

Evaluation of Saturates/Aromatics/Resins/Asphaltenes (SARA) Fractionation of Asphalt Binders in Louisiana

Introduction

Conventional asphalt binders typically consist of five categories of hydrocarbon molecules: saturates, aromatics, resins, asphaltenes, and polymers. To identify these components, the state of Louisiana uses Gel Permeation Chromatography (GPC), a technique that separates molecular components in binder samples based on size. While GPC has significantly advanced the field of binder characterization, the method relies on the assumption that molecular size directly correlates with and accurately represents the specific chemical categories of the asphalt molecules. Although chemical properties vary across molecule types, each category typically spans a range of molecular sizes. While medium to large molecular weight components are generally assumed to be asphaltenes and polymers, this assumption is often inaccurate because maltene fractions (i.e., saturates, aromatics, and resins) can also contain large molecules. A more accurate way to distinguish these components is to leverage their chemical solubility in different solvents. This method, called SARA (saturates, aromatics, resins, and asphaltenes) fractionation, separates the binder fractions by using hexane and toluene as a solvent, taking advantage of the components' varying levels of solubility.

Thin-Layer Chromatography coupled with Flame-Ionization Detection (TLC-FID), performed using an Iatroscan system, provides a micro-scale alternative to conventional SARA fractionation. This method utilizes capillary action to significantly reduce both solvent consumption and analysis time. In this approach, quartz rods (Chromarods) coated with an asphalt solution are partially submerged in a sequence of solvent development tanks. As the solvents migrate up the rods via capillary action, they separate the binder into its constituent fractions. The rods are then passed through a hydrogen flame, which combusts the components; a sensor records the resulting flame intensity, which is directly proportional to the concentration of each specific binder fraction. Typical GPC and Iatroscan systems are shown in Figure 1. Given the significant impact of chemical composition on asphalt binder performance, a thorough comparison of these characterization methods is essential to understand their distinct capabilities and the relative differences in their results.

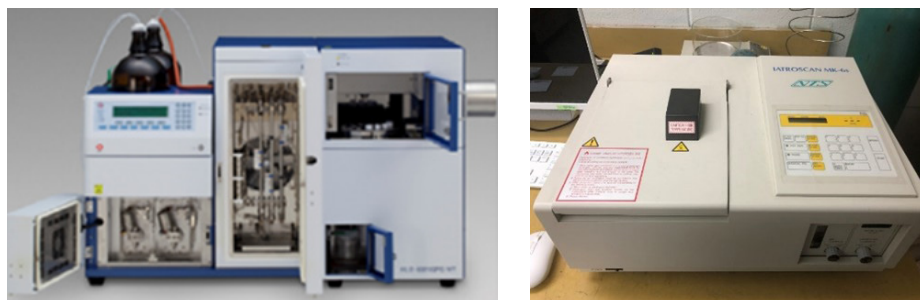


Figure 1. GPC system (left); Iatroscan system (right)

Objective

The objective of this project was to evaluate asphalt binder characterization using SARA fractionation via Thin-Layer Chromatography with Flame Ionization Detection (TLC/FID), and to analyze these results alongside available Gel Permeation Chromatography (GPC) data. The primary focus of this study was to investigate the sensitivity and capability of the TLC/FID-based SARA method in detecting variations in the chemical composition of asphalt binders.

Principal Investigator

Saman Salari, P.E.
225-767-9128

LTRC Contact

Moses Akentuna, Ph.D., P.E.
225-767-9151

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Scope

This study involved collecting asphalt binders from various terminal and plant-blend suppliers. SARA fractionation via TLC/FID was performed on these samples to establish a detailed chemical profile of the binders currently utilized throughout Louisiana. These results were compared with DOTD GPC characterization data to evaluate the effectiveness of the methodologies in detecting binder modifications. Ultimately, this comparative analysis enhanced testing proficiency and supported DOTD's efforts to ensure the reliability and quality of materials utilized in state paving projects.

Methodology

A total of 46 asphalt binder samples were collected from various suppliers across Louisiana. These binders, representing a range of collection intervals and PG classifications, were evaluated using each characterization method to compare their relative efficacy in identifying molecular components.

GPC was performed on all samples to separate the components of the asphalt binder based on molecular weight. This methodology categorized the components into three distinct groups: polymers, asphaltenes, and maltenes. SARA fractionation was conducted via TLC/FID using two distinct approaches. In the first approach, asphaltene components were screened out to allow the limited rod length to be used exclusively for the three maltene components (i.e., saturates, aromatics, and resins). Consequently, the resulting graph consisted of three peaks, one for each component. This approach was designated as the 3-peak method. The second approach, known as the 4-peak method, did not filter out the asphaltenes and produced a graph containing four distinct peaks.

Conclusions

Based on these findings, GPC is valuable for analyzing larger molecular components, such as asphaltenes and polymer additives, whereas SARA methods are better suited for evaluating smaller molecular fractions, such as maltenes. Although both SARA methods demonstrated reasonably comparable performance, the 4-peak method, due to its elimination of pre-separation steps, was found to be more convenient for practical applications. Specific observations from the study are outlined below:

Chemical Characterization and Source Fingerprinting

Comparative analysis of PG 67-22, PG 70-22M, and PG 76-22M binders confirmed that GPC and SARA fractionation serve distinct, complementary roles. GPC proved most robust for identifying binder grade and modification levels. By isolating the Large Molecular Size (LMS) fraction, GPC

effectively stratified binders by polymer content, showing a clear progression from unmodified PG 67 (< 4.5% LMS) to PG 76 (> 8% LMS). Conversely, SARA fractionation provided a chemical fingerprint of the base binder source, independent of modification:

- **Sup2 Source:** A high-saturate (~10%), paraffinic source with potential for physical hardening and reduced adhesion.
- **Sup6 Source:** A high-aromatic, solvated system (Saturates < 8%) relying on solvency rather than resinous peptization to disperse polymers.
- **Sup3 Source:** A chemically heavy, structured binder with the highest asphaltene and resin contents (4-peak), indicating strong peptization and rutting resistance.
- **Sup5 Source:** Defined by a high resin load (~30% in 4-peak), acting as a robust sol-type binder with high colloidal stability.

SARA Fractionation: 3-Peak vs. 4-Peak

A critical divergence exists between SARA fractionation methods. The 3-peak method, which relies on manual filtration, consistently overestimates aromatics and underestimates resins due to light resin co-elution and physical entrapment within the polymer-asphaltene matrix. In contrast, the 4-peak method utilizes in-situ separation to provide superior resolution for modified binders, enabling accurate classification of high-polarity fractions. However, the 4-peak method faces specific limitations when applied to high-polarity binders: (1) the retention of polar components at the origin; (2) heteroatom interference with quantification; and (3) sensitivity to sample spot size. To enhance the reproducibility of the 4-peak method, modern protocols recommend the use of automated spotting devices and the doping of Chromarods with Copper (II) Sulfate solution.

Recommendations

Based on these findings, GPC is valuable for analyzing larger molecular components, such as asphaltenes and polymer additives, whereas SARA methods are better suited for evaluating smaller molecular fractions, such as maltenes. Although both SARA methods demonstrated reasonably comparable performance, the 4-peak method, due to its elimination of pre-separation steps, was found to be more convenient for practical applications.