

# FILTERING QUALITY OF RAW SUGAR: INFLUENCE OF STARCH AND INSOLUBLE SUSPENDED MATTER

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## Abstract

The influence of starch and insoluble suspended matter on the filtration behaviour of processed and unprocessed raw sugar liquor has been examined. In the C.S.R. Filterability Test, which utilises unprocessed, raw liquor, the amount of suspended matter present is a factor of paramount importance, whereas starch is shown to have minimal effect on the test filterability figure, within the starch range studied (up to 400 ppm). The second half of the paper deals with filtration of steady-state carbonated liquor. The starch content is shown to have a profound effect on the filterability of the processed liquor. However, the influence of insoluble suspended matter is of much less importance. The mechanism of starch interference in carbonation is briefly discussed.

## Introduction

That aspect of sugar quality which concerns itself with the assessment of filtration characteristics of raw sugar is one of considerable importance. Much thought and considerable effort have been expended in the past in finding ways of improving filtering quality, both in this country and elsewhere<sup>1 3 9 10 11 21 35</sup>. However, certain facets of our knowledge remain incompletely understood and the subject requires further examination.

The sugar industry has, in the past, relied mainly on filterability tests based on the filtration performance of a raw melt under standard conditions of concentration and temperature (e.g. 60° Brix at 20°C), the solution being filtered through a suitable filter medium at constant pressure (e.g. diatomaceous earth or millipore filter at 3,45 bar (50 lb/in<sup>2</sup>). The test filterability is then calculated as a function of the volume of filtrate collected after a specified time. When compared to refinery filtration data, results from this type of test show low concurrent reliability. Moreover, there is the additional objection that a test based on the "specified time" principle is not time-independent and, therefore, cannot reflect accurately the behaviour of a constant pressure refinery filter<sup>29</sup>.

The laboratory test which is used in South Africa, i.e. the C.S.R. Filterability Test<sup>20</sup> belongs to this category. It has proved to be of very limited use in assessing the refinery filtration quality of South African raw sugar. As far as refinery processed liquor is concerned, the pattern of filtration behaviour is complicated by the choice of purification processes, e.g. carbonation, phosphatation and the large variation of conditions employed within these processes. Nevertheless, various impurity factors associated with raw sugar

have been tentatively linked with poor filtering quality (of both processed and unprocessed liquor) and of these, starch and insoluble suspended matter are probably most notorious.

Insoluble suspended matter in a raw sugar solution results when the particulate impurities occluded within the crystal are released and dispersed on dissolution of the crystal in water. The particle size and surface charge of this matter is such that it remains stably dispersed as colloidal particles of up to 300-400 μm in diameter. The chemical nature of this material has been investigated widely<sup>7 8 17 22 25 31</sup> and polysaccharides, silica and lipids and other substances have been isolated. A partial size characterisation has also been attempted by light scattering<sup>32</sup> on the smaller suspended matter present, viz. approximately 10 μm and below.

Starch is present in the raw sugar crystal by virtue of the fact that it is preferentially occluded during sucrose crystallisation. It is composed of two major components: straight-chain amylose and branched-chain amylopectin. The most important physico-chemical properties of starch, with reference to its role in filtration, are probably the ratio of amylose: amylopectin, the molecular weight size range of these fractions and the variation in charge characteristics with pH, in solution.

The content of this paper is divided into two parts for convenience. The first part of our investigation of filterability concerns the examination of the respective roles played by the two factors previously discussed, i.e. insoluble suspended matter and starch, in the C.S.R. Filterability Test, where the test solution is non-carbonated. Part II deals with their respective influence on the filtration behaviour of liquor carbonated in the laboratory under steady state conditions. The conclusions at the end of the paper attempt to compare and contrast the results of Parts I and II.

## Part I: Filterability of Raw Liquor

The test solution in the C.S.R. Filterability Test consists of a 60° Bx raw sugar solution at standard conditions of temperature and pH (20°C at pH = 9,0). The experimental investigation of the effect of amount of suspended matter, its particle size distribution and quantity of starch present, on the test, was performed also on a 60° Bx raw sugar solution. The main technique used to alter amounts of suspended matter and starch in the raw sugar solutions, was ultrafiltration,<sup>15 28</sup> as described in the following section.

**Experimental**

The particle size distribution of insoluble suspended matter in certain samples of very high pol (V.H.P.) raw sugars was determined by using Sartorius cellulose nitrate membrane filters. The technique utilises a pressure unit at 2,07 bar (30 lbs/in<sup>2</sup>) which pumps a measured volume of 60,0° Brix liquor at 25°C from a reservoir through a previously tared 142mm diameter membrane filter of selected pore size. The filter is supported in a stainless steel holder and the filtrate volume passed is noted. The suspended matter caught up on the filter is measured in mg/litre of solution passed after washing the filter with 5 l. of hot distilled water (70°C) to remove adhering sucrose. The dried filter is weighed under standard conditions.

The systematic removal of suspended matter was studied by using increasingly smaller filter sizes on one sample of recycled solution. The removal of starch by the filters was also studied by checking the starch analysis on each filtrate. To prevent particle build up on the external surface of the filter it was necessary to monitor the filtration rate accurately. Particle build-up, which leads to a subsequent decrease in the average pore or leakage diameter, is manifested by a noticeable drop in flow rate. Steps can thus be taken to ensure that particles removed under constant flow rate only, are measured.

The removal of starch was also studied by an alternative membrane filtration technique involving vacuum filtration (15mm Hg) through a 50mm diameter filter.

**Results**

With membrane filters it is possible to study particle distributions in the range 20 µm down to 0,45 µm. Particles above 20 µm are found in very small numbers in all V.H.P. sugars investigated and only a few low density particles are found in the 300-400 µm size range. In the experimental work, these particles were often ignored after it was shown that their influence on the filterability test was negligible. Statistically, the particle count best follows a log normal distribution; this type of distribution is common for particles produced by comminution.

An analysis of the log normal probability graphs of the four V.H.P. sugars examined, viz. TS, DL, SZ, AK, indicated that on average, the samples possess a geometric mean particle size diameter of approximately 0,6 µm, within the particle range measured, i.e. between 20 µm and 0,45 µm. Occasionally, when the particle count was low enough, it was possible to extend the range down to 0,20 µm. Normally the combined effect of partial filter blockage and high solution viscosity create very high flow resistance through the 0,20 µm filter.

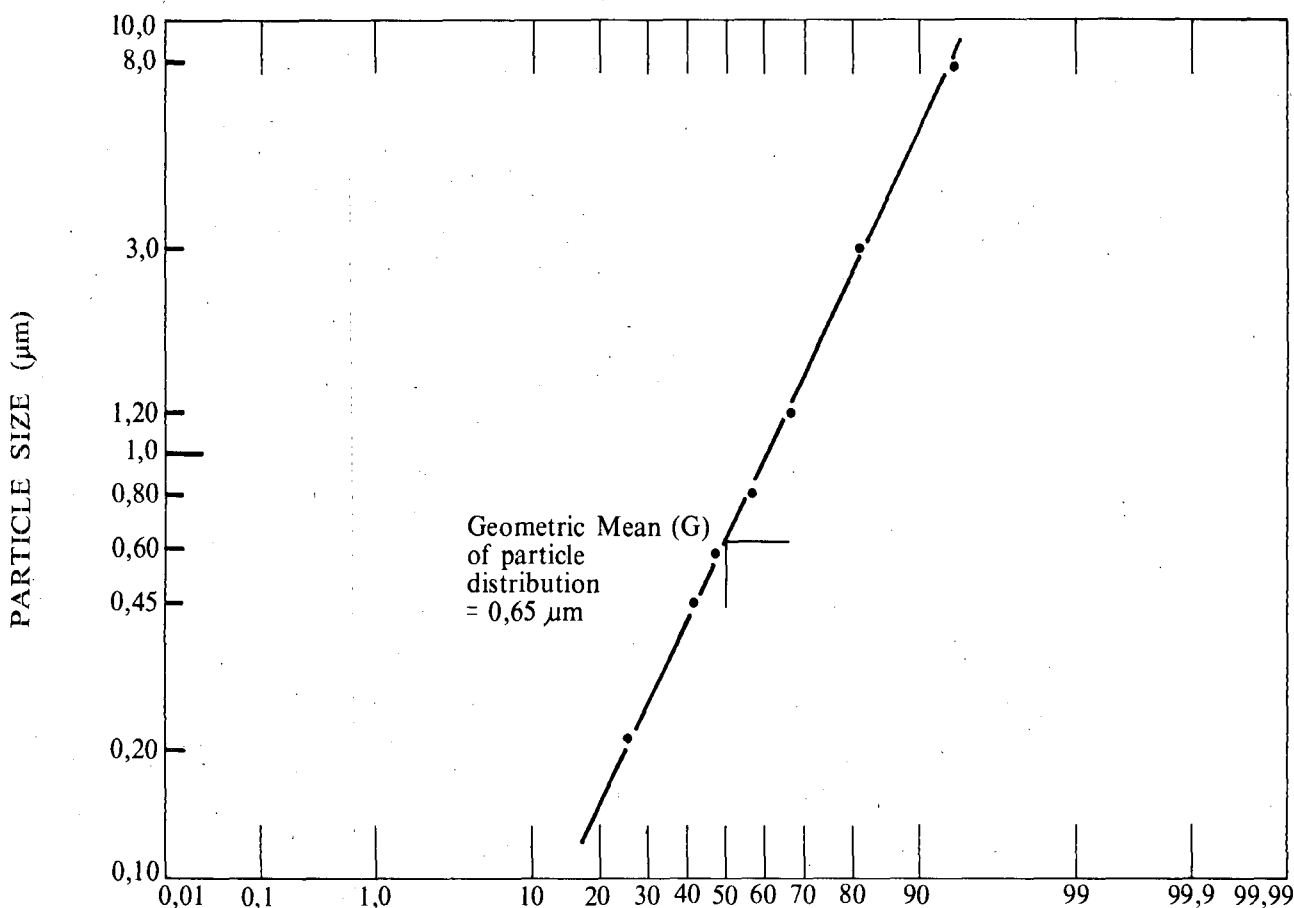


Figure 1. Log Normal probability graph : weight undersize distribution. Insoluble suspended particles in raw sugar size range, 0,20 µm to 20,0 µm. Sample : AK

