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IMPURITY TRANSFER DURING A-MASSECUITE BOILING

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Abstract

The transfer of impurities, particularly colour, from mother liquor to crystal was investigated on a pilot-plant scale by boiling syrup samples from four selected factories at regular intervals throught the season. Since all the boiling conditions were kept constant, changes in the crystal quality were caused only by changes in the syrup itself. Crystal quality was found to be strongly affected by seasonal factors and by cane quality.

Introduction

Although crystallisation is a powerful purification process, impurities can still be found in crystals. Three mechanisms have been proposed[1] to explain the presence of impurities in the sucrose crystal. These mechanisms are absorption, inclusion and co-crystallisation.

Many authors[2, 3, 4] show that the distribution of an impurity between the crystalline solid and the interfacial liquid from which it grows cannot be described in terms of usual phase diagrams. There are kinetic processes taking place at the interface resulting in changes in concentrations and other properties of the interfacial medium. Powers[4] for example stresses that the molecular properties at the crystal/massecuite interface must be considered. Thus, the process cannot be treated only as a simple entrapment of mother liquor into the crystal.

Attempts have been made[4] to classify liquid inclusions according to their appearances. It was found that most of them fell into one of three groups, viz. random unsymmetric positions, hour glass shapes and small veil-like shapes. These liquid inclusions are believed to be caused by etch pits, which are formed during periods of subsaturation and are then overgrown, thus sealing in interfacial liquid when growth starts again. This mechanism could be expected to produce the random type of inclusion although the more regular type could also result from the possiblity of heating to local subsaturation as the massecuite traverses the heating surface of the pan, followed by a rapid increase in concentration to substantial supersaturation as the material rises to the surface, the process being then repeated. Powers[4] notes that the composition of the included material will not be the same as that of the mother liquor because of the interfacial kinetic processes mentioned earlier.

The effect of operational factors on the introduction of impurities into the sucrose crystal have been investigated by many workers[5-9]. Work in England[5] and Italy[6] has shown that, although the same basic mechanism may be responsible for the presence of impurities in the sucrose crystal, there have been indications that important differences exist between cane and beet sugars and between white and raw sugars. This must therefore be considered when published data are reviewed. It should also be noted that it is often difficult or even impossible to change one variable without affecting many others. Temperature is an obvious example as it affects viscosity, supersaturation and other factors.

Moritsugu[7] shows that, other conditions being the same, stirring increases the crystallisation rate without increasing the entrapment of impurities.

Mantovani[8] stresses the importance of the physical characteristics of the solution. Viscous solution for example enchances droplet capture.

Australian workers[9] note that dissolution followed by regrowth results in fluid inclusions and that as the dissolution rate increases, so does the rate of inclusion. This agrees well with the observations of Powers.

Growth rate is generally recognised[6, 8, 9] as being one of the more important factors as far as the introduction of impurities in crystals is concerned. Different crystal faces will show inclusions depending on their growth rates, with fast growing faces showing more inclusions.

Work based on white beet sugar has shown[1] that the amount of impurities trapped by the crystal increases with crystal size. Moritsugu and Payne[7] and Guo and White[10] reached a similar conclusion with cane sugar crystals.

It is evident from this very brief review of the literature that the amount of impurity trapped into the sucrose crystal will be controlled by two main factors. The first is the quality of the feed material from which the crystals are made while the second is an operational factor consisting of the conditions (eg temperature, crystallistaion rate, stirring) under which crystallisation takes place. It is therefore evident that an investigation into the transfer of impurities during A-boilings should consist of two main parts. This paper deals with the first factor, namely the effect of the syrup quality.

Experimental procedure

Objectives

The main objective of this investigation was to study the effect of syrup quality on the transfer of selected impurities during boiling of A-massecuites. The other conditions should thus be kept constant which is best done at pilot-plant scale.

Pilot plant

The Sugar Milling Research Institute (SMRI) pilot batch pan was used for all the boilings. The pan itself has been described elsewhere[11].

Major changes were made to the pan instrumentation, which now consists of the following:-

(a) Conductivity measurements using a conventional two electrode system situated in the pan saucer.

