USING CELLULOSE FILTERS IN THE SOLUBILITY TESTING OF ASPHALT CEMENT

By

GEORGE RAY MURRELL

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

1968

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
May, 1969

USING CELLULOSE FILTERS IN THE SOLUBILITY

TESTING OF ASPHALT CEMENT

Thesis Approved:

Phillip L. Marker
Thesis Adviser

R L Janes

N. D. Durham
Dean of the Graduate College

TO MY WIFE:

for her patience, sacrifice,

understanding, and

encouragement

ACKNOWLEDGMENTS

The author wishes to express gratitude and sincere appreciation to the following individuals:

To his major advisor, Professor Phillip G. Manke, for his consultation and expressed interest throughout this research.

To his committee members, Professor R. L. Janes, and Professor M. Abdel-Hady, for their interest and assistance.

To fellow graduate students, Captain R. Matalucci and Samuel Ng, for their help in taking pictures.

To his parents, Lucille and Ray Murrell, for being good examples from which to learn.

To Mrs. Nancy Wolfe for typing the manuscript.

To Mr. Eldon Hardy for assistance in preparation of graphical portions of this thesis.

To Gordon Eubanks for his help with the computer program.

To Dan Marks for his help in getting my paper in to the Graduate Office.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Modern asphalt highways require high quality materials. Since good quality asphalt cement is a necessity, several standard tests have been devised and employed to estimate asphalt quality. One such test which has been used for many years is the determination of the proportion of bitumen soluble in carbon tetrachloride. Probably the first reference to this test was made in 1908 by Clifford Richardson (1). In 1923, Richardson's solubility test was tentatively adopted by the American Society for Testing and Materials (2). In 1927, this procedure was accepted in substantially unchanged form as an A.S.T.M. standard test procedure with the designation D 165-27 (3). This test was slightly revised in 1942. In 1966 A.S.T.M. adopted a similar test called "Solubility of Bituminous Materials in Organic Solvents" under the designation D 2042 (4).

In the present method, D 2042, four solvents can be used. These are carbon disulphide, carbon tetrachloride, benzene and trichloroethylene. Two of these solvents are used to find the proportion of bitumen soluble in carbon tetrachloride. To find this proportion, a sample of asphalt cement is dissolved in carbon disulfide and another sample is dissolved in carbon tetrachloride. These solvent-asphalt cement solutions are poured through filters consisting of asbestos mats prepared in Gooch crucibles. Insoluble portions of both solutions are

retained on the filters and the percent of insoluble material on a weight basis can be determined from the filter and crucible weights before and after the filtration process. The proportion of bitumen soluble in carbon tetrachloride is the per cent by weight of the sample soluble in carbon tetrachloride divided by the per cent by weight of sample soluble in carbon disulfide.

This paper is primarily concerned with the filter media, and therefore, only one solvent was used. Because of the high flammability and toxic nature of carbon disulfide, carbon tetrachloride was selected for the tests. If the asphalt cement samples are assumed to be 100% bitumen, then the percentage of the sample soluble in carbon tetrachloride can be called the proportion of bitumen soluble in carbon tetrachloride.

There are many inherrent drawbacks in the use of asbestos filters. The asbestos filter is difficult to make, and its effectiveness depends a great deal upon the ability of the operator to prepare the filter mat. Even if the operator's procedure is good, there is still present an inability to make a uniform size filter with constant pore diameter. Another weakness of asbestos filters is the small amount of soluble bitumen which is irreversibly adsorbed by the asbestos fibers (4). Still another disadvantage of the asbestos filter involves the thickness of the filter mat. The standard test method does not specify a minimum length of asbestos fiber to be used. Different lengths of fiber can cause differential thicknesses of mats having approximately the same weight, thus affecting the efficiency, and effectiveness of the filtering media.

This paper proposes a method of filtration using Millipore membrane filters or other similar type filters. Millipore filters are

porous membranes composed of pure and biologically inert cellulose esters (5). These cellulose filters are quite uniform in size, and they allow a large rate of flow through the filter as compared to the slower rate of the asbestos mat. Few fluids, including those used in this test, will attack the cellulose filter. These filters are also quite applicable to gravimetric analysis because of the filter's almost complete destruction after ignition, yielding a residual of only a few micrograms. All particles larger than the pore sizes of the filter are retained in such a manner as to allow inspection under a microscope. The filter itself will become transparent if it is immersed in an oil of matching refractive index.

The objective of this paper is to show statistically that the cellulose filter can yield results which are more reproducible than those obtained using the asbestos filter, and to point out other desirable characteristics of the cellulose filters related to subsequent analysis of the cake (insoluble material retained on the surface of the filter).

A series of tests using four different pore size Millipore filters as well as the standard asbestos filter were conducted. Different sizes of cellulose filters were used in order to arrive at a pore size having approximately the same retention capacity as the asbestos filter. Three different penetration grade asphalts were used in these tests to determine if consistency of the asphalt cement had any effect upon the results.

A computer program was developed to compare the means and variances of the data. The mean of twelve determinations of solubility was computed for each filter. The Millipore filter size with a mean closest to that of the asbestos filter was chosen for the analysis of variances

using the F test. A comparison of variances indicated which of the respective filters yielded results with the lowest deviation. Results indicated that the Millipore filter could successfully be substituted for the asbestos filter without sacrificing any objectives of the standard test.

CHAPTER II

REVIEW OF LITERATURE

Interpretation of Solubility Tests

In the past there appears to have been some discrepancy with regard to the purpose of solubility tests for asphalt cements. The purpose of A.S.T.M. D 165 was to determine the proportion of bitumen that is soluble in carbon tetrachloride (3). The word bitumen can be misleading when connected with A.S.T.M. D 165. Bitumen is defined as being hydrocarbon material of natural or pyrogenous origin, or combinations of both, frequently accompanied by their nonmetallic derivatives, which may be gaseous, liquid, semisolid, or solid, and which is completely soluble in carbon disulfide (6). The purpose of A.S.T.M. D 165 implied that the sample used was 100% bitumen and neglected the fact that other contaminants or extraneous insoluble materials might have been present in the sample.

Most specifications for asphaltic materials include a minimum percent of sample (bitumen + other extraneous materials) soluble in carbon tetrachloride. The Texas Highway Department in their manual of test procedures includes a solubility test identical with A.S.T.M. D 165 (7). The purpose of this test as listed in the Texas Highway Department manual is to detect any contamination of asphalt due to extraneous materials, such as coal tar, salt, and other mineral matter. This interpretation of the carbon tetrachloride solubility test A.S.T.M.

D 165 is in agreement with the purpose of the specifications concerning the minimum per cent of sample soluble in carbon tetrachloride.

The California State Highway Department also includes in their manual of test procedures an asphalt cement solubility test (8). The purpose of this test, as stated in the manual, is to determine whether an asphalt has been overheated or "cracked" during production. Such treatment will cause the formation of an excessive amount of material known as carbenes (asphaltic material soluble in carbon disulfide and insoluble in carbon tetrachloride).

In this procedure the carbon disulfide test must be run in conjunction with the carbon tetrachloride test. There is no concern about non-asphaltic materials such as salt which are contained in the sample.

Broome (9) stated that, in general, the higher the carbene content the more highly metamorphosed (changed in structure) is the bitumen. Asphaltic bitumens do not show this change in structure unless they have been overblown or overheated (cracked in the manufacturing process).

Information on the reliability of asbestos filter mats is presented in an article in Sewage and Industrial Wastes titled "Suspended Solids Determination" (10). Asbestos filters in Gooch crucibles were used in sewage filtration. To ascertain whether or not pieces of asbestos fiber were being washed out of the Gooch crucibles during filtration, a series of tests were conducted using distilled water as the filtering material. Asbestos mats were prepared in Gooch crucibles and ignited in the same manner as in asphalt cement solubility tests. Distilled water was passed through the asbestos mats after they had cooled to room temperature. The filters were then dried in an oven and

again cooled to room temperature. It was shown that in all cases the filters lost weight when distilled water was passed through them. In one case, the filter mat lost 0.0044 grams from its original weight of 0.1112 grams. This was a reduction in weight of 3% which could not be tolerated. It was suggested that the diameter of the openings in the Gooch crucible be reduced to prevent loss of the asbestos fibers. However, in the solubility testing of asphalt cement, it would not be possible to reduce the Gooch crucible openings without a reduction in the already very slow flow rate.

In A.S.T.M. test D2042 a table is presented showing estimates of standard deviations for the test when conducted using correct lab procedure. If a series of solubility tests are performed, the calculated standard deviation must be multiplied by $\left[1+1/4(N-1)\right]$ before comparing it with values listed in the tables. N is the number of solubility determinations used to make the standard deviation calculation. The correction factor approaches one when a large number of determinations are made. This follows one of the rules of statistics, i.e., to get a representative sample a large number of determinations must often be made. Also given in the table are values of repeatability and reproducibility. Repeatability values are maximum differences which should be tolerated within one laboratory, while reproducibility values are maximum differences which should be tolerated between laboratories.

New Methods of Testing

Varma and Sheffert (11) suggested that cellulose membrane filters be used in solubility testing of asphalt cement. The method suggested is similar to the method employed in this paper. Membrane filters with

0.8 micron pore size were used to compare their retention capacity to that of the standard asbestos mats. Results indicated a high correlation factor of 0.812 between the data of both filters. A paired t test was also employed to analyze the data. At the 50 per cent confidence level the calculated t value was less than the critical value for 9 degrees of freedom. There was no investigation in this paper comparing the variances and standard deviations of both filter types. The number of solubility determinations was small, and therefore any type of variance analysis might have been meaningless. They suggested that a controlled series of tests be conducted with known levels of carbon tetrachloride-insoluble material. This type of controlled test probably should be performed using minerals as the insoluble material since the use of insoluble asphalt particles (carbenes) would not be practicable because of the difficulty in obtaining them without the use of a filtering procedure similar to the one under consideration.

