A METHOD OF DETERMINING SEVERAL VISCOSITIES SIMULTANEOUSLY.¹

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IN the course of an investigation on the action of various substances on serum, it became advisable to determine simultaneously the viscosity of several admixtures of reagent and serum. The ordinary modified Poiseuille (so-called Ostwald) viscometer, which has been used so largely in the past, was not suitable for the work in hand, as with such an apparatus it was necessary to determine the density of the liquid as well as to take the viscosity readings. Fortunately, however, a method, due to Scarpa (1910¹), was available in which it was not necessary to determine the density of the liquid. It consists in measuring the time, t_1 , which is occupied in drawing up, through a vertical capillary tube, sufficient liquid to fill a bulb at the top of this tube, and the time, t_2 , which this volume takes in flowing out from the bulb under the weight of the liquid. Under constant conditions, the viscosity is proportional to the expression $\frac{t_1 t_2}{t_1 + t_2}$. A further advantage of the method is, that it is immaterial whether exactly equal volumes of liquid are used in the different experiments.

For the purposes of the investigation undertaken by the author, the principle of Scarpa's method was employed, but the form of the viscometer and the general arrangement of the apparatus were modified, and, as a further development, a method was devised for determining the viscosity of several liquids simultaneously.

The quantity of liquid, *e.g.*, serum, used in determining the viscosity by means of the apparatus herein described was 2 c.c. for each determination. This amount was a convenient one for the investigation in hand, but there is no reason why an apparatus should not be made on the same lines in which the quantity of liquid used would be much smaller, say 1 c.c. or even less. The serum to be examined was run by means of a pipette into a test-tube 25 cms. long and 1.4 cm. wide (see Fig. 1). The viscometer proper consisted of two pieces of glass tubing (one of which was of capillary tubing 0.34 mm. in bore, and the other of ordinary tubing 4 mm. in bore), joined together in the blow-pipe flame and blown out at the joint into a bulb. The bulb was about 1 c.c. in capacity, and its shape was that suggested by two cones placed base to

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Fig. 1.—Type of viscometer in which a separate determination of the density of the liquid under investigation is not required. All that is necessary is to take the times of flow from the lower to the upper mark, and the time of flow from the upper to the lower mark.

Fig. 2.—Viscometer suitable for testing the action of reagents or liquids under investigation. Having determined the viscosity of, say, serum by means of this apparatus, a known portion is removed by means of a pipette graduated in one-hundredths of a c.c., and an equal quantity of the reagent added. The viscosity of the mixture is then redetermined.

base (1916²). The shape of the bulb differed from that of Scarpa, who apparently used one more nearly spherical. According to Applebey (1913³), the main factor in securing the efficiency of a modified Poiseuille viscometer (the same applies to the apparatus used by Scarpa) is the character of the joins between the capillary and the bulb. For the preservation of a proper flow, it is necessary that the joins should be even and without irregularity, and that the change of diameter should be gradual. The lower end of the capillary dipping into the liquid was cut off square. The length of the capillary was 10.5 cms. Immediately above the bulb was a constriction bearing an etched ring. Another ring was etched below the bulb, at the point where the normal diameter of the capillary commenced. It was the times taken for the liquid to flow between these two marks, both upwards and downwards, that provided the data for each experiment. The rubber stopper supporting the viscometer had a shallow V-shaped slit cut in its side, so that when the apparatus was assembled the pressure of the air inside and outside was always equal during the upward or downward flow of the serum in the capillary. The pressure of the air in the viscometer proper was kept constant by means of the mechanism described later.

In some of the experiments in hand it was necessary to take the viscosity of the serum, then to remove a small known portion, and replace this by an equal quantity of the reagent, *e.g.*, mustard gas, whose action one was investigating. The form of the apparatus described above did not lend itself very well to this type of work, inasmuch as it was troublesome to disassemble the apparatus, and, moreover, some of the liquid was liable to be lost owing to the fact that, when the capillary was withdrawn, its lower end sometimes inadvertently touched the side of the test-tube. This loss of liquid prevented one from adjusting with sufficient accuracy the relative strengths of the liquid and reagent. To remove this disadvantage the following apparatus was designed (Fig. 2).

The test-tube was replaced by a U-tube, one limb of which was 14 mm. wide, and the other 7 mm. The viscometer was carried by the wider tube. The rubber stopper was also conveniently replaced by a hollow ground-glass one, blown round the upper part of the viscometer proper. As the serum to be investigated was in such amount that it did not completely fill the bend of the U-tube, the presence of the air in both limbs was always the same during an experiment, and equal to that of the atmosphere. There was no need, therefore, for a slit to be made in the side of the stopper. By means of pipettes of 1 c.c. capacity, and graduated in one-hundredths of a c.c., it was a simple matter to withdraw a known volume of serum without disassembling the apparatus, and add an equal quantity of reagent through the narrow limb of the U-tube.

