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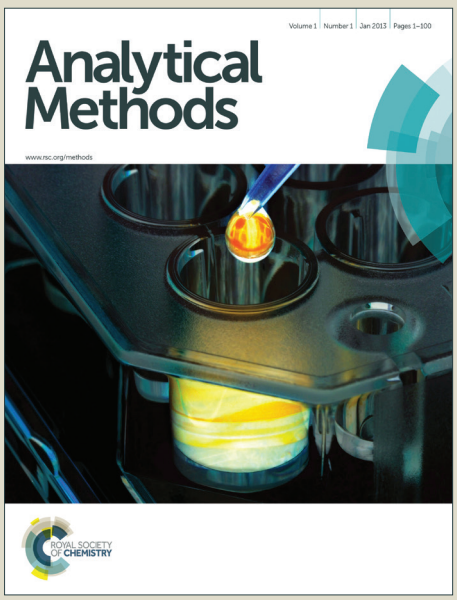

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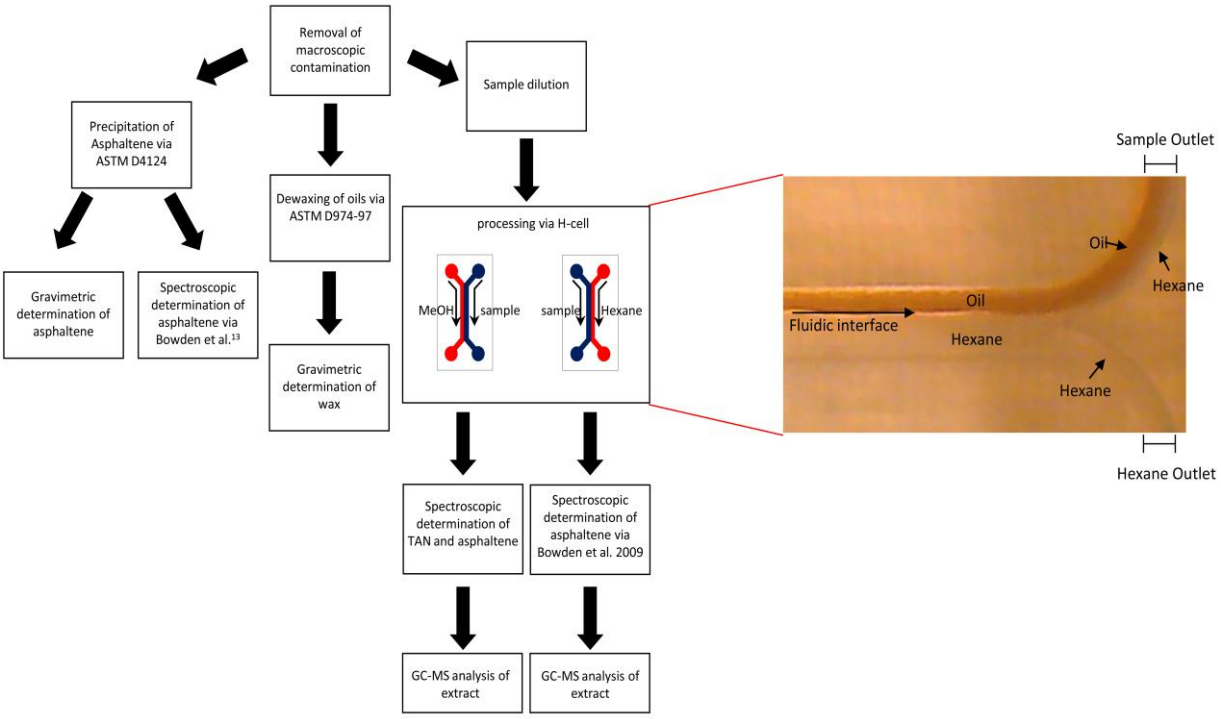

Analytical scheme for H-cell capable of performing rapid and accurate asphaltene and TAN assays.

Simultaneous and rapid asphaltene and TAN determination for heavy petroleum using an H-cell

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Abstract

Characterising the asphaltene and carboxylic acid (naphthenic acid) content of crude oil is important for petroleum production, transport, storage and environmental science. This is because, the proportion of asphaltene and the concentration of acidic compounds in petroleum can be used to characterise viscosity (e.g. producibility), refining potential (e.g. its value) and chemical recalcitrance and thus behaviour as a contaminant. Here we present an assay for determining the proportion of asphaltene and total acid number (TAN) of petroleum. The method utilises a microfluidic component called an H-cell and produces an asphaltene-free fraction, either hydrocarbon or methanol-soluble, that can be forwarded for further advanced analysis and used to determine asphaltene content and TAN value. The H-cell method depends on a diffusion-based separation that is only practical when a sample is manipulated at a microscale and thus is fundamentally different to previous methods for assaying these parameters that utilise solubility- or chromatography-based methods. Comparisons of asphaltene and TAN measurements derived from the H-cell based assay have very high correlations with the ASTM D4124 and ASTM D974-97 methods. Therefore rapid and simultaneous determination of asphaltene content and TAN value can be achieved by an H-cell based format. While this format is suited to miniaturisation and point of need analysis, the main benefit of the H-cell method might be its capacity to provide new analytical windows.

1.0 Introduction

The fractionation of petroleum into its constituent parts falls into two basic categories; thermally driven distillation processes applied in refining and trading petroleum as a commodity and chemical methods applied to evaluate oil and gain crucial technical information that can answer problems encountered during oil exploration, production, transportation and environmental remediation[1]. Of the chemical assays reported for asphaltene analysis, the SARA (Saturates, Aromatics, Resins and Asphaltenes) scheme is currently at the fore[1-4]. Standard methods for asphaltene analysis define asphaltene as the component of petroleum that is insoluble when diluted with an excess of *n*-alkane solvent; within ASTM D4124[2] this is hexane although other solvents may be chosen[1].

A standard method for assaying the acidity of crude oil (ASTM 974-975) is the Total Acid Number (TAN) – number of milligrams of potassium hydroxide required to neutralise the acidity in a gram of petroleum. Particularly when hydrogen sulphide is absent, it is the carboxylic acids (naphthenic acids) present in petroleum that are often responsible for its acidic behaviour and thus corrosion during petroleum transport, storage and refining[6]. Furthermore, the carboxylic acids within petroleum may combine with salts to create surfactants and emulsifying agents that are important for determining the interaction of petroleum with aqueous phases[7]. Carboxylic and naphthenic acids can be extracted from petroleum by ion exchange methods[8,9], and the yields obtained generally, although not always, correlate with TAN number.