In Fig. 1, a typical log normal probability graph is shown. From the straight line graph it is possible to calculate the geometric mean particle size diameter of the sample (AK) at  $0,65 \pm 0,05 \mu\text{m}$ . This figure compares favourably with that published by Tu<sup>30</sup> ( $0,8 \mu\text{m}$  for Hawaiian commercial sugars) using a light scattering technique and measuring over a slightly different size range.

Other figures for geometric mean particle size diameter are published in Table I. Considering the size range of particles measured, there is small variation in magnitude between the geometric mean of the four different samples.

The adsorption and retention of starch by the cellulose nitrate membrane filters was also studied concurrently with particle removal. The amount of starch retained by each filter was calculated by measuring the difference in magnitude between starch concentration in the liquor before and after filtration, for each membrane filter used in sequence. Table I contains the results of this investigation.

It is noted from the contents of Table I that starch removal by filtration does not become significant for any one sugar until a small filter size is reached. In fact, less than 20% of the starch in each case is removed by a filter corresponding in pore size to the geometric mean particle size diameter (e.g. AK starch retention averages 17% on a  $0,6 \mu\text{m}$  filter, whereas the

geometric mean particle size diameter =  $0,65 \pm 0,05 \mu\text{m}$ ).

If starch is not associated to any great extent with suspended particles of dimension greater than  $0,6 \mu\text{m}$ , these particles have, at least, a very important role in the laboratory filterability test. This was shown by examining the change in filterability with removal of suspended matter by ultra-filtration. The results of a typical investigation showing the relationship between the "increase in test filterability" gained by removing a certain amount of suspended matter with membrane filters of specific pore size and the "weight of matter removed", can be seen in Fig. 2.

Other V.H.P. sugars examined give a relationship of a nature similar to that shown in Fig. 2. In fact, for all the samples examined, it was possible to calculate an average correlation coefficient relating cumulative weight of suspended matter removed and increase in test filterability due to its removal, at 0,96. In the example in Fig. 2, it is of interest to note that removal of all suspended matter greater than  $0,45 \mu\text{m}$  in diameter results in an increase in test filterability of 24 units (out of a theoretically maximum possible of 52). However, at the same time only 10% of the total starch present is retained by the filters (allowing that the amylose : amylopectin ratio does not change significantly during filtration, thus introducing error in the starch analysis).

#### Filtering quality of raw sugar

TABLE I  
Starch Retention by Membrane Filters

Filter size Sartorius Membrane Filter	% Starch retained above filter size							
	TS		AK		SZ		DL	
	P	V	P	V	P	V	P	V
8 $\mu\text{m}$	0	0	5	3	0	0	0	0
3 $\mu\text{m}$	0	0	5	6	0	0	0	7
1,2 $\mu\text{m}$	0	0	10	8	5	3	9	7
0,8 $\mu\text{m}$	0	0	10	11	10	4	9	14
0,6 $\mu\text{m}$	2	10	15	19	19	15	25	16
0,45 $\mu\text{m}$	10	11	20	19	25	24	25	21
0,20 $\mu\text{m}$	25	18	37	43	34	39	45	37
original starch conc. i.e. 100% ( $\pm 10$ ppm)	132 ppm		94 ppm		114 ppm		84 ppm	
Insoluble Suspended Matter: Geom. Mean Particle Size ( $\pm 0,05 \mu\text{m}$ )	0,44 $\mu\text{m}$		0,65 $\mu\text{m}$		0,66 $\mu\text{m}$		0,70 $\mu\text{m}$	
Lab. Filt. Test %, of original VHP sugar ( $\pm 2,0$ )	55,0		62,0		55,0		53,0	

P = Pressure filtration 2,07 bar (30 lb/in<sup>2</sup>)

V = Vacuum filtration (15 mm Hg)

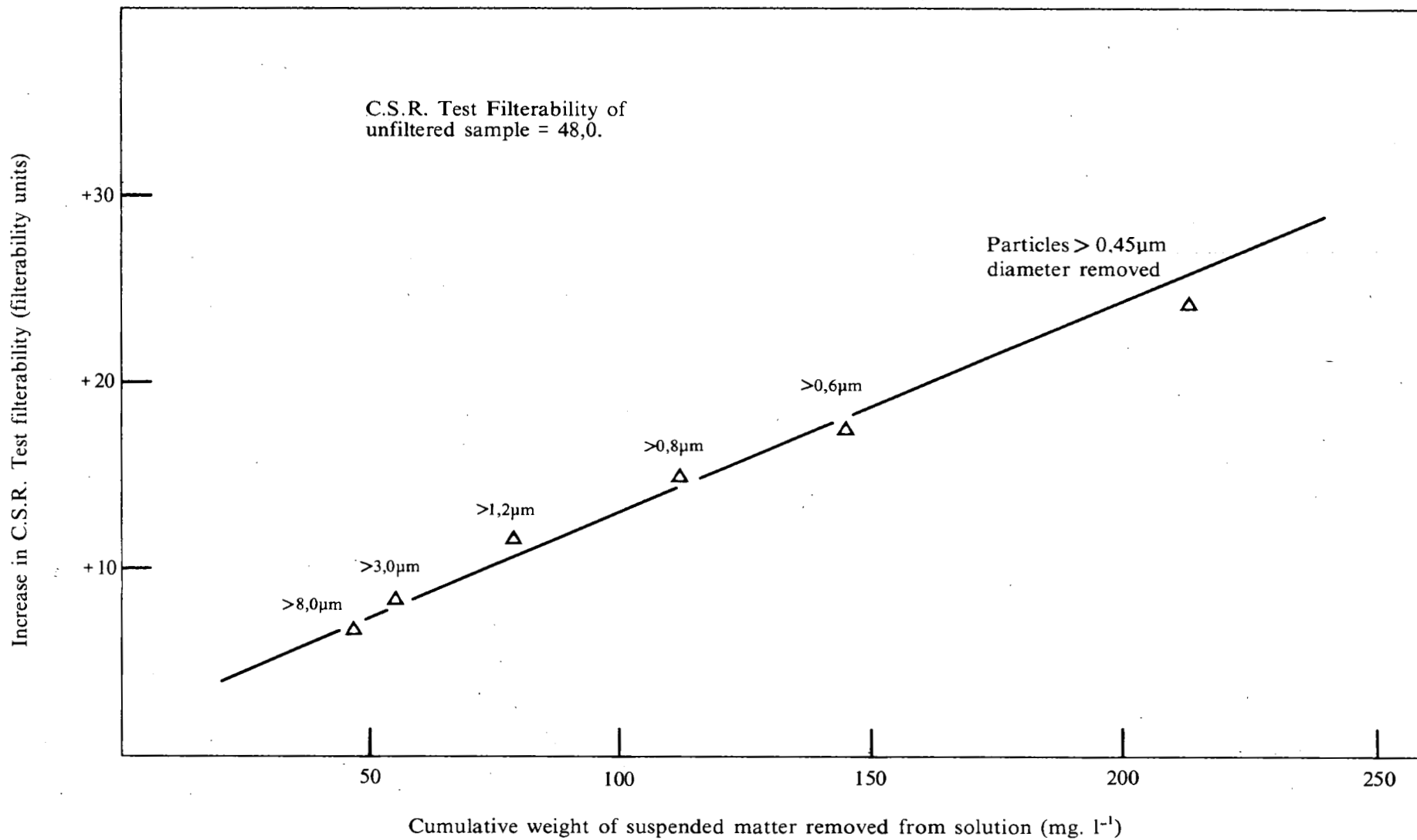


Figure 2. Relationship between increase in C.S.R. test filterability and cumulative weight of insoluble suspended matter removed from solution by ultrafiltration.

