CONSTITUENTS IN RAW SUGAR THAT INFLUENCE REFINING

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ABSTRACT

The present status in identification of the minor constituents in cane sugars and the effect of these constituents on refining is reviewed. Discussed are ash constituents, including heavy metals; colorants and floc constituents. Analytical methods for these minor constituents are described, and results show them to be in the ppm range in raw sugars and well below 1 ppm in refined sugars. These minor constituents will become even more important as standards for refined sugar are tightened and increasingly affect farmers, millers, and refiners alike.

INTRODUCTION

When analysing cane juice by the standard analytical procedures, which were described by Roberts and Martin, one can account for all but about 3 or 4% of the juice in terms of known compounds such as sugars, water, starch, gum, dextran, protein, fat, wax, carboxylic acids, amino acids and ash. The unknown 3 or 4% is greatly reduced in the processing of the juice so that the unidentified substances are only in the ppm range in refined sugar. It is to these unknown minor constituents that the refiner must direct his attention.

The known constituents in cane juice or raw sugar have a known effect upon refining. They may be troublesome, but at least the refiner knows what the trouble is, what causes it, and what he can do about it, and whether it is worth doing anything about.

No one knows all the trouble that is caused by the unknown minor constituents, but color results from these materials and we do know what trouble this causes. Color is the key component in refining sugar. Every sugar refinery is run to obtain a product of sufficiently low color value. All the other components, such as invert and ash, are handled easily enough, but every refinery struggles to remove the color.

Although color is the key component, relatively little is known about the chemical compounds that make up the colorant: their origin, their eventual destination, or their properties. With no knowledge about what specific materials make up the colorant, no specific method can be used for removal. Instead, general methods must be used. The principal methods are adsorption onto carbon, ion exchange, bleaching and crystallisation.

If more were known about the individual chemical compounds making up the colorant, it would probably be easier to prevent its formation or to remove it. The waste and sometimes destruction of sucrose and the expense entailed in the general decolorisation procedures could be reduced.

But color is not the only thing in that small unknown fraction of minor
constituents in sugar. There must be compounds structurally similar to the colorants but not colored, color precursors, substances that produce flavor and odor, perhaps even toxic substances such as pesticide residues or heavy metals.

For further advancement in cane sugar processing, these unknown constituents will first have to be identified, then analytical procedures must be developed so that they can be easily measured. Only then can improved processing be realised. Many minor constituents have already been identified; for example Roberts and Martin\textsuperscript{16} reported a long list of known compounds.

It is worthwhile reviewing briefly the present status in identification and measurement of these minor constituents, describing some of the recent advances, and considering what use can be made of this new information.

\textbf{ASH CONSTITUENTS}

Although measurement of ash is routinely used in processing control, only rarely are the individual ash constituents considered. Practical analytical methods for all the major ash constituents are handbook information,\textsuperscript{14} and Carpenter \textit{et al}\textsuperscript{14} showed that the balance of polyvalent anions with polyvalent cations can have a spectacular effect on color removal by bone char. This balance determination requires the measurement of total ions (which can double as an ash determination), chloride and calcium. In every refinery calcium is added in the form of lime, but the control is based on pH, not on calcium.

By controlling calcium, particularly to avoid an unfavorably low level, good decolorisation by bone char can be assured. At present only a few refineries practice this method, but many more could use it to achieve better control over the still little understood bone char process.

Very recently considerable concern has arisen over what were formerly very minor ash constituents, namely heavy metals. In a recent survey by Pommez and Clarke,\textsuperscript{16} a raw sugar and a refined sugar were examined for 25 heavy metals. The only toxic heavy metals above the detection limit were: chromium, selenium, antimony, nickel, cadmium, barium, copper, tin, lead.

Conspicuous by their absence were such famous poisons as arsenic and mercury.

Some of the heavy metals are not toxic but are essential to growth. These are generally referred to as trace elements. A few elements — those that are toxic at high levels but essential at low levels — appear in both categories. The desirable trace elements found in sugar were:

- vanadium, cobalt, selenium (also toxic)
- chromium (also toxic), copper (also toxic), molybdenum
- manganese, zinc, tin (also toxic)
- iron

All of the toxic heavy metals present were well below the level of concern in refined sugar, but unfortunately the essential trace elements were also very low, below the effective dietary supplement range.

In another study by Clarke \textit{et al},\textsuperscript{16} the levels of various metals were charted from the raw sugar through the refinery to the refined product. Samples from different types of refineries were studied. Table 1 shows a typical set of results.
for a few metals from a refinery that used phosphate clarification and bone char. Analysis was by atomic absorption spectrophotometry, with the sample in solution atomised in a graphite furnace. The major removal of all of these metals was in the affination and clarification stages. Iron and manganese levels were further considerably reduced by passage over bone char. In some cases the copper level increased between liquors entering pans and refined sugar, probably because of the large quantities of copper in the surfaces to which the hot liquor was exposed.