Varma and Sheffert listed several advantages of membrane filters: larger quantities can be filtered, membrane filters can be preserved for future reference, filtration can be done in the field, results are more reproducible, and the test is quicker. The need for field testing is questionable, particularly since a 12 hour minimum waiting period is prescribed for the solutions, but it is true that filtration in the field would be a faster operation using the membrane filters.

A preliminary study on the use of this type of filter in the solubility testing of asphalt cement was made at Oklahoma State University in 1965. The object of the work was to measure retention capacity, but not reproducibility of results. Filters of 0.45 and 1.2 micron diameters were used in the tests conducted and two penetration

grades of asphalt were employed to determine what effect asphalt consistency had on the retention capacity of the filters.

Olienses (12) developed a test similar in purpose to the solubility test. This test, first published in 1933, is called the Oliensis Spot Test (13). This test also serves to detect in a qualitative manner asphalts that in the process of refining have been subjected to a degree of overheating or cracking sufficient to have affected their normal quality. Samples which have been overheated will show up positive by the spot test. This test has been used for years by many laboratories, but it is probably less exact than the solubility test.

Theory of Filtration

The word "filter" is derived from the Latin word filtrum, meaning felt or compressed wool. The word filter was first used in connection with the filtration of certain liquids through some type of felt or cloth (14). For many years the most common filter medium was a type of cloth. It was later discovered that liquids could be forced more easily through these cloth filters using pressure. These pressure filters were first used in beet-sugar filtration (15). Pressure filtration usually involved either a large continuous head or a mechanical pressure applied to the filter.

Box filters (filters which are held together by a container) were developed partly to be used in pressure filtration. Gooch (15) developed a modification of the box suction filter for use in solid determination. The most common filters used in the Gooch box were asbestos mats. Dr. Julius Lowe first described asbestos filters saying that they had the advantage that they could be used to filter corrosive

liquids.

At the same time that different filtering methods were being developed, theories were being introduced to explain the filtration processes. Genter (16) first pointed out that filtrate flow occurred simultaneously with solid packing of particles into the cake (material retained on the filter). Genter noticed that certain properties of the solids involved determined filtration rate, speed of cake formation, and other variables of filtration. Some variables of filtration were listed as; effective filter area, filtration pressure, nature of the solids, water or solution present in the sludge and filter cake and its density, rate of solids deposited in the filter cake, resistance of filter base to filtrate flow, time by which rate factors are measured, coefficient of viscosity of filtrate or sludge moisture, and temperature.

One of the earliest formulas related to filtration was developed by Poiseuille (17). He published a formula for eddyless flow of liquids under pressure through capillary tubes. This equation proved to be correct also for flow through sand and various porous media. The equation is:

$$V = Pr^4 / 8Lu$$

where:

V = flow velocity

P = pressure difference at tube ends

r = internal capillary radius

L = length of opening

u = viscosity of the fluid.

The Poiseuille equation was approximate if there was no build-up of particles on the filter. Ruth (18) developed the following equation to take into account this particle build-up:

$$(V + C)^2 = (2A^2P/\alpha Z)\left[(1 - ms)/P^s\right](\theta + \theta_o)$$

where:

V = filtrate volume

C = filtrate volume to produce a cake equal in resistance to the filter cloth

A = filter area

P = filtration pressure

α = average specific resistance of dry solid

Z = relative viscosity

m = ratio of wet (solute-free) to dry cake weight

s = weight fraction of solids in the sludge

θ = filtering time

θ_o = theoretical time to form a cake of resistance equal to cloth resistance present at the start of filtration.

This equation is quite similar to the one developed by Sperry (19).

Hatschek (20) published an article in 1908 which took a less theoretical approach to the science of filtration. He was of the opinion that the filtration process should be considered a simple mechanical process, as the main operation was passage of a particle through a porous medium. He stated that effectiveness of the filter was directly related to the particle size and shape of the material being retained on the filter. This was because the settlement of particles on the filter formed orifices through which the remaining

material had to pass. After a layer of cake developed, it was relatively unimportant what sizes of pores were contained in the filter if the cake orifices had diameters smaller than the filter pore diameters.

Hatschek reported that irregular shaped particles required much larger pore openings than uniformly shaped ones. This was because of the interlocking of the irregular shaped particles to form compact layers which greatly reduced the flow. He also noticed that in many cases elongated particles seemed to align themselves with their long axis in the direction of flow. This alignment was attributed to the tendancy of the particles to seek a position offering minimum resistance to flow of the liquid. Hatschek further pointed out that the filters would only retain particles whose smallest diameter was larger than the diameter of the filter pores and that the resistance to flow increased as the size of particles deposited decreased.

Sperry (21) published later articles on principles of filtration under constant pressure conditions. He stated that there were two changing processes in filtration, 1) build-up of a cake of particles, and 2) rate of flow of liquids travelling through the filter.

In some cases it may be desirable to determine pore sizes of certain filters involving extremely small pores. These pore size determinations can be made with Skan-Ruska mercury intrusion measurements of pore radius using the following relationship (5):

$$r = - \frac{2\gamma \cos \theta}{P}$$

where:

r = pore radius

P = pressure

γ = coefficient of surface tension of mercury

θ = contact angle with respect to the filter matrix.

Pore-size distribution curves can be plotted from data obtained using the above formula.

Filtration for Solids Recovery

The primary objective of a solubility test is to collect the suspended solids in a solution on a filter. In a 1923 article, Donald and Hunneman (22) presented many of the principles governing the recovery of solids. They gave four different methods of extracting solid materials from the filtrite. They were constant pressure, constant rate, with a filter aid, and without a filter aid. Donald and Hunneman mentioned that filter aids would reduce or increase filtering rates. They used silica as a filtering aid. Silica impurities increased rates of a clay filtration and prevented any dense consolidation of clay particles, thus reducing clogging of the filter. Presence of magnesium in caustic calcium carbonate solutions had the opposite effect and was decidedly detrimental to flow.

Temperature is an important factor in collection of solids and changing of flow rates of the filtrate. High temperatures decrease viscosity and therefore increase the rate of flow, thus, high temperatures can sometimes be used to speed up the filtration process. However, caution must be employed as flow rates may tend to become too fast for the filter medium employed. Fast flow rates may cause particles to hit the filter with enough momentum to cause embedment in the pores of the filter. A great deal of particle embedment can render the

filter ineffective.

Different filtration methods also effect rates of filtration. Press filters (flow increased by mechanical pressure) tend to force particles closer together, clogging the filter. Gravity filters (filters subjected to large filtering head) pack a cake of much less density. Continuous (flow changes directions to allow for cleaning of filter without stopping process) filters are the most advantageous filters when considering rate. A cake is not allowed to build-up to decrease the rates.

Although many methods may be employed to increase flow rates, the efficiency factor should not be overlooked. Collection of desired particles must be the most important factor. If proper retention can be accomplished with increased flow, then flow rates should be increased.

Many factors of solids determination were taken into consideration when cellulose filters were formed. The high temperatures necessary to speed filtrate flow will not affect the cellulose filters. The rigidity of the filter reduces embedding of particles in the pores to hamper flow. A filter aid is not needed to increase flow rates because of the cellulose filter's high porosity. High efficiency of solids collection can be achieved using cellulose filters even at high flow rates.

CHAPTER III

EXPERIMENTAL PROCEDURE

Equipment

The filtering apparatus assembly used in the standard test is shown in Figure 1. The assembly consists of a Gooch crucible, rubber tubing, filter tube, neoprene stopper, and a 500 milliliter filtering flask. Specifications for these component parts are listed in the A.S.T.M. test method D 2042-66.

The assembly of the Millipore filtering apparatus is shown in Figure 2. The assembly consists of a 300 milliliter pyrex funnel, a base with coarse-graded fritted support for the filter, an anodized aluminum spring-action clamp, a neoprene stopper, and a 500 milliliter filtering flask.

The two filtering assemblies were attached to a one-third horsepower Century vacuum pump and a vacuum pressure of 0.6 pounds per square inch was applied to both filtering assemblies during filtration. Figure 3 shows the Century vacuum pump and mercury monometer used to measure the vacuum pressure being applied to the apparatus.

All weighing was performed using a W. H. Curtin analytical balance capable of weighing to the nearest 0.0001 of a gram (Figure 4). A small 660 watt Humboldt oven was used to dry the filters (Figure 5).

