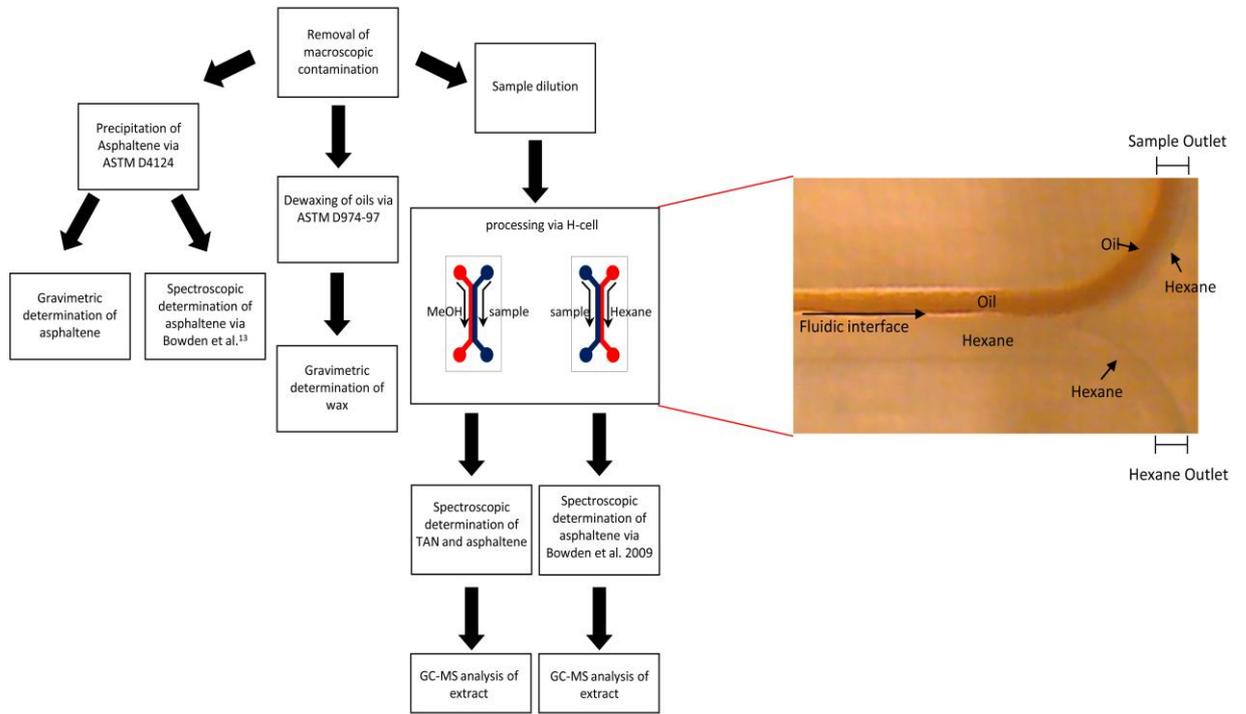


TABLE OF CONTENT ENTRY



2

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

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

20

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24

25 Abstract

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

47

48 1.0 Introduction

49 The fractionation of petroleum into its constituent parts falls into two basic
50 categories; thermally driven distillation processes applied in refining and
51 trading petroleum as a commodity and chemical methods applied to evaluate
52 oil and gain crucial technical information that can answer problems
53 encountered during oil exploration, production, transportation and
54 environmental remediation¹. Of the chemical assays reported for asphaltene
55 analysis, the SARA (Saturates, Aromatics, Resins and Asphaltenes) scheme
56 is currently at the fore¹⁻⁴. Standard methods for asphaltene analysis define
57 asphaltene as the component of petroleum that is insoluble when diluted with
58 an excess of *n*-alkane solvent; within ASTM D4124² this is hexane although
59 other solvents may be chosen¹.

60

61 A standard method for assaying the acidity of crude oil (ASTM 974-975) is the
62 Total Acid Number (TAN) – number of milligrams of potassium hydroxide
63 required to neutralise the acidity in a gram of petroleum. Particularly when
64 hydrogen sulphide is absent, it is the carboxylic acids (naphthenic acids)
65 present in petroleum that are often responsible for its acidic behaviour and
66 thus corrosion during petroleum transport, storage and refining⁶. Furthermore,
67 the carboxylic acids within petroleum may combine with salts to create
68 surfactants and emulsifying agents that are important for determining the
69 interaction of petroleum with aqueous phases⁷. Carboxylic and naphthenic
70 acids can be extracted from petroleum by ion exchange methods^{8,9}, and the
71 yields obtained generally, although not always, correlate with TAN number.