Complexity in handling and assaying petroleum derives from its chemical heterogeneity, varying physical properties (e.g. viscosity and density) and the sensitivity of methods to a wide range interferences (some of these factors are described from the perspective of an oil field operative in the opening chapter Mullins[4]). The latter can include non-petroleum and non-liquid materials, such as inorganic minerals and compounds that become entrained within petroleum during its production, refining and transport. The consequences of these are that asphaltene data appears to have considerable noise and this can

produce notable variation in the application of methods between laboratories – particularly with regard to TAN values[9]. The effect of this is the widespread and prolific modification of methods to create a range of propriety-assays and discipline specific methods. Examples of this include alternatives to the TAN assay (Horvath-Gumulka test – Naphthenic Acid Number and Carboxylic Acid Number[1]), utilisation of different solvents for analytical handling of asphaltene e.g. toluene or dichloromethane[4], and the widespread use of heptane over hexane by academic laboratories in preparing asphaltene-free fractions for biomarker analysis[10]. Thus while assaying petroleum for sale as a commodity mandates standardisation of assay formats (e.g. the use of ASTM methods) day to day problem solving and research drives considerable analytical development for what would generally be considered basic assays.

In this paper we investigate the application of an H-cell based method to determine asphaltene and carboxylic acid content for a range of petroleum-types. Within an H-cell, two fluids are flown in hard contact with each other, and analytes are permitted to diffuse from one fluid to the other[11]. To extract specific fractions from petroleum previous work has used hexane[12] and methanol[13], but only for a limited number of samples. The asphaltene assaying method used here[12,13] is fundamentally novel in that it does not strictly fall into either the thermal (evaporative) or chemical (chromatography or solubility) based methods[1] for fractionating petroleum, instead it depends on the varying rates of diffusion of different petroleum components within liquids to achieve separation[11-13]. For a range of sample types we have used two assay formats; 1) one using hexane to determine asphaltene content and 2) another using methanol to simultaneously determine asphaltene content and TAN number. Despite the potential of H-cell based methods, given the inherently complex nature of petroleum and potential interferences, a key need is to evaluate the robustness of the H-Cell methods when applied to a range of heavy petroleum - both naturally occurring and anthropogenically extracted from the subsurface. There is also a need to scope and document the analytical window provided by H-cell methods with regard to petroleum, and heavy petroleum.

2.0 Method

Analytical procedures are summarised in Fig. 1, and the methods employed at each stage are described in the following sections.

2.1 Samples

The petroleum samples used in this study represent a range of physical types from tar through to conventional oil (Fig. 2). Twelve petroleum samples were chosen for analysis (Table 1). Produced oils were analysed dead (they were degassed by exposure to ambient conditions) and taken from a stock collection at the University of Aberdeen. Seep samples and naturally occurring bitumen were analysed in the condition in which they were collected, except where obvious physical interferences were present; e.g. dead insects, sediment etc.

Two samples (Boa A & B) possessed high wax content. The wax component of petroleum is known to be a significant interference during asphaltene determination. To provide an assessment of this interference the sample was split, and the aliquot dewaxed prior to further analysis. Wax was removed from the waxy oils using the method detailed in ASTM D721-06[14]. Briefly; an oil sample is dissolved in a 3:1 Methyl Ethyl Ketone/Toluene mix and cooled to -32 °C. The precipitated wax is recovered by filtering the solution. The percentage of wax filtrate retained on the filter was determined gravimetrically, after it had been dried in a desiccator for 24 hours.

2.2 Asphaltene and SARA Analysis

The % asphaltene content of samples and SARA composition was obtained using ASTM D4124[2]. The oils were separated into component constituents of asphaltene and maltene using excess hexane in a 1:40 oil/ hexane ratio. Silica gel column chromatography was then used to separate the maltene fraction into saturate, aromatics, and resin components. The amount of each fraction, including the asphaltene fraction, was deduced gravimetrically.

2.3 TAN analysis

The ASTM D974-97[5] method was used to perform total acid number measurements. In summary, about 2 gram of oil is dissolved in 250ml conical flask using 100ml solution of titration solvent (toluene 500ml, water 5ml and propan-2-ol 495ml). P-Naptholbenzein solution was used as an indicator. The mixture (a yellow-orange coloration) was titrated with potassium hydroxide solution in small increments until the end point was indicated by a colour change. A blank titration was performed and the Total Acid Number calculated using the prescribed formula.

2.4 Petroleum Acid Fraction Extraction - Ion Exchange Solid-Phase Extraction

Carboxylic acids contained in the acid fraction of 9 crude oils were extracted using the Ion Exchange Chromatography (IEC). The Solid-Phase Extraction (SPE) method described in Jones et al.[8] was used on oil samples. In summary, a SAX quaternary amine SPE ion exchange column was conditioned with 40ml of *n*-hexane. One gram of oil, spiked with 75µg of 1-adamantanecarboylic acid and 50µg 5β-cholanic acid (recovery standards), was pipetted onto the column and allowed to adsorb. After eluting non-acid fractions with *n*-hexane and DCM, an acid fraction was eluted with a mixture of diethyl ether and 2% formic acid. The acid fraction was reduced to dryness in a rotor-evaporator and the recovered acid-fraction re-dissolved in methanol for spectroscopy and then redissolved in DCM prior to derivatisation with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) to convert alkenoic acids to their silyated ethers and esters for GC-MS analysis.

2.5 Gas Chromatography-Mass Spectrometry

GC-MS analysis was performed using an Agilent 6890N GC fitted with a J&W DB-5 phase 50 m length column (0.25 mm id, 0.25 µm film thickness) connected to a 5975 MSD and a quadruple mass spectrometer operating in SIM mode (dwell time 0.1 s/ion and ionisation energy 70 eV). Samples were injected manually using a split/splitless injector operating in splitless mode (purge 40 ml min^{-1} for 2 min). The temperature program for the GC oven was 80 – 295 °C, holding at 80 °C for two minutes, rising to 10 °C min^{-1} for 8 min and then 3 °C min^{-1} and finally holding the maximum temperature for 10 min.

Compounds were identified by comparing retention times to well-characterised materials that served as reference samples.

