LABORATORY MANUAL FOR AUSTRALIAN SUGAR MILLS

VOLUME 1

THE STANDARD LABORATORY MANUAL FOR AUSTRALIAN SUGAR MILLS

VOLUME I
PRINCIPLES AND PRACTICES

BUREAU OF SUGAR EXPERIMENT STATIONS
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PREFACE

THE STANDARD LABORATORY MANUAL FOR AUSTRALIAN SUGAR MILLS

The Division of Sugar Mill Technology was created in 1929 and one of the early duties of divisional staff was to introduce a definite plan for mill control. Such a scheme was not possible at that time due to the confusion of methods employed and the lack of specific standards.

In 1930, Mr Norman Bennett (then Mill Technologist) instituted the Mutual Control scheme to which the majority of Queensland mills voluntarily subscribed. Subsequently, all mills in Queensland and in New South Wales became involved in the scheme.

Later, the Division undertook the calibration of all glassware used by the industry in order to assist mills in obtaining standardised equipment. At the present time, only measuring instruments that are certified by BSES to be within the required limits of accuracy can be used for the determination of the brix, pol and fibre content of cane for payment purposes.

This combination of standardised methods and properly calibrated instruments has directly or indirectly contributed to the high standard of milling efficiency achieved by Australian mills.

During the past 14 years, since the fifth edition of the Laboratory Manual for Queensland Mills was published, the technology of the cane sugar industry has changed considerably. Many new items of apparatus have been introduced into sugar mill laboratories and analytical methods and techniques have been modified to take advantage of this improved equipment. A revision of the Manual is therefore timely and it has been produced in a format different from that of previous editions. As well as the obvious change to A4 size paper, the manual is being produced in two volumes.

Volume I — Principles and Practices includes, as its title implies, the text book section of the old manual. The present manual has been enlarged to cover techniques and instruments such as chromatography and the 'electronic' balance. The text has been extensively reviewed and updated and should remain current for a number of years.

Volume II — Analytical Methods contains a description of the analytical methods and the reference tables. For ease of use in the laboratory, the methods are set out in the standard format recommended by the International Commission for Uniform Methods of Sugar Analysis. Methods have been reviewed and have been brought up to date wherever required.

Since the Manual has been prepared using computer methods, updating of copy will be a simpler task than in the past. This has been done with a view to making more frequent revisions of the text, particularly of the volume containing the analytical methods.

The responsibility for reviewing the last edition of the Laboratory Manual for Queensland Sugar Mills and preparing the text for this publication was accepted by a group comprising:

Mr P. G. Atherton	BSES
Mr D. H. Foster	Sugar Research Institute
Mr L. K. Kirby	BSES
Mr J. B. Lee	CSR Limited
Mr A. P. Saranin	The Central Sugar Cane Prices Board
Mr B. D. Sockhill	Pioneer Sugar Limited

Assistance with writing and checking of various sections of the text has been given by a number of members of staff of BSES, Sugar Research Institute and CSR Limited. Staff from CSIRO Central Measurement Laboratory assisted with reviewing several chapters and the Committee is particularly grateful to Dr David Prowse who completely revised the chapter on analytical balances.

BSES Publications Officer, Mr P. J. Knight, was responsible for supervising the production of the Manual after the Committee had reached consensus on the text.

As well as these contributors, thanks are due to the distributors of laboratory apparatus and equipment who provided illustrations for some sections of the text.

Owen W. Sturgess,
Director of Sugar Experiment Stations.

INSTRUMENTATION

In this Manual, reference has been made to equipment supplied by specific manufacturers and a number of illustrations of this equipment are included.

This must not be construed as a recommendation for that particular instrument as these references have been employed only to illustrate certain features or principles of operation.

CHAPTER I

DEFINITIONS

WHILE the majority of definitions from the previous edition have been carried forward, several general terms which have recently come into prominence and some of the more important definitions associated with milling, diffusion and waste water treatment have been added.

ABSOLUTE JUICE

All the solids in solution in the cane, together with all the water in the cane:

i.e. absolute juice = cane − fibre.

ABSOLUTE TEMPERATURE (Kelvin, K)

This is temperature referred to absolute zero. The unit of absolute or thermodynamic temperature, the kelvin, is defined in terms of the triple point of water. It is related to Celsius by the following equation:

$$K = °C + 273.15$$

It should be noted that the degree sign is not used with the kelvin scale.

APPARENT

The word apparent is applied to figures and analyses based on brix and pol, as distinct from dry substance and sucrose, for example, apparent purity. Brix and pol analyses are still used by many mills for factory control purposes, and unless a specific instance arises where pol and brix have to be divorced from sucrose and dry substance, the term 'apparent' is often omitted.

ASH

Carbonated ash: The residue remaining after incineration at 450° C.

Conductometric ash: The conductometric ash of a product is the figure arrived at by correlating the specific conductance of the solution of that product with its sulfated ash.

Sulfated ash: The residue remaining after incineration at the specified temperature or temperatures of a sample which was pretreated with sulfuric acid.

Ash % impurities: The calculated ash expressed as a percentage of dry, non-sucrose impurities in the sample.

$$\text{Ash \% impurities} = \frac{\text{ash}}{100 - (\text{sucrose} + \text{water})} \times 100$$

BACK ROLLER JUICE

The juice expressed between the top and delivery rollers of *ANY* mill of a tandem. The term is synonymous with last expressed juice only when it refers to the last mill of a tandem.

BAGACILLO

Very small particles of bagasse separated either from preclarification juices or from the final bagasse for filtration or other purposes.

BAGASSE

The residue after extraction of juice from cane in one or more mills. Hence the terms, *first mill* bagasse, *second mill* bagasse etc. and in the case of the last mill *final* bagasse or simply *bagasse*, are used.

BOD (Biochemical oxygen demand)

The amount of oxygen required to oxidise biologically the organic matter in a waste stream, over a stated period of time, under standard conditions.

BRIX

The brix of a solution is the concentration (in g solute per 100 g solution) of a solution of pure sucrose in water, having the same density as the solution at the same temperature. If refractive index be adopted as an alternative basis of comparison the value derived should be termed *refractometer brix*.

Obviously, for solutions of pure sucrose in water, the brix is equal to the dry substance, but in the presence of soluble impurities this may not be, and usually is not the case. Although gases and insoluble solids in suspension may alter the density of a solution the term brix refers exclusively to soluble solids.

CANE

The raw material delivered to the mill, including clean cane stalk, trash, tops, and any other extraneous matter.

Clean cane stalk: Cane which has been cut above the highest subterranean roots; has been topped below the level of the growing point; has no leaves or adhering foreign matter and has not died and dried out.

Extraneous matter: Any solid material delivered with cane stalk, including dead and dried out stalks, dirt, roots, trash and tops.

Cane tops: The portion of the stalk above the natural breaking point, plus all green leaves and sheaths attached to that part of the stalk.

Trash: Leaves and sheaths delivered with the cane stalk.

CANE SUGAR

Sucrose, the pure chemical compound with the formula $C_{12}H_{22}O_{11}$.

C.C.S. (Commercial cane sugar)

The estimated yield of cane sugar from sugarcane, determined as prescribed in the Regulation of Sugar Cane Prices Act and the Regulations made thereunder.

$$\text{Commercial cane sugar} = \text{pol in cane} - \frac{\text{impurities in cane}}{2}$$

where

$$\text{Impurities in cane} = \text{brix in cane} - \text{pol in cane}$$

$$\text{Brix in cane} = \text{brix in first expressed juice} \times \left(\frac{100 - (\text{fibre} + 3)}{100}\right)$$

$$\text{Pol in cane} = \text{pol in first expressed juice} \times \left(\frac{100 - (\text{fibre} + 5)}{100}\right)$$

Historically, the c.c.s. formula was originally enunciated by Dr Gustav Kottmann of the Colonial Sugar Refining Company Limited (today CSR Limited) around 1888. The formula estimated 'pure obtainable cane sugar' or POCS. The formula was based on four assumptions:

(i) that 25% of the soluble impurities in cane is removed by clarification;

(ii) that the remaining 75% of the soluble impurities is eliminated in molasses;

(ii) that the molasses is exhausted to 40 true purity;

(iv) that there is no loss of sucrose in manufacture other than in molasses.

It can readily be calculated that, if X is the amount of impurities entering the factory, 0.75 X will carry with it 0.5 X of sucrose at 40 true purity.
So, theoretically:

$$\text{Recoverable sucrose} = \text{sucrose entering} - \frac{\text{impurities}}{2}$$

In practice, the recovery is affected by both the content and the nature of the impurities present.

The 3 and 5 factors which are used in the expressions to determine the brix and pol in cane from the analysis of first expressed juice were also developed by Kottmann. These were the rounded figures obtained after averaging trial data from mills operating in Kottmann's time.

CLARIFIED JUICE

Juice which has passed through the clarifiers. This juice is fed to the evaporators and as such can also be referred to as *effet supply juice* or *ESJ*.

COD (Chemical oxygen demand)

The amount of oxygen required to oxidise chemically the organic impurities in a liquid waste stream.

COEFFICIENT OF WORK

The percentage ratio of the weight of 94 n.t. sugar produced to the weight of c.c.s. in the cane from which the sugar was derived. So:

$$\text{Coefficient of work} = \frac{\text{tonnes 94 n.t. sugar made}}{\text{tonnes c.c.s. in cane}} \times 100$$

(A discussion on this formula is contained in the chapter entitled *'Calculations involved in chemical control'*.)

COMPRESSION RATIO (MILLING)

The no-void volume of original cane, divided by the volume occupied by the bagasse (or cane) at the conditions being considered.

CONDENSATE

Water which has been condensed, either from vapour liberated from boiling juice, or from steam.

CONDUCTOMETRIC ASH — See ASH.

CRYSTAL CONTENT

The percentage by weight of crystalline sugar present in a massecuite, magma or similar material.

CYCLONE PURITY OF MOLASSES

The purity of the mother liquor extracted from a sample of massecuite. The mother liquor sample is usually obtained by a pressure filtration process and is referred to as *pressure filter molasses* or *PFM*.

DEWATERING MILL(S)

Milling unit(s) immediately following the diffuser and from which the extracted juice is returned directly to the diffuser. This juice is called 'press juice'.

DEXTRAN

A high molecular weight polysaccharide formed by the action of certain species of bacteria, mainly leuconostoc mesenteroides, on sucrose.

DIFFUSION

A time dependent process of pol extraction relying chiefly on countercurrent washing. It may be either cane or bagasse diffusion.

DILUTION INDICATOR (DI)

A factor used to forecast the keeping and handling quality of raw sugar. It is the ratio of moisture to impurities expressed as a percentage.

$$\text{Dilution indicator} = \frac{\text{moisture}}{100 - (\text{pol} + \text{moisture})} \times 100$$

A value of dilution indicator below 40 is considered satisfactory, for values between 40 and 50 the keeping quality of the sugar is doubtful, while for values above 50 the probability of deterioration is considerable.

DILUTION WATER

The quantity of added imbibition or maceration water which is present in mixed juice. Dilution water is usually expressed as *dilution % first expressed juice.*

DRAFT

The ratio of the mass flow rate of diffuser juice to the mass flow rate of cane or bagasse subjected to diffusion. In the case of a cane diffuser, draft is the ratio of mixed juice to cane.

$$\text{Draft} = \left(1 - \frac{F_i}{F_o}\right) + M \times F_i$$

where F_i = fibre fraction of material entering the diffuser (cane or bagasse) In cane diffusion, F_i = fibre fraction in cane

F_o = fibre fraction of final bagasse

M = maceration water applied per unit fibre.

DRY SUBSTANCE

The weight of material remaining after drying the product examined under specified conditions, expressed as a percentage of the original weight. The determination of dry substance represents an attempt to measure the *total solids*, both soluble and insoluble, or, in the absence of insoluble solids, *the total soluble solids*. The degree of accuracy achieved depends upon the constitution of the sample and the drying technique.

ESCRIBED VOLUME

The volume escribed by a pair of mill rollers in a given time. Escribed volume is equal to the roller length multiplied by the work opening multiplied by the surface speed of the rollers.

EXPECTED PURITY (SRI)

A formula derived to postulate an attainable standard of exhaustion for any given sample of final molasses.

$$\text{Expected purity} = 40.67 - 17.80 \log x$$

where x = reducing sugar/ash ratio; reducing sugars being measured by the method of Lane and Eynon and ash by double sulfation.

EXTRACTION (POL)

The percentage of pol extracted from the incoming material by a diffuser or by a train of mills either individually or cumulatively. Analogous definitions apply to *sucrose extraction, brix extraction,* and *juice extraction,* the juice, in the case of the last mentioned, being undiluted juice.

EXTRANEOUS MATTER - See CANE.

FIBRE

Technically, fibre is the dry, water-insoluble matter in the cane. For commercial purposes a standard method of determination of fibre % cane is specified.

FILLING RATIO

A term used in milling calculations to define the ratio between the no-void volume of fibre passing between a pair of rollers in a given time, and the escribed volume for the same period of time. Filling ratio is actually volumetric coefficient divided by fibre density.

FILTER CAKE

The washed residue discharged from mud filters.

FILTRABILITY

The filtrability of a raw sugar is measured by comparing the filtration rate of the sugar with that of a standard sucrose solution under specified conditions. The result is expressed as a percentage of the filtration rate of the standard sugar.

FILTRATE

Liquid separated from filter cake at the mud filters and returned to process.

FIRST EXPRESSED JUICE

The juice expressed by the feeding devices and the first two rollers of the first three-roller mill of a milling tandem. For cane payment purposes it is defined as the aggregate of all juice expressed at or before the feed opening of the first three-roller mill including all the juice extracted by the feeding devices.

HYGROSCOPIC WATER

The brix-free water adsorbed by cane fibre, the amount of which varies with the condition of the solution with which the fibre is in contact. For sugar solutions of low brix and at normal temperatures, such as those experienced in bagasse analysis, hygroscopic water is assumed to be 25% on fibre.

IMBIBITION

The process whereby water or juice is added to bagasse to dilute the juice contained therein.

IMPURITIES (SOLUBLE)

A collective term for all substances other than sucrose present in the total soluble solids contained in a sample; sometimes expressed as a percentage of the whole material, as in the c.c.s. formula, and sometimes as a percentage of the total soluble solids as in:

$$\text{Impurities} = 100 - \text{purity}.$$

INVERT SUGAR

The equimolecular mixture of glucose and fructose which results from the hydrolysis or inversion of sucrose.

LAST EXPRESSED JUICE

The juice expressed between the top and delivery rollers of the final mill in a tandem.

MACERATION

The process in which the bagasse is steeped in an excess of water or juice, generally at a high temperature. The water added for this purpose is termed maceration water.

MAGMA

A mixture of sugar crystals with a liquid such as syrup, juice or water.

MASSECUITE

The mixture of sugar crystals and mother liquor discharged from a vacuum pan. Massecuites are classified according to descending purity as first, second, etc., or A, B, etc.

MILLING LOSS

The percentage ratio of pol in bagasse to fibre in bagasse.

MIXED JUICE

The mixture of juices leaving the milling train or a cane diffuser for further processing.

MOLASSES

The mother liquid separated from a massecuite. It is distinguished by the same term as the massecuite from which it was extracted.

MUD SOLIDS

Insoluble matter other than bagacillo in clarifier mud, filter cake and associated materials.

NET TITRE

An empirical figure used to determine the value of raw sugar to a refiner. The equation used is intended to compensate for the presence of reducing sugar and ash which reduce refined sugar yields, and reads as follows:

Net titre (n.t.) = pol − reducing sugars − (5 × ash)

In Australia sugars of various qualities are reduced to a common basis of 94 n.t. by the formula:

$$\text{Tonnes 94 n.t. sugar} = \text{tonnes actual sugar} \times \frac{\text{actual n.t.}}{94}$$

NORMAL WEIGHT

That weight of pure sucrose which, when dissolved in water to a total volume of 100 mL at 20° C, gives a solution reading 100 degrees of scale when examined in a saccharimeter, in a tube 200 mm long, at 20 °C.

The normal weight according to the International Sugar Scale is 26.000 g weighed in air with brass weights.

NO-VOID VOLUME

The volume of cane (or bagasse) calculated on the basis that it consists of juice and fibre only i.e. that all air and/or other gas has been removed.

OTHER ORGANIC MATTER (OOM)

The sum of the constituents of raw sugar other than pol, reducing sugars, ash and water:

i.e. OOM = 100 - (pol + reducing sugars + ash + water).

POL

The pol of a solution is the concentration (in g solute per 100 g solution) of a solution of pure sucrose in water having the same optical rotation as the sample at the same temperature. For solutions containing only pure sucrose in water, pol is a measure of the concentration of sucrose present; for solutions containing sucrose and other optically active substances, pol is the algebraic sum of the rotations of the constituents present.

POL IN OPEN CELLS (POC)

The percentage of broken cells in a sample of prepared cane, as determined by a standard method of analysis.

PRIMARY JUICE

All the juice extracted without dilution.

PRIMARY MUD

The underflow discharged from a clarifier prior to the addition of bagacillo.

PURGING EFFICIENCY

A term indicating centrifugal performance. It is the percentage ratio of impurities leaving in molasses to the impurities entering in massecuite.

PURITY

Two classes of purity — *apparent* and *true* purity — are recognised. Ideally, purity is the percentage of sucrose in the total solids in a sample. The purities mentioned above are derived as follows:

$$\text{Apparent purity} = \frac{\text{pol} \times 100}{\text{brix}}$$

$$\text{True purity} = \frac{\text{sucrose} \times 100}{\text{dry substance}}$$

The term purity alone generally signifies apparent purity.

REABSORPTION FACTOR

The ratio between the no-void volume of bagasse leaving a mill opening in a given time, and the escribed volume for the opening, over the same period of time.

RECOVERY

The ratio of sucrose actually recovered to that entering, expressed as a percentage. Overall recovery is the percentage ratio of pol actually recovered in sugar to total pol entering in cane.

REDUCED EXTRACTION

A formula used to express normal mill extractions on a common basis of 12.5% original fibre in cane. The formula is usually expressed in the general form:

$$\text{Reduced extraction} = 100 - \frac{(100 - \text{extraction})(100 - \text{fibre})}{7 \times \text{fibre}}$$

REDUCING SUGARS (RS)

The reducing substances in cane and sugar products calculated as invert sugar. The most familiar examples of sugars having reducing power are glucose (dextrose) and fructose (laevulose).

REDUCING SUGAR/ASH RATIO

The ratio between reducing sugars and ash.

REFRACTOMETER BRIX - See BRIX.

REMELT

A solution of low grade sugar in either syrup, clarified juice or water.

RESIDUAL JUICE

The juice left in bagasse after milling.

SEED

Fine sugar crystals, generally suspended in a liquid medium, in which case the mixture is known as *seed slurry*. Seed is used either to provide the crystal surface for deposition of sucrose, or to promote spontaneous crystal formation from a super-saturated solution. The latter is referred to as *shock seeding*.

SET OPENING

The distance between the tips of the teeth of a pair of rollers. Where the roller teeth are set in mesh, this distance will be negative.

STATISTICAL TERMS

See introduction to Volume II 'Analytical methods'.

SUCROSE

The pure chemical compound with the formula $C_{12}H_{22}O_{11}$. This is commonly referred to in the industry as pure cane sugar.

SUGAR

The crystals of sucrose, together with any adhering molasses, as recovered from the massecuites. The various grades are commonly identified in terms of the grade of massecuite processed, or in terms of the avenue of disposal of the sugar — so: A sugar, C sugar, shipment sugar.

SUSPENDED SOLIDS

Insoluble solids in juice or other liquid, removable by mechanical means.

SYRUP

The concentrated sugar solution leaving the evaporators.

TOTAL DISSOLVED SOLIDS (TDS)

The quantity of dissolved material present in a sample of water, as determined gravimetrically by oven drying.

TOTAL SUGARS

The combined percentages of sucrose and reducing sugars in a sample.

TURBIDITY

A measure of the material in suspension in a sugar solution as determined by a spectrophotometer.

UNDILUTED JUICE

The juice expressed by the mills or retained in the bagasse, corrected for dilution water. For purposes of calculation the brix of the undiluted juice is taken to equal that of the primary juice, or in Queensland, the first expressed juice.

VISCOSITY

The viscosity of a fluid is a measure of the internal friction of a fluid in motion. The unit of dynamic viscosity is the pascal second (Pa.s) which is the viscosity of a fluid for which a tangential force of one newton applied over an area of one square metre produces a laminar flow with a shear rate of one reciprocal second. For a newtonian liquid the viscosity is constant at all shear rates. For a non-newtonian liquid, viscosity will vary depending on shear rate.

VOLUMETRIC COEFFICIENT

A term used to designate the fibre loading of a mill opening. It is quoted as kilograms of fibre per cubic metre of escribed volume.

WORK OPENING

The mean opening between a pair of mill rollers. This opening takes into account the set opening and the allowance for mill grooving. No allowance is made for juice grooves, but where a dirty top roller is employed, this must be taken into account.

WORK RATIO

Where a three-roller mill has rollers of equal circumference rotating at a common speed, this ratio is the ratio between the feed work opening and the delivery work opening. Where openings with rollers of different diameter or different peripheral speed are to be compared, it is necessary to calculate the ratio from the two escribed volumes.

CHAPTER II

OPTICAL INSTRUMENTS

In general, the optical properties of sugar solutions afford rapid and convenient methods for their analysis. The dependence of refractive index on the concentration of dissolved solids (brix) and of optical rotation on the concentration of sucrose (pol) has led to the widespread use of the refractometer and polarimeter (saccharimeter) in the sugar industry. Other optical instruments in general use include the spectrophotometer, which is used mainly for concentration and turbidimetric determinations, and the microscope, which finds many uses, for example in the examination of raw sugar for grain quality. In this chapter a detailed description of each of these instruments is provided.