72

73 Complexity in handling and assaying petroleum derives from its chemical
74 heterogeneity, varying physical properties (e.g. viscosity and density) and the
75 sensitivity of methods to a wide range interferences (some of these factors are
76 described from the perspective of an oil field operative in the opening chapter
77 Mullins⁴). The latter can include non-petroleum and non-liquid materials, such
78 as inorganic minerals and compounds that become entrained within petroleum
79 during its production, refining and transport. The consequences of these are
80 that asphaltene data appears to have considerable noise and this can

81 produce notable variation in the application of methods between laboratories
82 – particularly with regard to TAN values⁹. The effect of this is the widespread
83 and prolific modification of methods to create a range of propriety-assays and
84 discipline specific methods. Examples of this include alternatives to the TAN
85 assay (Horvath-Gumulka test – Naphthenic Acid Number and Carboxylic Acid
86 Number¹), utilisation of different solvents for analytical handling of asphaltene
87 e.g. toluene or dichloromethane⁴, and the widespread use of heptane over
88 hexane by academic laboratories in preparing asphaltene-free fractions for
89 biomarker analysis¹⁰. Thus while assaying petroleum for sale as a commodity
90 mandates standardisation of assay formats (e.g. the use of ASTM methods)
91 day to day problem solving and research drives considerable analytical
92 development for what would generally be considered basic assays.

93
94 In this paper we investigate the application of an H-cell based method to
95 determine asphaltene and carboxylic acid content for a range of petroleum-
96 types. Within an H-cell, two fluids are flown in hard contact with each other,
97 and analytes are permitted to diffuse from one fluid to the other¹¹. To extract
98 specific fractions from petroleum previous work has used hexane¹² and
99 methanol¹³, but only for a limited number of samples. The asphaltene
100 assaying method used here^{12,13} is fundamentally novel in that it does not
101 strictly fall into either the thermal (evaporative) or chemical (chromatography
102 or solubility) based methods¹ for fractionating petroleum, instead it depends
103 on the varying rates of diffusion of different petroleum components within
104 liquids to achieve separation¹¹⁻¹³. For a range of sample types we have used
105 two assay formats; 1) one using hexane to determine asphaltene content and
106 2) another using methanol to simultaneously determine asphaltene content
107 and TAN number. Despite the potential of H-cell based methods, given the
108 inherently complex nature of petroleum and potential interferences, a key
109 need is to evaluate the robustness of the H-Cell methods when applied to a
110 range of heavy petroleum - both naturally occurring and anthropogenically
111 extracted from the subsurface. There is also a need to scope and document
112 the analytical window provided by H-cell methods with regard to petroleum,
113 and heavy petroleum.

114

115 2.0 Method

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

118

119 2.1 Samples

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

128

129 Two samples (Boa A & B) possessed high wax content. The wax component
130 of petroleum is known to be a significant interference during asphaltene
131 determination. To provide an assessment of this interference the sample was
132 split, and the aliquot dewaxed prior to further analysis. Wax was removed
133 from the waxy oils using the method detailed in ASTM D721-06¹⁴. Briefly; an
134 oil sample is dissolved in a 3:1 Methyl Ethyl Ketone/Toluene mix and cooled
135 to -32 °C. The precipitated wax is recovered by filtering the solution. The
136 percentage of wax filtrate retained on the filter was determined gravimetrically,
137 after it had been dried in a desiccator for 24 hours.

138

139 2.2 Asphaltene and SARA Analysis

140 The % asphaltene content of samples and SARA composition was obtained
141 using ASTM D4124². The oils were separated into component constituents of
142 asphaltene and maltene using excess hexane in a 1:40 oil/ hexane ratio.
143 Silica gel column chromatography was then used to separate the maltene
144 fraction into saturate, aromatics, and resin components. The amount of each
145 fraction, including the asphaltene fraction, was deduced gravimetrically.

146

147 2.3 TAN analysis

148 The ASTM D974-97⁵ method was used to perform total acid number
149 measurements. In summary, about 2 gram of oil is dissolved in 250ml conical
150 flask using 100ml solution of titration solvent (toluene 500ml, water 5ml and
151 propan-2-ol 495ml). P-Naptholbenzein solution was used as an indicator. The
152 mixture (a yellow-orange coloration) was titrated with potassium hydroxide
153 solution in small increments until the end point was indicated by a colour
154 change. A blank titration was performed and the Total Acid Number calculated
155 using the prescribed formula.

156

157 *2.4 Petroleum Acid Fraction Extraction - Ion Exchange Solid-Phase Extraction*

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

171

172 *2.5 Gas Chromatography-Mass Spectrometry*

173 GC-MS analysis was performed using an Agilent 6890N GC fitted with a J&W
174 DB-5 phase 50 m length column (0.25 mm id, 0.25 µm film thickness)
175 connected to a 5975 MSD and a quadruple mass spectrometer operating in
176 SIM mode (dwell time 0.1 s/ion and ionisation energy 70 eV). Samples were
177 injected manually using a split/splitless injector operating in splitless mode
178 (purge 40 ml min⁻¹ for 2 min). The temperature program for the GC oven was
179 80 – 295 °C, holding at 80 °C for two minutes, rising to 10 °C min⁻¹ for 8 min
180 and then 3 °C min⁻¹ and finally holding the maximum temperature for 10 min.