Sample : TS

Certain investigations elsewhere have given similar results. Tu<sup>32</sup> using a centrifugation technique has shown that a correlation coefficient of -0,96 exists for the total amount of suspended matter in solution and the laboratory test filterability. His results cover the differing amounts of suspended matter in a selection of commercial sugar of differing filterabilities, rather than a detailed examination of the suspended matter in each sugar. On a similar exercise, Yamane<sup>36</sup> produced a correlation coefficient of -0,92 (the filterability tests used in both instances differ somewhat in technique from the C.S.R. Filterability Test).

In this work we were not able to detect any critical particle size where filter efficiency would be at its lowest, even although this particle size does exist in theory for every particle distribution<sup>23</sup>. Rather, it would appear from our results that as far as the filterability test is concerned, the total weight of suspended matter is the most important factor. This work indicates that improvement in laboratory test filterability is associated with the removal from the sugar solution of insoluble suspended particles of a size greater than 0,5  $\mu\text{m}$  and that these particles themselves contain, or are associated with, very little of the starch content. This conclusion was further ratified by examining the 60° Brix filtrate resulting after the test filterability. The quantity of starch retained by the Celite filter aid during the test was determined by analysing the sample liquor before, and the filtrate after, the test. The results of this investigation are contained in Table II, below.

The results in Table II suggest that in sugars of average and above laboratory test filterability, the starch present in solution will pass through the filter bed unchanged and unhindered during the test.

It was actually possible to calculate the maximum amount of starch adsorption one would expect under filterability test conditions. At

pH = 9, i.e. the pH at which the test is performed, it has been shown that starch has a negative charge<sup>12 13</sup>. From streaming potential studies, it has also been shown<sup>2</sup> that under conditions of filtration, Celite filter aid, at pH = 9, acquires a negative charge (zero point of charge is at pH = 8,2<sup>26</sup>). This mutual charge repulsion means that starch is unlikely to be attracted strongly to the dicalite surface. In fact, one can calculate from adsorption data by Somasundaran<sup>27</sup> that in a raw sugar solution (pH = 9,0) containing 150 ppm of starch, only 6-7 ppm are likely to be absorbed by the dicalite surface during filtration. This adsorption figure is within the experimental error of starch analysis and probably accounts for the "trace" amounts of starch retained, in Table II. The calculation makes the reasonable assumption that the sucrose present will not interfere with the adsorption equilibrium.

Assuming that this amount of starch does adsorb, it is possible to calculate the likely increase in filter resistance due to a lowering of the dicalite bed streaming potential<sup>2 24</sup>. In fact, change in filter resistance is found by calculation to be negligible, as borne out by our test filterability experiments. It was also possible to predict by calculations from adsorption isotherm data<sup>27</sup> that starch concentrations of much greater magnitude would also have negligible effect on the testfilterability figure. This last point was examined experimentally. Samples of a high starch content Glendale sugar were prepared in which part of the starch content had been hydrolysed enzymatically. The results are in Fig. 3, (see overleaf)

The result of this experiment shows that there is no significant change in laboratory test filterability as the starch content of a raw sugar is varied experimentally between the limits 40-400ppm. This fact confirms the conclusion which has been drawn from the preceding experimental work, i.e. starch has minimal influence on laboratory test filterability.

#### Filtering Quality of raw sugar

TABLE II  
Starch Retention by Celite 505 Filter Aid

Sample	Laboratory Test Filterability %	Starch Conc. ppm		
		Filterability test solution before test (X)	Filterability test solution after test (Y)	Retained by Celite 505 Filter bed (X-Y)
AK	56,5±2,0	105±10ppm	100±10ppm	Trace
TS	48,0 "	158 "	155 "	Trace
SZ	52,0 "	110 "	100 "	Trace

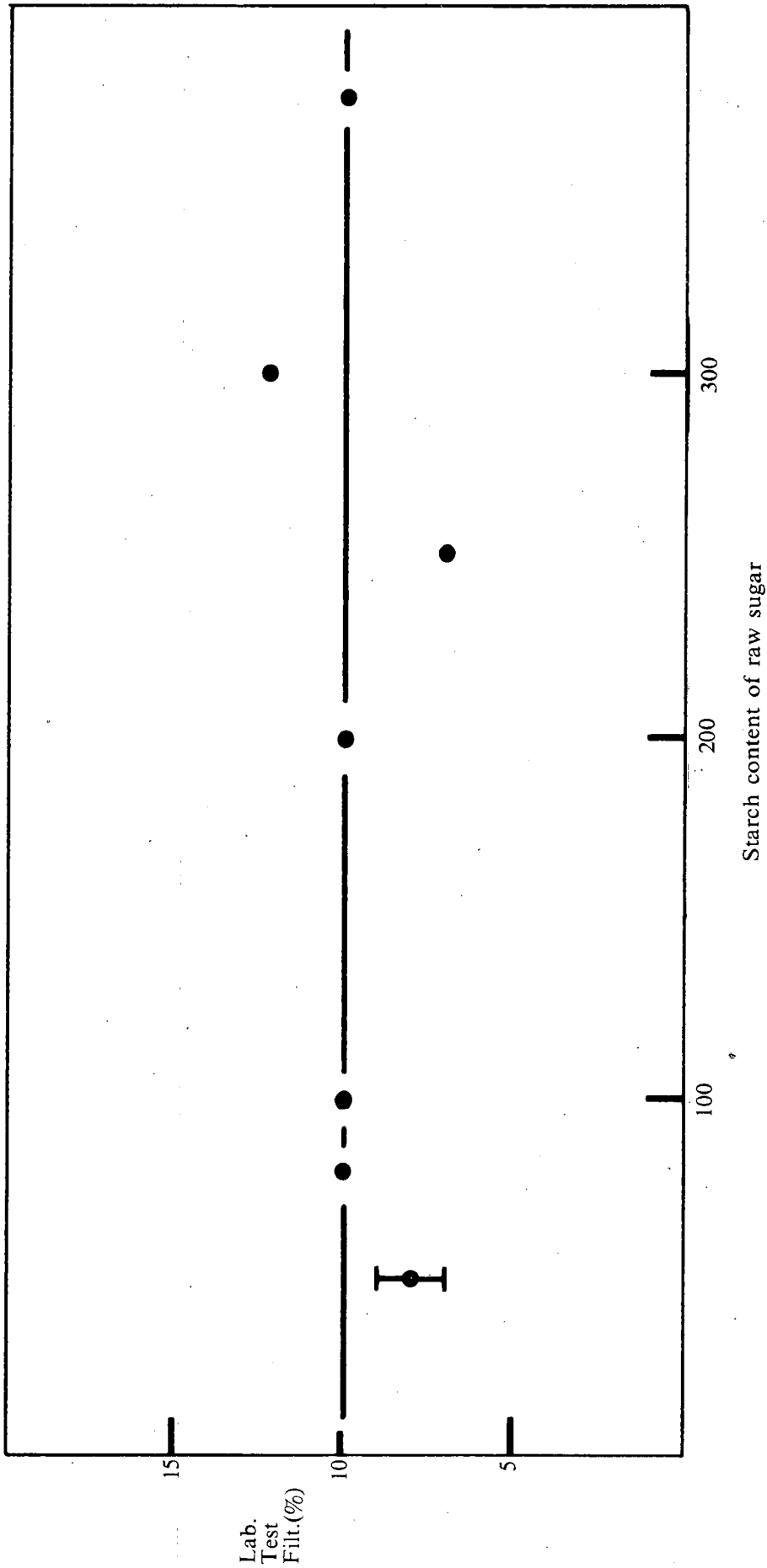


Figure 3. Relationship between laboratory test filterability and starch content of raw sugar. (A.A.M)

Sample : GD low pol.

## Part II : Filterability of Steady-State Carbonation Liquor

In order to maximise the influence of suspended insoluble matter and starch in the carbonation and filtration of laboratory carbonated liquor the choice of reaction conditions is important. It is necessary to ensure that minimum variation attends the carbonate crystal growth due to factors other than those two under scrutiny. Conditions for growth and precipitation of the carbonate crystal were thus standardised to ensure a steady-state environment during the reaction. The choice of conditions of pH, temperature, lime concentration and rate of CO<sub>2</sub>/air gas flow were mainly dictated by the necessity of creating a carbonate crystalline precipitate which would yield a constant, unvarying average specific filter resistance " $\alpha_c$ ", under filtration conditions. For example, a pH must be chosen which is far enough below the critical flocculation pH of CaCO<sub>3</sub> (pH = 10,1), such that  $\alpha_c$  does not vary. Similarly, it is also necessary to choose a suitable "% CaO on solids" which again gives a constant  $\alpha_c$ . The choice of reaction conditions of pH = 8,5 and lime addition of "1% CaO on solids" ensures that the calcium carbonate crystals formed are fully "gassed-out".

