

DEVELOPMENT OF A REPRODUCIBLE IATROSCAN  
METHOD TO CHEMICALLY CHARACTERIZE ASPHALT

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ABSTRACT

A rapid, reproducible method has been developed which quantitatively separates an asphalt into four generic fractions. This paper describes the impact of variables such as spotting technique, humidity, sample size, etc. on the quantitative reproducibility of the TLC-FID technique. With minor modifications, this method is being evaluated by the Asphalt Roofing Manufacturers Association (ARMA) as their standard Iatroscan method.

INTRODUCTION

The ability to predict the performance of a finished product that has been prepared from an asphalt and to understand the effects of various processing steps and modifications of asphalts requires a knowledge of the chemical composition of the asphalt. Since asphalts are complex mixtures of thousands of different compounds, separation of this material into each individual moiety would overwhelm currently available chromatographic data systems not to mention the analyst as well as the asphalt chemist. A better approach would be to separate the asphalt into groups or classes of compounds similar to the Corbett method.

Recently, a new technique which couples thin layer chromatography with a flame ionization detector has been introduced by Iatron Laboratories, Inc. The unit is called an Iatroscan. This unit takes advantage of the high separation power, simple and rapid operating procedures, and small sample size of the thin layer technique and couples that to the excellent quantitation of a flame ionization detector. With the Iatroscan all sample components are accessible to the detector.

Model compounds were used to develop a separation scheme that fractionates an asphalt into four reasonably distinct chemical classes. Although the precision for the same time period, one to three days, was generally excellent; within a matter of months it was apparent that the repeatability of week-to-week and month-to-month data was very poor. For example, a Cross roofers flux was analyzed on two different dates. As the results that are given in Table 1 indicate, the precision for both dates is excellent; however, the repeatability was unsatisfactory. By contrast, analysis of a synthetic standard which contained four distinctly different compounds with respect to polarity showed no day-to-day repeatability problems. See Table 2. This data clearly points to the fact that the chromatography was not adequate to affect the same separation day after day.

Thus, studies were conducted to examine the impact of various chromatographic parameters on repeatability. The most obvious parameters to study are: humidity, sample size and spotting technique.

## EXPERIMENTAL

### Apparatus:

All data was generated on a Iatroscan model Mark IV. The instrument was set up according to the manufacturer's specifications. The hydrogen gas flow rate was set to 160 mL/min and the air flow rate was set to 2.0 L/min. Flow rates were read from the bottom of the balls located inside the Iatroscan gauges. The chromarods were blank scanned twice prior to spotting. All scans were made at 30 seconds per scan. The unit was interfaced to a Hewlett Packard 1000 Data System.

### Procedure:

The manufacturer's procedures were followed to start up the Iatroscan. The chromarods were blank scanned twice at 30 seconds/rod to remove contaminants.

Samples were prepared by dissolving 150 mg/20 ml of carbon disulfide.

A sequential solvent development technique was used to separate the asphalt into four fractions.

1. N-heptane 8.5 cm
2. Toluene 4.5 cm
3. Tetrahydrofuran 2.0 cm

A constant humidity chamber was used to deactivate the chromarods to a constant state prior to each development step. Also, the rods were suspended over the solvent vapors for fixed time periods prior to development. After each development step, the rods were dried in an oven at 60°C for one minute.

Only the areas of the four main peaks are used in the calculation. Report the normalized area percent of each peak. Peak 1 should be reported as saturates. Peak 2 should be reported as naphthene aromatics. Peak 3 should be reported as polar aromatics. Peak 4 should be reported as asphaltenes.

## DISCUSSION

### Development of Separation Scheme

The Iatron Company supplies both alumina and silica chromarods. Model compounds were used to evaluate the ability of these adsorbents to resolve compounds representing saturates, aromatics, polars and asphaltenes. Nujol, an infrared spectroscopy mulling oil, was used to simulate the saturates and 1-phenyltridecane was used as the model for the aromatic fraction. The 1-phenyltridecane was at best partially resolved from the Nujol on the alumina adsorbent. A much better separation was obtained using the silica adsorbent with all other parameters being held constant. See Figures 1 and 2.