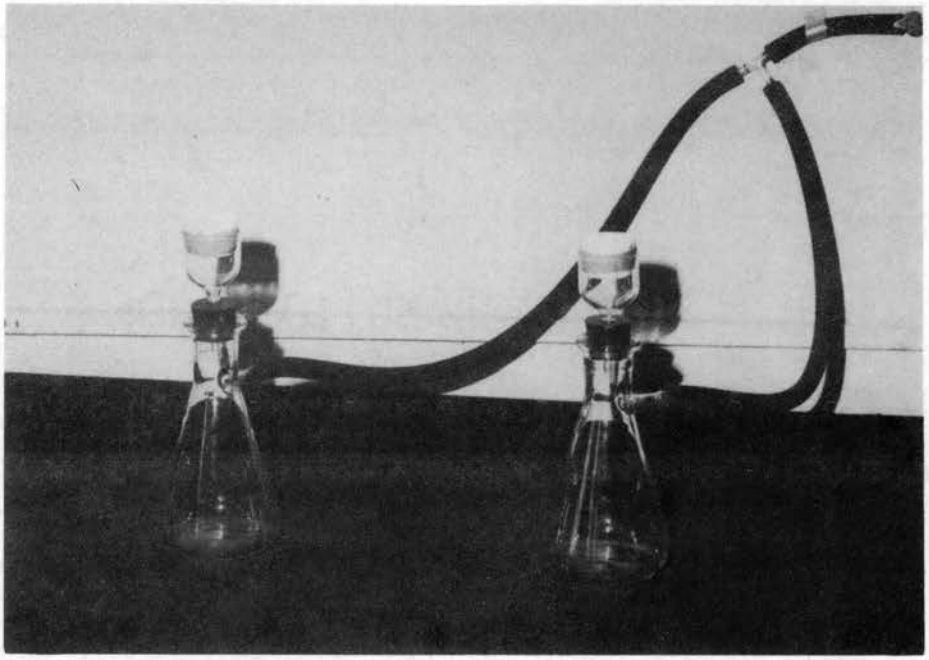

Figure 1. Standard Filtering Apparatus

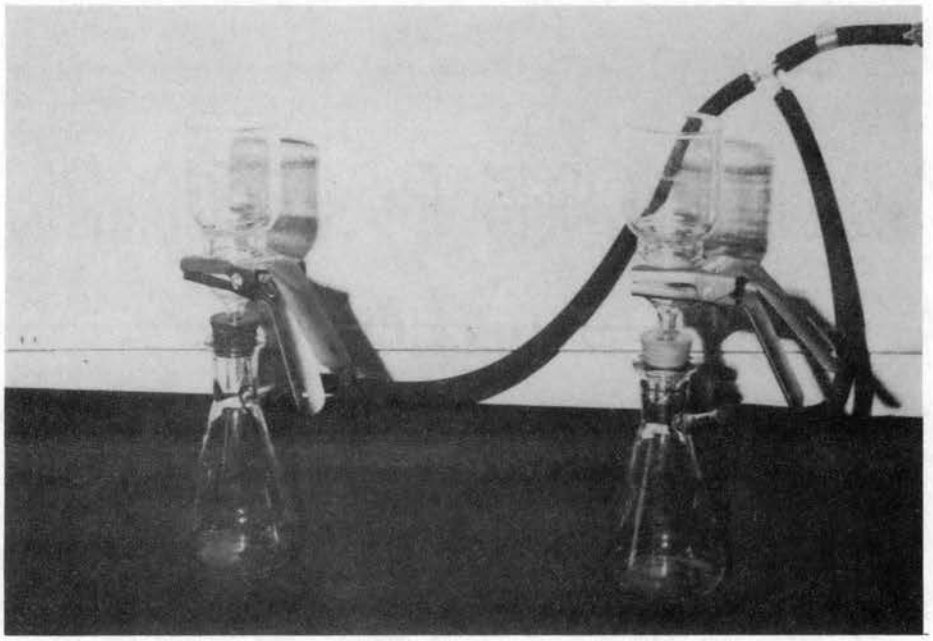

Figure 2. Millipore Filtering Apparatus

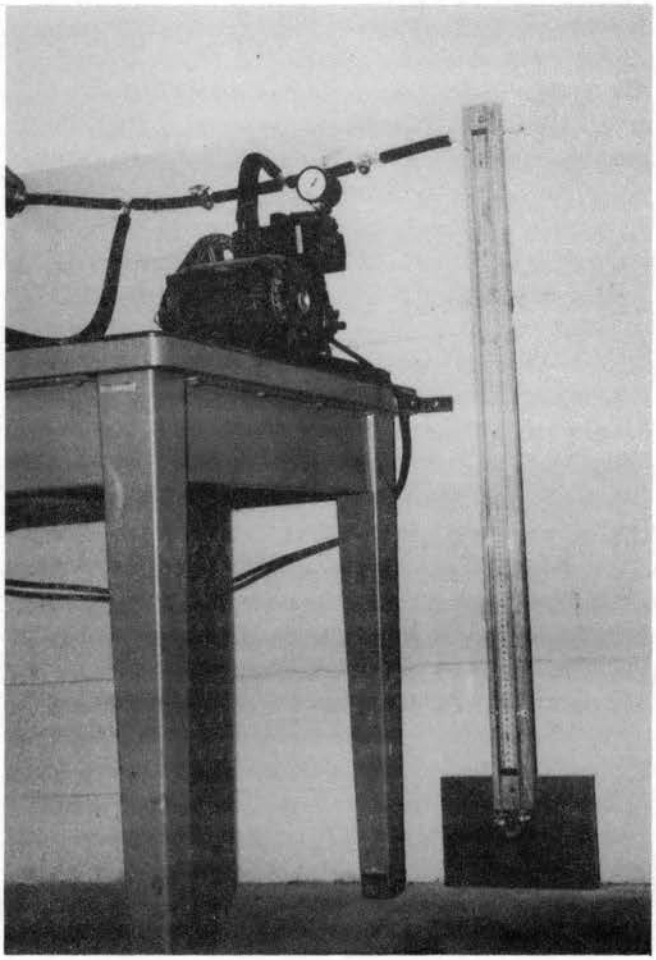

Figure 3. Pump and Manometer for Applying and Regulating Vacuum Pressure

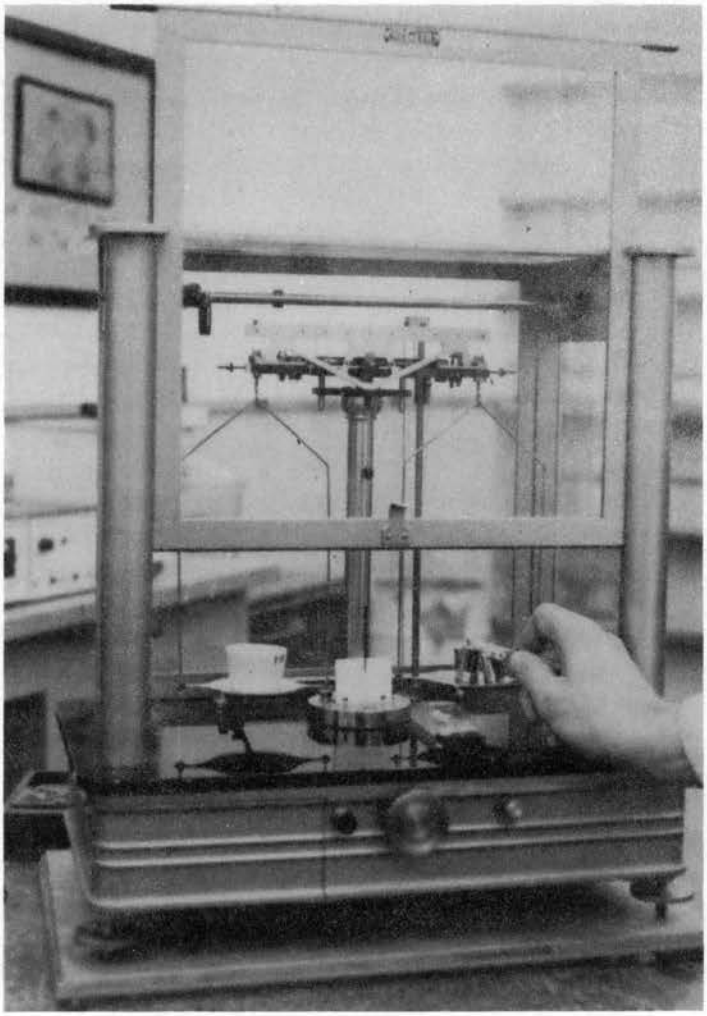

Figure 4. Weighing Gooch Crucible.

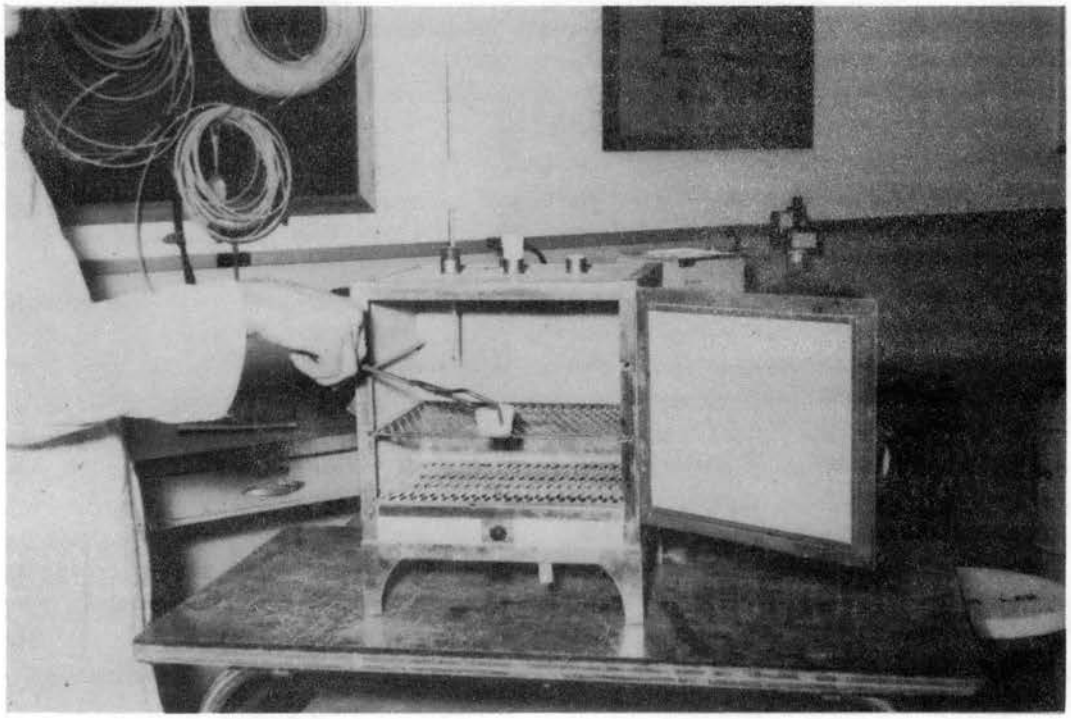

Figure 5. Removing Dry Crucible from Oven

Materials

Asphalt cements with 60-70, 85-100, and 200-300 penetrations were used to determine the effect of consistency on retention capacity.