During a part of the investigations it was necessary to be able to test the effect of varying strengths of reagent on one and the same samples of serum. For this purpose the apparatus depicted in Fig. 3 and Fig. 4 was designed.

The essential part of this apparatus is shown in Fig. 3. It consisted of a series of five two-way taps, the single tubes on the lower side of which were separately connected by rubber tubing to the respective viscometers, while the front tubes on the upper side were all connected to one single tube above,

Fig. 3.—The apparatus essential to the method for determining several viscosities simultaneously. During the upward flow of the serum the two-way taps are turned on to the aspirator, while during the downward flow of the serum they are turned on to air.

which was closed at one end and open at the other. The open end was connected by means of pressure tubing to the aspirator used for maintaining a constant negative pressure above the surface of the serum in the viscometer proper. The back tubes on the upper side of the series of two-way taps were each left open to the air, but bent at a right angle at the upper end, so as to prevent dust from settling into them.

The general build of the apparatus is shown in Fig. 4. As will be seen from the sketch, the viscometers and the two-way taps connected to them were supported in a water thermostat by a framework. The upper part of the framework was of wood, and the lower part of metal

Fig. 4.—General scheme of apparatus for determining viscosities. With the apparatus, as sketched, five viscosities can be determined separately simultaneously, or in groups of less than five. With this method also a separate determination of the density of each fluid is not required.

covered with aluminium paint to prevent rusting. The framework was also provided with suitable grooves and metal spring clamps for maintaining the viscometers in a constant vertical position. The viscometers were well immersed in the water, rather more so than shown in the sketch.

The water thermostat was of the constant level type, with glass windows at the front and back, and was kept at a constant temperature within at least one-fortieth of a degree Centigrade, by means of a sensitive toluol regulator. During an experiment the water in the thermostat was kept circulating by blowing in bubbles of air. For this purpose a mechanism similar to that described by Findlay (1914⁴) was used. Between the thermostat and the aspirator, used for producing a constant negative pressure, was placed a sheet of asbestos, which was specially useful when experiments were made at higher temperatures.

At the time of designing the apparatus for producing the constant negative pressure required for drawing the serum up the viscometer, the original article by Scarpa was not available. The method designed and shown in Fig. 4 was different, therefore, from that used by Scarpa, but was found to work very satisfactorily. It consisted of an aspirating bottle of about 8 litres in capacity, provided at its upper aperture with a well-fitting rubber stopper, through which passed a T-piece. One limb of the T-piece was connected by pressure tubing to a water manometer, and the other limb through a three-way tap to the viscometer. The lower aperture of the aspirating bottle was closed with a rubber stopper bearing a single-way tap. To the outer end of this tap was attached a short length of rubber tubing. When first filling the aspirator with the necessary quantity of water for producing a partial vacuum, the short length of attached rubber tubing was connected to the laboratory water-tap, and water run through the lower aperture until the vessel was about one-third full. In the meantime care had to be taken that the three-way tap above the aspirator was turned so as to connect the air in the interior of the aspirator with that of the exterior. As soon as sufficient water was run into the aspirator the lower single-way tap was turned off, and its attached rubber tubing made to dip into water contained in a wide shallow vessel. The upper three-way tap was now turned so as to connect the aspirator with the rest of the apparatus as far as the two-way taps above the viscometers. The lower single-way tap was then turned on, and the water allowed to flow from the aspirator into the wide shallow vessel until the difference of the two levels of water was such that the manometer registered about 250 mm. The pressure was then exactly adjusted to 250 mm. by using a lens for the reading of the millimetre scale, and by adding to or removing the requisite quantity of water from the wide shallow vessel by means of a pipette. As a medium for the manometer, water was preferred to mercury, since it was thirteen times more sensitive.

In making the routine determination of viscosities, 2 c.c. of the liquid under investigation were first pipetted into the respective test-tubes, and the viscometer proper then firmly fixed therein. The test-tubes were next clamped in a vertical position in the thermostat, and the viscometers connected through the rubber tubing to the two-way taps above, which were then turned on to air. The test-tubes and their contents were then allowed sufficient time to acquire the temperature of the thermostat. In the meantime the aspirator was adjusted to a negative pressure of 250 mm. of water. In order to wet the viscometers previous to taking readings, all five were connected to the aspirator at one time, and the liquid in each drawn well above the upper mark and allowed to flow out again. The two-way tap above viscometer A was now turned on to the aspirator, and, at the moment the liquid passed the lower mark of the viscometer, the stop-watch was started. The stop-watch used was an accurate one, graduated in one-tenths of a second, and bearing two independent fingers on a large dial for recording seconds and fractions of a