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

183

184 *2.6 Microfluidic Separation*

185 Microfluidic separation followed the method presented in Bowden et al.¹³
186 using an H-cell with the following channel dimensions: channel length 20 mm,
187 width 260 μm and 60 μm depth. Microfluidic chips were fabricated by Dolomite
188 microfluidics from sodalime glass. The H-cell was held in a Mitos chip
189 interface fitted with a multiflux 4-way linear connector. Heavy oils with API's <
190 23° were diluted with hexane to lower the viscosity and improve sample
191 manipulation (typical dilution factor of 1:5). Lighter oils (API's > 34°) were
192 analysed with limited dilution (1:1 to 1:0). Methanol and Hexane were used as
193 the extracting solvents and were pumped through the device with samples
194 introduced as slugs for discrete batch analysis and processing. Solvents were
195 pumped continuously through the microfluidic chip to establish optimal wetting
196 characteristics within the channel and limit interaction between the oil and the
197 sides of the channel (interface can occur via viscous effects caused by the
198 adsorption of asphaltene and wax precipitates on the sides of channels).
199 Three residence times were investigated; 2.8, 5.6 and 11.3 seconds –
200 residence time is a key operational parameter within a Y- or H-cell and
201 represents the maximum time that a particle will spend at the interface
202 between two fluid streams¹⁵. The ratio of the flow rates between petroleum
203 and extracting solvent was in the order of 1:6, this parameter governs the
204 separation of the fluid streams at the downstream-end of the H-cell. The
205 stability of the interface between the fluids was visually monitored at the down
206 stream end of the device during experiments (Fig. 2).

207

208 *2.7 Determination of asphaltene content by UV-Vis absorption spectra*

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

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

223

224 3.0 Results

225 *3.1 Comparison of spectroscopic and gravimetric determination of Asphaltene*

226 The H-cell based assay utilises differences in adsorption in the 290 to 410 nm
227 range for whole and asphaltene-free oils to determine asphaltene content ¹³.
228 This element of the assay was investigated separately from H-cell
229 parameters. It was found that a relatively high correlation ($r = 0.95$, $n = 13$
230 which is significant with an alpha value greater than 0.001) could be obtained
231 between the gravimetric and spectroscopic analysis of the products of ASTM
232 D4124² (Data shown in supplementary information 1). However, a notable
233 under-prediction occurred and the limit of detection was 4 %, e.g. when
234 gravimetric analysis returned 4 % asphaltene the spectroscopic method
235 presented in Bowden et al.¹³ detected no asphaltene. This is significant
236 because petroleum with an asphaltene content of 5 % would be considered
237 asphaltic.

238

239 The limit of detection was improved by aggregating the asphaltene spectra of
240 all twelve samples to produce an “averaged asphaltene spectra” in the range
241 290 to 410 nm. Results for this approach are shown in Fig. 3 and data
242 approach a 1:1 gradient, whilst the intercept of a straight line fitted to the data
243 suggests a minimum detection limit of less than 1 %. Variance in the data is
244 also well explained using this approach ($r = 0.97$, $n = 13$, which is significant
245 with an alpha value greater than > 0.001). At present we have not determined
246 the exact cause for this improvement, but it is likely that the improvement
247 achieved by using averaged asphaltene spectra reflects the difficulties
248 inherent to chemically separating and characterising a pure asphaltene

249 fraction of oil by ASTM D4124². Numerous studies have shown that
250 asphaltene subfractions can be highly variable and can contain many non-
251 macromolecular compounds that have little similarity to classic models of
252 asphaltenes but that can precipitate with an asphaltene fraction (e.g. non-
253 macromolecular heteroatomic compounds that are insoluble in hexane¹⁶).
254 Asphaltic oils would be expected to yield purer asphaltene, e.g. relatively
255 speaking they are less affected by interfering compounds. Averaged
256 asphaltene spectra were therefore used when analysing the products of H-cell
257 separations.

258

259 *3.2 Comparison of H-cell based measurement of asphaltene with ASTM* 260 *D4124*

261 Predictions of asphaltene content produced by the H-cell processing of oils
262 were compared to results obtained from ASTM D4124². The correlation
263 between the results of the standard and H-cell method, for all three H-cell
264 residence times using either hexane or methanol as the solvent, were
265 significant indicating that the different methods are at least comparable
266 (significant for an alpha value of 0.001, $r = 0.99$ and $n = 9$). Thus a calibration
267 of the standard ASTM method to the H-cell method can be achieved. Based
268 on the intercepts of straight-lines fitted to the raw data (Figure 4), the best
269 detection limits were obtained for residence times of 5.6 seconds; the limit of
270 asphaltene-detection when hexane was used was less than 1 % and when
271 methanol was used was less than 0.3%. (Data for other residence times is
272 shown in supplementary information 2 and 3 and results listed Table 1).

273

274 Asphaltenes are not the only high molecular weight and poorly soluble
275 component of petroleum that forms a solid precipitate. The wax components
276 of oil can variably co-precipitate with asphaltene during ASTM D4124² to
277 cause an erroneous assay. Waxes are held to be hydrocarbon compounds
278 with high molecular weights – typically saturated compounds such as *n*-
279 alkanes or structurally similar compounds. Asphaltenes are held to be
280 heteroatom-containing compounds, with an aromatic nucleus and a disputed
281 high molecular weight, (in excess of 550 amu⁴). The difference between the
282 two compounds classes is important because the factors that increase the

283 stability of one compound type may destabilise the other (for example
284 blending a waxy oil with lower molecular hydrocarbon compounds may help
285 solubilise wax but could destabilise asphaltene). Two waxy-oils were
286 processed (Boa A, 9.3% and Bob B, 13% wax). For a residence time of 5.6
287 seconds, a comparison of dewaxed and pristine samples (that still have their
288 wax content and have not been dewaxed via ASTM D721-06¹⁴) suggests that
289 waxy samples assay with 1.5 to 1 % more asphaltene than would be expected
290 (Table 1).

