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DETERMINATION OF THE SPECIFIC GRAVITY OF MICRO QUANTITIES OF BITUMINOUS SUBSTANCES

by

Rodney Edgerton Cox

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Transportation Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964

TABLE OF CONTENTS

INTRODUCTION

With the ever-increasing demand for better and, at the same time, more economical roads and highways for use by the automobile, bitumen is being looked to as the answer to this requirement. This material, in its various forms, is widely distributed throughout the world as asphalt, coal, petroleum, natural gas, maltha and in many other less common forms. It has been known of and used by man for centuries as a cementing, preserving and water proofing agent. It was not, however, until the nineteenth century that a bituminous material was used in the United States for road work. Rock asphalt was imported and successfully used in sidewalk construction in Philadelphia, Pennsylvania during the year 1838. In 1870, the first asphalt pavement was laid in Newark, New Jersey by a Belgian chemist, Professor E. J. De Smedt. The success of the Newark experimental road had much to do with the Congress authorizing the use of imported Trinidad Lake asphalt for the paving of Pennsylvania Avenue in Washington, D.C. in the year 1876.

The use of natural asphalts sufficed up until the development and subsequent expansion of the petroleum industry. The large annual consumption of petroleum by the gasoline engine added further emphasis to the utilization of the asphaltic material which remained as a residue after the fractional distillation of petroleum crude. The production of asphalt refined from crude petroleum has increased from approximately 20,000 tons in 1902 to 3,000,000 tons in 1924. Since 1924, the rate has increased steadily to about 9,000,000 tons in 1946 and then more than doubled to about 19,000,000 tons by 1956 (2).

The rapid expansion of the asphalt industry has been a constant challenge to both the engineer and the chemist. It soon became apparent to both that some asphalts were well suited for highway use and others, unexplainably, were not. The wide variety of sources and greater refinements in applications have created a pressing need for better and more detailed understanding of the composition and behavior of these materials. Tests which were once satisfactory are no longer adequate today due to the wide variety of sources and diverse methods of production and refining. For this reason, new tests to determine specific properties, composition and behavior of an asphalt are essential and imperative for its scientific application.

The Bituminous Research Laboratory of Iowa State University, under the direction of Professor Ladis H. Csanyi, has been investigating this problem since the Laboratory's inception. The opinion persists that a comprehensive knowledge of asphaltic constituents and their respective composition and properties is the key to the control and understanding of the behavior of asphalts.

Many investigations have been made to determine the composition of asphalts and what effect its various constituents have upon its physical properties and behavior. Asphalt has long been known to be a complex mixture of hydrocarbons which, depending upon the source and method of production, vary in molecular size and structure. But to date, the composition and structure of these hydrocarbons has not been definitely established. One accepted concept of the composition of asphalt indicates that it consists of carbon and hydrogen in major quantities and oxygen, sulphur, nitrogen and some metals in minor quantities (8). The manner and the proportions in which these elements are combined to form asphalt is not clearly understood nor determined.

Many methods are used to separate asphalt into its constituents among which are selective solvation, chromotography, electrophoresis, colorimeter, polography, and electrical means. Of these, the selective solvent method is most commonly used and favored. The constituents secured, however, depend largely upon the solvent and adsorptives used in the process. But even this method is not entirely dependable within desired limits of accuracy and time.

After looking over the methods used and considering the limitations of each, Csanyi launched a study in 1957 to determine the feasibility of separating asphalts into their several constituents by electrical means (5). The fundamental concept of the study was predicated on the belief that if the electro-chemical bonds could be sufficiently weakened, offset, or reversed by an imposition of an electrical current, the constituent compounds of the asphalt could be readily separated.

Early work by Csanyi and Bassi (5) established that asphalts could be separated into a number of different constituents in four hours or less by electrical means, and that continuing research was indicated and worthwhile. In 1959 and 1961, the Bituminous Research Laboratory was awarded National Science Foundation research grants NSF G 9101 and NSF 19781 respectively to continue study and development of the electrolytic method of analysis of asphalts. The work performed under these grants was divided into two parts. The first part was aimed at developing the electrolytic cell and its operation. The second part was aimed at analyzing and determining the composition and some of the properties of the constituents separated during the operation of the cell.

One important property of the asphalt's constituents separated during the operation of the cell was not readily obtainable by using known or standard tests. This missing, but necessary, property was the constituent's specific gravity which, due to the minute quantities of material recovered from the cell, could not be readily determined.

Since the specific gravity of each constituent was a desired part of the Laboratory's overall study, the development of a suitable method for determining this physical property and the subsequent testing of a range of test asphalts was undertaken by the author.

PURPOSE AND SCOPE

The extensive research investigation into the constituents of asphalts which has been undertaken by the Bituminous Research Laboratory of Iowa State University, in addition to other properties, required the specific gravity of each constituent that was to be separated during electrolysis.

This investigation, part of National Science Foundation grant NSF 19781, is a study made to develop a suitable and accurate method of determining the specific gravities of micro quantities of asphaltic materials ranging in weights of between 0.9 gram and 0.001 gram. After development of a test method, the test procedure was to be applied to the separated constituents of a series of test asphalts. Test results were expected to be within repeatable specific gravity limits of 0.005 as established by ASTM standards (1).

The asphaltic materials used in this research investigation were donated by commercial manufacturers from their facilities located in Wyoming, Kansas, Texas and Canada. Standard ASTM tests showed the materials to be typical of the asphalt industry (Table 1).

A Kansas asphalt, designated number six in the study, was chosen as a statistical control in all phases of the

Table 1. Properties of test asphalts

Asphalt number	Source	Penetration	Softening point °F	Flash point °F	Fire point °F	Oleinsis spot test	Percent asphaltenes	Viscosity (Brookfield) centipoise at 280°F	Surface tension dynes/cm at 280°F	Specific gravity
1	Wyoming	95	113	565	635	Neg	15.94	175	31.0	1.016
2	"	134	110	540	620	Neg	15.28	143	29.8	1.017
3	"	240	101	535	590	Neg	14.24	85	30.8	1.025
4	Kansas	40	138	675	705	Neg	18.80	450	31.4	1.016
6	"	60	124	630	700	Neg	17.20	250	32.0	1.001
7	"	84	120	640	700	Neg	16.25	190	32.3	1.008
8	"	125	115	630	695	Neg	14.27	160	29.2	1.013
9	"	250	104	615	680	Neg	13.55	72	31.4	1.012
21	"	46	130	586	630	Neg	19.90	365	35.5	1.019
22	"	98	119	578	680	Neg	15.16	185	33.9	1.014
23	"	130	113	550	648	Neg	15.79	133	30.9	1.007
24	"	245	105	630	690	Neg	13.25	110	33.0	1.003
31	Texas	240	104	548	610	Neg	13.50	122	32.8	1.022
34	Canada	137	112	620	690	Neg	12.90	180	34.0	1.012
35	"	250	115	600	665	Neg	12.62	52	31.1	1.012

entire investigation. This choice was considered to be excellent for this portion of the project since asphalt number six had a specific gravity of 1.001 which was closest of all the test asphalts to 1.000.

DEVELOPMENT OF METHOD

In order to tie the overall project of the Bituminous Research Laboratory's separation of asphalt into its constituents by electrical means together, all sample specimens were prepared in exactly the same manner during all portions of the project. This procedure, which is outlined below, is given in full detail in reference 4.

Sample Preparation

A standard asphalt solution of five (5) grams of asphalt dissolved in 95 ml of chemically pure benzene was first prepared. Thirty ml of this standard solution was then added to 270 ml of pure methanol. The 300 ml of electrolyte formed was then placed in a cylindrical jar cell (Plate 1) which was then covered by a flat nonconducting plate fitted with two electrical terminals. The two terminals, which were connected to two removable electrode holders, were set to hold the electrodes 1/2 inch apart. Two one inch wide by two inch long sheet platinum electrodes were then inserted into the holders and the cell connected to a power unit and a current recorder (Plate 3).