Similarly, model compounds were used to verify that the solvent development scheme separates the asphalt into saturates, aromatics, polars and asphaltenes. Neat solvents of increasing polarity were selected as opposed to solvent blends that contain low concentrations of the strong solvent. This eliminates the hassles of accurately generating and maintaining this solvent blend. The solvents selected are N-heptane, toluene and tetrahydrofuran (THF). With this system, all saturated hydrocarbons are eluted in the first peak. Fused ring

aromatics, alkyl substituted aromatics plus thiophenes are eluted with toluene in peak number 2. Nitrogen and oxygen heterocyclic aromatic compounds plus compounds which have polar functional groups such as hydroxyl, amines (primary and secondary), carboxylic acids, ketones, etc., are eluted with THF as peak number 3. The peak at the origin is most likely metal complexes and salts. Table 3 gives the peak location of various compounds.

#### Impact of Relative Humidity on Quantitation

Different concentrations of calcium chloride in water were used to prepare 30%, 65% and 100% relative humidity (R.H.) chambers. The same asphalt was analyzed at these three relative humidities. The results are given in Table 4. Dramatic changes in the concentrations of the naphthene aromatics (NA) and polar aromatics (PA) were observed. At 30% R.H., the NA are 39.3% compared to 55.5% NA at 100% R.H. The PA are 28.5% at 30% R.H. and 18.6% at 100% R.H. Clearly, higher relative humidities deactivate the chromarods, thereby allowing more of the polar aromatics to be moved with the toluene solvent front. Thus, it is imperative that the laboratory be maintained at a constant relative humidity or the methodology include constant humidity chambers.

#### Impact of Sample Size on Quantitation

To study the impact of sample size on quantitation, different concentrations of the same asphalt were prepared in carbon disulfide. The initial study covered the range of 20 to 100 micrograms of asphalt on the chromarods. At these loadings, baseline resolution between the polar aromatics and asphaltenes was not achieved. In addition, peaks were distorted and, in some cases, the peaks split into doublets. Also, rescan of these rods produced as high as 15% residue. Clearly for quantitative purposes this is not acceptable.

The next set of data spanned the range of 5 to 15 micrograms in 2.5 microgram increments. The data is given in Table 5. From this data, it appears that the optimum sample size is in the 7.5 to 12.5 microgram range. Rescan of these rods gave less than one percent residue.

#### Impact of Spotting Technique

Two spotting techniques were studied. The first technique involved the application of the sample on the chromarod as a discrete spot using a microliter syringe. This approach has two drawbacks. First, it would be difficult to ensure that the sample spot for all ten rods in a rack will remain constant with respect to the flame profile of the detector. Second, a spot does not give the sample full access to the total surface of the chromarod. The second spotting technique was to apply the sample as a narrow band around the circumference of the chromarod. Chromatograms for the spot and ring technique are illustrated in Figures 3 and 4, respectively. The loss of resolution between the asphaltene and polar aromatic peaks plus the band distortion of the asphaltene peak in the chromatogram of the sample applied as a spot indicates that breakthrough of the asphaltenes into the polar aromatics has occurred. Thus, optimum chromatography was obtained by applying the sample as a band rather than a discrete spot.

#### CONCLUSIONS

The Iatroscan method separates asphalts into four reasonably distinct groups of compounds: saturates, aromatics/thiophenes, polars and asphaltenes.

The repeatability of this technique has been improved by controlling the

following variables: relative humidity, sample size and spotting technique.