2.6 Microfluidic Separation

Microfluidic separation followed the method presented in Bowden et al.[13] using an H-cell with the following channel dimensions: channel length 20 mm, width 260 μm and 60 μm depth. Microfluidic chips were fabricated by Dolomite microfluidics from sodalime glass. The H-cell was held in a Mitos chip interface fitted with a multiflux 4-way linear connector. Heavy oils with API's < 23° were diluted with hexane to lower the viscosity and improve sample manipulation (typical dilution factor of 1:5). Lighter oils (API's > 34°) were analysed with limited dilution (1:1 to 1:0). Methanol and Hexane were used as the extracting solvents and were pumped through the device with samples introduced as slugs for discrete batch analysis and processing. Solvents were pumped continuously through the microfluidic chip to establish optimal wetting characteristics within the channel and limit interaction between the oil and the sides of the channel (interface can occur via viscous effects caused by the adsorption of asphaltene and wax precipitates on the sides of channels). Three residence times were investigated; 2.8, 5.6 and 11.3 seconds – residence time is a key operational parameter within a Y- or H-cell and represents the maximum time that a particle will spend at the interface between two fluid streams[15]. The ratio of the flow rates between petroleum and extracting solvent was in the order of 1:6, this parameter governs the separation of the fluid streams at the downstream-end of the H-cell. The stability of the interface between the fluids was visually monitored at the down stream end of the device during experiments (Fig. 2).

2.7 Determination of asphaltene content by UV-Vis absorption spectra

UV-Vis absorption spectra were obtained for the products of SARA fractions and off-line for microfluidic chip effluents using a USB4000 Ocean Optics spectrometer measuring within the wavelength range of 178-890 nm, in effect, operating the spectrometer as a single-beam spectrometer. Integration time was 500 ms and four scans were averaged to produce a single spectrum. Samples were diluted in solvent to increase volume for ease of sample

manipulation. Spectra were normalised, smoothed and then cropped (290nm to 410 nm range) and the difference between whole oil and maltene spectra used to obtain the proportion of asphaltene in a sample as described in Bowden et al.[13]. The same spectral acquisition parameters were utilised for the determination of methanol extractables, except in this instance the absolute units of absorption used were measured at 205.4 nm and a calibration curve obtained using the acid fraction obtained by ion exchange chromatography.

3.0 Results

3.1 Comparison of spectroscopic and gravimetric determination of Asphaltene

The H-cell based assay utilises differences in adsorption in the 290 to 410 nm range for whole and asphaltene-free oils to determine asphaltene content [13]. This element of the assay was investigated separately from H-cell parameters. It was found that a relatively high correlation ($r = 0.95$, $n = 13$ which is significant with an alpha value greater than 0.001) could be obtained between the gravimetric and spectroscopic analysis of the products of ASTM D4124[2] (Data shown in supplementary information 1). However, a notable under-prediction occurred and the limit of detection was 4 %, e.g. when gravimetric analysis returned 4 % asphaltene the spectroscopic method presented in Bowden et al.[13] detected no asphaltene. This is significant because petroleum with an asphaltene content of 5 % would be considered asphaltic.

The limit of detection was improved by aggregating the asphaltene spectra of all twelve samples to produce an “averaged asphaltene spectra” in the range 290 to 410 nm. Results for this approach are shown in Fig. 3 and data approach a 1:1 gradient, whilst the intercept of a straight line fitted to the data suggests a minimum detection limit of less than 1 %. Variance in the data is also well explained using this approach ($r = 0.97$, $n = 13$, which is significant with an alpha value greater than > 0.001). At present we have not determined the exact cause for this improvement, but it is likely that the improvement achieved by using averaged asphaltene spectra reflects the difficulties inherent to chemically separating and characterising a pure asphaltene

fraction of oil by ASTM D4124[2]. Numerous studies have shown that asphaltene subfractions can be highly variable and can contain many non-macromolecular compounds that have little similarity to classic models of asphaltenes but that can precipitate with an asphaltene fraction (e.g. non-macromolecular heteroatomic compounds that are insoluble in hexane[16]). Asphaltic oils would be expected to yield purer asphaltene, e.g. relatively speaking they are less affected by interfering compounds. Averaged asphaltene spectra were therefore used when analysing the products of H-cell separations.

3.2 Comparison of H-cell based measurement of asphaltene with ASTM D4124

Predictions of asphaltene content produced by the H-cell processing of oils were compared to results obtained from ASTM D4124[2]. The correlation between the results of the standard and H-cell method, for all three H-cell residence times using either hexane or methanol as the solvent, were significant indicating that the different methods are at least comparable (significant for an alpha value of 0.001, r = 0.99 and n = 9). Thus a calibration of the standard ASTM method to the H-cell method can be achieved. Based on the intercepts of straight-lines fitted to the raw data (Figure 4), the best detection limits were obtained for residence times of 5.6 seconds; the limit of asphaltene-detection when hexane was used was less than 1 % and when methanol was used was less than 0.3%. (Data for other residence times is shown in supplementary information 2 and 3 and results listed Table 1).

Asphaltenes are not the only high molecular weight and poorly soluble component of petroleum that forms a solid precipitate. The wax components of oil can variably co-precipitate with asphaltene during ASTM D4124[2] to cause an erroneous assay. Waxes are held to be hydrocarbon compounds with high molecular weights – typically saturated compounds such as *n*-alkanes or structurally similar compounds. Asphaltenes are held to be heteroatom-containing compounds, with an aromatic nucleus and a disputed high molecular weight, (in excess of 550 amu[4]. The difference between the two compounds classes is important because the factors that increase the

stability of one compound type may destabilise the other (for example blending a waxy oil with lower molecular hydrocarbon compounds may help solubilise wax but could destabilise asphaltene). Two waxy-oils were processed (Boa A, 9.3% and Bob B, 13% wax). For a residence time of 5.6 seconds, a comparison of dewaxed and pristine samples (that still have their wax content and have not been dewaxed via ASTM D721-06[14]) suggests that waxy samples assay with 1.5 to 1 % more asphaltene than would be expected (Table 1).

3.3 Hexane extracts analysis

In addition to permitting an analysis of asphaltene content the hexane extract obtained by diffusive separation within an H-cell is effectively asphaltene-free and readily amenable for GC-MS analysis[12]. Ion chromatograms of the hexane extracts and the saturate fraction (obtained via the SARA-scheme and ASTM D4124[2]) of sample Brid E are compared in Figure 5. Superficially they appear similar, expect that *n*-alkanes with a carbon number greater than twenty nine are not prominent on the 85 *m/z* ion chromatograms of H-cell extracts. Additionally, H-cell fractions with the shortest residence times have the lowest abundance of higher carbon number *n*-alkanes. This could be of concern when making use of petroleum-biomarker proxies and parameters that utilise homologous series of compounds, as these parameters are sensitive to differences of a single carbon number. Little variation in the relative proportions of the acyclic isoprenoids pristine and phytane is observed as a function of residence time, and similarly the proportion of these isoprenoids relative to their neighbouring *n*-alkanes also varies little (Figure 5). Thus when preparing a sample for GC-analysis, longer residence times would be needed if the final focus of analysis was on higher carbon number biomarkers such as hopanes or similar terpanes.