Voltage was then applied to the cell and adjusted to that desired for test. As the analysis continued, the

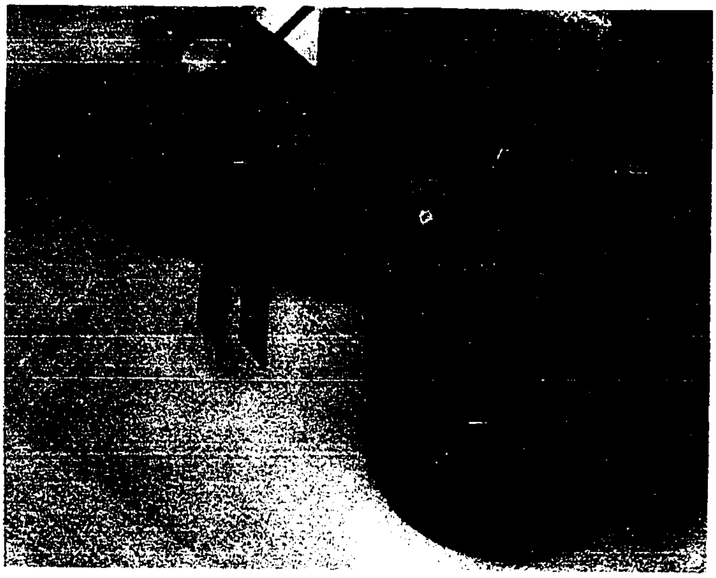


Plate 1. The spring clip removable electrode holders, the cell with electrolyte and the magnetic stirrer.

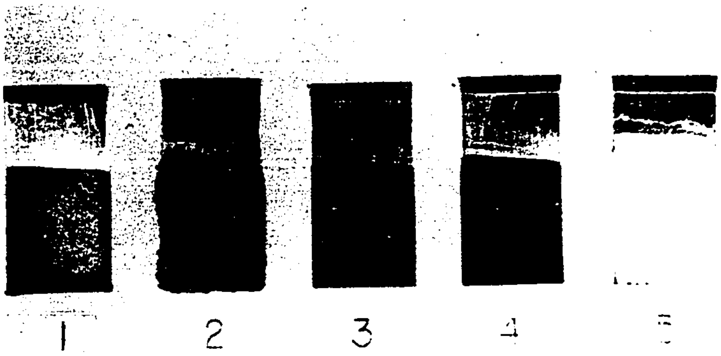


Plate 2.
1. Negative electrode with constituent A
2. Negative electrode with constituent B
3. Negative electrode with constituent C
4. Negative electrode with constituent D
5. Positive electrode with constituent E

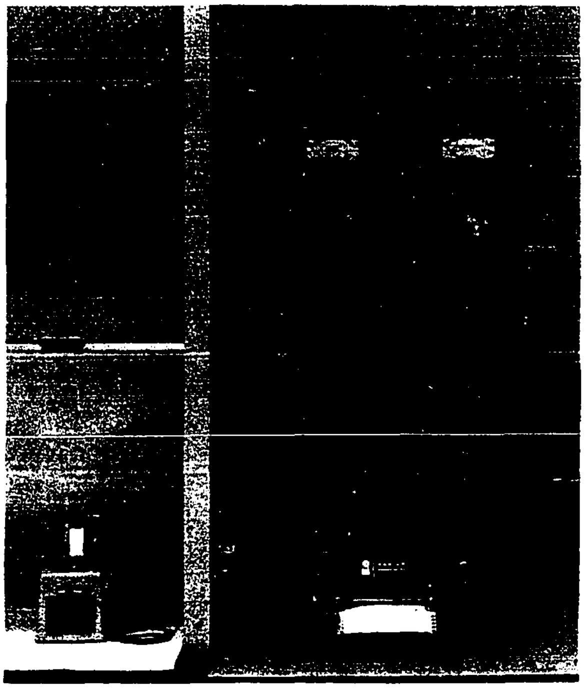


Plate 3. Analytical equipment: power unit, current recorder and cell on stirrer under hood.

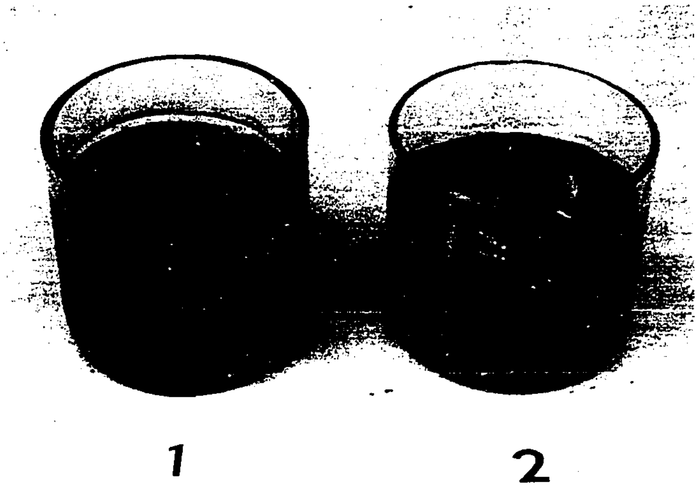


Plate 4. Electrolyte. 1 at beginning and 2 at end of analysis.

current graph on the recorder was watched to locate a significant change in the rate of change of current passing through the cell. When a change in the rate of change occurred, indicating a change in constituent (Fig. 2), the voltage was turned off. The removable electrode carrying the deposit was then removed and a fresh one inserted in its place. The same procedure was repeated until the recorder indicated no further change in the rate of current passing through the cell. The electrolyte of the cell at this point had cleared from its original dark color to one of a light amber in appearance (Plate 4). The cell and its amber colored liquid was then placed in an air dryer to evaporate the solvent from the remaining solute.

The electrodes carrying the deposits (Plate 2) were then coded with the letters "A" through "D" in the order the constituents separated from the original asphalt during electrolysis. The small quantity of material collected on the second electrode during the entire separation process was coded as constituent "E." Material clinging to the magnetic Stirrer's spinner (Plates 1 and 3) after separation was coded "F" and the residue remaining in the jar cell after air drying was coded as constituent "G." All constituents were tested for molecular weight refractive index, radio activity count, percent carbon, percent hydrogen and I. R. trace as part of the overall project.

Since very small quantities of constituents were obtained during the separation and since specific gravity is an essential property, a special means of determining this value was essential to complete the initial study.

First Trial Method

After a detailed review of the various methods of determining the specific gravities of various materials, three methods appeared to have the greatest possibility of being adapted to the problem of micro quantities of asphaltic materials.

The first method to be tried was that of dissolving the asphalt in a solvent of known specific gravity and determining the specific gravity of the resulting mixture. It then followed that the unknown specific gravity of the solute could be calculated by the formula

$$G_{AB} = \frac{W_A + W_B}{\frac{W_A}{G_A} + \frac{W_B}{G_B}} \qquad \text{(Eq. 1)}$$

where:

A is the solute

B is the solvent

AB is the solvent-solute liquid

W_A is the weight of the solute

W_B is the weight of the solvent

G is the specific gravity

This method, although theoretically possible, proved to be too difficult due chiefly to the rapid rate of solvent evaporation during the necessary handling and weighing operations. This evaporation caused large fluctuations in the resulting calculation of the solute's specific gravity as a result of the imbalance between the amount of solute compared to the excess of solvent. After many attempts at solving the inherent problems of this method, it was finally abandoned in favor of another method.

Second Trial Method

The second method of test was an application of Archimede's principle of buoyancy. Since all of the asphaltic constituents were believed to have a specific gravity reasonably close to that of 1.000, its buoyant characteristics in water were measured. A large cylindrical column of glass was filled with doubly distilled freshly boiled water, and the constituent immersed in it. The behavior of the asphalt specimen gave a clue as to its relationship with water. If it sank, its specific gravity was greater than that of water and if it floated to the surface, its specific gravity was less than that of water. The specific gravity of the water was then altered by titrating a liquid of either higher or lower specific gravity into the water depending on the action of the asphalt specimen. The results expected would be that when the constituent would remain suspended in the liquid, neither rising nor falling, its specific gravity would be the same as that of the liquid. It would then be an easy matter of determining the liquid's specific gravity to complete the test. The method proved too unreliable, however, due probably to concentration gradients existing in the cylinder.

A modification of the second method utilizing the principles of Stoke's Law was tried. In the turbulent region (particles over 2,000 microns) the law is (7)

$$V = ksD \qquad \text{(Eq. 2)}$$

where:

V is the terminal velocity

D is the particle diameter, microns

k is a constant

s is the specific gravity of the particle

Here again, consistent results could not be obtained within the desired degree of accuracy. This attempt initially showed much promise and with the development or purchase of accurate measuring devices to measure the terminal velocity and particle diameter, the method could probably be refined to the application of micro quantities.

Actual Method of Test

The third test method and the one finally adopted for this research was an application of the displacement method. Initial tests were far from encouraging, but examination of the variables involved showed that the small amount of asphalt constituents available were beyond the accurate sensitivity range of the weighing balance (0.0001 grams). Temperature fluctuation was also not believed to be adequately controlled for the exact liquid volume measurements that were necessary. With proper instrumentation and controls, it was felt that this method possessed promise and could be developed.

