

PRELIMINARY STUDY ON THE EXTRACTION OF SOME IMPURITIES FROM CANE DURING DIFFUSION

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Abstract

Experimental methods for the study of the extraction of brix and of a number of impurities from cane, under conditions simulating diffusion, are described. The effects of changes in pH and temperature and of cane quality factors such as the presence of tops or trash, are studied.

Introduction

The ultimate performance criterion for a sugar factory is the overall recovery of sugar of the required quality. There is a need, therefore, to investigate not only the extraction of sucrose, but also that of impurities, particularly those which are known to affect sugar quality.

Cane quality, as affected by tops, trash, soil, or deterioration, and actual process conditions in the factory (for example pH, temperature, retention times) are two major factors which influence both the type and the quantity of the impurities present in the extracted juices. These factors have been investigated by a number of workers. Graham *et al*⁷ investigated juice qualities at two diffuser factories; Buchanan and Jullienne² used a laboratory pilot diffuser, while Rein¹⁰ used both a laboratory batch diffuser and a pilot diffuser in a sugar factory. More recently, impurities concerned with colour have been investigated by a number of overseas workers.^{3,5,6,9,12,13} These investigations were aimed at establishing the types of colorants found in cane, in juices and in sugar, and at developing analytical techniques for their quantification.

The present study is concerned with the effect of cane quality and of process conditions on the extraction of brix, pol and a number of impurities related mainly to colour. Colour bodies found in the affinated sugar crystal can originate from the cane itself or may have been formed during the process, either from coloured compounds originally present in some other form in the cane or from colourless precursors. These bodies persist throughout the process and are not eliminated by the final crystallisation step. They are thus the most troublesome and their presence in the cane and juice should be prevented or reduced as far as possible. Smith^{12,13} and others^{4,5,6,8,11} have identified some of the major classes of compounds present in cane, juices and sugar crystals. Phenolic compounds form one of these classes, two-thirds of the colour in sugar crystals having been found to be due to phenolics and to cane pigments of the flavonoid type. Curtis and Paton⁵ identified a number of phenolic acids in juices, raw and refined sugars. Flavonoid types of pigments have been found even in refined sugar⁹. Of the colorants developed during the process, melanoidins are, in general, Maillard-type reaction products formed by the reaction of amine groups with sugar groups. Since amine compounds come from the plant, this type of colorant is also plant derived⁴.

As a result of these findings, total phenols, anthocyanins (plant pigments falling in the flavonoid class) and amino-nitrogen were selected as the three broad classes of compounds to be monitored. The availability of relatively simple and fast analytical techniques was another criterion used in the selection of these particular classes. In addition, the optical absorbances in the visible and ultra-violet ranges of the spectrum were also measured, since these are widely used to measure colour.

Since the trend in South Africa is towards the extraction of

juice from cane by diffusion, the experimental approach was designed to simulate diffusion.

Experimental Procedure

The laboratory diffusers consist of five 6 litre stainless steel, jacketed vessels. One such vessel is shown in Figure 1. A stirrer is used to ensure good mixing of the cane pulp and water, and samples of juice may be withdrawn when required.

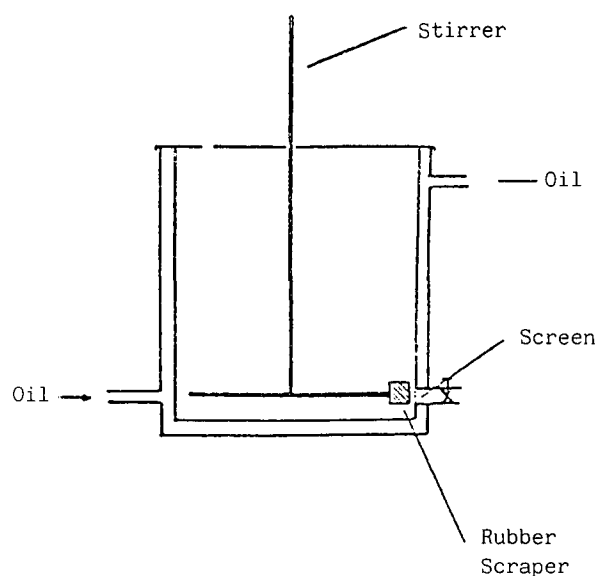


FIGURE 1 Diffusion vessel

A stainless steel screen at the inlet to the sampling pipe prevents it from becoming choked by fibre. The rubber scraper is necessary to ensure the flow of samples. There is a facility to introduce a temperature probe and/or pH electrode in the cane/water mixture.

