

EXPERIENCES IN IMPLEMENTING THE CORBETT-SWARBRICK
PROCEDURE FOR SEPARATION OF ASPHALT INTO FOUR
GENERIC FRACTIONS

by

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Submitted for

Presentation and Publication
The Transportation Research Board Annual Meeting
January 1987

August 1986

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ABSTRACT

This paper presents an evaluation of the Corbett-Swarbrick procedure for separation of asphalt into four generic fractions. The Corbett-Swarbrick procedure, currently accepted as an ASTM standard (ASTM D4124-82) has been submitted for revision to the ASTM committee. The revised procedure involves considerably modifications to the existing standard.

Oregon State University together with Oregon State Highway division have implemented both procedures (current ASTM standard and the revised procedure) and used them on a routine basis in an ongoing research program. The implementation of both procedures created a number of difficulties. Most of these difficulties were related to the the interpretation of the standard and the lack of more complete information associated with the several steps to follow when performing the entire test.

The purpose of the paper is to present the major difficulties encountered with the implementation of the test and present some recommendations for future revisions of the current standard. Several aspects of the test procedure are analysed, such as: the method used for asphaltene precipitation, filtration, solvent concentration and some problems related to the use of alumina and the chromatographic column.

INTRODUCTION

Oregon State University (OSU) and Oregon State Highway Division (OSHD) are involved in an ongoing program to monitor the effects of the environment 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 throughout this paper.

With the repetition of many tests, it was found that, even with improvements made to expedite the procedure, the test was still lengthy (two days work per test), expensive to run, and relative hazardous due to the large amount of solvents handled. Further, even though the ASTM procedure was followed in both laboratories (OSU and OSHD) reproducibility of the results was poor.

The standard test ASTM D4124-82 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 ASTM D4124, Method-B throughout this paper) is not yet a standard, it was decided to adopt it instead of the current standard procedure (Method A) originally described in ASTM D4124-82.

The implementation of both, the present standard and the new short procedure, created a number of difficulties. Most of these difficulties

were related to the interpretation of the standard and the lack of more complete information associated with the several steps to follow when performing the test. Also, the research team had little previous experience with such test procedures.

Difficulties with the test procedure encountered in the present research are not new but have seldomly been reported. Nevertheless it was found by personal contact that a number of laboratories that have implemented the test procedure have had similar difficulties. Further, most reseachers have deviated from the standard procedure and adopted various different laboratory techniques to yield the required fractions.

The purpose of this paper is to present the major problems encountered with the implementation of the test and present some recommendations for future revisions of the ASTM chemical fractionation procedure.

THE CORBETT SWARBRICK PROCEDURE

Currently accepted as ASTM D4124, this is essentially a selective adsorption-desorption column chromatographic technique (1) as shown in Figure 1. The asphaltenes are first separated based on their solubility in a non polar 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 petrolene 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, naphtene-aromatics, and polar-aromatics.

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

- a) The fractionation scheme separates asphalt into less complex and more homogeneous fractions. The generic fractions are in themselves still complex mixtures of molecular groups and not well defined chemical species.
- b) The asphaltene fraction in this method differs from all the asphaltene fractions given by other methods because the precipitating solvent is n-Heptane.
- c) The method itself has been used in several research projects (1,2,3) presenting one important advantage, that is, the method is considered to be non-destructive and further separation or analysis can be done over the remaining fraction.
- d) The method is lengthy. this is also true for most of the chemical composition analysis available for asphalt materials. This last is applicable for Method-A of the procedure which is the present ASTM standard. The short procedure (Method-B) is relative short as compared with the present standard.

This paper discuss the problems referring to the small column (Method-B). Nevertheless, 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 to be similar in both cases.

The overall significance of this reduction are summarized in Table 1. The values shown in Table 1, represent the differences experienced at Oregon State laboratories (ODOT and OSHD) when running both methods on a routine basis. The values given are similar to those experienced by other

laboratories.