After thorough deliberation and discussion between the author and the Director of the Bituminous Research Laboratory, the decision was made to refine the displacement method and further attempts to develop additional methods or to refine the first two methods were dropped. The equipment and controls utilized, as well as the method of test, are set forth below.

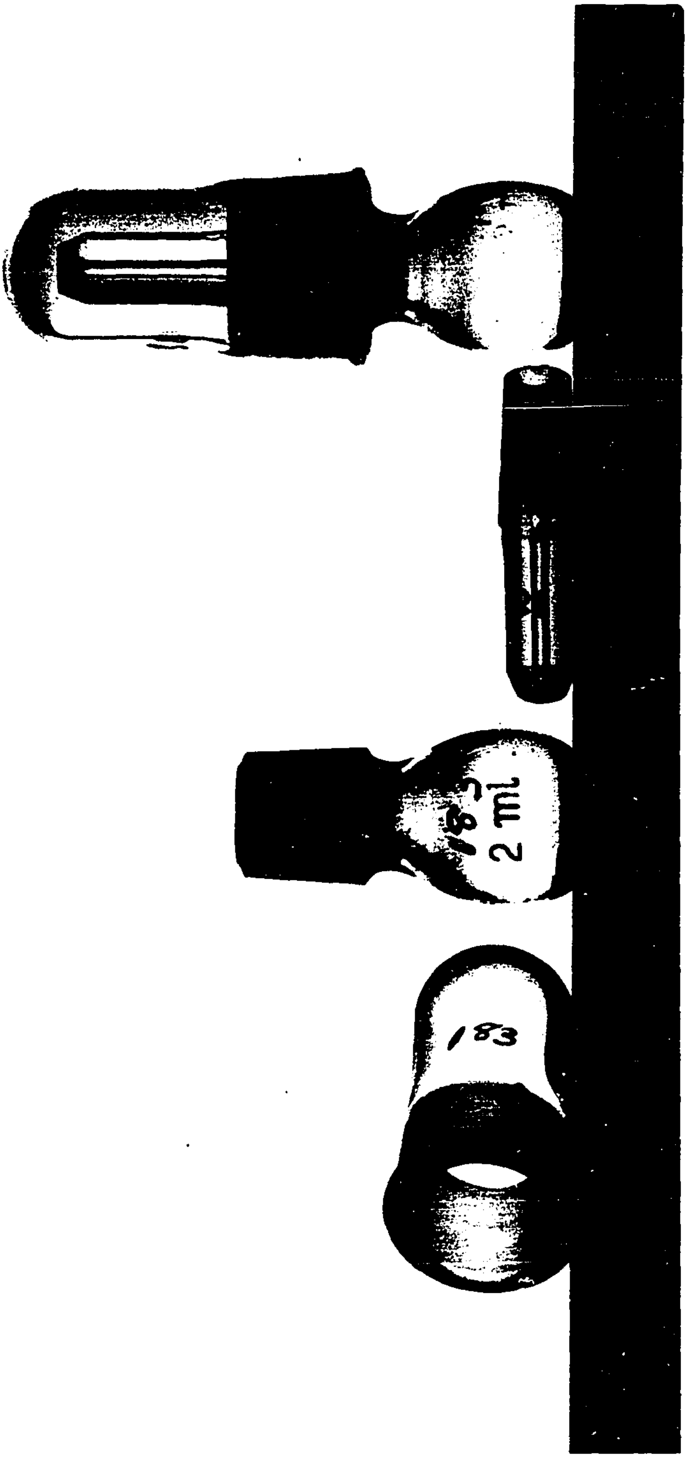
Test equipment

Certain items of test equipment are essential to gain the necessary degree of accuracy for the test. A discussion of the equipment used during the research followed by the actual test procedure is presented in that order.

Pycnometer The two milliliter capacity glass pycnometers utilized were obtained from the Scientific Glass Apparatus Company, Inc., Bloomfield, New Jersey. They consisted of three pieces, namely, base, stem and cap (Plate 5). The neck portion of the base is carefully ground both inside and out to insure a tight seal between the ground surfaces of the stem and cap. During all phases of testing, it was found to be essential that parts of the pycnometer did not come into direct contact with researcher's bare skin. This problem, which was imposed by the extreme sensitivity of the automatic balance, was solved by the use of both tweezers and disposable latex gloves whenever it became necessary to handle the pycnometers.

Automatic micro weighing balance All weight recordings were accomplished on a Mettler Automatic Micro Weighing Balance model M-5 distributed in the United

Plate 5. Assembled and unassembled 2 ml pycnometers.


185
2 ml
183

States by the Mettler Instrument Corporation of Highlstown, New Jersey. This piece of laboratory equipment weighs up to 20 grams with a sensitivity of one millionth (0.000001) of a gram. In order to gain the full potential of the balance, it was necessary to place the equipment in a climatized room with a constant temperature of $75^{o}F$ and the relative humidity maintained below 40 percent. Initial weight measurements indicated that the equipment bench upon which the balance was resting was not solid enough. This situation was corrected by adding additional bracing under the bench and anchoring the bench to both the floor and the wall. Subsequent measurements were still found to be unsatisfactory, however, for the balance was thrown off by the building vibrations induced by the heating and ventilation systems. This final problem was solved by placing the balance on a marble slab which in turn was insulated from the equipment bench by rubber insulators.

Oven A thermostatically controlled laboratory oven capable of maintaining a temperature of $100^{o}F \pm 2^{o}F$ was used to evaporate the CCl_4 solvent from the mixture of asphalt and CCl_4.

Syringe Two standard laboratory syringes of 5 ml capacity were necessary. One syringe was used to handle CCl_4 and the other for handling distilled water.

Water bath A Magni Whirl water bath manufactured by the Blue M Electric Company of Chicago, Illinois was used. The basic equipment was modified by adding three coils of 1/2 inch brass tubing below the water level of the bath. Water from the University's water supply system was constantly fed through the coils and exhausted into a sink drain in order to maintain a stable temperature within the bath regardless of room temperature. To further insure uniformity of the water bath's temperature, a motor driven propeller was added to supplement the magnetic stirring device of the bath. Motor speed was adjusted by utilizing a variable transformer. With these described modifications, water temperature was maintained at $25^{\circ}C$ with $\pm 0.1^{\circ}C$ variance.

Desiccator A laboratory desiccator was used to protect the pycnometers from dust and other foreign material when they were not in use. A tray of activated silica gel desiccant was utilized to control the humidity within the desiccator.

Still A simple still was constructed to produce distilled water. Water used in the testing phase was doubly distilled and then freshly boiled prior to testing to insure purity and a uniform quality at all times.

Specific gravity determination

Each of the constituents, A through G, were individually dissolved in 2 ml of carbon tetrachloride and transferred by syringe into a tared pycnometer base. Extreme care was taken to insure that the solution did not come into contact with the ground glass surface of the pycnometer's interior. The pycnometer base was then placed in an oven and dried to a constant weight at 100°F. Drying time was found to vary for each constituent as indicated in Fig. 1. To establish uniformity, 48 hours of 100°F drying was used in all tests to insure that all of the carbon tetrachloride solvent had been removed.

After drying to a constant weight, the entire pycnometer containing the constituent was transferred to a climatized weighing room where the temperature was maintained at 75°F and the relative humidity below 40 percent. When the pycnometer had come to room temperature, it was weighed on a micro balance to the nearest one millionth (0.000001) of a gram. Weighing procedure followed was to zero the balance, weigh the pycnometer and then recheck the zero of the balance. If a zero balance check was not obtained, the procedure was repeated until an exact zero check was made.

