

# Experiences with the Corbett-Swarbrick Procedure for Separation of Asphalt into Four Generic Fractions

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The Corbett-Swarbrick procedure for separation of asphalt into four generic fractions is evaluated. This procedure, currently accepted as an ASTM standard (ASTM D 4124-82), has been submitted to the ASTM committee for revision. The revised procedure involves considerable modifications to the existing standard. Oregon State University and the Oregon State Highway Division have implemented both procedures (the current ASTM standard and the revised procedure) and routinely used them in an ongoing research program. A number of difficulties have been experienced with both procedures. Some of these difficulties are related to interpretation of the standard, and some were due to the inexperience of the research team with the test procedures. The purpose of this paper is to present some of the ways the research team solved the major difficulties encountered with the implementation of the test. Several aspects of the test procedure are analyzed: method used for asphaltene precipitation, filtration, solvent concentration, and some problems related to the use of alumina and the chromatographic column.

Oregon State University (OSU) and the Oregon State Highway Division (OSHD) are involved in an ongoing program to monitor environmental effects on asphalt pavements. This involves the use of routine test procedures for asphalts and mixtures, laboratory aging procedures, and the implementation of a chemical test for asphalt fractionation. The Corbett-Swarbrick method of separating asphalt into four generic fractions was selected for implementation by both OSU and OSHD. Initially, the procedure documented in ASTM 4124-82, Separation of Asphalt into Four Fractions, was used. This procedure is referred to as Method A.

With the repetition of many tests, it was found that, even with improvements made to expedite the procedure, the test was still lengthy (2 days' work per test), expensive to run (Table 1), and relatively hazardous because of the large amount of solvents handled.

The standard test (ASTM D 4124-82) has been submitted for revision to ASTM Committee D04.47. The revised procedure involves considerable modifications to the existing standard. Although this new procedure (referred to as ASTM D 4124, Method B throughout this paper) is not yet a standard, it was

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TABLE 1 COMPARISON OF METHOD A AND METHOD B

Item	Method A	Method B
Column length	1000 mm	500 mm
Column volume	754 cm <sup>3</sup>	200 cm <sup>3</sup>
Material cost, 1985 (alumina plus solvents)	\$40.00	\$15.00
Number of tests a day (one person)	0.5 test/day	2 tests/day
Other relative savings		Energy Nitrogen Laboratory space Asphalt sample

decided to adopt it instead of the current standard procedure (Method A) originally described in ASTM D 4124-82.

The implementation of both the present standard and the new short procedure created a number of difficulties. Some of these difficulties were related to interpretation of the standard, and some were due to the inexperience of the research team with such test procedures.

It was found by personal communications that a number of laboratories that have implemented the test procedure have had difficulties similar to those experienced by the OSU-OSHD team. Further, it appears that most researchers have deviated from the standard procedure and adopted various techniques to yield the required fractions.

The purpose of this paper is to present the major problems encountered by the OSU-OSHD team with the test and present some solutions that were developed.

## CORBETT-SWARBRICK PROCEDURE

Currently accepted as ASTM D 4124, this procedure is essentially a selective adsorption-desorption column chromatographic technique (1) as shown in Figure 1. The asphaltenes are first separated from the other fractions by precipitation in a nonpolar paraffinic solvent (*n*-heptane). This removes the most polar and least soluble asphalt components so that further separation is possible of the remaining fraction known as petrolenes (maltenes). The remaining petrole fraction is then adsorbed on a chromatographic column (alumina is used as the adsorbent phase) and sequentially desorbed with solvents of increasing polarity. The three fractions obtained from the petrolenes are saturates, naphthene aromatics (*n*-aromatics), and polar aromatics (*p*-aromatics).

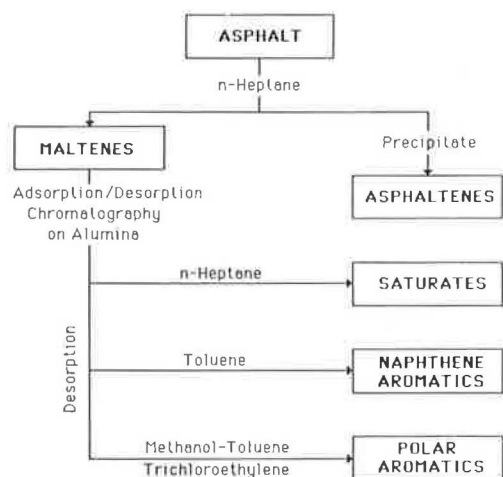


FIGURE 1 Corbett-Swarbrick scheme.

