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Phenol-selective mass spectrometric analysis of jet fuel†

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Bromobenzyl compounds react selectively with phenols *via* the Williamson ether synthesis. An imidazolium charge-tagged bromobenzyl compound can be used to reveal phenol impurities in jet fuel by analysis *via* electrospray ionization mass spectrometry. The complex matrix as revealed by Cold EI GC/MS analysis is reduced to a few simple sets of compounds in the charge-tagged ESI mass spectrum, primarily substituted phenols and thiols. Examination of jet fuels treated by different refinery methods reveals the efficacy of these approaches in removing these contaminants.

Introduction

Phenols are a class of compound found within petroleum at variable concentrations, depending on the provenance of the crude oil. Jet fuel (b.p. range 170–270 °C) is the petroleum fraction most likely to encounter phenol contamination (phenol itself has a boiling point of 182 °C), and phenols are particularly problematic in the formation of jet fuel surface deposits.[1] Phenols are the major oxygen-containing chemical and corrosion source in jet fuel,[2] but their analysis is a significant challenge due to their structural similarity and low relative concentration.[3] In order to facilitate the selective detection of phenols in petroleum fractions, a variety of approaches have been tried, with mass spectrometry being especially popular.

Gas chromatography/mass spectrometry (GC/MS) is a standard analytical method for phenols. Acidic compounds including phenols are usually derivatized prior to GC/MS analysis, by a range of different processes including silylation,[4] microwave-assisted silylation,[5] acylation,[6] alkylation[7] and esterification,[8] among others.[9] Ferrocenecarboxylic acid chloride was reported to react with phenols and the resulting esters were detected by GC with atomic emission detection (AED) in the iron-selective detection mode.[10] Shi and co-workers also successfully applied negative-ion GC/APCI-MS to determine phenolic compounds in coal tar samples.[11] The complexity of petroleum products has also led to GC × GC methods being applied to their study with good success.[12]

A two-step derivatization of alcohols into charged ammonioacetyls by reaction with bromoacetylchloride and amines has been reported as an effective means of producing intense signals in MALDI mass spectra.[13] 1,2-Dimethylimidazole-4-sulfonyl chloride (DMISC) has been shown to react selectively with phenol, and the products exhibited improved sensitivity in LC/ESI-MS studies.[14] DMISC was similarly employed to analyse 1-hydroxypyrene in human urine.[15] Flow injection analysis coupled with acetic anhydride acetylation of phenols in a K_2CO_3-buffered alkaline medium followed by membrane introduction mass spectrometry enabled fast, accurate and sensitive quantitation.[16] CO_2 laser ablation of the frozen water matrix, followed by resonance-enhanced multiphoton ionization technique coupled with reflectron time-of-flight mass spectrometry, has been applied to the analysis of water polluted with phenol molecules.[17]

Petroleomics as a discipline arrived soon after Fenn first analyzed a petroleum sample with ESI-MS,[18] revealing the extreme complexity of the polar components of such mixtures. Ultra-high resolution spectra, obtainable on high-field FTICR machines, are capable of separating literally thousands of elemental compositions present in petroleum, both polar (using ESI-MS) and non-polar (field desorption and atmospheric pressure photoionization, among others).[19] Such analyses pick out all abundant components, including phenols, but are not routine unless one has access to an FTICR instrument, which remain relatively rare. These analyses do not distinguish different types of compound, so something with the formula $C_xH_yO_z$ with 4 or more double bond equivalents might not be a phenol – it could be an alcohol, an ether or a carbonyl-containing compound.

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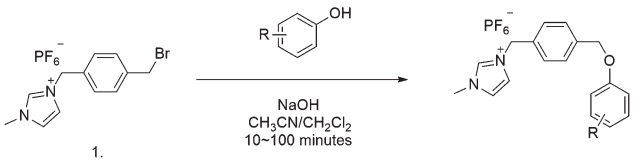
A host of non-mass spectrometric methods has determined the concentration of phenols in complex matrices. Electron capture gas chromatography was used in conjunction with α-bromo-2,3,4,5,6-pentafluorotoluene derivatization to determine phenols and mercaptans in river water.[20] Total phenolics in wine and other extracts were determined by the Singleton–Rossi method (colorimetry with phosphomolybdic/phosphotungstic acid reagents) as early as 1965.[21] An amperometric biosensor based on covalently immobilized tyrosinase on the surface of graphite electrode was described for the selective detection of phenol and several phenolic compounds in a flow system.[22] Various extraction methods, such as two-trap tandem extraction[23] or two-step liquid–liquid extraction,[24] were used in conjunction with HPLC analysis for determining phenols in water samples. A resonance light scattering (RLS) method involving the use of graphene quantum dots (GQDs) successfully analyzed phenols in different types of industrial water.[25] UV/Vis spectroscopy detected phenols in wastewater.[26]