PROPERTIES OF LIGHT

The propagation of light, or electromagnetic radiation, can conveniently be described as a transverse wave. The latter may be represented as a set of points that oscillate in the same plane across an axis such that at any instant they follow a sine function that intersects the axis. The wave motion generated by this oscillation is similar to that which travels along a rope or string when one end is suddenly jerked sideways. The oscillating points of the transverse wave can be taken to describe the vibration of the electric vector of light. Light also has a magnetic vector which vibrates in phase with the electric vector, and in a plane which is perpendicular to that of the electric vector and to the direction of travel. However, it is the electric vector which affords light its properties which are of interest in this chapter. The principle of a light wave is illustrated by reference to Figure II-1.

The distance AB in Figure II-1 represents the amplitude of the wave. The intensity of the wave as perceived by the eye or other detector is proportional to the square of the amplitude. The distance CD, which represents one complete oscillation of the electric vector (E) is known as the wavelength and is denoted by the symbol λ. Wavelengths are normally expressed in nanometres (1 nm = 10^{-9} m) or angstroms (1 Å = 10^{-10} m). Under the SI system the nanometre is the correct unit. The number of complete oscillations per second is the frequency, denoted by ν and measured in hertz, Hz (cycles per second). Therefore, the velocity (v) at which the wave advances is given by

$$v = \nu\lambda$$

Ordinary visible white light is a combination of all wavelengths in the approximate range 400 to 700 nm.

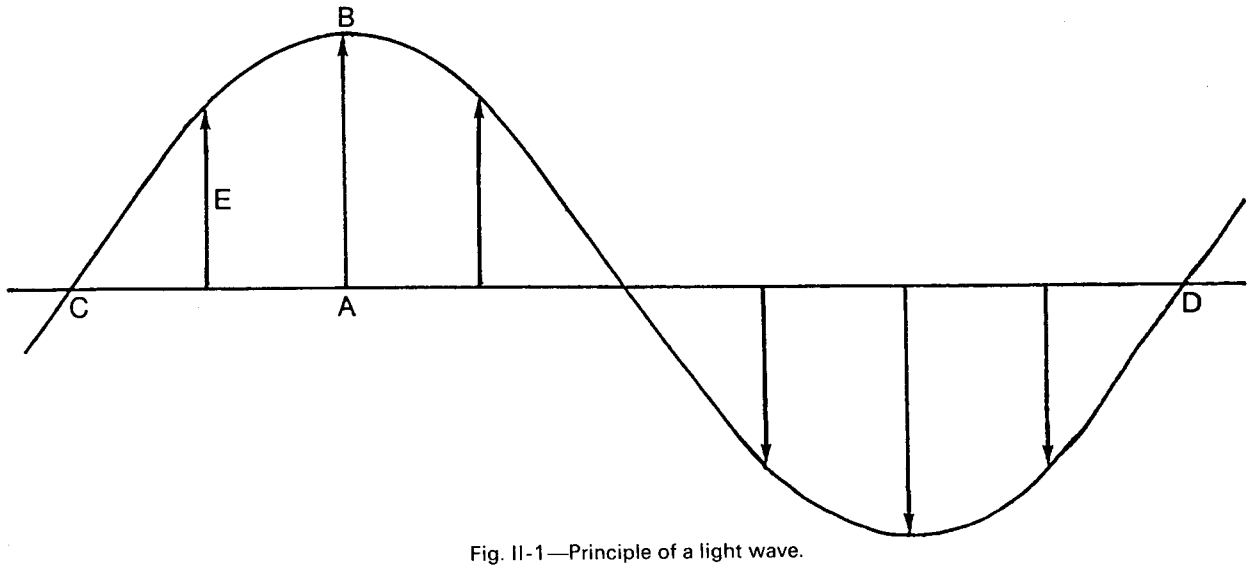


Fig. II-1—Principle of a light wave.

Isolated wavelengths are perceived by the eye to have colour but appear white in ordinary light due to mixing with a complementary wavelength, or colour. The various colours and their wavelengths are shown in the accompanying table.

Wavelength (nm)	Colour	Complementary colour
400-435	violet	yellow-green
435-480	blue	yellow
480-490	green-blue	orange
490-500	blue-green	red
500-560	green	red-violet
560-580	yellow-green	violet
580-595	yellow	blue
595-610	orange	green-blue
610-680	red	blue-green
680-700	red-violet	green

When a substance absorbs certain wavelengths from white light incident upon it, the light which is transmitted or reflected is perceived by the eye to have the colour which is complementary to that absorbed. For example, a pigment which appears red to the eye absorbs blue-green light and vice versa.

The velocity of light in a vacuum (c) is constant at all wavelengths and has a value of 2.9979×10^8 m.s^{-1}. In transparent matter however, the velocity is lower and varies with the wavelength of the light and the type and concentration of matter. The change in velocity when leaving one medium and entering another causes the light to deviate from its original path, and it is this property which allows the estimation of the total dissolved solids in a solution by refractometry. The more concentrated the solution, the lower the velocity and the greater the deviation.

When a single atom in a light source emits a pulse of radiation, the plane in which the electric vector oscillates maintains a constant angle or azimuth with respect to the direction of travel. This angle may have any value. Consequently, when a large number of atoms are emitting light, the angles are randomly distributed and the light is said to be *unpolarised* (Figure II-2 a). The electric vector of light has components in the two dimensions at right angles to the direction of propagation (Figure II-2 b) and it is possible to remove one of these components by various means to give a beam of light in which the electric vectors all have the same angle. The light is then said to be *plane polarised* (Figure 2 c). Depending on their structure, some molecules have the ability to rotate the plane of polarisation in one direction or the other and are said to be optically active. Sugars are amongst this class of molecules. Polarimetric determinations of concentration are based on the fact that the degree of rotation is proportional to the concentration of the optically active substance.

A molecule has electronic energy by virtue of the unceasing motion of its electrons. The electronic energy associated with a particular bond (or group of bonds) within a molecule will at any instant have one of several discrete values characteristic for that molecule. At ambient temperature most bonds are in their lowest energy or *ground* state. The bond may move from one of these energy levels to another only by a sudden jump involving the absorption or emission of a quantity of energy which is exactly equal to the energy difference between the two levels. This energy may be in the form of light having a frequency which is related to the difference in energy between the two states (ΔE) by the formula:

$$\nu = \frac{\Delta E}{h} \qquad \text{where h = Planck's constant.}$$

The dependence of the amount of light of appropriate frequency absorbed in transitions to higher energy levels on the concentration of the absorbing species is defined by the Beer-Lambert law:

$$\log \frac{I_o}{I_t} = \varepsilon c_1 t/10$$

where I_o and I_t are the intensities of the incident and transmitted light respectively, ε is the molecular extinction coefficient, c_1 is the concentration of the absorbing species (in mol.L^{-1}) and t is the thickness of the absorbing medium (in mm). This is the fundamental equation for spectrophotometric analysis. The term $\log \frac{I_t}{I_o}$ is known as the optical density (D). The transmittance (τ) is defined as the ratio of the intensity of the transmitted to that of the incident light $\frac{I_t}{I_o}$

Hence $D = -\log \tau$.

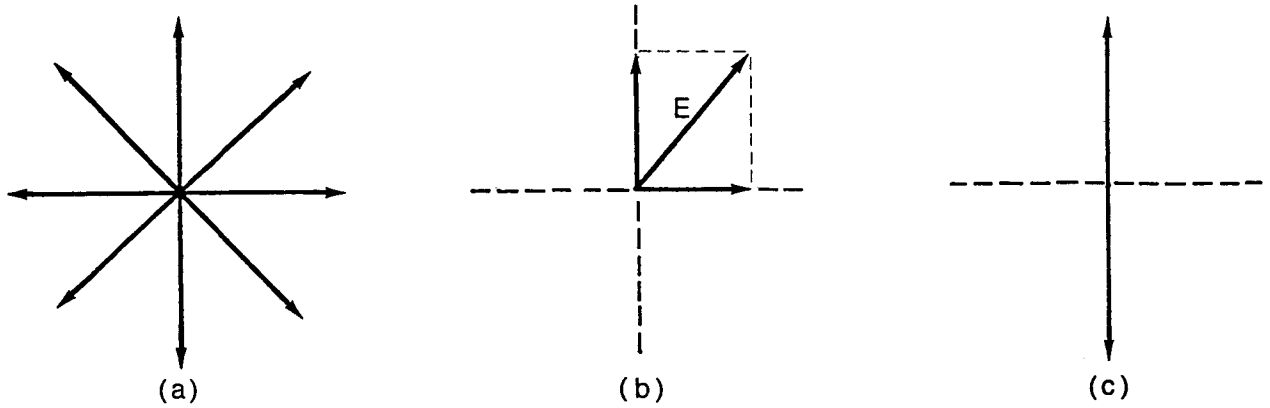


Fig. II-2—(a) Unpolarized light.
(b) Resolution of electric field into its components.
(c) Plane polarized light.

REFRACTIVE INDEX

In a homogeneous medium light travels in straight lines. If, however, a beam of light in one medium meets the surface of a second medium, it will in general be refracted or bent from its original path because of the different velocities of light in the different media. The incident ray of light, denoted by LO in Figure 3, arrives at the boundary between the media M_1 and M_2 in a direction represented by the angle LOP between the ray and the normal (perpendicular) to the boundary. This angle is called the angle of incidence, i. Some of the light is reflected along OL′ at the same angle i on the opposite side of the normal. The remainder of the light, however, is transmitted into the second medium along OS, which makes an angle SOQ with the normal. This is called the angle of refraction, r. If this angle is smaller than the angle of incidence, the first medium is said to be the rarer medium and the second the denser. This terminology relates to the effect, discussed earlier, that as the concentration and hence the density of a medium increases, the speed of light in it decreases.

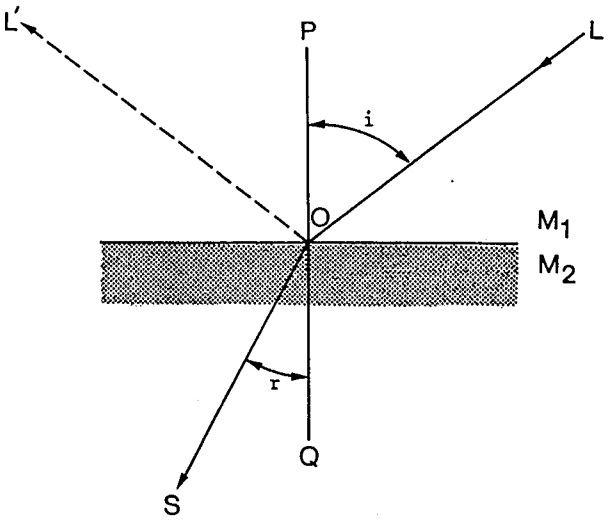


Fig. II-3—Illustrating the law of refraction.

The angles of incidence and refraction are related by the expression

$$n_1 \sin i = n_2 \sin r$$

where n_1 and n_2 are constants describing each medium; they are the refractive indices of the media. For any transparent medium, the refractive index is the ratio of the speed of light in air to its speed in the medium (v). Thus, a 'denser' medium, in which light has a lower speed, has a higher refractive index than a 'rarer' medium.

For a stricter theory, the refractive index should be defined with respect to speed of light in vacuum rather than in air, namely

$$n = c/v.$$

This is the absolute refractive index and it is 1.000 28 times the refractive index relative to air, 1.000 28 being the absolute index of air itself. For practical purposes, however, it is always the index relative to air that is used and this is what is meant by the simple term 'the refractive index'.

Another way of writing the relation between the angles of incidence and refraction is

$$\frac{\sin i}{\sin r} = n$$

where $n = n_2 / n_1$ and is the ratio of the two refractive indices or the relative refractive index. This ratio is the same whether absolute indices or indices with respect to air are used.

Since the speed of light in any medium other than vacuum varies with wavelength, so does the refractive index. Light of different wavelengths is therefore refracted by different amounts. When a beam of white light, which is a mixture of all visible wavelengths, is refracted at a boundary, it is spread out into a series of colours, known as a spectrum. This is the phenomenon of dispersion. When a refractive index of a material is quoted, it is therefore desirable to specify the wavelength for which it has been measured. Certain spectral wavelengths are known by letters, for example, the D wavelength of a sodium lamp, and n_D denotes the refractive index when using this light source. Important wavelengths are:

Symbol	Wavelength (nm)	Colour	Element
C	656.3	red	hydrogen
C′	643.8	red	cadmium
D	589.3	orange	sodium
d	587.6	yellow	helium
e	546.1	green	mercury
F	486.1	blue	hydrogen
F′	480.0	blue	cadmium

When the wavelength is not specified, it is commonly the D index that is meant. Although useful for measurements of moderate accuracy, this is really two lines, close together. The modern tendency, particularly for accurate work, is to replace the D line by either the helium d line or the mercury e line.

The dispersion of a medium has traditionally been given by the difference between the refractive indices for the blue and red lines of the hydrogen spectrum, i.e. $n_F - n_C$. However, this is now being replaced by the lines of cadmium, i.e. $n_{F'} - n_{C'}$.

The refractive index of a material also varies with the temperature and a complete description of a refractive index should also include this, as, for example $n^{20°}$. The rate of variation for glass is small, between 1×10^{-6} and 6×10^{-6} per degree Celsius, and is usually positive, the index increasing as the temperature increases. For liquids, the rate of change is much greater and in the opposite sense; an increase of temperature by 1 °C decreases the refractive index of water by 8×10^{-5}. For sugar solutions the temperature coefficient is of a similar order, increasing with increasing concentration; for organic liquids it is usually even greater.

THE REFRACTOMETER

For the most accurate measurements of refractive index the material, if a solid, is made into the form of a prism. If liquid, it is poured into a hollow prism. The deviation of the light through the prism is then measured. For routine measurements of refractive indices of liquids, however, methods based on the critical angle are used.

Critical-angle refractometers

When light passes from a rarer to a denser medium, the angle of refraction is smaller than the angle of incidence. Thus, while all values up to 90° are possible for the angle of incidence, until the incident light grazes the boundary surface, the angle of refraction has a maximum value that is smaller than this. This maximum value is the critical angle r_c and is the angle of refraction that corresponds to an angle of incidence of 90°. Then

$$\sin i = 1$$

and $$n_1 = n_2 \sin r_c.$$

Thus an unknown index n can be found by measuring the critical angle r for light refracted from the sample into a denser medium of known index n_2.

The method is illustrated in Figure II-4(a), where M_1 is the rarer and M_2 the denser medium. The light is incident from the rarer medium and rays O_1 -O_3 are shown at increasing angles of incidence. A small amount of the energy from each ray is reflected at the boundary; the rest is transmitted in the refracted ray. The ray O_3 arrives at an angle of incidence of 90° and is therefore the critical ray. No light from M_1 can penetrate into M_2 at a larger angle of refraction. Hence, if the emergent light into M_2 is viewed by a telescope aimed along the direction O_3, the observer will see light on one side of the field of view, darkness on the other. Obviously, it is impossible for the telescope to be inside the denser medium M_2, but this medium can be made as a prism, the second surface of which refracts these emergent rays into the air. This second refraction will change the direction of the critical ray but the final direction will still depend only on the known refractive index of the prism M_2 and the unknown index of the sample M_1. The angle of the critical ray is measured and the index n_1 of the sample found from tables provided with the refractometer, or the instrument is calibrated to read, instead of angle, the index n_1 directly or a brix value derived from n_1.

The reverse process to that described above is shown in Figure II-4(b). In this case the light is incident from the denser medium and the rays O_1 -O_3 are again part reflected and part refracted at the boundary, passing into the rarer medium at a larger angle to the normal until, for O_3, the angle of refraction has reached 90° and the ray leaves grazing the boundary. The angle of incidence for this ray is thus the critical angle. If the angle of incidence is increased further, as in O_4 , no light can be refracted into the rarer medium. All the energy is reflected at the boundary giving the phenomenon known as total internal reflection. Again if the light emerging in the denser medium, now the reflected light, is examined by a telescope aimed along O_3, a divided field of view is seen with one side brighter than the other. The brighter side, at angles greater than O_3, corresponds to rays for which there is total reflection, while the darker side corresponds to partial reflection. For this case

$$\sin r = 1$$

and $$n_1 = n_2 \sin i_c.$$

The critical angle is now an angle of incidence. Since on reflection, the angles of incidence and reflection are equal in magnitude, the unknown refractive index is found from a measurement of the angle of reflection that corresponds to this critical angle of incidence, i_c.

For either method of critical-angle refractometry, the solid or liquid sample M_1 is placed on a prism of the material M_2. For the first method, the boundary is illuminated from the sample; for the second, from the prism. In both cases the illumination should cover a range of angles: in the first case right up to 90° incidence, and in the second the range must include the critical angle. The emergent light, refracted or reflected according to the method, is examined through a telescope, the

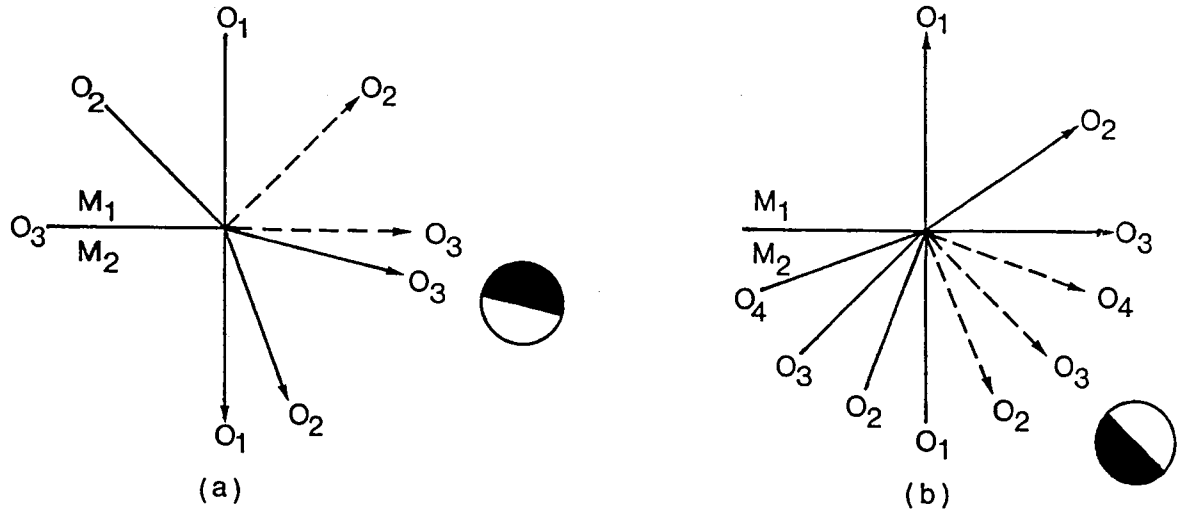


Fig. II-4—Illustrating the measurement of critical angle
(a) by transmission.
(b) by reflection.

inclination of which can be altered to set it in the direction of the critical ray. The field of view of the telescope has a lighter and a darker side and the boundary between them is set on a pair of cross lines in the telescope eyepiece.

In the first method, the darker side of the field would be completely dark, but for scattered light. In the second method there is only the less obvious distinction between total and partial reflection. Therefore, the first method is by far the more sensitive method of measurement and it is the one normally used. The second method is only used when the specimen is so strongly absorbing (e.g. a sample of molasses) or scattering, that insufficient light can be sent through it to the boundary.

Measurement of the critical angle is the basis of operation of most refractometers. Such instruments are known as Abbe refractometers. The principle of operation of a refractometer of this type is shown in Figure II-5 for the usual measurement on a reasonably clear liquid. A drop of sample is placed between two hinged prisms whose surfaces come together to spread the sample into a thin film. Light enters through the bottom prism (A) and is scattered by the ground surface (CD) in contact with the sample so that the sample is subjected to incident light at all angles up to 90°. The top prism (B) gives the critical refraction. In the figure the thickness of the sample is greatly exaggerated, and in practice the rays PQ and P'Q' are almost parallel to the prism surface EF. These rays enter prism B at the critical angle and are brought to a focus along a line at L in the eye-piece of a telescope. Other rays are focused to the left of L, so that L represents the boundary between light and dark fields. This boundary is set to intersect the centre of a pair of cross lines by adjusting the angle between the prisms and the telescope. The latter angle is used to give a direct measure of either refractive index or brix.

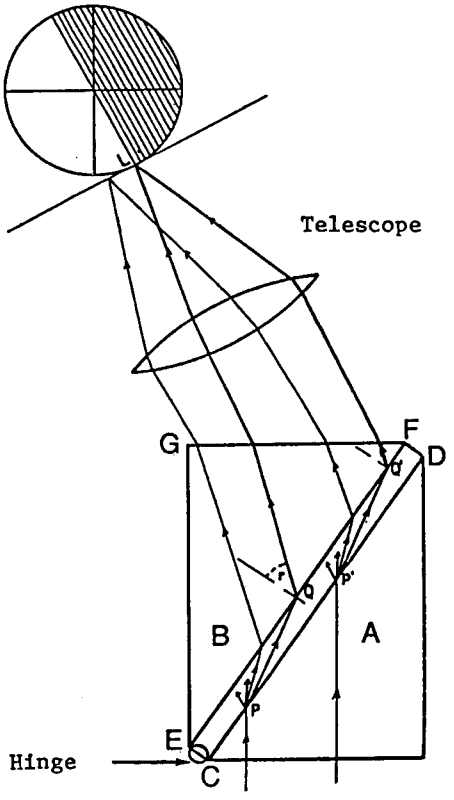


Fig. II-5—Principle of the Abbe refractometer.

When a strongly absorbing sample is to be measured, the prisms are rotated and opened up so that the surface EF of prism B faces upwards. The sample is placed on the latter surface. Light enters prism B through its surface EG and that which is totally internally reflected passes through FG to the telescope. Prism A is not used in this measurement.