After recording the weight of the asphaltic

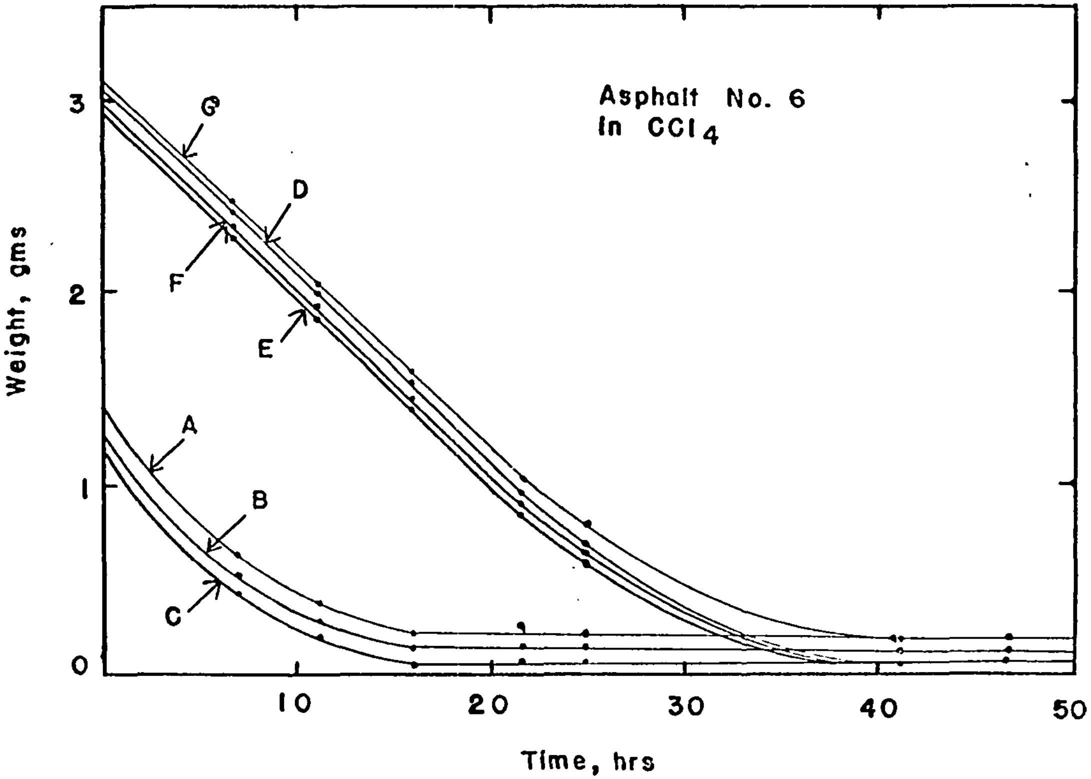


Fig. 1. Rate of evaporation of solvent from solution

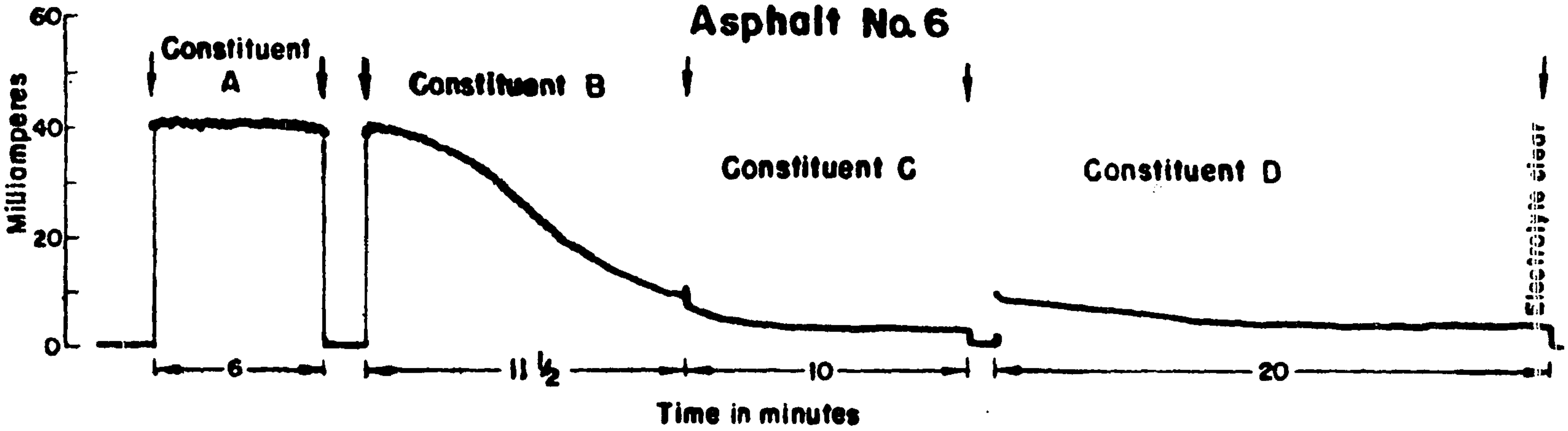


Fig. 2 Current variation and constituent end points during analysis

constituent and the pycnometer, the pycnometer was filled with freshly boiled doubly distilled water at 25°C, the stem inserted, and the base and stem portions completely immersed for not less than thirty minutes in a closed beaker of freshly boiled doubly distilled water which was maintained at 25°C by a water bath. With the pycnometer and its contents at 25°C, the top of the pycnometer's stem was exposed and immediately wiped dry so that the meniscus in the stem's bore was flush with the top surface of the stem. The pycnometer was then removed from the water bath and chilled so as to reduce the water's volume and thereby draw the meniscus down into the stem's bore to prevent evaporation from the exposed surface. The pycnometer was then carefully dried and the cap firmly emplaced to prevent evaporation (Plate 5). The pycnometer was then transferred back to the climatized weighing room, allowed to attain room temperature, and weighed to the nearest one millionth (0.000001) of a gram using the zero recheck technique of weighing previously described.

The specific gravity of the asphaltic constituent was then calculated by the formula

$$G = \frac{a}{b - (c - d)} \qquad \text{(Eq. 3)}$$

where:

G is the specific gravity of sample

a is the weight of the asphalt, grams

b is the volume of the pycnometer, ml

c is the weight of asphalt, pycnometer and water, grams

d is the weight of asphalt and pycnometer, grams

In order to verify the ASTM's ± 0.005 reproducibility limits on the calculated specific gravity, three separate and independent tests were run on each specimen.

TEST RESULTS

The objective of this research was twofold. The primary concern of the investigator was to determine the specific gravities of a series of test asphalt constituents that had been separated from the base asphalt in a secondary cell by electrolysis. Before these specific gravities could be determined, however, it first became necessary to develop a suitable method for determining this property, as discussed in previous chapters.

The test data presented in Table 2 are the result of running forty repetitive tests on micro quantities of the control asphalt number six to determine the specific gravity of each sample.

Table 3 is the result of the specific gravity determinations of each constituent of each of fifteen test asphalts. The values presented are the result of averaging three separated and independent tests on each constituent.

Table 2. Specific gravity determinations of control asphalt

Test number n	Sample weight, gms W_A	$\frac{1}{W_A^2}$	Specific gravity G
1	0.037319	719	1.001772
2	0.254222	16	1.002050
3	0.111452	81	1.001717
4	0.002521	100,000	0.991349
5	0.002220	100,000	1.016949

Table 2. (Continued)

Test number n	Sample weight, gms W_A	$\frac{1}{W_A^2}$	Specific gravity G
6	0.166501	36	1.001781
7	0.021895	2,083	1.001968
8	0.256753	15	1.002190
9	0.374474	7	1.002101
10	0.060366	275	1.002624
11	0.001919	250,000	0.973124
12	0.002149	250,000	1.021874
13	0.092945	116	1.001347
14	0.027105	1,370	1.000148
15	0.265489	14	1.002189
16	0.267290	14	1.001184
17	0.253199	16	1.001887
18	0.148231	46	1.001155
19	0.000819	1,666,666	0.977327
20	0.004208	50,000	0.992219
21	0.153030	43	1.001001
22	0.050042	400	1.000980
23	0.372441	7	1.000865
24	0.157759	40	1.002070
25	0.011694	7,142	0.999658
26	0.006783	20,000	1.000395
27	0.018324	3,030	1.002517
28	0.168111	35	1.001292
29	0.043253	535	1.001923
30	0.338935	9	1.001513
31	0.226905	19	1.000851
32	0.019367	2,632	0.999845
33	0.004848	50,000	0.996301
34	0.017294	3,333	1.004414
35	0.206319	23	1.001563
36	0.002082	25,000	0.982075
37	0.436349	5	1.001545
38	0.146253	47	1.001321
39	0.020092	2,500	1.000149
40	0.178519	31	1.001751
		2,536,305	

$$\overline{\frac{1}{W_A^2}} = 63,408$$

Table 3. Specific gravity determinations of asphalt constituents

Asphalt no.	Constituent A	B	C	D	E	F	G
1	1.1474	1.0512	0.9568	0.6186	0.8797	0.8624	1.0082
2	1.1191	1.0738	0.9349	0.9422	0.8051	1.0716	1.0374
3	1.1453	1.0793	0.9781	0.8066	0.8887	1.5912	1.0186
4	1.0312	1.0381	1.0477	1.0613	1.3812	0.7629	1.0499
6	1.0133	1.1028	1.0841	1.0752	0.9965	1.1903	1.0283
7	0.9237	1.0686	1.1153	1.0432	0.9442	0.9010	1.1145
8	1.0652	1.0837	1.0645	1.0368	0.9796	1.1266	1.0739
9	0.9969	1.1179	1.0446	0.9154	0.9337	0.9024	1.0553
21	1.0193	1.0625	1.0686	1.1109	0.9949	0.8443	1.0705
22	1.1010	1.0836	1.1151	0.9837	0.8779	0.8101	1.1726
23	1.1835	1.0218	1.0068	1.0272	1.0339	1.0045	1.0391
24	1.0335	1.0164	1.0039	1.1534	1.1277	1.0327	1.0026
31	1.0252	1.0033	1.0283	1.0214	1.0406	1.2779	1.0152
34	1.0275	1.0144	1.0160	0.9584	1.0637	1.0084	1.0700
35	1.3109	1.0082	1.0215	1.3914	1.3706	1.0515	0.9558

DISCUSSION OF TEST RESULTS

To prove the reliability of the test data and procedure, the author requested and received the assistance of Doctor Herbert T. David, Professor of Statistics, Iowa State University. Dr. David suggested that reliability of the test could be determined by utilizing a procedure for estimating the coefficient of variance of a series of triplicates by a disqualification test that he had developed in conjunction with two other associates (6). This coefficient of variance could then be equated to the variance of a number of specific gravity determinations of the control asphalt for which the specific gravity was known. This procedure was excellent for the developed data since a triple measurement of all weight determinations had been carried out during the entire investigation.