### Experimental

#### (i) Apparatus

The apparatus which was set up to create and maintain the chosen conditions of steady state carbonation is shown schematically in Fig. 4. The basic reactor consists of a 15cm diameter cylindrical vessel (a) with a No. 4 sinter glass base (b) through which a 10% CO<sub>2</sub>/air mixture flows at a constantly monitored rate, measured by flow meter (c). This whole assembly is immersed in a thermostat bath (d) and the contents of the reaction vessel, which consist of 1,5 litres of a 60,0° Brix solution (e) of the sugar under study, are held at 80,0°C under reaction conditions. The milk-of-lime solution (S.G. = 1,039) is sufficiently dilute to compensate for loss of water by the reaction mixture at 80°C, during the reaction time of 90 mins  $\pm$  3 mins. It is held in slurry form by gentle stirring in the lime tank (f) and it is introduced into the reaction vessel through a small tap, the tube of which has been shortened to minimise sedimentation of the lime particles. The lime slurry drops onto a slowly rotating impeller blade (g) which is positioned some 3 cm above the reaction solution. This blade serves the dual purpose of adequately dispersing the lime onto the surface of the liquor and of breaking up foam which may form during the reaction and create a nuisance. No mechanical stirring of the solution is necessary since the turbulence created by the gas flow suffices.

Control of pH is manual. Gas flow and lime addition may be regulated by hand to keep the pH within  $\pm$  0,05 unit limit of 8,5. The high temperature Ag-AgCl Beckman electrode system (h) was found to have high stability over the whole course of the reaction. An accurate thermometer (i) which

monitors the internal reactor temperature completes the apparatus, (for fig. 4, see overleaf).

#### (ii) Reaction procedure

The carbonation reaction is initiated by raising the pH of the 60,0° Bx reaction liquor at 80°C (typically pH = 6,3 for a V.H.P. sugar) by lime addition, to pH = 8,5. This addition takes place at a carefully controlled rate over a 5,0 min. period. Sufficient nucleation of calcium carbonate is created by this procedure to produce seed crystals enough for the whole reaction. These crystals are now grown under the steady-state conditions of pH = 8,5 at 80°C with a gas flow averaging 850 ml/min of a 10% CO<sub>2</sub>/air mixture. Lime addition continues at a measured rate until the prescribed volume of 150ml has been added. Occasionally, the evaporation of water from the reaction surface becomes excessive and the brix must be re-adjusted to 60,0 by the addition of a small quantity of distilled water at approximately 80°C. Also, on occasion, the gas flow may require adjusting during the reaction, to ensure that the reaction time limits are not exceeded. This requirement occurs particularly in the case of high starch sugars. At the end of the reaction, the pH is dropped to 8,0 at which pH the liquor is filtered.

#### (iii) Influence of suspended matter

The effect which suspended matter has on the carbonation reaction and subsequent filtration of the reaction mixture was studied by altering the amount of matter in the 60° Bx solution before the reaction. Particles of various sizes were systematically removed from the sugar solution by using membrane filters as described in Part I, Experimental. The filtered liquor was introduced into the reaction vessel in the normal experimental volume of 1,5 litres.

#### (iv) Influence of starch

The starch content of the raw liquor was increased by addition of potato starch (AR grade). This starch has an amylose : amylopectin ratio of 20 : 80, which is almost identical to that of the sugar sample (TS) which formed the bulk of this study. A weighed amount of starch necessary to increase the total concentration of starch in the 60° Brix reaction liquor to a desired value, for example 300ppm on brix, was mixed with the required amount of distilled water and autoclaved at 1,38 bar ( $\approx$  20 lb/in<sup>2</sup>) for ten minutes. This ensures complete dissolution of the starch. The resultant solution is used to dissolve the raw sugar sample to the required concentration of 60,0° Bx. This solution is now ready for use in the carbonation reactor. For reaction runs which demanded a concentration of starch in solution less than that already present in the raw sugar in its original state, starch was hydrolysed by enzymatic destruction. This process was best accomplished at 30° Bx with a retention time of 1 hour at 76°C with a suitable quantity of enzyme. The liquor was then concentrated under vacuum to 60° Bx for use in the reactor. Starch analyses were performed colorimetrically by a standardised method<sup>19</sup>.

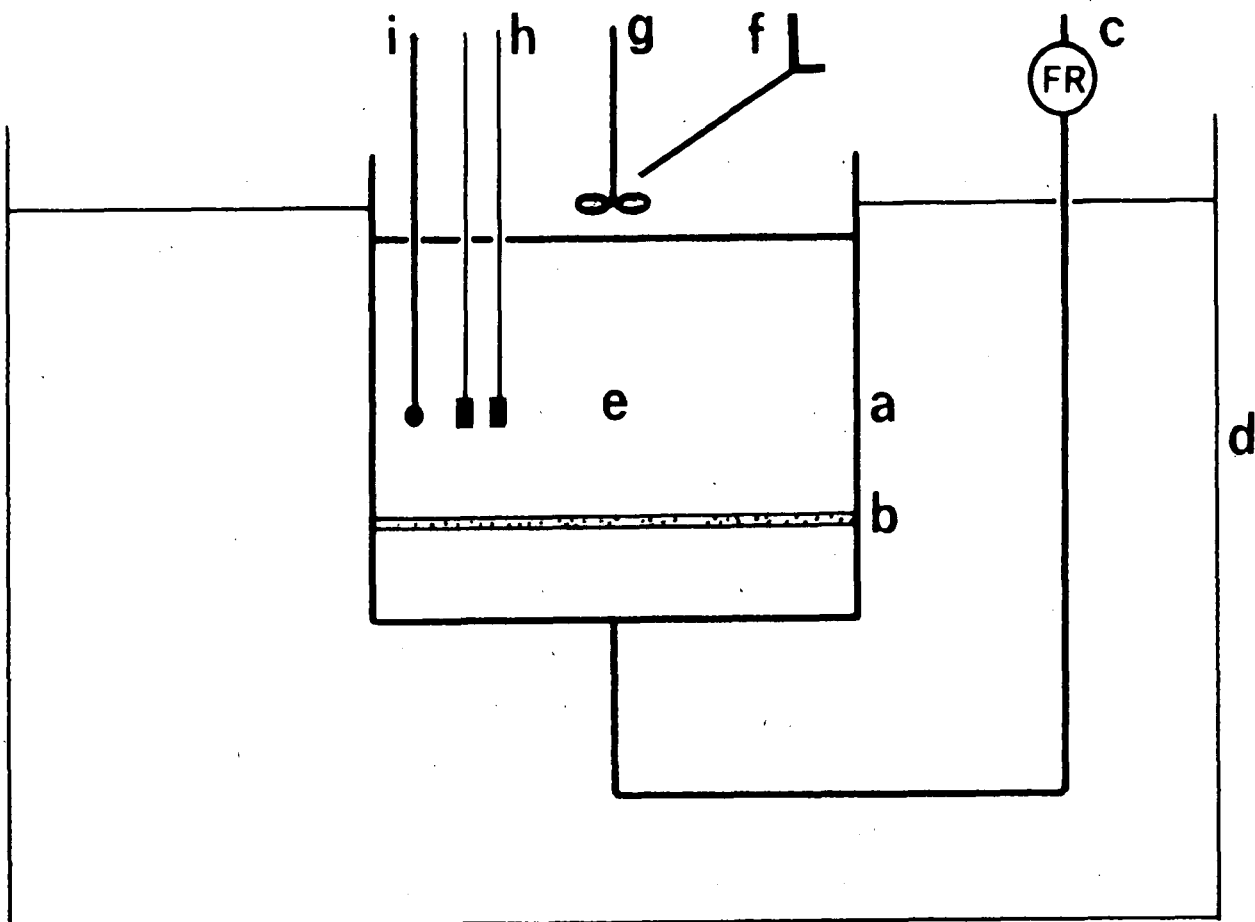


Figure 4. Schematic Diagram of Carbonatation Apparatus.

- |                        |                           |
|------------------------|---------------------------|
| (a) reactor vessel     | (f) lime tank             |
| (b) No. 4 glass sinter | (g) foam impeller blade   |
| (c) flow meter         | (h) pH electrodes         |
| (d) thermostat bath    | (i) thermometer (+0,1C°). |
| (e) reaction solution  |                           |

*(v) Filtration*

The filtration apparatus consists of a conventional cylindrical pressure unit, fitted with an enclosing water jacket. The unit is maintained during the filtration procedure at 80,0°C by circulating water through the jacket. On completion of the carbonatation reaction a charge of liquor (200ml) of pH = 8 is pumped out of the carbonatation reactor and into the filtration unit which is fitted with a 5,5cm No. 42 Whatman filter paper. Immediately a stirrer with a polythene impeller is inserted into the filtration unit and filtration time  $t = 0$  is taken the moment this stirrer is switched on. Stirring is necessary at this stage to ensure that the filter cake forms in a uniform layer when pressure is applied. After 4,0 minutes, the stirring ceases and in the next 1,0 minute the liquor is allowed to settle during which time the pressure head is fitted to the unit. A 250ml measuring cylinder is positioned underneath the unit such that it can collect the filtrate from the outlet. On the time mark  $t = 5,0$  mins., pressure is applied at a constant rate of 0,345 bar per 6 secs. ( $\cong 5$  lb/in<sup>2</sup> per 6 secs), such that at the end of 1 min., i.e. when  $t = 6,0$  mins the pressure is 3,45 bar ( $\cong 50$  lb/in<sup>2</sup>). The filtrate volume is timed on 10ml volume increments and the results are tabulated.