291

292 *3.3 Hexane extracts analysis*

293 In addition to permitting an analysis of asphaltene content the hexane extract
294 obtained by diffusive separation within an H-cell is effectively asphaltene-free
295 and readily amenable for GC-MS analysis¹². Ion chromatograms of the
296 hexane extracts and the saturate fraction (obtained via the SARA-scheme and
297 ASTM D4124²) of sample Brid E are compared in Figure 5. Superficially they
298 appear similar, expect that *n*-alkanes with a carbon number greater than
299 twenty nine are not prominent on the 85 *m/z* ion chromatograms of H-cell
300 extracts. Additionally, H-cell fractions with the shortest residence times have
301 the lowest abundance of higher carbon number *n*-alkanes. This could be of
302 concern when making use of petroleum-biomarker proxies and parameters
303 that utilise homologous series of compounds, as these parameters are
304 sensitive to differences of a single carbon number. Little variation in the
305 relative proportions of the acyclic isoprenoids pristane and phytane is observed
306 as a function of residence time, and similarly the proportion of these
307 isoprenoids relative to their neighbouring *n*-alkanes also varies little (Figure 5).
308 Thus when preparing a sample for GC-analysis, longer residence times would
309 be needed if the final focus of analysis was on higher carbon number
310 biomarkers such as hopanes or similar terpanes.

311

312 *3.6 Determination of TAN value using a methanol extract*

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

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

323

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

333

334 Previous work linking concentrations of naphthenic acids in petroleum to TAN
335 values^{9,17} has used correlations between IEC yields and TAN value rather
336 than concentrations of specific compounds. This is because the identification
337 of compounds types that contribute most to crude oil acidity has been
338 inconclusive – e.g. *n*-alkanoic acids have been shown to contribute little to the
339 proton donating ability of crude oil and therefore have little influence on TAN
340 value¹⁷. They were utilised in this study because of the highly diagnostic M-15
341 ions produced by BSTFA-derivatised alkanolic acids during electron impact
342 ionisation mass spectrometry. To convert methanol extract yields to a TAN
343 equivalent a straight-line equation derived from IEC-acid fraction yields and
344 TAN values was used^{8,9,17}. The TAN values obtained via ASTM D974-97⁵ are
345 compared to H-cell predictions of TAN value in Fig. 6b - see Supplementary
346 Information 5 for other residence times. There are notable outliers, but
347 generally, data fall in the same sequence as those determined via ASTM
348 D974-97⁵ (e.g. the most acidic sample determined via ASTM D974-97⁵ is the
349 most acidic sample according to the H-cell method).

350

351 4.0 Discussion

352 4.1 Precision and sensitivity of H-cell method

353 A residence time of 5.6 seconds has the most repeatable measurement (%
354 relative standard deviation of 19% compared to 25% for both 2.8 and 11.3
355 seconds and 34% for the SARA method) (Table 2). Low repeatability for
356 ASTM D4124² likely derives from difficulty in weighing small amounts of
357 asphaltene in asphaltene poor samples. Measurement accuracy of the H-cell
358 method is also indicated by limits of detection (Table 2), where as low as
359 0.05% asphaltene in oil can be detected depending on the solvent used.
360 Sensitivity for asphaltene prediction is higher for methanol than for hexane.
361 Repeatability of TAN data is best at 11.3 seconds compared to other
362 residence times (although reasonable for 5.6 seconds) (table 2) but low when
363 compared to ASTM D974-97⁵. H-cell method appears sensitive at detecting
364 very low acid concentrations in oils, typically detecting acid content which can
365 be equivalent to as low as ~0.001mg of potassium hydroxide per gram of oil
366 however; this is a combined assay for both acids and alcohols.

367

368 4.2 Other considerations

369 For conventional asphaltene determination, the wax content of crude oil is a
370 known potential interference because of the formation of microcrystalites of
371 wax¹⁸. Previous work suggested that the formation of large asphaltene
372 aggregates that, in common with wax crystalites are a solid phase, are larger
373 and slower diffusing than their constituent molecules, did not impinge on the
374 production of an asphaltene-free fraction and thus asphaltene determination
375 via an H-cell¹². The results presented here suggest that waxes within oils
376 interfere slightly in the determination of asphaltene content; a 1 to 1.5 % over
377 estimation of asphaltene content was found for waxy oils. This over estimation
378 is relatively minor; by way of example, this is less than the error introduced by
379 various oil field sampling methods¹⁹, but significant within the context of the
380 generally high accuracy seen in Fig. 4 and table 2. The main cause of over
381 estimation is that wax compounds, as straight chain *n*-alkanes, contribute to
382 the spectra of the whole oil in a similar way to the saturate fraction of a non-
383 waxy oil (Fig. 8). Fig. 9 presents diffusive mixing times for *n*-alkanes within the
384 H-cell, and from this it could be concluded that both waxes and particularly