Reagent grade carbon tetrachloride was used as the solvent for all solutions.

Four different pore size Millipore filters were used along with the standard asbestos filter. The cellulose filters had a diameter of 47 millimeters and pore sizes of 0.45μ, 0.80μ, 1.2μ, and 3.0μ. The standard filter mats were formed from acid washed Gooch grade asbestos (amphibole) fibers.

Procedure

The filtration procedure using asbestos filters corresponded to that prescribed in A.S.T.M. test method D 2042-66. This standard test does not specify exact details as to operating procedure and preliminary tests were made to determine the best procedures for forming the asbestos mat filters. These procedures were then employed to achieve uniform mat thicknesses and ensure reproducible results.

It was found that a dry weight of about 0.53 grams of asbestos would produce a filter weight of 0.5 ± 0.1 grams after ignition and cooling. The asbestos fibers were placed in a 125 ml Erlenmeyer flask and mixed with enough distilled water to make a slurry. The slurry was then decanted into the Gooch crucible using a glass stirring rod placed over the top of the flask. The mat was washed thoroughly with distilled water and a light suction of about 0.6 pounds per square inch was used to remove the excess water. The filter was dried in an oven and then ignited over a bunsen burner. The ignition of the asbestos

mat over a bunsen burner follows the prescribed procedure in A.S.T.M. D 165-42. Ignition of the filter is shown in Figure 6.

The solutions used for filtration were obtained by adding about 100 milliliters of carbon tetrachloride to a flask containing approximately two grams of the asphalt cement sample. The solution was allowed to stand about 24 hours in subdued light before filtering. Following the 24 hour waiting period, a stirring rod was used to decant the solutions through the filters. The material clinging to the sides of the flask were washed into the filtering apparatus using a squeeze bottle filled with carbon tetrachloride.

The asphalt-carbon tetrachloride solutions were decanted through the cellulose filter until all insoluble matter was washed from the solution bottle in the same manner as with the asbestos filters. Insoluble matter on the filter was washed until the filtrate was substantially colorless. After all remaining solvent passed through the filter, the filter was taken from the holder and placed in a warm place to dry. After all solvent odor was gone from the filter, it was then placed in an oven at 110°C for 20 minutes. The filter was then cooled in a desiccator and weighed. Drying and weighing was repeated until a constant weight (±0.3 milligrams) was obtained.

Twelve determinations with each of the asphalt cements were made using each pore size of Millipore filter and the asbestos filter. All weighings were made to the nearest 0.0001 of a gram.

Calculations

The calculations for the proportion (per cent) of the asphalt sample insoluble in carbon tetrachloride were made using the following

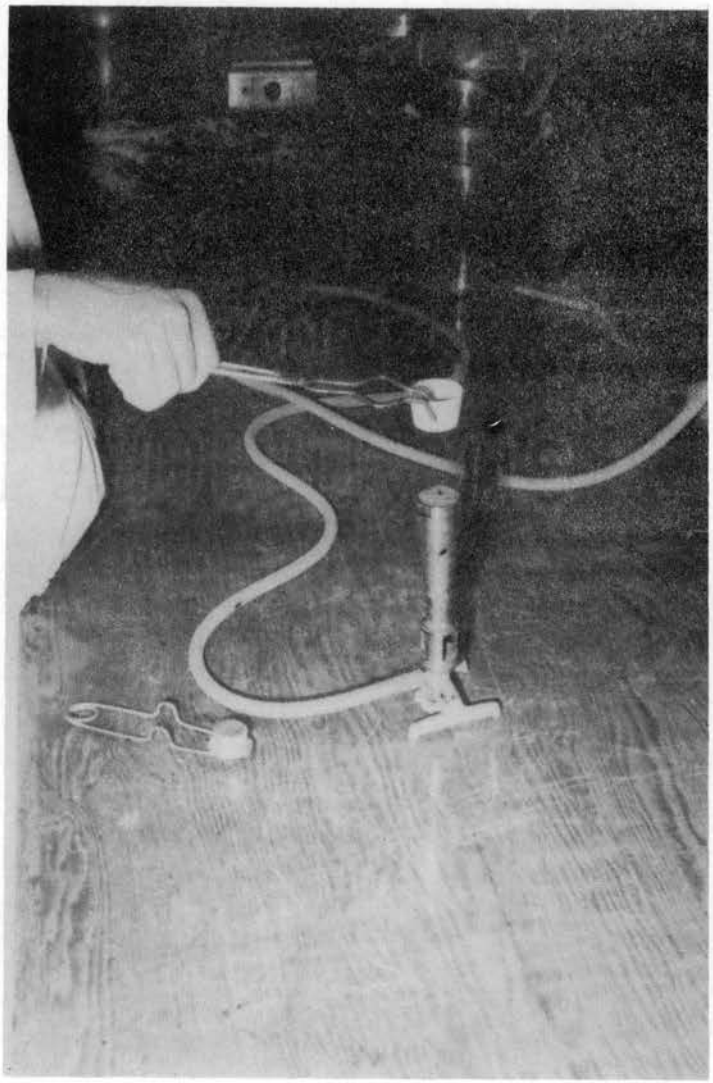

Figure 6. Igniting Asbestos Mat

relationship:

$$\text{proportion insoluble} = I/S \times 100$$

where:

I = weight of insoluble proportion (weight retained on the filter)

S = total weight of asphalt sample.

The mean of twelve determinations was found using the following formula:

$$\text{mean} = \sum_{i=1}^{12} X_i/12$$

where

X_i = i^{th} determination (i^{th} percentage of insolubility).

The variance of twelve determinations was found from:

$$S^2 = \text{variance} = 12 \cdot \sum_{i=1}^{12} X_i^2 - \left(\sum_{i=1}^{12} X_i\right)^2/12(12-1)$$

where:

X_i = i^{th} determination (i^{th} percentage of insolubility).

A sample data sheet and computer program used to calculate means, variances, and the F random variable are contained in the Appendix. The F random variable is calculated by the following formula:

$$F = S_1^2/S_2^2$$

where:

S_1^2 = variance of the asbestos determinations

S_2^2 = variance of the cellulose determinations.

CHAPTER IV

DISCUSSION

General

The cellulose filter procedures used in this study to determine the solubility of asphalt cements were quite satisfactory. The equipment was relatively easy to set up and use, and the required testing time was considerably shorter than that time for the asbestos filtration. Although there were no cost studies done for this paper, it appears that the total cost for both filtering operations was approximately the same; but the shorter time required to conduct tests using cellulose filters might be considered a reduction in cost.

Asbestos filters do not lend themselves to subsequent examimations for the purpose of identifying the retained material. Much of this material is retained within rather than on the filter and the filter cannot be removed from the Gooch crucibles without destroying the mat. All of the cellulose filters were saved in a covered container which kept them free of dust particles contained in the air. This saving of the used cellulose filters proved to be a great advantage because of the post test examination of filters and material contained on them. Figure 7 shows 0.45, 0.80, 1.20, and 3.00μ pore size filters which were used in tests with the 200-300 penetration asphalt cement. As the pore size diameter becomes smaller the color of the filter