3.6 Determination of TAN value using a methanol extract

To evaluate the feasibility of predicting TAN value from an H-cell extract, the yield of methanol was first compared to the concentration of naphthenic acid obtained by Ion Exchange Chromatography (IEC). The greatest yields of methanol-extractables were obtained for H-cell residence times of 5.6

seconds (Fig. 6a – see Supplementary Information 4 for other residence times), but a significant correlation (alpha value greater than 0.01) between H-cell and IEC yields was observed for residence times of both 5.6 and 11.3 seconds. Detection limits (e.g. the value at which IEC yields an acid fraction but the H-cell method would not) decreased from 4.6 mg/g through 4.4 mg/g to 3.4 mg/g for residence times of 2.8, 5.6 and 11.3 seconds.

GC-MS analysis of BSTFA derivatised H-cell and IEC fractions revealed that both fractions are similar (both contain *n*-alkanoic acids and *n*-alkanols), but that the H-cell extract contained far greater proportions of *n*-alkanols (Fig. 7). This is a reasonable finding as methanol would not be expected to offer much selectivity in terms of preferably solubilising alkanols over alkanoic acids, and the two compound classes would have similar diffusivities. The presence of other compound-types such as alcohols in addition to naphthenic acids explains the relatively high yields obtained for the H-cell extracts in comparison to acid fractions obtained by ion exchange chromatography.

Previous work linking concentrations of naphthenic acids in petroleum to TAN values[9,17] has used correlations between IEC yields and TAN value rather than concentrations of specific compounds. This is because the identification of compounds types that contribute most to crude oil acidity has been inconclusive – e.g. *n*-alkanoic acids have been shown to contribute little to the proton donating ability of crude oil and therefore have little influence on TAN value[17]. They were utilised in this study because of the highly diagnostic M-15 ions produced by BSTFA-derivatised alkanoic acids during electron impact ionisation mass spectrometry. To convert methanol extract yields to a TAN equivalent a straight-line equation derived from IEC-acid fraction yields and TAN values was used[8,9,17]. The TAN values obtained via ASTM D974-97[5] are compared to H-cell predictions of TAN value in Fig. 6b - see Supplementary Information 5 for other residence times. There are notable outliers, but generally, data fall in the same sequence as those determined via ASTM D974-97[5] (e.g. the most acidic sample determined via ASTM D974-97[5] is the most acidic sample according to the H-cell method).

4.0 Discussion

4.1 Precision and sensitivity of H-cell method

A residence time of 5.6 seconds has the most repeatable measurement (% relative standard deviation of 19% compared to 25% for both 2.8 and 11.3 seconds and 34% for the SARA method) (Table 2). Low repeatability for ASTM D4124[2] likely derives from difficulty in weighing small amounts of asphaltene in asphaltene poor samples. Measurement accuracy of the H-cell method is also indicated by limits of detection (Table 2), where as low as 0.05% asphaltene in oil can be detected depending on the solvent used. Sensitivity for asphaltene prediction is higher for methanol than for hexane. Repeatability of TAN data is best at 11.3 seconds compared to other residence times (although reasonable for 5.6 seconds) (table 2) but low when compared to ASTM D974-97[5]. H-cell method appears sensitive at detecting very low acid concentrations in oils, typically detecting acid content which can be equivalent to as low as ~0.001mg of potassium hydroxide per gram of oil however; this is a combined assay for both acids and alcohols.

4.2 Other considerations

For conventional asphaltene determination, the wax content of crude oil is a known potential interference because of the formation of microcystalites of wax[18]. Previous work suggested that the formation of large asphaltene aggregates that, in common with wax crystallites are a solid phase, are larger and slower diffusing than their constituent molecules, did not impinge on the production of an asphaltene-free fraction and thus asphaltene determination via an H-cell[12]. The results presented here suggest that waxes within oils interfere slightly in the determination of asphaltene content; a 1 to 1.5 % over estimation of asphaltene content was found for waxy oils. This over estimation is relatively minor; by way of example, this is less than the error introduced by various oil field sampling methods[19], but significant within the context of the generally high accuracy seen in Fig. 4 and table 2. The main cause of over estimation is that wax compounds, as straight chain *n*-alkanes, contribute to the spectra of the whole oil in a similar way to the saturate fraction of a non-waxy oil (Fig. 8). Fig. 9 presents diffusive mixing times for *n*-alkanes wihtin the H-cell, and from this it could be concluded that both waxes and particularly

wax-precipitates would not be expected in the extracting phase. As waxes will not have defused to the asphaltene-free extract, their contribution to the final spectra is missing and the proportion of asphaltene over estimated (the amount of maltene fraction is underestimated). From an applications perspective it would be beneficial to have an *a priori* knowledge of wax content prior to sample analysis.

Unlike ion exchange chromatography, an H-cell, using methanol as an extracting solvent, does not separate *n*-alkanoic acids from mixtures containing *n*-alkanols and *n*-alkanoic acids (Fig. 7). The effects created by the presence of *n*-alkanols within methanol extracts can by adjusted by using the straight line relationship shown in Fig. 6a to recalibrate results. Thus from the perspective of producing a proxy for TAN, the presence of alcohols in methanol-extracts is not a significant interference. However alcoholic compounds such as phenols despite being classed as corrosive have not been shown to be significant contributors to TAN value in the same way as carboxylic acid species[17]. Compounds such as phenols, although not detected in the small volumes analysed by GC-MS in this instance, would be expected to partition to the methanol phase of an H-cell extract. Longer term, this aspect of the H-cell separation procedure could be developed to try and obtain a broader spectrum assay for polar compounds in petroleum.