The statistical approach suggested was to detect whether or not any of the unusual observations noted during the tests were the result of normal experimental variation or were due to faulty procedure or other aberration and should therefore be discarded. The theory requires three measurements of an operation be taken and the ratio, r, of the range, R, of the three values to the average, $\overline{X}$, of the three values be computed. R is calculated as the difference between the largest and smallest value of the triplicate series. Thus,

$$r = \frac{R}{\overline{X}} = \frac{X_{max} - X_{min}}{(x_1 + x_2 + x_3)/3} \qquad \text{(Eq. 4)}$$

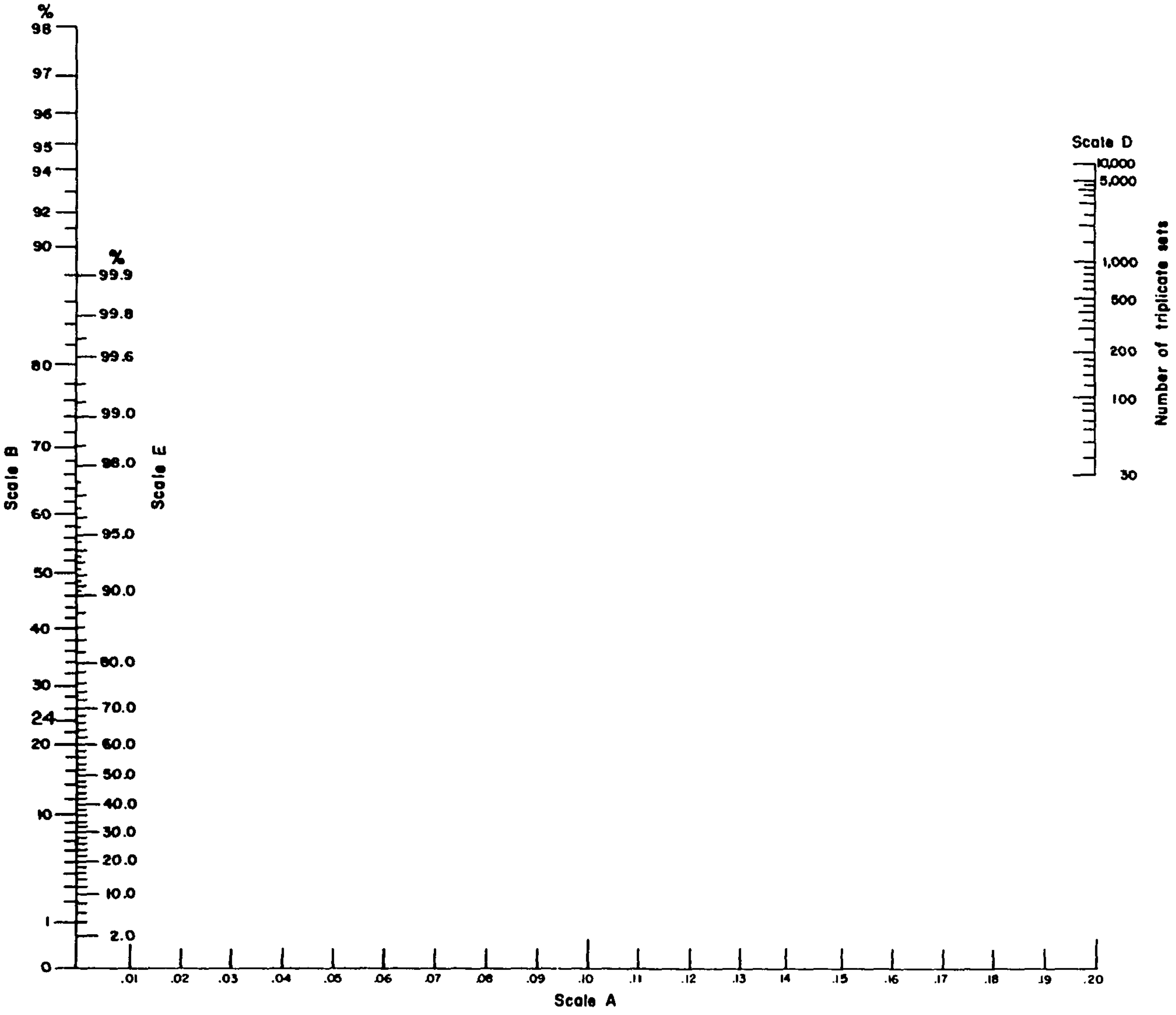
Each r value obtained is then arranged in ascending order of magnitude and thirty approximately equal spaced r values chosen. For each selected r value, the number of other r values less than it is designated as n and this value is increased by 1/2 with the result expressed as a percentage of the total number, N. That is compute

$$\frac{100(n + 1/2)}{N}$$

Each r value is then plotted against its corresponding percentage on a specially developed nomograph (Fig. 3), using scale A for the r values and scale B for the percentages. The points so obtained are then fitted with a straight line passing through the origin which is called the CV line. If the plotted points lie reasonably close to the straight line, the constancy of the coefficient of variance is established and the proposed test is considered applicable (6).

Outliers will tend to enlarge r if they are present which will cause an arched rather than a straight line. In such cases, the points farthest from the origin should

Fig. 3. Nomograph for graphical determination of outliers


%
98
97
96
95
94
92
90
80
70
60
50
40
30
24
20
10
1
0
Scale B
%
99.9
99.8
99.6
99.0
98.0
95.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
2.0
Scale E
.01
.02
.03
.04
.05
.06
.07
.08
.09
.10
.11
.12
.13
.14
.15
.16
.17
.18
.19
.20
Scale A
Scale D
10,000
5,000
1,000
500
200
100
30
Number of triplicate sets

be excluded from the straight line fit.

The coefficient of variance itself is estimated by the value of scale A at which the CV line attains a height of 24 on scale B (6).

Tables 4, 5 and 6 represent a series of triplicates that indicate the quantity (c - d) in the previously discussed specific gravity formula

$$G = \frac{a}{b - (c - d)} \qquad \text{(Eq. 3)}$$

The quantity (c - d) represents the weight of water that was added to the pycnometer and its asphalt specimen. Since this process represents the operator and equipment variables encountered during the test, it was decided to utilize these test values to establish the coefficient of variance for the test procedure.