Ultimately, several of these techniques have proven less selective than required for the analysis of phenolic species in the highly complex matrix of petroleum fractions.[27] Trace impurities exist within finished product from a refinery[28] such as thiols, naphthenic acids, alcohols, alkylphenols, and amines.[29] As such, the ideal technique for the analysis of phenolic constituents of petroleum fractions should be both resilient to interaction with other functional groups, as well as sensitive and quantitative with the application of a suitable method. An early effort to develop derivatization methods for selective ESI-MS analysis of phenols involved the use of dansyl chloride (5-(dimethylamino)naphthalene-1-sulfonyl chloride), which has been shown to form a sulfonate with phenol species which may then protonated under slightly acidic conditions for detection *via* mass spectrometry.[30] It has been reported that dansyl chloride will also derivatize thiols, so the resulting mass spectrum required careful interpretation. Beyond this difficulty, the addition of acid alone may result in a highly complex spectrum due to the abundance of basic amines or other oxygen-containing molecules present within the sample. Dansyl chloride derivatization of chlorophenols followed by sensitive and specific LC-MS/MS detection has been reported.[31]

Another method to detect phenols is simply through exploitation of the acidity of the hydroxyl group. With strong base, deprotonation produces a phenolate detectable in the negative ion mass spectrum. Early attempts using a variety of bases have shown some success using sodium or potassium hydroxide as the base of choice.[32] Strong bases also deprotonate alcohols, thiols, and (especially) naphthenic acids present in the fraction, and the lack of selectivity using this approach poses a problem for MS analysis.

Here, we investigate the use of a imidazolium-based charged tag (**1**) that reacts with phenols *in situ* for mass spectrometric detection in the positive ion mode (eqn (1)). The charge-tagged derivatization approach enhances analyte signal by producing very high ionization efficiency, thanks to high surface activity of the cation and reduced ion pairing thanks to the non-coordinating anion.



(1)

This reaction is an *O*-alkylation of the phenol, a reaction that is fairly slow with weak bases[33] but that can be accelerated with stronger ones. It is an example of a Williamson ether synthesis,[34] a reaction that is largely free from side reactions and whose kinetics can be altered readily through manipulation of solvent and base.[35] The reaction proceeds *via* S_N2 displacement of an alkyl halide by an alkoxide (in this case a phenoxide). We designed the charged tag to be remote from the reactive site (the C–Br bond) and unreactive towards base or any other competing side reactions. Additionally, these imidazolium-type charge tags exhibit high surface activity because of their bulk and hydrophobicity, and we have paired them with a non-coordinating anion to reduce the strength of ion pairing. The Williamson ether synthesis is much faster for phenols than for alcohols, and as such acts as a selective reagent for the derivatization of phenols (so much faster that the synthesis of the charged tag was performed in methanol, with no appreciable reactivity). The approach is similar to one we took for the selective analysis of thiols, wherein we employed a charge-tagged disulfide.[36]

Experimental

Chemicals and solvents were purchased from Aldrich and used without subsequent purification. Jet fuel samples were gifts of the Imperial Oil Products and Chemicals Division (Sarnia, Canada). ^{1}H NMR spectra were obtained on a Bruker 300 MHz instrument as $CDCl_3$ and CH_3OD solutions. ESI-MS of synthetic products were collected in the positive ion mode on a Waters Micromass Q-TOF *micro* mass spectrometer using solutions prepared in HPLC grade acetonitrile and dichloromethane. Capillary voltage: 3000 V. Cone voltage: 16 V. Extraction voltage: 0.5 V. Source temperature: 90 °C. Desolvation temperature: 190 °C. Cone gas flow rate: 100 L h^{-1}. Desolvation gas flow: 200 L h^{-1}. Collision voltage, 2 V (for MS experiments); collision voltage, 2–80 V (for MS/MS experiments); microchannel plate detector (MCP) voltage, 2700 V. The instrument provides resolution of approximately 6000 FWHM at m/z 500 and is calibrated routinely to <10 ppm using a sodium iodide calibration solution. Pressurized sample infusion (PSI) experiments used identical instrument settings. For PSI experiments, the reaction vessel was pressurized using 3 psi of nitrogen. A magnetic stirring hot plate and stir bar provided stable reflux conditions. Mass-to-charge ratio values were calculated using chemcalc.org.[37]

Cold EI GC/MS data were obtained on an AXION iQT GC/MS instrument from PerkinElmer (Waltham, Massachusetts,

USA) which equipped with a Clarus 680 gas chromatograph from PerkinElmer (Waltham, Massachusetts, USA). The mass spectrometer was tuned using perfluorotributylamine (PFTBA) solution. The injector is programmable split/splitless (PSS) injector connected with a PerkinElmer Elite™-5MS (PerkinElmer, length 30 m, inner diameter 250 mm, film thickness 0.25 μm) non-polar capillary column cross-bonded with 5% diphenyl/95% dimethyl polysiloxane. The jet fuel sample X1 was diluted 100 times with hexane before analysis. The sample (0.5 μL) was injected at 220 °C, the temperature program in the GC oven was 40 °C for 1 minute, followed by ramping at 20 °C min^{-1} to a final temperature of 260 °C, which was held for 1 minute. The transfer line temperature was 250 °C and source temperature was 200 °C. Make up gas flow was 50 mL min^{-1}. Axion eCipher software was used for post processing data application for identification of compounds.