4.3 Applications

The asphaltene content and acidity of petroleum is used to inform decision making for oilfield (often termed the upstream sector of the petroleum industry), refinery (the downstream sector) and natural or environmental science applications. Conventional methods typically yield this information subsequent to laboratory analysis. Recent work has sought to develop methods to provide this information at point of need and hopefully more rapidly[13,20]. In the case of oilfield applications varying asphaltene contents can be used to predict variation in the physical properties of petroleum in the subsurface; an example of this includes subsurface intervals within oil reservoirs that contain exceptionally viscous or even solid petroleum (tar-

mats). These intervals, aside from containing immobile bitumen may even constitute barriers to flow, can be identified by a simple chemical assay[21]. Aside from this special case, it is also not uncommon for subsurface accumulations of petroleum to be the product of complex filling histories – e.g. oil of different types migrated to its current position at varying times, and was then variably altered in different regions of the subsurface[22]). Chemical assays (notably asphaltene content) are often a viable and far less costly proxy for identifying and characterising variation than physical measurements. More recently the role of organic acids within petroleum in influencing wetting behaviour and the final level of oil recovery has been highlighted by laboratory studies[23]. Therefore the simultaneous and rapid measurements of both asphaltene and acid content would be extremely useful for appraising oilfield potential and in particular what fraction is ultimately recoverable.

Further into the life of an oilfield, the actions (workovers) initiated by operators to improve oil production often result in transient changes in the composition of produced fluids e.g. increased concentrations of corrosive surfacting agents or asphaltene as a consequence of the removal of blockages[6]. Chemical measurements performed at point of need could help engineers identify when the deleterious effects of such interventions had abated. Similar benefits could also be envisioned for point of need assays performed for the purposes flow assurance in refineries.

For natural and environmental science applications, the asphaltene and TAN number are useful because changes in both parameters can be linked to oil degradation. Asphaltene is the recalcitrant proportion of petroleum and thus within spilled petroleum asphaltene concentrations rise as other components are degraded[24]. Organic acid concentrations initially rise as oil is degraded, likely because of a contribution from hydrocarbon-metabolites formed by microbial activity. In the terminal stages of petroleum degradation the concentration of organic acids has been observed to decrease[25]. Repeated simultaneous measurements of asphaltene and TAN values via an H-cell would therefore record the attenuation of oil-spills and possibly help differentiate fresh from degraded petroleum. Measuring the asphaltene and

TAN content of petroleum thus provides a rapid method of characterisation – e.g. helping to distinguish fresh from weathered petroleum.

5.0 Conclusion

An H-cell based method for separating heavy petroleum can be optimised to yield proxy measurements of asphaltene and the carboxylic acid content of petroleum (which can be expressed as a TAN value). Detailed analysis of the extracts produced by the H-cell demonstrates that the method, because it utilises microscaled diffusion, provides an analytical window that is inherently different to distillation and chemical based methods for assaying heavy petroleum, The H-cell method gives better accuracy for measuring asphaltene when compared to a gravimetric-based methods like ASTM D4124[2]. The capability of this technique to provide rapid simultaneous TAN and asphaltene proxy measurements has the potential to impact both petroleum and environmental science.

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Figure captions

Figure 1: Schematic representation of the analytical scheme used during this study, illustrating the alternative analysis methods employed for heavy petroleum.

Figure 2: LHS - Variation in the sample type used for this study that ranges from solid through to viscous liquid petroleum. RHS - Image of H-cell device in operation. Labelled is the interface between the two fluids and the fluids exiting the device. Note that the relative pressure of the two fluid streams is set so that some of the extracting phase exits through the sample outlet. This

represents a factor of safety to ensure that none of the asphaltene containing sample unintentionally exits with the sample phase needs to be asphaltene-free.

Figure 3: Graph comparing spectroscopic and gravimetric determination of asphaltene. Raw data (filled black circles) and data recalibrated using straight-line fitted to raw data (Hollow circles).

Figure 4: Comparison of percentage asphaltene predicted by the H-Cell method with ASTM D4124[2]. LHS – analyses using hexane as the extracting solvent and for a residence time of 5.6 seconds; RHS – analyses using methanol as the extracting solvent and for a residence time of 5.6 seconds.

Figure 5: m/z 85 Ion chromatograms of the H-cell hexane extracts and hydrocarbon fraction yielded by ASTM D4124[2]. Data are shown for sample Bride E for the H-cell residence times indicated. Carbon numbers correspond to those of the n-alkane homologous series.

Figure 6: a) Comparison of the yield of methanol extractables at 5.6 seconds with acid-fraction yields obtained by ion exchange chromatography[8]. b) Acid fraction yields at 5.6 seconds expressed as TAN values using approach presented in Borgund, et al.[9], and Meridith, et al.[17] with TAN values obtained by ASTM D974-97[5].

Figure 7: *m/z* Ion chromatograms for methanol extracts and acid fractions obtained by IEC. Plotted ions in the range *m/z* 285 to 341 correspond to the M-15 ions for BSTFA derivatised n-alkanols and n-alkanoic acids.

Figure 8: Absorption spectra of various fractions of oil in the 280-410 nm wavelength range. Note: Wax spectra are similar to that of maltene fraction (de-asphaltened oil) causing over estimation of asphaltene content.

Figure 9: Scatter plot of the relative abundance of *n*-alkanes in H-cell extracts (relative to the abundance of the compound in the fraction produced by column chromatography) plotted by carbon number. Also shown is the calculated diffusive mixing times[15] shown for key *n*-alkanes.