To measure the D index, a sodium lamp is used as the light source. When white light is used, the boundary becomes a band of colours since a different critical angle is obtained for each wavelength. To compensate for this dispersion, Abbe refractometers are equipped with a pair of compensating or *Amici* prisms. These prisms, which are placed on the telescope tube in front of the objective, can be rotated simultaneously in opposite directions to produce variable dispersion. This is adjusted to compensate for the dispersion of the critical refraction.

The sample should be kept at a constant temperature during the measurement by circulating water at a constant temperature through the metal mountings which carry the prisms. When a measurement has been made, the liquid should be removed from the prism surfaces with absorbent paper, the surfaces washed with a suitable solvent (usually water or alcohol) and dried with a soft cloth. As the prisms are made of a soft flint glass, they are easily scratched and great care must be taken not to wipe grit across their surfaces or close them with dust in between. A scratched or pitted prism will give an indistinct boundary, and repolishing is expensive.

The adjustment of the refractometer should be checked periodically on a sample of known refractive index. This can be the glass test piece provided with the instrument, freshly distilled water free from air ($n_D^{20°}$ = 1.3330) or another liquid that has been specially calibrated. When using liquids as standards, it is essential to control their temperature to that for which they have been calibrated. Provided the sample gives a clear boundary between the light and dark fields, an Abbe refractometer should be capable of measuring its refractive index to an accuracy of about ±0.0002 (±0.1° brix).

There are, however, more accurate critical angle refractometers which can measure the refractive index of solutions to an accuracy of ±0.000 04 (less than 0.02° brix). One such instrument is the dipping or immersion refractometer (Figure II-6). This instrument is supplied with a series of interchangeable prisms, each one covering a portion of the total range of 1.32 to 1.64 refractive index. These prisms may or may not be water jacketed to permit temperature control. If not, the refractometer is used with the measuring prism dipping into the solution to be tested. Flow through cells are also available for these instruments. It must be stressed that constant temperature control is essential for precise measurement.

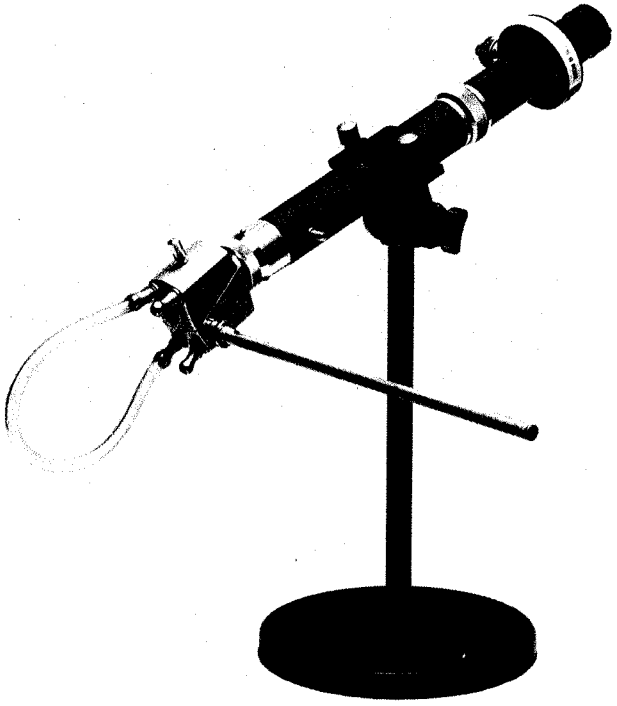


Fig. II-6—Immersion refractometer with temperature controlled prism by Carl Zeiss, W. Germany.

Table VIII shows the relationship between the concentration and the refractive index of sugar solutions at 20 °C. This relationship varies only slightly for different sugars, so the refractometer is quite satisfactory for determining the total sugars present in a solution of mixed sugars. Where it is necessary to correct refractometer results for temperature, the refractometer reading is converted to its corresponding brix value and the correction for refractometer brix shown in Table IX is applied. With respect to speed, ease of manipulation, and amount of sample required, this procedure is superior to specific gravity methods.

With impure sugar solutions, such as molasses, it is found that the refractive index affords a closer approximation to the actual amount of dry substance present than does the specific gravity. The percentage dry matter in massecuites or moist sugars can be determined with the refractometer after dissolving all soluble matter in a known amount of added water. Since the refractometer indicates the amount of dissolved solids only, any insoluble matter which is present will introduce an error in the estimation of dry substance. Where dark-coloured solutions are being examined, it is often difficult to eliminate completely the effects of dispersion. This may be corrected in some degree by dilution with water, but with impure solutions an error is introduced just as in the case of specific gravity determinations. A close approximation is obtained if a solution of pure sugar is used for the dilution.

Most modern refractometers can be obtained with a brix scale for the direct determination of the brix of sugar solutions. The hand refractometer, of which one type is illustrated in Figure II-7, is useful for the approximate

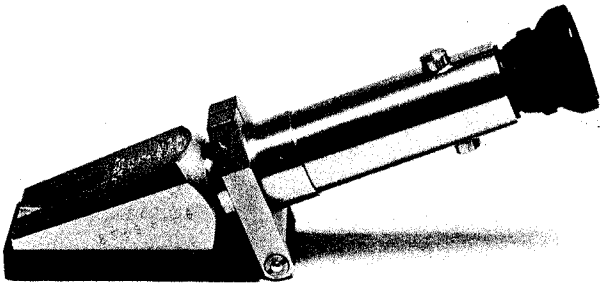


Fig. II-7—Hand refractometer by Atago Optical Works, Japan.

checking of brix, particularly for maturity testing in the field. When a sample is introduced, the eye placed to the telescope will see a division line between light and dark fields superimposed on a scale of the type shown in Figure II-8. The scale is read at the junction of the two fields. These instruments are made to cover various ranges of brix, e.g. 0-30°, 0-50°, 40-80°.

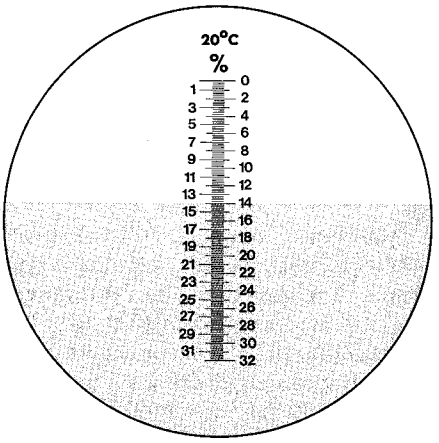


Fig. II-8—Typical field of a hand refractometer.

So long as an adequate number of stalks is suitably sampled, it is possible to obtain a reasonably accurate estimate of the dry substance present in the juice from a crop using the hand refractometer. Also, the measured concentration of solids from the several portions of the stalk of cane provides a useful guide in the determination of the state of maturity of the crop. The instrument is also of great value in affording a rapid estimate of the relative sugar content of large numbers of cane seedlings when these are being selected for further trials.

Automatic refractometers

Automatic refractometers are designed primarily to eliminate human error in the determination of the boundary line position. Typically, the refractive index, or brix, is determined automatically from one of two types of measurements made by an array of photodiodes:

(i) The lateral shift, or sometimes the dispersion, of the transmitted beam as a result of refraction;

(ii) The critical angle, when the light is incident through the prism support and the emergent beam is tangential to the interface.

Measurement by the 'transmission principle' (i) is probably the most precise of these methods; however, it is only suitable for light-coloured solutions. For dark-coloured solutions it is essential to use small measuring cells and this can cause difficulty if any particulate matter is present. Measurements obtained with automatic refractometers using the 'critical angle principle' (ii) are usually unaffected by colour, turbidity and aeration.

The Atago DBX-50 automatic digital refractometer, which has a range of 0 to 50° brix operates on the 'critical angle principle'. Light from an incandescent lamp is directed by a lens system into a glass prism which is in contact with a liquid sample (Figure II-9). The portion of the beam which has an angle of incidence greater than the critical angle undergoes total internal reflection and is directed on to the detector via the objective lens. When the angle of incidence is less than the critical angle, however, the light is refracted into the sample. The shaded area in Figure II-9 represents the portion of the beam which is removed from the view of the detector when a sample of 25° brix is placed on the prism. This instrument reads to one decimal place and has an accuracy of ±0.1°. It is therefore unsuitable for use when high precision is required. However, it has a number of features which make it particularly suited to process control work. Also, water cooling or temperature corrections are not required since the measured value of brix is automatically converted into the value at 20 °C.

The Refractomat automatic refractometer, which has a digital brix display and automatic temperature compensation, also operates on the critical angle principle. This instrument is available in two versions; a laboratory model for batch measurements and a process model for continuous monitoring of process streams. The sensing head of the latter model may be installed directly into a pipe system, bypass etc. The laboratory model has a range of 0 to 45° brix whereas the process model can be adapted to application between 0 and 90° brix. The Refractomat reads to two decimal places and has an accuracy of ±0.05° brix.

PLANE POLARISED LIGHT

Plane polarised light is obtained from natural light by means of a polariser, a system that transmits vibrations in one direction only. Since the random vibrations of natural light can be resolved into two components along two directions at right angles and these two components are, on the average, equally intense, a perfect polariser will transmit half the intensity of natural light.

The light reflected from the boundary between two transparent media is plane polarised for a certain angle of incidence, but only a small part of the intensity is reflected. A more efficient polariser is made from *dichroic* films. A dichroic material is one that transmits light plane polarised in a certain direction (with respect to the orientation of the material molecule) and absorbs that polarised in the direction at right angles. The early experiments on polarised light used the dichroic crystal tourmaline as polarisers. As it proved difficult to produce large dichroic crystals artificially, later crystalline polarisers were made from small crystals embedded in a plastic sheet, all aligned in the same direction by stretching the sheet. This was the original form of polaroid, the crystals used being herapathite or iodosulfate of quinine.

However, these microcrystalline sheet polarisers are now quite obsolete. The present-day polarisers made by the Polaroid Corporation and others use a molecular dichroic material. A sheet of polyvinyl alcohol is stretched to align the molecules and then its surface is converted into a dichroic material by treatment either with iodine or oxygen to give a polaroid sheet. For use in optical instruments, the sheet polariser is cemented between discs of glass.

The properties of sheet polarisers vary somewhat, depending on the dichroic material used and how much of it there is on the sheet. All absorb some of the plane polarisation that they should transmit and transmit a small amount of the polarisation they are intended to absorb. Good sheet polarisers, however, are now almost as good as the polarising prisms described later and are

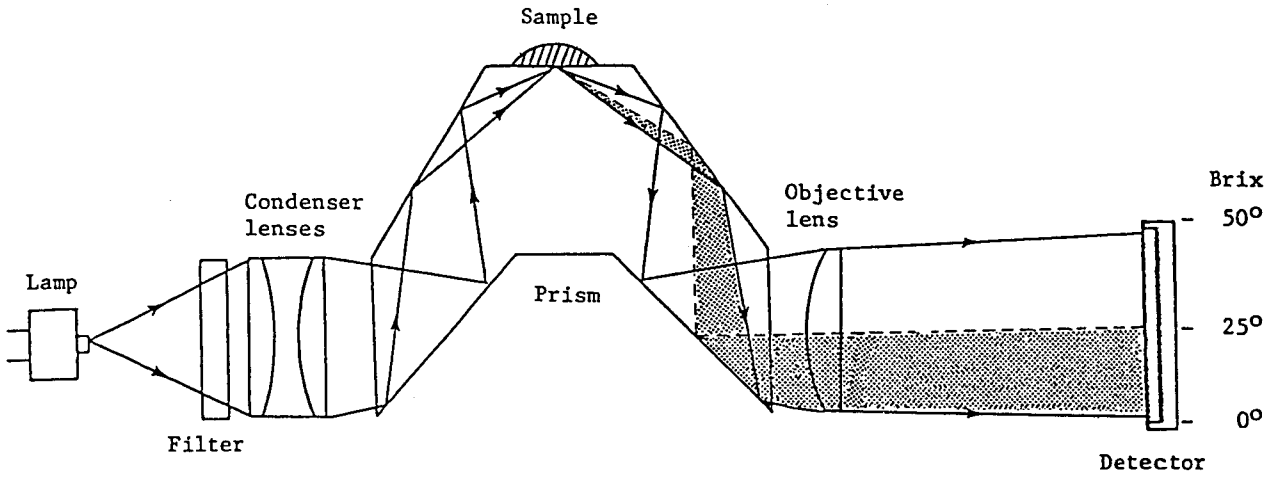


Fig. II-9—Principle of the Atago DBX-50 Digital Refractometer.

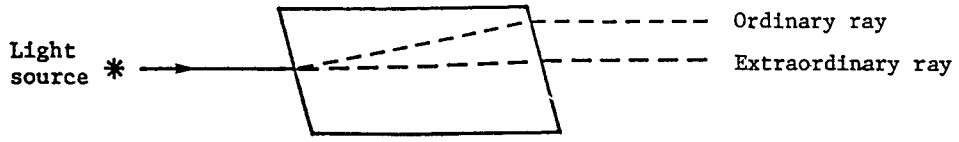


Fig. II-10—Illustrating double refraction of light in calcite.

gradually replacing these prisms in polarimeters and other optical instruments.

Prism polarisers are made from transparent crystals that have the property of being *birefringent* or *doubly-refracting*. The crystal commonly used is calcite or Iceland spar, a clear form of calcium carbonate that cleaves readily into rhombohedra. If an object is viewed through such a crystal, a double image is seen. Both images are found to be plane polarised with their polarisations at right angles. The crystal thus splits natural light into two plane polarised rays and refracts these rays in different directions. (A dichroic crystal does the same splitting, but it absorbs one ray.)

Each crystal has a direction known as the *optic axis*, fixed with respect to the rhombohedral planes, in which both rays have the same refractive index, 1.658 for calcite. In other directions, one ray still has the same refractive index; it is called the ordinary ray. The other ray, however, the extraordinary ray, has a refractive index that varies with direction from 1.658 to 1.486 and so does not obey the simple law of refraction. In Figure II-10 the effect of sending a beam of light through a crystal of calcite is illustrated.

The natural light is split into two polarised beams that leave the crystal with a slight separation, about 1/9 of the distance travelled through the crystal. This separation is usually too small to be useful for making a polariser, and before such a crystal of calcite may be utilised for this purpose, one set of emergent rays must be eliminated. One method is to use the phenomenon of total internal reflection, and this is usually accomplished by the method devised by Nicol. A crystal is selected (Figure II-11) of which the length is about three times the width. The crystal is then halved in the direction AC. The cut surfaces are next polished and reunited with Canada balsam which has a refractive index of about 1.54. A beam of light PR entering such a crystal (Figure II-11) is resolved into two rays, RO and RE. That which is the more highly refracted (the ordinary ray, RO) meets the film of Canada balsam AC at an angle of incidence greater than the critical angle and is completely reflected and thus eliminated. The extraordinary ray RE is less highly refracted, and emerges as plane polarised light from the end surface of the composite prism.

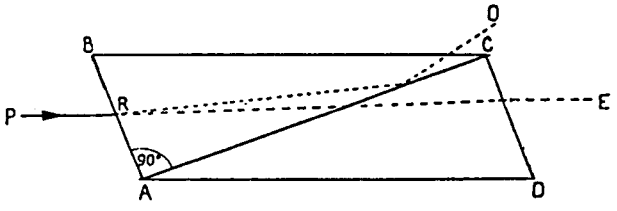


Fig. II-11—Illustrating the principle of the Nicol prism.

It should be noted that the separation of the two rays and the elimination of the ordinary ray are achieved by the half prism ABC and the film of Canada balsam. The other half prism ADC serves only to restore the extraordinary ray to its original direction, and to protect the film of Canada balsam.

This early type of Nicol prism does not need to be ground and polished on the outside faces, only along the diagonal - where the two half prisms are cemented with the Canada balsam. It has the disadvantages of a small useful angle and of displacing the beam of light to one side. It is now replaced entirely by rectangular prisms, with all faces polished. These are, however, still sometimes called 'nicols'.

A combination of two polarisers in series is the basis of a polarimeter. When light from the first polariser proceeds to a second polariser, known as an *analyser*, it is completely transmitted if the polarising directions of the two are parallel (Figure II-12 a), losses in imperfect polarisers being neglected. If, however, the analyser is rotated about the light beam (Figure II-12 b), the intensity of the emergent light will decrease until the two polarising directions are at right angles, when the light is extinguished. In the first position, the polarisers are said to be *parallel*; in the second, they are said to be *crossed*.

Optical activity

Quartz is also a crystal that is birefringent with about one-twentieth the birefringence of calcite. As with calcite, this effect is greatest in directions at right angles to the optic axis. Along the optic axis of a quartz crystal, however, a new effect occurs; if plane polarised light is sent through a crystal in this direction, the angle at which the light is polarised is changed. The amount of change depends on the thickness; the direction of polarisation rotates around the ray like a corkscrew as the light proceeds through the quartz.

This property of rotating the plane of polarisation is known as *optical activity*. It is possessed by certain crystals and also by some liquids and solutions, including sugar solutions. Materials such as glass that are not ordinarily optically active can rotate the plane of polarisation when they are placed in a magnetic field which is in the same direction as the light; this is known as the *Faraday effect*.

The amount of rotation depends directly on the thickness of the sample through which the light passes and, in the case of a solution, on the concentration of the optically active substance in the solution. It also depends on temperature and wavelength, so these must be specified. An active substance in solution is characterised by its *specific rotation*, i.e. the rotation of a solu-

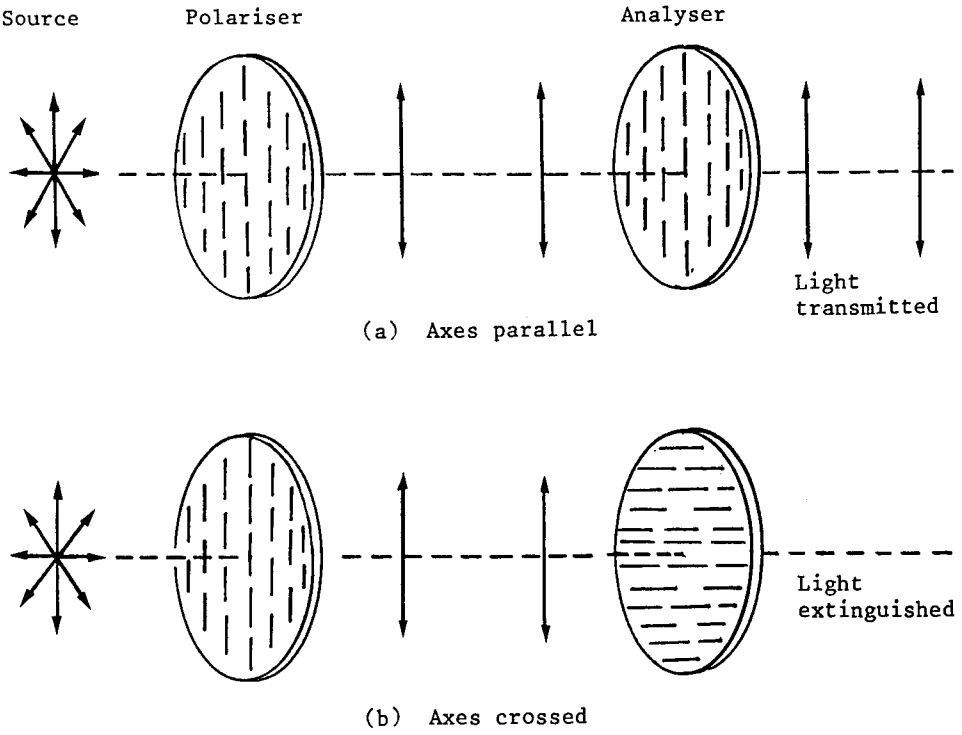


Fig. II-12—Illustrating the principle of polarizer and analyzer using polaroid sheets.

tion having a concentration of 1 g.mL^{-1} and a length of 100 mm. For the D line at 20 °C this is written α_D^{20}. If a sample has a concentration c (in g.mL^{-1}, weighed in vacuo) and a length l (in mm), the angular rotation will be

$$\theta = \alpha_D^{20}\ cl/100$$

θ being measured in degrees. In the case of the Faraday effect, the amount of rotation depends on the field strength and its length, and therefore for an electromagnetic coil, on the current in the wire and the number of turns. A normally non-optically active substance, such as glass or air, when placed in an electromagnetic coil is characterised by its *Verdet constant* V, i.e. the rotation caused by the substance in a field having a strength of 0.0001 Tesla and a length of 10 mm. The angular rotation can be expressed as

$$\theta = V_D^{20}\ Hl \times 10^3$$

where H is the field strength in Tesla and l is the length in mm.

The measurement of this rotation is the technique of polarimetry; it is a method of measuring the concentration of a substance of known specific rotation when placed in a tube of known length. The values of α_D^{20} for some common sugars are:

Sucrose	+66.54	Fructose	−92.5
Glucose	+52.5	Invert	−20.0

A solution of sucrose or glucose, which has a positive specific rotation, rotates the plane of polarisation in a clockwise direction when viewed towards the light source, and is said to be *dextrorotatory*. Fructose, on the other hand, rotates the plane in an anti-clockwise direction and is said to be *laevorotatory*. Crystals of quartz occur in two different forms that are either dextro- or laevorotatory. They are called right-handed and left-handed quartz. In the case of the Faraday effect, the direction of rotation depends upon the direction of the magnetic field and therefore, for an electromagnetic coil, on the direction of the current in the coil.

In polarimetry, the sample is placed in a cell of known length between two polarisers which are set in the crossed position. The extra rotation of the analyser required to restore extinction after the sample is introduced is a measure of the rotation of the sample. Alternatively, the rotation of the plane of polarised light may be compensated for by a plate of quartz of variable thickness. The latter principle of balancing is sometimes employed in automatic polarimeters, but instead of quartz, a rod of glass in a variable magnetic field gives a Faraday rotation; the current required to produce the field provides a measure of the sample rotation.

