INFRARED PHOTOMETRIC MEASUREMENT OF
THE SATURATION TEMPERATURE AND
SUPERSATURATION OF SYRUPS

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ABSTRACT

This paper describes experiments with the infrared photometric measurement of supersaturation of a sugar syrup, which is based on the fact that a scan against temperature of light transmission of seeded syrup has a minimum at its saturation temperature. The supersaturation of sugar syrup was obtained by determining its saturation temperature along with its actual temperature, and then using sucrose solubility data. The photometric measurement, while it is direct, operates in a batchwise (scanning) manner. The apparatus includes a heating stage assembly and a dedicated TP-801 computer with A/D converter for data logging and processing. It is stated that, with good equipment and a responsive thermal probe, the measurement time could be reduced to about 5 min. An examination of a variety of methods for seed preparation was carried out, and seed crystals of 38 to 75 μm, dispersed with a little surfactant and crystallization inhibitor, is found suitable. The systematic errors of the measurement are analyzed in some depth. The magnitude of these is shown to depend on the size and quantity of seed, pre-crystallization delays, thermal probe delays, etc. It is concluded that the theoretical estimate of the error in the saturation temperature could be as low as -0.5 K, implying an error in the supersaturation value of some 0.0015 units. Some theoretical aspects of the measurement are discussed. Diffusion layering is examined and considered to be helpful in amplifying the photometric discontinuity at the saturation point. The rate of change of the light transmission with temperature above the saturation temperature, i.e. the slope of the X/Y trace) is considered to be proportional to the seed number density divided by its mean size. Finally, suggestions have been made for the use of the equipment off-line, as well as for modifications of the equipment to enable on-line measurements to be made from sugar pans. If on-line measurement could be accomplished it is said to represent a major advance towards optimal control of sugar pan boiling operations.
Supersaturation is the most important control variable for sugar crystallization in vacuum pans but its direct measurement has long been an insolvable problem. Although indirect measurements based on conductivity or rheological measurements on massecuite are widely used, they cannot give the real value of concentration or supersaturation. During the 1980s some hundreds of boiling pans in China have been fitted with microcomputer-based control apparatus, but these are run to simulate good manual methods of boiling since there is a lack of direct measurement of supersaturation, both off-line and on-line. There are some laboratory methods but these are time consuming and do not present the results to the pans as voltage or current signals.

About ten years ago Wright reported on the photometric method for the determination of the saturation temperature of syrups or molasses. In this method the seeded syrups were heated past their saturation point while their light transmission characteristics were recorded against temperature on an X-Y recorder. The saturation temperatures were detected by observing transmission minimums on the scan traces (Wright). This method is a direct physical measurement of the saturation temperature. However, it is realized that the supersaturation value, related to this, is of more concern in the operation of crystallization in sugar factories.

In the present paper an infrared photometric method for measuring the supersaturation as well as the saturation temperature of the sugar syrup is described. The systematic measurement errors which are influenced by the seed crystal size, the dispersant, and by pre-crystallization are analyzed, and the detailed mechanism of the photometric measurement is discussed.

**EXPERIMENTAL METHOD**

**Apparatus**

The project was aimed at the research and development of a photometric method for determining supersaturation, using an infrared light beam transmitted through a one to three millimetre layer of syrup sample seeded with 5-20% of fine crystals (38 to 75 μm). The detail of the heating stage assembly is shown in Figure 1. The light transmission was detected with a photodetector and the sample temperature with a semi-conductive thermometer. The electrical signals from these were transmitted to a TP-801 single board computer (with a Z80 CPU chip). A schematic diagram of the measurement system is shown in Figure 2. When the seeded sample was heated it was found that the transmitted light signal decreased steadily until
the saturation temperature was reached. At this point there was an abrupt change and the signal rapidly increased. The minimum point on the trace corresponded to the saturation temperature. The computer was programmed to assign the saturation temperature \((T_{sa})\) at this point. The signals for light transmission and temperature were plotted on an X-Y recorder and monitored by a double-trace oscilloscope to see if any disturbances existed. A second temperature (signal or key-input) was supplied to the computer to represent...
the bulk temperature (I) of the syrup. After serial table checks and digital calculations, the computer output was actuated and this included:

- the saturation temperature \( T_{\text{sat}} \),
- the actual operating temperature \( T_{\text{act}} \),
- the subcooling temperature difference \((T_{\text{sat}} - T_{\text{act}})\) \( \Delta T \),
- the concentration difference (driving force for crystallization) \( \Delta C \), and
- the supersaturation coefficient \( SS \).