Some important aspects of the test may be summarized as follows:

- The fractionation scheme separates asphalt into less complex and more homogeneous fractions. The generic fractions are still complex mixtures of molecular groups, not well-defined chemical species.
- The precipitated asphaltene fraction in this method differs from the asphaltene fractions given by other methods because the precipitating solvent is *n*-heptane whereas other procedures use *n*-hexane and *n*-pentane.
- The method, which has been used in several research projects (1-3), presents one important advantage: it is considered nondestructive, and further separation or analysis can be done with the remaining fraction.
- The method is lengthy, as are most of the chemical composition analyses available for asphalt materials. Method A of this procedure, which is the present ASTM standard, is particularly lengthy; it takes approximately 2 days to complete one test. The short procedure (Method B) is relatively quick compared with the standard procedure (Method A); an experienced technician can usually perform two tests per day.

The problems encountered with the small column (Method B) are discussed in this paper. Method A, which uses a 1000-mm column, is essentially a large-scale test compared with Method B, which uses a 500-mm column. Thus, the problems could be considered similar in both cases.

The significant changes between Methods A and B are summarized in Table 1. The values shown represent experience at the ODOT and OSHD laboratories when both methods were used routinely.

## IMPLEMENTATION

### Asphaltene Precipitation

Four factors are to be considered during asphaltene precipitation for more uniformity in the standard procedure (4):

- Solvent concentration: Speight et al. (5) recommend that the asphalt/paraffin concentration be greater than 30 mL

of solvent per gram of asphalt. The standard procedure uses 100 mL/g. This concentration was found to be satisfactory because it permits better stirring, and, provided this concentration is always used, no variations in asphaltene precipitated will occur.

- Stirring time: Speight et al. (5) recommend that this be greater than 8 hr. The standard recommends 30 min. The stirring time of 30 min has also been found to be insufficient for aged, recovered, and blown asphalts (5). The stirring device used could also influence the total amount of time required for asphaltene precipitation. For 2 to 3 g of asphalt (amount required in Method B) at the concentration of 100 mL/g, 2 to 3 hr of stirring with an air-powered device has been found to be sufficient for all asphalts used to date by the authors.

- Time of contact between asphalt and solvent: This includes stirring time plus settling time and should not be longer than 20 hr (5). If asphaltene precipitation is perfectly achieved during stirring, the authors believe that overnight settling should not be a requirement. Instead, other filtering devices could be used so that a quick separation of asphaltenes could be made as soon as precipitation is finished. The filtering apparatus used by the authors will be outlined in the next section.

- Temperature during precipitation: Use room temperature (5). The standard procedure recommends warming the asphalt in the flask before pouring the precipitating solvent. Also, the standard specifies that during stirring the solvent should be kept at a temperature near its boiling point (approximately 90°C). No heat application is recommended by the authors because of the direct effect that this has on the final asphaltene portion. It has been observed that warming the flask before and during stirring causes the amount of asphaltenes sticking to the glass to increase considerably. The asphaltenes sticking to the glass are not removable with *n*-heptane. However, asphaltenes adhering to the glass may be dissolved in toluene and recovered by solvent removal to improve the repeatability of the results.

### Filtration Procedure

The filtration procedure described here does not correspond to the one given in the standard. The method described here is cheaper and more rapidly performed. Also, it has been observed that it yields the same proportion of asphaltenes.

The proposed procedure uses at least two filtration phases. The first phase is intended to collect the bulk of the precipitated asphaltenes immediately after stirring so that chances for the

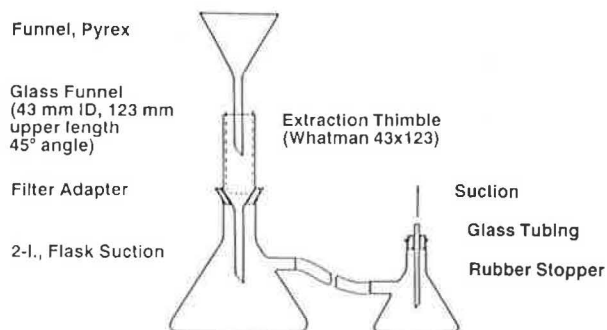


FIGURE 2 Filtration, first phase (slow procedure).

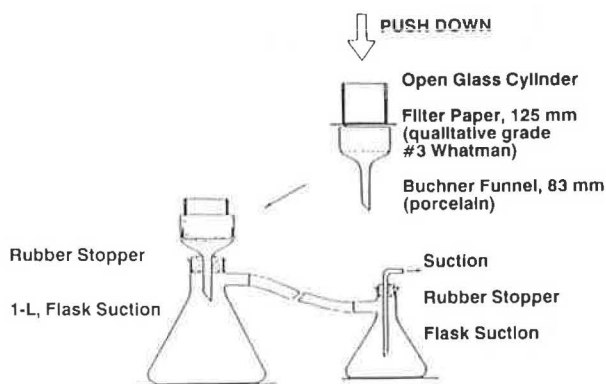


FIGURE 3 Filtration, first phase (quick procedure).

asphaltenes to stick to the glass are reduced. Also, there is no need to wait 12 hr for the settlement of the asphaltenes. Figures 2 and 3 show alternate first phase filtration methods. The second phase follows exactly the filtration procedure described in the original standard ASTM D 4124-82 (Figure 4). These procedures are described in more detail elsewhere (4).