The final reaction solution in the PSI experiment was collected and diluted to 10 ppm using HPLC grade acetonitrile. The diluted reaction solution was analysed in the positive ion mode on an Exactive Plus Orbitrap Mass Spectrometer from Thermo Fisher Scientific (Waltham, MA, USA) using the integrated syringe pump. The mass spectrometer was tuned using a proprietary calibration mix solution (Thermo Fisher Scientific, Waltham, MA, USA) for each ionization mode. Flow rate was set to 50–100 μl min^{-1}, ESI spray voltage was set to 3.5 kV and capillary temperature was set to 250 °C. Sheath and auxiliary gas flow rates and auxiliary gas temperature were set to obtain stable ion fluxes, resulting in values of ~30, 10 and 175 °C respectively. Automatic gain control (AGC) target was set to 1e6 with 50 ms max injection time and TIC variation was <13%. Data was collected over the mass range of *m*/*z* 133–2000 in the profile mode.

3-(4-(Bromomethyl)benzyl)-1-methylimidazolium hexafluorophosphate, 1

1-Methylimidazole (0.46 mL, 5.77 mmol, 99% Sigma-Aldrich) was reacted with excess α,α′-dibromo-*p*-xylene (2.049 g, 7.76 mmol, 97% Sigma-Aldrich) through gentle reflux under argon for about 14 hours in 50 mL of THF, a synthesis based on a standard laboratory preparation of imidazolium-based ionic liquids.[38] A white powder was recovered from acetonitrile through vacuum filtration and vacuum dried for 1 day. The 3-(4-(bromomethyl)benzyl)-1-methylimidazolium bromide (0.220 g) and 25 mL of 50% (v/v) aqueous methanol were added to a round bottomed flask, followed by sodium hexafluorophosphate (0.330 g). The solution was stirred for 12 hours. A white powder was recovered from the reaction solution *via* vacuum filtration. 0.686 g (yield = 28.9%) of final product was obtained. NMR data ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 3.93 (s, 3H), 4.59 (s, 2H), 5.41 (s, 2H), 7.61–7.40 (m, 6H), 8.95 (s, 1H). QTOF ESI(+): $[M]^+$ *m*/*z* 265.1; ESI(−): $[M]^-$ *m*/*z* 145.1.

1-Methyl-3-(4-(phenoxymethyl)benzyl)-1*H*-imidazol-3-ium hexafluorophosphate(v), 2

3-(4-(Bromomethyl)benzyl)-1-methylimidazolium hexafluorophosphate (0.100 g, 0.243 mmol) was reacted with excess phenol (0.0343 g, 0.365 mmol, 1.5 eq.) and excess sodium hydroxide (0.194 g, 4.86 mmol, 20 eq.) in a round bottom flask at room temperature for 30 minutes in 5 mL acetonitrile. The reaction solution was filtered and the filtrate was vacuum dried and washed by ether and vacuum dried. The powder was redissolved in a minimum amount of acetonitrile and white crystals were precipitated after leaving the solution at 4 °C overnight. The crystals were recovered from reaction solution through vacuum filtration, yield 17%. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 3.90 (s, 3H), 5.05 (s, 2H), 5.29 (s, 2H), 6.94–7.50 (m, 11H), 8.64 (s, 1H). QTOF ESI(+): $[M]^+$ *m*/*z* 279.4.

ESI-MS reaction monitoring using pressurized sample infusion

As described elsewhere,[39] a 20 mL Agilent headspace vial was filled with 15 mL of an acetonitrile/CH_2Cl_2 mixture (v/v = 4 : 9) and between 20–30 equivalents of sodium hydroxide. The vial was equipped with a magnetic stir bar, and a rubber stopper wrapped with Taegaseal PTFE tape. PEEK tubing was fed from the vial to the ESI-MS source and the headspace vial pressurized using 3 psi of nitrogen gas. The solution was stirred without heat using a magnetic stirrer. 2 mL of the analyte solutions of interest were injected *via* syringe.

Results and discussion

Cold EI GC/MS analysis

Before analyzing samples using the charge-tagging approach, we characterized the samples of interest using a well-established mass spectrometric approach. However, the GC/MS spectrum is sufficiently dominated by the hydrocarbons that the small amounts of phenols and other functionalized molecules could not be picked out in this simple analysis (ESI Fig. S3†), and distinguishing them would require the application of ultra-high resolution mass spectrometry or GC × GC methods.