(b) Massecuite temperature, measured by a semiconductor sensor extending for about 5 cm into the massecuite.

(c) Stirrer torque measurement, which is done electronically, from the DC motor.

(d) Pan absolute pressure which is measured electronically.

(e) Boiling point elevation which is the difference between the massecuite temperature measured in (b) and the boiling temperature of water at the same absolute pressure.

The measurements are converted to 0 to 10 V, which are then fed into a data logging computer through an A/D card. The five quantities mentioned above are displayed numerically and graphically on the computer monitor. The measurements are stored on disc and can be printed if desired.

Syrup (at 65°C) is fed into the pan through a needle valve, using the pan vacuum to draw in the feed. The syrup is sieved (100 mesh) prior to being used as small particles of bagacillo or scale tend to block the feed valve. A dripper is used to assess the feed rate visually.

It is also possible to adjust the heat input into the pan through a thyristor control and to change the rotational speed of the stirrer.

Syrups used

Factories were selected to represent an inland diffusion factory, namely Union- Co-operative (UC), which has shown low sugar colours; diffusion factories on the north and south coasts, namely Amatikulu (AK) and Sezela (SZ), and finally a milling factory, Darnall (DL).

Syrup was catch sampled from the evaporator last effect, on a twice monthly basis, sent to the SMRI and boiled the next day. The period May to November 1986 was covered.

Analytical procedures

(a) **Affinated sugar:** The sugar crystals are separated from the massecuite by centrifuging the hot massecuite in a laboratory centrifuge. This also yields the mother liquor.

The sugar is removed from the basket and an equal mass of saturated refined sugar solution is added. The sugar and syrup are mixed by hand. This magma is then centrifuged again, the sugar removed, spread on a clean sheet of paper and allowed to air dry.

The sugar crystals are then affinated according to the ICUMSA cane sugar method[12]. This affination step is very important because the mother-liquor can be one hundred times more coloured than the crystal. Thus, small amounts of mother-liquor left on the crystal cause large errors.

All the sugar analyses reported here were done on this affinated sugar.

(b) **Absorbances:** A solution of about 5 brix is made which is then filtered through a 0,45 μm membrane. The filtrate is adjusted to pH 7 with HCl or NaOH (0,05M) and the brix is read. The absorbance at 420 nm, in a 10 mm cell is then read and the absorbance units are calculated by multiplying the spectrophotometer reading by 1 000 and dividing by the concentration in g solids cm^{-3} (obtained from the brix reading and the appropriate table). The filtrate pH is then adjusted to 4 and the procedure repeated. Finally, the procedure is repeated at 9 pH.

(c) **Total phenols and amino nitrogen:** Total phenols by the Folin-Ciocalteu and Liebermann methods and amino nitrogen by the ninhydrin method are determined in dilute, filtered solutions. These analyses are done on a Technikon Auto-Analyser. The results are reported as ppm on brix.

(d) **Indicator values** (IV): Indicator value is given by the ratio (absorbance pH 9)/(absorbance pH 4) and is used to differentiate between classes of phenolics. Plant pigments have IV values of 7-13 while factory formed colour has IV values of 1-5.

(e) **Crystal size distribution** (CSD): CSD's are determined on the crystals from each boiling and on the Hulett superfine sugar used as seed. This yields average width and length, based on the measurement of 400 crystals with a Kontron Image Analyser.

(f) **Crystallisation rate:** Mass and brix balances have been used to calculate the mass of crystal produced during each boiling. The boiling time is also recorded for each run. It is then possible to calculate the crystallisation rate.

Results and Discussions

Operational conditions

Fifty-one boilings were done during the investigation. Means and 5 % confidence intervals for some important operational factors are given in Table 1.

Table 1

Means and 5 % confidence intervals

Crystal width (μm)	382 ± 12
Crystallisation rate (kg. $s^{-1} \cdot m^{-2}$)	$3,6 \times 10^{-5} \pm 1,6 \times 10^{-6}$
Exhaustion	61,9 ± 1,2
Syrup purity	85,0 ± 0,5

Controllable factors such as stirring rate and vacuum were kept within narrow limits and it is concluded that operational factors were controlled satisfactorily. This conclusion is strengthened by the absence of a significant correlation between, for example, syrup purity and crystallisation rate and between other pairs of factors which should affect each other, if their ranges had been wide enough. Similarly there is no correlation between affinated sugar colour (pH 7) and any of the factors shown in Table 1.