**TABLE 1. Heavy metals in a phosphatation-bone char refinery.**

<table>
<thead>
<tr>
<th></th>
<th>Fe ppm</th>
<th>Cu ppm</th>
<th>Mn ppm</th>
<th>Cr ppm</th>
<th>Ag ppm</th>
<th>Pb ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw</td>
<td>6.86</td>
<td>1.07</td>
<td>2.91</td>
<td>0.09</td>
<td>0.007</td>
<td>0.25</td>
</tr>
<tr>
<td>refined</td>
<td>6.14</td>
<td>0.99</td>
<td>1.06</td>
<td>0.03</td>
<td>0.006</td>
<td>0.18</td>
</tr>
<tr>
<td>phosphated</td>
<td>2.26</td>
<td>0.29</td>
<td>0.38</td>
<td>0.008</td>
<td>0.006</td>
<td>0.02</td>
</tr>
<tr>
<td>char filtered</td>
<td>0.60</td>
<td>0.29</td>
<td>0.05</td>
<td>0.005</td>
<td>0.006</td>
<td>0.01</td>
</tr>
<tr>
<td>refined</td>
<td>0.14</td>
<td>0.11</td>
<td>0.02</td>
<td>0.004</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td>detection limit</td>
<td>0.001</td>
<td>0.000 2</td>
<td>0.000 2</td>
<td>0.001</td>
<td>0.000 6</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Levels of metals in raw sugars entering the refineries covered a wide range. Differences could be due to soil and weather conditions in the field and to the type and quality of processing in the mills. However, the various combinations of processes in the refineries all gave refined sugars with metals at about the same levels, despite differences in the raw sugar.

For the fact that heavy metals are no problem the cane sugar industry can be collectively thankful. However, the “safe” levels tend to decrease toward the detection limit. As more sensitive analytical methods are developed it can be expected that problems will arise. The industry must continue to monitor its products by the latest available methods to stay one jump ahead of any possible “scare” that could have catastrophic effects on sugar sales, bring stringent regulations, and precipitate major reorientation of processing.

**COLORANTS**

**Identification**

At the 1971 meeting of ISSCT Farber and Carpenter reported on the identification of several plant pigments that occur in raw and refined cane sugars. This work has been continued, and the identity of 21 of these minor constituents whose source is the cane plant is now known.

It is interesting to consider the types of compounds found: every compound contained a ring structure. The simplest structure was quinic acid, which has a saturated ring. This compound is common to many plants.
Splitting one water out of quinic acid gives shikimic acid, which is considered to be involved in the biosynthesis of aromatics.

All of the other compounds identified were aromatic. Seven of the compounds were benzoic acid derivatives or their corresponding aldehydes:

- Vanillic acid
- Vanillin
- 3,4-dihydroxybenzoic acid
- 3,4-dihydroxybenzaldehyde
- p-Hydroxybenzoic acid
- p-Hydroxybenzaldehyde
- Syringic acid

Since none of these compounds is colored, they are not considered pigments. However, these compounds do have flavor and odor, and can have deleterious effects on products made from sugar.

Six of the compounds identified were cinnamic acid derivatives and their corresponding alcohols or esters:

In addition, 3 compounds were coumarin derivatives, but coumarin can be considered the product of ring closure of o-hydroxycinnamic acid.
Three compounds were flavonols.

\[
\begin{align*}
\text{coumarin} & : R_1 \quad R_2 \\
\text{umbelliferone} & : \text{OH} \quad \text{H} \\
\text{esculin} & : \text{OH} \quad \text{O-glucose}
\end{align*}
\]

These last 3 classes of compounds are all colored, generally yellow, and are more strongly colored at higher pH. The flavonols are generally more deeply colored than cinnamic acid derivatives.

All 21 of the above compounds were found in the cane plant, 10 were found in raw sugar, and 4 in refined sugar.

The plant pigments thus far identified are undoubtedly only a small fraction of all the compounds present, many of which will surely be other derivatives in these same classes. It will be interesting to see which additional classes of plant pigments are discovered.

There are, however, 2 other types of colorants, not plant pigments, that may account for a large fraction of the sugar colorant. These are melanoidins, the reaction products of amines with reducing sugars, and caramels, the decomposition products of sucrose.

Binkley and Cookson et al. have studied these other classes of colorants extensively but still have not identified the chemical species of the colorants. They believe that other colorants are far more important than the plant pigments. The melanoidins are undoubtedly very dark, but to the refiner the most important colorants are not necessarily the most highly colored but the most difficult to remove and thus the most often found in refined sugar.

Melanoidin and caramel-type color is undoubtedly being made from sugar at all stages of processing. Anet has proposed one route in which fructose under acidic conditions forms 3,4-dideoxyglucosulose-3-ene (DGU)

\[
\text{CH}_2\text{OH}
\]

\[
\text{O}
\]

\[
\text{OH}
\]
as a precursor to 5-hydroxymethyl-2-furfural (HMF)

\[
\text{HOCH}_2\text{C}=\text{O}
\]

which in turn is a precursor to color.

The first step in this mechanism is the inversion of sucrose. The second step is the acid-type decomposition of fructose. However, this representation is vastly oversimplified, because 13 different unidentified materials that have been detected in acid fructose solutions all convert to DGU.