*Calculation of filtration rates*

The method used to measure the filtration rate of the carbonatated liquor was based on calculating the incremental rise in filter cake resistance with time.

The equation governing the relationship between filtration rate and the specific filter resistance of an incompressible filter cake may be expressed in the form <sup>14</sup>

$$\frac{d\theta}{dV} = \frac{\alpha_c \eta M V}{A^2 P} + \frac{\alpha_s \eta}{AP} \quad \dots (1)$$

where  $\frac{d\theta}{dV}$  = reciprocal filtration rate

$\alpha_c$  = average specific filter cake resistance

$\alpha_s$  = average specific septum resistance

$\eta$  = solution viscosity (taken as  $\cong 60,0^\circ$

Bx pure sucrose solution)

M = mass of cake-forming solids

V = cumulative volume of filtrate

P = applied pressure

A = filter cake area

In order to express the reciprocal rate in terms of a filterability index, it is necessary to relate the factors on the right hand side of Eq. (1) to the

filter throughput. This has been simplified by Bennett<sup>4</sup> who defines sugar throughput as "Q" and shows that on integrating Eq. (1), that

$$Q^2 = \frac{k}{\alpha_c M} \quad \dots (2)$$

Now, the average specific filter resistance,  $\alpha_c$ , is a measure of the resistance to flow across the filter cake and the conc. of the solid phase, M, in the unfiltered liquor can be taken as equal to the concentration of calcium carbonate crystals.

i.e.  $\alpha_c M$  = total resistance to flow/unit vol. filtrate

The reciprocal of this expression measures the ease of flow of liquid through the filter cake and it has been termed the filterability, "F"<sup>4</sup>.

$$\text{i.e. } F = \frac{1}{\alpha_c M} \quad \dots (3)$$

Substituting this expression of Eq. (2), it can be shown that

$$F \propto Q^2 \quad \dots (4)$$

It is obviously more convenient to express this as

$$\sqrt{F} \propto Q \quad \dots (5)$$

$\sqrt{F}$ , which gives a measure of the filter throughput, is termed the "index of filterability"<sup>6</sup>.

In order to calculate F, and subsequently  $\sqrt{F}$ , it is necessary to substitute Eq. (3) in the general rate relationship, Eq. (1).

$$\text{i.e. } \frac{d\theta}{dV} = \frac{\eta}{F A^2 p} V + k'$$

A plot of  $\frac{d\theta}{dV}$  against V, should give a straight line graph where

$$\text{the slope "m"} = \frac{\eta}{F A^2 p}$$

In our whole series of experiments  $\eta$ , A and P were kept constant.

$$\text{i.e. } F = \frac{0,995 \times 10^{-12}}{m} \text{ c.g.s. units}$$

where "m" = slope of graph of  $\frac{d\theta}{dV}$  against V

This expression was used to calculate values of F, and hence  $\sqrt{F}$ .

It is convenient to express this index of carbonatation filterability,  $\sqrt{F}$ , as a percentage of that of refined sugar. The filtration rate of a sample of double washed refined sugar (first boiling), containing negligible amounts of starch and insoluble matter was measured by the standard procedure, as described. A figure of  $9,5 \times 10^{-5}$  cm was produced and this was taken as 100% carbonatation filterability.

All other filterabilities are relative to this figure and are designated "f<sub>c</sub>", i.e. carbonatation filterability per cent.

$$\text{where } f_c = \frac{\sqrt{F}}{9,5 \times 10^{-5}} \times 100\% \quad \dots (6)$$

$$\text{from (3) } f_c = \frac{\left(\frac{0,995 \times 10^{-12}}{m}\right)^{1/2}}{9,5 \times 10^{-5}} \times 100\%$$

$$\text{i.e. } f_c = \frac{1,05}{m^{1/2}} \quad \dots (7)$$

It is thus possible to calculate the value of the carbonatation filterability, "f<sub>c</sub>", of a sample of carbonatated liquor, by measuring the slope, "m", of the graph  $\frac{d\theta}{dV}$  against V, and substituting this value in Eq. (7).

**Results**

The results in this section refer to a complete investigation of the influence of starch and insoluble suspended matter on one V.H.P. sugar. The general conclusions which have been drawn from this one set of data have been checked against data from other South African V.H.P. sugars and found to be wholly representative.

*(i) Influence of insoluble suspended matter on "f<sub>c</sub>"*

The determination of the carbonatation filterability per cent, f<sub>c</sub>, begins by determining the slope, m, of the  $\frac{d\theta}{dV}$  against V graph. Typical filtration data appear in Table III.

This data refers to the standard V.H.P. sugar where all insoluble particles greater than 3,0 μm are removed by ultrafiltration before the liquor is carbonatated. A note is taken of the starch concentration before and after carbonatation.

This procedure is completed in turn for all the TS samples which have been processed by ultrafiltration before the liquor is carbonatated. Fig. 5 shows a selection of this data drawn graphically.

From Fig. 5, it can be seen that as more and more suspended matter is removed by each filter in turn, the value of the slope "m" decreases. As "m" decreases, the value of "f<sub>c</sub>" must increase, i.e. the filtration quality of the carbonatated liquor increases.

Substituting values of "m" from Fig. 5, in Eq. (7) it is possible to calculate the carbonatation filterability, f<sub>c</sub>, for each line on the graph. The values gained in this way are shown in Table IV.

The results in Table IV indicate that removal of suspended matter down to 0,2 μm in diameter from the raw liquor does have a considerable effect on the subsequent filtering quality of the liquor when carbonatated. The actual amounts of suspended matter removed by each membrane filter was measured by the technique described in Part I, Experimental. The relationship between

*Filtering quality of raw sugar*

**TABLE III**  
**Carbonatation : Experimental Data**

Run A32	:TS (Feb. sample)
Conditions	:All particles >3,0 μm removed by ultrafiltration
Reaction solution	:1,5 l., 60° Bx at 80°C
Gas flow	:Average 850ml/min., 10% CO <sub>2</sub> air mixture
Residence time	:92 minutes
Starch in liquor	:105ppm after ultrafiltration
Filt.pressure	:50 lbs/sq.in (3,45 bar)

Filtrate Vol (ml)	time(θ) (min.sec.)	Δθ (secs)	Δθ / ΔV (secs.ml <sup>-1</sup> )	V plotted (ml)
ΔV=10ml	40	6.15		
	50	6.32	17	1,7
	60	6.52	20	2,0
	70	7.14	22	2,2
	80	7.40	26	2,6
	90	8.8	28	2,8
	100	8.40	32	3,2
	110	9.14	34	3,4
	120	9.50	36	3,6
	130	10.31	41	4,1
	140	11.13	42	4,2
	150	11.58	47	4,5
	160	12.46	46	4,8
	170	13.40	54	5,4

Starch in filtrate : 60 ppm

*Filtering quality of raw sugar*

**TABLE IV**  
**Carbonatation filterability of membrane filtered sugar**

Sample	Ultrafiltration Treatment	√F x 10 <sup>-5</sup> cm	Carbonatation Filterability (f <sub>c</sub> )
TS	All particles > 40 μm removed	3,91	41,0±1,0%
	All particles > 20 μm removed	4,03	42,5 "
	All particles > 3 μm removed	4,46	47,0 "
	All particles >0,8 μm removed	4,70	49,5 "
	All particles >0,45μm removed	5,40	57,0 "
	All particles >0,20μm removed	5,75	60,5 "