TEST IMPLEMENTATION AND DISCUSSION

Asphaltene Precipitation:

Four factors are to be considered during asphaltene precipitation for more uniformity of the standard procedure (5). These are:

- a) Solvent concentration: Reference (4) recommends that the asphalt/paraffin concentration should be greater than 30 mL of solvent per g of asphalt . The standard procedure uses 100 mL/g of asphalt. This concentration was found to be satisfactory since it permits better stirring and provided this concentration is used always, no variations in asphaltene precipitated will occur.
- b) Stirring time: This should be greater than 8 hrs (4). 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 the asphaltene precipitation. For 2 to 3 g of asphalt (amount required in Method-B) at the above concentration of 100 mL/g , 2 to 3 hours of stirring (respectively) with an air powered device has been found to be sufficient for all asphalts used to date by the authors. The use of an ultrasonic bath after that period of time could improve the efficiency of the precipitation.
- c) Contact time between asphalt and solvent: This includes stirring time plus settling time. This should not be greater than 20 min. (4). If the asphaltene precipitation is perfectly achieved during

the stirring process the authors believe that overnight settling should not be a requirement. Instead, other filtering devices could be use so that a quick separation of asphaltenes could be made as soon as the precipitation is finished. The filtering apparatus used by the authors will be outlined in the next section.

- d) Temperature during precipitation: Use room temperature (4). The standard procedure recommends the warming of the asphalt in the flask before pouring the precipitating solvent. Also, the standard specifies that during the stirring process, the solvent should be kept at a temperature near its boiling point (approximately 90 C). None of the heating application is recommended by the authors due to the direct effect that this has on the final asphaltene portion. By warming the flask before and during the stirring process it has been observed that the amount of asphaltene sticking to the glass will considerably increase. The asphaltene sticking to the glass are not removable with n-Heptane.

Filtration Procedure

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

The proposed procedure considers the use of at least two filtration phases. The first phase is intended to collect the bulk of the the

precipitated asphaltenes immediately after the stirring process so that chances for the asphaltenes to stick to glass are reduced. At the same time, there is no need for waiting 12 hours for the settlement of the asphaltenes (Figure 2 and 3). The second phase follows exactly the filtration procedure described in the original standard ASTM D4124-82 (Figure 3).

These procedures are described in more detailed in reference (5).

Removal of Residual Solvent of Asphaltenes

The standard procedure calls for the use of 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 recommends to use 60 C until constant mass is achieved.

Column and Alumina

Special problems were encountered by the authors during the present research 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 under the above specifications could be obtained directly from the manufacturer. Nevertheless, it was found that the 'quality' of the alumina will vary among manufacturers and within the production lots of one manufacturer.

Table 2 shows results of a number of tests performed with one asphalt

but with alumina samples of two different manufacturers (Manufacture A and B). Further, alumina samples from manufacture 'A' were obtained from three different lot productions. The results shown 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 prior to any the test whose results are given in Table 2.

The explanation to the above 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 (5,6,7). The size and surface area is controlled basically by the selection of an 80-200 mesh alumina. The moisture content is controlled by calcining the material at 413 C for 16 hours.

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 solution to this problem was to retreat the alumina according to the specification given in the standard (413 C for 16 hours) and store in a vacuum dessicator. Unfortunately, the standard is not clear in specifying the above treatment as essential. This may have caused other researchers to have the same problem as was found later by the authors through personal contact.

The alumina from manufacturers 'A' and 'B' was retreated and tested using another asphalt. The results are shown in Table 3 and shows that there are no major variations among the different sources of alumina used

if they are recalcined before performing the test.

Another problem encountered by other researchers is the filling of the column with the alumina. The dry pack method was preferred by the OSU/ODOT team as described in reference (9), and found to be easily accomplished.

Cutting Point and Elution Time

The total elution time was reduced considerably in the present research by applying continuous vacuum to the column after recovering the first and second fraction at the specified elution rate of 5 mL/min. The procedure is briefly explained as follow: " After collecting the second fraction (Naphtene-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 reaches the bottom of the alumina bed." Since it is easy to remove the alumina when is in slurry state, it is recommended to add 150 mL of recovered n-Heptane to the top of the trychloroethylene so that this solvent is left in the column for easy cleaning.

The use of vacuum to extract the last fraction is also favorable since it has been found (5) that all losses of the Corbett procedure comes from the Polar-Aromatics which are retained in the alumina after the elution in the column.

