bactericide. These show carbon isotope values of methane of -65 to -70‰ while the sample that was frozen at -80°C has a carbon isotope value of -46.8‰ (Figure 1b). In short, the results for the samples that were kept at ambient temperature and the samples kept at -18°C , regardless of bactericide being added or not, show the samples to contain mainly biogenic gas while the methane from the sample that was kept at -80°C shows that this contains thermogenic gas.

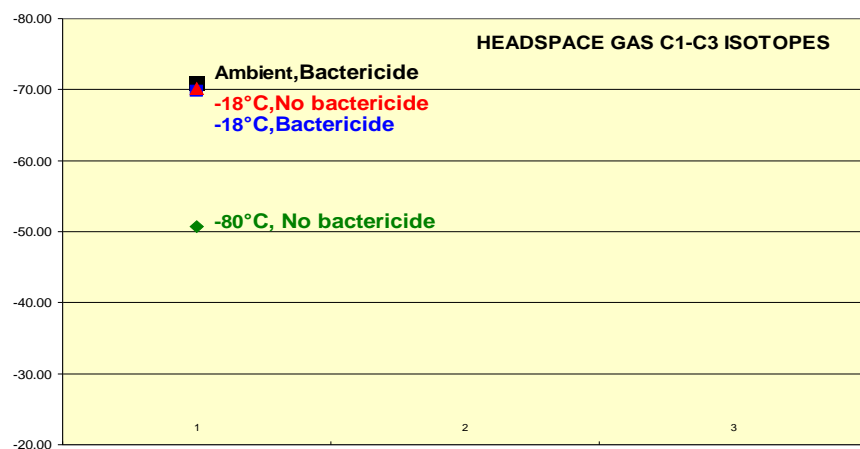
Similar results are also seen for the adsorbed gas analyses where the samples ‘preserved’ at ambient temperature using a bactericide or frozen to -18°C with or without the use of a bactericide give similar carbon isotope values, approximately -58‰ while the sample kept at -80°C shows carbon isotope values of -44‰ (Figure 1c).

It is therefore clear that the ‘preservation’ using a bactericide, even if the sample is frozen to -18°C , does not in fact adequately preserve the sample. The bacteria are still active and will destroy the higher molecular weight components and generate biogenic methane. This is not surprising since the clay will not get into suspension when shaken, only remaining as a solid lump in the can. The bactericide will only kill the bacteria on the outside of this, while the bacteria inside the lump of clay will not be affected.

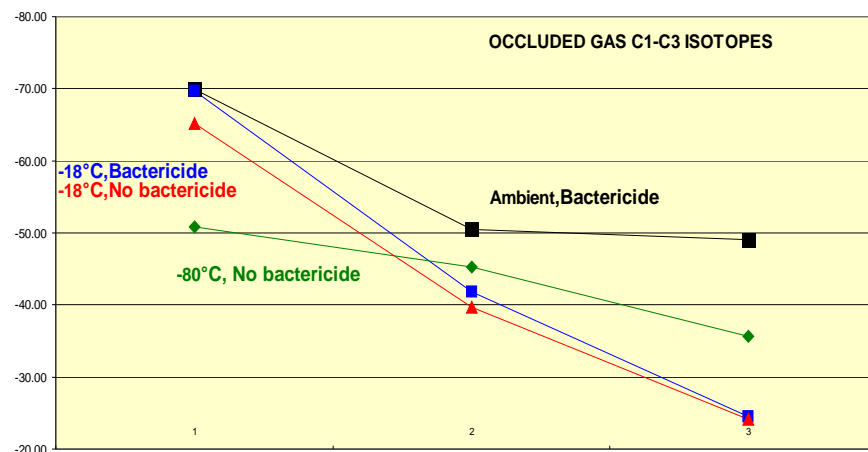
Type of corer	No. Cores collected	Average water depth (m)	Total time used (hrs)	Average penetration (m)	Average core length (m)	Average distance from target (m)
Gravity corer	10	964	9.5	4.9	4.7	6.3
Piston corer	10	964	22	5.1	4.9	6.5

Table 1. Comparison of sampling data from gravity and piston coring.

a.



b.



c.

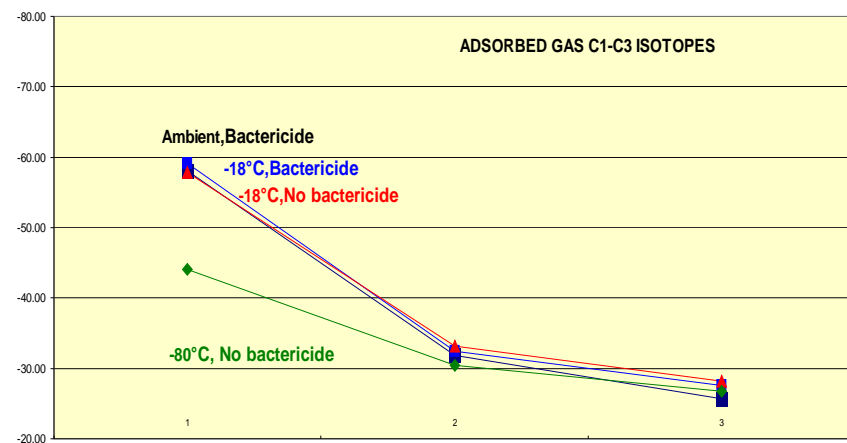


Figure 1. GC-IRMS data of gases in surface geochemical samples using different preservation methods.

Analysis of Samples

The most used analyses for surface geochemical samples lately have been analysis of gases by gas chromatography (GC), analysis of liquid hydrocarbons by solvent extraction using (GC) and Total scanning fluorescence (TSF). If indications of seeped hydrocarbons are detected, combined gas chromatography – mass spectrometry (GC-MS) is used. Below we will examine the different type of analyses and give recommendations regarding what to use.

