Chemical class separation of petroleum and wax analysis

Paul Sutton[a], Steven J. Rowland[a] and Neil Chilcott[b]

[a]School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, UK PL4 8AA (E: pasutton@plymouth.ac.uk; S.Rowland@plymouth.ac.uk)

B KAT [Kernow Analytical Technology], Unit 2B, Rural Workshops, North Petherwin, Cornwall, UK PL15 8TE (E:analysis@kat-lab.com)

Proposal

A. Class-type separation of petroleum using ion exchange (IEX) solid phase extraction (SPE) and analysis of amenable fractions using high temperature gas chromatography with flame ionisation detection (HTGC-FID)

B. Wax analysis using (HTGC-FID)

A. Class-type separation of petroleum using ion exchange (IEX) solid phase extraction (SPE) and analysis of amenable fractions using high temperature gas chromatography with flame ionisation detection (HTGC-FID)

- *Sequential strong cation exchange (SCX), strong anion exchange (SAX) and adsorption on silica (Si) fractionation of crude oil (Figure A1)*
- *Variant used commercially for $C_{80\text{-}82:0\text{-}8}$ ('Arn') tetraacids (12 years; Sutton & Rowland, 2014)*
- *API gravity 12.1-38.3°, TAN 0.1-3.6 mg KOH, S 0.25-2.7%, asphaltene 0-11%*
- *Immature to late maturity oils, biodegradation 0.9-8.2 and absent pristane/nC_{17} ratio*
- *Gravimetric determination of fractions (Table A1; quantitatively important)*
- *Procedure lends itself to 'read-across'*
- *Can be readily implemented in any laboratory*
- *Mass balance when evaporative losses accounted for*
- *Relatively quick sample preparation time, low solvent use*
- *Non-destructive*
- *Fractions available for toxicity testing (toxicity identification evaluation; rule in/out)*
- *Fractions available for molecular identification*
- *Most fractions amenable to GC, use HTGC for >C_{30}*

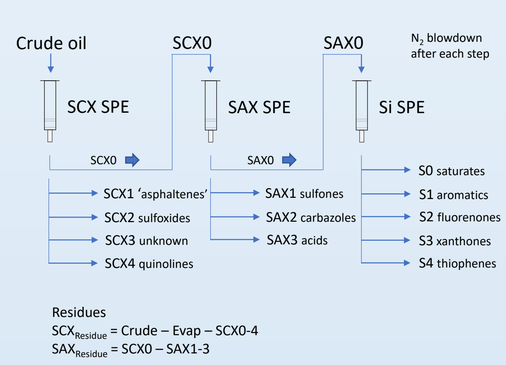


Figure A1. Flow diagram for gravimetric class type IEX SPE separation of crude oil

Table A1. Chemical class fractions obtained from crude oil using IEX SPE and the analytical techniques used to characterise them (Robson et al 2017, Robson 2018)

Fraction			Eluent	'Class'	Analysis
SCX1			Toluene	"Asphaltenes"	??
SCX2			THF	Sulfoxides	GC
SCX3			THF/H_2O/2% ammonia	No model compounds	??
SCX4			THF/H_2O/5% ammonia	Quinolines	LC-MS
SCX0 (unretained)	SAX1		Toluene	Sulfones	GC
	SAX2		THF	Carbazoles	GC
	SAX3		THF/H_2O/FA	Naphthenic acids	GC (TMS)
	SAX0 (unretained)	S0	*N*-hexane	"Saturates"	GC
		S1	DCM/*n*-hexane 1:4	"Aromatics"	GC
		S2	DCM/*n*-hexane 1:1	Fluorenones	GC
		S3	DCM	Xanthones	GC
		S4	THF	Thiophenes	GC

B. *Wax analysis*

- *Requires special precautions due to wax deposition*
- *T-SEP® 'Topping' procedure improves 'high-end' sensitivity (Figure B1)*
- *Gravimetric determination of 'total' wax*
- *Condensates, liquid and waxy oils, oily waxes and wax deposits*
- *Merge WHOLE and TOPPED n-alkane integrals, plot weight % (Figure B2)*
- *External semi-quantitation based on sensitivity of in-house n-alkane ($nC_{10\text{-}30,40,50,60}$) standard*
- *Used commercially for 14 years*