Fraction Concentration

The solution concentration of the Petrolenes and its subsequent fractions is done most quickly and efficiently with the use of a

rotovapor plus Nitrogen. The standard procedure should be more explicit with the concentration requirements since, the use of a rotovapor presents considerable advantages particularly to this test procedure. Some of these advantages are:

- a) Materials are concentrated in shorter time.
- b) Less chance to overheat the concentrated solution.
- c) When the solution is composed of several solvents of different boiling points (e.g. Polar-Aromatics), there is no danger of explosion.
- d) No air pollution at all.

SUMMARY

Asphalt materials are recognized to be fairly complex substances where there are a large number of parameters to be considered when performing any test so that meaningful repeatability and reproducibility of the results can be achieved.

The ASTM D4124-82 is only one example of a test for asphalt materials which is insufficiently explained causing many researchers to deviate from the standard procedure. The problems reported in the present paper are basically related to the interpretation of the standard. The fact that important requirements are left as notes or footprints instead of been contained in the body of the procedure creates unnecessary room for different application of the test method. It is recommended that the standard include on the body of the text all statement regarding the requirements of the materials used in the test procedure particularly the necessity to recalcine the alumina prior to the test.

For the asphaltene precipitation it is not recommended to warm the asphalt sample at any stage of the procedure. Thus, eliminating the warming of the flask prior to the test and eliminating the a vapor bath to keep the solvent near to its boiling point.

A quicker and simpler procedure is proposed so that the filtration of the asphaltenes can be done immediatly after the asphaltene precipitation. This filtering procedure eliminates the necessity of settling the asphaltenes for longer periods which in the author's opinion is not necessary if the precipitation of the asphaltenes has been completly achieved during the stirring process. The other advantages of the proposed procedure are: less chances of having asphaltene losses, less chances of clogging the filtering device and less time to perform the test.

Either when using the large column (Method-A) or the small column (Method-B), a third of the total time spent distilling the three fractions contained with the petrolenes, could be reduced by applying vacuum to the chromatographic column after recovering the Saturates and N-Aromatics. This, will also reduce the losses of the P-Aromatic fraction.

The proposed procedure (Method-B), present a number of advantages over the current standard. Some of these advantages era given in Table 1.

REFERENCES

- (1) L. W. Corbett, "Composition of Asphalt Based on Generic Fractions, Using Solvent Deasphalting, Elution-Adsorption Chromatography, and Densimetric Characterization", *Analytical Chemistry*, Vol.41,1969, pp. 576-579.
- (2) L. W. Corbett, "Relationship Between Composition and Physical Properties of Asphalt", *Proceeding of the Association of Asphalt and Paving Technology*, Vol 39, 1970, pp. 342-346
- (3) L. W. Corbett and R. M. Menz, "Asphalt Binder Hardening in the Michigan Test Road After 18 years of Service", *TRB-554*, pp. 27-34
- (4) J. G. Speight, R. B. Long and T. D. Trowbridge, "Factors Influencing the Separation of Asphaltenes from Heavy Petroleum Feedstock", *Fuel*, Vol. 63, May 1984 pp. 616-620.
- (5) G. Thenoux, C. A. Bell, J. E. Wilson, D. Eakin and M. Schroeder, "Evaluation of Asphalt Properties and their Relationship to Pavement Performance", *Interim Report to Oregon Department of Transportation, Salem, Oregon, FHWA-OR-RD-86-02, Feb.1986.*
- (6) S. Hala, M. Kuras and M. Popl, "Analysis of Complex Hydrocarbon Mixtures", Vol. XIII, Elsevier Scientific Publishing Co., 1981, pp. 116-120.
- (7) R. L. Pecsok, L. D. Shield, T. Cairns and I. G. McWilliam, *Modern Methods of Chemical Analysis, Second Edition, John Wiley and Sons, 1976, pp. 56.*
- (8) F. A. Cotton, G. Wilkinson, "Advanced Inorganic Chemistry", Fourth Edition, John Wiley and Sons, 1979, pp. 329-330.

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- (9) D. L. Pavia, G. M. Lampman and G. S. Kriz, Organic Laboratory Techniques, Second Edition, Saunders College Publishing, 1982, pp. 560-568.

ACKNOWLEDGMENTS

The work presented in this paper was conducted as part of a Highway Planning and Research (HP&R) Project funded through the U.S. Department of Transportation Federal Highway Administration (FHWA), and Oregon Department of Transportation.

The authors are grateful for the support and encouragement of Glen Boyle and his staff in the mix design unit of Oregon state Highway Division. We are also grateful to the Department of Civil Engineering, Oregon State University for provision of laboratory facilities.