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

391

392 Unlike ion exchange chromatography, an H-cell, using methanol as an
393 extracting solvent, does not separate *n*-alkanoic acids from mixtures
394 containing *n*-alkanols and *n*-alkanoic acids (Fig. 7). The effects created by the
395 presence of *n*-alkanols within methanol extracts can be adjusted by using the
396 straight line relationship shown in Fig. 6a to recalibrate results. Thus from the
397 perspective of producing a proxy for TAN, the presence of alcohols in
398 methanol-extracts is not a significant interference. However alcoholic
399 compounds such as phenols despite being classed as corrosive have not
400 been shown to be significant contributors to TAN value in the same way as
401 carboxylic acid species¹⁷. Compounds such as phenols, although not detected
402 in the small volumes analysed by GC-MS in this instance, would be expected
403 to partition to the methanol phase of an H-cell extract. Longer term, this
404 aspect of the H-cell separation procedure could be developed to try and
405 obtain a broader spectrum assay for polar compounds in petroleum.

406

407

408 *4.3 Applications*

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

419 mats). These intervals, aside from containing immobile bitumen may even
420 constitute barriers to flow, can be identified by a simple chemical assay²¹.
421 Aside from this special case, it is also not uncommon for subsurface
422 accumulations of petroleum to be the product of complex filling histories – e.g.
423 oil of different types migrated to its current position at varying times, and was
424 then variably altered in different regions of the subsurface²²). Chemical
425 assays (notably asphaltene content) are often a viable and far less costly
426 proxy for identifying and characterising variation than physical measurements.
427 More recently the role of organic acids within petroleum in influencing wetting
428 behaviour and the final level of oil recovery has been highlighted by laboratory
429 studies²³. Therefore the simultaneous and rapid measurements of both
430 asphaltene and acid content would be extremely useful for appraising oilfield
431 potential and in particular what fraction is ultimately recoverable.

432

433 Further into the life of an oilfield, the actions (workovers) initiated by operators
434 to improve oil production often result in transient changes in the composition
435 of produced fluids e.g. increased concentrations of corrosive surfacting agents
436 or asphaltene as a consequence of the removal of blockages⁶. Chemical
437 measurements performed at point of need could help engineers identify when
438 the deleterious effects of such interventions had abated. Similar benefits could
439 also be envisioned for point of need assays performed for the purposes flow
440 assurance in refineries.

441

442 For natural and environmental science applications, the asphaltene and TAN
443 number are useful because changes in both parameters can be linked to oil
444 degradation. Asphaltene is the recalcitrant proportion of petroleum and thus
445 within spilled petroleum asphaltene concentrations rise as other components
446 are degraded²⁴. Organic acid concentrations initially rise as oil is degraded,
447 likely because of a contribution from hydrocarbon-metabolites formed by
448 microbial activity. In the terminal stages of petroleum degradation the
449 concentration of organic acids has been observed to decrease²⁵. Repeated
450 simultaneous measurements of asphaltene and TAN values via an H-cell
451 would therefore record the attenuation of oil-spills and possibly help
452 differentiate fresh from degraded petroleum. Measuring the asphaltene and

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

455

456 5.0 Conclusion

457 An H-cell based method for separating heavy petroleum can be optimised to
458 yield proxy measurements of asphaltene and the carboxylic acid content of
459 petroleum (which can be expressed as a TAN value). Detailed analysis of the
460 extracts produced by the H-cell demonstrates that the method, because it
461 utilises microscaled diffusion, provides an analytical window that is inherently
462 different to distillation and chemical based methods for assaying heavy
463 petroleum, The H-cell method gives better accuracy for measuring asphaltene
464 when compared to a gravimetric-based methods like ASTM D4124². The
465 capability of this technique to provide rapid simultaneous TAN and asphaltene
466 proxy measurements has the potential to impact both petroleum and
467 environmental science.

468

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544 Figure captions

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

548

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

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

557

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

561

562 Figure 4: Comparison of percentage asphaltene predicted by the H-Cell
563 method with ASTM D4124². LHS – analyses using hexane as the extracting
564 solvent and for a residence time of 5.6 seconds; RHS – analyses using
565 methanol as the extracting solvent and for a residence time of 5.6 seconds.

566

567

568 Figure 5: m/z 85 Ion chromatograms of the H-cell hexane extracts and
569 hydrocarbon fraction yielded by ASTM D4124². Data are shown for sample
570 Bride E for the H-cell residence times indicated. Carbon numbers correspond
571 to those of the n-alkane homologous series.

572

573 Figure 6: a) Comparison of the yield of methanol extractables at 5.6 seconds
574 with acid-fraction yields obtained by ion exchange chromatography⁸. b) Acid
575 fraction yields at 5.6 seconds expressed as TAN values using approach
576 presented in Borgund, et al.⁹, and Meridith, et al.¹⁷ with TAN values obtained
577 by ASTM D974-97⁵.