Temperature is controlled by pumping hot oil through the jackets. The oil temperature is maintained at the desired level by a conventional thermostat bath. The heated parts of the equipment are lagged.

All metal parts in contact with the cane/water mixtures are made of stainless steel, because cane colour constituents react with iron to produce a brown colouration and this does not occur with stainless steel.

In all cases it was necessary to analyse the juice samples immediately they were withdrawn from the diffusion vessels because the usual juice preservatives were found to interfere with the subsequent analytical methods. In the case of total phenols and anthocyanins, the simple methods used will cause some overlap and a loss of specificity. It is more correct therefore to consider these analyses as yielding Folin-Ciocalteu positive compounds and lead precipitable/alcohol soluble compounds, rather than total-phenols and anthocyanins.

The experimental approach has been designed to investigate the effects of cane quality and of process conditions on both the rate at which the constituents are being extracted, and on

their final concentrations in the juice. The theory used to calculate these quantities is based on the work of Rein¹⁰ and Spiro^{14,15,16} who worked on tea and coffee. The theory is briefly described in Appendix 1.

In the case of the rate determinations, the effect of temperature and pH were investigated, using a cane quality which was maintained at a reasonably constant level, by freezing (-10°C) sub-samples of the prepared cane for subsequent runs. In all cases, the cane consisted of a mixture of clean cane plus 5% tops and 5% trash by mass. Three main series of factorially designed runs were conducted, one finely prepared cane using a Jeffco cutter-grinder and the other two with a coarser preparation using a modified Waddell shredder. The level of cane preparations in the latter two cases was reasonably typical of actual industrial practice.

Only Jeffco prepared cane was used for the equilibrium experiments in which the effects of pH, temperature, tops and trash on the concentrations of the selected constituents, were investigated.

Results

The results from the first set of experiments, which include the rate measurements, are considered first. Calculation of the experimental error showed that only the total concentration after 60 minutes (C_{60T}) and the fraction of material available through the diffusion mechanism, α , were sufficiently precise for the results to be meaningful. The precision for C_{60T} was $\pm 5\%$. The high and low levels of temperature and pH used in these tests are given in Table 1.

TABLE 1
High and low levels of pH and temperatures

| | pH | Temperature (°C) |
|------------|-----|------------------|
| High level | 7,2 | 82 |
| Low level | 5,7 | 60 |

All pH values quoted here were measured at the temperature of the extract. The mean effect of temperature and pH on the finely and coarsely prepared cane were similar. The results for the coarse preparation are given in Table 2, where anthocyanins are expressed as anthocyanin units on juice, total phenols and amino nitrogen as ppm on juice. The optical absorbances have been averaged to give absorbance units on juice, in the visible and ultra violet regions.

TABLE 2

Effect of temperature and pH on total concentration after 60 min. (coarsely prepared cane)

| Analysis | Temperature | | | pH | | | | |
|----------------------------|----------------------|--------------------|--------------|------------------|--------------------|--------------|-------|------|
| | Mean of high and low | Difference (H - L) | % Difference | Mean of high low | Difference (H - L) | % Difference | | |
| Brix | 3,31 | 3,14 | +0,18 | + 6 | 3,21 | 3,23 | -0,02 | -0,6 |
| Anthocyanins | 0,16 | 0,14 | +0,02 | +14 | 0,15 | 0,14 | +0,01 | +7 |
| Total Phenols | 202 | 175 | +27 | +15 | 182 | 193 | -10 | -5 |
| Amino Nitrogen | 33 | 32 | +1 | +3 | 32 | 33 | - 1 | -3 |
| Absorbance: visible region | 1,76 | 1,42 | +0,34 | +24 | 1,62 | 1,55 | +0,07 | +5 |
| Absorbance: UV region | 7,38 | 5,73 | +1,65 | +29 | 6,71 | 6,38 | +0,33 | +5 |