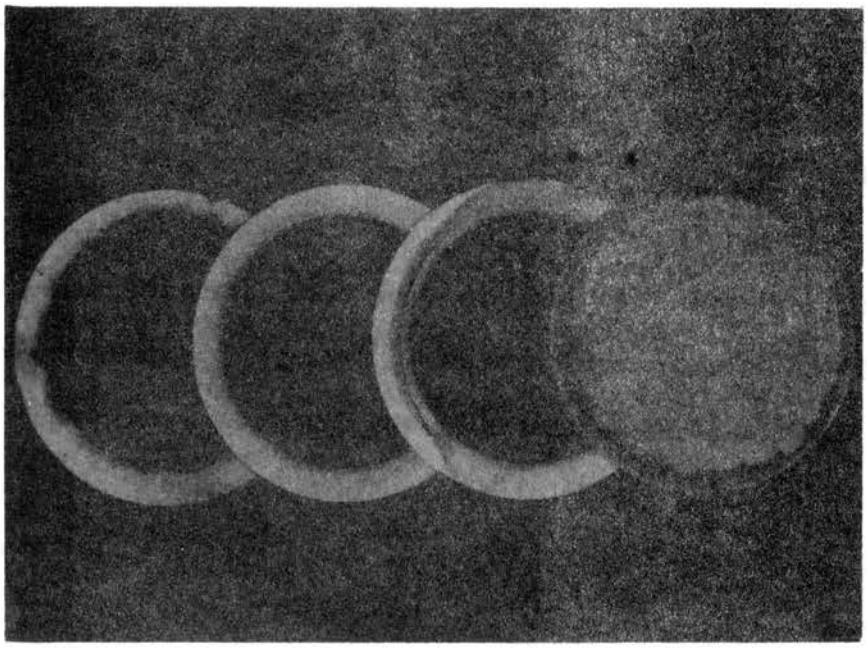

Figure 7. Used Cellulose Filters - 0.45, 0.8, 1.2, and 3.0μ Pore Sizes

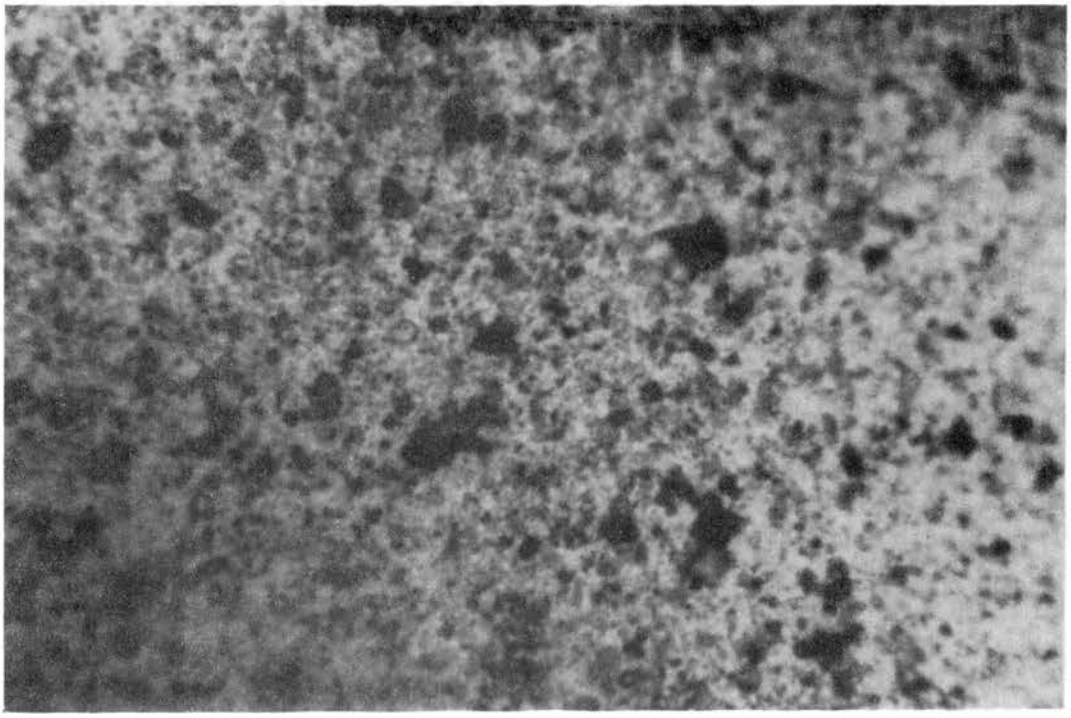

Figure 8. Photomicrograph of .45μ Filter Above

to employ on the solubility test data indicated a need for a comparison of means and variances. Since four pore size cellulose filters and the standard asbestos filter were used in this study for comparative purposes, there was a need to determine which pore size cellulose filter had approximately the same retention capacity as that of the asbestos mat's. Means were computed to estimate the retention capacity of each filter. Table I shows insolubility values for all filters which were used to compute the means. Table II is the listing of means of both cellulose and asbestos filters. The means of all filters for each penetration grade asphalt cement are plotted in Figure 9.

The higher penetration asphalts seemed to have higher degrees of insolubility, although, this might not always be the case. It is important to note that all means of a given penetration grade asphalt cement follow a certain trend, i.e., high or low. This is probably due to different processes and temperatures undergone in the manufacture of each asphalt. The 200-300 penetration asphalt might have undergone higher temperatures during refining, causing more of the asphalt to "crack" and form insoluble carbenes.

The plot in Figure 9 indicates that the cellulose filter having a similar retention capacity as the asbestos filter is either the 0.8μ or 1.2μ pore size. In two cases the 1.2μ filter's mean is closest to the asbestos mat's mean, and in one case the 0.8μ filter's mean is closest to the asbestos mat's mean. In view of this information, it is recommended that the 1.2μ filter be used as a substitute for the asbestos mat filter. For the comparison of variances, the 0.8μ pore size filter was used when its mean was closest to the mean of the asbestos filter. In the other two cases the 1.2μ pore size cellulose filter was

TABLE I

DETERMINATIONS OF INSOLUBILITY

60-70 Pen. A.C.

Filter Type	Test Number											
	1	2	3	4	5	6	7	8	9	10	11	12
0.45μ	0.1747	0.1427	0.1501	0.1678	0.1644	0.1264	0.1508	0.1457	0.1417	0.1601	0.1555	0.1425
0.80μ	0.1033	0.1826	0.1317	0.1046	0.1100	0.0654	0.0659	0.1275	0.1155	0.0741	0.1240	0.0935
1.20μ	0.0377	0.0502	0.0700	0.0812	0.0722	0.0555	0.0532	0.0592	0.0532	0.0352	0.1175	0.0487
3.00μ	0.1017	0.1045	0.0884	0.0780	0.0718	0.0968	0.1038	0.0802	0.1057	0.0439	0.0837	0.0639
Asbestos	0.0101	0.0203	0.0655	0.0854	0.1743	0.1392	0.0698	0.0725	0.1844	0.2054	0.2195	0.2438

85-100 Pen. A.C.

0.45μ	0.1545	0.1289	0.2383	0.2231	0.1676	0.1497	0.1968	0.2316	0.2822	0.2226	0.1838	0.2319
0.80μ	0.1463	0.1325	0.1327	0.1746	0.1783	0.1577	0.3314	0.1686	0.1398	0.1284	0.1277	0.1318
1.20μ	0.0877	0.1003	0.0933	0.1023	0.1299	0.0488	0.0930	0.1176	0.1528	0.0945	0.1047	0.0901
3.00μ	0.0647	0.1022	0.0851	0.0831	0.0739	0.0764	0.0601	0.1008	0.1038	0.0929	0.0844	0.0897
Asbestos	0.0640	0.1118	0.2044	0.2185	0.2699	0.1162	0.0364	0.0120	0.0872	0.1434	0.1055	0.1421

200-300 Pen. A.C.

0.45μ	0.3470	0.3524	0.3196	0.3654	0.2891	0.2721	0.3204	0.2882	0.2803	0.3921	0.2720	0.2494
0.80μ	0.2313	0.2637	0.2798	0.1997	0.2097	0.2291	0.2760	0.2581	0.2998	0.2534	0.3006	0.2213
1.20μ	0.1616	0.1430	0.1426	0.1684	0.1299	0.1585	0.1813	0.1441	0.1749	0.1613	0.1485	0.1423
3.00μ	0.1321	0.1246	0.1300	0.1343	0.1771	0.1212	0.1127	0.0936	0.1287	0.1177	0.1698	0.1229
Asbestos	0.1454	0.0913	0.0744	0.1414	0.2691	0.1496	0.1344	0.2920	0.3138	0.2935	0.1519	0.1814

TABLE II

MEANS AND VARIANCES

	Filter Type	Mean	Variance
60-70 Pen.	0.45μ	0.1519	
	0.80μ	0.1082	0.0011
	1.20μ	0.0611	
	3.00μ	0.0852	
	Asbestos	0.1242	0.0064
85-100 Pen.	0.45μ	0.2009	
	0.80μ	0.1625	
	1.20μ	0.1013	0.0006
	3.00μ	0.0848	
	Asbestos	0.1257	0.0058
200-300 Pen.	0.45μ	0.3123	
	0.80μ	0.2519	
	1.20μ	0.1547	0.0002
	3.00μ	0.1304	
	Asbestos	0.1865	0.0069

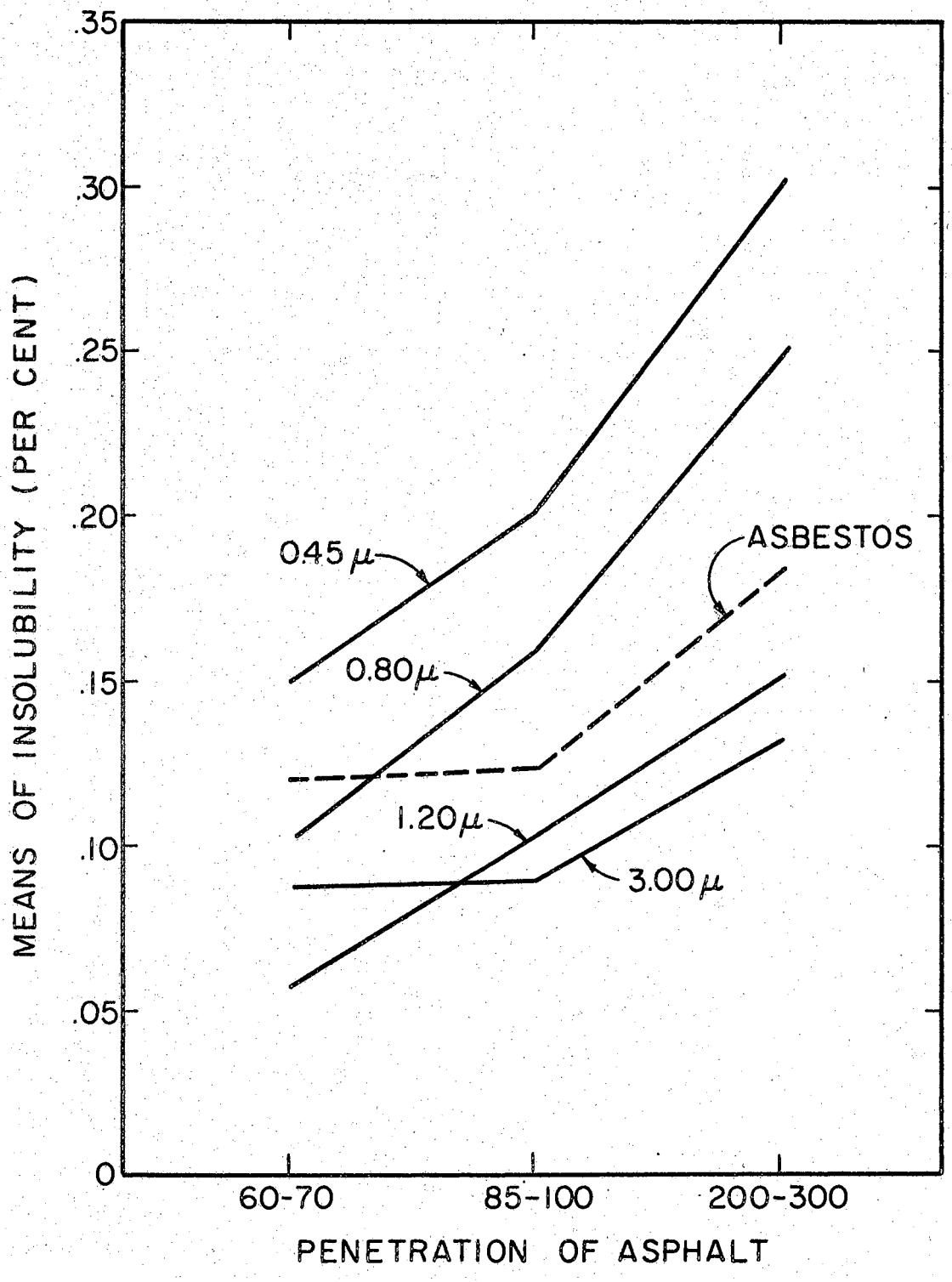

Figure 9. Means of Samples

used for the variance comparison.