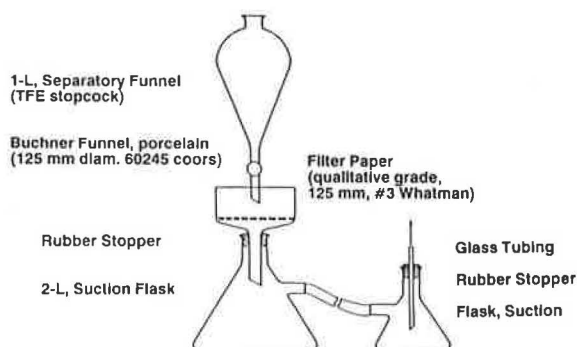


FIGURE 4 Filtration, second phase.

#### Removal of Residual Solvent from Asphaltene Fraction

The standard procedure calls for the use of an oven temperature of 104°C to remove the solvent from the recovered asphaltene fraction. It has been observed that asphaltenes have very unstable weight if heated at higher temperatures (above 60°C) or heated for longer periods. The authors recommend using 60°C until constant mass is achieved. However, through personal contact with H. Plancher at the Western Research Institute, Laramie, Wyoming, it was discovered that the instability of asphaltene weight is due to occluded resins, which may be removed by further washing of the asphaltenes with *n*-heptane.

#### Column and Alumina

Problems were encountered with the alumina used as the adsorption-desorption material in the chromatographic column. Alumina is specified in the standard as "F-20 chromatographic grade calcined at 413°C for 16 hours." The standard suggests

that the alumina may be obtained directly from the manufacturer. However, it was found that the quality of the alumina varies among manufacturers and within the production lots of one manufacturer.

Table 2 gives results of a number of tests performed with one asphalt but with alumina samples of two different manufacturers (Manufacturers X and Y). Further, alumina samples from Manufacturer X were obtained from three different lot productions. The results given in Table 2 indicate that the alumina as it is received from the supplier does not comply with the specifications and has different adsorptive capacity. It should be noted that the alumina was not calcined before any of the tests the results of which are given in Table 2.

TABLE 2 COMPARISON OF ALUMINA OBTAINED FROM DIFFERENT MANUFACTURERS AND DIFFERENT LOT PRODUCTIONS

Fraction	Manufacturer			
	X			
	Lot Number			
	X1 <sup>a</sup> (%)	X2 <sup>b</sup> (%)	X3 <sup>c</sup> (%)	Y <sup>d</sup> (%)
Asphaltenes	15.21	15.53	15.67	15.08
Saturates	23.24	15.84	10.65	12.77
Naphthene aromatics	45.10	44.02	38.21	40.91
Polar aromatics	15.61	22.85	35.08	29.91
Total	99.34	98.24	99.11	98.67

<sup>a</sup>Average of six tests.

<sup>b</sup>Average of three tests.

<sup>c</sup>Average of two tests.

<sup>d</sup>One test.

The explanation of this problem, which caused considerable delay in the test program, was that the adsorptive capacity of alumina is a function of moisture content, size, and surface area (4; 6; 7, p. 57). Size and surface area are controlled basically by the selection of an 80-200 mesh alumina. Moisture content is controlled by calcining the material at 413°C for 16 hr.

Although alumina is calcined before being packed in sealed bottles, the packing procedure probably is not carried out under vacuum conditions. Thus, during transportation and storage, the material can adsorb various amounts of water. The effect of this phenomenon is variable polarity in the alumina and erratic adsorption behavior. It is also possible that variations in particle size distribution (within specification) and impurities in alumina from different sources will influence the results of the tests.

The solution to this problem was to re-treat the alumina according to the specification given in the standard (413°C for 16 hr) and store it in a vacuum desiccator. Unfortunately, the standard is not clear in specifying such treatment as essential, which may cause other researchers to have the same problem.

The alumina from Manufacturers X and Y was re-treated and tested using another asphalt. The results, given in Table 3, indicate that there are no major variations among alumina from different sources if they are recalculated before the test is performed.

