Enhanced SARA And PIN Group-Type Separations And Quantification In Crude-Oil And Condensate Characterization

K. K. (Adry) Bissada¹, Ewa B. Szymczyk¹, L. M. (Mike) Darnell¹ and David G. Nolte²

¹Petroleum Systems & Geochemistry Institute, University of Houston, Houston, Texas; ²Ontario-Texas Technology Development, Houston, Texas.

Analysis of crude oils and bitumens provides important geochemical information for assessing source-rock potential and crude-oil provenance in petroleum-systems analysis projects and for understanding and predicting asphaltene, paraffin and heavy organics deposition ("arterial blockage") in production, transportation and processing operations. An essential step in this analysis is the group-type separation of the components of the petroleum fluid into Saturated hydrocarbons, Aromatic hydrocarbons, Resins, and Asphaltenes (SARA fractions), and the further separation of the Saturates into n-Paraffins, Iso-paraffins and Naphthenes (PIN fractions). Conventional methods of group-type separation and quantification entail complex procedures involving preliminary "de-asphaltening" with a suitable flocculating or precipitating agent (e.g. n-pentane) and subsequent separation of the soluble portion (Maltenes) into Saturate, Aromatic and Resin fractions using open-column elution chromatography or medium-pressure liquid chromatography (Fig. 1).

Further separation of the Saturates into individual PIN fractions is even more complex, often entailing urea adduction or molecular sieve occlusion of n-Paraffins and subsequent decomposition of the adducts to recover the Paraffins (Fig. 2).
Extensive observations on the effectiveness of these separation procedures revealed serious inadequacies in both open-column and medium-pressure liquid chromatography. The most significant problem is the extensive cross contamination of the separated “SARA” fractions as revealed by gas-chromatography, gas-chromatography/mass spectrometry, infra-red spectroscopy, UV spectroscopy and, most vividly, by HPLC re-chromatography of fractions derived from the traditional separation methods (Fig. 3 and 4).

Figure 3. Evidence of cross-contamination in conventional SARA separation

Figure 4. HPLC re-chromatography of typical “SARA” fractions pre-separated by conventional column chromatography (pre-separation by commercial service lab).

The second most serious problem in conventional group-type analysis is quantification of the yields from these processes. The traditional methods are both difficult and grossly inaccurate. The different fractions do not have common chromophores or properties that allow quantification by typical detectors used for liquid chromatography. Generally, it is performed by gravimetric means, which are
tedious, slow and require removal of solvents by evaporation before the weighing step. This results in significant losses of light components (~ C15-) from the recovered fractions (Fig. 5).

Figure 5. Loss of volatile fraction (C_{15-}) during solvent evaporation in gravimetric quantification

Experiments on adaptation of multidimensional high-performance liquid chromatography (HPLC), and customization of Evaporative Light Scattering Detection (ELSD) techniques that preclude the need for solvent evaporation and weighing of residues, lead to the development of two practical, semi-preparative processes for group-type separation and quantitative analysis of bitumens and petroleum fluids. The SARA HPLC process fractionates an oil sample into all four SARA fractions without prior de-asphalteneing (Fig. 6). It requires about 60 minutes per run. The PIN HPLC process separates the

Figure 6. Multidimensional SARA HPLC separation process

further into the n-Paraffins, the Iso-Paraffins and the Naphthene fractions with excellent purity (Fig. 7). The PIN process requires about 70 minutes per run. All steps for the two processes are controlled automatically by a programmable microprocessor that switches valves and solvents as required by the program.
Figure 7. Multidimensional PIN HPLC separation process

Extensive testing of chromatographic performance using infrared and NMR spectroscopy, FID/PID GC, GC/MS, and solubility/non-solubility criteria showed radically improved purity of separations and significantly enhanced precision (Figs. 8 and 9). Furthermore, the analysis time is considerably shortened (SARA 60 minutes; PIN 70 minutes).

Figure 8. High-purity separation of SARA group-types by multi-dimensional SARA HPLC
Figure 9. Enhanced separation of Saturates into n-Paraffins, iso-Paraffins, and Naphthenes by multi-dimensional P-I-N HPLC.

Twenty replicate samples of a C_{15+} Bitumen of the New Albany Shale (Illinois) were separated by HPLC, measured, recombined, then re-separated by the open column method. The results of these tests show much higher precision for HPLC than the open-column method (Fig. 10).

Figure 10. Improved precision in multi-dimensional SARA HPLC analysis relative to conventional procedures

Quantification of the products of the HPLC separations is done in solution using an Evaporative Light Scattering Detector technique that precludes the need for solvent evaporation and weighing of residues. Because the ELSD process is extremely sensitive and the semi-preparative multi-dimensional HPLC processes yield several orders of magnitude too much product fractions for the detector, we have developed a rapid, simple technique that entails injection of a 100µl aliquot of the solutions from the HPLC fractions into the ELSD solvent stream as it passes through the injection port nebulizer of the ELSD detector (Fig. 11). Detector response is calibrated using synthetic solutions of the various group-types in ranges of concentration as customarily encountered in most crude oils.
Figure 11. ELSD Quantification of SARA or PIN fractions

Mass-balance computations indicated essentially full recovery (Fig. 12). Because the ELSD method avoids evaporation and weighing steps, it is less susceptible to errors stemming from loss of light components. Thus, it is especially suitable for analyzing light crudes, condensates, diesel, and other refined light hydrocarbon fluids.

Figure 12. Comparative performance of conventional vs. ELSD quantification procedures in SARA/PIN group-type analysis