The syrup purity showed a small seasonal trend which could have influenced the results. The effect of this trend on syrup colour was investigated by recalculating colours based on non-pol rather than brix. The differences obtained were considered far too small to explain the trends discussed in the following sections.

Colours

Individual affinated sugar colours, namely 51 observations at each of the 3 pH values, were regressed against the corresponding syrup colours. The results are shown by equations 1, 2 and 3.

$$\text{Affinated sugar (pH 4 colour)} = -20,7 + 0,0148 \times \text{Syrup pH 4 colour} \quad (n = 51;\ r = 0,68) \qquad (1)$$

$$\text{Affinated sugar (pH 7 colour)} = 15,8 + 0,0129 \times \text{Syrup pH 7 colour} \quad (n = 51;\ r = 0,72) \qquad (2)$$

$$\text{Affinated sugar (pH 9 colour)} = 54,1 + 0,0126 \times \text{Syrup pH 9 colour} \quad (n = 51;\ r = 0,66) \qquad (3)$$

The regression coefficients are fairly low, and the residuals show a clear time trend. Time was therefore introduced into the regression, using the calendar month number, M (e.g. May = 5, June = 6 etc.). Equations 4, 5 and 6 were obtained.

$$\text{Affinated sugar (pH 4 colour)} = 534,2 + 0,0009664 \times \text{Syrup pH 4 colour} - 120,5 \times M + 7,02 \times M^2 \quad (n = 51;\ r = 0,82) \qquad (4)$$

$$\text{Affinated sugar (pH 7 colour)} = 813,8 + 0,008085 \times \text{Syrup pH 7 colour} - 172,5 \times M + 9,81 \times M^2 \quad (n = 51;\ r = 0,83) \qquad (5)$$

$$\text{Affinated sugar (pH 9 colour)} = 2278,6 + 0,008851 \times \text{Syrup pH 9 colour} - 517,9 \times M + 30,3 \times M^2 \quad (n = 51;\ r = 0,84) \qquad (6)$$

The fits are now better and the residuals are normal, showing that time is a significant factor.

Average monthly colours have been calculated in Table 2.

Table 2

Monthly average colours

Month	Sugar			Syrup		
	pH 4	pH 7	pH 9	pH 4	pH 7	pH 9
May	253	422	1058	15377	28717	69340
June	143	266	696	10430	20060	52988
July	145	250	567	9938	17875	48388
Aug.	123	206	538	11143	18571	50743
Sept.	128	218	584	11676	20794	59712
Oct.	147	263	694	11195	21837	61552
Nov.	188	314	827	13130	25232	63429

These values have been plotted in Figure 1, the time trend being clearly evident.

Colour transfer

Colour transfer is the ratio of the colour of affinated sugar to that of the syrup. It thus represents the proportion of colour impurities that entered the crystal. Since the transfer is a ratio, analytical and experimental errors tend to be higher. It is therefore better to look at the monthly average, given in Table 3.

Table 3

Colour transfers monthly average

	Colour Transfer		
Month	pH 4	pH 7	pH 9
May	0,0164	0,0147	0,0153
June	0,0136	0,0132	0,0130
July	0,0145	0,0143	0,0122
Aug.	0,0110	0,0109	0,0103
Sept.	0,0109	0,0105	0,0097
Oct.	0,0127	0,0116	0,0113
Nov.	0,0138	0,0122	0,0133

These results in Table 3 have been plotted in Figure 2 and indicate two trends. Firstly, the pH 4 colour transfer is higher than the pH 9 one. This will be discussed later. Secondly, there is again a significant time trend, with high transfers in May and November and low transfers in August/September, which indicates that there could be a direct relationship between the colour transfer and the syrup colour.

Indicator values

Average values for the colour transfers and for indicator values are given in Table 4.