DISCLAIMER

The opinions expressed in this paper are those of the authors and not necessarily those Federal Highway Administration (FHWA), Oregon Department of Transportation (ODOT) and Oregon Department of Transportation.

TABLE 1: OVERALL SIGNIFICANCE OF THE CHANGES

	METHOD "A"	METHOD "B"
COLUMN LENGTH	1.0 m	0.5 m
COLUMN VOLUME	754 cc	200 cc
MATERIAL COST (ALUMINA PLUS SOLVENT)	\$ 40.00	\$ 15.00
TIME FOR ONE LABORATORY TECHNICIAN (NUMBER OF TESTS PER DAY)	0.5 tests	2.0 tests
OTHER SAVINGS:	--	ENERGY
	--	NITROGEN
	--	LAB. SPACE
	--	ASPHALT SAMP.

TABLE 2. COMPARISON OF ALUMINA OBTAINED FROM DIFFERENT MANUFACTURERS AND DIFFERENT LOT PRODUCTION

FRACTIONS	MANUFACTURER "A"			"B"
	LOT NUMBER			
	X	Y	Z	
ASPHALTENES	15.21%	15.53%	15.67%	15.08%
SATURATES	23.42%	15.84%	10.65%	12.77%
N-AROMATICS	45.10%	44.02%	38.21%	40.91%
P-AROMATICS	15.61%	22.85%	35.08%	29.91%
TOTAL	99.34%	98.24%	99.11%	98.67%
AVERAGE OF:	6 tests	3 tests	2 tests	1 test

TABLE 3. COMPARISON OF ALUMINA OBTAINED FROM FROM DIFFERENT MANUFACTURERS BEFORE AND RETREATMENT

FRACTION	MANUFACTURER "A"		MANUFACTURER "B"	
	RETREATMENT		RETREATMENT	
	NO	YES	NO	YES
ASPHALTENES	13.83%	13.73%	13.47%	13.72%
SATURATES	16.76%	11.35%	14.14%	11.26%
N-AROMATICS	44.42%	24.65%	36.29%	24.24%
P-AROMATICS	23.01%	49.30%	36.05%	49.07%
TOTAL	98.02%	99.03%	99.95%	98.29%
AVARAGE OF:	2 tests	2 tests	1 test	1 test