Variances

Once the cellulose filter with a mean closest to that of the asbestos filter's mean was determined, an analysis of variance was needed to indicate which type filter's results tended to be more reproducible. The F test was chosen to determine reproducibility of insolubility determinations.

The F test is stated in Theorem 7.5 contained in Probability and Statistics for Engineers by Miller and Freund (23). The theorem reads: "if S_1^2 and S_2^2 are the variances of independent random samples of size n_1 and n_2, respectively taken from two normal populations having the same variance, then

$$F = S_1^2/S_2^2$$

is a value of a random variable having the F distribution with the parameters $v_1 = n_1 - 1$ and $v_2 = n_2 - 1$."

The population spoken of in the theorem refers to all values of insolubility which could be determined from each penetration grade asphalt. Populations for all of the filters are infinite, since the number of determinations of insolubility which could be made is infinite. If a population is infinite, it is impossible to observe all its values. Thus, it is usually necessary to use a sample as part of the population, and infer from its results pertaining to the entire population. Sample data must be representative of the entire population. It was assumed from the beginning of the analysis that all samples taken for the insolubility tests were representative. The

actual means and variances of populations are parameters of the population. Calculated means and variances from sample data are the statistics of the data. The means and variances calculated for this paper are statistics of the data obtained.

There are two assumptions made in the above theorem. One is that the data comes from normal populations. The second assumption is that both populations have the same variance.

The first assumption can be justified because most errors of measurement and a large variety of physical observations have approximately normal distributions; therefore it was assumed that the insolubility determinations comprised a normal population. The top graph shown in Figure 10 is a curve representing a normal population. The curve indicates that most of the values or members of a population occur at a central point and decrease as shown on each side of the central point. The normal curve can be closely represented by a group of rectangles as illustrated in the graph.

Insolubility determinations with the 1.2μ cellulose filter and the asbestos filter using the 85-100 penetration asphalt were examined to see if they approximated a normal distribution. Although twelve determinations using each filter does not represent an entire population, the determinations might indicate whether there was a trend toward a normal population. The data from the 1.2μ filters and the asbestos filters was divided up into five equal intervals. The number of determinations falling into each interval was counted and plotted as a rectangle as drawn in Figure 10. The number of determinations falling into each interval is called the class frequency. As shown, there was a trend toward normality which validates the use of the F test.

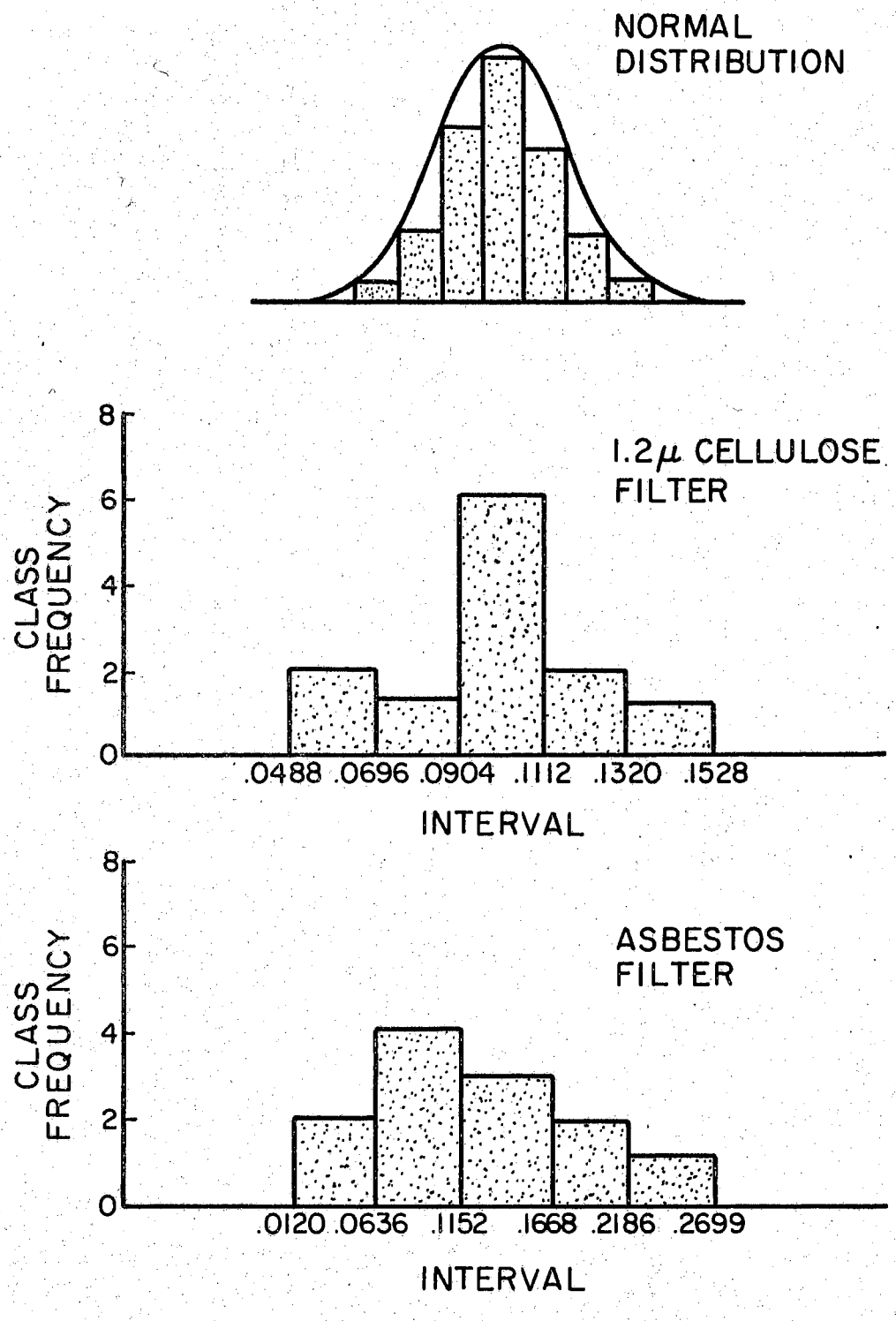

Figure 10. Sample Distributions

Concerning the second assumption, the actual variances of insolubility determinations are identical if the samples for testing of both type filters come from the same source or population. In the tests conducted for this paper the samples were taken from the same population.

The listing of computed variances is shown in Table II. Figure 11 is a graphical representation of the variances. Variances of the asbestos filters are quite high in comparison with the variances of the cellulose filters.

The F random variables were determined using a computer program that was to make the statistical computations involved in this study. Since the calculated F random variable (S_1^2/S_2^2) is set up to be a ratio of the variance of the asbestos filter determinations divided by the variance of the cellulose filter determinations, there is a value (determined by the $F_{0.99}$ distribution for v_1 and v_2 equal to 11 degrees of freedom) which the calculated random variable cannot exceed without the conclusion being made that the variances are significantly far apart. Since the three calculated values of the F random value (6.0, 9.1, and 34.5) are larger than $F_{0.99}$ for $v_1 = 11$ and $v_2 = 11$ (4.47), then the conclusion must be made that the variance of the asbestos filter determinations is significantly larger than the variance of the cellulose filter determinations. Because the asbestos filter produced insolubility values with larger variance, a final conclusion can be made that the test results using the cellulose filters are more reproducible than those obtained using the asbestos filter.