578

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

582

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

586

587 Figure 9: Scatter plot of the relative abundance of *n*-alkanes in H-cell extracts
588 (relative to the abundance of the compound in the fraction produced by
589 column chromatography) plotted by carbon number. Also shown is the
590 calculated diffusive mixing times¹⁵ shown for key *n*-alkanes.

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Table 1: Sample Descriptions and Analysis Details

Sample*	Type [†]	API ^{††}	TAN mg KOH/g	Wax %	Asph ₁ [‡] %	ICE acid fraction* mg/g oil	H-cell analyses [°] (%)									
							Dilute [°]	RT: 2.8			RT: 5.6			RT: 11.3		
								Hex	MeOH	Hex	MeOH	Hex	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 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.	

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*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, except 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.

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Table 2: Precision and Sensitivity

Method	RT(s)	RSD (%)		LoD		
		Asph	TAN	Asph%	Methanol	TAN
				Hexane		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			

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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.

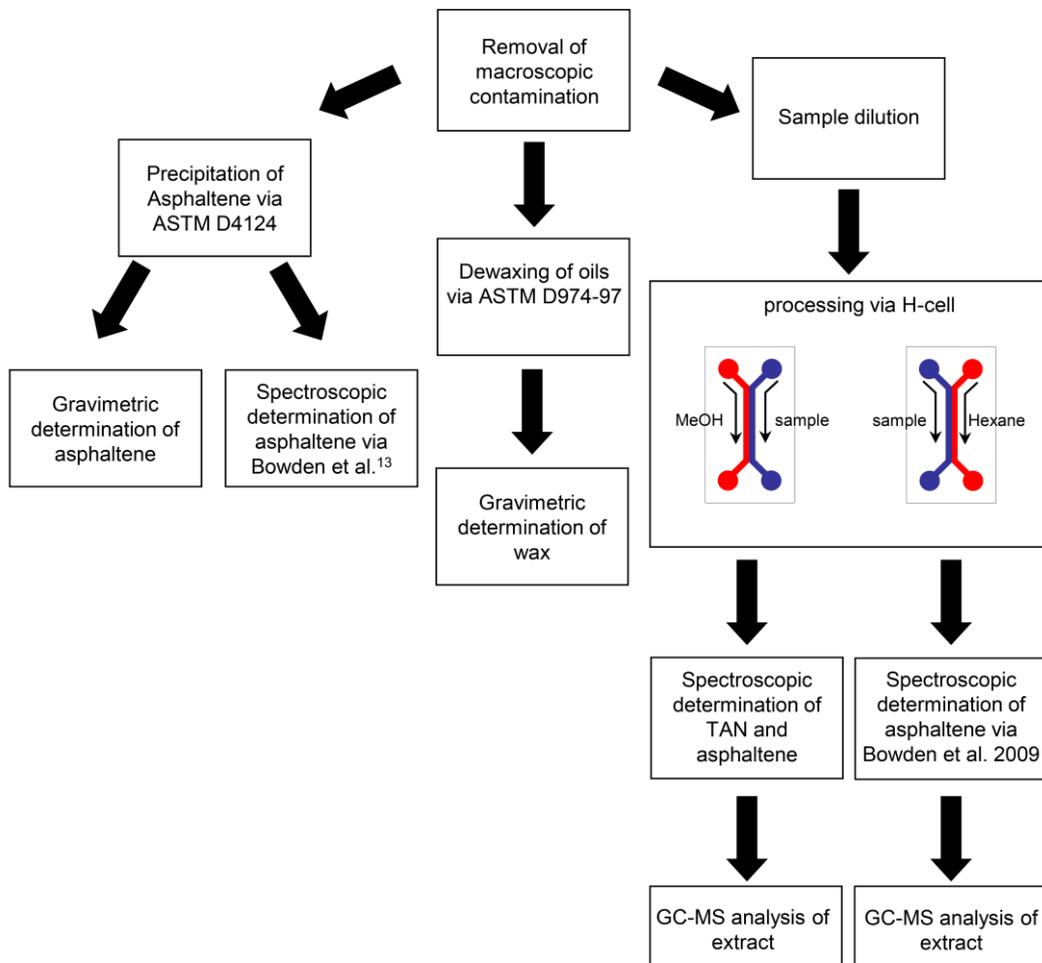


Fig 2.

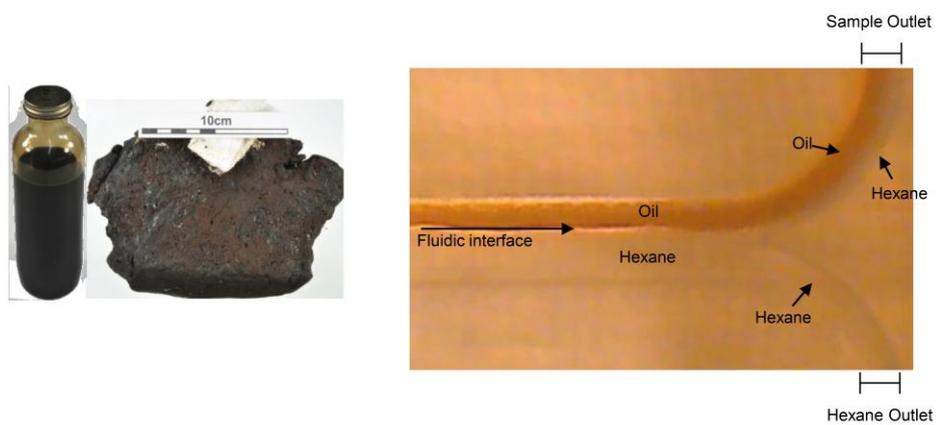


Fig 3.