Gas Analysis

Over the years there have been two different lines of thought regarding the analyses that should be used, either just headspace gas or all three fractions; e.g., headspace gas, occluded gas and adsorbed gas. Using just headspace gas has been recommended by the organisations that preserve the samples by adding a bactericide and freezing to -18 to -25°C while different organisations have reported using all three fractions; i.e., headspace gas, occluded gas and adsorbed gas. Bjørøy and Ferriday (2008) reported analysis of 100 samples where different preservation techniques were used. Regarding the fractions that were preserved by adding a bactericide and freezing to -18°C, significant amount of gases were found in the occluded gas; i.e., all the free gas in the samples will not go into the headspace even after shaking of the cans. Therefore we cannot recommend using just headspace gas for the determination of free gas in surface geochemistry samples.

Analysis of all three fractions of gases has always been used when the samples have been frozen to -80°C (Emmel et al., 1985; Bjørøy and Løberg, 1993; Bjørøy et al., 1999; Bjørøy and Ferriday, 2003). The reason for this is to get an evaluation of the total amount of free gas in the sample at the time of collection by analysing the headspace and occluded gas and get an evaluation of the amount and composition of the gas that has percolated through the sample over geological time by analysing the adsorbed gas. Typical results of headspace gas, occluded gas and adsorbed gas in a surface geochemical sample are shown in [Figure 2](#). We therefore recommend that all three gas fractions be analysed to get a complete picture of the gases in the sample at the time of collection.

As mentioned above, carbon isotope analysis is the best analysis to determine if the gases are thermogenic, biogenic or a mixture of these. All surface geochemical samples which show indications of containing seeped hydrocarbons from gas GC should therefore undergo carbon isotope analysis. It is strongly recommended to use a combined gas chromatographic – isotope ratio mass spectrometer (GC-IRMS) for such analysis since this type of instrument will give data for C₁–C₄ in a single run. Example of this is shown in [Figure 1](#).

Solvent Extraction

Solvent extraction and analysis of the solvent to determine if the samples contain seeped liquid hydrocarbons started in the early 1980s (Brooks et al., 1987; Kennicutt et al., 1987), and hexane was used as solvent. In most cases the total sample was used for the extraction; i.e., larger particles were not removed from the sample before they were crushed and extracted. Bjørøy and Ferriday (2002) reported testing of samples where the whole sample

was analysed and where the particles $> 63 \mu\text{m}$ were removed before extraction, either by scraping the sample with a spatula on a $63 \mu\text{m}$ sieve or by washing the sample using temperate water over a $63 \mu\text{m}$ sieve. Samples from the North Sea, Norwegian Sea, Norwegian Barents Sea, Atlantic margin and South China Sea have been analysed. For most of the samples there were only minor differences in the amount of extract from the three fractions, except for the samples from the Norwegian Barents Sea (Figure 3). The samples from the Norwegian Barents Sea were found to contain a large percentage of shale particles, shale which had been removed from outcrops on the islands in the northern part of the Barents Sea during the last ice age and dumped in the Barents Sea when the ice melted. The gas chromatograms of the three fractions of one of the samples from the South China Sea are shown in Figure 4, while the gas chromatograms of the three fractions from one of the samples from the Barents Sea are shown in Figure 5. The interpretation of the three gas chromatograms is that oil has seeped to the surface; i.e., it did not matter if the larger particles had been separated from the sample before it was extracted while the interpretation of the three gas chromatograms of the three fractions of the sample from the Barents Sea give a different interpretation. The gas chromatogram of the fraction where the particles $> 63 \mu\text{m}$ were not removed would be interpreted to show an oil seeping to the surface while the two fractions where the particles $> 63 \mu\text{m}$ have been removed would be interpreted to contain only reworked organic material. This shows therefore that it is important to remove reworked material from the samples before they are extracted. Correspondingly, we recommend that all the samples are either scraped on a $63 \mu\text{m}$ sieve or washed using temperate water through a $63 \mu\text{m}$ sieve before being dried and crushed for extraction.

As mentioned above, hexane was normally used as a solvent from the early days of using solvent extraction to remove liquid hydrocarbons from the surface geochemistry sediments. Hexane is also used as a solvent with extraction of sediments where there has been an oil spill. However, Logan et al. (2009) reported that dichloromethane (DCM) may be more effective for the extraction of UCM (unresolved complex mixture) material in some cases. To evaluate the effect of the two solvents 7 samples were each split in two and each sub-sample extracted with hexane and DCM before the extract was analysed by GC. The results from this experiment are shown in Figure 6. As expected it is found that extraction with DCM gives a larger yield of extractable organic matter (EOM) (Figure 6a). The same is found for the UCM while the yield of $\text{C}_{10}\text{--C}_{35}$ hydrocarbons is approximately the same for the two sub-samples. However, when examining the gas chromatograms of the two sub-samples, it is clearly seen that the gas chromatograms of the hexane extracts are far cleaner and easier to interpret than when DCM is used as solvent (Figure 7). There are also some components present in the gas chromatograms of the sub-samples that were extracted with DCM that are not seen in the sub-samples extracted with hexane. Based on these analyses it is evident that both DCM and hexane can be used as solvent to extract seeped hydrocarbons from a surface geochemical sample. However, we recommend using hexane since it is easier to interpret the gas chromatograms; besides that, it is more likely that DCM will extract components from the sample that do not belong to the seeped liquid hydrocarbons, rather than to the recent organic matter.



Figure 2. Typical gas chromatograms of headspace gas, occluded (interstitial) gas, and adsorbed gas in a sample with seeped hydrocarbons.