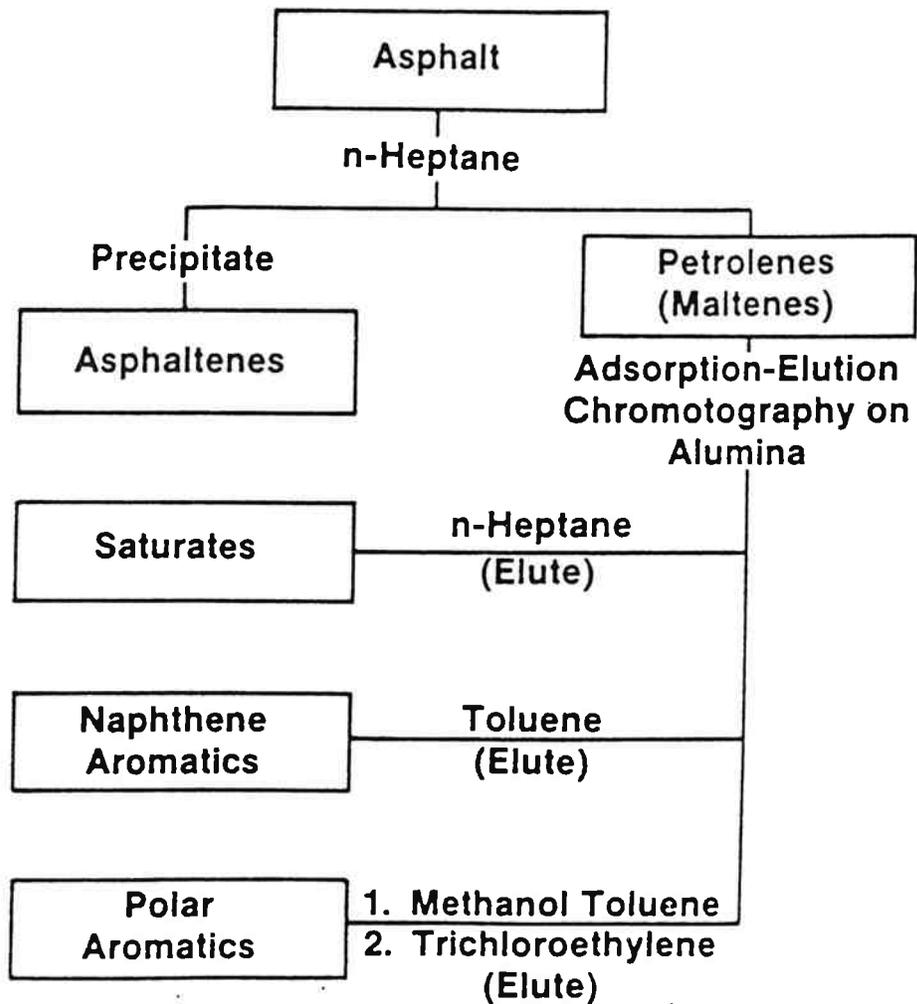


FIGURE 1 : CORBETT-SWARBRICK SCHEME

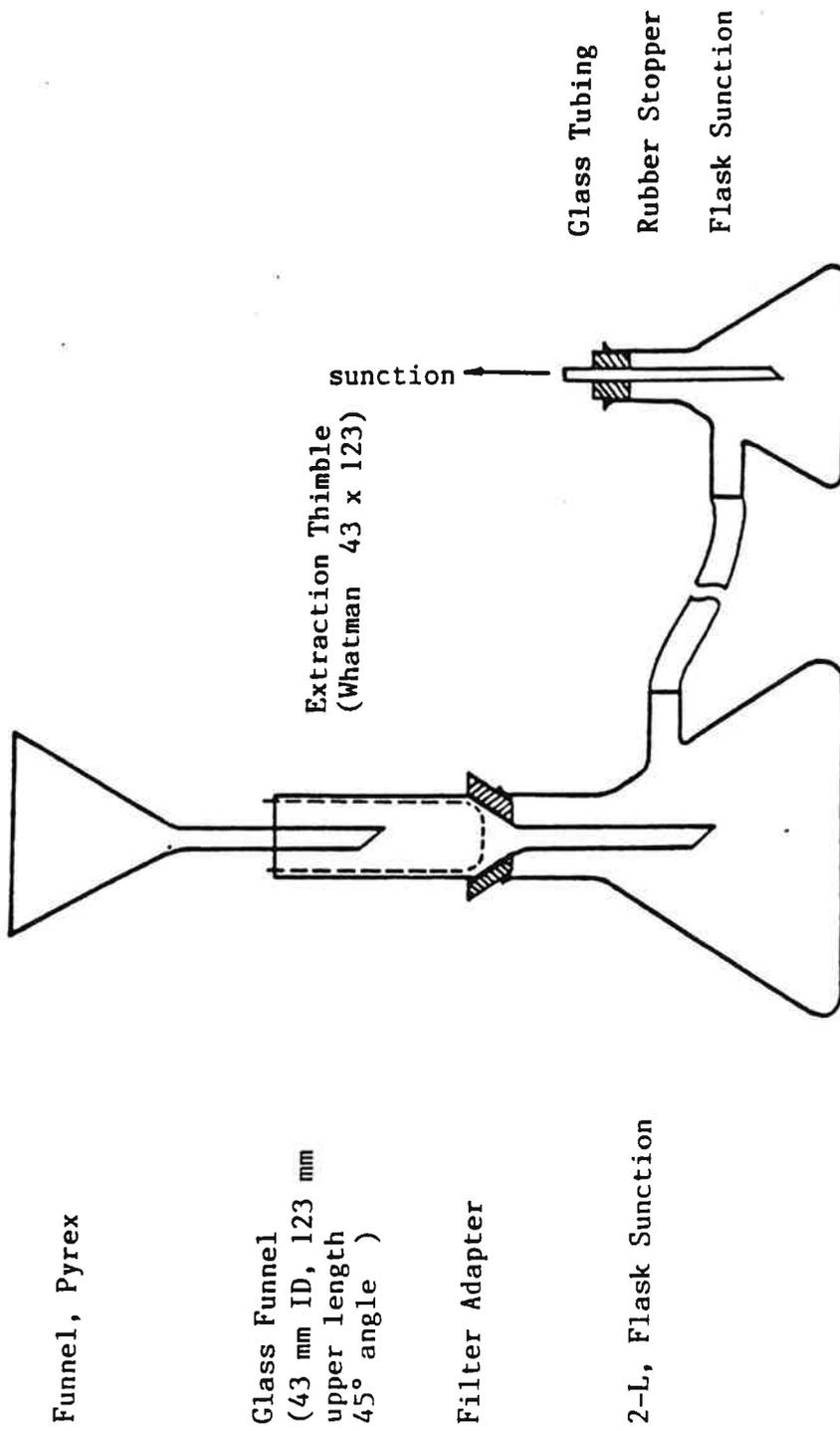