The variation of rotation with the wavelength of the light used is known as *rotatory dispersion*. It has the practical result that measurements of rotation must be made with monochromatic light, as are measurements of refractive index. Traditionally, the D line of sodium has been used, but there is a modern tendency to use the e line of mercury (546.1 nm) for very accurate measurements; it must be remembered that the specific rotations for these two lines are quite different. Quartz and sugar solution have similar rotatory dispersions, at least in the red-to-yellow part of the spectrum, and hence white light that has been passed through an orange filter (e.g. dichromate solution) may be used in those instruments which employ quartz compensators and are used exclusively for measurements on sugar solutions (saccharimeters).

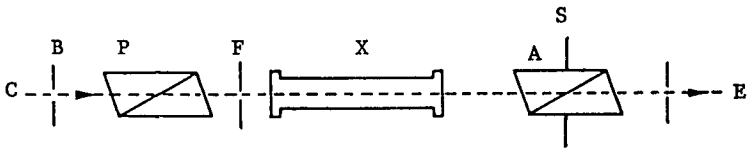


Fig. II-13—Essential parts of a simple polarimeter.

THE POLARIMETER

The essential parts of a visual polarimeter are shown in Figure II-13. An aperture B is illuminated by a source of monochromatic light C, either directly or through a lens which focuses C on B. The light passes on through a fixed polariser P, with a field stop F, and an analyser A which may be rotated. The latter is fitted with a scale S on which the rotation can be read; it is usually graduated so that the crossed position of the analyser corresponds to the zero of the scale. The light is viewed by the eye E of the observer. If a cell X containing an optically active solution is now placed between the polariser and analyser, it will be found that the light is no longer extinguished by A, which will have to be rotated to a new orientation to restore extinction. The angle through which the analyser is rotated is the rotation of the specimen. The scale S, as well as being marked in angular degrees, is often also marked in terms of the International Sugar Scale discussed later.

A simple polarimeter of this type would not be very accurate, because setting an instrument to extinguish light cannot be done with high precision. It is well known in the technique of measurement that a setting to a maximum or a minimum, such as this, is less precise than a balancing of two quantities to equality or coincidence. An example of the latter is the matching of the intensities of two adjacent fields of view. Settings of this last type are known as null settings.

The eye looking through the polarimeter has a field of view located at the stop F near the fixed polariser. To convert the instrument into one with a null setting, this field may be split into two parts, with the polarisations of these two parts differing by a small angle. As the analyser is rotated, first one field, then the other is extinguished. When the analyser is crossed with the direction midway between the two polarisations, the two fields have equal intensity. This is illustrated in Figure II-14. A setting to this position is thus a null setting and is much more accurate than a simple setting to extinction.

The angle between the polarisations of the two fields is known as the *half-shadow angle*. Theory shows that, the smaller the half-shadow angle used, the greater is the sensitivity of the instrument. However, the smaller this angle, the closer the two sides of the field are to extinction at the balance point, and the less light there is available to judge the balance. Since the sensitivity also depends on the light intensity, when the light source is as bright as can be obtained, a compromise is required on the half-shadow angle between the loss of sensitivity due to too large an angle and the loss due to too little light. In practice angles of 1° to 10° are used. In the saccharimeter described later an angle of about 7° to 8° has been found to be a good compromise for accuracy and available light.

The most common method of obtaining the split field is by use of the Lippich polariser, shown in Figure II-15. In front of the main polariser is placed a smaller polariser covering half the field. This is rotated through the half- shadow angle from the main polariser. This rotation changes the direction of polarisation across this half of the field and also slightly reduces the intensity.

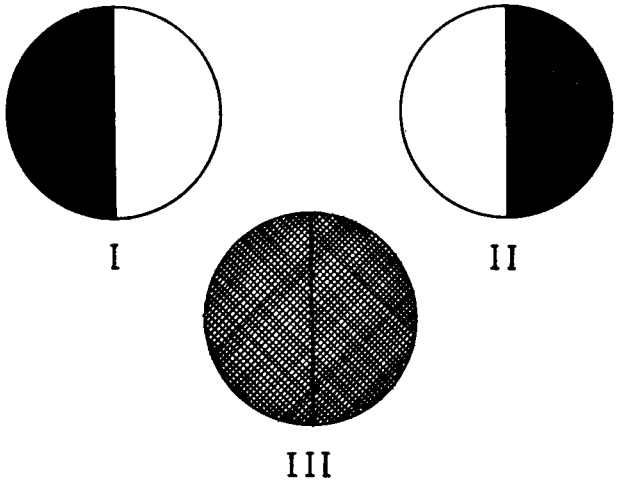


Fig. II-14—Appearance of a null intensity setting.

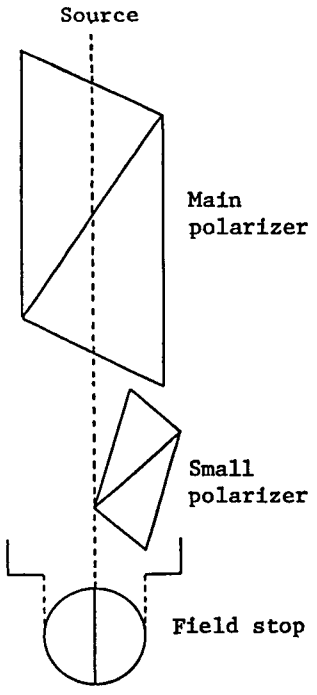


Fig. II-15—Construction of a Lippich polarizer.

The reduction of intensity affects the position of the setting slightly; it is no longer exactly midway between the angles at which the two fields extinguished. The small polariser is also tilted slightly so that the observer does not look along its face (and hence see a broad band separating the two fields) but sees only a sharp edge. The Lippich system has the advantage that the half-shadow angle is adjustable and can be altered to suit the intensity of the illumination.

THE SACCHARIMETER

Formerly, a saccharimeter was considered to be a polarimeter graduated not in angular degrees but in relative concentration of sugar or *degrees of sugar*, °S. However, some polarimeters today have both angle and sugar scale graduations and modern automatic polarimeters can be arranged to display the rotation in any chosen unit. This applies equally whether the sample rotation is compensated for by turning the analyser prism, or by placing a suitable amount of optically active substance, such as a piece of quartz, or a glass rod in a magnetic field, immediately before a fixed analyser.

Therefore it seems best to describe a polarimeter with a sugar scale merely as a sugar polarimeter and to confine the term saccharimeter to an instrument which by virtue of its principle of operation should be used only on sucrose solutions. Accordingly, it is becoming common to reserve the name saccharimeter for an instrument that uses a quartz-wedge compensator.

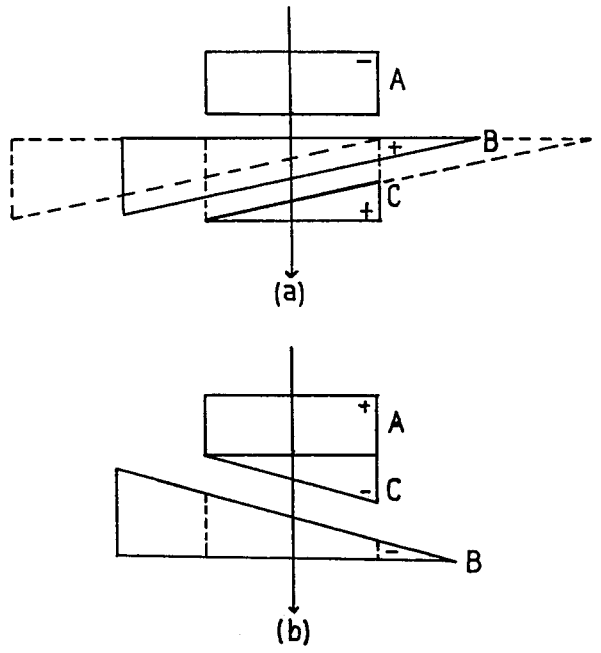


Fig. II-16—Construction of a single wedge quartz compensator
(a) Dextrorotary (+) system.
(b) Laevorotary (—) system.

The *quartz-wedge compensator* in its simplest form consists of two wedges of quartz (B and C) of equal angle mounted so that one can be moved past the other, as shown in Figure II-16. The pair of wedges then acts as a parallel-sided plate of quartz of adjustable thickness and it gives a controlled rotation to the light going through it. At a certain setting, the dextrorotation of wedges B and C in Figure II-16 (a) exactly neutralises the laevorotation of a fixed quartz plate (A). If a tube of dextrorotatory sugar solution is placed between the polariser and plate A, the optical neutrality is destroyed and it is necessary to decrease the thickness of the quartz plate by adjusting the position of B with respect to C until balance is restored. If the sugar solution is laevorotatory, the thickness of the wedge must be increased. In a laevorotatory wedge system [Figure II-16 (b)] the compensating motion of B is the reverse of that for the dextrorotatory system.

The optical system of a saccharimeter is shown in Figure II-17. The lens A condenses white light from a clear filament lamp onto the aperture in B; the light passes through the orange filter C and is brought to a focus at the objective of the telescope by a lens D; E is the polariser (with fixed half-shadow angle); F is a stop to limit the size of the light beam and G is a glass protecting plate. The sugar solution under examination is contained in the cell H; I is a second protecting plate; J and N are stops for cutting out stray light; K, L, and M make up the quartz-wedge compensator; O is the analyser; P the objective of the viewing telescope; Q a field stop in the focal plane of the eye-piece; and R and S form the eye-piece of the telescope. A saccharimeter in common use is shown in Figure II-18.

The scale is usually graduated from −30 °S through zero to +105 °S (with extended graduations at both ends), or occasionally, from −150 °S to +150 °S. The angular rotation that corresponds to 100 °S depends on the length of cell used, the normal weight specified for the instrument, and on the wavelength for which the rotation is measured.

Effect of illumination

As stated earlier, the rotatory dispersion of sucrose solution is close, but not exactly equal to that of quartz, sucrose having the greater dispersion. The difference in the two dispersions is greatest for blue light and hence the quartz-wedge saccharimeter is designed for use with white light filtered to remove the blue end of the spectrum. Therefore, a movable glass filter is usually built into the saccharimeter. This filter transmits red, orange, and yellow light but absorbs the rest of the spectrum; the transmitted radiation has a mean wavelength of about 600 nm.

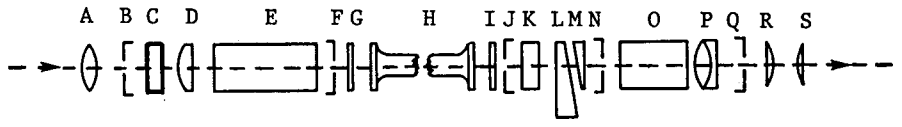


Fig. II-17—The essential parts of a saccharimeter.

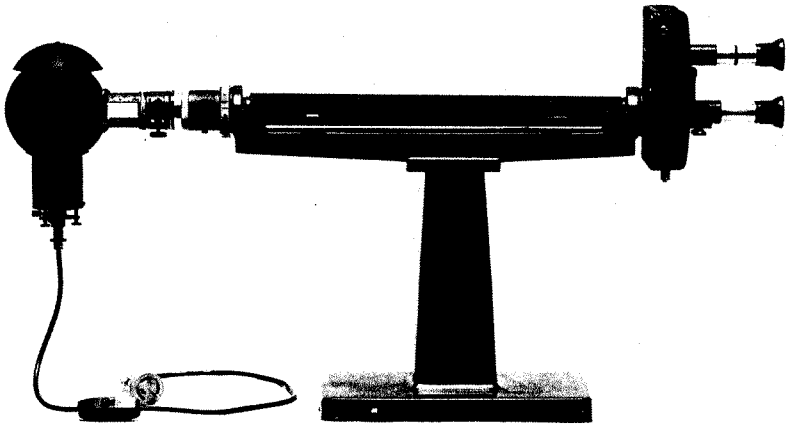


Fig. II-18—Schmidt and Haensch saccharimeter.

If white light is used without a filter, a saccharimeter will give readings that are in error by about +0.12 °S at the 100 °S point. Only when the solution is coloured and acts as its own filter should the filter be omitted. If a sodium lamp is used with a quartz-wedge saccharimeter, there is again a small error, now about +0.003 °S at 100 °S, whether a filter is used or not.

AUTOMATIC POLARIMETERS

The modern tendency in optical measuring instruments is to replace the eye by some photoelectric detector. Such instruments do not require as highly skilled an observer and are less fatiguing to use. In addition, the results obtained are more reliable and often more accurate and, being in the form of an electrical signal, can be recorded by means of the large variety of data-recording equipment now available. If calculations are made on the results, this is done by connecting in the appropriate calculating circuits and the result is obtained with very little delay. An automatic polarimeter is normally used with a flow-through cell so that samples can be readily introduced and flushed away; many installations use an automatic sample feeder which introduces samples to the instrument at regular intervals of, say, 60 seconds and actuates the read-out device. Certain instruments allow the polarisation to be recorded continuously as the sample flows through the cell.

A photoelectric polarimeter could be made by using a conventional split-field polariser and taking the light from each half of the field to a separate photocell. At the balance point, the two electrical signals from the photocells would be equal. Such a system would give continuous D.C. signals from the photocells and would require D.C. amplifiers, which are notoriously more unreliable and more unstable than A.C. amplifiers.

Modern automatic polarimeters, therefore, use A.C. balancing. Instead of a field split in space and two photocells, one photocell is used with a field 'split in time'. The plane of polarisation changes backwards and forwards between the two positions it would have for the split field, either in jumps or continuously. The electrical signal from the photocell then consists of a D.C. background on which is superimposed an alternating current of the same frequency as that at which the polarisation is being switched. This A.C. component of the signal is an error signal, becoming zero at balance. The instrument balances itself by using the error signal to drive the balancing system; when the error signal vanishes, this drive stops. It is thus a servo-system.

In order to oscillate the direction of polarisation, one of three methods is used. The first uses a synchronous motor to rotate the polarising prism backwards and forwards. The second uses a rotating plate, around the edge of which is a series of holes, each covered by a quartz plate. The latter are of equal thickness and alternately dextro- and laevorotatory. As the carrier plate rotates, the quartz plates pass in turn in front of the polariser to give a polarisation which is alternately dextro- and laevorotatory.

The third method makes use of a Faraday cell, or modulator. As stated earlier, if a glass rod with light passing through it is placed in a magnetic field, the field being in the direction of the light, the plane of polarisation of the light is rotated by an amount that depends on the type of glass and the strength of the magnetic field. Very dense flint glasses give the largest rotation. The sense of rotation depends on the direction of the field and, if this is alternated, the rotation alternates. To give an oscillating direction of polarisation the glass rod is enclosed in a solenoid through which passes an alternating current.

The polarimeter is balanced in one of three ways; either a conventional analysing prism is rotated, or compensating quartz wedges are driven up and down, or a D.C. Faraday cell is used as a compensator to balance the rotation due to the sample. The rotating analyser is turned to balance by a motor that is driven by the amplified error-signal, and the rotation can be read from an angle scale. The compensating quartz wedges are driven to balance by a motor in a similar fashion to the rotating analyser, and the sugar value of the rotation of the sample is read from a linear scale. In the case of the D.C. Faraday cell, the current required to cause compensation provides a measure of rotation.

The Schmidt and Haensch Polartronic Universal (Figure II-19) is one of a number of precision automatic instruments currently available. Three operating modes can be selected: α mode (optical rotation displayed in angular degrees), °S mode (per cent of normal weight of sucrose) and °S x 2 mode. The latter mode, which simply involves doubling the measured °S value, is useful for work with half the normal weight or for work with a measuring tube of half the originally intended length, for example when there is excessive light absorption. The standard instrument is equipped with a digital data output for connection to a printer or a data acquisition unit. It has a measuring range of ±70° or ±170 °S and reads to two decimal places in all modes. The accuracy is ±0.01° or ±0.01 °S.

The standard light source for this instrument is a halogen lamp with an interference filter which emits radiation of wavelength 546 nm. The halogen lamp requires no warm-up time, has a long lifetime and is relatively inexpensive. The instrument can also be fitted with a different interference filter to obtain light having the 589 nm wavelength. Alternatively, the 546 and 589 nm emissions may be obtained using the optional mercury and sodium spectral lamps respectively. The 589 nm emission has been adopted for use in Australia.

The Polartronic Universal incorporates a Faraday modulator for polarisation oscillation and a rotating analyser for balancing. The latter is under the control of a photomultiplier, which is essentially a combined detector and high-gain amplifier (see later). The instrument is fitted with an automatic sensitivity control for examination of light-absorbing samples; absorptions up to 99% can be tolerated. This control also compensates for ageing of the light source and photomultiplier.

Effects of birefringence

Some materials, such as glass, become doubly refracting if they are strained. If plane polarised light passes through such strained glass, it may come out elliptically polarised, that is, the electric vector may vibrate in an ellipse at right angles to the direction of travel. This is due to out-of-step recombination of the rays as they leave the glass. If the glass is now followed by an analyser, the intensity seen varies as the analyser is rotated, but it no longer drops to zero at any position; the extinction is only partial, not complete. At the position of minimum intensity, the analyser is crossed with the direction of the longer axis of the ellipse of polarisation. This may not be in the same direction as the original linear polarisation, so that the strained glass has introduced an error into the measurement. It is not possible to eliminate this error by re-adjusting the zero of the polarimeter since the direction of the ellipse and hence the error can change when the sample is introduced and rotates the polarisation.

These errors due to birefringence can be caused by strained glass in the end plates of the sample cells or in other protective plates between the polariser and the analyser. In visual polarimeters and saccharimeters they are not usually large enough to be serious, but in automatic polarimeters, where the accuracy of angle measurement must be greater to allow for the shorter sample, they can be significant. The errors interact so that strain in glass plates before and after the compensation cell can give rise to two sets of errors, one fixed, the other depending on the sample. To avoid birefringence errors in automatic polarimeters, not only must all glass used be very well annealed, but it must also be mounted without strain and cleaned correctly; wiping with a circular motion introduces less birefringence than wiping always in the one direction.

Standardisation of polarimeters

Just as the reading of a refractometer is checked periodically by making a measurement on a test piece, a polarimeter should be checked regularly with a standard of known rotation. For visual polarimeters, this is a quartz control plate, that is, a plate of quartz of known rotation mounted in a tube that fits into the polarimeter in place of the sample cell. These control plates are normally made close to 25 °S, 50 °S, 75 °S and 100 °S and the last two at least should be available for use. The quartz control plates are themselves checked by a standardising laboratory. In Australia, the recognised standardising laboratories are CSIRO Division of Applied Physics and BSES.

The International Sugar Scale

At the 1932 meeting of the International Commission for Uniform Methods of Sugar Analysis (ICUMSA), the following resolutions were agreed to:

(1) That the Commission adopt a standard scale for the saccharimeter and that the scale be known as

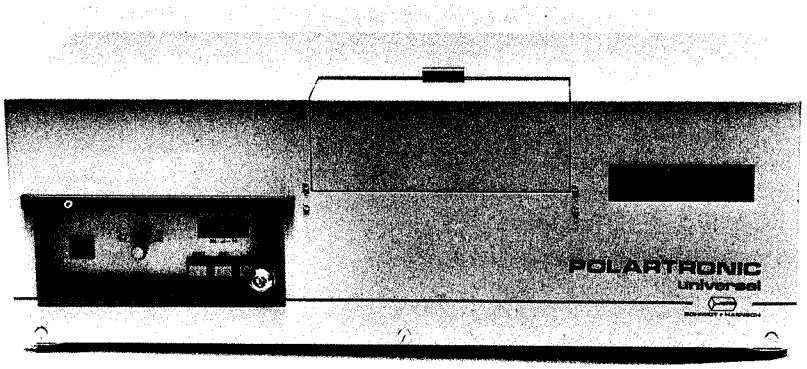


Fig. II-19—Schmidt and Haensch Polartronic Universal automatic polarimeter.

the 'International Sugar Scale'. Rotations expressed in this scale shall be designated as degrees sugar (°S).

(2) That the polarisation of the normal solution (26.000 g of pure sucrose dissolved to 100 mL, in a 200 mm tube at 20 °C using white light and a dichromate filter as defined by the Commission) be accepted as the basis of calibration of the 100° point on the International Sugar Scale.

(3) That the following rotations shall hold for the normal quartz plate of the International Sugar Scale:

Normal quartz plate = 100 °S = 40.690° ± 0.002° (λ = 546.1 nm) at 20 °C
Normal quartz plate = 100 °S = 34.620° ± 0.002° (λ = 589.3 nm) at 20 °C

This definition of the 'International Sugar Scale' does not, however, make mention of the rotations of the normal sugar solution, at the normal temperature, for the mercury light and sodium light of the wavelengths 546.1 nm and 589.3 nm respectively. These values were, however, determined by F.J. Bates (Circular of the National Bureau of Standards C440) and are as follows:

Normal sugar solution = 100 °S = 40.763° (λ = 546.1 nm) at 20 °C
Normal sugar solution = 100 °S = 34.617° (λ = 589.3 nm) at 20 °C

The difference between the rotations of the normal quartz plate and the normal sugar solution at each wavelength is due to differences in their rotatory dispersion curves.

At the 1962 ICUMSA meeting it was considered that the 1932 definition of the sugar scale precluded the calibration of a polarimeter, without quartz-wedge compensation, in °S, independently of the wavelength employed. This also applied to existing automatic photoelectric polarimeters. It was also considered that the definition should have a higher accuracy than is possibly obtainable in the measurements of practical saccharimetry. Accordingly, it was resolved that the 1932 definition of the normal sugar solution be redrafted as follows:

'The normal sugar solution is defined as 26.0160 g of pure sucrose, weighed in vacuo, dissolved in pure water at 20.00 °C to 100.000 mL. This corresponds to a concentration of 26.000 g of sucrose, weighed with brass weights in air, under normal conditions (101 kPa pressure, 20 °C, 50% relative humidity) in 100.000 mL of solution at 20 °C.'