Synthesis and characterization of charged tag 1

The charged tag used in this study was prepared by alkylation of methylimidazole using 1,4-di(bromomethyl)benzene. Salt metathesis of the resulting bromide with $NaPF_6$ generated the more soluble hexafluorophosphate salt. In the presence of base and a phenol, this compound produces an aryl ether (eqn (1)). Both the charged tag (**1**) and the product of its reaction with phenol (**2**) were fully characterized, including by X-ray crystallography (Fig. 1, and ESI Tables S3–S15†).

We conducted a variety of experiments to determine the reactivity of the tag towards different phenols: phenol, *o*-cresol, 2,3-dimethylphenol, 1-naphthol and 2,4-dimethylphenol (Fig. 2). The limit of detection was determined to be 8 μM for phenol and the limit of quantitation for the same analyte to be 30 μM (see ESI† for more details).

The fastest reacting phenols were 1-naphthol and the two dimethylphenols (2,3- and 2,4-). All three of these reactions were complete within 10 minutes and exhibited pseudo-first

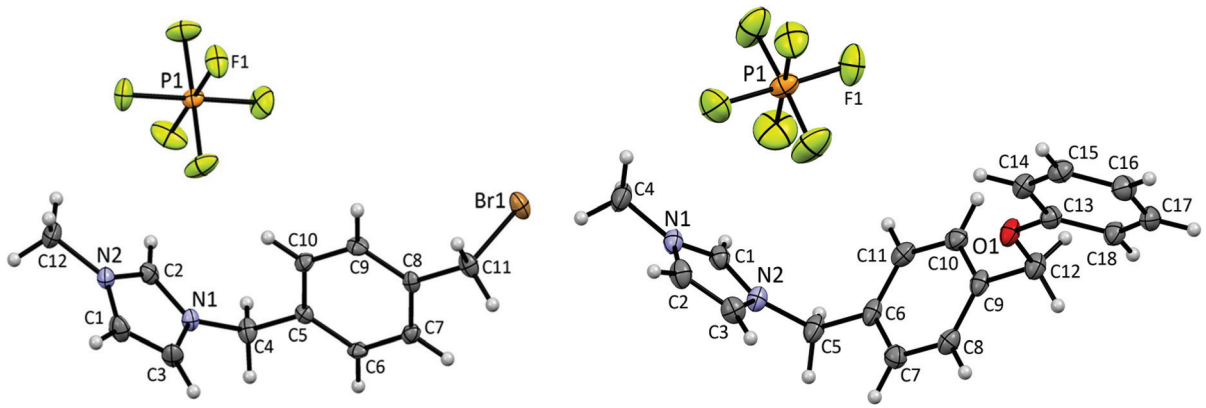


Fig. 1 Left: X-ray crystal structure of charged tag **1**. Key bond lengths and angles: average P–F: 1.5908(18) Å; N1–C1: 1.327 (3) Å; N1–C2: 1.373(3) Å; N1–C4: 1.462 (3) Å; N2–C1: 1.317(3) Å; N2–C3: 1.364(4) Å; N2–C12: 1.469(3) Å; Br1–C11: 1.971(3) Å; C8–C11–Br1: 109.88(17)°; N1–C4–C5: 112.0(2)°. Right: X-ray crystal structure of the product of the reaction between the charged tag and phenol, **2**. Key bond lengths and angles: average P–F: 1.5845(2) Å; N1–C1: 1.319(3) Å; N1–C2: 1.372(4) Å; N1–C4: 1.459(4) Å; N2–C1: 1.325(4) Å; N2–C3: 1.380(4) Å; N2–C5: 1.472(3) Å; O1–C13: 1.371(3) Å; O1–C12: 1.435(3) Å; O1–C13: 1.371(3) Å; C13–O1–C12: 117.6(2)°; N2–C5–C6: 111.6(2)°.

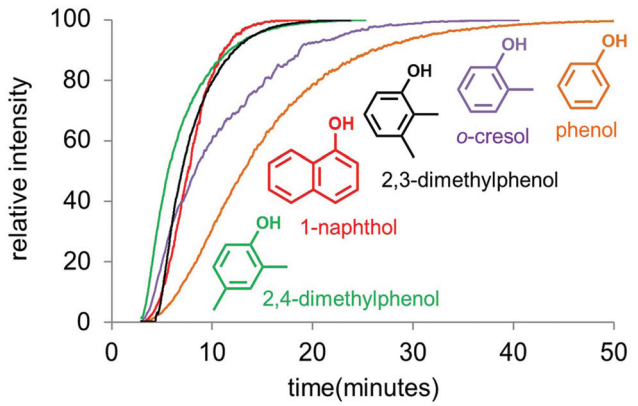


Fig. 2 Increase in *O*-alkylation products over time, monitored in real time by pressurized sample infusion ESI-MS.

order kinetics. The *ortho*-cresol was slightly slower (first order, but complete in 20 minutes) and phenol was the slowest (also first order, but complete in 30 minutes). Clearly, the steric bulk of the substituents exert little influence on the reaction, but the electronic properties of the phenol do seem to be important. The more electron-rich the phenol, the faster the reaction, because the basicity of the phenol parallels its efficacy as a nucleophile (*i.e.* the less acidic the phenol, the faster the reaction).