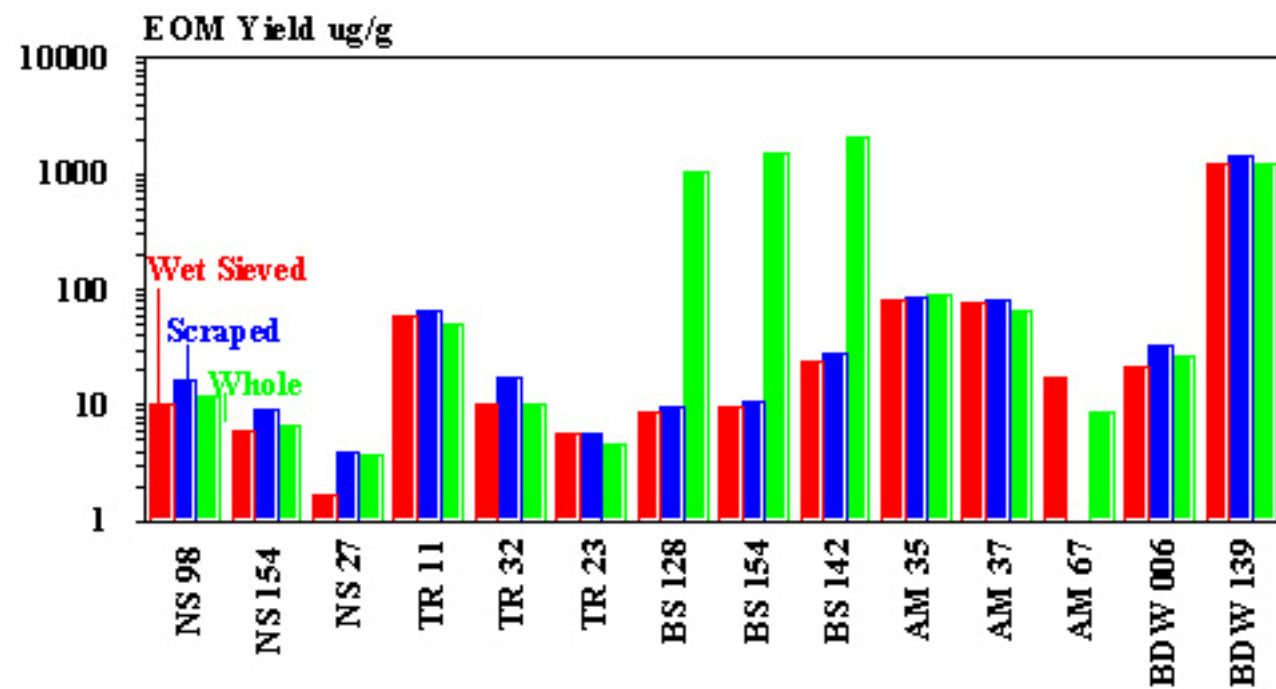


Figure 3. EOM yield variation in sample preparation.

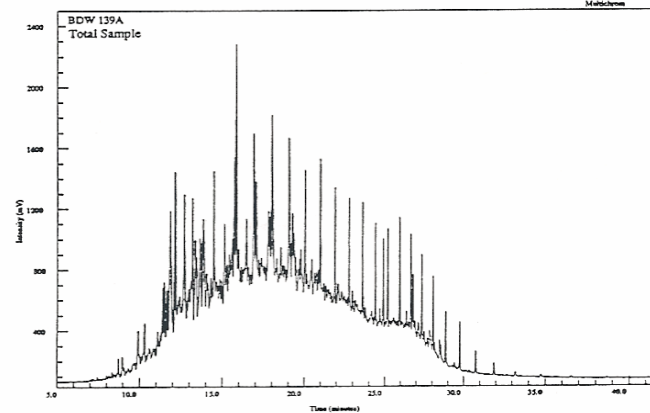
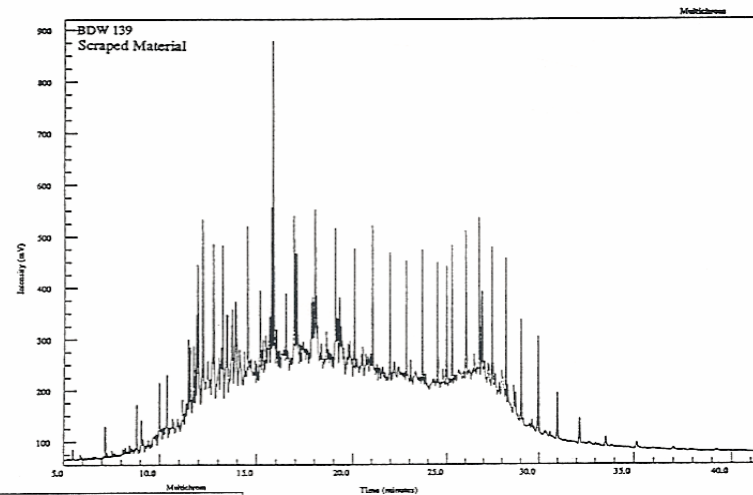
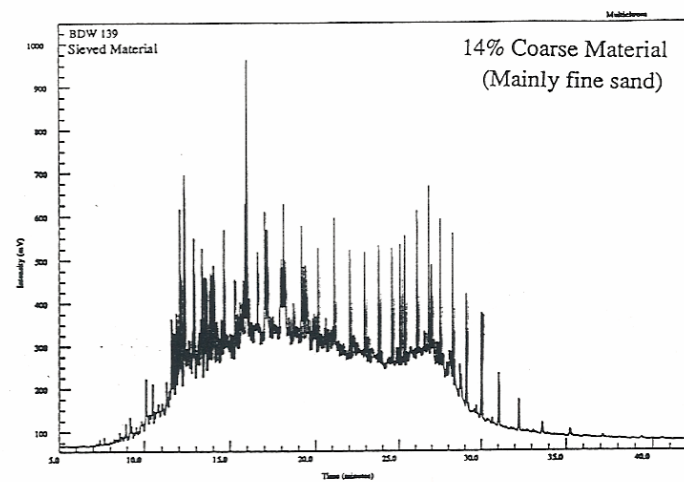