It was also recommended that further investigations be carried out on the optical rotation of the normal sugar solution at exactly defined wavelengths, preferably in the region of the yellow-green mercury line. Also, it was recommended that the studies should include factors relating to the purity of sucrose, as it plays an important part in the definition of the 100 °S point. The results of these studies should provide a basis for a physically exact definition of the normal sugar solution, not limited to any one principle of measurement.

Following on reports of these studies, a new definition of the 100 °S point was adopted at the 1966 meeting of ICUMSA; that is, 'The basis of the 100 °S point of the International Sugar Scale is the optical rotation of the normal weight of sucrose dissolved to 100.000 mL, at the wavelength of the green line of the mercury isotope ^{198}Hg = 546.2271 nm, 20.00 °C and 200.000 mm tube length.' Also, for these standard conditions, the 1970 meeting adopted the following rotation value:

$$\alpha^{20.00\ °C}_{546.2271\ nm} = 40.765 \pm 0.001°$$

The latter meeting also adopted the following values for quartz control plates of the sugar value of 100.00°S for saccharimeters equipped with quartz-wedge compensation.

$$\alpha^{20.00\ °C}_{546.2271\ nm} = 40.692°$$
$$\alpha^{20.00\ °C}_{589.4400\ nm} = 34.619°$$

The small differences between these values and those of the 1932 definition are due to differences between the new and the old values obtained for the rotation of the normal sugar solution.

Another recommendation adopted at the 1966 meeting was that by means of the following formula the rotation values of the normal sugar solution may be calculated for wavelengths other than the 546.2271 nm determined, but to be limited to the range 540 to 590 nm, until further notice.

$$\frac{\alpha_\lambda}{\alpha_{546.2271\ nm}} = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} + \frac{d}{\lambda^8}$$

where
$a = -1.7982 \times 10^{-3}$
$b = +2.76532 \times 10^{5}$
$c = +6.55736 \times 10^{9}$
$d = +1.03825 \times 10^{19}$
λ = wavelength in vacuo in nm.

The mean wavelength of filtered yellow sodium light is taken as $\lambda = 589.4400$ nm in vacuo. From the above equation the angular rotation corresponding to the 100°S point for this wavelength is:

$$\alpha^{20.00\ °C}_{589.4400\ nm} = 34.616 \pm 0.001°$$

The wavelengths mentioned in the 1966 recommendations are referred to vacuum.

Polarimeter tubes

Tubes for use with polarising sugar solutions in visual polarimeters or saccharimeters are usually supplied in three lengths—400 mm, 200 mm and 100 mm, and may be of glass or metal with screw or slip caps. For accuracy they must conform to three general requirements.

(1) The length of the tube should be accurately known;

(2) The ends of the tube and the surface of its cover glasses must be plane parallel;

(3) The tube must be centred evenly in its mountings.

The tube of 200 mm length is used for the normal weight of all saccharimeters but tubes of 400 mm length are commonly used for dilute solutions such as bagasse extracts. If, due to depth of colour of the solution, a short tube is employed, the errors in observation are proportionately higher and short tubes are only used when absolutely necessary.

The specifications for polarimeter tubes and cover glasses can be found in Table XXV and it should be remembered that, when fitting cover glasses to polarimeter tubes, undue strain on the glass should be avoided. The rubber washers, which lie between the cover glass and the metal cap, should also be inspected to ensure that they are still compressible and that they lie flat in the cap.

Various forms of polarimeter tube are used and these may be seen in Figure II-20. Figure II-20a shows the plain glass polarimeter tube, while Figure II-20b shows a tube with an enlarged end. This modification offers the advantage that entrapped air bubbles can be manipulated into the enlarged end of the tube, where they offer no obstruction when reading. Figure II-20c shows an illustration of Pellet's flow-through tube. This continous tube is commonly used for juice testing purposes in connection with c.c.s. determinations, but its use should be restricted to this purpose, for when successive solutions which differ markedly in density are to be observed, considerable risk of error is introduced. Figure II-20d shows a jacketed tube used when polarisation temperature must be controlled e.g. during sucrose determinations using the Clerget method.

Temperature effects

When a sugar solution is made up and measured at temperatures other than 20 °C, the reading obtained will be influenced by the temperature difference on the instrument, the apparatus used in making up the solution, and the substance in solution. Therefore, the reading obtained must be corrected to 20 °C to give the true polarisation in °S of the solution and, in addition, this corrected polarisation reading must be corrected further if the solution was not made up at 20 °C.

R.A.M. Wilson (1965) of the Colonial Sugar Refining Co. Ltd (now CSR Ltd.) classified the corrections for temperature effects into the 'polarisation reading correction' based on the temperature of the solution when taking a reading and the 'solution preparation correction', based on the temperature at which the solution is made to the mark when the solution is prepared by a weight/volume method. The first correction is subdivided into the effects on polarisation of temperature of the substance and of the instrument; the instrument effect being applicable only when quartz-wedge saccharimeters are used. The temperature coefficients for each factor involved are shown in temperature correction equations, and it is possible to obtain combinations of the equations for practical applications for substance effect, instrument effect, and solution preparation correction if necessary.

The various factors involved in temperature corrections to be applied to the reading obtained when sugar solutions are polarised at temperatures other than 20 °C, and the equations involved for the two classifications are as follows:

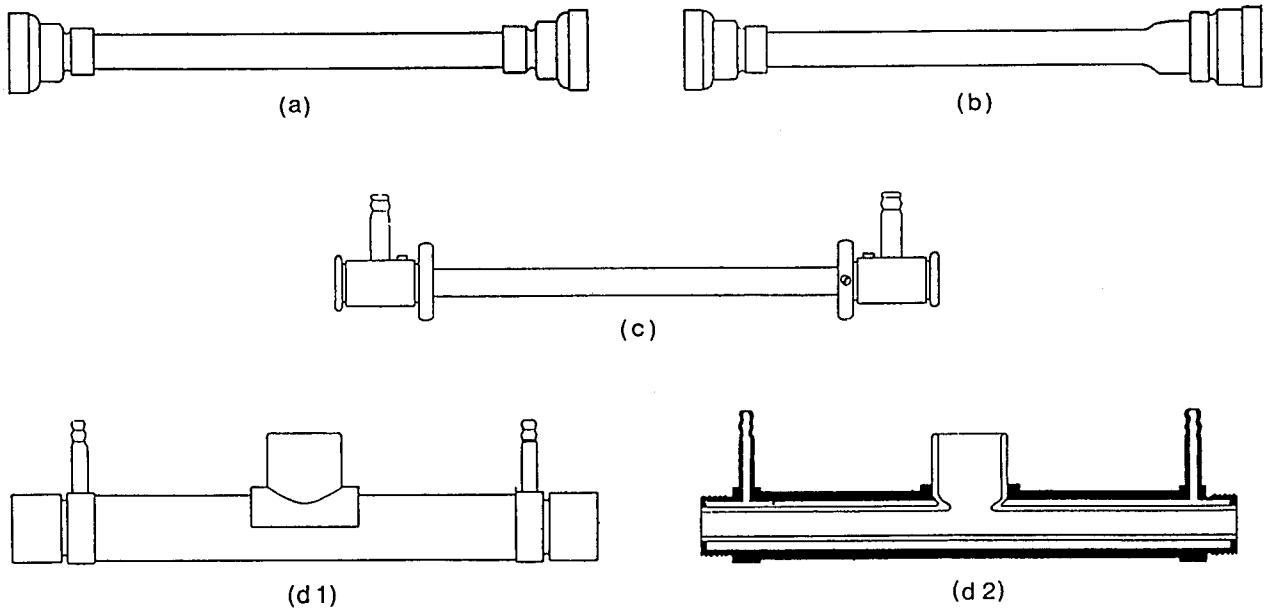


Fig. II-20—Types of polarimeter tube.

1. *Polarisation reading corrections*	Correction equation
(a) Substance effect	
(i) Quartz control plate—specific rotation	$P_{20} = P_T - 0.000\,144\ P_{20}\,(T_r - 20)$
(ii) Sucrose—specific rotation	$P_{20} = P_T + [0.000\,184 - 0.000\,006\,3\,(T_r - 20)]\ NS\ (T_r - 20)$
(iii) Reducing sugars—specific rotation	$P_{20} = P_T - 0.004\ NR\ (T_r - 20)$
(iv) Solution concentration	$P_{20} = P_T + [0.000\,29 + 0.000\,006\,6\ (T_r - 20)]\,(T_r - 20)$
(v) Tube length expansion and contraction	
glass	$P_{20} = P_T - 0.000\,008\ P_{20}\,(T_r - 20)$
stainless steel	$P_{20} = P_T - 0.000\,017\ P_{20}\,(T_r - 20)$
(b) Instrument effect	
(i) Compensator—specific rotation	$P_{20} = P_T + 0.000\,144\ \eta\ P_{20}\,(T_P - 20)$
(ii) Scale expansion and contraction	
glass	$P_{20} = P_T + 0.000008\ \eta\ P_{20}\,(T_P - 20)$
metal	$P_{20} = P_T + 0.000018\ \eta\ P_{20}\,(T_P - 20)$
(iii) Quartz-wedge expansion and contraction perpendicular to the optical axis	$P_{20} = P_T - 0.000\,013\ \eta\ P_{20}\,(T_P - 20)$
2. *Solution preparation corrections*	
(i) Solution expansion	$P_{20} = P_T - [0.000\,29 + 0.000\,006\,6\,(T_m - 20)]\,P_{20}\,(T_m - 20)$
(ii) Flask volume expansion and contraction	$P_{20} = P_T + 0.000\,025\ P_{20}\,(T_m - 20)$

Nomenclature

P_{20} = polarisation at 20 °C (°S)
P_T = polarisation at T °C (°S)
T_r = temperature of solution or quartz plate when reading the polarisation (°C)
N = normality of solution. A normal solution contains 26 g of sample in 100 mL of solution
S = weight % sucrose in the sample
R = weight % reducing sugar in the sample
T_P = temperature of polarimeter (°C)
T_m = temperature of solution when making to the mark (°C)
η = constant equal to 1 for quartz-wedge saccharimeters and equal to 0 for other types of polarimeters and saccharimeters.

Following on the work of Wilson and a submission to ICUMSA in 1966 by the Australian National Committee of ICUMSA, the following simplified formulas were adopted as usually sufficient for temperature corrections to the polarisation of raw sugar. For other products, for quartz control plates and for high precision work, appropriate formulas may be obtained by suitable combination of the equations above.

For quartz-wedge saccharimeters the temperature correction to be made to the observed polarisation shall be:

$$(t_r - 20)\,(0.000\,33\ S - 0.004\ R)$$

where

t_r (°C) is the temperature of the solution as read in the saccharimeter
S is the approximate % sucrose in the sample
R is the approximate % reducing sugars (as invert sugar) in the sample.

For sugar polarimeters (without quartz-wedge compensation) the correction to be made to the observed polarisation shall be:

$$(t_r - 20)\,(0.000\,19\ S - 0.004\ R)$$

where the symbols are as defined above.

For accurate work it is desirable that control of temperature to 20.0 ± 0.5 °C be obtained for all polarimetric analyses of sugar solutions, thus eliminating any major temperature corrections.

THE SPECTROPHOTOMETER

The simplest method for estimating the concentration of a coloured substance is to make a visual comparison with a series of standard colours using a *colorimeter* or colour comparator. Natural or artificial white light is generally used as the light source. In effect, a colorimeter measures the degree of complementary colour absorbed by the sample. When the eye is replaced by a photoelectric cell, thus largely eliminating the errors due to the personal characteristics of each observer, the instrument is termed an *absorptiometer*. The photoelectric cell affords a direct measure of light intensity and hence absorption, rather than colour. For this reason, an absorptiometer may be used to measure the absorption of light in the ultraviolet as well as the visible region of the spectrum. This instrument usually employs light contained within a comparatively narrow range of wavelengths furnished by passing white light through appropriate filters.

An instrument which employs more nearly monochromatic light of continuously variable wavelength is termed a *spectrophotometer*. This instrument, which is

essentially a refined absorptiometer, provides the most accurate means for determining concentration by the light absorption technique. The basic features of an ultraviolet-visible spectrophotometer are shown in Figure II-21 and are described below.

Light source

A deuterium lamp is normally used to produce ultraviolet light (180 to 370 nm) while a tungsten or tungsten-iodine lamp is used to produce light spanning the visible and extending into the near-infrared region (370 to 1000 nm). Use of a tungsten lamp has the disadvantage that the tungsten filament vaporises and the vapour fixes onto the inner surface of the bulb. The resulting decrease in light transmission causes overheating and deterioration of the filament. A tungsten-iodine lamp on the other hand contains a mixture of inert gas and a trace quantity of iodine which greatly reduces the rate of vaporisation of the tungsten filament and hence provides for a longer source life.

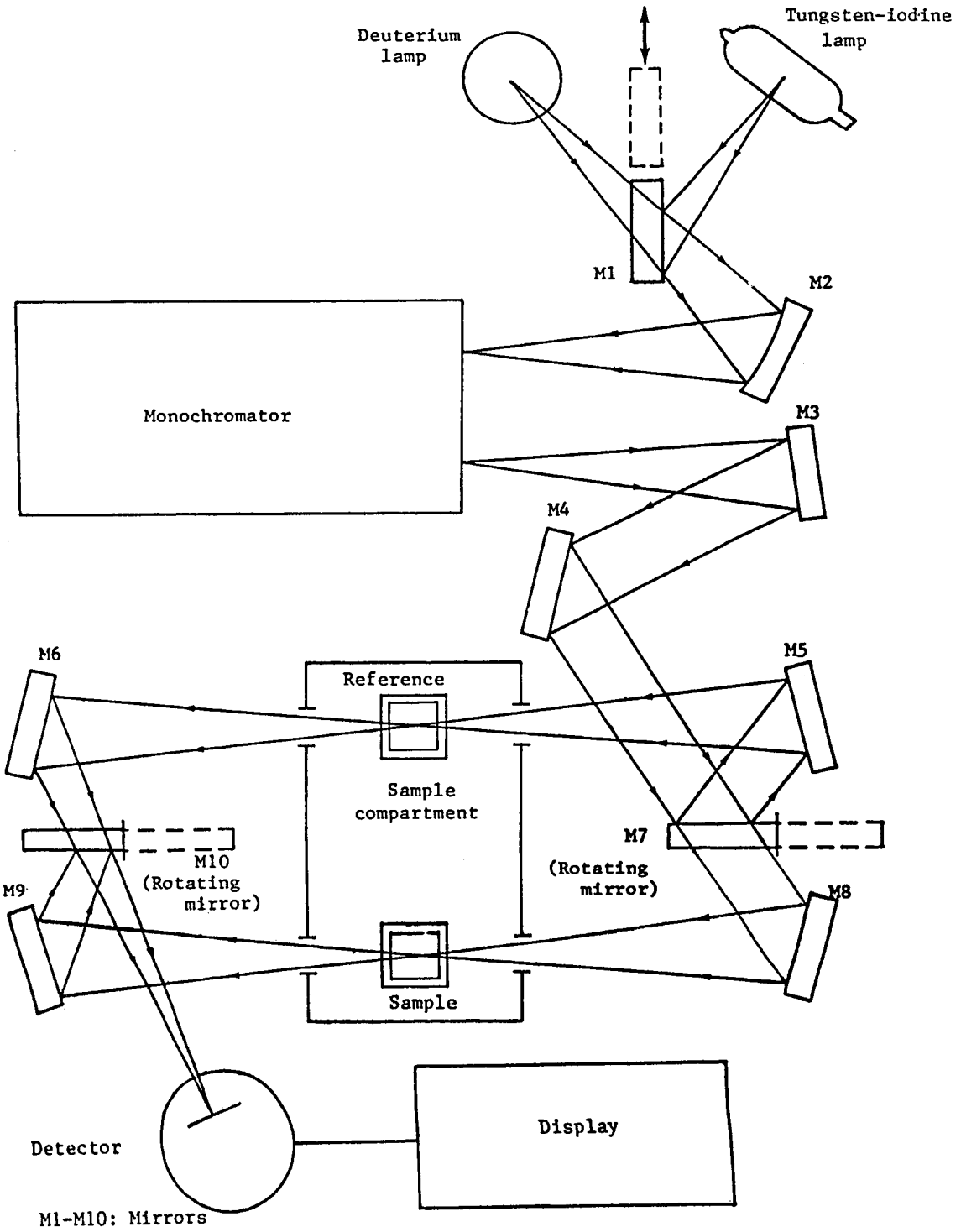


Fig. II-21—Basic features of an ultraviolet-visible spectrophotometer.

Monochromator

A monochromator is a device for dispersing the polychromatic light from the source into its component wavelengths and for selecting a narrow range (band) of these wavelengths. Monochromators are usually classified into prism and grating types, depending on the type of dispersion element used. In a prism monochromator (Figure II-22), light from the source passes through the entrance slit and is made into a parallel beam by a concave mirror. The light is then dispersed by a silica or glass prism and reflected back towards the exit slit via the concave mirror as a continuous series of convergent monochromatic beams. The wavelength of the light coming out of the exit slit is changed by rotating the prism.

A disadvantage of prism monochromators is that a complicated cam system is necessary in order to obtain a linear wavelength scale. This is because the dispersion of the prism varies with wavelength. Non-linear dispersion also means that the resolution, that is, the smallest wavelength interval for which two adjacent absorptions can be recognised as separate absorptions, is not uniform over the entire spectral region for a fixed bandwidth. The bandwidth may generally be decreased and hence resolution increased by decreasing the width of the exit slit of the monochromator. However, the output energy from the monochromator is proportional to the square of the slit width and hence reductions in the latter may result in large reductions in output energy.

In a grating monochromator, light from the source passes through the entrance slit and is made into a parallel beam by a concave mirror. The light is then incident upon a diffraction grating which disperses and reflects the light back towards the exit slit by the same or a different mirror. Some typical optical arrangements of grating monochromators are shown in Figure II-23. A diffraction grating consists of a reflecting surface on which a large number of parallel grooves (500 to 2000 per mm) have been ruled. Commercially available gratings are usually replicas duplicated from the master on a thin synthetic resin film cemented to a thick glass plate of small coefficient of expansion. Figure II-24 shows such a grating in cross-section.

The dispersion of light by a diffraction grating is due to interaction between the light and grooves, and the dependence of the extent of this interaction on wavelength. This dependence is described by the following equation:

$$m\lambda = d(\sin i + \sin \theta)$$

where i and θ are the angles of incidence and diffraction respectively, d is the distance between grooves and m is the order of diffraction (0,±1,±2 ...). Hence the first order angle of diffraction for light of wavelength λ is the same as the second order angle of diffraction for light of wavelength $\frac{1}{2}\lambda$ and so on. In order to obtain only the first order diffracted light of wavelength λ, the second and higher order diffracted light is excluded by means of order sorting filters.

The main advantage of grating monochromators over prism monochromators is greater dispersion and hence better resolution in the visible and near- infrared regions. Also, the dispersion of grating monochromators is almost constant over the useful wavelength range.