Phenols are an acidic component of petroleum (part of why they can be a problem). As such, we examined a jet fuel sample in the negative ion mode, with base, to examine the speciation and see if the phenol components were discernable even without a charged tag. The results (see ESI†) show that spectra are typically dominated by trace amounts of other anions (such as PF_6^-, or the phenol antioxidants added to rubber septa), and the spectra clearly contain species which are not simple phenols (in ESI-MS, ions with even-numbered *m*/*z* values implicate the presence of atoms other than just C, H and O).

When we examined a solution of jet fuel in the positive ion mode by ESI-MS it showed the presence of polyethylene glycols (PEGs) in the range *m*/*z* 250–550, corresponding to the Na^+ and K^+ adducts of $H(OCH_2CH_2)_nOH$ (n = 3–13) (Fig. S5, ESI†). Addition of NaOH caused an increase in intensity of the sodiated PEGs. We checked blanks and they contained no PEGs, so we can be sure they came from the sample, suggesting that they are introduced in low quantity at some stage during the extraction or refining process. No other peaks of note were observed, suggesting that the amount of basic material in the sample was low (aside from the PEGs).

Despite the apparent prominence of the peaks above and the good signal-to-noise ratio, addition of the charged tag to this mixture suppressed their appearance, a result that is quite reasonable considering the purposefully-designed high surface activity of the charged tag. The charged tag immediately begins reacting with the phenols present to generate an assembly of different but related species (Fig. 3). The most prominent of these are derived from variously alkylated phenols, of general formula $C_6H_5(CH_2)_nOH$ (where n = 2–9). This distribution reaches a maxima at n = 5. We are not able to differentiate between isomers, so for example the n = 3 compound could include contributions from five different phenols substituted with three methyl groups, ten different phenols substituted with one ethyl and one methyl group, or three different phenols substituted with a propyl group.

In the same mass range, we also observed two less abundant series of compounds whose composition was not obvious. As such, we turned to high resolution analysis to assist us in the assignment. Orbitrap analysis supported the assignment of the primary series as based on phenols, but the smaller series did not contain O at all; instead, one series was attributable to $C_nH_{2n+2}S$ (n = 9–14) and the other $C_nH_{2n}S$

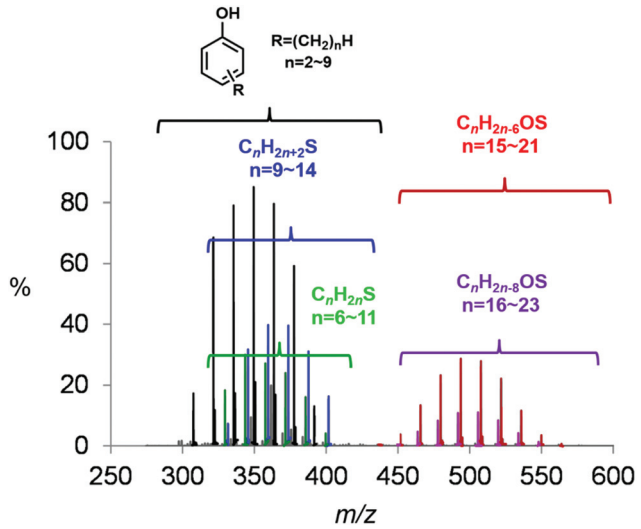


Fig. 3 ESI mass spectrum of sample B after reaction with **1** in the presence of NaOH. Five distinct product series were observed, which have been colour-coded and labelled with the empirical formula of the reacting species.

(n = 6–11). Because they reacted with the charged tag, we can assume these must be thiols rather than thioethers. The saturated series might be branched or linear, whereas the unsaturated series could either contain a double bond or be cyclic. Product ion MS/MS experiments do not provide structural information on the thiol, because the first fragmentation to occur is always benzylic C–S cleavage, with the charge being retained by the tag (hence all subsequent fragmentations are of the tag, not the target). The mass accuracy of the Orbitrap is within a few parts per million, and so can distinguish unambiguously between one sulfur (31.9721 Da) and two oxygen atoms (31.9898 Da). There are narrower mass splits than this in jet fuel, notably SH_4 and C_3 (0.0034 Da),[40] but even at the masses being considered here (3–550 Da), this difference represents a mass error of 6–11 ppm.