Anetl has also shown that this same intermediate, DGU, can be formed through the Maillard reaction in which the amine fraction splits off, leaving DGU, with the amine then free to repeat the process.

Another mechanism of colorant formation involving amines is through the formation of reductones, reviewed by Hodge. However, the exact compounds involved and the resulting colorant have not been identified.

There is another whole realm of color formation in the alkaline range which has been much studied. Fleming et all have evaluated many of the properties of the colorant and color precursors, but the exact mechanism of formation and nature of the colored products still remain elusive.

If the mechanism of the color formation could be better described or the precursors identified, then it might be possible to interrupt the mechanism to save sucrose or to otherwise react the intermediates to avoid color.

Measurement

Once some colorants are identified, the next step is to devise simple practical analytical procedures so that the compounds can be followed through processing to determine how much of a problem they actually are.

Chromatography. One obvious analytical technique is gas chromatography; however, Godshall showed as many as 80 peaks in cane sugars by gas chromatography, so that peak identification is difficult at best. By using a preliminary solvent extraction for partial separation she was able to reduce the peaks to a manageable number. Her results for 4 compounds, given in Table 2, show that these minor constituents average several ppm in raw sugar but are reduced to well below 1 ppm in refined sugar.

**TABLE 2.** Minor constituents in sugar by gas chromatography

<table>
<thead>
<tr>
<th></th>
<th>malic acid</th>
<th>parahydroxyacid</th>
<th>palmitic acid</th>
<th>oleic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw sugar A</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>raw sugar B</td>
<td>0,39</td>
<td>0,93</td>
<td>3,8</td>
<td>6,6</td>
</tr>
<tr>
<td>refined sugar C</td>
<td>&lt;0,01</td>
<td>&lt;0,07</td>
<td>&lt;0,01</td>
<td>&lt;0,07</td>
</tr>
<tr>
<td>refined sugar D</td>
<td>&lt;0,01</td>
<td>&lt;0,07</td>
<td>0,31</td>
<td>0,36</td>
</tr>
</tbody>
</table>

Fluorescence Methods. Another technique that has analytical possibilities for these minor constituents is fluorescence. Since fluorescence was used extensively in the work in which these materials were detected and identified in sugars, it would seem natural to use it to measure them. Carpenter and Wall in two
papers[17]. Explored the fluorescence in sugar solutions, defined its range, and showed that the fluorescence of many of these minor constituents coincided with the usual fluorescence of sugars. They also showed that fluorimetry was an extremely sensitive technique, far more sensitive than colorimetry for the very low concentrations.

More recently the fluorescence method has been applied directly to electrophoregrams. This technique combines the superior resolving power of high voltage electrophoresis as developed by Gross[12] with the high sensitivity of fluorescence. The sugar solution is extracted at a suitable pH and brix with a solvent selected to give substantially 100% extract of the minor component in question.

Note that this technique would not be possible if the constituent had not been identified. Identification of the constituents is a prerequisite to developing methods for their analysis.

Unfortunately there is no universal solvent or set of conditions, a different extraction has to be made for nearly every different constituent. The extracted component is run on high voltage electrophoresis,[9] and the resulting electrophoregram is evaluated with a fluorescence densitometer to obtain quantitative results.

Some results are shown in Table 3.

These results are at the same level as those obtained for different compounds by gas chromatography.

**Table 3.** Minor constituents in sugar by fluorescence densitometer

<table>
<thead>
<tr>
<th>chlorogenic acid</th>
<th>unbelliferone</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>raw sugar E</td>
<td>4.6</td>
</tr>
<tr>
<td>raw sugar F</td>
<td>3.2</td>
</tr>
<tr>
<td>raw sugar G</td>
<td>0.07</td>
</tr>
<tr>
<td>refined sugar H</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

**Floc Constituents**

Another area that may be elucidated by identification of constituents in sugar is the nature of beverage floc. The floc problem has been "solved" many times but has not been eliminated. Floc formation seems to result from a combination of several factors and conditions. As the various minor constituents are identified and brought under control the floc problem may vanish without any necessity for its real nature to ever be explained.

**Conclusion**

Around the world the specifications for refined sugars are surely going to become increasingly restrictive. Under these conditions of tightened control farmers, millers and refiners alike are all going to have to pay more attention to the complete composition of sugar, especially the minor constituents.

**References**


COMPONENTES DEL AZUCAR CRUDO QUE INFLUYEN EN LA REFINACION

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RESUMEN

Se hace una revisión del estado actual de la identificación de los componentes menores en los azúcares de caña y el efecto de estos componentes en la refinación. Los componentes que se discuten son componentes de la ceniza, incluyendo a metales pesados, colorantes y componentes floculantes. Se describen métodos de análisis para estos componentes menores y los resultados indican que se encuentran en la escala de ppm en los azúcares crus y muy por debajo de 1 ppm en azúcares refinados. Estos componentes menores llegarán a tener mayor importancia a medida que se exijan especificaciones más estrictas para el azúcar refinado y llegarán a afectar a los caficultores, los fabricantes de crudo y los refinadores.