Table 4

Overall average, colour transfers and IV's

	Average 51 Observations
pH 4 Colour transfer	0,0130
pH 7 Colour transfer	0,0121
pH 9 Colour transfer	0,0116
IV Syrup	5,1
IV Affinated sugar	4,6

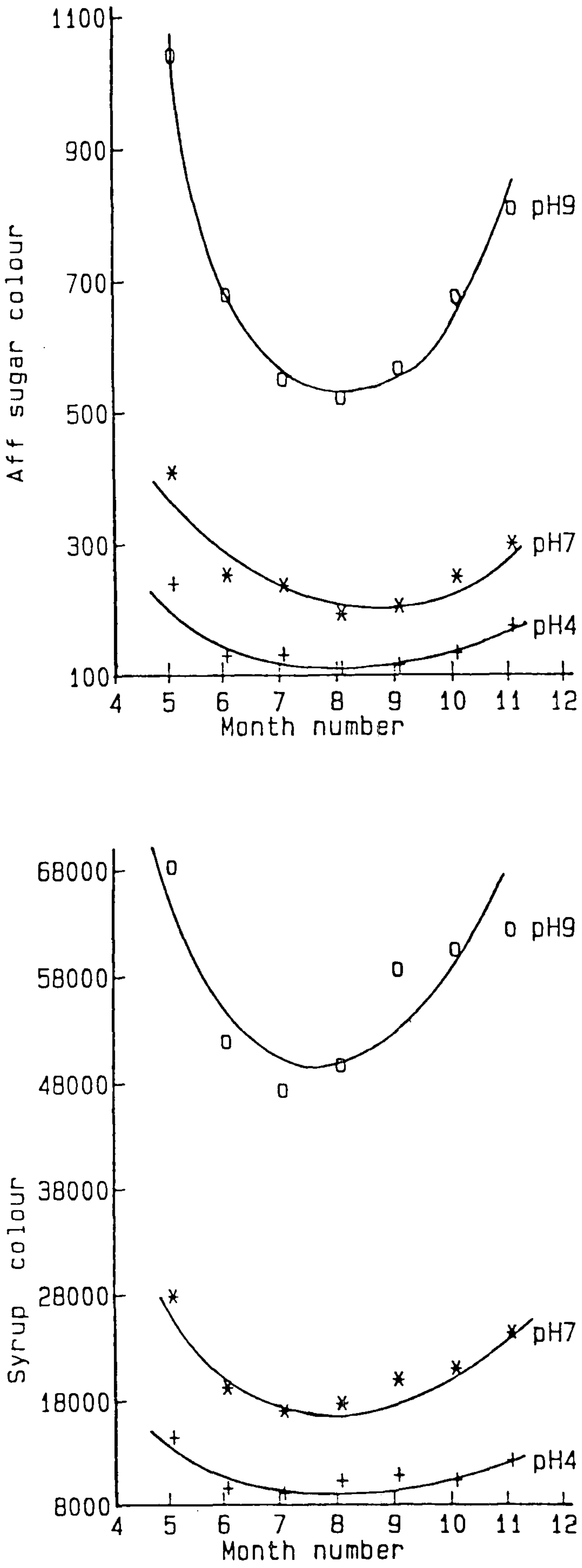

FIGURE 1 Syrup and affinated sugar colours plotted against time of the year.