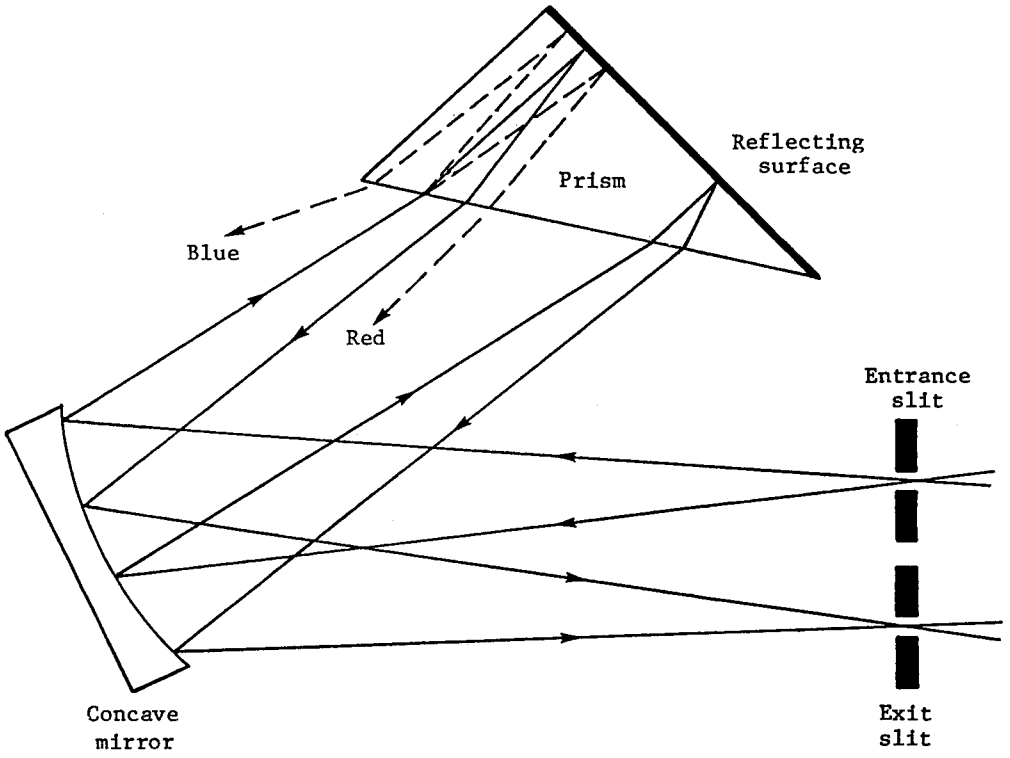
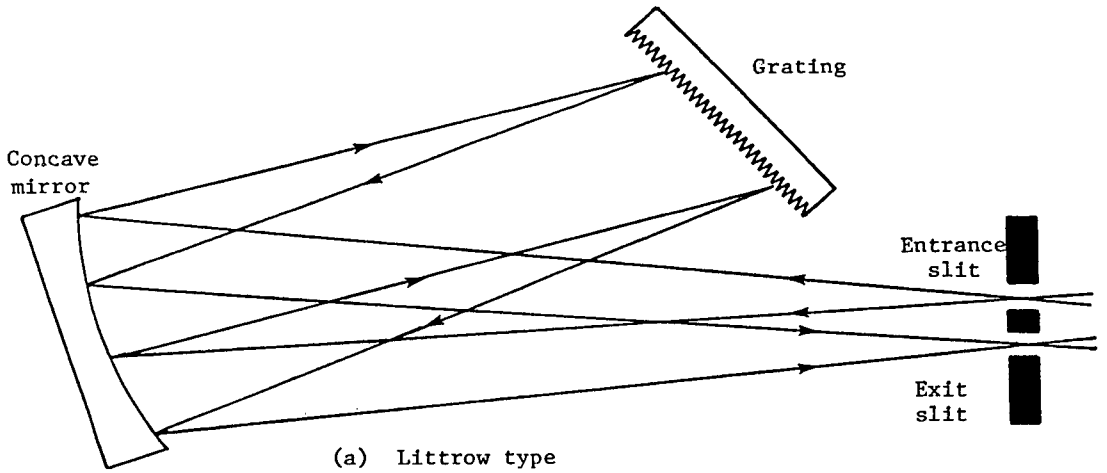
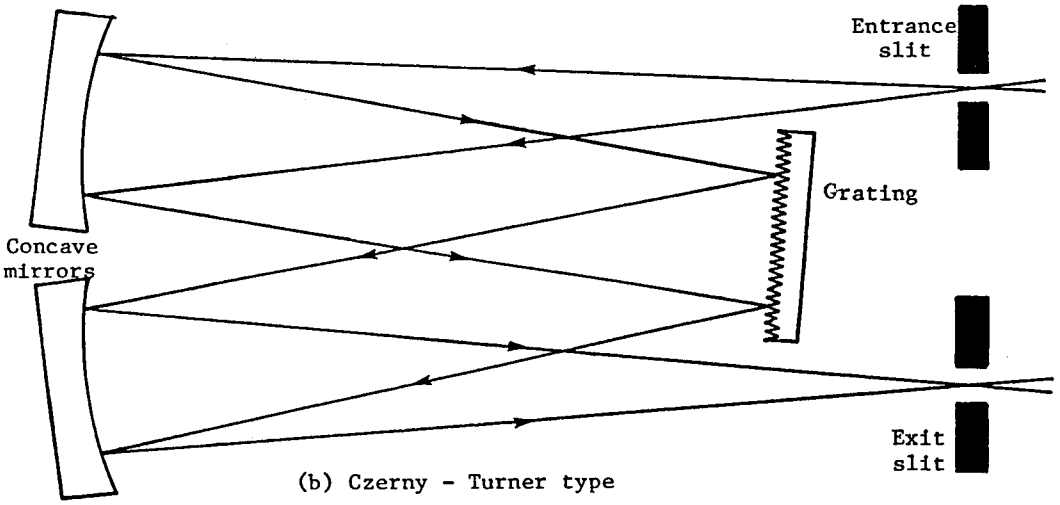


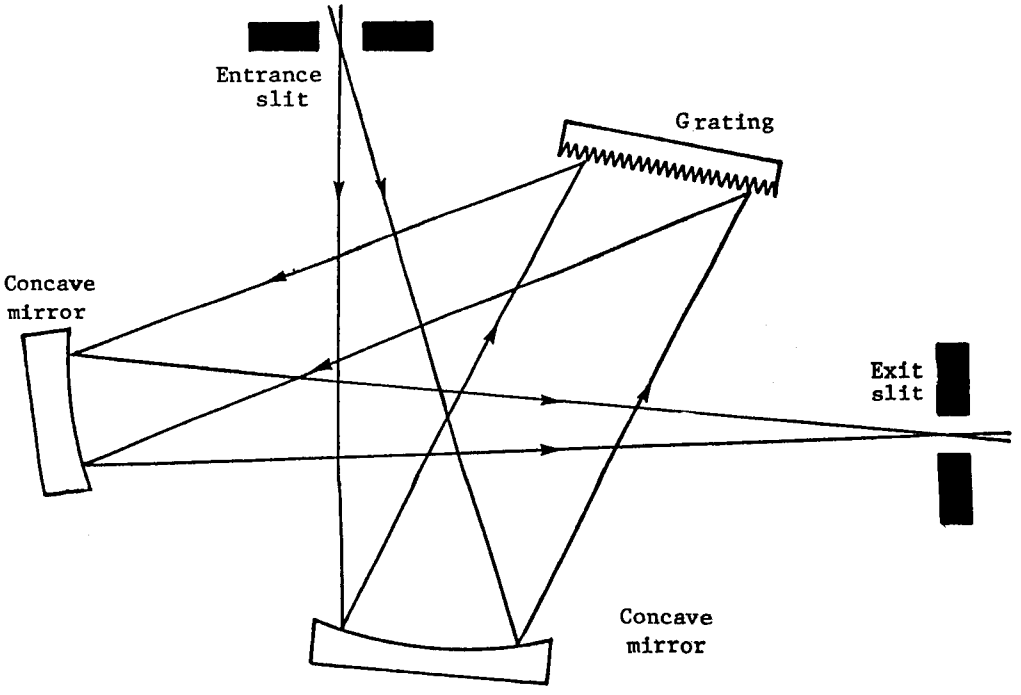
Fig. II-22—Littrow Mount prism monochromator.



(a) Littrow type



(b) Czerny - Turner type



(c) Crossed Czerny - Turner type

Fig. II-23—Typical optical arrangements of grating monochromators.

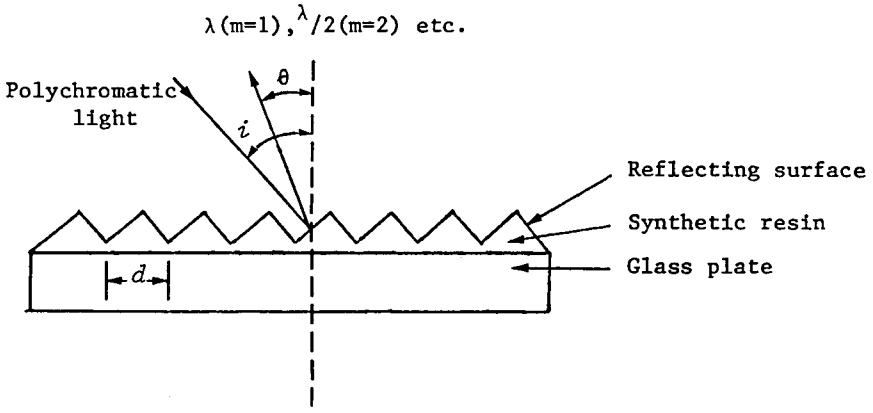


Fig. II-24—Diffraction grating.

Sample compartment

In double-beam instruments, light from the monochromator is directed alternately to the sample and reference cells by a rotating mirror (Figure II-21) or split into sample and reference beams by a half-silvered plate. The sample cell contains the dissolved sample while the reference cell contains the solvent alone. In this way the optical density (D) or transmittance (τ) of the sample at any wavelength is determined by measuring the intensity of the light emerging from the sample (I_t) and reference cells (I_0). In single-beam instruments, absorption by the solvent is compensated for by placing a cell containing the solvent alone in the beam and adjusting the instrument zero to 100% transmittance or zero optical density. This procedure must be repeated for each wavelength at which measurements are carried out.

Although sample cells are available in various shapes and dimensions, the most popular is the 10 mm square cell with a height of 45 mm. When the sample concentration is very low or the absorbance is too small for adequate detection, a cell having a longer optical path is effectively used. Cells are made from glass, which transmits in the 340 to 2500 nm range, or quartz, which transmits in the 180 to 2500 nm range. The careful matching of sample and reference cells, that is, selecting cells which have equal optical path lengths, is essential for accurate work.

Detector

The detectors of spectrophotometers convert optical signals (intensity) into electric signals and are therefore referred to as photodetectors. Various types of photodetectors are in common use, including silicon photocells, phototubes and photomultipliers. A silicon photocell employs a semiconductive surface for light detection. A phototube employs a photocathode and anode to which a constant voltage is applied so that light incident upon the photocathode liberates electrons which flow towards the anode. The electric current thus produced is very weak and amplification is therefore required. A photomultiplier on the other hand is a combination of a phototube and a high-gain amplifier.

As shown in Figure II-25, a photomultiplier has a photocathode and nine dynode plates which greatly

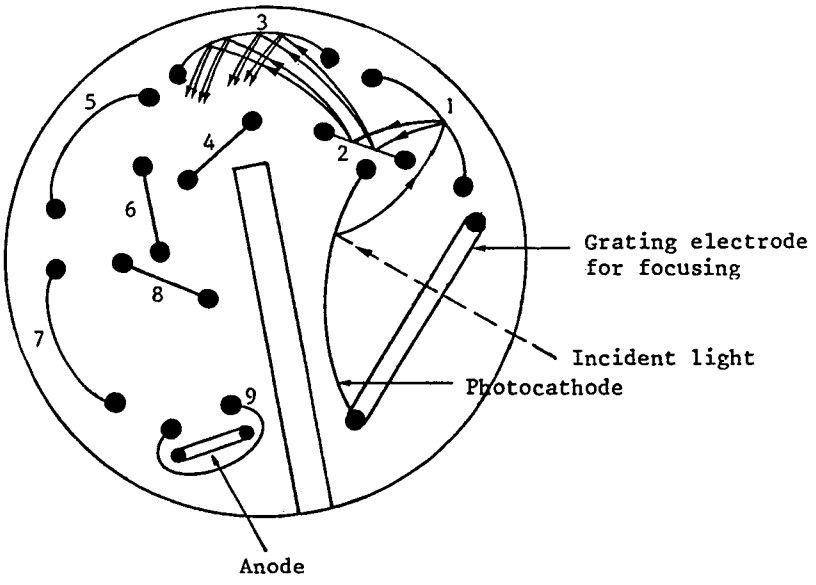


Fig. II-25—Photomultiplier.

increase the number of electrons generated by the photocathode. That is, there is a nine-step amplification. The anode is grounded and a negative high voltage of − 200 to −1000 V is applied to the cathode. This voltage is divided by serial resistors and applied to the dynodes in such a way that the voltage applied to each becomes progressively less negative.

Double beam systems can have a single-detector system which detects the sample and reference beams alternately, or a double-detector system in which the beams are sensed by two independent detectors. In single-detector systems a rotating mirror causes the sample and reference beams to enter the detector alternately. For the double-detector system it is necessary to select a pair of well-matched detectors to ensure high accuracy. The latter should also have good stability.

Turbidity measurement

Spectrophotometers are also used to measure the turbidity of such mill products as evaporator supply juice (ESJ). For this determination the wavelength is set at 975 nm, well into the infrared region to avoid the effect of juice colour, and the amount of radiation absorbed, read as optical density, gives a measure of turbidity. For convenience, turbidity is usually recorded in turbidity units (TU) where one TU = 1000 x optical density/mm. A description of the CSR turbidimeter (Figure II-26) is as follows.

Inside the head, the measuring light beam is passed through the centre of the flow cell (heavy duty borosilicate glass tubing of 20.4 mm inside diameter) from the front to the rear, at 90° to the flow of the sample. The light source is a modulated light emitting diode (LED). Because of the relatively narrow bandwidth, no filters are required to eliminate unwanted wavelengths. In the rear of the head a phototransistor detects the light level transmitted through the flow cell and sample (I_t). A second phototransistor is placed above the LED to obtain a reference level of the light emitted from the LED (I_o). The signals from the signal and reference phototransistors are sent to the electronics module for processing. A tungsten lamp is placed behind the glass cell in order that the operators may view the sample and monitor the condition of the flow cell.

The ESJ sample is usually taken from the clarifier weir box and then conveyed to a suitable location for the turbidimeter head along a gravity feed sample line capable of supplying about five litres of ESJ per minute.

The output of the clarifier should not contain any bubbles. Although the turbidimeter electronics are designed to have little response to a small quantity of bubbles passing through the light beam, a large quantity will be seen as high turbidity. This problem may be overcome by passing the ESJ along two to three metres of horizontal 25 mm sample line immediately before the turbidimeter head. With the correct flow rate, this allows the bubbles to float to the top of the sample line where they do not intersect the narrow light beam passing through the centre of the flow cell.

A pneumatically operated 25 mm ball valve placed in the sample line near the turbidimeter head allows the ESJ flow to be turned off. Water is connected into the sample line by a second ball valve. At regular intervals (normally every one or two hours) the sample line is closed and the water valve is opened automatically. Clean water then flushes through the cell for 30 seconds

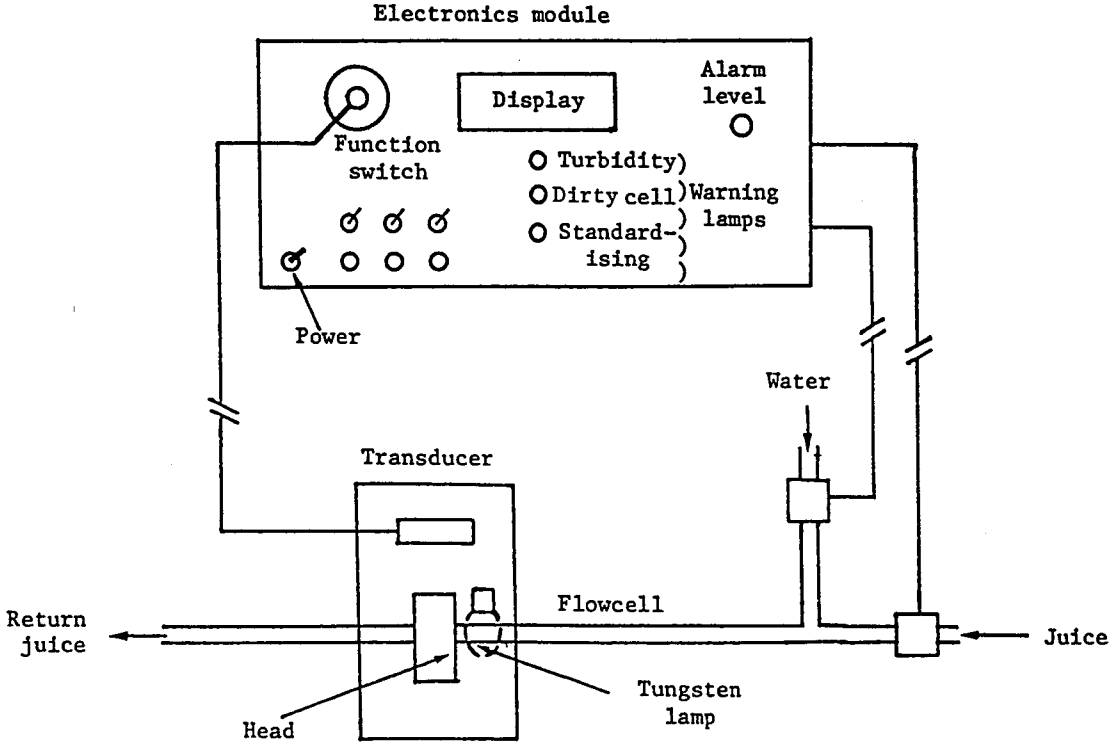


Fig. II-26—CSR Turbidimeter.

which helps to remove built-up scale from the flow cell walls. At the end of the flushing period the water is stopped for a further 15 seconds and the electronics makes an automatic correction for the build-up of scale on the cell walls. This reading is taken as the new zero turbidity reference. The juice valve then re-opens to continue monitoring the ESJ.

The electronics module receives the signals from the reference and measuring phototransistors. It amplifies and demodulates the signals, computes the logarithm of their ratio (optical density) and displays the results in turbidity units (TU) on a digital panel meter.

The electronics module also drives the LED and tungsten viewing lamp in the head, controls the automatic water standardising cycle, applies the automatic cell correction to compensate for scale build-up on the flow cell, and provides 0-10 V and 4-20 mA outputs for recorders and remote displays.

Three warning lamps are provided on the front panel. There is a standardising lamp which indicates when the instrument is carrying out a water flushing and standardising cycle, a dirty flow cell lamp to indicate when the flow cell has more than 10 TU of dirt on the walls, and a turbidity alarm to indicate when the turbidity of the juice sample is greater than the adjustable alarm level set point. A remote alarm (e.g. flood lamps) of up to one ampere at 240 volts can also be connected.

A function switch on the front panel allows the turbidity of the sample (in TU) and various internal parameters to be displayed. The latter include the alarm level set point, the +15 V and −15 V supply voltages, the cell correction (in TU) being applied to compensate for dirt on the flow cell, and the signal levels from both the measuring and reference phototransistors. The latter are transmittance values and will be nominally 100.0%.

Apart from switches, connectors and one relay, the electronics are solid state throughout. Almost all of the electronics are mounted on three plug-in printed circuit boards, which are easily replaced by removing the right-hand front panel. An extension board is provided to allow testing of the circuits outside the instrument.

NEPHELOMETRY

A nephelometer is an instrument which measures the light scattered by suspended particles from a beam of light passing through a suspension. The amount of light scattered is dependent upon the size of the particles and their geometric shape and concentration. The technique is generally restricted to measurements on relatively dilute suspensions since it relies on the incident and scattered light penetrating the liquid medium. However, the RIMCO nephelometer developed by CSIRO uses fibre optics to measure the light scattered back from a very thin layer of sample immediately in front of the probe and can therefore be used in virtually opaque systems containing several per cent of suspended solids.

THE MICROSCOPE

In sugar factory operations the most important use of the microscope is for the examination of proof samples withdrawn from vacuum pans and for the determination of the sizes of crystals in sugar, massecuite, magma, seed, etc. For these purposes a comparatively low order of magnification is required. The microscope is also used in the determination of saturation temperature by the optical method and has numerous other casual uses for which a fairly high degree of magnification is required. Hence, whilst the provision of a simple low powered microscope for use on the pan stage is universally accepted, there is also need for a more versatile instrument of better quality for laboratory use.

The structure and operation of the microscope

The essential parts of the monocular microscope in general use in the sugar laboratory are illustrated in Figure II-27. The heavy base of cast metal A supports a short rigid upright pillar B to which the arm or limb D is hinged at C. The arm, which is conveniently curved for easy grasping by the hand when the microscope has to be moved from place to place, is also of heavy metal and the hinge C should allow only a stiff movement in a vertical plane and no movement whatsoever sideways. At the upper end the arm bears the tubular body E, which carries the magnifying lenses. Just near the hinge, the stage F is rigidly attached to the arm. Beneath the stage and fitted to it is the condenser G, commonly known as the substage condenser, and below that the double mirror H, which is flat on one side and concave on the other. Movement of the tubular body down to, and up from, the stage is provided by a coarse adjustment operated by turning the milled head I and a fine adjustment working through a smaller head J. At the top the tubes of most microscopes are fitted with a graduated draw tube K so that the distance between the eye- piece L and the nose-piece M in which the objectives N are mounted, can be varied to suit the recommendations of the manufacturer of the lenses. The eye-piece fits easily into the top of the tube. The objectives do not fit directly into the tube, but are screwed into the revolving nose-piece. This may hold from one to four objectives. For purely routine use at the at the one magnification a single-objective nose-piece is quite suitable, but when a range of magnification is required the multi-objective nose-piece is essential in that it allows the ready changing of objectives without risk of damage to the object and with a minimum of delay. The substage condenser is not necessary with low-power objectives (when the concave side of the mirror performs the same function), but it is essential for high-power objectives which must have a concentrated beam of intense light. The condenser must be used only with the plane mirror, otherwise it loses much of its efficiency. The rack and pinion gear O is used for moving the condenser up and down and there is usually some provision for swinging the condenser out of the optical axis when not required. The vertical movement of the condenser is very important because the system of lenses forming the condenser has to be focused just as carefully as the objectives if a high-quality image of the object is to be obtained. The iris diaphragm P used to regulate the amount of light coming into the condenser, is an integral part of it and is operated by a small lever facing towards the front of the instrument.