second, and one finger on a small dial for recording minutes. Both large fingers were set going together in a superimposed position, by pressing the primary spring connected with the winding screw. One of the fingers could be stopped at any moment by pressing a secondary spring a little to one side of the primary. On again pressing the secondary spring, the finger it controlled rejoined the primary finger, which had kept on going in the meantime. This starting and stopping of the secondary during the progress of the primary finger could be repeated as often as desired. When the watch was to be stopped finally, the primary spring was pushed. Both fingers then stopped. Another push of the primary spring brought the two fingers to zero. The first viscometer having been started, the second two-way tap was turned on to the aspirator, and the time at which the liquid passed the lower mark recorded by means of the secondary spring on the stop-watch. The secondary finger having been made to rejoin the primary, the third viscometer was started at the time recorded as before. This process was repeated until all five viscometers had been started. The moment the liquid in the first viscometer had passed the upper mark, the secondary spring was pressed and the time recorded. The two-way tap was then turned away from both the aspirator and the air. The secondary finger having been made to rejoin the primary, the reading for the second viscometer was recorded, and the two-way tap turned off. In this way all five viscometers were successively dealt with. The record obtained in one experiment was as follows :—

READING.	VISCOMETER.				
	A.	B.	C.	D.	E.
Initial time in seconds (lower mark)	0·0	18·9	30·8	43·8	59·0
Final time in seconds (upper mark)	188·0	224·7	264·0	235·8	276·4
Difference = t_1 . . .	188·0	205·8	233·2	192·0	217·4

To obtain readings for t_2 , the two-way taps were consecutively turned on to the air, and the stop-watch used as before for recording the times at which the respective liquids passed the upper and lower marks on the viscometers. For example, in the above experiment, the readings for t_2 were as follows :—

READING.	VISCOMETER.				
	A.	B.	C.	D.	E.
Initial time in seconds (upper mark)	0·0	28·8	59·4	80·2	95·1
Final time in seconds (lower mark)	178·0	205·8	268·6	259·0	296·9
Difference = t_2 . . .	178·0	177·0	209·2	178·8	201·8

In order to increase the accuracy of the readings, a lens was used when watching the liquid flow past the mark.

Each reading was repeated at least three times and the average taken. That

the method was capable of a considerable degree of accuracy is shown by the following figures, taken from the experiment referred to above:—

READING.	VISCOMETER.									
	A.		B.		C.		D.		E.	
	t_1	t_2	t_1	t_2	t_1	t_2	t_1	t_2	t_1	t_2
First . . .	188.0	178.0	205.8	177.0	233.2	209.2	192.0	178.8	217.4	201.8
Second . . .	187.8	177.8	205.0	176.2	233.6	209.8	192.4	178.2	217.8	201.6
Third . . .	187.6	178.2	205.0	176.4	233.0	209.0	191.8	178.4	217.0	201.6
Average . . .	187.8	178.0	205.2	176.5	233.3	209.3	192.1	178.4	217.1	201.7

Having obtained the necessary data for each liquid, the viscosity relative to water was calculated from the following formula:—

$$\text{viscosity} = \frac{t_1 t_2}{t_1 + t_2} \times \frac{T_1 + T_2}{T_1 T_2}$$

where t_1 = time of upward flow of unknown ;

t_2 = time of downward flow of unknown ;

T_1 = time of upward flow of distilled water ;

T_2 = time of downward flow of distilled water.

The constant $\frac{T_1 + T_2}{T_1 T_2}$ has to be determined for each viscometer,

but, once obtained, it is recorded, and merely requires checking from time to time. Hence the formula resolves itself into—

$$\frac{t_1 t_2}{t_1 + t_2} \times K.$$

For the determination of K one may use distilled water or some substance, such as aniline, whose viscosity has been accurately determined and recorded. Aniline (1913⁵) is particularly suitable, as it can be readily obtained in a high state of purity. If η is the viscosity of the standard other than water, then—

$$K = \frac{\eta (t_1 + t_2)}{t_1 t_2}$$

where t_1 and t_2 represent the times of upward and downward flow of that standard. If water is used as a direct standard, it should be recently distilled, and allowed to stand over night in a large vessel. This will allow any particles present in the water to sediment to the bottom, so that the required volume of water can be pipetted from the upper stratum.

The times for t_2 with distilled water in the apparatus used varied with the viscometer from 94.5 to 101.8 seconds, and the values of K were as follows :—

Viscometer.	K .
A	0.02172
B	0.02064
C	0.01838
D	0.01916
E	0.01793

One further point requires mention. Occasionally, when the liquid had finished flowing downwards in the viscometer, a small bubble of air was left in the capillary. To provide for the removal of this bubble, a short length of rubber tubing was fixed on to the air outlet of the three-way tap placed above the aspirator. By turning the three-way tap so as to connect the viscometer with this short length of tubing, and then blowing gently through or squeezing the tube, an air bubble in any of the viscometers could readily be removed.

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