These results show that temperature has a marked effect on absorbances, both in the visible and ultra violet regions. An increase of 22°C, from 60 to 82°C, caused the measured absorbances to rise between 20 and 30%. Anthocyanins and total phenols increased less, averaging about 15%. Brix on the other hand, increased by about 5% for the same increase in temperature, while amino nitrogen did not change.

The effect of pH was less evident. Anthocyanins, total phenols and amino nitrogen showed no significant changes. The absorbances, however, nearly always increased with increasing pH, although the increases were not always significantly larger than the experimental error. On average, an increase in pH from 5,7 to 7,2 could result in absorbances increasing by about 5%. As could be expected, pH had no effect on brix.

The effect of cane preparation on α , the fraction of the constituent extracted by diffusion after 60 minutes, to the total amount extracted, is shown in Table 3.

TABLE 3
Values of α for finely and coarsely prepared cane

| Brix | | Anthocyanins | | Amino Nitrogen | | Total Phenols | | *9-380 | | **9-420 | |
|--------|--------|--------------|--------|----------------|--------|---------------|--------|--------|--------|---------|--------|
| fine | coarse | fine | coarse | fine | coarse | fine | coarse | fine | coarse | fine | coarse |
| 0,04 | 0,13 | 0,13 | 0,29 | 0,08 | 0,14 | 0,23 | 0,32 | 0,22 | 0,21 | 0,12 | 0,19 |
| 0,05 | 0,13 | 0,28 | 0,45 | 0,10 | 0,15 | 0,22 | 0,40 | 0,18 | 0,11 | 0,13 | 0,22 |
| 0,14 | 0,13 | 0,30 | 0,28 | 0,10 | 0,13 | 0,23 | 0,32 | 0,28 | 0,26 | 0,18 | 0,21 |
| 0,12 | 0,13 | 0,44 | 0,35 | | 0,05 | 0,14 | 0,30 | 0,23 | 0,27 | 0,23 | 0,17 |
| 0,06 | 0,14 | 0,30 | 0,39 | | 0,24 | | 0,31 | 0,18 | 0,23 | 0,08 | 0,26 |
| 0,09 | 0,16 | 0,28 | 0,32 | | 0,23 | | 0,34 | 0,24 | 0,25 | 0,17 | 0,24 |
| 0,08 | 0,15 | | 0,33 | | 0,17 | | 0,31 | 0,18 | 0,26 | 0,19 | 0,27 |
| 0,08 | 0,16 | | | | 0,16 | | 0,34 | 0,31 | 0,25 | 0,30 | 0,25 |
| 0,09 | | | | | | | | | | | |
| 0,08 | | | | | | | | | | | |
| 0,06 | | | | | | | | | | | |
| + 0,08 | 0,14 | 0,29 | 0,34 | 0,09 | 0,16 | 0,20 | 0,33 | 0,23 | 0,24 | 0,18 | 0,23 |

* Optical absorbance, at 380 nm and pH 9

** Optical absorbance, at 420 nm and pH 9

+ Mean values

The differences between the means for each analysis were tested using a t-test. The differences between the mean values for the coarse and fine preparations were statistically significant in the case of brix and total phenols. In the case of brix, which in these experiments comprised between 85 and 90% of the sucrose, the fine preparation results in more than 90% of the material being available through the washing mechanism, during the first 4 to 5 minutes of the 60 minute extraction. Coarse preparation reduces this amount to 85% showing that, even then, the major proportion of the sucrose is extracted in the washing step. Amino-nitrogen, is the only other constituent for which results are comparable. They were not statistically significant, probably because of the small number of observations.

As far as the anthocyanins, total phenols and optical absorbances are concerned, the values of α now range from 0,2 to 0,3 showing that even with fine preparation, diffusion has relatively more importance. Except for total phenols, the difference between the values of α for fine and coarse cane preparations were no longer found to be statistically significant.