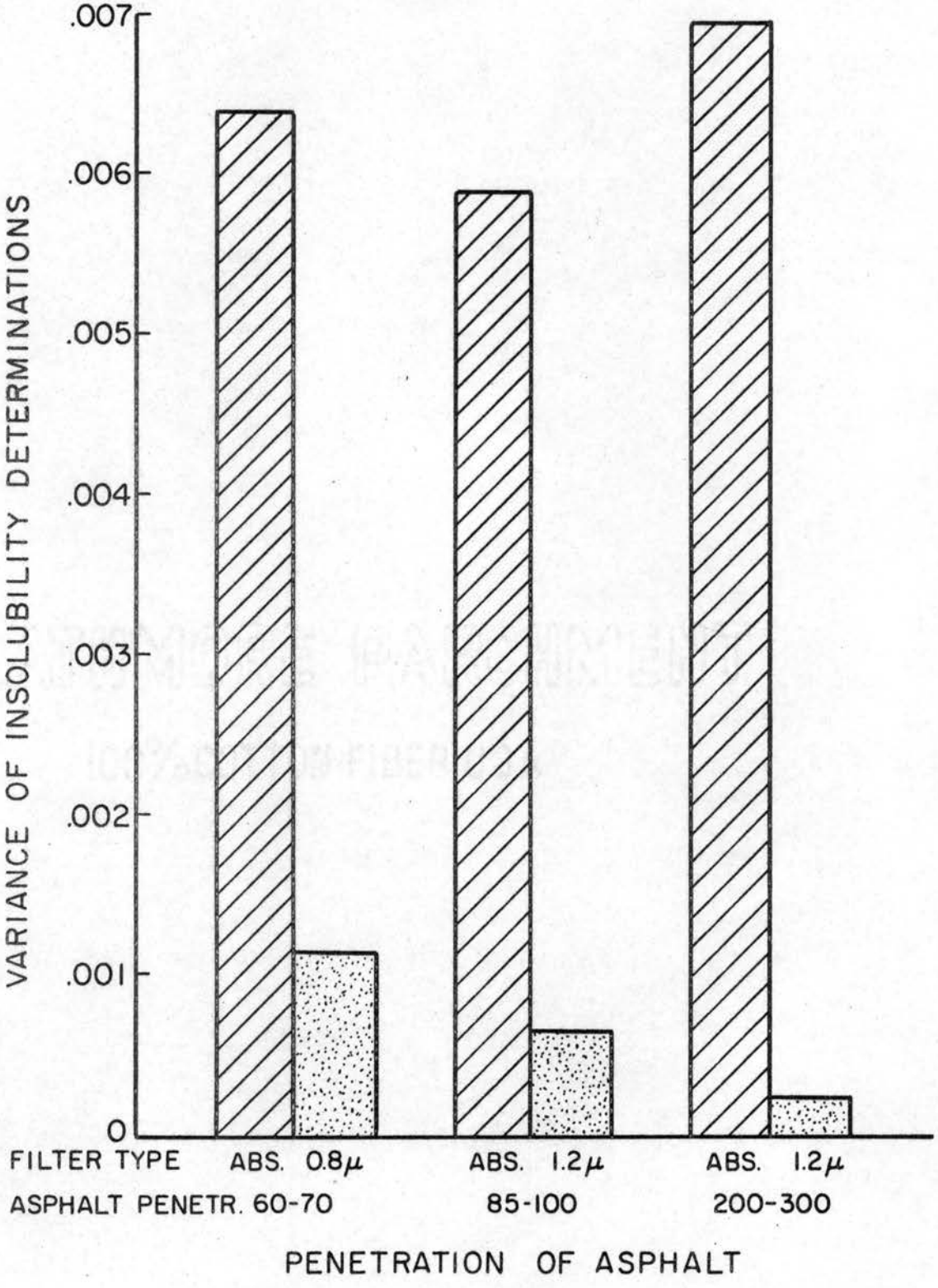

Figure 11. Variances

CHAPTER V

SUMMARY AND CONCLUSIONS

The purpose of this study was to compare cellulose membrane filters and asbestos filters in the solubility testing of asphalt cements. From this study the following conclusions can be made:

(1) Asbestos fibers are non-uniform in shape and size.

(2) Non-uniform pores are obtained from the prepared asbestos mat.

(3) The operator has little control over the thickness of the asbestos mat.

(4) Holes and thin spots are often formed as the solution is poured through the asbestos mat.

(5) Particle size retention capability varies for the asbestos filter.

(6) The performance of the asbestos filter mat depends a great deal upon the techniques of the operator.

(7) The preparation of the asbestos mat is quite time-consuming.

(8) A small amount of bitumen is irreversibly adsorbed by the asbestos mat and not by the cellulose membrane.

(9) The flow rate through the cellulose filter is much faster because of the high percentage of pores contained in the filter.

(10) Cellulose filters are applicable to gravimetric analysis

because of the filter's almost complete destruction after ignition, yielding a residual of only a few micrograms.

(11) The cellulose filter becomes transparent when immersed in an oil of matching refractive index, therefore lending the filter to study under the microscope.

(12) If properly supported Millipore filters will withstand at least 10,000 pounds per square inch differential pressure without significant distortion of the pore structure.

(13) The 1.2μ pore size cellulose filter has approximately the same retention capacity as that of the asbestos mat.

(14) The cellulose filter's results are by far more reproducible than those of the asbestos filter.

The following recommendations are made with regard to further study in the field which this paper was concerned:

(1) Investigation as to content could be made of insoluble portions of asphalt using the microscope.

(2) Controlled levels of insolubility could be employed to further test the effectiveness of the different filters. It is recommended that some type of mineral or salt be used for the tests.

(3) Tests could be conducted using different amounts of pressure to see if this had any effect on retention capacity of the cellulose filters.

(4) A gravimetric analysis of insoluble portions of asphalt cements could be made using the cellulose membrane filters.

A SELECTED BIBLIOGRAPHY

(1) Richardson, Clifford. The Modern Asphalt Pavement, 2nd Ed. New York: John Wiley and Sons, 1968.

(2) American Society for Testing and Materials, Proceedings of A.S.T.M., Vol. 23 (1923), 754-755.

(3) American Society for Testing and Materials, 1927 Book of A.S.T.M. Standards, Part II (1927), 487-488.

(4) American Society for Testing and Materials, 1967 Book of A.S.T.M. Standards, Part 11 (1967), 606-609.

(5) Millipore Filter Corporation, Techniques for Microbiological Analysis, ADM 40 (1965).

(6) American Society for Testing and Materials, 1966 Book of A.S.T.M. Standards, Part 11 (1966), 12.

(7) Texas Highway Department Materials and Tests Division, Manual of Testing Procedures (June, 1962).

(8) California Department of Public Works, Materials Manual of Testing and Control Procedures (January, 1956).

(9) Broome, D. C. The Testing of Bituminous Mixtures, 2nd ed. London: Edward Arnold and Company, 1949.

(10) Degen, Jerome and Frederick E. Nussbeger, "Notes on the Suspended Solids Determination." Sewage and Industrial Wastes, Vol. 28, No. 2 (February, 1956), 237-240.

(11) Varma, M. M. and P. C. Sheffert. "Using a Cellulose Membrane for Determining the Carbon-Tetrachloride-Insoluble Portion of Bitumens." Materials Research and Standards, Vol. 3, No. 7 (July, 1963), 560-561.

(12) Olienses, G. L. Director of Research for Lloyd A. Fry Roofing Company, private correspondence (August 15, 1968).

(13) American Association of State Highway Officials, Standard Specifications for Highway Materials and Methods of Sampling and Testing, Part II (1961), 199-201.

(14) Bolton, H. C. "Ancient Methods of Filtration." Popular Science Monthly, XVI (1880), 495-502.

(15) Dickey, George D. and Charles L. Bryden. Theory and Practice of Filtration, 2nd ed. New York: Guinn Company, 1949.

(16) Genter, A. L. "Principles and Factors Influencing Vacuum Filtration." Sewage Works Journal, Vol. 13, No. 4 (1941), 1164-1204.

(17) Poiseiulle, J. L. "Recherches experimentales sur le mouvement des liquides dans les tubes de tres-petits diametres." Comptes Rendus, Vol. 15 (1842), 1167-1187).

(18) Ruth, B. F. "Studies in Filtration." Industrial and Engineering Chemistry, Vol. 27 (1935), 708-723.

(19) Sperry, D. R. "The Principles of Filtration." Metallurgical and Chemical Engineering, Vol. 15 (1916), 198-203.

(20) Hatschek, E. J. "The Mechanism of Filtration." Society of Chemical Industry, Vol. 27 (1908), 538-544.

(21) Sperry, D. R. "Analysis of Filtration Data." Industrial and Engineering Chemistry, Vol. 36 (1935), 323-329.

(22) Donald, M. B. and R. D. Hunneman. "Investigation of the Application of the Lewis Formula." Transactions of Industrial and Engineering Chemistry, Vol. 1 (1923), 97-112.

(23) Miller, Irwin and John E. Freund. Probability and Statistics for Engineers, 1st ed. Englewood Cliffs: Prentice-Hall, 1965.

APPENDIX

TABLE III

MEANS AND VARIANCES PROGRAM

```
0001          101 FORMAT(1H1,14X,56HSTATISTICAL ANALYSIS WITH ASBESTOS AND CELLULOSE      000
                 C FILTERS,/22X,43HIN THE SOLUBILITY TESTING OF ASPHALT CEMENT/)          005
0002          102 FORMAT(24X,21HTHIS TEST IS FOR THE ,1X,2A4,1X,7HASPHALT/)            010
0003          103 FORMAT(20X,47HTHE PROPORTION INSOLUBLE MEAN BY FILTER NUMBER /)      015
0004          104 FORMAT(28X,29HSIZE IN MICRONS          MEAN/)                        020
0005          105 FORMAT(33X,F5.2,12X,F7.4)                                            025
0006          106 FORMAT(5X,3HTHE,F5.2,66H MICRON CELLULOSE FILTER HAS A MEAN CLOSES   030
                 CT TO THE ASBESTOS FILTER//)                                         035
0007          107 FORMAT(9X,30HA STATISTICAL ANALYSIS ON THE ,F5.2,28H MICRON CELLUL   040
                 COSE FILTER AND,/21X,42HTHE ASBESTOS FILTER PRODUCED THESE RESULTS/  045
                 C)                                                                   046
0008          108 FORMAT(28X,31HSIZE IN MICRONS         VARIANCE)                      050
0009          109 FORMAT(35X,4HF = ,F5.3/34X,12HF(.05) =2.69///29X,27H***** MEANS AS   055
                 CBESTOS FILTER)                                                      060
0010          201 FORMAT(2A4,I2)                                                       065
0011          202 FORMAT(8X,12F6.0)                                                    070
0012              DIMENSION CARBS(12,5),TABLE(5),AVG(5),TYPE(2)                        075
0013              TABLE(1)=0.45                                                        085
0014              TABLE(2)=0.80                                                        090
0015              TABLE(3)=1.20                                                        095
0016              TABLE(4)=3.00                                                        100
0017              TABLE(5)=9999999.0                                                   105
0018           20 READ(5,201)TYPE,LAST                                                 110
0019              IF(LAST.EQ.1) CALL EXIT                                              113
0020              WRITE(6,101)                                                         115
0021              WRITE(6,102)TYPE(1),TYPE(2)                                          120
0022              WRITE(6,103)                                                         125
0023              WRITE(6,104)                                                         130
0024              DO 30 J=1,5                                                          135
0025           30 READ(5,202) CARBS(1,J),CARBS(2,J),CARBS(3,J),CARBS(4,J),CARBS(5,J)   140
```