All of these compounds are in a predictable mass range for jet fuel. However, there exists an additional pair of series of related compounds approximately 150 Da higher in mass, and like the two previous thiols, these differ in mass from each other by 2 Da. Orbitrap analysis provides the formulae as containing both O and S, $C_nH_{2n-8}OS$ (n = 16–23) and $C_nH_{2n-6}OS$ (n = 15–21). Assignment is a challenge because both phenols and thiols can react with the charged tag, but the level of unsaturation points towards the compounds being phenols (double bond equivalents = 4, compared to 4 and 5 in the case of these series). The combinatorial possibilities of these formulae are sufficiently high that speculation on structure would be very prone to error, and we have not endeavored to make structural assignments for these series. They are not any more amenable to MS/MS analysis than the lower mass ions. We also know that they are not byproducts of derivatization, because they do not appear at all in some samples that do contain some of the lower mass species (*vide infra*).

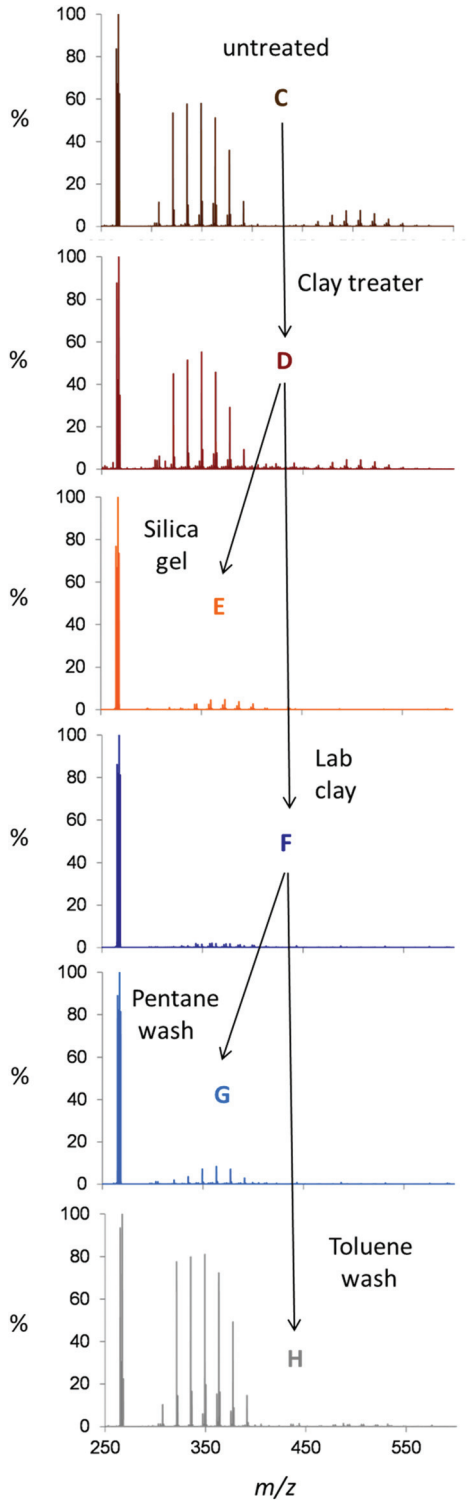


Fig. 4 Selective phenol analysis of a series of jet fuel samples. The untreated sample (C) is treated with clay, after which spectrum (D) is provided (reduced phenol content). Further treatment with either silica gel (E) or lab clay (F) resulted in much lower phenol content. Washing the lab clay with pentane recovered little phenol (G), but a toluene wash recovered most of it.

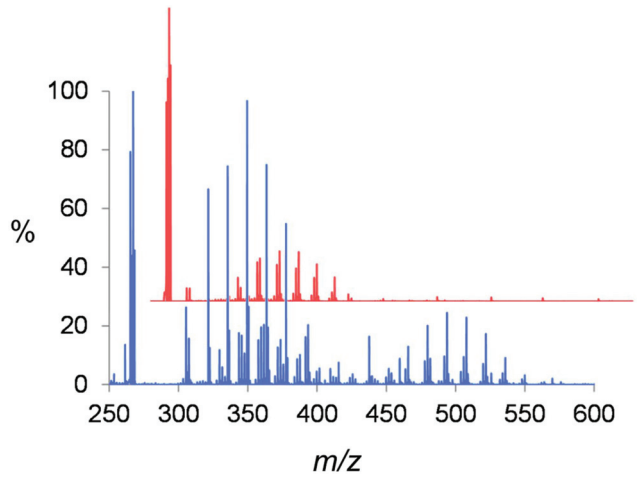


Fig. 5 Jet fuel sample X2 before (blue) and after (red) stirring in the presence of alumina for 40 hours.

In a refinery environment, petroleum streams undergo various processes to remove undesired contaminants, and phenols and thiols alike fall into this category of compound. Fig. 4 outlines the changes in detected analytes depending on treatment. Untreated sample C is the same as shown in Fig. 3, but the unreacted charged tag **1** is also shown in the spectrum to provide an indication of the relative abundance of the products. Clay treatment (sample D) exhibits reduced phenol concentrations (by about 20%), and the sulfur-containing compounds are reduced by >50%. Silica gel treatment (sample E) removes nearly all phenols as does lab clay (sample F). Washing the lab clay with pentane (sample G) removed some of the adsorbed phenols from the clay, or in the case of toluene (sample H), substantially more. None of the higher sulfur-containing compounds were removed however, suggesting that these had a higher affinity for the lab clay than the lower mass phenols.