The second set of experiments deals with the measurement of concentrations in cane/water mixtures, after equilibrium has been reached. This part of the investigation is far from complete, but has generated some interesting preliminary results. Since this approach yields the concentration of material in the cane, results for pol and brix can be compared with those obtained by Direct Analysis of Cane (DAC) (Figure 2).

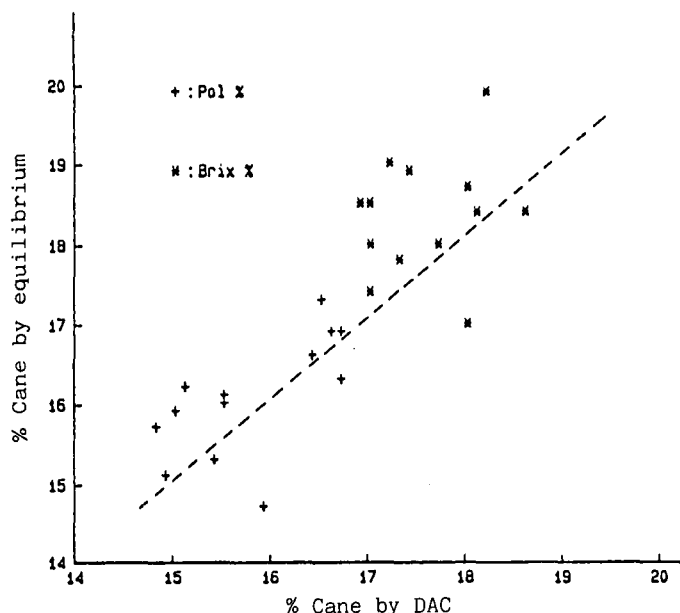


FIGURE 2 Comparison of pol and brix extraction against the routine DAC procedure.

These results show that there is evidence of bias, with the equilibrium values being generally higher than those of the DAC. The reasons for this need to be investigated, but it is evident that the agreement between the two approaches is sufficiently good to warrant further investigations into the equilibrium method.

A series of 13 runs was carried out, involving clean cane, clean cane plus tops and clean cane plus trash. Temperatures and pH values were also varied. In all cases the cane was prepared by using the Jeffco shredder and 10% by mass of tops or trash was added. The tops, trash and the subsequent mixtures with cane were analysed for moisture, thus permitting accurate mass balances to be computed on a dry matter basis.

Although the experimental approach was a factorial design, the results were analysed by means of a multilinear regression. The range of the independent variables is given in Table 4 and some of the results are shown in Table 5. In all cases the number of observations was equal to 13.

TABLE 4
Range of the variables for the equilibrium tests

| Variable | Lowest | Highest | Mean |
|------------------|--------|---------|------|
| Temperatures(°C) | 57 | 79 | 67 |
| pH (at T°C) | 5,4 | 7,3 | 6,4 |
| Tops % * | 0 | 9,4 | 2,7 |
| Trash % ** | 0 | 20,1 | 5,7 |

* Tops % expressed as dry matter from tops % total dry matter in the clean cane + tops mixture

** Trash % expressed as dry matter from trash % total dry matter in the clean cane + trash mixture

TABLE 5

Relationships between temperature, pH, tops, trash and concentrations in cane

| | |
|--------------|--|
| Brix % cane | = 14,9 + 0,06 × T - 0,04 × trash |
| Pol % cane | = 15,0 + 0,03 × T - 0,11 × tops - 0,08 × trash |
| Anthocyanins | = -0,8 + 0,01 × T + 0,1 × pH + 0,03 × trash |
| T.phenols | = 19 + 7,5 × T + 102 × pH + 12 × tops + 23 × trash |
| A 9-380 | = 2,5 + 0,17 × T + 0,48 × Tops + 0,30 × trash |
| A 9-320 | = -25,0 + 0,62 × T + 2,5 × pH + 0,56 × trash |

In Table 5, the temperature (T) is expressed in degrees celsius. The pH is expressed in pH units, measured at T°C. Tops and

trash are expressed as dry matter from tops or trash as a percent of total dry matter. Finally, A 9-380 and A 9-320 are optical absorbances, expressed as absorbance units on cane, measured at a pH value of 9, at wavelengths of 380 and 320 nm respectively.