Table 1  
 Repeatability of the Iatroscan Analytical Results  
 for a Given Asphalt Sample

|    | <u>Dec 1988</u> |     | <u>March 1989</u> |     |
|----|-----------------|-----|-------------------|-----|
|    | $\bar{X}$       | SD  | $\bar{X}$         | SD  |
| SA | 3.0             | 0.3 | 3.0               | 0.3 |
| NA | 29.0            | 0.6 | 44.0              | 1.0 |
| PA | 56.0            | 1.0 | 41.0              | 1.1 |
| AS | 12.0            | 0.9 | 12.0              | 0.8 |

Table II  
 Repeatability of the Iatroscan Analytical Results  
 for Synthetic Standards

|               | <u>April 1989</u> |      | <u>May 1989</u> | <u>June 1989</u> |
|---------------|-------------------|------|-----------------|------------------|
|               | $\bar{X}$         | S.D. |                 |                  |
| Nujol         | $\bar{X}$         | 20.6 | 20.8            | 20.8             |
|               | S.D.              | 0.9  | 0.8             | 0.7              |
| Polystyrene   | $\bar{X}$         | 29.2 | 28.0            | 28.7             |
|               | S.D.              | 0.7  | 0.6             | 0.7              |
| Vegetable Oil | $\bar{X}$         | 21.4 | 24.0            | 20.9             |
|               | S.D.              | 0.4  | 0.5             | 0.5              |
| Rhodamine     | $\bar{X}$         | 28.7 | 27.2            | 29.6             |
|               | S.D.              | 0.4  | 0.6             | 1.1              |

Table III  
Iatroscan Analysis of Model Compounds

| Compound                         | Saturate | Aromatic | Peak Location |            |
|----------------------------------|----------|----------|---------------|------------|
|                                  |          |          | Polar         | Asphaltene |
| Nujol                            | x        |          |               |            |
| 1-phenyltridecane                |          | x        |               |            |
| 7,8-benzoquinoline               |          |          | x             |            |
| 3-pentadecylphenol               |          |          | x             |            |
| Thianthrene                      |          | x        |               |            |
| 6-methylquinoline                |          |          | x             |            |
| Phthalazine                      |          |          | x             |            |
| 4,4-dihydroxydiphenylmethane     |          |          |               | x          |
| Naphophthalein                   |          |          | x             |            |
| 4-hydroxybenzyl alcohol          |          |          | x             |            |
| p-nitrobenzoic acid              |          |          | x             |            |
| 4,4-dimethyldianiline            |          |          | x             |            |
| 4-(P-nitrophenylazo) resorcinol  |          |          | x             |            |
| Rhodamine B                      |          |          |               | x          |
| Vegetable Oil                    |          |          | x             |            |
| Low molecular weight polystyrene |          | x        |               |            |
| Anthracene                       |          | x        |               |            |

Table IV  
Effect of Humidity  
on Iatroscan Results

|                 | Relative Humidity |      |      |
|-----------------|-------------------|------|------|
|                 | 30%               | 65%  | 100% |
| Saturates       | 16.5              | 13.5 | 15.5 |
| Aromatics       | 39.3              | 46.5 | 55.5 |
| Polar Aromatics | 28.5              | 25.0 | 18.6 |
| Asphaltenes     | 14.8              | 13.0 | 10.5 |

Table V

## EFFECT OF SAMPLE SIZE ON QUANTITATION

| <u>COMPONENT</u> | <u>SAMPLE SIZE</u>         |                              |                             |                               |                             |
|------------------|----------------------------|------------------------------|-----------------------------|-------------------------------|-----------------------------|
|                  | <u>5 <math>\mu</math>G</u> | <u>7.5 <math>\mu</math>G</u> | <u>10 <math>\mu</math>G</u> | <u>12.5 <math>\mu</math>G</u> | <u>15 <math>\mu</math>G</u> |
| SA               | 16.8                       | 18.2                         | 17.8                        | 19.8                          | 20.1                        |
| NA               | 23.2                       | 26.3                         | 27.6                        | 27.6                          | 27.4                        |
| PA               | 34.5                       | 34.6                         | 34.3                        | 32.7                          | 36.5                        |
| AS               | 25.5                       | 20.9                         | 20.3                        | 19.9                          | 16.0                        |