Figure 4. Gas chromatograms of total extracts of one sample from the South China Sea. Different sample preparation

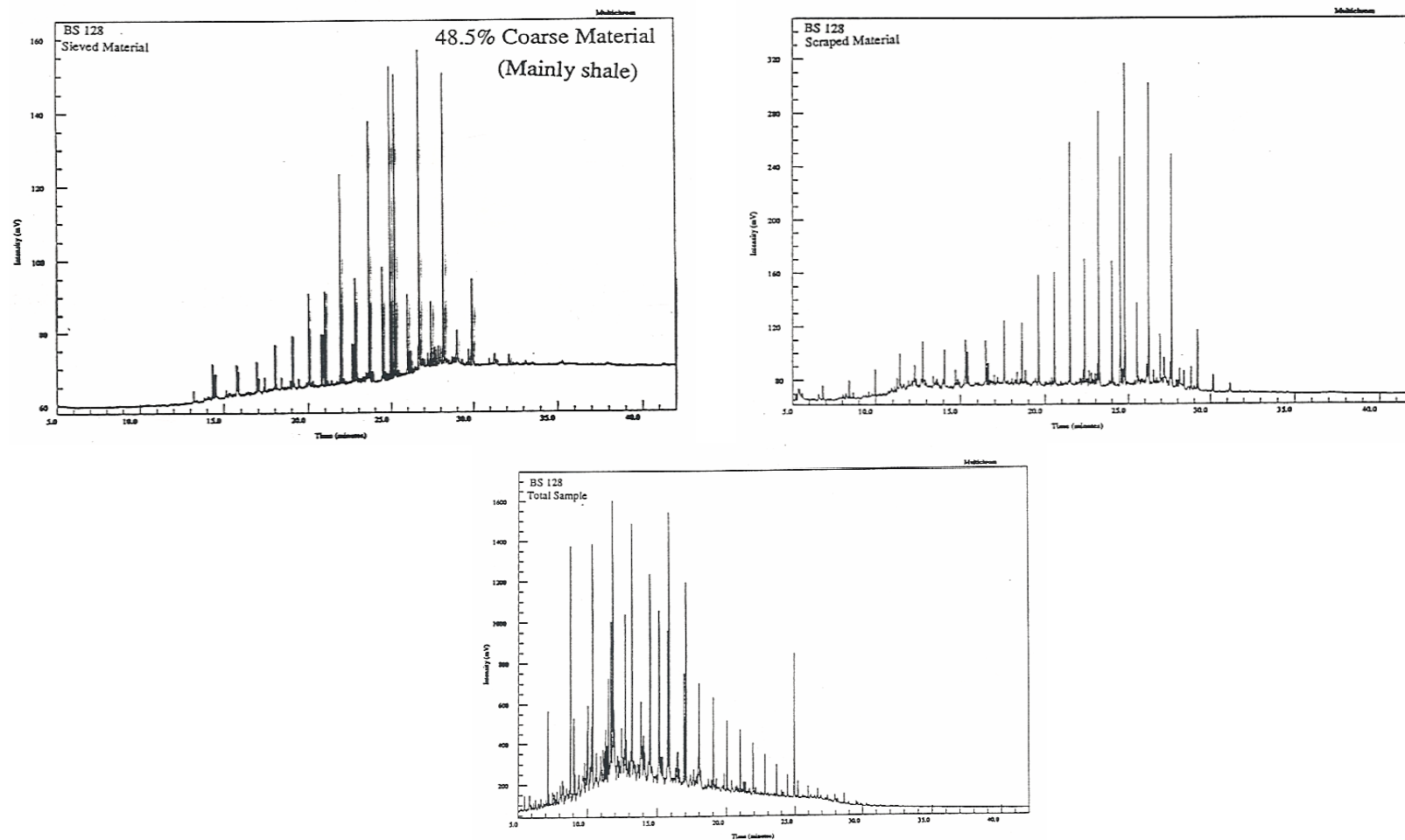


Figure 5. Gas chromatograms of total extract of one sample from the Norwegian Barents Sea. Different sample preparations.

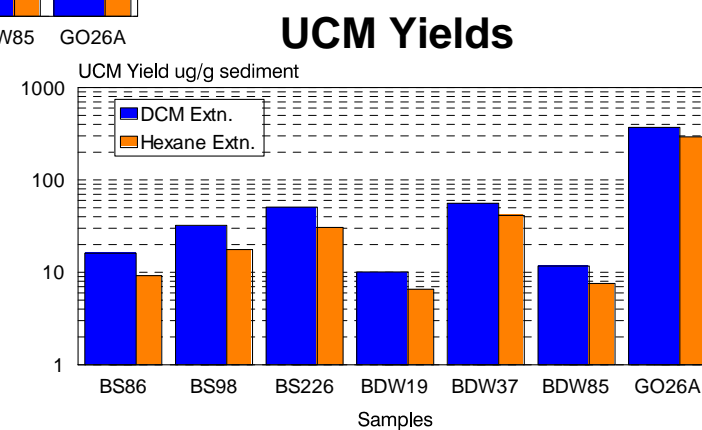
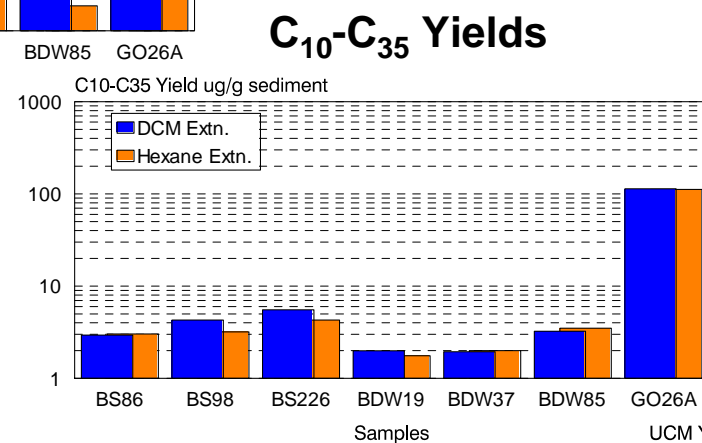
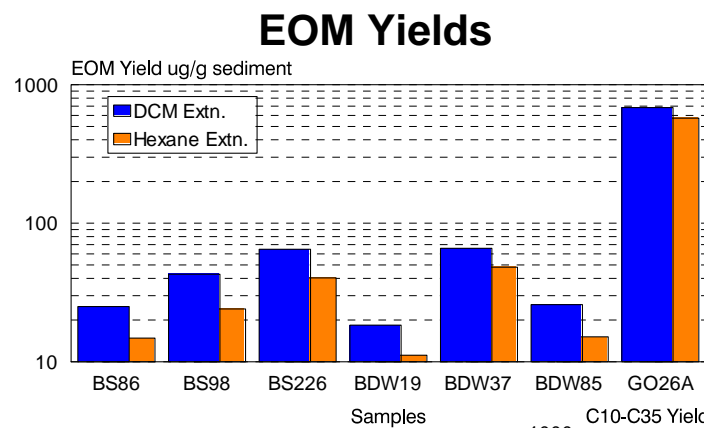