TABLE III (Continued)

```
      C,CARBS(6,J),CARBS(7,J),CARBS(8,J),CARBS(9,J),CARBS(10,J),CARBS(11,
      CJ),CARBS(12,J)
0026   DO 50 J=1,5
0027   SUM=0.0
0028   DO 40 I=1,12
0029 40 SUM=SUM+CARBS(I,J)
0030   AVG(J)=SUM/12.0
0031 50 WRITE(6,105) TABLE(J),AVG(J)
0032   BEST=AVG(1)
0033   DIFF=ABS(AVG(5)-BEST)
0034   J=1
0035   DO 60 I=2,4
0036   CHECK=ABS(5)-AVG(I))
0037   IF(CHECK.LT.DIFF) GO TO 55
0038   GO TO 60
0039 55 DIFF=CHECK
0040   BEST=AVG(I)
0041   J=I
0042 60 CONTINUE
0043   WRITE(6,106) TABLE(J)
0044   WRITE(6,107) TABLE(J)
0045   WRITE(6,108)
0046   SUM1=0.0
0047   SUM2=0.0
0048   DO 70 I=1,12
0049   SUM1=SUM1+CARBS(I,5)**2
0050 70 SUM2=SUM2+CARBS(I,5)
0051   VARI=(12.0*SUM1-SUM2**2)/132.0
0052   SUM1=0.0
0053   SUM2=0.0
0054   DO 80 I=1,12
0055   SUM1=SUM1+CARBS(I,J)**2
```

TABLE III (Continued)

```
0056              80 SUM2=SUM2+CARBS(I,J)                                    305
0057                 VAR2=(12.0*SUM1-SUM2**2)/132.0                          310
0058                 WRITE(6,105) TABLE(J),VAR2                              315
0059                 WRITE(6,105) TABLE(5),VAR1                              320
0060                 F=VAR1/VAR2
0061                 WRITE(6,109) F                                          330
0062                 GO TO 20                                                335
0063                 END
```

TABLE IV

FLOW CHART OF PROGRAM

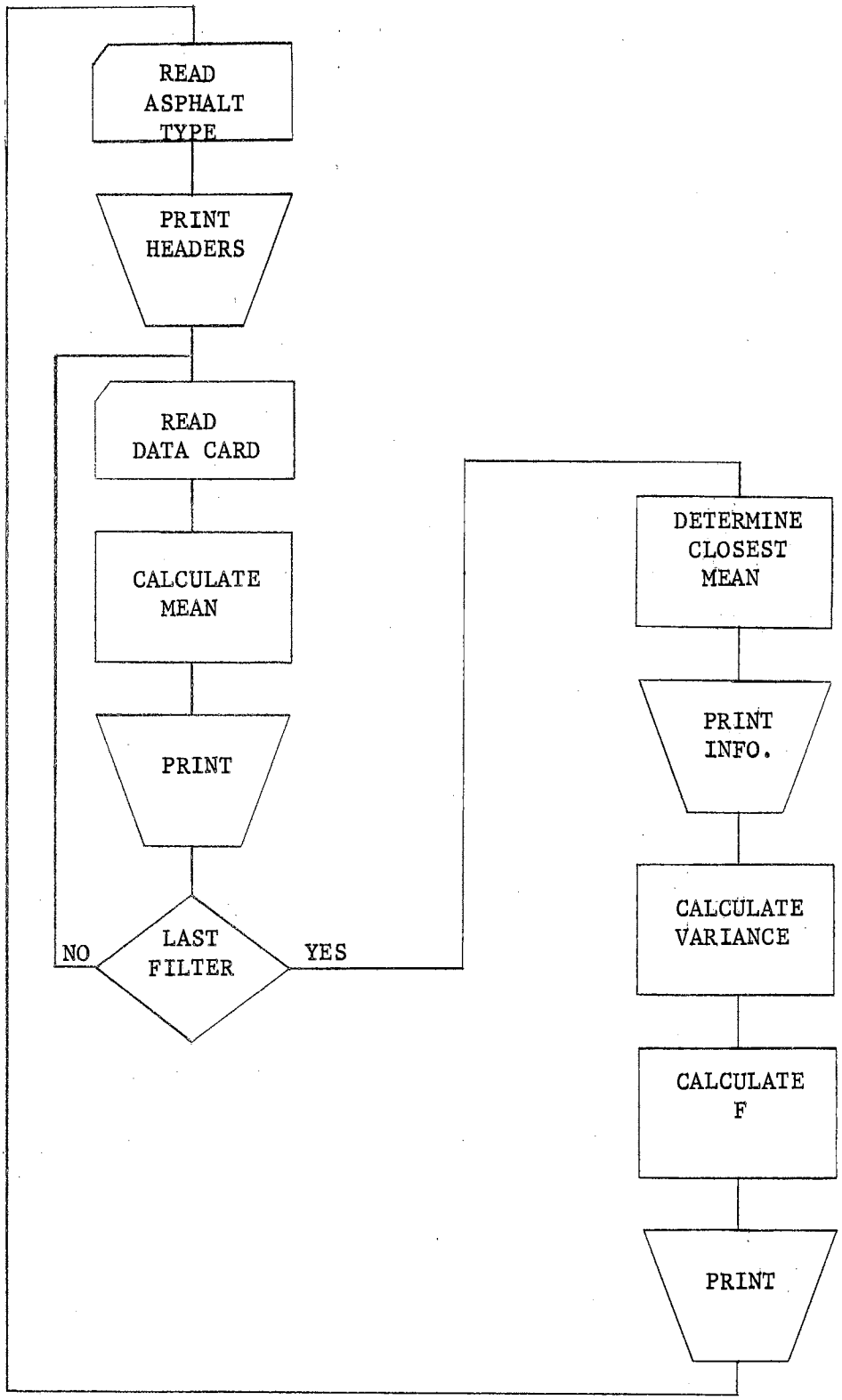

TABLE V

SAMPLE DATA SHEET

Test No.	Pen. of Asphalt Sample	Method of Filtration	Weight of Empty Flask	Wt. of Flask + Sample	Wt. of Asphalt Sample Col 5-4	Wt. of Millipore Filter	Wt. of Gooch Crucible	Wt. of Col. 7or8 + Insoluble Matter	Wt. of Insoluble Matter Col 9-8 or Col 9-7	Proportion Insoluble (Per Cent) $\frac{\text{Col 10}}{\text{Col 6}} \times 100$
1	2	3	4	5	6	7	8	9	10	11
1	85-100	asb	85.0120	87.0667	2.0547		18.9376	18.9418	.0042	.2044
2	85-100	asb	72.3170	74.3305	2.0135		19.5007	19.5051	.0044	.2185
3	85-100	.45μ	84.5628	86.5667	2.0039	.0964		.0994	.0030	.1497
4	85-100	1.2μ	83.4306	85.4782	2.0476	.0789		.0799	.0010	.0488
5	85-100	asb	85.0113	86.9745	1.9632		18.5690	18.5743	.0053	.2699
6	85-100	asb	72.3159	74.2940	1.9781		19.0495	19.0518	.0023	.1162
7	85-100	.45μ	84.5624	86.5944	2.0320	.0954		.0994	.0040	.1968
8	85-100	1.2μ	83.4303	85.4726	2.0423	.0791		.0810	.0019	.0930
9	200-300	.45μ	85.0114	87.4027	2.3913	.0943		.1026	.0083	.3470
10	200-300	1.2μ	72.3164	74.2954	1.9790	.0815		.0847	.0032	.1616
11	200-300	.45μ	84.5632	86.6914	2.1282	.0944		.1019	.0075	.3524
12	200-300	1.2μ	83.4310	85.4582	2.0272	.0819		.0848	.0029	.1430
13	200-300	.45μ	81.4544	83.4876	2.0332	.0966		.1031	.0065	.3196
14	200-300	1.2μ	71.9149	73.9478	2.0329	.0794		.0823	.0029	.1426

VITA

George Ray Murrell

Candidate for the Degree of

Master of Science

Thesis: USING CELLULOSE FILTERS IN THE SOLUBILITY TESTING OF ASPHALT CEMENT

Major Field: Civil Engineering

Biographical:

Personal Data: Born in Sentinel, Oklahoma, March 23, 1945, the son of Mr. and Mrs. Ray Murrell.

Education: Graduated from Altus High School, Altus, Oklahoma, in May, 1963; received the Bachelor of Science degree from Oklahoma State University in January, 1968, with a major in Civil Engineering; completed requirements for the Master of Science degree from Oklahoma State University in May, 1969, with a major in Civil Engineering.

Professional Experience: Engineering Aid, U.S. Soil Conservation Service, Summer 1963-65; Engineering Technician IV, Alaska Highway Department, Summer 1967; graduate research assistant, School of Civil Engineering, Oklahoma State University, 1968-69.