SARA Analysis in a Flash

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Chromatography Application Note AN130

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Abstract

Crude oil and associated bitumens are some of the most complex mixtures in the world. Crude oil is the feedstock of the petrochemical industry which produces fuels, solvents, lubricants, fertilizers, and plastics. Bitumens are a component of crude oil and are used often in road construction, and thus are important for infrastructure. Results from analysis of saturates, aromatics, resins, and asphaltenes (SARA) are valuable for understanding the aging process of bitumens and have been associated with mechanisms of roadway weathering and decay. SARA analysis of crude oils provides information about processing the feedstock. Flash chromatography with Evaporative Light Scattering Detection (ELSD) was found to be an efficient means of both separating the SARA components and quantifying them. In addition, the automatic solvent switching during a run allowed resolution of the SARA components.

Background

The flash chromatography procedure described herein can be used as an orthogonal approach to the traditional, yet time consuming and expensive, TLC-FID procedure[1]. The flash chromatography procedure provides similar data, while also allowing for bulk separation and collection of the various SARA components for further characterization, if desired. Flash chromatography has also been used to resolve SARA components in crude oil using a similar procedure as in this application note[2], although different solvents were used.

Experimental, results and discussion

Bitumens

For studies of bitumen aging, approximately 0.2 g of asphalt binder were dissolved in chloroform and loaded onto a 5-g solid load cartridge. A 12 g RediSep Gold® silica column was used for separation. A series of gradients were used with solvent changes to elute the different components. The Combi*Flash*® NextGen 300+ system (PN 685250001) with ELSD (PN 605257001) was run in column volumes (CV), as working in CV allows easy scale-up to a larger column without changing the method — the elution time of a compound in CV is the same whether a column is small or large.

The following gradient table was used:

Table 1: Bitumen Study Gradients

Gradient segment length (CV)	A solvent	B solvent	% B solvent
Start	*n*-Heptane	Toluene	0
5	*n*-Heptane	Toluene	0
0	*n*-Heptane	Toluene	20
7	*n*-Heptane	Toluene	20
0	*n*-Heptane	Toluene	100
5	*n*-Heptane	Toluene	100
0	Toluene	Tetrahydrofuran	0
0	Toluene	Tetrahydrofuran	100
6	Toluene	Tetrahydrofuran	100
0	*n*-Heptane	Toluene	0
2	*n*-Heptane	Toluene	0

The column was run at 30 mL/min with a 6-minute equilibration in *n*-heptane prior to the gradient.

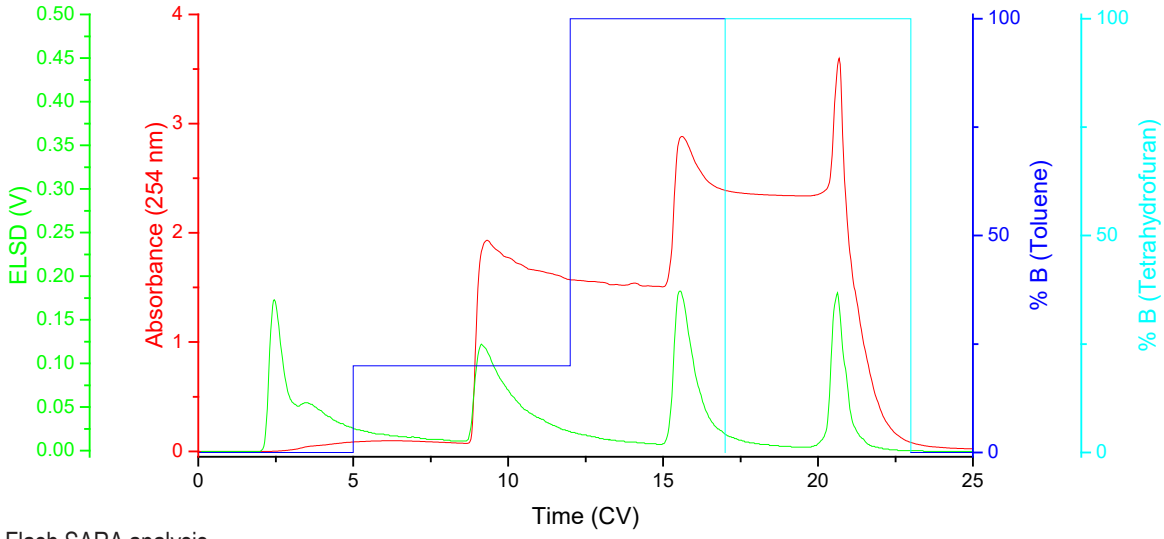
The solvents were assigned to the flowing solvent inlet lines:

Table 2: Solvent Assignment

Solvent Inlet	Solvent
1	*n*-Heptane
2	Toluene
3	Tetrahydrofuran
4	[unused]

Detection and peak collection used the ELSD (spray chamber = 20 °C, drift tube = 60 °C). UV-vis detection at 254 and 200–800 nm was set to "monitor," so no peak collection was triggered by the UV detector. The UV traces verified that the solvent changes were occurring. Pure *n*-heptane was used, as was un-stabilized tetrahydrofuran. As the TLC method used silica, it was easy to transfer the method to a column.

The gradient method was determined empirically to create conditions for all samples. The gradient is intended to minimize time, sharpen peaks, and resolve the peaks from one another. Compared to the traditional Iatroscan procedure (ca. 3-hour total time, from sample preparation and TLC development to analysis), flash-SARA provides results in 30 minutes; that is, 1/6th the time.



Flash SARA analysis

Atmospheric residue maltenes

Atmospheric residue maltenes (AR maltenes) is the oil obtained from the bottom of the atmospheric distillation unit for crude oil. Another group[2] used flash chromatography to resolve AR maltenes into separate samples for further analysis. They loaded 0.1 to 0.3 g maltenes onto an 80 g RediSep silver column with ELSD. The column was run at 25 mL/min with the gradient listed below.

This procedure produced saturated compounds eluting in the hexanes, followed by two groups of aromatic compounds, with polar compounds eluting in the ethyl acetate and methanol. Note that it would be better to return to hexanes via a toluene or ethyl acetate intermediate because methanol and hexanes are not miscible.

Table 3 Maltenes Study Gradients

Gradient segment length (CV)	A solvent	B solvent	% B solvent
Start	Hexanes	Toluene	0
7	Hexanes	Toluene	0
0	Hexanes	Toluene	5
7	Hexanes	Toluene	5
0	Hexanes	Toluene	30
7	Hexanes	Toluene	30
0	Hexanes	Toluene	100
7	Hexanes	Toluene	100
7	Hexanes	Ethyl acetate	100
7	Ethyl acetate	Methanol	100
2	Hexanes	Toluene	0

Conclusion

Flash chromatography is a fast, easy, and reliable method for SARA analysis. The purified fractions may also be used for further analysis of a particular class of compounds. Redi*Sep* columns provide good resolution, solid load cartridges, while the ability to change solvents during a run on the NextGen 300+ system allows for semi-automated operation and data collection. Evaporative light scattering detection permits measurement of the eluting bitumen compounds in the presence of solvents that absorb UV light.

Notes

1. Masson, J-F; Price, P.; Collins, P. Dynamics of Bitumen Fractions by Thin-Layer Chromatography/ Flame Ionization Detection. *Energy & Fuels* 2001, **15**, 955-960
2. Kim, E.; EunJi E.; Serah S.; Park,J-I; Kim, S. Characterization of Petroleum Heavy Oil Fractions Prepared by Preparatory Liquid Chromatography with Thin-Layer Chromatography, High-Resolution Mass Spectrometry, and Gas Chromatography with an Atomic Emission Detector. *Energy Fuels* 2016, **30**, 2932–2940

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January 17, 2023; revised September 2023