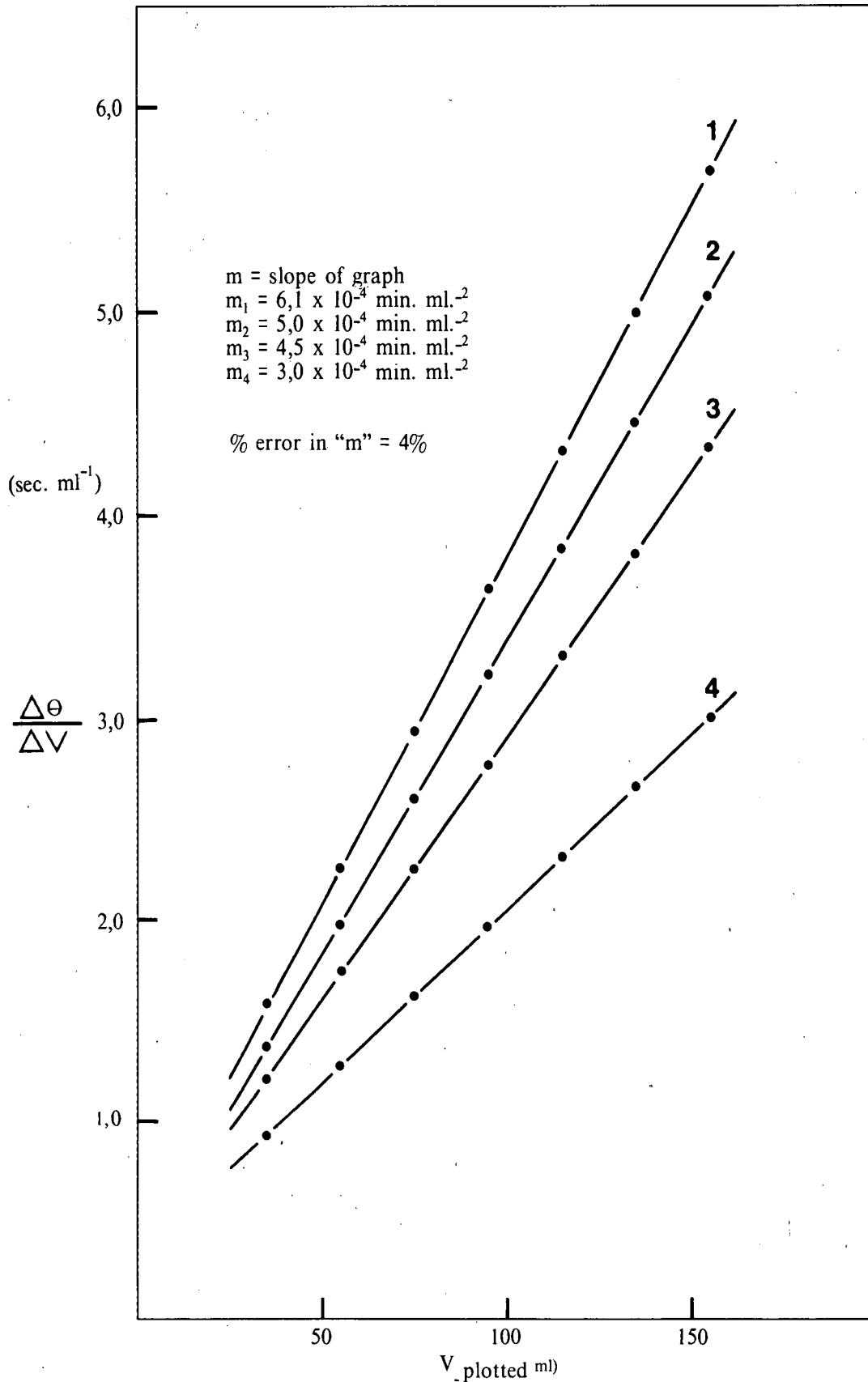


Figure 5. Determination of "m" from plot of carbonatated liquor filtration data.

1. TS, unfiltered sample
2. TS, all particles  $> 3,0 \mu\text{m}$  removed
3. TS, all particles  $> 0,80 \mu\text{m}$  removed
4. TS, all particles  $> 0,20 \mu\text{m}$  removed

total weight of suspended matter removed and subsequent improvement in carbonatation filterability, due to this removal, was investigated. The results are shown in Fig. 6, opposite

In Fig. 6, the correlation coefficient between "increase in carbonatation filterability" and "cumulative weight of particles removed" is calculated as  $r = 0,96$ . However, membrane filtration tends to remove a certain amount of starch, especially when filters with very small pore sizes are used. Starch is removed by the 0,45  $\mu\text{m}$  and 0,20  $\mu\text{m}$  filters and these raw sugar liquors before carbonatation have a starch concentration which has dropped from 120ppm to 105ppm and 85ppm respectively. As will be shown later, 15-25ppm of starch can have a small but measurable effect on the carbonatation filterability. When the 0,45  $\mu\text{m}$  and 0,20  $\mu\text{m}$  points in Fig. 6 are "corrected" for starch influence, the correlation coefficient rises to 0,98.

#### (ii) Influence of starch on " $f_c$ "

The effect which starch has on the carbonatation filterability of the standard sample of V.H.P. sugar was studied by adding various amounts of potato starch to the sugar, to give starch concentrations of 150, 200, 250... 550ppm total starch. Carbonatation of these samples was performed under the standard conditions set and the filtration characteristics of the resultant liquors were investigated. At a starch concentration of 120ppm in raw sugar solution, the carbonatation process removed only 50% of the starch present. However, at the 500ppm level, the amount of starch removed had risen progressively to 80%, i.e. 400 ppm went into the filter cake. For a study of samples with less starch than the original concentration, it was necessary to reduce the starch count enzymatically, as described. To calculate " $m$ " values, the graphs of  $\frac{d\theta}{dV}$  against  $V$  were plotted, as in Fig. 7. (see p14)

Fig. 7 shows that for starch concentrations of 300ppm or less the straight line plots indicate that the filter cake is behaving according to the tenets of Eq. (1). However, at starch concentrations of the order of 500ppm, Eq. (1) no longer holds since the cake has lost its incompressibility due to its high starch content and " $m$ " is no longer constant but increases with time. The influence of starch concentration on " $f_c$ " can be seen clearly by plotting "total starch conc." against values of " $f_c$ " as in Fig. 8. (see p15)

Between starch concentrations of 85ppm and 300ppm, there is good correlation between the total starch present in the raw sugar and the " $f_c$ " value (corr. coefficient = -0,98). The very pronounced effect of starch in this region can be illustrated by comparing the " $f_c$ " values at the 125ppm and 275ppm levels in Fig. 8. The value of the carbonatation filterability has dropped from 38,0 to 18,5, i.e. effectively, the filter throughput/unit time has decreased by more than 50% of its former value. Moreover, the sample with 275ppm of starch will tend to blind the filter much more

quickly than the lower starch sample due to a faster increase of " $m$ " with time, as discussed before with reference to Fig. 7.

The correlation coefficient between total starch and " $f_c$ " value over the total starch concentration range studied i.e. 85ppm to 500ppm, is -0,93. The drop in correlation coefficient from -0,98 to -0,93 is due to the value of " $f_c$ " corresponding to the 500ppm starch conc. level in Fig. 8 being higher than expected. However, the value " $f_c$ " = 18,5 represents only the filtration rate at time " $t$ "  $\rightarrow 0$ , since it was derived from the tangential value of " $m$ " at " $t$ " = 0. As time " $t$ " increases, " $m$ " also increases (e.g. in Fig. 7  $m_{4b} > m_{4a}$ ) and hence " $f_c$ " decreases. In fact, after 30 minutes filtration time, " $f_c$ " has dropped from 18,5 to 15,0, and after 45 minutes to 14,0. (When  $f_c = 14,0$ , corr. coefficient rises from -0,93 to -0,95).

#### (iii) Relative influence of starch and suspended matter on " $f_c$ "

It is interesting to compare the relative effectiveness of an incremental decrease in starch or suspended matter content, on the value of " $f_c$ ". In order to increase the value of " $f_c$ " by 10 units (i.e. from 41,0 to 51,0 or from 0 to 10 on the  $\Delta f_c$  axis on Fig. 6) it is necessary to remove from solution by ultrafiltration, prior to carbonatation, a certain weight of suspended matter, calculated from Fig. 6, as 140 mg.l<sup>-1</sup>. In essence this means having to remove from solution all particles greater than 0,70 $\mu\text{m}$  ( $\pm 0,05 \mu\text{m}$ ). Even on a laboratory scale this process proves time-consuming and troublesome. However, from Fig. 8, it is seen that the same effect (i.e. increase in " $f_c$ " of 10 units) may be achieved by merely lowering the starch content from e.g. 200ppm to 130ppm.

From such considerations it is obvious that as far as the filtering quality of carbonatation liquor is concerned, the starch content of the original raw sugar, from which the liquor is derived is far more influential than the suspended matter content. This conclusion is in direct conflict with the findings of the laboratory filterability test. Starch influence was found to be inconsequential but suspended matter content the major factor of importance.

#### (iv) Carbonate crystallisation and starch

It is obvious from these results that the mechanistic influence which starch exerts in steady-state carbonatation is of fundamental importance. Within the range, 100-300ppm, starch concentration, the initial interference is probably with carbonate nucleation, resulting in variation in particle size and shape. Evidence has been proposed for this elsewhere<sup>5, 34</sup>. However, at high starch concentrations viz. 500ppm, there is perhaps an added surface chemistry effect which may account for the compressibility factor inherent in high starch cake behaviour.