FIGURE 2 : FILTRATION, FIRST PHASE

(Slow procedure)

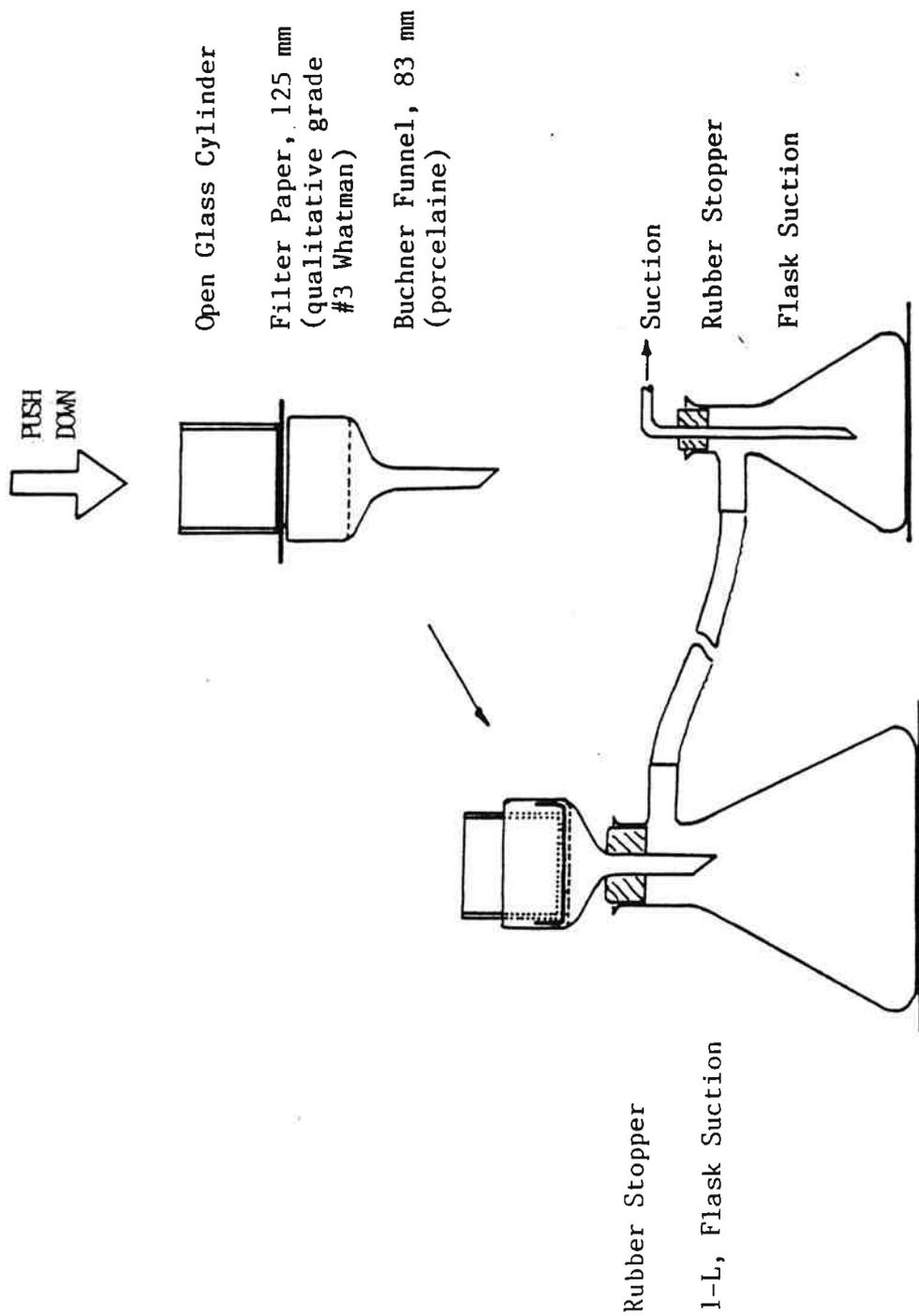


FIGURE 3 : FILTRATION, FIRST PHASE
 (Quick procedure)