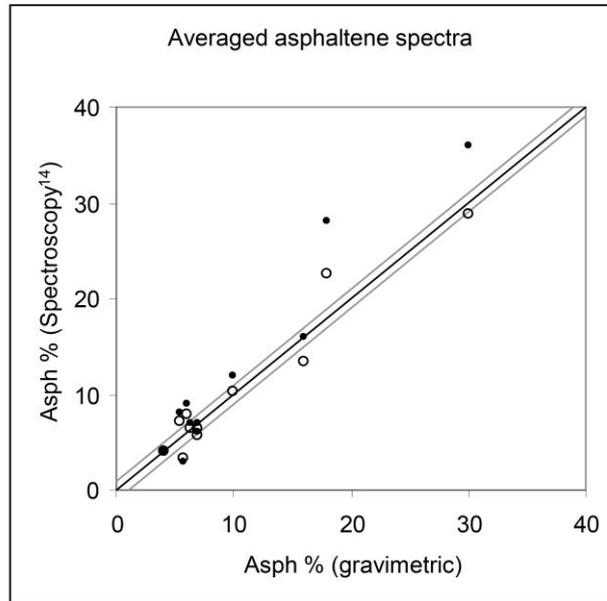


Fig 4.

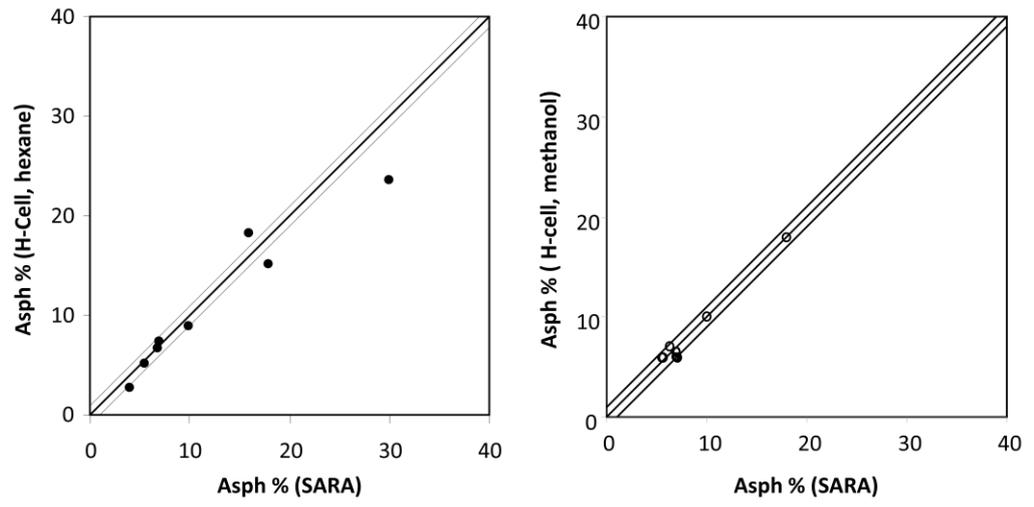


Fig 5.

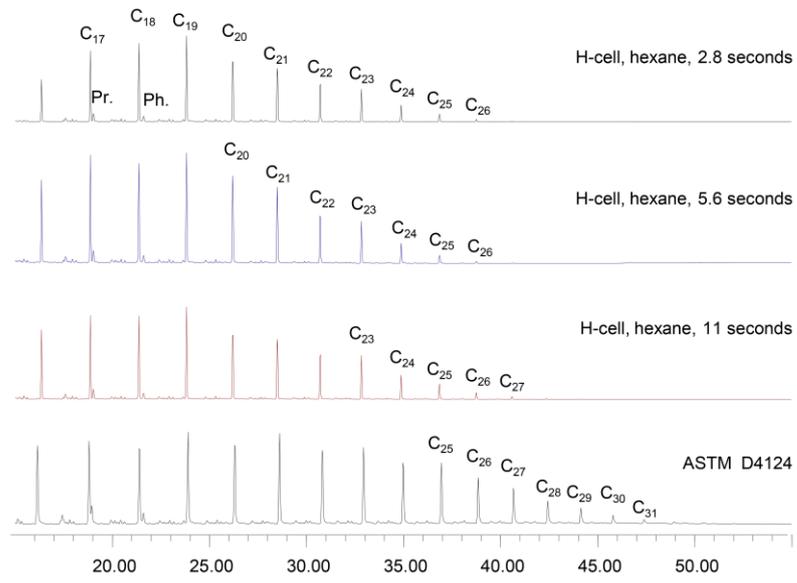
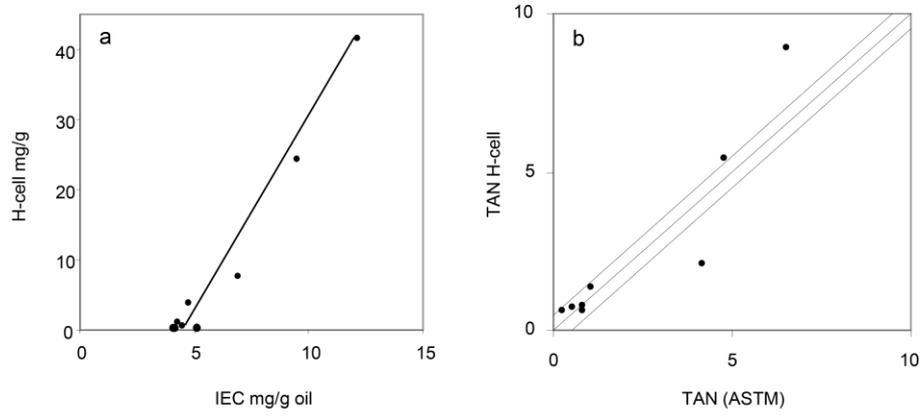