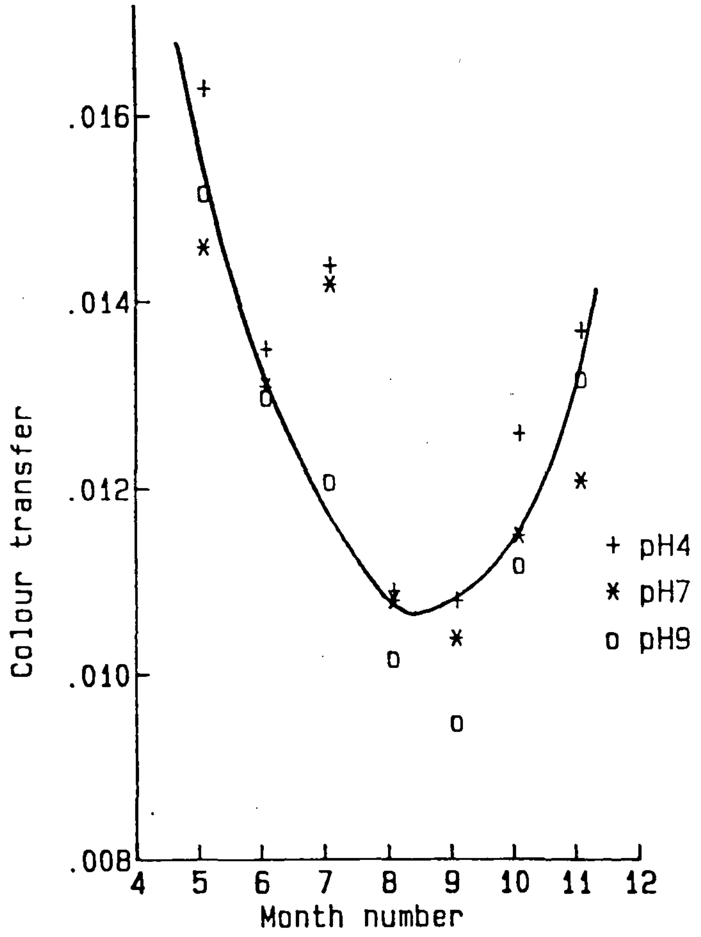

FIGURE 2 Colour transfers plotted against time of the year.

It is evident that the IV of the affinated sugar is lower than that of the syrup. This implies that the pH 4 colour transfer is higher than that of the pH 9 colour, which is also evident from Table 4.

These results indicate that there are concentrations and other processes taking place at the crystal liquid interface, as mentioned earlier in the paper.

Phenolics and Amino nitrogen

Monthly averages for the Folin-Ciocalteu phenolics, expressed as ppm caffeic acid on brix, averages for Liebermann phenolics, expressed as ppm gallic acid on brix, and averages for amino nitrogen on brix, are given in Table 5.

Table 5

Averages for phenolics and Amino-nitrogen

Month	Syrup			Aff. sugar		
	Caffeic acid	Gallic acid (ppm on brix)	Amino nitrogen	Caffeic acid	Gallic acid (ppm on brix)	Amino nitrogen
May	5314	1355	592	64,6	21,6	7,6
June	4580	770	780	69,1	12,2	6,9
July	5179	952	767	75,1	15,9	6,6
Aug.	4746	970	799	58,4	12,9	5,6
Sept.	4552	991	883	57,4	13,9	7,3
Oct.	5289	1115	860	67,7	16,1	6,5
Nov.	6676	1240	743	83,6	20,8	5,9

It is evident that the phenolics show trends similar to that of the absorbance, namely higher levels at the beginning and end of the season.

Amino nitrogen however shows different trends, the concentrations in syrup being highest in mid-season while that in affinated sugar stays fairly constant around 7 ppm.

The effects of phenolics on affinated sugar colours were investigated by regressing the affinated sugar pH 7 colour against the phenolics and amino nitrogen in syrup. The plots are shown in Figure 3.

The regressions obtained with these monthly averages were as follows:

$$\text{Affinated sugar (pH 7 colour)} = 47{,}3 + 0{,}0398 \times \text{ppm caffeic acid on brix in syrup} \quad (n = 6;\ r = 0{,}82) \tag{7}$$

$$\text{Affinated sugar (pH 7 colour)} = 24{,}3 + 0{,}282 \times \text{ppm gallic acid on brix in syrup} \quad (n = 7;\ r = 0{,}76) \tag{8}$$

$$\text{Affinated sugar (pH 7 colour)} = 804{,}7 - 0{,}681 \times \text{ppm amino-nitrogen on brix in syrup} \quad (n = 7;\ r = 0{,}89) \tag{9}$$

These results show that affinated sugar colour increases as the concentration of phenolics in syrup increases. Equation 9 however, shows that sugar colour decreases with increasing amino nitrogen in syrup. A possible explanation for this would be that lower levels of amino nitrogen could result from the occurrence of Maillard type reactions which are known to consume amino nitrogen and form colour bodies which would then be incorporated into the crystal. High levels of amino nitrogen in syrup on the other hand could be due to the absence of these reactions resulting in lower levels of colour.