We did our own in-house experiments with the jet fuel, leaving the fuel to stir for 40 hours in the presence of alumina. This removed nearly all of the higher mass species and about three quarters of the lower mass phenols (Fig. 5).

Conclusions

We have developed a rapid, selective and chromatography-free mass spectrometric analysis of a highly complex matrix. While derivatization is common in ESI-MS, this methodology in petroleomics is less commonly explored. The results from analysis of jet fuels at different treatment stages are consistent with effective if not quantitative removal of phenols from the petroleum matrix. The selective nature of the above techniques is useful not only in petroleomics, but to other ESI-MS users working in other contexts as it allows them to quickly and easily detect specific chemical moieties in complex matrices.

Conflicts of interest

Imperial Oil partially funded this research through their University Research Award program and GBM is an employee.

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References

1 (*a*) L. M. Balster, S. Zabarnick, R. C. Striebich, L. M. Shafer and Z. J. West, *Energy Fuels*, 2006, **20**, 2564–2571; (*b*) S. Zabarnick, *Ind. Eng. Chem. Res.*, 1994, **33**, 1348–1354; (*c*) E. G. Jones and L. M. Balster, *Energy Fuels*, 2000, **14**, 640–645; (*d*) W. F. Taylor, *Ind. Eng. Chem., Prod. Res. Dev.*, 1974, **13**, 133–138; (*e*) M. Sobkowiak, J. M. Griffith, B. Wang and B. Beaver, *Energy Fuels*, 2009, **23**, 2041–2046; (*f*) M. Commodo, I. Fabris, C. P. T. Groth and Ö. L. Gülder, *Energy Fuels*, 2011, **25**, 2142–2150.

2 Y. Zhang, Q. Shi, A. Li, K. H. Chung, S. Zhao and C. Xu, *Energy Fuels*, 2011, **25**, 5083–5089.

3 R. C. Striebich, J. Contreras, L. M. Balster, Z. West, L. M. Shafer and S. Zabarnick, *Energy Fuels*, 2009, **23**, 5474–5482.

4 (*a*) A. Kovácsa, M. Mörtlb and A. Kendea, *Microchem. J.*, 2011, **99**, 125–131; (*b*) T. G. Sobolevsky, A. I. Revelsky, B. Miller, V. Oriedo, E. S. Chernetsova and I. A. Revelsky, *J. Sep. Sci.*, 2003, **26**(17), 1474–1478.

5 T. Chu, C. Chang, Y. Liao and Y. Chen, *Talanta*, 2001, **54**, 1163–1171.

6 A. Dobos, E. Hidvégi and G. P. Somogyi, *J. Anal. Toxicol.*, 2012, **36**, 340–344.

7 C. Schummer, O. Delhommea, M. R. B. Appenzeller, R. Wennig and M. Millet, *Talanta*, 2009, **77**, 1473–1482.

8 M. C. Pietrogrande, D. Bacco and M. Mercuriali, *Anal. Bioanal. Chem.*, 2010, **396**, 877–885.

9 E. L. B. Lourenco, A. Ferreira, E. Pinto, M. Yonamine and S. H. P. Farsky, *Chromatographia*, 2006, **63**, 175–179.

10 J. Rolfes and J. T. Andersson, *Anal. Chem.*, 2001, **73**, 3073–3082.

11 S. Ma, C. Ma, K. Qian, Y. Zhou and Q. Shi, *Rapid Commun. Mass Spectrom.*, 2016, **30**, 1806–1810.

12 (*a*) G. S. Frysinger and R. B. Gaines, *J. High Resolut. Chromatogr.*, 1999, **22**, 251–255; (*b*) J. J. Harynuk, A. D. Rossé and G. B. McGarvey, *Anal. Bioanal. Chem.*, 2011, **401**, 2415–2422; (*c*) T. Dijkmans, M. R. Djokic, K. M. Van Geem and G. B. Marin, *Fuel*, 2015, **140**, 398–406; (*d*) B. Omais, N. Charon, M. Courtiade, J. Ponthus and D. Thiébaut, *Fuel*, 2013, **140**, 805–812; (*e*) B. Omais, M. Courtiade, N. Charon, D. Thiébaut, A. Quignard and M. C. Hennion,

J. Chromatogr., A, 2011, **1218**, 3233–3240; (*f*) T. C. Tran, G. A. Logan, E. Grosjean, D. Ryan and P. J. Marriott, *Geochim. Cosmochim. Acta*, 2010, **74**, 6468–6484; (*g*) T. C. Tran, G. A. Logan, E. Grosjean, J. Harynuk, D. Ryan and P. J. Marriott, *Org. Geochem.*, 2006, **37**, 1190–1194.