Figure 6. Extraction data using DCM and hexane as solvent on 7 different samples.

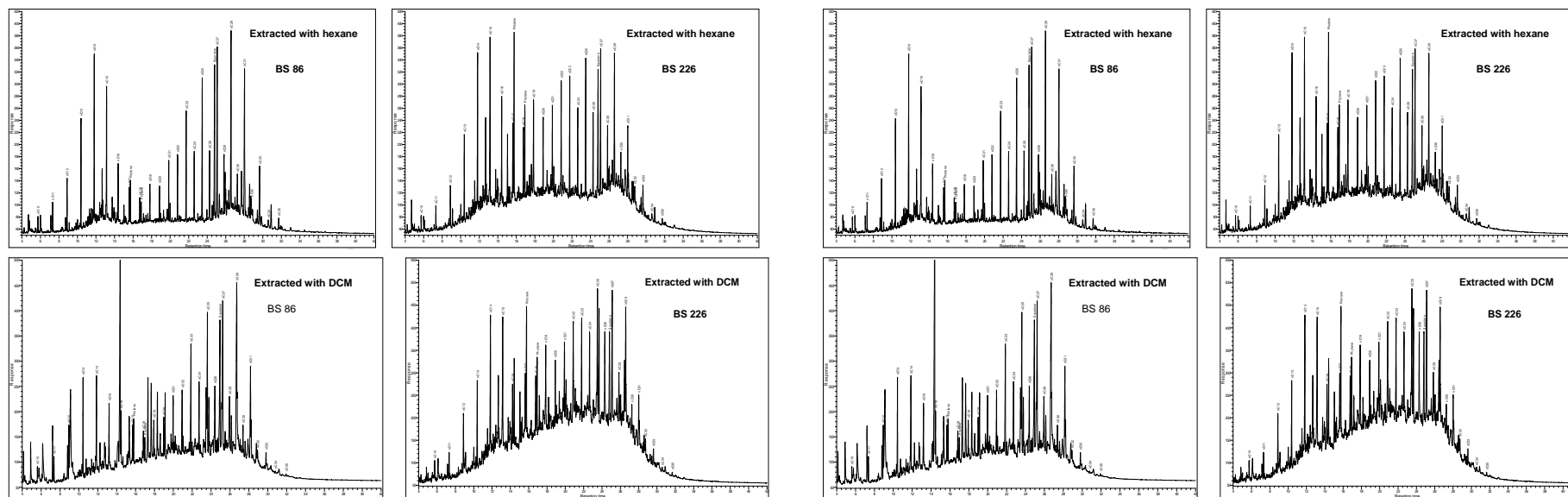


Figure 7. Comparison of gas chromatograms of samples extracted with hexane and DCM.

Gas Chromatographic Analysis of Extract

GC analysis of the whole extract has been undertaken since the late 1980s (Brooks et al., 1986) and has been an ubiquitous technique for most surveys in the 1990s and later (Abrams, 1996; Abrams and Narimanov, 1997; Bjørøy et al., 1999; Cameron et al., 1999; Cole et al., 2001a,b; Bjørøy and Ferriday, 2003; Logan et al., 2009; Bjørøy et al., 2009). The gas chromatograms will clearly show if a sample contains only hydrocarbons from recent organic matter, if there is a mixture of recent organic matter and seeped hydrocarbons, or if it contains mostly seeped hydrocarbons and if the seeped hydrocarbons have been biodegraded or not and how severely the biodegradation is. Examples of gas chromatograms of extracts of surface geochemistry samples are shown in [Figure 8](#). We believe, based on analysing thousands of surface geochemistry samples, that the GC analysis of the solvent extracts is the most significant analysis to determine whether or not a surface geochemical sample contains seeped oil or condensate and if this has been biodegraded or not. This analysis should be undertaken on all offshore surface geochemical samples.

Total Scanning Fluorescence (TSF) analysis

TSF analysis detects and measures organic compounds containing one or more aromatic functional groups and was used to determine if a surface geochemical sample contained seeped hydrocarbons by Brooks et al., (1983) and has been used in numerous studies since then. However, a number of

authors have since showed that the TSF can give data which does not agree with the GC analysis of the same sample (Barwise and Hay, 1966; Edwards and Crawford, 1999; Abrams et al., 2001; Bjorøy and Ferriday, 2002; Logan et al., 2009). What these authors found was that in many cases TSF would show data that indicated the sample contained seeped oil while the GC analysis showed that there were no indications of the sample containing seeped oil. In other cases, TSF indicated that there were no seeped hydrocarbons in the sample while the GC analysis showed the opposite--or the two methods could also agree. Examples of such samples are shown in Figure 9. Based on findings described in the literature together with hundred of similar findings in our own studies for various places around the world, such as the Atlantic Margin, The Barents Sea, The North Sea, Caspian Sea, Offshore West Africa and South China Sea, we recommend that TSF is not used as a screening tool to evaluate whether or not surface geochemical samples contain seeped liquid hydrocarbons.