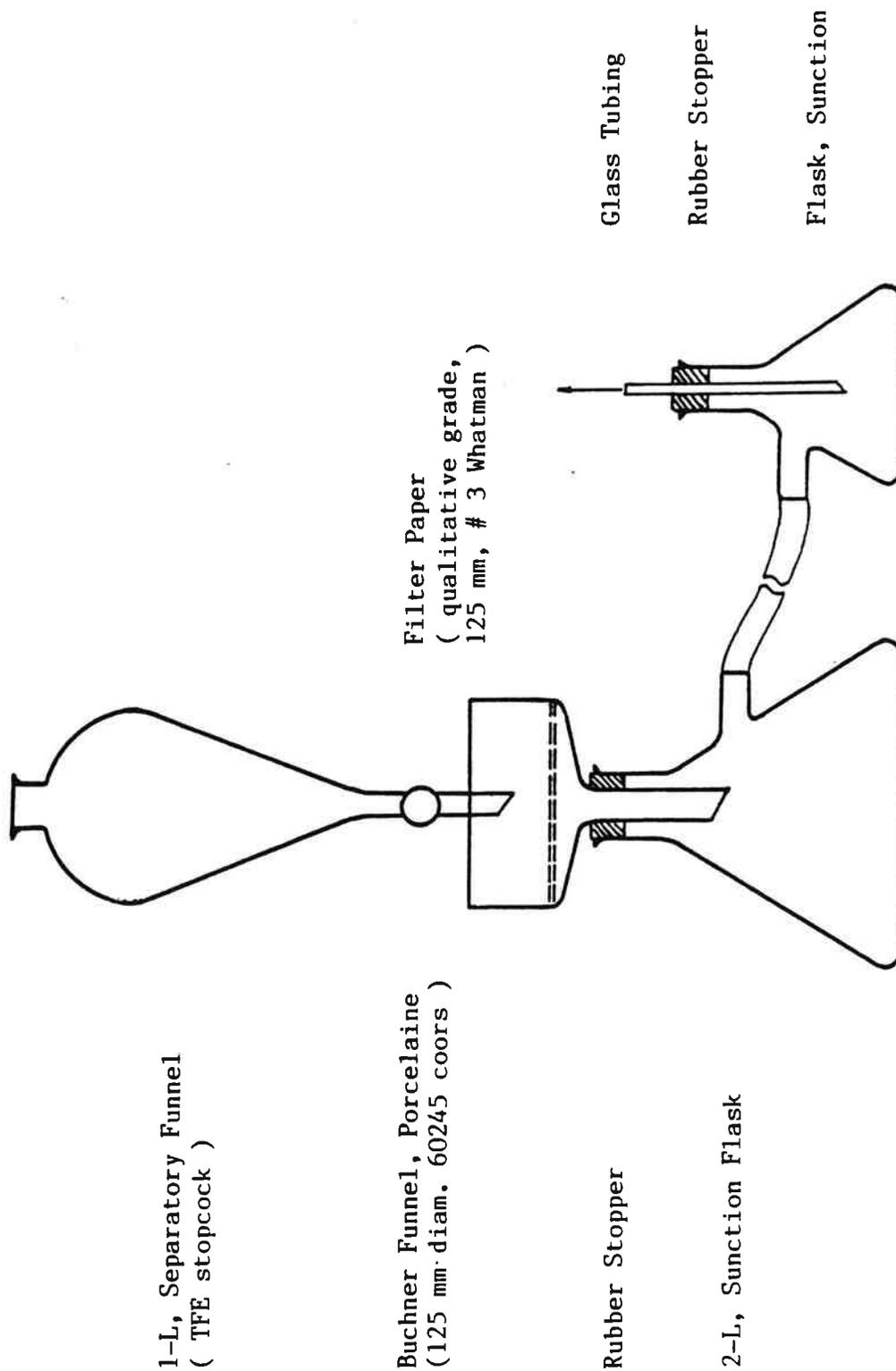
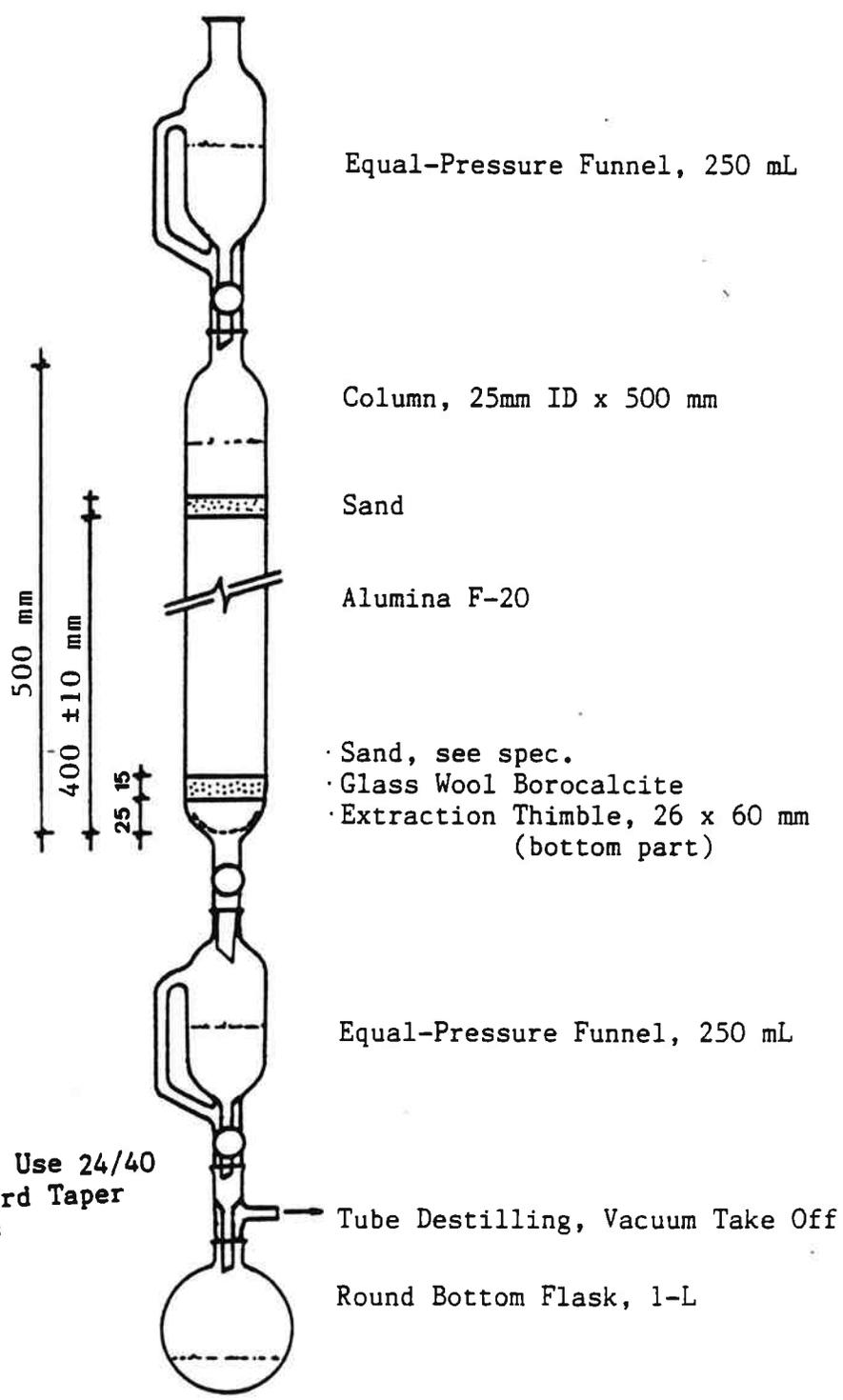


FIGURE 4 : FILTRATION, SECOND PHASE



Note : Use 24/40 Standard Taper Joints

FIGURE 5 : CHROMATOGRAPHIC COLUMN