TABLE 3 COMPARISON OF ALUMINA OBTAINED FROM DIFFERENT MANUFACTURERS BEFORE AND AFTER RE-TREATMENT

Fraction	Manufacturer			
	X		Y	
	Re-treatment <sup>a</sup>		Re-treatment <sup>b</sup>	
	No (%)	Yes (%)	No (%)	Yes (%)
Asphaltenes	13.83	13.73	13.47	13.72
Saturates	16.76	11.35	14.14	11.26
Naphthene aromatics	44.42	24.65	36.29	24.24
Polar aromatics	23.01	49.30	36.05	49.07
Total	98.02	99.30	99.95	98.29

<sup>a</sup>Average of two tests.

<sup>b</sup>One test.

Another problem encountered was the filling of the column with alumina. The dry-pack method was preferred by the OSU-ODOT team (8, pp. 560–568) and found to be easily accomplished. Use of vibration during packing has a substantial effect on ease of packing.

### Cutting Point and Elution Time

The total elution time was reduced by about one-third in this study by applying continuous vacuum to the column after recovering the saturates and the *n*-aromatic fractions at the specified elution rate of 5 mL/min. The procedure is briefly explained as follows: "After collecting the second fraction (*n*-aromatics), load the column with the last solvent, open widely valves A and B [Figure 5], and close valve C. Apply continuous vacuum to the column until trichloroethylene is recovered."

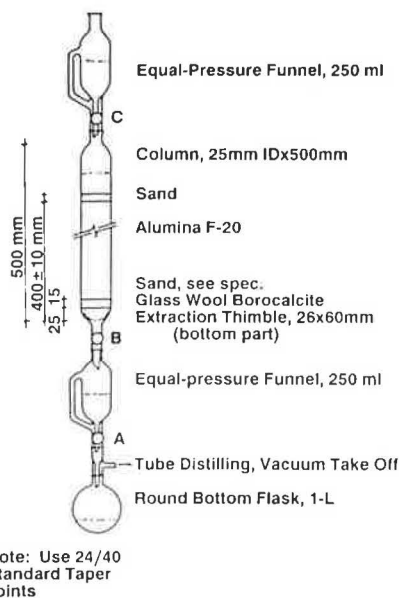


FIGURE 5 Chromatographic column.

The use of vacuum to extract the last fraction is also advantageous because it has been found (4) that all losses of the Corbett-Swarbrick procedure come from the *p*-aromatics that are retained in the alumina after elution in the column. The vacuum procedure appears to reduce these losses.

### Fraction Concentration

The solution concentration of the petrolenes and their subsequent fractions is done most quickly and efficiently with the use of a rotovapor plus nitrogen. The standard procedure should be more explicit about concentration requirements because the use of a rotovapor presents considerable advantages in this test procedure:

- Materials are concentrated in a shorter time,
- There is less chance of overheating the concentrated solution, and
- There is no air pollution at all.

### SUMMARY

Described in this paper are experiences in implementing the Corbett-Swarbrick procedure, currently ASTM standard method D 4124-82, for the fractionation of asphalt. A proposed procedure (Method B) was compared with the current standard method (Method A) and found to offer several advantages (Table 1), especially a decrease in testing time and a decrease in the cost per test.

The ASTM D 4124-82 procedure leaves room for users of the Corbett-Swarbrick method to deviate from the standard procedure, particularly those users who may be inexperienced with this type of test. It should be recognized that many state highway agencies, which may wish to adopt this test, may have experience only with the more common physical tests used for asphalt.

Some of the problems reported in this paper are related to the interpretation of the standard. However, some were due to the inexperience of the research team. One such problem was their failure to recognize that the alumina used in the chromatographic column must be recalcined before it is used, even if its container appears to be perfectly sealed. It is recommended that the standard include in the body of the text a statement regarding the need to recalcine the alumina before testing.

Other problems and recommendations for their solutions are summarized next in the hope that others will benefit from the experience gained by the authors.

For the asphaltene precipitation it is best not to warm the asphalt sample at any stage of the procedure; eliminate the warming of the flask before the test and eliminate the vapor bath to keep the solvent near its boiling point.

A quicker and simpler method is proposed that allows the filtration of the asphaltenes to be done immediately after asphaltene precipitation. This filtering procedure eliminates the necessity of settling the asphaltenes for longer periods, which, in the authors' experience, is not necessary if precipitation of the asphaltenes has been completely achieved during the stirring process. The other advantages of this method are fewer chances of having asphaltene losses, fewer chances of clogging the filtering device, and less time to perform the test.

When using either the large column (Method A) or the small column (Method B), one-third of the total time spent distilling the three fractions contained in the petrolenes could be reduced by applying vacuum to the chromatographic column after recovering the saturates and *n*-aromatics. This will also reduce losses of the *p*-aromatic fraction.

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