Of the two main components of starch, branched-chain amylopectin is a more "compact" molecule than straight-chain amylose and should

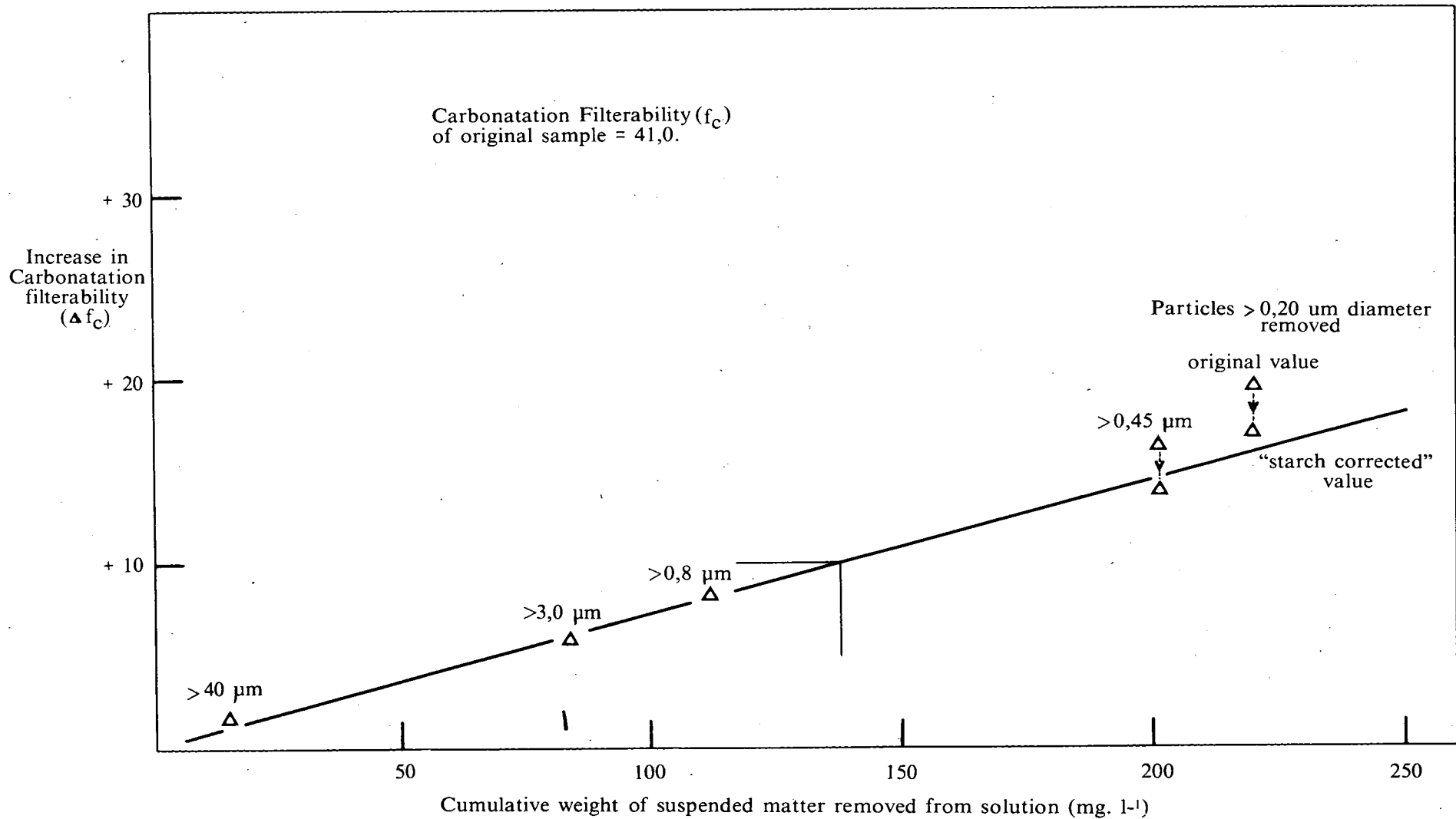


Figure 6. Relationship increase in carbonatation filterability and cumulative weight of insoluble suspended matter removed from solution by ultrafiltration.

Sample = TS.

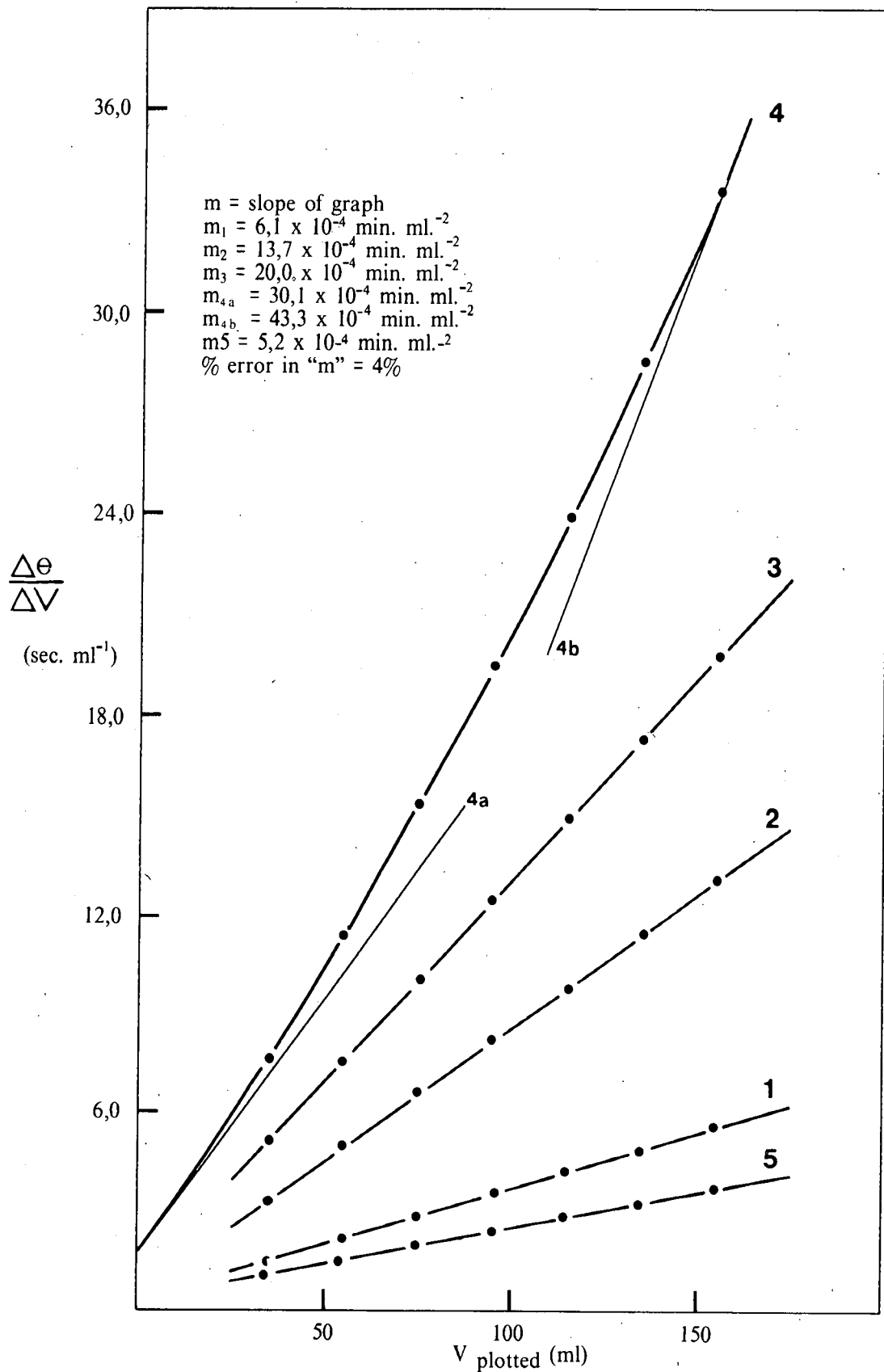


Figure 7. Determination of "m" from plot of carbonated liquor filtration data.

1. TS, original starch, 120 ppm,
2. TS, starch added, total 180 ppm,
3. TS, starch added, total 235 ppm,
4. TS, starch added, total 500 ppm,
5. TS, starch reduced to 85 ppm.