Phenolics and amino nitrogen transfers do not show clear trends with time of the year or against concentrations in syrup. On average, however, the Liebermann phenolics (expressed in ppm gallic acid) showed a higher average transfer (0,0151) than the Folin-Ciocalteu phenolics (0,0131) indicating that the Liebermann phenolics are preferentially incorporated into the crystal.

Individual mills

Overall averages for some selected results, on a mill basis, are given in Table 6.

Table 6

Mill averages

Mill	Syrup					Sugar	
	Purity	Colour pH 7	IV	ppm gallic acid on brix	ppm amino nit. on brix	Colour pH 7	IV
DL	83,2	20771	4,3	950	900	260	3,8
SZ	84,8	23341	4,8	1150	665	287	4,3
AK	85,4	22970	5,3	1169	718	273	4,8
UC	87,4	17153	5,7	889	967	208	5,3

The UC results are particularly noticeable. The syrup has the highest purity, lowest colour and highest amino nitrogen content while the UC sugar shows the lowest colour. It is generally accepted that the cane quality at UC is one of the best in the industry and this must have had a pronounced effect on the syrup quality.

The DL result was somewhat different from those of AK and SZ, particularly as far as the phenolics and amino nitrogen are concerned. Since DL is the only milling factory in the selected group, this could be the cause of the differences. This aspect however needs to be investigated further.