**Solubility theory**

Solubility theory states that the solubility coefficient of sucrose is defined as the ratio of the actual concentration \( C \) (expressed as the sucrose/water ratio by analysis) to that of the saturation concentration at the actual temperature \( T_{\text{act}} \) or \( C_s(T_{\text{act}}) \). The value \( C \) can be equated to the saturation concentration at the measured saturation temperature \( T_{\text{act}} \) or \( C_s(T_{\text{act}}) \). Supersaturation is thus a defined measurement involving the expression of two measurable variables (temperature and concentration) in two states (actual or saturated). For pure sugar syrups the two temperature measurements can be transformed into saturation concentration values using solubility expressions, such as that of Charles\(^3\), and the ratio of the two saturation concentration values is the supersaturation value.

Impurities generally change the solubility coefficient of sucrose but, with the relatively small differences between actual temperature and saturation temperature observed in pan boiling syrups, we can make the approximation that the solubility coefficient is independent of temperature. This assumption is supported by the work of Jesic\(^4\). It provides a basis for the estimation of the supersaturation of an actual boiling syrup from its actual temperature \( T_{\text{act}} \) and its saturation temperature \( T_{\text{sat}} \), using the same transform to saturation concentrations and the ratio of the latter exactly as if the syrups were pure sucrose.

**Experimental results**

The sugar syrup or massecuite was sampled from the vacuum pan and placed into the sample cell and mixed with a small amount of specially prepared seed without the introduction of air bubbles. A cover glass was then positioned and the cell placed in the heating stage. The special lid (with the centrally-mounted phototransistor) was added and the measurement sequence commenced.

It was found best to sieve the dry sugar powder before use, collecting the fractions \( 150 - 75 \) + 38 \( \mu \)m in size. This fraction was blended with a little dispersant to form a fondant paste. The dispersant served to assist the blending of the seeds into the syrup sample and had to be chosen to have
no significant effects on sucrose solubility. A dispersant which inhibits pre-crystallization but not dissolution, such as caramel, gives an added advantage. Traces from measurements made with a variety of dispersants are shown in Figure 3a to 3d. Computer outputs are attached to most of the traces; these should need no further interpretation. The syrups were previously equilibrated at the temperature indicated by the dotted lines on the traces. The dotted lines thus approximately indicate the saturation temperature. Acetylacetone was found to be a good dispersant, as were some surfactants with a little caramel mixed in.

Another group of measurements was made in which seeds of different size fraction were used. The range covered was 38 to 250 μm size. Traces from these measurements are shown in Figure 4. Traces made with coarse seeds were too flat to give a definite light transmission peak. The sensitivity of the response improved as the seed size was reduced, and the fraction 75 + 38 μm size was found to give the best trace. The error due to the Gibbs-Thompson "enhanced solubility" effect, as discussed below, is still insignificant for the latter seed size.

Error analysis

The measurement errors on the saturation temperature, which contribute to the errors of the supersaturation estimate include:

(a) that due to the Gibbs-Thompson (enhanced solubility) effect,
(b) that due to pre-crystallization of the sample during the measurement
(c) that due to temperature lags in the probes, and
(d) random error arising from analogue to digital conversion.

Enhanced solubility error

With respect to error (a), an analysis of the saturation temperature depression due to the enhanced solubility of the small seed crystals (Qin²) showed that this is approximately given by the value $8.67 \times 10^3 T_{sa} L^2$, where $T_{sa}$ is the true saturation temperature (in K) and $L$ is the mean seed size (in μm).
FIGURE 3. Some measurement traces showing the effect of the choice of dispersant.
Thus, for a seed size greater than 30 μm the temperature depression is less than 0.01 K. An error of 0.1 K (just large enough to become noticeable) would not occur until the seeds were less than 3 μm in size. This error tends to underestimate the true saturation temperature.