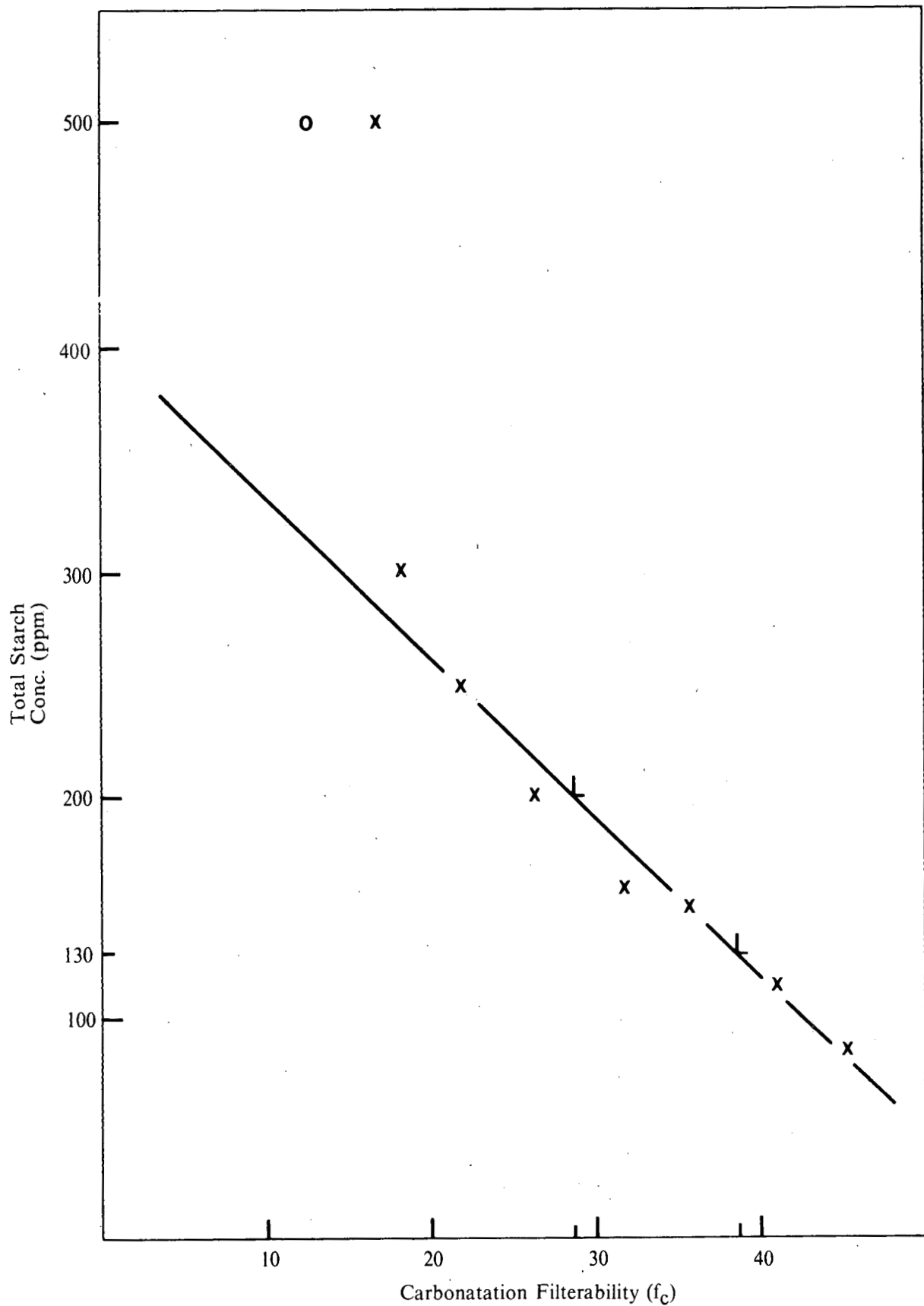


Figure 8. Relationship between total starch content of raw sugar and carbonatation filterability, ( $O - f_c$  at 500 ppm starch, when "m" is calculated at time "t" + 45 mins)

Sample = TS

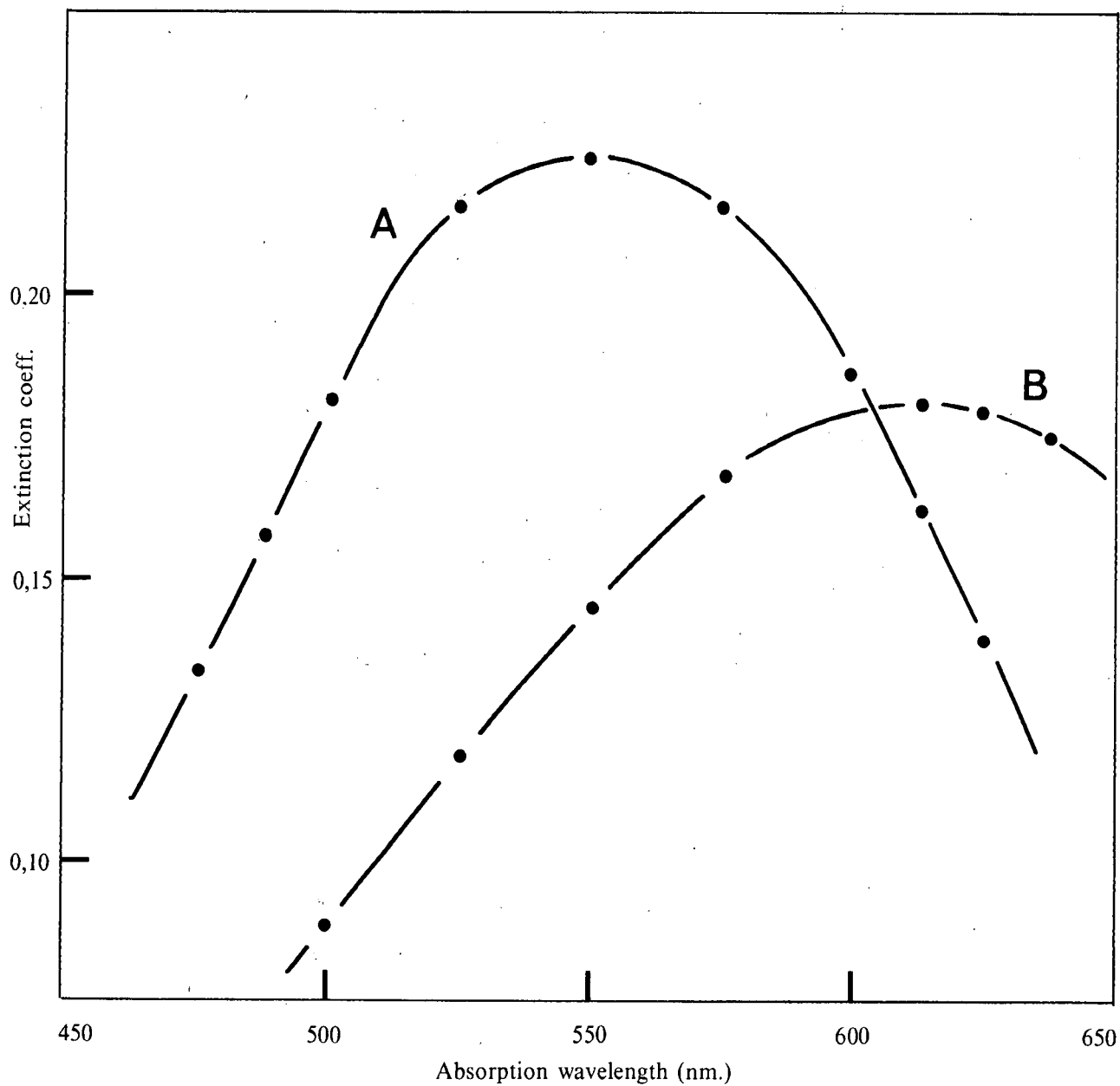


Figure 9. Absorption spectra of the iodine complex of starch derived from carbonate crystal.

A = Starch from  $\text{CaCO}_3$  Crystal interior — very high amylopectin content.  
 B = Starch from  $\text{CaCO}_3$  Crystal surface — very high amylose content.

Sample = TS.

possess a higher charge density. Thus amylopectin would be more likely to be taken up in the crystallisation process either by acting as charged nuclei or by chemisorption onto the growing crystal face. Amylose, on the other hand, with a much lower charge density would be more likely to adsorb onto the outer surfaces of the carbonate crystal and be held by much weaker physical forces. In this position it may influence the surface characteristics of the crystal<sup>18 33</sup>

In fact, the distribution of starch in the cake was examined experimentally. By boiling the cake in water it was possible to desorb starch from the outer surfaces of the carbonate crystal, showing that the binding forces must have been rather weak. The absorption maximum (at  $\lambda = 620$  nm) of the starch-iodine complex formed from this solution indicated that the starch was largely composed of amylose (max. absorption pure amylose,  $\lambda = 625$ nm)<sup>16</sup>. It was possible to release the starch held within the crystal matrix only by dissolving the carbonate lattice with dilute hydrochloric acid at 4,0°C. On forming the iodine complex after neutralisation, this starch component was found to be almost pure amylopectin (absorption max.  $\lambda = 550$ nm; absorption max for pure potato starch amylopectin,  $\lambda = 550$ nm)<sup>16</sup>. The absorption spectra are shown in Fig. 9, opposite

### Conclusions

The most interesting points, which have arisen in the results of Parts I and II, with reference to starch and insoluble suspended matter, have been those which have highlighted the essential differences in behaviour between carbonated and non-carbonated liquor during filtration. The results from Part I indicate clearly that a filterability test, which relies in principle on a filtration rate measurement of a raw sugar solution, will provide at best an estimation of the amount of suspended matter in solution. This estimation, if required, could perhaps be achieved much more easily using a turbidity meter.

The influence of starch on the laboratory test filterability has been shown to be insignificant. Under the conditions of the test, starch does not, in fact, cannot create any adverse filtration effect (except that which may arise from a small increase in viscosity) because of its inability to adsorb onto the filter aid so causing changes in filter resistance and cake streaming potential.

In steady-state carbonation, insoluble suspended matter does have an influence on the filtration rate, as evidenced by the high correlation coefficient. However, unless the quantity present exceeds inordinate proportion the effect on filtration performance is bound to be small. Starch, however, according to the results of Part II is of no inconsiderable consequence to the filtration performance of steady-state carbonated liquor. At moderate levels (150ppm) its effect is already significant; at higher levels (500 ppm) the effect is very pronounced. With reference to high-starch carbonation filter cake, a preliminary examination of the mechanistic influence of starch has shown that the distribution of amylose and amylopectin within the carbonate

crystal matrix, may be of considerable importance to the physical properties of the filter cake.

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