Table 1: Sample Descriptions and Analysis Details

Sample*		Type†	API††	TAN mg KOH/g	Wax %	Asph‡ %		ICE acid fraction● mg/g oil	Dilute○	H-cell analyses○ (%) RT: 2.8 Hex	RT: 2.8 MeOH	RT: 5.6 Hex	RT: 5.6 MeOH	RT:11.3 Hex	RT:11.3 MeOH
Beatrice Oilfield, Moray Firth, UK	Boa A	Stock Oil	38°	n.d.	9.3	4	*1*	n.d.	1:1	4(4.5)^{w}	n.d.	2(3)^{w}	n.d.	4(5)^{w}	n.d.
	Bob B	Stock Oil	38°	n.d.	13	5.5	*7*	n.d.	1:1	5.5(5)^{w}	5	5(5)^{w}	6	4.5 (4.5)^{w}	n.d.
Siljan, Sweden	Sil C	Stock Oil	15-20°	5.3	n.d.	10	*12*	9.51	1:3	10	10	10	10	10	n.d.
Wytch farm, Dorset	Sher D	Stock Oil	37°	5.17	n.d.	18	*25*	6.89	1:2	17	18	18	18	18	n.d.
	Brid E	Stock Oil	38°	0.55	n.d.	6.9	*8*	4.28	1:1	6.9	6	7	6.5	6	n.d.
	From F	Stock Oil	38°	1.08	n.d.	7	*1*	4.77	1:2	n.d.	7	n.d.	6	n.d.	n.d.
Bengal fore-deep	Syl G	Stock Oil	28.3°	0.84	n.d.	5.7	*5*	4.17	1:½	n.d.	5.7	n.d.	6	n.d.	n.d.
	BM J	Stock Oil	n.a.	0.84	n.d.	6	*2*	5.15	1:2	n.d.	n.d.	n.d.	n.d.	n.d.	7
Murchison Field, North Sea	Oryx L	Stock Oil	38°	0.55	n.d.	6.3	*6*	4.5	1:½	n.d.	7	n.d.	6.5	n.d.	5.5
	Oryx M	Stock Oil	38°	0.28	n.d.	7	*10*	4.1	3:1	7	6.3	8	7	7	5
Thurso, Sutherland, UK	Cait	Fresh, Seep	n.d.	n.d.	n.d.	16	*12*	n.d.	1:5	16	n.d.	22	n.d.	18	n.d.
Pitchford Bridge, Shropshire, UK	Pit Br	Fresh, Seep	n.d.	6.57	n.d.	30	*37*	12.13	1:10	30	n.d.	29	n.d.	38	n.d.

*Sample name and code referred to in text. †Stock samples are taken from a stock collection held at the University of Aberdeen; Fresh Seep samples were collected during fieldwork. ††API values were taken from the information listed with samples in the collection, expect for seep samples. ‡The first asphaltene value was obtained using ASTM D4124, the second as described in text. ●Acid fraction obtained by ion exchange chromatography (solid phase extraction).○ Dilution factor of samples to solvent (v/v), RT = residence time of particle in H-cell, hex = hexane used as extracting solvent, MeOH = methanol used as extracting solvent, n.d. = not done, ()^{w}= Asphaltene data for waxy samples.

Table 2: Precision and Sensitivity

Method	RT(s)	RSD (%)		LoD		
		Asph	TAN	Asph%		TAN
				Hexane	Methanol	mgKOH/g
H-cell	2.8s	25	13	0.5	0.3	0.9
	5.6s	19	11	0.1	0.05	~0.001
	11.3	25	7	0.9	0.1	~0.001
ASTM D4214		34				
ASTM D974-9726			4			

RT = residence time of particle in H-cell, Asph = Asphaltene, TAN = Total Acid number, RSD (%) = Relative standard deviation expressed in percentage, LoD = Limit of Detection.

Fig 1.

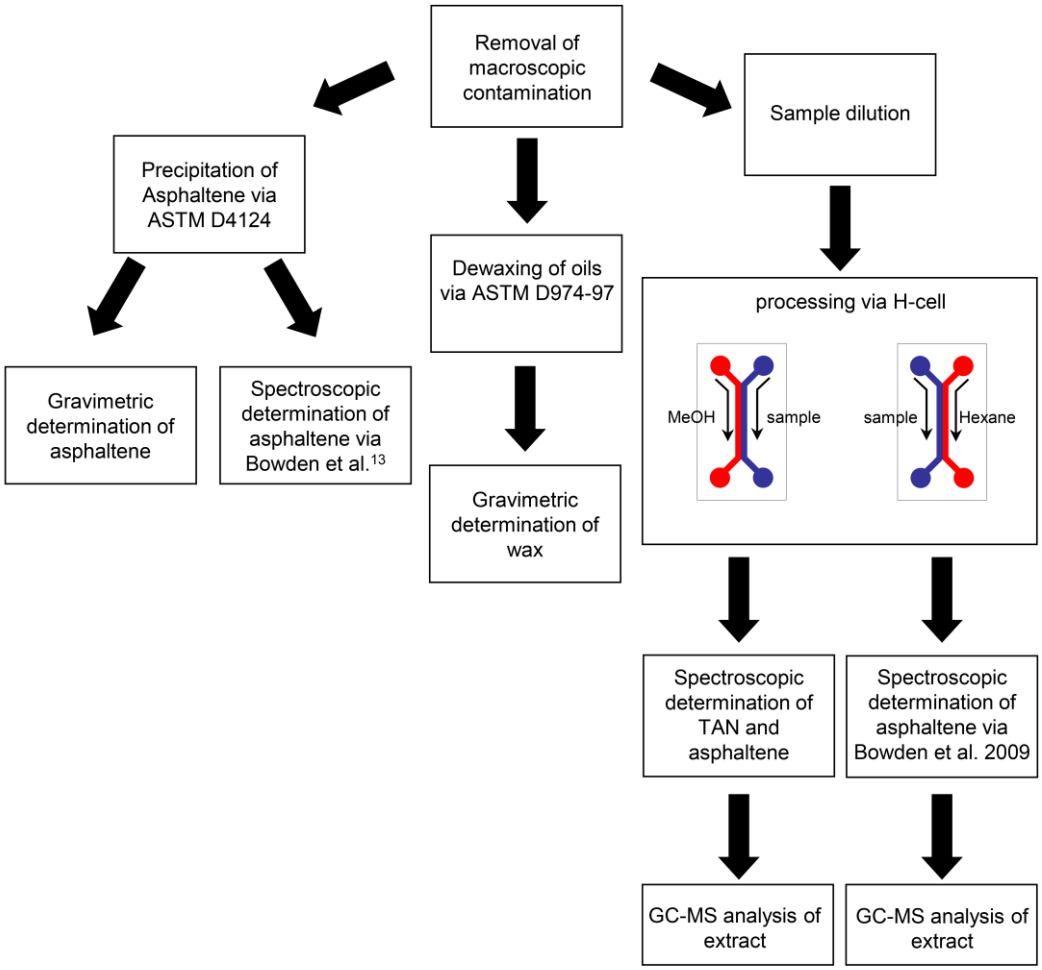

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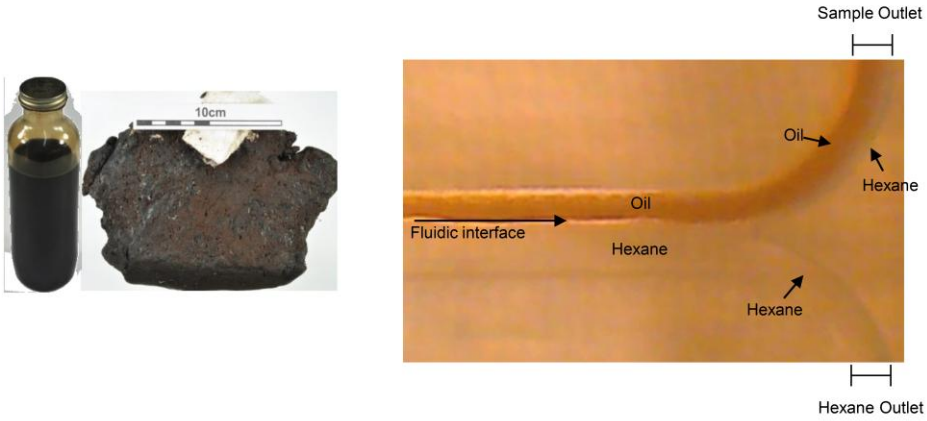
Fig 2.