Fig 6.



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Fig 7.

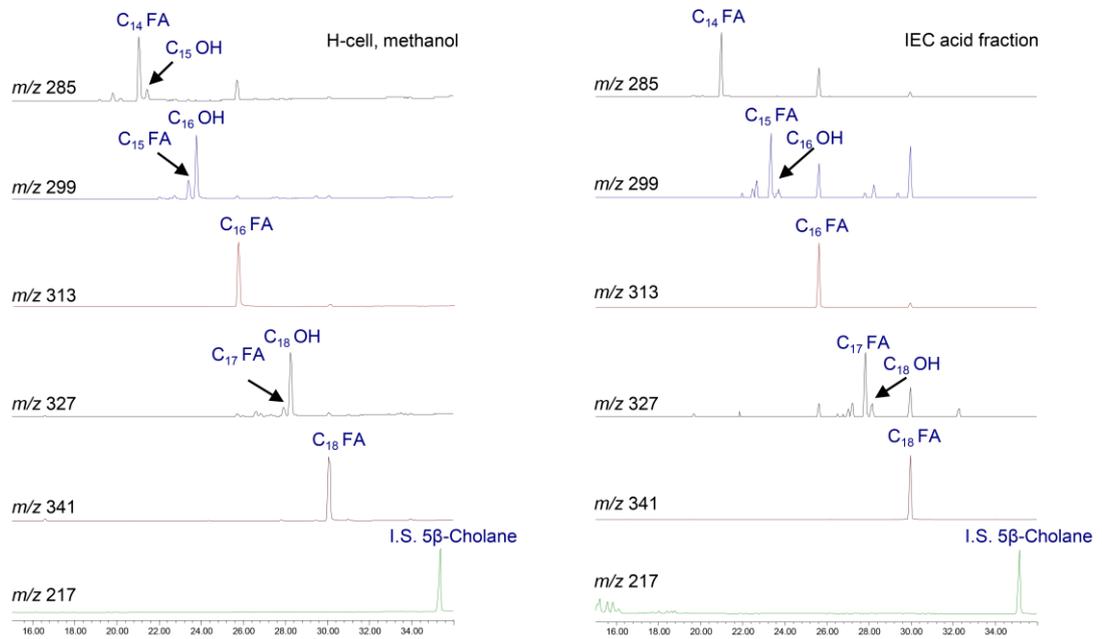


Fig 8.

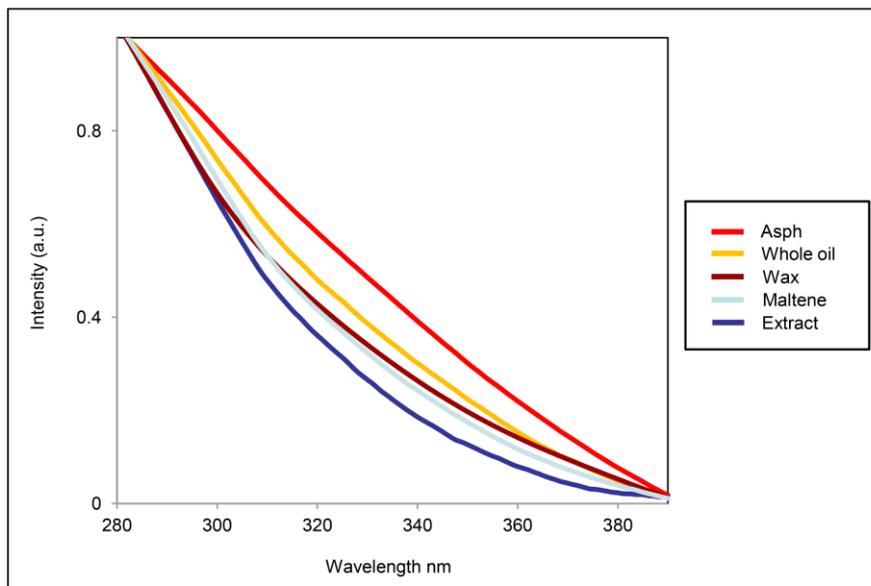


Fig 9.