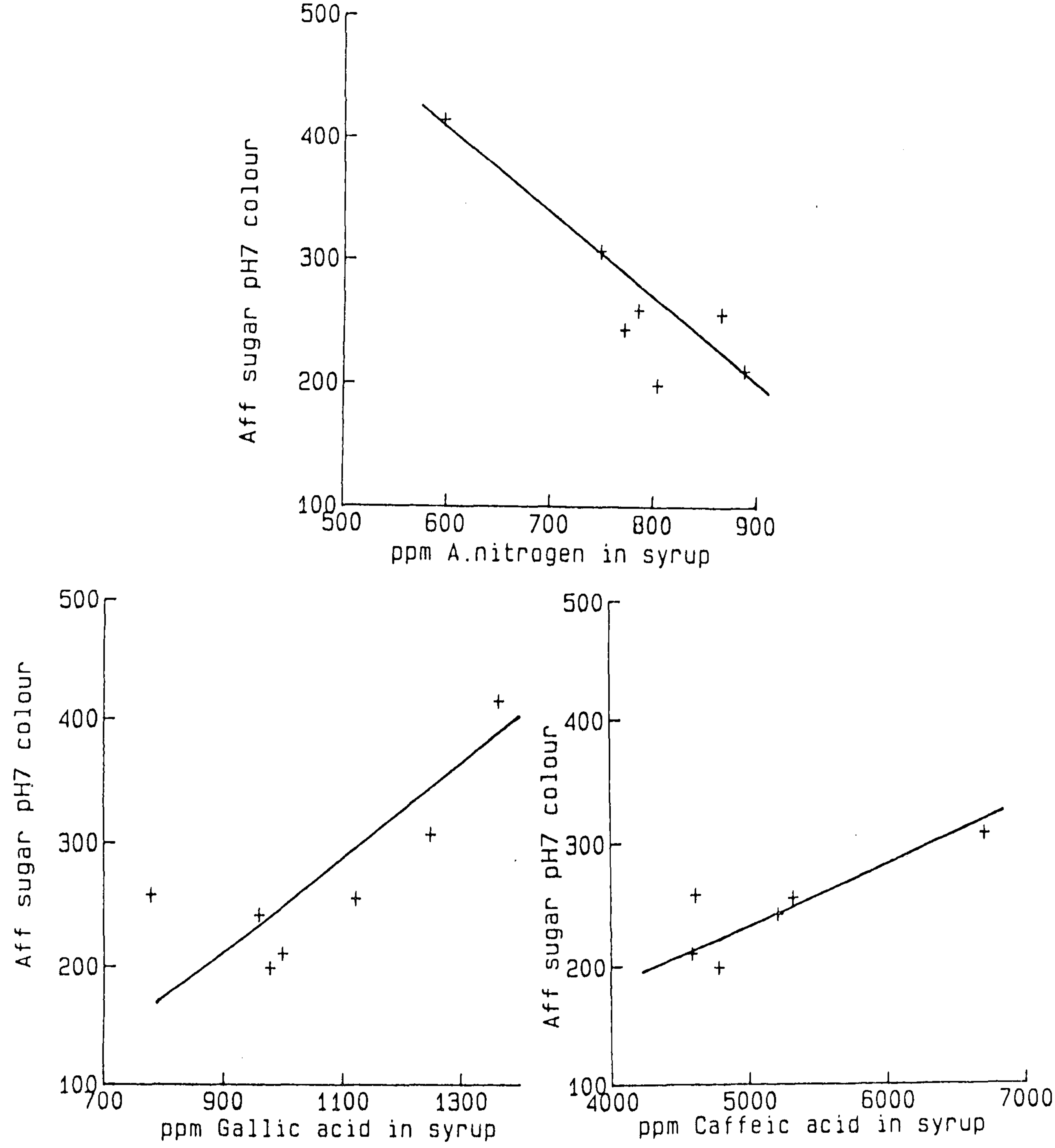

FIGURE 3 Affinated sugar colour (pH 7) plotted against phenolics and amino-nitrogen in syrup.

Conclusion

The basic requirement of this investigation, namely the use of standard and reproducible boiling conditions, has been achieved satisfactorily. This would not have been possible without the instrumentation installed at the beginning of the project. Since boiling conditions were kept constant, changes in sugar quality can only be due to the syrup itself.

Of the two factors found to affect syrup quality, namely its mill of origin and the time of the year, the latter has by far the larger effect. Thus the mills cause differences around 40 % whereas the time of the year results in differences ranging from 50 to 75 %.

Syrup colour correlates well with time of the year, equation 10 showing the result for pH 7 colour:

$$\text{Syrup (pH 7 colour)} = 79428 - 15190 \times M + 940 \times M^2 \quad . \; . \; . \; . \; . \quad (10)$$

$$(n = 7;\ r = 0{,}92)$$

where the syrup colours used are the monthly averages (Table 2) and M is the month number, with M = 5 representing May etc.

Sugar quality is dependent not on syrup quality only but also on a time factor. Good fits are obtained when the sugar colours are regressed against corresponding syrup colours and month number as shown by equations 4, 5 and 6. Equation 5 is shown here again.

$$\text{Sugar (pH 7 colour)} = 813{,}8 + 0{,}008085 \times \text{Syrup pH 7 colour} - 172{,}5 \times M + 9{,}8 \times M^2 \quad (n = 51;\ r = 0{,}83) \qquad (5)$$

Colour transfers are not the same at the 3 pH's, with pH 4 colour showing a value higher than that of pH 9. This is also evident when sugar and syrup IV's are compared. These results indicate that there are dynamic processes taking place at the crystal/mother liquor interface. Colour transfers were not constant throughout the test period but showed trends similar to that of the syrup colour. Although there is no strong evidence at this stage, it appears that the colour transfer could be directly proportional to the syrup colour. This conclusion however needs to be investigated in detail.

The importance of phenolics in juice and sugar colour has been stressed by many workers. The results obtained here show significant positive correlations between affinated sugar colour and the concentration of phenolics in syrup.

The results obtained with amino nitrogen are particularly interesting in that the correlation between affinated sugar colour and the concentration of amino nitrogen in syrup is statistically significant and negative, as shown by Equation 9.

Since Maillard type reactions consume amino nitrogen and form colour, the results indicate that low levels of amino nitrogen in syrup imply that these reactions have taken place, destroying amino nitrogen and forming colour which can then be included in the crystal.

The importance of cane cleanliness is highlighted when the syrup and sugar colours from UC are compared with those of the other 3 mills.

Finally, the results given here represent only the effects of syrup quality. Effects due to operational factors such as stirring rate, temperature and crystallisation rates, which form part of the other half of this work, still need to be studied.

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