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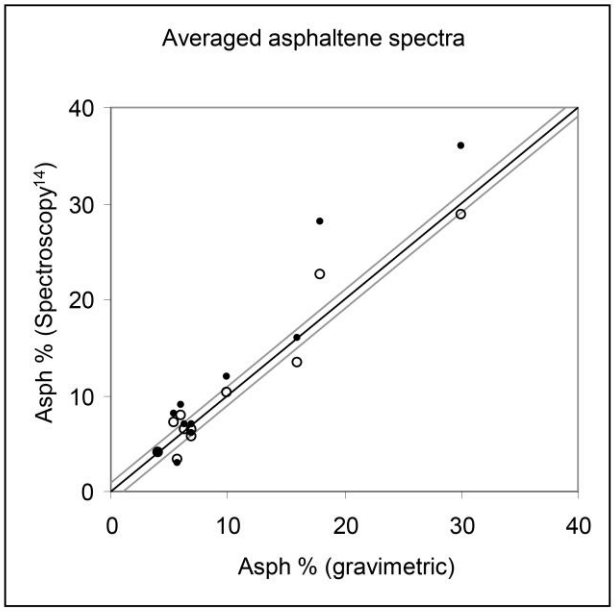

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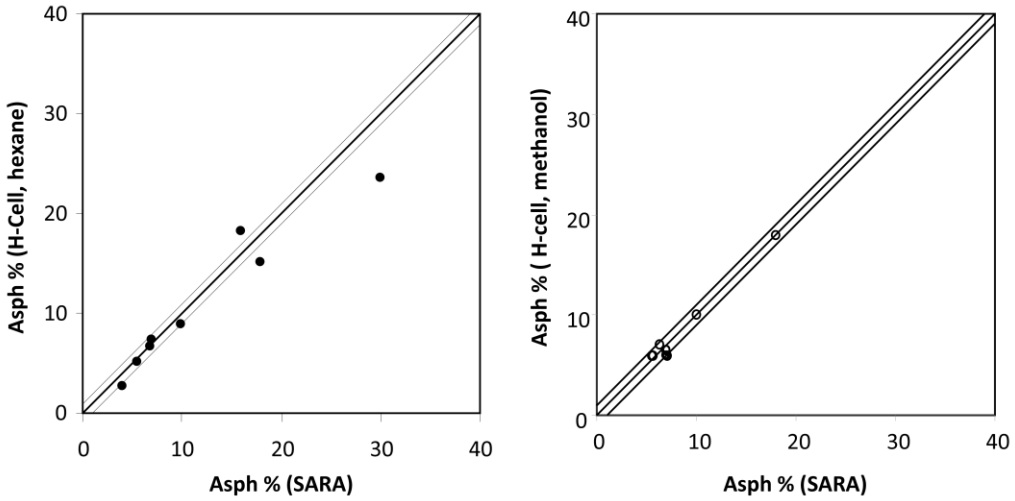

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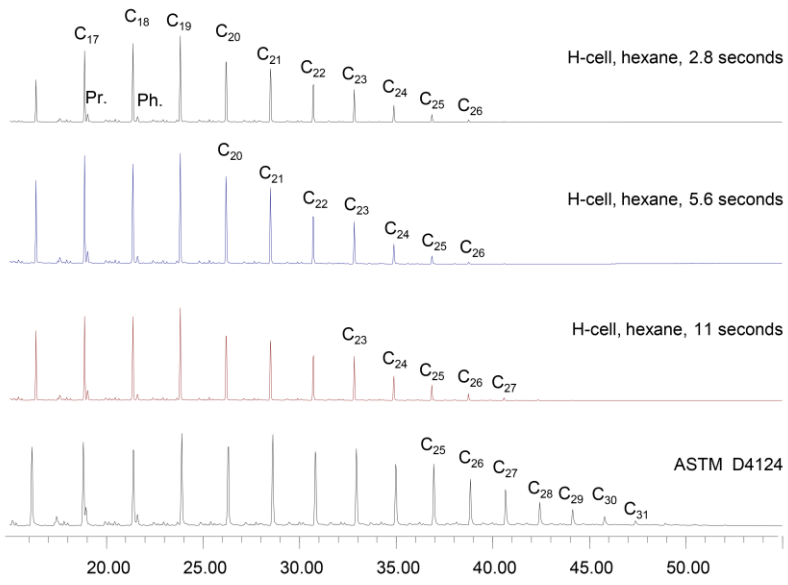

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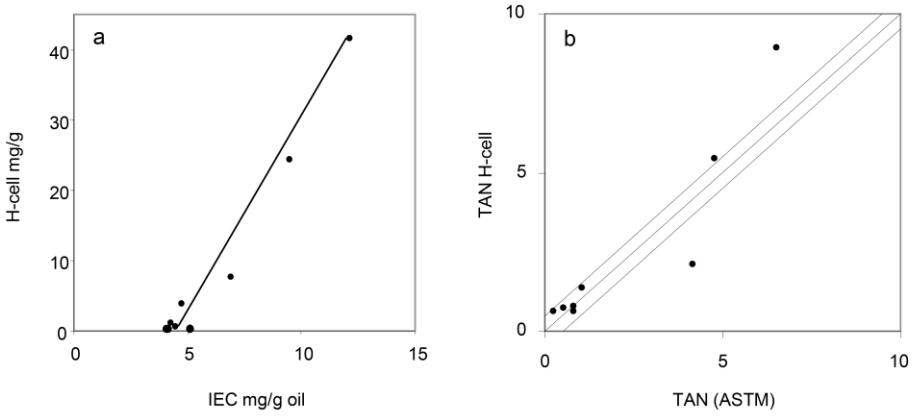

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Fig 7.