General principle of operation: By suitable positioning of the mirror in relation to the condenser and the source of light, rays of light are reflected from it and into the condenser where they are focused, both to cover the object and fill the objective. The object is mounted on a glass slide, usually measuring 76 x 26 mm, held firmly by spring clips to the stage, and for satisfactory examination should be either comparatively transparent, or consist of small particles separated by clear liquid. A glass cover slip (0.17 mm thick) is placed over the object, unless a 'no cover glass' objective is used. The light passing through the mounted object enters the objective, the function of which is to form an enlarged image of the object for further magnification by the eye-piece. The lens of the eye collects the light rays coming through the eye-piece and projects an image on the retina which the brain records as an object situated about 250 mm away from the eye. The image seen by looking down a microscope is inverted and if one wishes to move an object from, say, the left edge of the field of view to the centre,

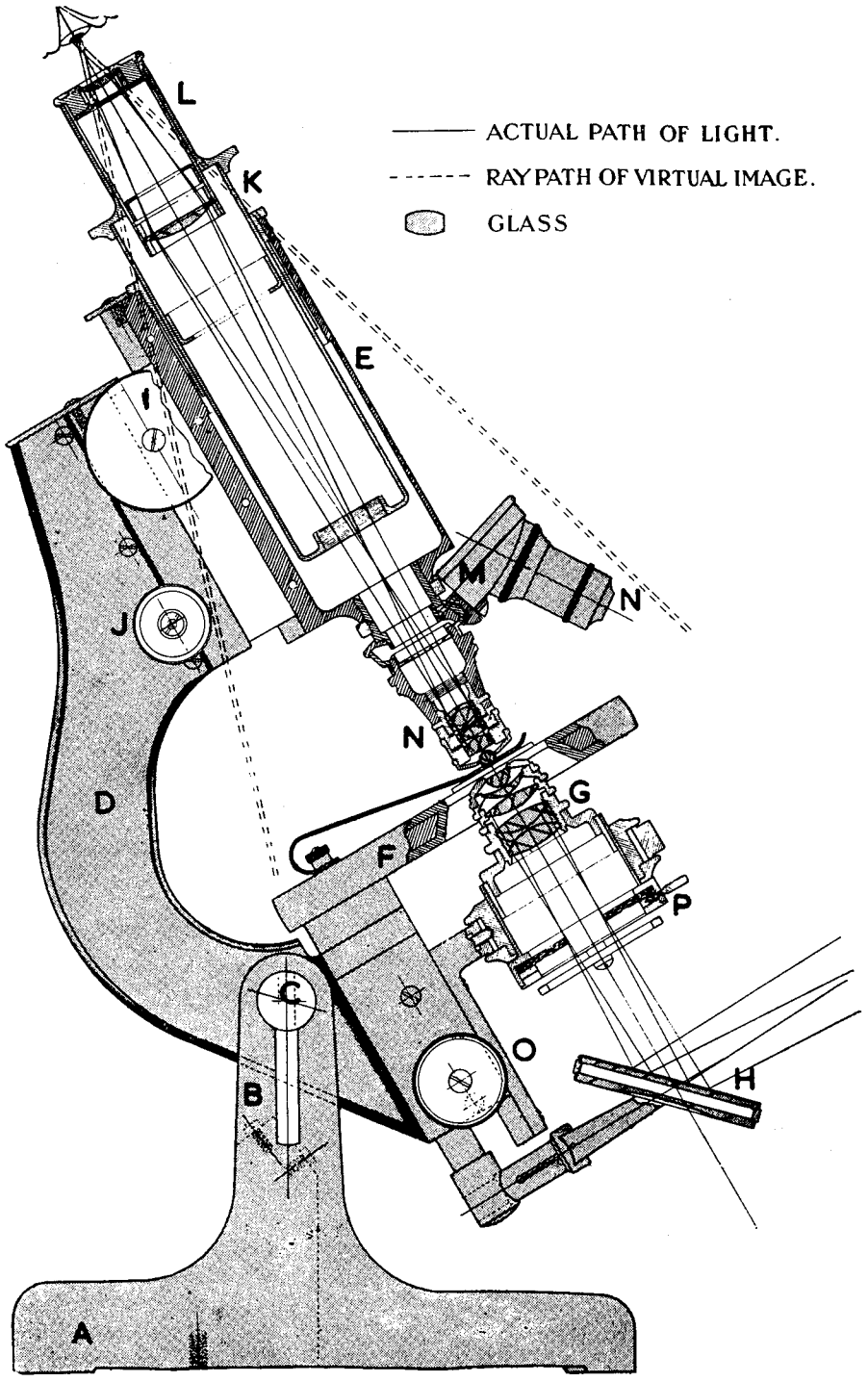


Fig. II-27—Essential parts of a microscope.

one must move the stage (and slide) from right to left and not left to right. The same reversal, of course, occurs for other movements also.

Lenses and magnification: The objectives are the most important components of the microscope since on their perfection depends the efficiency of the instrument. They each consist of a series of lenses in a brass cylinder and are made to give various degrees of magnification: the higher the magnification the more lenses have to be incorporated, and so the more expensive the objectives become. The lower powered objectives are known as 'dry' lenses, but objectives giving a magnification of 80 or more are usually 'oil immersion', that is they can only operate when a film of special oil, having a refractive index similar to that of glass, makes contact with both the front of the lens and the top of the glass slip covering the object. 'Water immersion' lenses are also available but these are rarer. Immersion lenses represent the peak of the lens maker's skill and are essential for critical work at high magnifications, but they are quite unnecessary for practical sugarhouse control, and the special conditions for their satisfactory use will not be considered here. Two types of dry lenses which are commonly available are the achromatic and apochromatic types. The apochromats are more corrected for colour errors inherent in any glass magnification system, but their advantage is only apparent in critical work at the higher magnifications. For the practical requirements of a sugar mill the much cheaper achromats are quite suitable. For photographic work the use of a plano lens, which has a flatter field than these lenses, is required. Objectives are designated by their magnifying power. The common objectives are the 10X and 40X lenses, and the 80X which is an immersion type. An objective is always designed to be used with a certain tube length, usually 170 mm, but objectives for a 240 mm length are also obtainable.

Like the objectives the eye-pieces are also compound lenses. Their function is to pick up the enlarged image of the object formed by the objective and magnify it still further. The total magnification thus obtained is the product of the objective magnification multiplied by the eye-piece magnification. Eye-pieces are made with various powers of magnification, 6X and 10X being the most common.

The table below shows the approximate magnification obtained with various objectives and eye-pieces.

Objective or initial magnification	Final magnification	
	6X eye-piece	10X eye-piece
10	60	100
20	120	200
40	240	400
80	480	800

Source of light: While ordinary daylight, not direct sunlight, is often used as a source of illumination for microscopic work, artificial light is preferred. Its use allows the general lighting in the room to be reduced to a comfortable level for microscope work and so extraneous annoying glare can be eliminated. It also gives the operator complete control over the intensity of the illumination and allows the microscope to be sited wherever convenient.

Operation: The microscope must be set on a firm table or bench at a comfortable height for the operator, and vibration from machinery, people walking on the floor, etc., eliminated as far as possible. An eye-piece and the objectives having been placed in position, the operator puts the microscope squarely in front of him with the mirror facing directly towards the source of light. The diaphragm P is opened to its fullest extent and the plane mirror adjusted so that the maximum amount of light is reflected through the condenser and the whole field of view is illuminated as evenly as possible. It is convenient at this juncture to focus an object on a slide with the low power objective even though the light may not be satisfactory. *When bringing an object into focus never rack the tube downwards with the eye looking through the eye-piece; always rack down carefully as close to the object as possible with the eye on a level with the stage and then rack upwards until the object is in focus.* Many expensive lenses and irreplaceable objects have been ruined by failure to obey this simple rule.

With the object in focus the condenser is then brought into focus also. This is done by moving the condenser upwards towards the slide and concurrently moving the mirror slightly from time to time until the edge of the lamp or the filament of the bulb or, if daylight is being used, a portion of the window frame or a mark on the window glass, comes into view. This image is then made to disappear by moving the condenser downwards slightly, and the illumination restored to its previous uniformity by manipulation of the mirror. The condenser is then transmitting the maximum amount of light, which in general will be too much for use with the low powers and should be reduced by use of the diaphragm, or a screen of ground or coloured glass inserted between the source of light and the mirror.

The coarse adjustment is operated by the milled head I and is all that is necessary for the lower powers. For the higher powers the fine adjustment J is necessary to bring the object into sharp focus. The low power objective should always be engaged first and should it be desired to view a section of the field in greater detail, the section is moved into the centre of the field, an objective of higher power turned into position, and the focus carefully adjusted. The low power is the reconnaissance lens and the examination of any object should commence with this before using the higher power.

Objects mounted on the usual 76 x 26 mm glass slides may best be observed by submerging them in a thin film of a colourless liquid and carefully placing a coverslip over the whole. For pan stage observations with very low powers a coverslip is not necessary, but crystals are seen much more clearly if mounted in a couple of drops of a saturated solution of refined sugar. Massecuites may be thinned down for examination by mixing with a

drop of the saturated solution. Black circular air bubbles may interfere with the observation of some preparations, but a drop of alcohol either neat or sugar-saturated will usually cause them to disappear.

Direct measurement of objects: It is frequently desired to measure accurately the dimensions of an object under the microscope. It is manifestly impossible to place a fine ruler in the same field and make direct readings as one would do were the object of a size easily measurable by comparatively gross instruments such as calipers and rules. Therefore, an eye-piece micrometer is used. This is preferably fitted to the eye-piece during manufacture but may be inserted by the user when making a measurement. It consists of a glass disc on one surface of which are accurately etched lines or squares of uniform spacing. To fit the micrometer, the top of the eye-piece is unscrewed and the micrometer dropped in to come to rest on a ledge within the eye-piece. The top is then replaced and the eye-piece looked into while held vertically over a source of light. The micrometer rulings should now be in sharp focus: if they are not, the micrometer may be found to have landed upside down on the ledge or it may be necessary to screw the top out slightly to give a sharp focus. It will be found that when properly positioned and in sharp focus the micrometer rulings will lie in the same plane as the image of the object and the size of the object in terms of divisions can be read directly. The apparent size of these divisions in millimetres is, however, not known and must be ascertained by reference to a stage micrometer. This consists of a stout 76 x 26 mm glass slide with a portion in the centre ruled accurately with lines a known distance apart. A common type has lines several millimetres long 0.1 mm apart with one 0.1 mm section subdivided into 0.01 mm. By focusing on this micrometer on the stage the eye-piece rulings can be superimposed on the scale readings and the value of the eye-piece micrometer divisions easily measured. This measurement of the apparent actual size of the eye-piece micrometer division is termed 'calibration' of the eye- piece micrometer and varies with the magnification, so a separate determination must be made for each combination of eye-piece and objective at a particular tube length. Eye-piece micrometers are not expensive and should be part of the equipment of every microscope: as a matter of fact they can be kept permanently in the eye-piece and so run no risk of being mislaid. The stage micrometers are more expensive but officers of BSES will be pleased to calibrate any microscopes and eye-piece micrometers upon request.

The projection microscope

A projection microscope is of value when a large image is to be thrown on a screen for demonstration purposes or on to a table for the purpose of making a drawing.

Outfits are available for converting a standard microscope into a projector, the main requirements being a stand to provide rigid mounting and an efficient illumination train of high intensity. Complete projection microscopes may also be obtained. Various models are available ranging from expensive high power units to much simpler ones when only low to medium magnification is required. A projection microscope is shown in Figure II-28.

This microscope is a type suitable for use in the examination of proof samples withdrawn from vacuum pans etc. The slide with the sample to be examined is placed on the stage and brought into focus on the viewing screen of about 180 mm diameter. The standard lens supplied (10X) is of sufficient power for pan stage operation; however, other objectives up to 40X are also available. A squared grid may be placed over the screen and calibrated for size depending on the objective used.

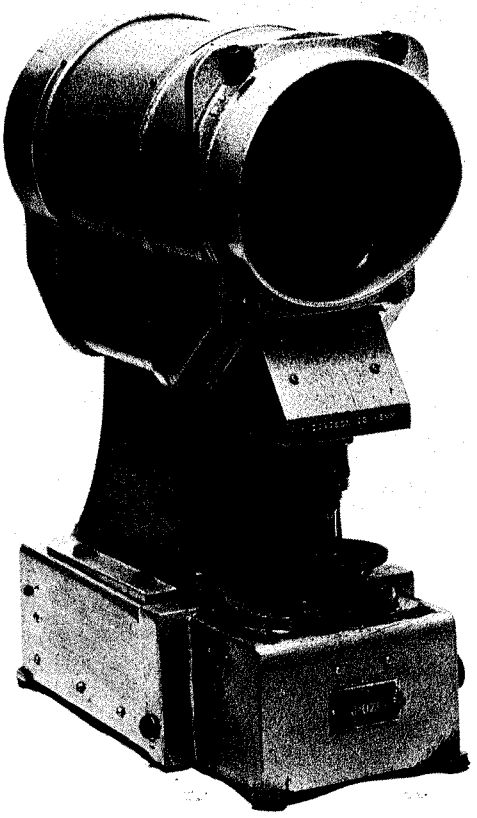


Fig. II-28—Projection microscope.

Photomicrography

Photomicrography is the process of recording on film the image produced by the microscope. The fact that a real image of the microscopical object is projected, without the aid of any equipment other than a brilliant source of illumination, by the eye-piece onto a screen located above it, makes photographic reproduction possible.

If a light-sensitive plate or film is substituted for the screen and all extraneous light excluded, a negative can be secured.

The simplest form of equipment consists of a light-tight box with a ground glass screen fitted into the top, which can be exchanged for a film pack or plate holder. The box is arranged over the microscope so that the image can be focused onto the screen, which is then exchanged for the film. The exposure can be made by turning the microscope light on for the required period.

Another simple method involves a camera with the lens removed, connected in a light-tight manner to the microscope tube. A single-lens reflex camera or one with a ground glass focusing screen is required so that accurate focusing on the focal plane of the camera can be done, for the point of best focus for the camera will not be identical with the best visual focus through the microscope. If a camera with a focal plane shutter is used this can be used for making the exposure, otherwise the microscope light can be used.

Complete photomicrographic equipment, ranging from extremely simple to very elaborate, is available from microscope manufacturers. If serious work is contemplated these commercial products are to be preferred, however very good results can be obtained with improvised outfits.

THE CARE OF OPTICAL INSTRUMENTS

All too frequently optical instruments are treated as though they were a piece of laboratory furniture and not as delicate instruments built by the manufacturers to a degree of high precision. If treated and used carefully the life of a good instrument is practically unlimited.

Optical instruments should be set up in situations which are not exposed to dampness or corrosive fumes, or subjected to jarring or vibration. In tropical conditions, dampness favours mould growth which etches the polished surfaces of prisms and lenses. It has been found in practice that mould growths on calcite prisms will render a saccharimeter useless within a short period of time from when they first become visible. If these are seen the instrument should be forwarded for attention to an instrument maker who is thoroughly conversant with it.

If the instrument is subjected to vibration or jarring the optical system may be thrown out of alignment. Where it is not practicable to build the laboratory sufficiently far from the mill to avoid all vibration, the instrument should be mounted on a suitable anti-vibration table.

The instrument should be examined regularly and kept scrupulously clean. This applies, in the case of saccharimeters, to splash glasses and the trough. If juice is allowed to accumulate in the trough, thus penetrating to the threads of the screw caps holding the splash glasses, great difficulty will be experienced when an attempt is made to remove them. In some saccharimeters the splash glass holder is held in position by means of a tension spring and is constructed for ready removal by the fingers. It should be maintained in such a condition.

The prisms of a refractometer should always be thoroughly cleaned (with lens tissue moistened with alcohol) and dried after use and a piece of lens tissue placed between the prisms before closing them. This assists in keeping the polished face of the measuring prism in good condition.

A microscope, even one in the cheaper range, is an instrument of precision and as such should be treated with every care, if it is to give satisfactory results over a long period. The operation and manipulation should be entrusted only to people who have shown themselves capable of handling it with the respect it deserves. Special precautions should be taken to ensure that dust is kept out of the lenses at all times. When not in use, objectives should be placed carefully in the small plastic or metal cans provided by the manufacturers. There should always be an eye-piece in position otherwise damaging grit is likely to enter the draw tube, body, nose-piece and objectives. Eye-pieces should never be left dismantled, for dust inside the eye-piece will spoil the image. The condenser remains attached to the microscope permanently and should be wiped over from time to time with a dust-free cloth, care being taken that the top lens surface is not scratched. The diaphragm and mirrors should be quite dry and dust-free. While a very small amount of lubrication is required for the adjustment threads and racks, oil or grease elsewhere is to be avoided at all costs. Not only is it unnecessary, but it damages lenses and specimens and in removing it permanent harm can easily occur to the instrument.

Care in the actual use of the microscope is also of importance in maintaining the instrument in a good working condition. It should never be subjected to sudden jolts or bumps and never allowed to get sticky or dirty. The underside of the slides should always be dry and clean before being placed on the stage and no liquid should be allowed to run off the mounted slide. The technique for avoiding the fouling of the front lens of the objective when bringing the object into focus has been explained and it should be followed at all times.

When not in continuous use, all optical instruments should be kept under a cover. At the end of the season they should be cleaned and stored away in a dry atmosphere.

CHAPTER III

MODERN BALANCES AND WEIGHING

IN the five years since 1978 there has been a radical change in balances, a change even greater than the introduction of the single-pan balance. The electromagnetic-force-compensation technique eliminates the knife edge and has been so successful that one major balance manufacturer ceased to manufacture mechanical balances with knife edges in 1983.

By itself the introduction of electromagnetic-force-compensation, though significant, would merely be the utilisation of another of the many properties that can be used as a means of weighing. The application of the microprocessor, however, has meant that it is possible to take the digital output signal from the balance and transform it into any unit, to collect these data for later analysis, and to use the balance as a process controller.

The introduction of this type of balance into a laboratory will not greatly change the weighing procedures compared with those used for mechanical single-pan analytical or top-loading balances. The differences are that the balance will read slightly more quickly, there are no knobs to turn to change weights, and the reading is displayed electronically.

PRINCIPLE OF THE ELECTROMAGNETIC-FORCE-COMPENSATION BALANCE

All balances of this type measure force, or weight, rather than mass, and it is this that determines the form of the balance.

Figure III-1 shows the principle of the balance and Figure III-2 gives a general view of a commercial balance. A coil, rigidly attached to the balance pan, is placed in the cylindrical gap of a magnet. When a mass is added to the pan a position sensor detects that the pan has been lowered and causes the current through the coil to be increased, providing a magnetic counter force which returns the balance pan to the original position. The compensation current is measured across a resistor R as a voltage and then read out on what is effectively a digital voltmeter. The compensation current is in direct proportion to the mass on the pan and so the actual mass may be obtained and processed, or displayed, as appropriate.

This type of system may be used to weigh masses up to about 1 kg. For higher maximum loads the heat produced in the coil, and the size of the magnet, cause problems and so, for these loads, levers are inserted into the system. Thus many balances use a mechanical lever so that the ratio of load to the force due to the coil is around ten to one.

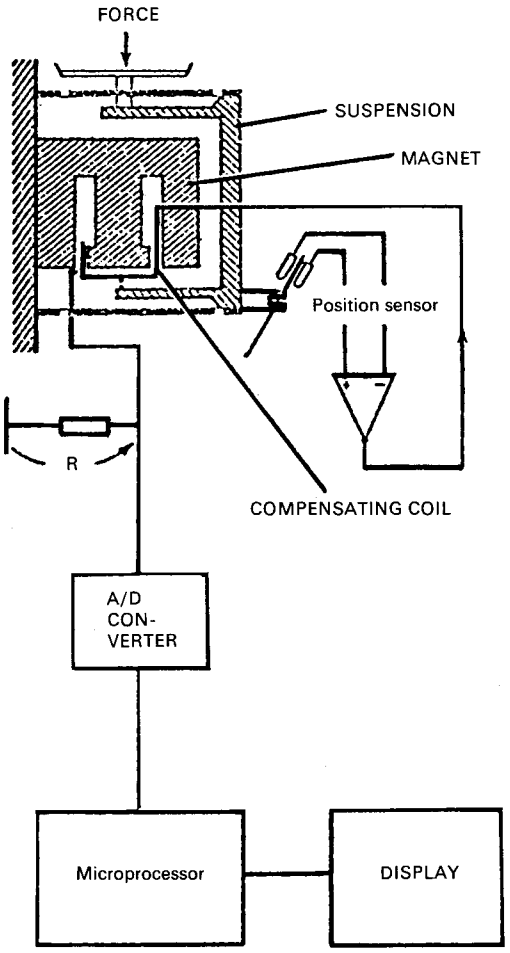


Fig. III-1—Basic diagram of an electromagnetic-force-compensated balance.

The temperature of the balance has been stabilised mainly by arranging for the current at no load to be −50% of the maximum. This means that heating starts immediately the balance is switched on. Most have a stabilising time of about half an hour. This is why it is important to switch these balances on in the morning and then to leave them on all day.

With precision amplifiers, changes in force of down to 3 parts in 10^7 can be detected while typical analytical balances are produced with resolutions of 6 parts in 10^7 i.e. they can weigh 160 g to 0.1 mg.

As stated above the balance measures force and hence the reading depends upon the value of gravity at the location. All balances need to be adjustable and some means for this must be provided by the manufacturer.

Some balances have a built-in calibration mass which can be applied at any time, others go through an automatic calibration procedure when switched on, while others require a mass to be added to the pan. Some of these balances require the calibration mass to be exactly equal to the nominal value. If another value is used the balance calibrates to this value assuming it to be the nominal value — a process which can lead to errors.

For electromagnetic-force-compensated balances there is no distinction in principle between analytical balances and top-loading balances. Because of the construction they are all of necessity top-loading balances with some analytical balances being specially designed so that the weighing is done below the force cell. This of course is not the case with mechanical single-pan balances where the construction of the analytical balance is completely different from that of the top-loading instrument.

Because the display on this type of balance can be zeroed at any load, merely by the touch of a button, there is no need for any special taring facility.

One of the big advantages of these balances is that the value can be read with a computer or small calculator. This means:

(i) The numbers can be recorded on a mass storage device or more permanently on a printer, eliminating transcription errors.

(ii) The computer can be programmed to do any necessary calculations with the numbers.

(iii) It is possible to increase the resolution of the balance. By arranging for the computer to automatically collect ten or more readings as fast as possible (usually less than one second per reading), and then averaging, it is possible to improve the resolution equivalent to another digit beyond the reading shown on the balance display. Whether the balance is sufficiently stable for this increased resolution to be meaningful is something only the user can decide.