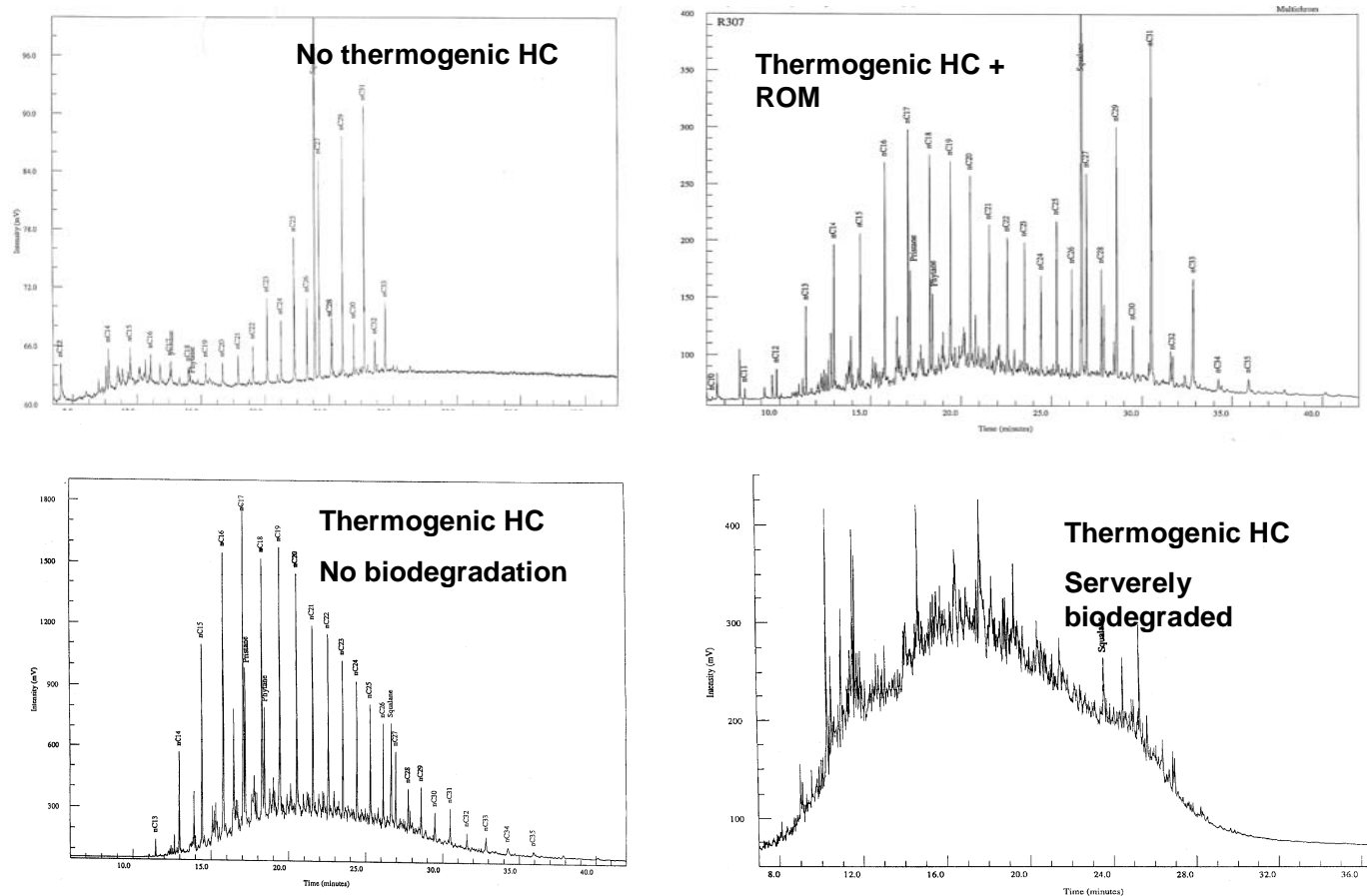


Figure 8. Typical gas chromatograms of different types of liquid hydrocarbons in surface geochemical samples.

GC-MS analysis

GC-MS analysis is a very valuable technique when evaluating the range of source types and maturities of seeped hydrocarbons in surface samples. Since the mid-1990s it has been common to report GC-MS data in surface geochemical surveys (Thrasher et al., 1996; Abrams and Narimov, 1997; Bjorøy et al., 1999, 2003; Cameron et al., 1999; Cole et al., 2001). There has been discussion regarding the work-up of the samples before the GC-MS analyses are performed, as well as discussions regarding the type of instrument that should be used; e.g., whether a low resolution instrument, a quadropole, can be used or whether a high resolution instrument, a magnetic sector instrument, should be used. There has also been discussion regarding the types of components that should be analysed by GC-MS; i.e., whether only the saturated compounds; e.g., the steranes and tritetpanes, or in addition the aromatic compounds. The answer to the latter discussion is clear. If the first is selected; i.e., analysis of only the saturated compounds, a significant amount of information will remain unrevealed, information that might help in identification of the type of source generating the hydrocarbons and its maturity.