Figure 4 represents the plotted r values computed from the data in Tables 4, 5 and 6. In order to utilize the established nomograph, the r values were coded by multiplying them by 0.23×10^4 to force them to fall within the limits of scale A. The coefficient of variance, as read off of Figure 4, yields a value of 0.04 which must be divided by 0.23×10^4 to obtain the true uncoded value. The true uncoded coefficient of variance from Figure 4 then is 17.32×10^{-6}. The scatter represented by the test data

Table 4. Triplicate determinations of weight of water added to pycnometer and constituent (c - d)

Constituent	Trial	Asphalt number				
		1	2	3	4	6
A	1	1.631913	1.681884	1.590440	2.011180	1.979019
	2	1.631909	1.681871	1.590416	2.011154	1.979053
	3	1.631950	1.681903	1.590464	2.011179	1.979024
	avg	1.631924	1.681886	1.590440	2.011171	1.979032
B	1	1.850548	1.864744	1.866679	1.779466	1.705926
	2	1.850607	1.864801	1.866649	1.779501	1.705901
	3	1.850708	1.864816	1.866658	1.779401	1.705921
	avg	1.850621	1.864787	1.866662	1.779456	1.705916
C	1	1.929239	2.094577	1.939209	1.940043	1.725562
	2	1.929250	2.094634	1.939198	1.940054	1.725587
	3	1.929303	2.094601	1.939129	1.940017	1.725573
	avg	1.929264	2.094604	1.939178	1.940038	1.725574
D	1	2.004836	2.036244	1.952745	1.976696	1.731327
	2	2.004859	2.036386	1.952749	1.976673	1.731251
	3	2.004840	2.036231	1.952741	1.976731	1.731256
	avg	2.004845	2.036287	1.952745	1.976700	1.731278
E	1	2.020383	2.088259	1.935714	2.008558	1.967061
	2	2.020315	2.088311	1.935711	2.008581	1.967041
	3	2.020490	2.088300	1.935756	2.008571	1.967048
	avg	2.020396	2.088290	1.935727	2.008570	1.967050
F	1	1.960288	2.006499	2.004265	1.955584	2.001175
	2	1.960211	2.006517	2.004242	1.955518	2.001267
	3	1.960311	2.006568	2.004264	1.955608	2.001293
	avg	1.960270	2.006528	2.004257	1.955570	2.001245
G	1	1.862454	1.776238	1.971777	1.858653	1.992592
	2	1.862358	1.776204	1.971801	1.858666	1.992643
	3	1.862364	1.776191	1.971777	1.858769	1.992622
	avg	1.862392	1.776211	1.971785	1.858696	1.992619

Table 5. Triplicate determinations of weight of water added to pycnometer and constituent (c - d)

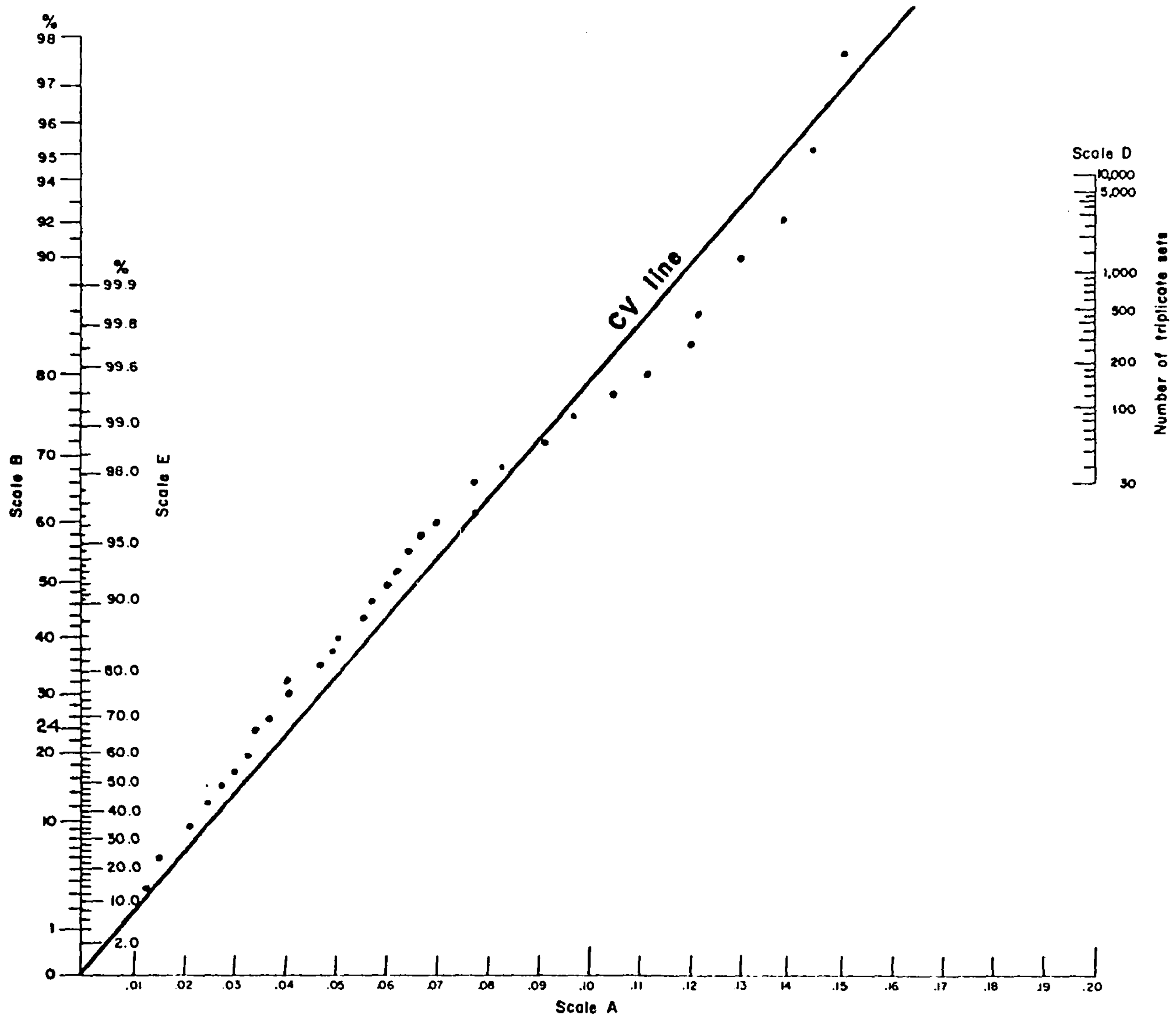
Constituent	Trial	Asphalt number				
		7	8	9	21	22
A	1	0.957029	1.824188	0.903859	1.999651	0.945014
	2	0.957066	1.824224	0.903808	1.999754	0.945077
	3	0.957016	1.824197	0.903817	1.999698	0.945092
	avg	0.957037	1.824203	0.903828	1.999701	0.945061
B	1	1.788025	1.706992	1.559359	1.826235	1.769431
	2	1.787965	1.706998	1.559385	1.826294	1.769419
	3	1.787929	1.706989	1.559348	1.826296	1.769527
	avg	1.787973	1.706993	1.559364	1.826275	1.769459
C	1	1.726739	1.743548	1.902165	1.778374	1.660163
	2	1.726704	1.743432	1.902188	1.778468	1.660099
	3	1.726648	1.743523	1.902169	1.778484	1.660083
	avg	1.726697	1.743501	1.902174	1.778442	1.660115
D	1	1.932463	1.883429	2.023400	1.544847	1.987653
	2	1.932436	1.883456	2.023389	1.544781	1.987688
	3	1.932442	1.883450	2.023456	1.544796	1.987681
	avg	1.932447	1.883445	2.023415	1.544808	1.987674
E	1	2.002560	1.965062	2.007569	1.966561	2.006101
	2	2.002546	1.965077	2.007548	1.966539	2.006083
	3	2.002535	1.965101	2.007575	1.966505	2.006053
	avg	2.002547	1.965080	2.007564	1.966535	2.006079
F	1	1.954563	2.000834	1.952448	2.005657	1.963500
	2	1.954580	2.000865	1.952501	2.005711	1.963454
	3	1.954579	2.000869	1.952383	2.005705	1.963441
	avg	1.954574	2.000856	1.952444	2.005691	1.963465
G	1	1.811551	1.881523	1.803176	1.845955	1.790679
	2	1.811551	1.881512	1.803206	1.845952	1.790682
	3	1.811497	1.881531	1.803212	1.845961	1.790652
	avg	1.811533	1.881522	1.803198	1.845956	1.790671

Table 6. Triplicate determinations of weight of water added to pycnometer and constituent (c - d)

Con-stit-uent	Trial	Asphalt number				
		23	24	31	34	35
A	1	1.969444	0.952602	0.947326	1.059067	1.967982
	2	1.969471	0.952573	0.947318	1.059096	1.967981
	3	1.969462	0.952568	0.947340	1.059104	1.968028
	avg	1.969459	0.952581	0.947328	1.059089	1.967997
B	1	1.854551	1.784752	1.825343	1.660789	1.779869
	2	1.854486	1.784745	1.825381	1.660710	1.779943
	3	1.854478	1.784744	1.825407	1.660781	1.779960
	avg	1.854505	1.784747	1.825377	1.660760	1.779924
C	1	1.837440	1.621652	1.764865	1.831801	1.815258
	2	1.837518	1.621599	1.764913	1.831814	1.815218
	3	1.837491	1.621588	1.764904	1.831863	1.815226
	avg	1.837483	1.621613	1.764894	1.831826	1.815234
D	1	1.902662	1.895900	1.823513	2.001632	1.934373
	2	1.902618	1.895989	1.823460	2.001601	1.934364
	3	1.902601	1.895961	1.823491	2.001588	1.934361
	avg	1.902627	1.895950	1.823488	2.001607	1.934366
E	1	1.951052	1.968664	1.992877	1.986011	1.966376
	2	1.951023	1.968743	1.992889	1.986015	1.966378
	3	1.951027	1.968780	1.992895	1.986043	1.966359
	avg	1.951034	1.968729	1.992887	1.986023	1.966371
F	1	1.970276	2.001596	1.967201	1.949536	1.989918
	2	1.970258	2.001549	1.967170	1.949514	1.989929
	3	1.970213	2.001541	1.967160	1.949525	1.989901
	avg	1.970249	2.001562	1.967177	1.949525	1.989916
G	1	1.797159	1.918368	1.806652	1.830959	1.806285
	2	1.797159	1.918433	1.806673	1.830944	1.806247
	3	1.797168	1.918444	1.806679	1.830917	1.806251
	avg	1.797162	1.918415	1.806668	1.830940	1.806261