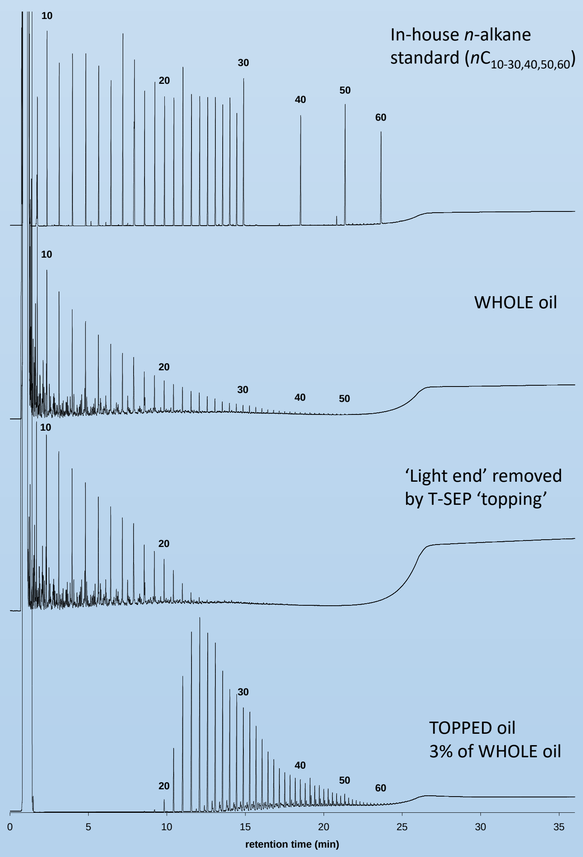


Figure B1. HTGC-FID chromatograms of *n*-alkanes in-house standard (top), Gulf of Mexico WHOLE crude oil (NIST 2779; upper), fraction removed by 'TOPPING' (lower), and the T-SEP® 'TOPPED' fraction (bottom). Numbers represent carbon number of *n*-alkane.

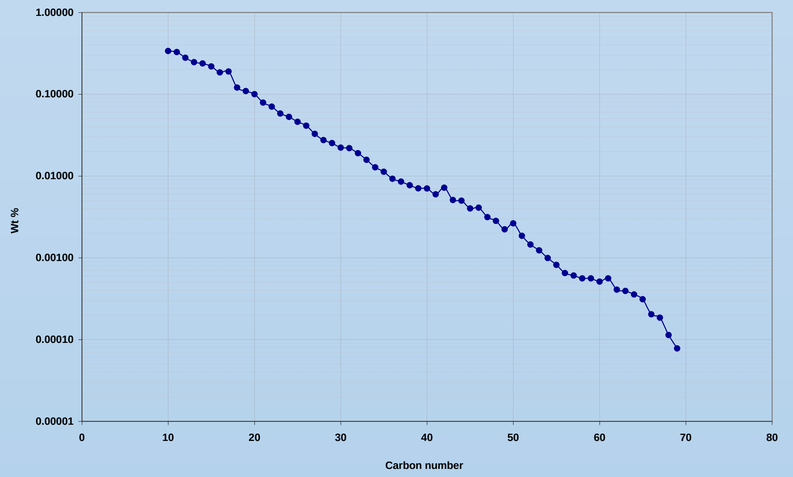
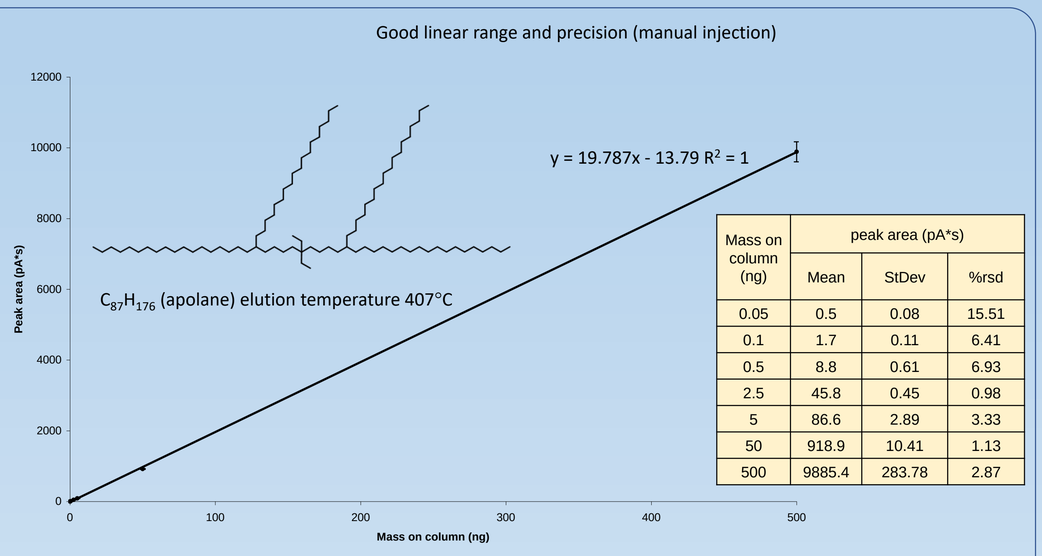


Figure B2. Weight percentage n-alkanes in Gulf of Mexico crude oil (NIST 2779)

HTGC-FID – Highlights

- *Good separation efficiency*
- *Robust using steel coated columns*
- *'Hot' injection of heated waxy samples*
- *Analysis up to ca. C_{100} with capillary column*
- *Four orders magnitude linearity (Figure 1)*
- *Good precision (%rsd)*
- *FID optimised LoD ca. 20 pg on column $C_{87}H_{176}$*



Mass on column (ng)	peak area (pA*s)		
	Mean	StDev	%rsd
0.05	0.5	0.08	15.51
0.1	1.7	0.11	6.41
0.5	8.8	0.61	6.93
2.5	45.8	0.45	0.98
5	86.6	2.89	3.33
50	918.9	10.41	1.13
500	9885.4	283.78	2.87

Figure 1. Calibration chart for $C_{87}H_{176}$ hydrocarbon apolane (n = 3 at each point)

References

Robson, W.J., Sutton, P.A., McCormack, P., Chilcott, N.P. and Rowland, S.J. (2017) Class type separation of the polar and apolar components of petroleum. *Analytical Chemistry* **89**, 2919-2927. [doi: 10.1021/acs.analchem.6b04202].

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