13 R. S. Borisov, D. I. Zhilyaev, N. Y. Polovkov and V. G. Zaikin, *Rapid Commun. Mass Spectrom.*, 2014, **28**, 2231–2236.

14 M. L. Salomonsson, U. Bondesson and M. Hedeland, *Rapid Commun. Mass Spectrom.*, 2008, **22**, 2685–2697.

15 L. Xua and D. C. Spink, *J. Chromatogr., B: Biomed. Appl.*, 2007, **855**, 159–165.

16 R. M. Alberici, R. Sparrapan, W. F. Jardim and M. N. Eberlin, *Environ. Sci. Technol.*, 2001, **35**, 2084–2088.

17 S. S. Alimpiev, V. V. Mlynski, M. E. Belov and S. M. Nikiforov, *Anal. Chem.*, 1995, **67**, 181–186.

18 D. Zhan and J. B. Fenn, *Int. J. Mass Spectrom.*, 2000, **194**, 197–208.

19 (*a*) A. G. Marshall and R. P. Rodgers, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 18090–18095; (*b*) A. G. Marshall and R. P. Rodgers, *Acc. Chem. Res.*, 2004, **37**, 53–59; (*c*) R. P. Rodgers, T. M. Schaub and A. G. Marshall, *Anal. Chem.*, 2005, **77**, 20A–27A; (*d*) M. P. Barrow, *Biofuels*, 2010, **1**, 651–655; (*e*) J. M. Purcell, C. L. Hendrickson, R. P. Rodgers and A. G. Marshall, *Anal. Chem.*, 2006, **78**, 5906–5912.

20 F. K. Kawahara, *Anal. Chem.*, 1968, **40**, 1009–1010.

21 K. Slinkard and V. L. Singleton, *Am. J. Enol. Vitic.*, 1977, **28**, 49–55.

22 F. Ortega, E. Domínguez, G. Jönsson-Pettersson and L. Gorton, *J. Biotechnol.*, 1993, **31**, 289–300.

23 A. D. Corcia, S. Marchese and R. Samperi, *J. Chromatogr., A*, 1993, **642**, 175–184.

24 M. Saraji and M. Marzban, *Anal. Bioanal. Chem.*, 2010, **396**, 2685–2693.

25 R. Sun, Y. Wang, Y. Ni and S. Kokot, *Talanta*, 2014, **125**, 341–346.

26 F. Martin and M. Otto, *Fresen. J. Anal. Chem.*, 1995, **352**(5), 451–455.

27 (*a*) J. Rolfes and J. T. Andemson, *Anal. Commun.*, 1996, **33**, 429–432; (*b*) H. L. Lochte, *The petroleum acids and bases*, Chemical Pub. Co, Inc., New York, 1955.

28 J. G. Speight, *Petroleum Refinery Processes. Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2005.

29 (*a*) J. G. Speight, *The Chemistry and Technology of Petroleum*, CRC Press, Taylor & Francis Group, Inc., Abingdon, 5th edn, 2014; (*b*) G. Alfke, W. W. Irion and O. S. Neuwirth, *Oil Refining. Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2007.

30 J. M. E. Quirke, C. L. Adams and G. J. Van Berkel, *Anal. Chem.*, 1994, **66**, 1302–1315.

31 M. Noestheden, D. Noot and R. Hindle, *J. Chromatogr., A*, 2012, **1263**, 68–73.

32 H. H. Schobert and C. Song, *Fuel*, 2002, **81**, 15–32.

33 G. Brieger, D. Hachey and T. Nestrick, *J. Chem. Eng. Data*, 1968, **13**, 581–582.

34 W. Williamson, *J. Chem. Soc.*, 1852, **106**, 229.

35 O. C. Dermer, *Chem. Rev.*, 1934, **14**, 385–430.

36 E. Janusson, G. B. McGarvey, F. Islam, C. Rowan and J. S. McIndoe, *Analyst*, 2016, **141**, 5520–5526.

37 L. Patiny and A. Borel, *J. Chem. Inf. Model.*, 2013, **53**, 1223–1228.

38 S. V. Dzyuba, K. D. Kollar and S. S. Sabnis, *J. Chem. Educ.*, 2009, **86**, 856.

39 (*a*) K. L. Vikse, M. P. Woods and J. S. McIndoe, *Organometallics*, 2010, **29**, 6615–6618; (*b*) K. L. Vikse, Z. Ahmadi, J. Luo, N. van der Wal, K. Daze, N. Taylor and J. S. McIndoe, *Int. J. Mass Spectrom.*, 2012, **323–324**, 8–13.

40 J. D. Byer, K. Siek and K. Jobst, *Anal. Chem.*, 2016, **88**, 6101–6104.