Σ averages/105 = $\bar{\bar{X}}$ = 1.831 gms

Fig. 4. Graphical determination of coefficient of variance


%
98
97
96
95
94
92
90
80
70
60
50
40
30
24
20
10
1
0
Scale B
%
99.9
99.8
99.6
99.0
98.0
95.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
2.0
Scale E
CV line
.01
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.03
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.12
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.14
.15
.16
.17
.18
.19
.20
Scale A
Scale D
10,000
5,000
1,000
500
200
100
30
Number of triplicate sets

plotted in Figure 4 is indicative of good test procedure (6), and it was not deemed necessary to pursue the matter further, but rely upon the graphically established coefficient of variance.

In order to bridge the area between the known and the unknown, forty (40) micro specific gravity determinations were made of the control asphalt number 6. Since the specific gravity of the control asphalt was known, the standard deviation and variance of the determinations were computed and the results are shown in Table 7.

If there were no measurement error at all during the weighing operations, the successive specific gravity determinations, G_i, would have the following structure:

$$G_i = \frac{W_{Ai}}{W_{wi} - (W_{wi} - \frac{W_{Ai}}{G_A})} \qquad \text{(Eq. 5)}$$

where:

W_{Ai} = weight of asphalt in the pycnometer

W_{wi} = weight of water that pycnometer holds when full

G_A = specific gravity of asphalt specimen

In the above equation, the subscript i is to indicate sources of variability which were introduced by varying the asphalt sample weights and utilizing different pycnometers in random fashion.

Table 7. Standard deviation of specific gravity determinations of control asphalt no. 6

Observation number n	Sample weight w	Specific gravity G	Deviation from mean $g=G-\overline{g}$ (+)	Deviation from mean $g=G-\overline{g}$ (-)	Deviation squared $g^2 \times 10^{-6}$
1	0.037319	1.001772	0.001800		3.24
2	0.254222	1.002050	0.002078		4.32
3	0.111452	1.001717	0.001745		3.05
4	0.002521	0.991349		0.008623	74.36
5	0.002220	1.016949	0.016977		288.22
6	0.166501	1.001781	0.001809		3.27
7	0.021895	1.001968	0.001996		3.98
8	0.256753	1.002190	0.002218		4.92
9	0.374474	1.002101	0.002129		4.53
10	0.060366	1.002624	0.002652		7.03
11	0.001919	0.973124		0.026848	720.82
12	0.002149	1.021874	0.021902		479.70
13	0.092945	1.001347	0.001375		1.89
14	0.027105	1.000148	0.000176		0.03
15	0.265489	1.002189	0.002217		4.92
16	0.267290	1.001184	0.001212		1.47
17	0.253199	1.001887	0.001915		3.67
18	0.148231	1.001155	0.001183		1.40
19	0.000819	0.977327		0.022645	512.80
20	0.004208	0.992219		0.007753	60.11
21	0.153030	1.001001	0.001029		1.06
22	0.050042	1.000980	0.001008		1.02
23	0.372441	1.000865	0.000893		0.80
24	0.157759	1.002071	0.002099		4.41
25	0.011694	0.999658		0.000314	0.10
26	0.006783	1.000295	0.000323		0.10
27	0.018324	1.002517	0.002545		6.48
28	0.168111	1.001292	0.001320		1.74
29	0.043253	1.001923	0.001951		3.81
30	0.338935	1.001513	0.001541		2.37
31	0.226905	1.000851	0.000879		0.77
32	0.019367	0.999845		0.000127	0.02
33	0.004848	0.996301		0.003671	13.48
34	0.017294	1.004414	0.0044442		19.73
35	0.206319	1.001563	0.001591		2.53
36	0.002082	0.982075		0.017897	320.30
37	0.436349	1.001545	0.001573		2.47

Table 7. (Continued)

Observation number n	Sample weight w	Specific gravity G	Deviation from mean $g=G-\bar{g}$ (+)	(-)	Deviation squared $g^2 \times 10^{-6}$
38	0.146253	1.001321	0.001349		1.82
39	0.020092	1.000149	0.000177		0.03
40	0.178519	1.001751	0.001779		3.16
Totals		39.998885	0.087883	0.087878	2569.93

$$\bar{g} = 39.998885/40 = 0.999972$$

$$s^2 = \Sigma\, g^2/n-1 = 2569.93/39 = 65.90 \times 10^{-6}$$

$$s = 8.12 \times 10^{-3}$$

Since there is a measuring error, just by the very nature of the process and equipment used, the actual structure of Equation 5 is:

$$G_i = \frac{W_{Ai} + \epsilon_i}{(W_{wi} + \partial_i) - (W_{wi} - \frac{W_{Ai}}{G_A} + \eta_i)} \qquad \text{(Eq. 6)}$$

where ϵ_i, ∂_i and η_i are expressions for the weighing errors. Since the specific gravity of asphalt, G_A, is in reality very nearly 1.000, Equation 6 can be written as

$$G_i = \frac{W_{Ai} + \epsilon_i}{W_{Ai} + \partial_i - \eta_i} = \frac{1 + \frac{\epsilon_i}{W_{Ai}}}{1 + \frac{\partial_i - \eta_i}{W_{Ai}}} \qquad \text{(Eq. 7)}$$

$$G_i = \frac{1 + \frac{\epsilon_i}{W_{Ai}}}{1 + \frac{\partial_i - \eta_i}{W_{Ai}}} \times \frac{1 - \frac{\partial_i - \eta_i}{W_{Ai}}}{1 - \frac{\partial_i - \eta_i}{W_{Ai}}} = \frac{(1 + \frac{\epsilon_i}{W_{Ai}})(1 - \frac{\partial_i - \eta_i}{W_{Ai}})}{1 - (\frac{\partial_i - \eta_i}{W_{Ai}})^2}$$

Since $(\frac{\partial_i - \eta_i}{W_{Ai}})^2$ is an extremely small term

$$G_i \doteq (1 + \frac{\epsilon_i}{W_{Ai}})(1 - \frac{\partial_i - \eta_i}{W_{Ai}}) \qquad \text{(Eq. 8)}$$

$$G_i \doteq 1 + \frac{\epsilon_i + \eta_i - \partial_i}{W_{Ai}} \qquad \text{(Eq. 9)}$$

If we now compute the variance affecting a particular G_i, then

$$s^2_{Gi} = (s_{Gi} - 1)^2$$

where s^2 represents the variance. It then follows that

$$s^2_{Gi-1} \doteq \overline{(G_i - 1)^2} - (\overline{G_i - 1})^2 \qquad \text{(Eq. 10)}$$

If the term $\epsilon_i + \eta_i - \partial_i$ in Equation 9 above is let equal to the term E_i, representing the combined measurement error, then Equation 10 can be rewritten as

$$s^2_{Gi} \doteq \overline{(E_i^2)(\frac{1}{W_{Ai}})^2} - [\overline{(E_i)(\frac{1}{W_{Ai}})}]^2 \qquad \text{(Eq. 11)}$$

Assuming statistical independence of the measurement errors and initial weights, $\overline{E_i}$ becomes equal to zero since there is a fifty percent probability of half of values being on one side of the mean as on the other side. For this reason Equation 11 can be written as

$$s^2_{Gi} \doteq E_i^2 \overline{(\frac{1}{W_{Ai}})^2}$$

$$s^2_{Gi} \doteq s^2_{Ei} \overline{(\frac{1}{W^2_{Ai}})} \qquad \text{(Eq. 12)}$$

Since there are three sources of error indicated in Equation 4, Equation 12 becomes

$$s^2_{Gi} = 3\sigma_m \overline{(\frac{1}{W^2_{Ai}})} \qquad \text{(Eq. 13)}$$

where σ_m represents the standard deviation of the entire population of which s represents a sample of 40. The coefficient of variance, CV_m, of the population, which has been estimated by the triplicate computations, multiplied by the average of the average of all the triplicate determinations of Tables 4, 5 and 6, $\bar{\bar{X}}$, should then equal the population's standard deviation. Thus,

$$s^2_{Gi} \doteq 3\ CV^2_m(\bar{\bar{X}})^2\ \overline{\left(\frac{1}{W_{Ai}}\right)^2} \qquad \text{(Eq. 14)}$$

The data accumulated during this investigation (Tables 2, 6 and 7 and Fig. 4) when entered into Equation 14 emits the following structure:

$$65.90 \times 10^{-6} = 3(17.32 \times 10^{-6})^2\ (1.831)^2\ (44.64 \times 10^3)$$
$$= 134.58 \times 10^{-6}$$

The above approximate equality means that the variance of the specific gravity determinations of the 40 runs of the control asphalt number 6 (Table 2) is 2.04 times better than would be predicted.