Pre-crystallization error: In literature on crystal nucleation, it is sometimes stated, without reference to the subcooling temperature, that a 10% error in the growth rate constant relating growth rate per unit area to the subcooling temperature ΔT, and F is the surface area of the fine seed crystals per unit mass of syrup. This error tends to underestimate the true saturation temperature.

For pure sucrose solutions at 343 K (70°C) and 5% by mass of seed of average size 38 μm, the expression for error (b), becomes $\Delta T \left[ e^{0.0097X} - 1 \right]$. With a subcooling of 20 K and a holding time of 15 min, the error due to pre-crystallization is estimated from this expression to be −0.05 K. With impure solutions the crystal growth rate constant $k$ is considerably reduced. As well, the average time and extent of subcooling during a typical measurement is less than the conditions considered above. All these factors would tend to reduce the magnitude of error (b) to below 0.05 K. A smaller size seed would increase the error in inverse proportion, as the crystal surface area is increased. This effect could be partly compensated for by reducing the amount of seed addition when using finer seed. On the other hand, the expressions above are based on the supposition that the solution around the crystals is of uniform concentration. The existence of a diffusion layer which has a lower concentration than that of the bulk solution will tend to inflate the pre-crystallization error.

Thermal probe error

Error type (c), that due to the lag in the sample probe temperature measurement while the temperature is rising at the measurement rate (0.5 to 2 K/min), can be appreciable and must be minimized by use of a low thermal mass type of thermocouple. With careful design (e.g. the use of a bare fine wire thermocouple junction) it can be reduced satisfactorily. This error tends to underestimate the true saturation temperature.

A/D Conversion error

Error type (d) is a random type, and would be a maximum of about 0.2 K if an eight-bit converter is used, scaling between 323 and 373 K (50 and
100°C). Use of a converter of a 12 bit (or higher) type would effectively eliminate this error.

**Summary of errors**

Other errors would involve the stability of the infrared source and photodetector, the presence of air bubbles (which tend to move, expand and change the light transmission unpredictably) and the effect of the seed dispersant.

In summary, most of the predictable errors tend to cause an underestimation of the saturation temperature. Pre-crystallization error could become important if a heavy seeding of ground slurry (5 μm) seed was used in high purity syrup, but this is not necessary and can be avoided. It is probably true that, with good technique, the cumulative underestimation error could be less than 0.5 K. The corresponding error in supersaturation coefficient would be about 0.003 times this, or 0.0015 units. It is anticipated, however, that the earlier assumption of “constant solubility coefficient with temperature for impure syrups” is not exact and would cause a larger error in the supersaturation estimation than this experimental error.

**Role of the Diffusion Layer**

The photometric method is based on the detection of the minimum value of the light transmission through seeded syrups as they are heated past their saturation temperature. When the diffusion layers around individual sugar crystals were observed with holographic interferometry it was found that the thickness of the layers changed markedly near the saturation point. This is shown for one set of observations in Figure 5. Because the layers distort the passage of light, acting as a lens with large curvature, they reduce the passage of light during the pre-crystallization phase and tend to increase it in the dissolution phase of the measurement. Thus the diffusion layer effect reinforces the photometric characteristics at the saturation point.

**Crystal Size and Number Density**

The transparency of the sample to infrared light is determined by its crystal content and syrup color for constant dimensions of the sample cell. When the sample temperature exceeds the saturation point the major mechanism of the observed increase in light transmission relates to the dissolution of the seed crystals. Qin considers that the rate of change with temperature (above the saturation temperature) of the light intensity absorbed by the crystal seed would be proportional to its effective surface area. Thus the slope of the X/Y trace above saturation would be proportional to the seed surface area,
FIGURE 5. Changes in the diffusion layer checked with holographic interferometry.
which in turn is proportional to the seed number density divided by the seed size $L$. This relationship may prove to be useful in some industrial applications of the photometric method in the future.