To test the different possible methods a suite of extracts from surface geochemical samples was selected. All the samples had been found by GC analysis to contain seeped oil. A portion of each extract was separated by MPLC into saturated and aromatic fractions before each fraction plus the original extracts were analysed both on a high resolution instrument and on a quadropole instrument. It became clear that it was impossible to analyse both saturated and aromatic compounds in a single run using a quadropole; i.e., the resolution was not good enough. If a quadropole instrument was going to be used, the extract needed to be separated into saturated and aromatic fractions. Even after such separation there were difficulties with some of the samples, especially regarding the steranes where it was not possible to separate the peaks of the different compounds. When the same samples were analysed using a high resolution instrument, it was found that it was not necessary to undertake the separation into saturated and aromatic hydrocarbon fractions. The resolution was just as good when using the whole extract as when analysing the separated fractions. Examples of sterane and triterpane fragmentograms using the whole extract on a high resolution instrument are shown in [Figures 10 and 11](#). There are also other limitations of performing the GC-MS analyses on separated extracts. Apart from the additional time and cost of the final analysis, it is a fact that many surface sediments yield insufficient weights of extracts to physically enable MPLC separation to be performed. In conclusion, therefore, the preferred analysis is of the whole extract using a high resolution GC-MS instrument.

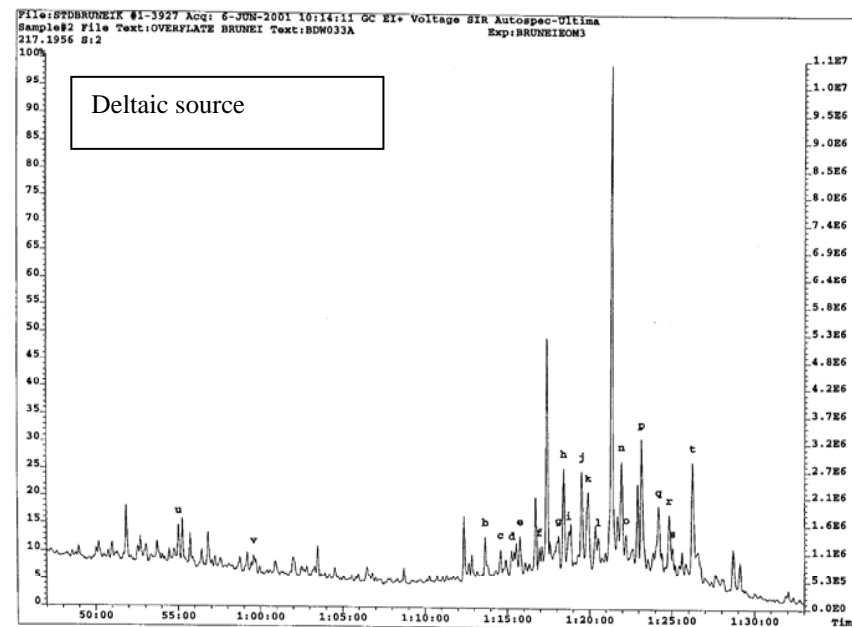
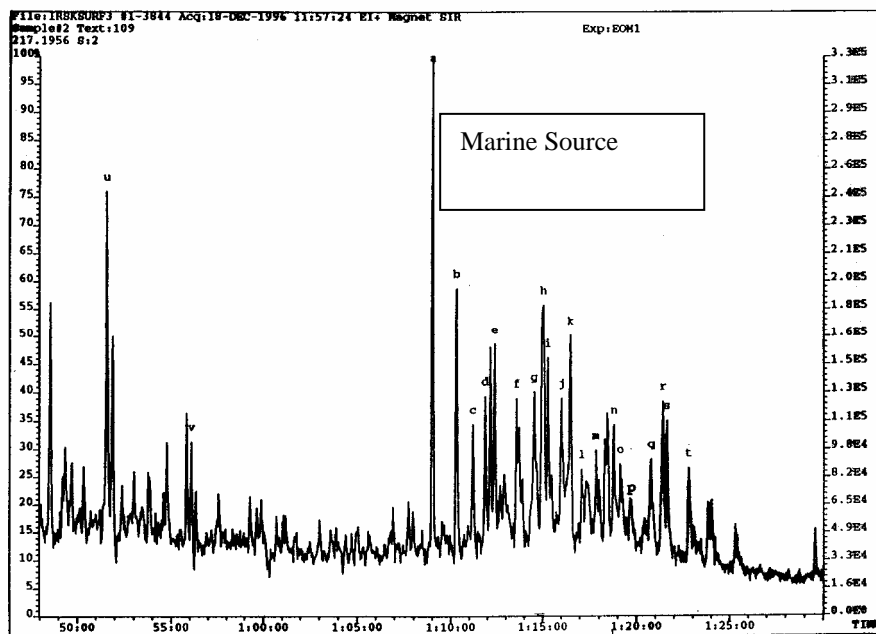


Figure 10. Example of steranes from high resolution GC-MS in surface geochemical samples.