Conclusion

The experimental approaches developed in this investigation have resulted in the quantification of the effects of a number of variables on diffusion juice quality. Although a number of points still need to be clarified or confirmed, the method is promising and has given meaningful answers, particularly as far as temperature, pH and cane preparation are concerned.

Temperature increases the juice colour significantly, without corresponding increases in pol extraction. Fine cane preparation on the other hand increases pol extraction, but does not have similar effects on impurities. The effects of pH are less pronounced but generally, increasing the pH increases the levels of the impurities present in the juice. Tops and particularly trash, increase juice colour significantly. It should be noted that, if all these effects are present simultaneously, colour increases would be quite substantial.

This project is continuing with experiments to investigate the effects of cane deterioration and cane age on the extraction of impurities.

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APPENDIX 1

Rein¹⁰ has shown that the extraction of brix from a cane/water mixture takes place through two parallel first order mechanisms. The first and quicker is a washing mechanism while the second is a diffusion mechanism.

Spiro^{14,15,16} derives two models for the extraction of soluble constituents from tea leaves and ground coffee. The first deals with the rate at which a constituent is extracted while the second describes the concentration of the constituent in solution at equilibrium. Spiro found that the extraction processes in tea and coffee were first-order. This approach therefore may be used with cane.

Using Spiro's theory, the following relation may be derived for a given mixture of prepared cane and water:-

$$\ln \frac{(C_{\infty})}{(C_{\infty} - C)} = k_1 \cdot t \quad \dots \dots \dots (1)$$

where C_{∞} = concentration of constituent in extract at equilibrium.
 C = concentration of constituent in extract at time t
 k_1 = 1st order rate constant.

Equation (1) shows that a plot of $\ln \frac{(C_{\infty})}{(C_{\infty} - C)}$ against t gives a straight line with slope equal to k_1 .

This approach requires the value of C_{∞} . Spiro found that for tea, a sample after 20 min of infusion was adequate. In the case of cane, much longer times would be necessary, particularly with coarsely prepared cane. These long retention times could result in excessive chemical and/or biological changes. Furthermore, they would not be representative of industrial retention times of about 60 minutes. This difficulty can be obviated by using a method developed by Guggenheim¹. This results in the relation:

$$\ln (C_{t + \Delta t} - C_i) = \ln (C_{\infty}(1 - e^{-k_1 \cdot \Delta t}) - k_1 t) \quad \dots \dots \dots (2)$$

Equation 2 shows that a plot of $\ln (C_{t + \Delta t} - C_i)$ versus t yields a straight line with slope $-k_1$ and intercept $\ln (C_{\infty} \cdot (1 - e^{-k_1 \cdot \Delta t}))$. It is noted that Δt must be constant.

This Guggenheim approach was utilised to determine the rate constants for both the washing and the diffusion stages.

However if it is only desired to determine the final equilibrium concentration, C_{∞} , then Spiro derives the following equation:-

$$\frac{1}{C_{\infty}} = \frac{V}{X_0 \cdot W} + \frac{1}{X_0} \frac{1 + Vn \cdot \rho_n - Y}{K \cdot \rho_s} - Vn \quad \dots \dots \dots (3)$$

where:
 C_{∞} = the concentration of the constituent in the extract, at equilibrium
 V = the volume of water
 W = the mass of cane
 X_0 = the concentration of the constituent in cane
 K = a partition coefficient
 ρ_s and ρ_n are densities of water and extract respectively

Vn and Y are properties of the cane/water mixture which are determined by experiment.

Equation 3 shows that if $1/C_{\infty}$ is plotted against $1/W$, a straight line is obtained with slope equal to V/X_0 .

Since V is known, X_0 can be calculated. This approach therefore permits the analysis of cane under specified conditions of temperature and pH.