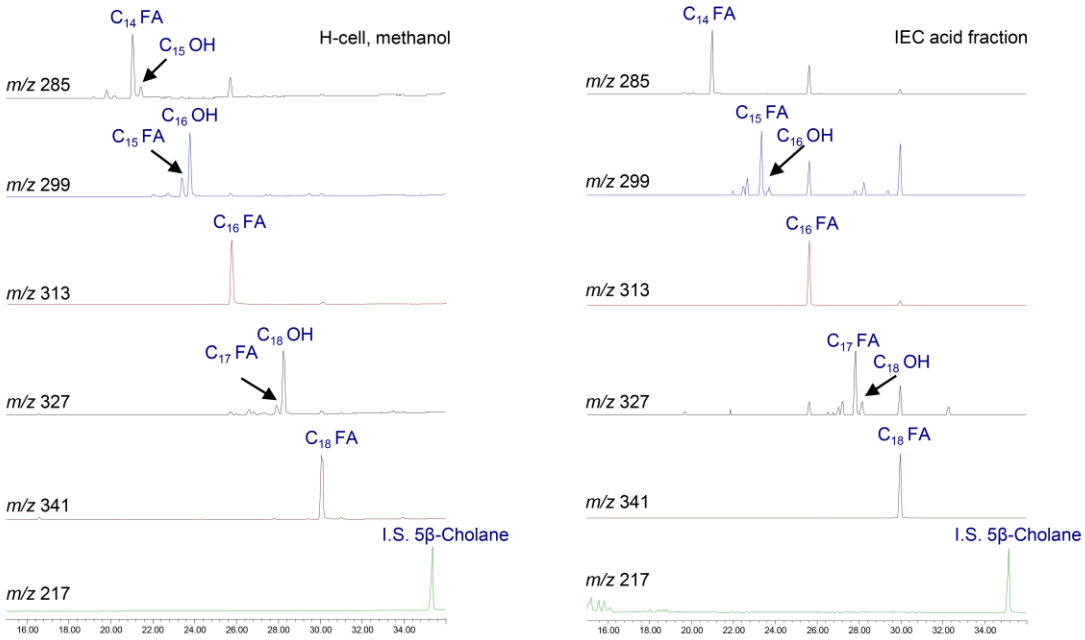

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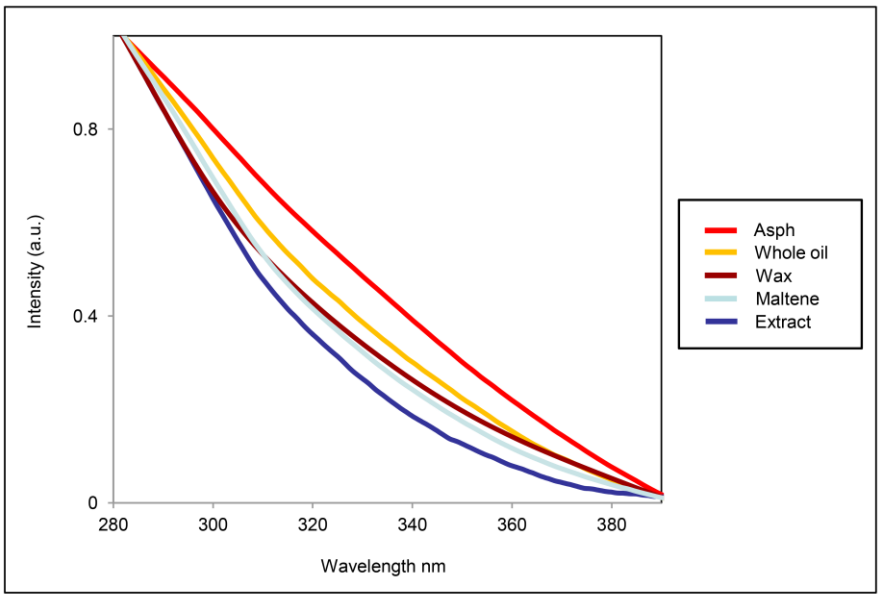
Fig 8.



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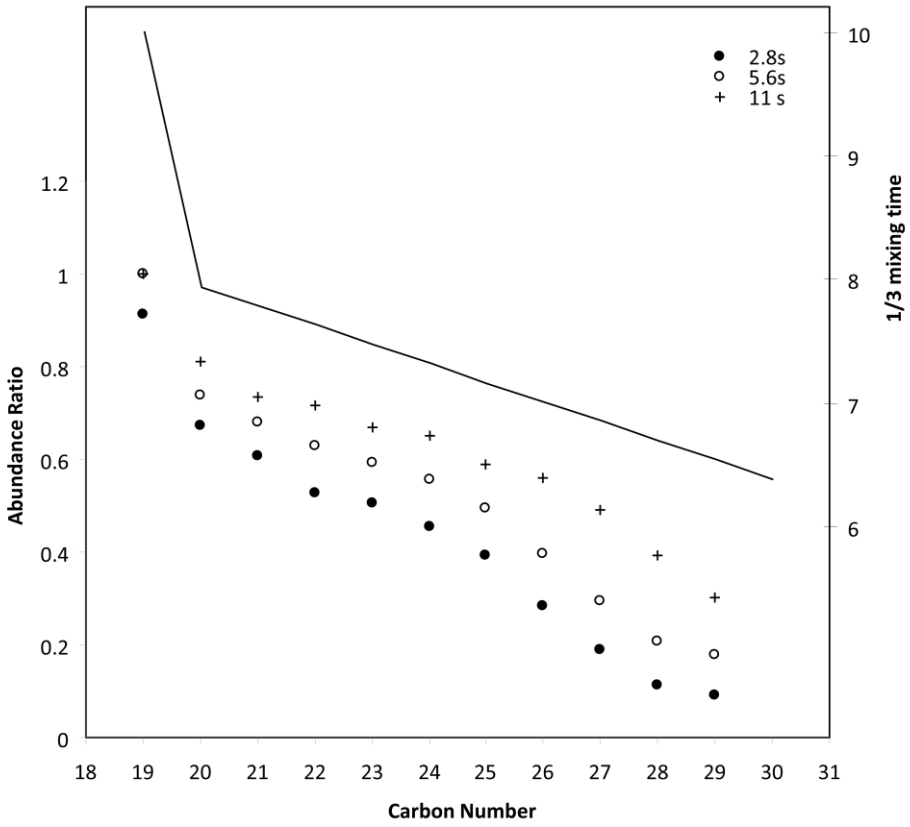

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