**Possibilities for on-line supersaturation measurement**

Sugar technologists have long searched for a direct measurement of the supersaturation of boiling syrup for improved crystallization control. As an off-line device the present photometric method makes it possible to determine saturation temperature and to estimate supersaturation. This would be useful as a research tool for the determination of seeding points for graining operations and for occasional characterization of other established on-line measurements such as conductivity or viscosity. However, the photometric method would be very much more useful if it could be adapted for on-line use on sugar vacuum pans.

For on-line applications the following factors need to be taken into consideration:

(a) A system for drawing a partly screened sample of mother liquor from the pan has to be designed,

(b) During the test the syrup sample extracted from the pan needs to be heated past the point of saturation. This would normally cause boiling if the sample was under the same vacuum as in the pan. Therefore the test measurement has to be done with a higher absolute pressure in the sample cell, and

(c) An addition of fine seed has to be made to the syrup sample. Care would have to be taken that the seed crystals are re-dissolved before the syrup sample is allowed to return to the pan, otherwise the fine grain would contaminate the pan.

One tentative idea for an on-line measurement system is shown in Figure 6. Syrup is continuously extracted from the pan, using a small pump and normally returns to the pan using a bypass loop. A computer controls two valves which allow a sample of the syrup to be injected with seed and pushed into the test stage. A computer-controlled photometric measurement is then taken. Any seeded syrup is reheated to dissolve the seeds before it is returned to the vacuum pan.
FIGURE 6. A possible arrangement for an on-line photometric supersaturation measurement.
SUMMARY AND CONCLUSIONS

The infrared photometric measurement of supersaturation of a sugar syrup is based on the fact that light transmission of syrup has a minimum at its saturation temperature. The supersaturation of sugar syrup can be obtained by determining its saturation temperature along with its actual temperature, and then using sucrose solubility data. The influence of impurities on this calculation can be disregarded if the solubility coefficient of the solution does not vary over the temperature range.

The photometric measurement, while it is direct, operates in a batchwise (scanning) manner. With good equipment and a responsive thermal probe it is considered that the measurement time could be reduced to about 5 minutes. After an examination of a variety of methods for seed preparation it is concluded that seed crystals of 38 to 75 µm are suitable, and these are best dispersed with a little surfactant and crystallization inhibitor (such as caramel) before addition to the measurement sample.

The apparatus requires a dedicated computer with A/D converter for data logging and processing. In the experiments described in this paper a TP-801 (Z-80 based) single board computer was used.

The systematic errors of the measurement have been analyzed in this paper. The magnitude of these depend on the size and quantity of seed, pre-crystallization delays, thermal probe delays, etc. It is considered that, with good equipment, the error in the saturation temperature could be as low as 0.5 K, leading to an error in the supersaturation value of some 0.0015 units.

Diffusion layering has been examined and considered to be helpful in amplifying the photometric characteristics at the saturation point. The rate of change of the light transmission with temperature above the saturation temperature (i.e. the slope of the X/Y trace) is considered to be proportional to the seed number density divided by its mean size. Finally, suggestions have been made for modifications of the equipment to enable on-line measurements to be made during sugar boiling operations. If on-line measurement could be accomplished it would represent a very considerable advance towards optimal control of sugar vacuum pans.

ACKNOWLEDGMENTS

The assistance of Dr. P. G. Wright of the Sugar Research Institute, Mackay, Australia, in preparing and editing this paper is gratefully acknowledged.
REFERENCES


NOMENCLATURE

\( C_s(T) \): saturation concentration at temperature \( T \),

\( C_s(T)_{sat} \): saturation concentration at temperature \( T_{sat} \),

\( C_s(T)_{act} \): saturation concentration at temperature \( T_{act} \),

\( \Delta C \): concentration difference,

\( F \): surface area of seed crystals per unit mass of syrup,

\( G \): growth rate constant, \( \text{mg} \text{ m}^{-2} \text{kg}^{-1} \text{min}^{-1} \),

\( H \): seed crystal mean size, \( \text{mg} \text{ m}^{-2} \text{kg}^{-1} \text{min}^{-1} \),

\( K \): supersaturation, ratio of \( C_s(T_{sat}) \) to \( C_s(T_{act}) \),

\( L \): temperature,

\( N \): seed crystal number,

\( T_{act} \): actual temperature,

\( T_{sat} \): saturation temperature,

\( DT \): subcooling temperature,

\( X \): time interval, \( \text{min} \).