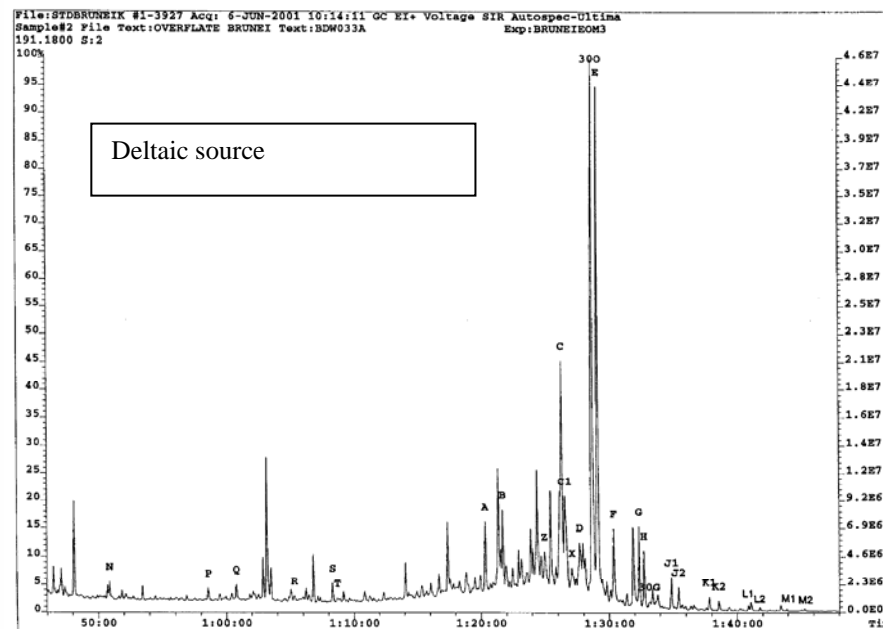
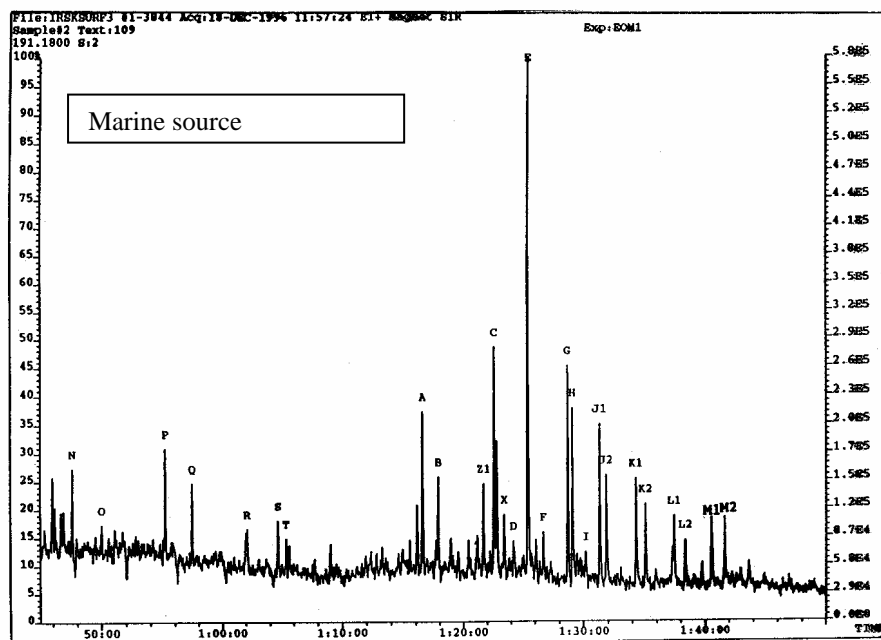


Figure 11. Example of triterpanes from high resolution GC-MS in surface geochemical samples.

Conclusions and Recommendations

The penetration of the sediment will only depend on the weight of the corer and the speed at which the corer enters the sediment, not on the type of corer; i.e., gravity or piston corer, when the core barrel enters the sediment at a speed of between 1.5 and 2.0 m/sec.

Analyses undertaken on samples collected by gravity coring and piston coring show basically no significant differences, neither for the gaseous hydrocarbons nor for the liquid hydrocarbons, clearly showing that there is no difference in the quality of the samples collected using the two different coring techniques. However, there is a marked difference between these techniques in the time needed to collect cores. Gravity coring is basically twice as fast as piston coring. There is also a significant difference in the weather window where cores can be collected. Gravity cores can be collected in rougher weather conditions than when a piston corer is used. We therefore recommend a gravity corer when sampling clayey sediments.

Regarding preservation of the samples, our data show clearly that the only method which will preserve the samples properly is to can the samples and freeze them to very low temperatures. The use of bactericide before freezing to -18°C , a procedure which has been commonly used by a number of companies, will not adequately preserve the samples' original hydrocarbons; i.e., stop any bacterial activity. If the samples are of clay, they will not go into suspension and the bacteria will still feed on the higher molecular weight hydrocarbon components and form biogenic methane. The results from the analysis of the gaseous fractions will therefore give the wrong results; i.e., the gaseous compounds analysed will not be those that were in the samples when collected but those that are in the samples after the bacteria have formed biogenic gaseous compounds. The use of a bactericide and freezing in normal household freezers (-18 to -25°C) should therefore never be used for preservation of surface geochemical samples if the samples are of clay. We therefore recommend that all samples are put into metal containers, flushed with nitrogen, sealed and frozen to -80°C .

Regarding the gas analysis, especially when the samples are preserved properly; i.e., frozen to -80°C , all three gas fractions should be analysed; e.g., headspace gas, occluded (interstitial) gas, and adsorbed gas, to get a complete set of data regarding the gases present in the sample at the time of collection and gases that percolated through the sample over geological time. If only headspace gas is analysed, a lot of information will be lost.

When extracting a sample, it is preferable to use hexane and not DCM since DCM will extract other components from the sample that do not come from the seeped hydrocarbons, and this may make interpretation more difficult. Also, to avoid contamination of the extract by reworked material all samples should be separated by sieving and only the $< 63\mu\text{m}$ fraction should be used. The GC analysis of the whole extract is the best analysis for determining whether or not the sample contains seeped hydrocarbons, if these are oil or condensate-related and if there is any biodegradation. We recommend that all the samples be extracted and analysed by GC.

TSF analyses have shown that they will at times give the wrong result; i.e., indicating seeped oil when there is only ROM in the samples and vice versa, showing only ROM when there are seeped hydrocarbons in the sample. We therefore do not recommend including TSF analyses in an analytical program for an offshore surface geochemical study.

To be able to determine the type of source and maturity of the seeped hydrocarbons, it will be necessary to undertake GC-MS analysis, and both the

saturated compounds (sterane and triterpanes) and the aromatic compounds should be analysed. We recommend undertaking the GC-MS analysis using the whole extract on a high resolution instrument.

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