Since there are apparent outliers in the 40 control tests which appear to be dependent upon sample weight, the 40 control specific gravities were plotted against their weight. The results of this analysis are shown in Fig. 5. The heavy horizontal lines of Fig. 5 represent ±0.005 from the true specific gravity of the control asphalt (1.001). If all specific gravities falling outside of these two limit lines are eliminated, it appears that 0.005 grams (5 mg) is the lower sample weight limit of the test.

When all specific gravities of Tables 2 and 7 which

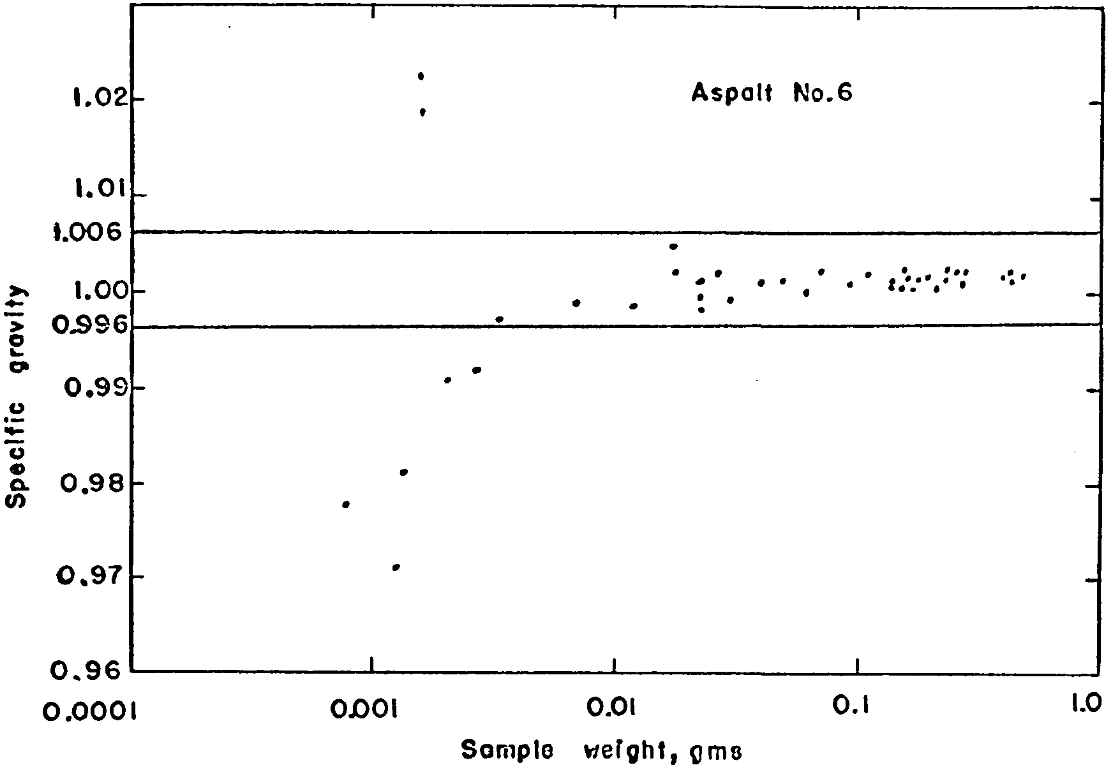

Fig.5. Accuracy limits of test procedure

have a sample weight of less than 5 mg are eliminated as outliers, the computed variance, s^2, is 3.55×10^{-6}. Using this refined data in Equation 14 yields

$$\begin{aligned} 3.55 \times 10^{-6} &= 3(17.32 \times 10^{-6})^2\,(1.831)^2\,(1.39 \times 10^3) \\ &= 4.19 \times 10^{-6} \end{aligned}$$

This approximate equality means that without outliers, the variance of the 40 control asphalt determinations is 1.18 times better than would be predicted.

These close equalities between the variance of the control data and that of the test data of Table 3 give a good indication of the validity of the overall test and serve as a double check of the coefficient of variance determined from Fig. 4. It should be noted that the 40 control asphalt specific gravity determinations were made at the end of the laboratory testing phase. The fact that the investigator's procedure of test had become more refined through experience probably accounts for the fact that the control asphalt specific gravity determinations were slightly better than would normally be predicted.

It is apparent that for this method of determining the specific gravity, the measurement error cannot be assessed without going through the detailed and somewhat complicated steps outlined. This limitation applies whenever a set of specific gravity determinations is made, even on the same material, if the sample weights are allowed to vary in the same series.

One source of error that has not been treated throughout the investigation is that the actual specific gravity of water at 25°C is not 1.000, but is in fact 0.997044. The reason for this error being carried is predicated on the fact that the ASTM test does not take this small error into consideration. Since one of the prime purposes of this research was to cover the area of sample weight below that of the ASTM test, it was felt that there was no reason to incorporate the factor into this investigation. The very small error introduced by neglecting this value can best be assessed by referring to Equation 5 which shows the almost total cancellation effect of the water weights in the developed formula. If desired, the true specific gravity of the water can be incorporated into the developed formula (Equation 3) as follows:

$$G = \frac{a}{\frac{b}{G_1} - (c - d)} \qquad \text{(Eq. 3a)}$$

where G_1 represents the specific gravity of the water at the test temperature.

CONCLUSIONS

This investigation to determine the specific gravity of micro quantities of bituminous materials indicates that the following conclusions can be drawn:

1. The method of test described is both practical and feasible for bituminous substances where quantities of material available for testing exceed 0.005 grams (5 mg).

2. For weights of material in excess of 5 mg, the method yields repeatable and reproducible specific gravity results within the desired ±0.005 tolerance established by ASTM.

3. The developed method of test compliments the ASTM specific gravity tests for bituminous materials since it covers an area of sample weights that cannot be tested by ASTM tests for bituminous materials.

4. With suitable equipment, the developed test can be performed with only a brief familiarization with the procedure since the required equipment and mathematics are extremely simple.

5. From the test results obtained, it appears that the test procedure is applicable to materials other than bituminous materials, but thorough testing would be necessary with respect to each specific material before a conclusion as to test validity could be established.

REFERENCES CITED

1. American Society for Testing Materials. A.S.T.M. standards on bituminous materials for highway construction, waterproofing, and roofing (with related information). 8th ed. Philadelphia, Pa., Author. 1960.

2. Asphalt Institute (College Park, Md.). Introduction to asphalt. Asphalt Institute Manual Series No. 5. 3rd ed. 1961.

3. Bassi, B. S. Separation of asphalt by electrical means. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

4. Csanyi, L. H. An electrolytic analysis of asphalts. Iowa Engineering Experiment Station. Oct. 1963.

5. ________ and Bassi, B. S. Analysis of asphalts by electrical means. Paper presented at the Association of Asphalt Paving Technologists, Montreal, Canada, Feb. 1958. (Mimeo. report.) Ames, Iowa, Iowa State University of Science and Technology. *ca*. 1958.

6. David, H. T., Davidson, D. T. and O'Flaherty, C. A. Pinpointing suspect triplicate unconfined compressive strength determinations. Paper presented at annual meeting of American Society for Testing Materials, Atlantic City, N.J., June 1962. (Mimeo. report.) Ames, Iowa, Iowa State University of Science and Technology. *ca*. 1962.

7. Marks, L. S. Mechanical engineer's handbook. 4th ed. New York, N.Y., McGraw-Hill Book Co., Inc. 1941.

8. Pfeiffer, J. P. The properties of asphaltic bitumen. New York, N.Y., Elsevier Publishing Co., Inc. 1950.

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