The document contains references and nomenclature related to sugar syrup and crystallization processes.
MESURES PHOTOMETRIQUES DANS L'INFRAROUGE POUR MESURER LA SRSATURATION ET LA TEMPERATURE DE SATURATION DES SIROPS

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On décrit des expériences photométriques en infrarouge pour la mesure de la sursoaturation des sirops sucrés, basée sur l'observation que la relation entre la temperature et la lumière transmise à travers un sirop ensemencé avec des petits cristaux, montre un minimum à la temperature de saturation. La sursoaturation du sirop est obtenue en servant de la temperature de saturation à la temperature de mesure, en comparaison avec les mesures de solubilité du saccharose. La mesure photométrique quoique directe, opère d’une manière discontinue. L’appareil comprend un élément chauffant et un ordinateur TP801 qui permet de recueillir et de manipuler les mesures. Avec un bon équipement et une sonde de temperature sensible, la mesure prend 5 min seulement. Une étude des méthodes pour l’ensemencement a montré que les cristaux doivent mesures 38 μm. Ils sont dispersés en servant d’une petite quantité de surfactant d’un produit pour empêcher la cristallisation. Les erreurs systématiques de la mesure sont analysées. Leur grandeur dépend de la grosseur et de la quantité des cristaux d’ensemencement, des délais de la pré-cristallisation, des délais causés par le capteur de temperature etc. On conclut que l’erreur théorique pour la temperature de saturation pourrait être seulement -0.5K, ce qui indique que l’erreur de la sursoaturation ne serait que de 0.005 unité. Des aspects théoriques de la mesure sont discutés. La diffusion en couche est examinée et peut servir pour amplifier la discontinuité photométrique à la saturation. La vitesse à laquelle la transmission de la lumière change en relation avec la temperature, en dessous de la temperature de saturation c’est à dire la pente de la graphique X/Y, est considérée comme étant proportionnel au nombre de cristaux d’ensemencement, divisé par la grandeur moyenne des cristaux. Des suggestions sont proposées pour que l’équipement soit utilisé en laboratoire et sur des cuves industrielles. Si cela est possible, cette technique deviendrait un outil très important pour le contrôle des cuves.
RESUMEN
Este escrito describe experimentos con fotometría infrarroja para medir la sobresaturación de melados de azúcar, basado en el hecho de que la observación del cambio de transmisión de luz de melados semillados tiene un mínimo a su temperatura de saturación. La sobresaturación de melados de azúcar fue obtenida, determinando la temperatura de saturación en conjunto con su temperatura actual y entonces utilizando la data de solubilidad de azúcar. La medida fotométrica es directa pero opera de una forma similar a la muestra. El aparato incluye una etapa de calentamiento y una computadora delidada estilo TP-801, con un convertidor A/D para adquisición de data y procesamiento. Se espera que con buen equipo y un sensor termico de respuesta rapida el tiempo de medida se pueda llevar a 5 minutos. Un examen de varios métodos para preparación de semilla fue realizado, y cristales de semilla de 38 a 75 μm mezclados con surfactante y inhibidor de cristalización se consideró satisfactorio. Los errores sistemáticos de las medidas fueron analizados en profundo. La magnitud de los cuales depende en la cantidad y el tamaño de la semilla, retardos en pre-cristalizacion, demoras en el sensor termico, etc. Se concluye que el probable error teórico en la temperatura de saturación puede ser tan bajo como de -0.5 K, esto implica un error en el valor de sobresaturación de 0.0015 unidades. También se discuten algunos aspectos teóricos del sistema de medida.