Figure 1

Iatroscan Separation of Model  
Compounds on Alumina Adsorbent

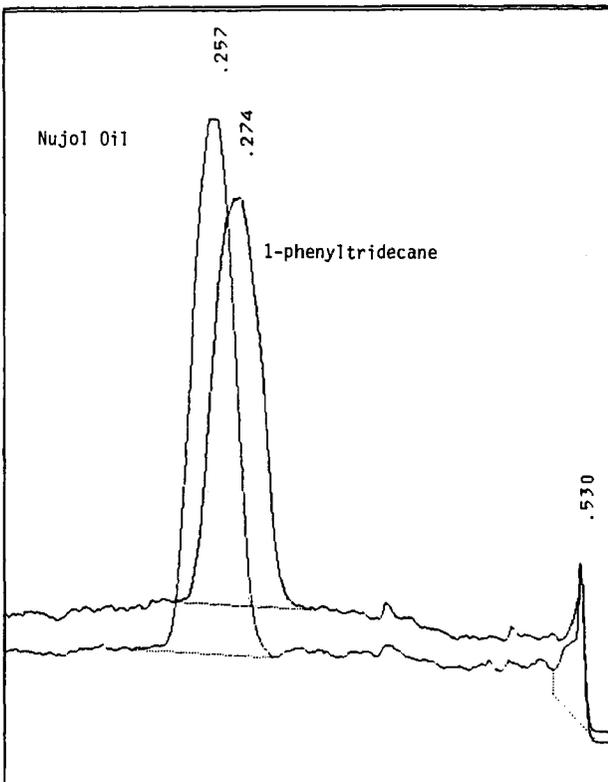


Figure 2

Iatroscan Separation of Model  
Compounds on Silica Adsorbent

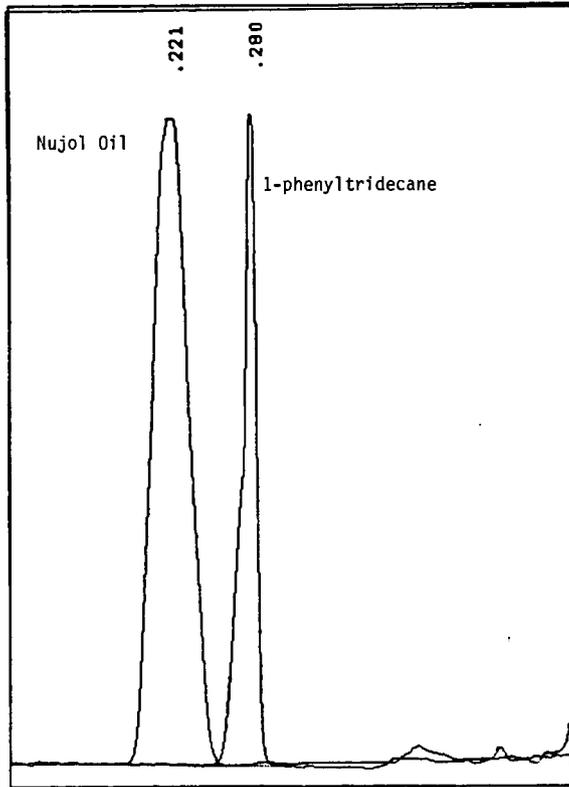


Figure 3

Sample Applied as spot

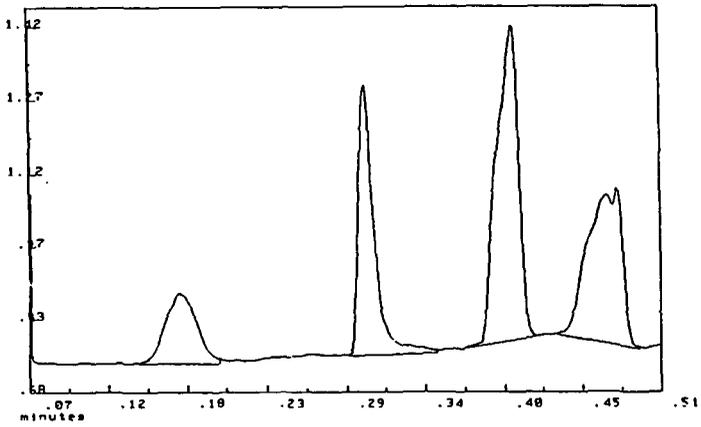


Figure 4

Sample Applied as Band