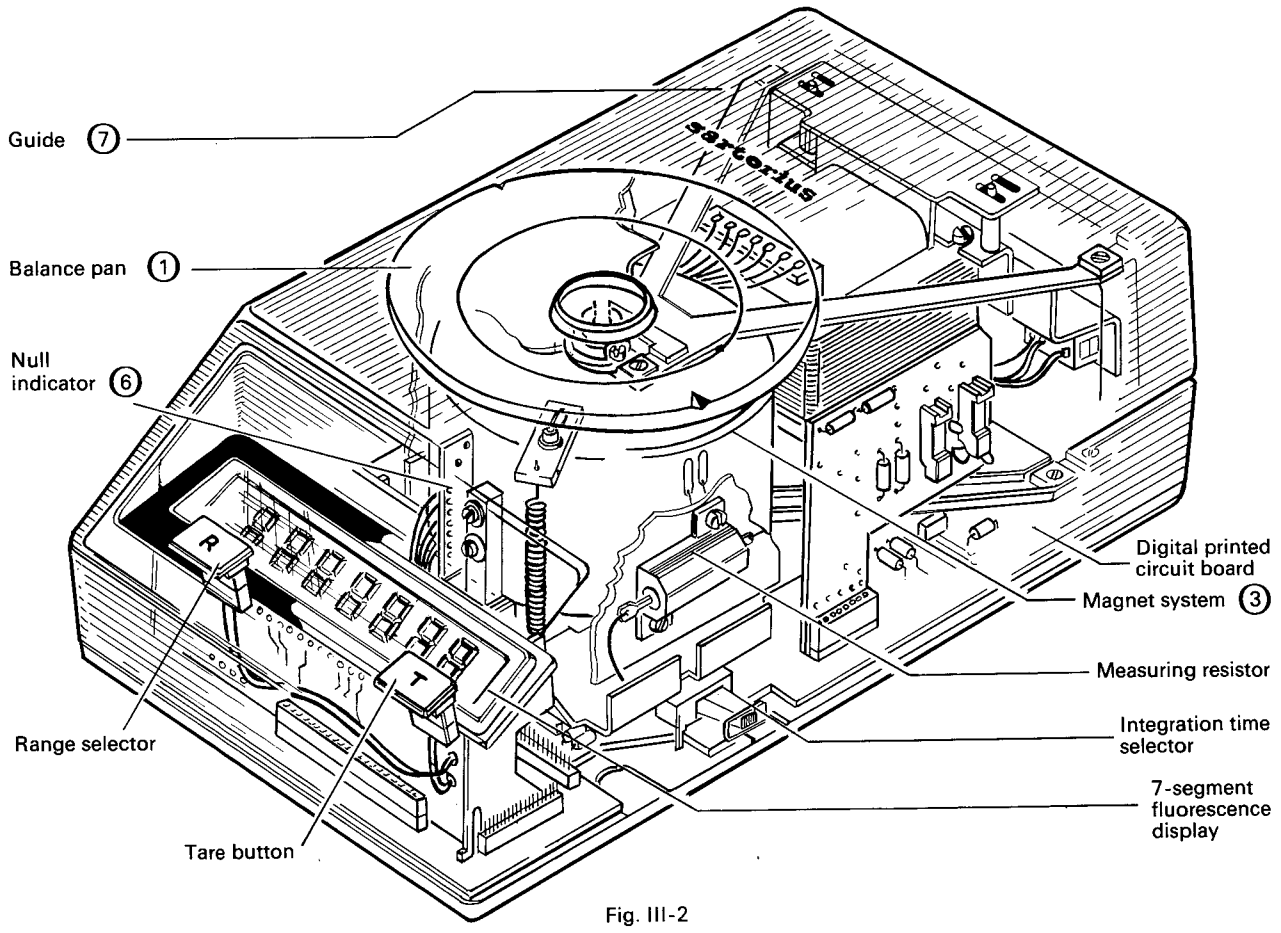


Fig. III-2

ERRORS

Below are listed the types of errors that can occur in a balance with electromagnetic-force compensation.

1. Temperature changes may alter the relative positioning of the position sensor. This will be seen as a zero drift. After warm-up this is usually small in a well-constructed balance.

   If either the value of the resistor R or the diameter of the coil changes with temperature then there will be a change in the sensitivity or span, resulting in a change in the reading which can only be detected by calibration.

2. There may be a lack of proportionality between current and load. This could be caused by changes in the resistance of R with different currents, by the feedback system failing to return the position sensor to null, by relative movement in the coil windings, or by mechanical errors in the lever system.

3. Similarly to mechanical single-pan balances, there could be an error due to the calibration mass.

4. For those balances that employ a lever, change in the lever ratio may occur.

5. These balances are sensitive to magnetic fields. A magnet near the balance case may produce permanent changes in both the reading and scale factor. The magnitude and sign of the changes depend on the strength, polarity and location of the magnet relative to the balance. These changes are permanent in that they remain after the magnet is removed. If the balance is zeroed and recalibrated then the effects of the magnetic field are eliminated. Magnetised objects should not be weighed on these balances without special precautions.

6. Small changes in the level of a balance alter the zero reading and the scale factor, but do not affect the other characteristics such as linearity and repetition. Most balances are provided with a level bubble and the balance should be carefully levelled prior to calibration or use. Within reasonable limits, the actual tilt of the balance is unimportant and the level bubble provides a means of returning the balance to the inclination in which it was calibrated, should it have been moved from that position. Some recent models of top-loading balances are not provided with any means of levelling, or level detection. For these balances care should be taken that the balance is either not moved, or that it is recalibrated (scale factor checked) after moving.

MASSES

In general the majority of modern balances do not need masses for routine weighing. Modern electronic balances should have a standard mass associated with them to check the calibration at regular intervals, as described in the next section.

Whatever standard masses are used they must conform with certain basic requirements. To ensure both long and short term stability the mass must be constructed in one piece from a hard inoxidisable material, the surface must be smooth and free from sharp edges and the material must be non-magnetic. These requirements are met by well-made masses of non-magnetic stainless steel containing approximately 25% chromium and 20% nickel and having a density between 7500 and 8000 $kg.m^{-3}$ at 20° C. Masses of this material are far superior to those of brass, either plain or with a protective plating.

Masses must never, under any circumstances, be touched with the fingers. They should be manipulated only with plastic-tipped or chamois-covered forceps.

CALIBRATION

Departure from nominal reading

The sensitivity of a mechanical or traditional balance is defined as the deflection produced by the addition of unit mass to the pan and is usually expressed in divisions per milligram. Sensitivity reciprocal, the more useful term, is the mass which must be added to the pan to change the reading by one scale division.

For balances operating on the principle of electromagnetic-force compensation this idea of sensitivity needs to be modified slightly. They no longer have scales, or scale divisions, but have digits on an electronic display. The display covers the whole weighing range of the balance and by suitable electronic adjustment, and the use of a standard mass, this display can be made equal to its nominal value at any predefined point. At other points in the range, linearity and other errors may cause the output to depart from its nominal value. So rather than talk about sensitivity it is probably easier to talk in terms of departures from nominal reading or linearity of the reading. Rather than measuring the sensitivity, the scale value is set using a standard mass, either exterior or interior to the balance, so that at this load each digit represents an exact fraction of a gram. Then the departures from nominal value at other loads are measured.

In general, the balance is adjusted by placing a known mass (usually maximum capacity) on the pan and adjusting the balance until it displays the value of the mass. Some balances have a built-in calibrating mass or an automatic calibrating cycle but whatever the system all balances should be checked to ensure that the calibration is correct and that the calibrating mass is unchanged.

The reading should be checked at a minimum of ten equally spaced steps over the range. There are two methods of doing this depending upon the masses available.

(a) A set of calibrated masses is available.

(i) Read the zero.

(ii) Place the known mass, M, for the first step, on the pan. Note the reading.

(iii) Remove the mass and read zero.

(iv) Place the known mass, 2M, for the second step, on the pan. Note the reading.

(v) Remove the mass and read zero.

(vi) Repeat through all the steps with the values 3M, 4M, ... until the capacity of the balance is reached.

From the known values of the masses the value of the departure from nominal value for each step is easily calculated. The departure from nominal should be close to zero and not change significantly with load.

(b) A set of calibrated masses is not available.

In this case an object of mass approximately equal to the desired calibration step is obtained along with supplementary objects that can be used as taring masses.

(i) Read the zero.

(ii) Place the mass on the pan and note the reading.

(iii) Remove the mass and add the supplementary objects until the same reading is displayed. This effectively becomes the new zero reading.

(iv) Add the mass to the pan, again noting the reading.

(v) Remove the mass and add more tare till the balance displays the reading given in (iv).

Repeat this procedure until the capacity of the balance is reached. By successively subtracting the 'zero' reading from the reading with the mass, the linearity or change in departure from nominal over the range of the balance can be calculated.

Method (b) does not require any calibrated masses, but by its nature is more time-consuming than (a). To check the calibration at maximum capacity it is still necessary to have a calibrated mass of this magnitude. Such a check should be carried out periodically (weekly). As mentioned above some balances require a calibrating mass equal to the nominal value. This is either provided with the balance or is built-in. In either case, because they are used regularly, the value of these masses can change and they should be checked periodically, preferably every three years. This is particularly necessary for balances with a resolution of 1 part in 10^6 or better.

A built-in calibrating mass is usually well protected and unlikely to change significantly unless the balance is in a harsh environment. However, it should be checked occasionally. This is done by calibrating the balance by the procedure nominated by the manufacturer and then weighing a standard mass, preferably of nominal value equal to the calibrating mass. If the value of the calibrating mass is correct then the balance will display the value of the standard mass.

Repeatability of reading

This is a measure of how consistently a reading is displayed by the balance, and is usually expressed as a standard deviation. There are a number of methods of measuring this standard deviation, but whatever method is adopted it should be measured in a realistic way. Because these balances do not weigh at constant load the effect of different loads on the repeatability is likely to be more significant than for substitution balances. So the repeatability of reading should be measured at more than one load.

All weighings involve a minimum of two readings — a zero reading and a reading with the mass to be measured. If this difference is measured a number of times it is a good measure of the repeatability of reading. In contrast to a mechanical balance, this type of balance has no arrestment; so the load on the balance must be disturbed in some way to measure any repeatability, which is desirable since this is the way the balance is used in practice.

Procedure:

(a) Zero the balance — reading Z_1

(b) Place mass m on the balance — reading m_1

(c) Remove m and read the balance — Z_2

(d) Replace mass m on the balance — m_2.

Do this n times; minimum $n = 10$,

$d_1 = m_1 - Z_1, \ldots\ldots, d_n = m_n - Z_n$

The standard deviation, σ, is given by

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (d_i - \bar{d})^2}{n-1}}$$

$$= \sqrt{\frac{n\Sigma d_i^2 - (\Sigma d_i)^2}{n(n-1)}}$$

where $\bar{d}$ is the mean of the d_i readings.

The balance should not be zeroed during this series of readings.

This procedure should be repeated for a number of different values of m, preferably, for example, near zero, half maximum load and maximum load.

Effect of off-centre loading

These balances require some form of mechanical parallel linkage to transfer the load on the pan to the transducer, so the effect of off-centre, or corner, loading may be quite significant. This effect is easily measured by placing a mass in the centre of the pan and then placing it near each of the corners in turn and reading the difference.

Most balance manufacturers recommend that this effect be measured at half or one third of the maximum load of the balance, or quote performance figures at this load. Larger loads are not necessary as this effect is not always linear with respect to either load or position, and varies from balance to balance. Hence this test does not produce figures that can be used to correct balance readings, but indicates the precision with which an object must be located on the balance pan for this effect to be negligible.

METHOD OF WEIGHING

In weighing with these balances the normal precautions for using a balance should be observed: it should be placed on a solid bench in an area free from draughts and vibration; the balance should be clean and the pan brushed prior to weighing.

The temperature of the room should be reasonably constant or vary only slowly during the day. Temperature differences, and air-conditioning, can cause convection currents which produce fluctuating forces on balance pans. For a balance with a pan diameter of 100 mm a draught velocity of 46 $mm.s^{-1}$ produces a force on the pan equivalent to a 1 mg mass. The air speed in an air-conditioned laboratory is typically about 300 $mm.s^{-1}$. This shows that for precision weighing, balance pans need to be enclosed.

Objects should never be weighed until they have attained the temperature of the balance case. Hot bodies should never be placed on the balance pan but should be allowed to cool, preferably in a desiccator, until they are approximately at ambient temperature.

Hygroscopic materials can only be weighed when contained in an airtight vessel. Under no circumstances should any chemical come into contact with the scale pan. All material to be weighed should be placed in a clean dry container of suitable material such as platinum, glass, aluminium etc. or in the case of non-hygroscopic crystals, a piece of clean dry paper. The container should be tared.

The operation of weighing is very simple. With no load, or with an object to be tared on the pan, the display is zeroed. The component to be weighed is placed on the pan or in the container and the reading noted when the display is steady. The component is removed and the zero reading noted — this is to allow for any zero drift. If the readings on the balance are likely to drift significantly, then the weighings should be made symmetrically with respect to time, that is, a second reading should be made on the component. Thus the readings could be made in the following order:

zero 1	(first reading with zero load — usually made equal to zero by taring)
reading 1	
reading 2	
zero 2	(second reading with zero load — not necessarily equal to zero)

with the component being removed from the balance between reading 1 and reading 2.

CALIBRATION OF MASSES

If it is desired to calibrate masses or to weigh accurately with these balances then the greatest accuracy will be achieved by using the balance as a comparator. By comparing the unknown masses with calibrated masses from a standard set and using the balance to display the small differences, any errors in linearity, uniformity of response or the calibration of the balance are eliminated. Provided the standard and unknown masses are of similar materials then this procedure eliminates any effects due to air buoyancy. This method is usually known as 'weighing by substitution'. First place the standard mass on the balance pan and either zero the display or note the reading; remove the standard and replace it with the unknown mass. Repeat the weighing with the unknown mass by lifting it off and then replacing it on the pan. Finally, remove the unknown and replace it with the standard mass. The difference between the means of the appropriate readings gives the difference in mass between the standard and the unknown, enabling the value of the unknown to be calculated.

AIR BUOYANCY

Because these balances actually measure force, the calibration will vary with gravity and a means of adjusting the calibration, or sensitivity, is provided for use when the balance is moved from one gravity field to another. The balance weighs in air but there is no compensation for buoyancy as there is with the single pan substitution balances, or two-pan balances, where the buoyancy of the object is effectively balanced against the buoyancy of stainless-steel standards situated inside the balance.

When the balance is calibrated with the standard mass, it is done in air of a certain density and so all weighings will be correct only if they are made in air of the same density. Under certain conditions this can lead to significant errors in precision weighing.

For a normal laboratory with reasonable temperature control the maximum range in air density is about 0.08 $kg.m^{-3}$ (due largely to changes in atmospheric pressure). If the balance is calibrated with a 100 g mass when the air density is 1.2 $kg.m^{-3}$ and then the 100 g mass is re-weighed when the air density is 1.28 $kg.m^{-3}$ then the change in reading on the balance would be equal to the change in air density multiplied by the volume of the mass, that is:

$$\delta M = (1.28 - 1.2)\,(0.1/8000)\ \text{kg} = 1\ \text{mg}$$

where 8000 $kg.m^{-3}$ is the effective density of the 100 g mass. By means of equation 2 from the following section, the reading on the balance would be

$$100\ \left(1 - \frac{1.2}{8000}\right) / \left(1 - \frac{1.28}{8000}\right) = 100.001\ \text{g}$$

or a change of 1 part in 10^5. This shows that air density needs to be considered if weighings are to be made to this accuracy or better. Thus, regardless of the calibration of the balance, if similar objects are to be accurately compared from weighings made at different times then changes in air density need to be allowed for, particularly for objects of low density. For example, if a 100 g object of density of around 1000 $kg.m^{-3}$ is weighed, and then re-weighed with an air density difference of 0.08 $kg.m^{-3}$ then the change in balance reading is 8 mg.

Table I gives values of the air density conditions to be expected in most laboratories. Intermediate values, to sufficient accuracy, can be obtained by simple linear interpolation.

TABLE I
Air density kg.m^{-3} (1 kg.m^{-3} = 0.001 g.cm^{-3})

Temp. °C	Relative humidity 30%	50%	70%	90%
	Pressure = 740 mmHg = 98 659 Pa			
10	1.212 63	1.211 49	1.210 35	1.209 22
15	1.190 87	1.189 32	1.187 76	1.186 21
20	1.169 65	1.167 56	1.165 46	1.163 37
25	1.148 88	1.146 09	1.143 31	1.140 53
30	1.128 48	1.124 81	1.121 14	1.117 48
35	1.108 36	1.103 57	1.098 79	1.094 02
40	1.088 41	1.082 23	1 076 07	1.069 91
45	1.068 53	1.060 63	1.052 75	1.044 89
	Pressure = 750 mmHg = 99 992 Pa			
10	1.229 05	1.227 91	1.226 77	1.225 63
15	1.207 01	1.205 45	1.203 90	1.202 34
20	1.185 51	1.183 41	1.181 32	1.179 23
25	1.164 47	1.161 68	1.158 90	1.156 11
30	1.143 81	1.140 14	1.136 47	1.132 81
35	1.123 44	1.118 65	1.113 87	1.109 10
40	1.103 25	1.097 07	1.090 90	1.084 75
45	1.083 13	1.075 23	1.067 35	1.059 49
	Pressure = 760 mmHg = 101 325 Pa			
10	1.245 47	1.244 33	1.243 19	1.242 05
15	1.223 13	1.221 58	1.220 03	1.218 48
20	1.201 36	1.199 26	1.197 17	1.195 08
25	1.180 06	1.177 27	1.174 48	1.171 70
30	1.159 14	1.155 47	1.151 80	1.148 14
35	1.138 52	1.133 73	1.128 95	1.124 18
40	1.118 09	1.111 91	1.105 74	1.099 59
45	1.097 74	1.089 83	1.081 95	1.074 10
	Pressure = 770 mmHg = 102 658 Pa			
10	1.261 88	1.260 75	1.259 61	1.258 47
15	1.239 26	1.237 71	1.236 16	1.234 61
20	1.217 21	1.215 12	1.213 02	1.210 94
25	1.195 64	1.192 85	1.190 07	1.187 29
30	1.174 47	1.170 80	1.167 13	1.163 47
35	1.153 60	1.148 81	1.144 03	1.139 26
40	1.132 92	1.126 74	1.120 58	1.114 43
45	1.112 34	1.104 44	1.096 56	1.088 70

AIR BUOYANCY AND WEIGHING

To assist in calculating the effects of air buoyancy, particularly for objects of differing densities, the following section discusses air buoyancy effects related to weighing in general.

When an object is weighed in air it experiences an upthrust or buoyant force (loss of weight) equal to the weight of air displaced. It is this buoyant force which causes many problems and much confusion in weighing. It is not practical to weigh in vacuum because of the surface effects that would occur on the objects being weighed. However, what is termed the 'true mass' of an object is the mass that would be measured in a vacuum, providing everything else (surface layers, etc.) was unchanged. Thus, in a standards laboratory, it is true mass values which are measured in calibrating primary standards and all other values are calculated from these.

The following nomenclature is used in this section:

ρ — air density, kg.m^{-3}
V — volume of a mass, m^3
d — density of a mass, kg.m^{-3}
M — true mass, kg.

If the mass is measured on a weighing system (e.g. a spring balance) the value obtained would be M*, where

$$M^* = M - \rho V$$
$$= M\left(1 - \frac{\rho}{d}\right)$$

If two objects, denoted by subscripts 1 and 2, are weighed, then the difference in mass is given by

$$\delta M = M_1 - M_2 - \rho_1 V_1 + \rho_2 V_2 \qquad (1)$$

Thus if M_1 is known then M_2 can be calculated provided that ρ_1, ρ_2, V_1 and V_2 are also known.

If the weighings are done at nearly the same time and under the same conditions, then $\rho_1 = \rho_2$, and if the masses are made of the same material then $V_1 \simeq V_2$ and (1) reduces to

$$\delta M = M_1 - M_2$$

This is the case which is normally encountered in the calibration of masses. When comparing objects made from differing materials, then $V_1 \neq V_2$, and the effect of air buoyancy must be calculated or be sufficiently small that it can be neglected for the accuracy required.

When the latter is done the value obtained is said to be the *mass (weight) in air* of the object. This is the value of the masses (usually stainless steel) required to balance the object in air of nominal density 1.2 kg.m^{-3}. Take as an example the weighing of a quantity of water M_w that balances a stainless steel mass M_{ss} of density 8000 kg.m^{-3}.

If $\rho = 1.2$ kg.m^{-3} then

$$M_w\left(1 - \frac{1.2}{1000}\right) = M_{ss}\left(1 - \frac{1.2}{8000}\right)$$

So

$$M_w = (1.001\ 05)M_{ss}\ \text{kg}$$

This means that if the stainless-steel mass balanced against the water is 1 kg, then because of the upthrust due to the air, the mass of water balancing the stainless steel is approximately 1.001 kg, i.e. a difference of 1 g in 1000 g. In this case the true mass differs from the mass in air by 1 g.

Because the density of the material used for masses changes from one set to another, the idea of an *apparent mass value* has arisen. The apparent mass, M_a, is the amount of any specified material which will balance the unknown in a specified atmosphere, $\rho_o = 1.2$ kg.m^{-3}, at the specified temperature t = 20° C.

For an object with a true mass M, made from material of density d_M, the calculated apparent mass value is:

$$M_a = M[1 - (\rho_o/d_M)] / [1 - (\rho_o/d_a)] \qquad (2)$$

where d_a is the density of the appropriate 'ideal' material. The internationally accepted value for d_a is 8000 kg.m^{-3} or 8.0 g.cm^{-3}, at 20° C. This is commonly called the *8.0 basis*. In Australia the CSIRO Division of Applied Physics calibrates all masses on this basis.

To convert from a true mass basis to the 8.0 basis, equation (2) gives:

$$M_{8\cdot0} = M\left(1 - \frac{1.2}{d_M}\right) / \left(1 - \frac{1.2}{8000}\right) \qquad (3)$$

For stainless steel of density 7800 $kg.m^{-3}$, equation (3) gives:

$M_{8\cdot0} = (0.999\ 996\ 15)M.$

When brass was used extensively for standard masses the mass basis then used was 8.4. To convert from 8.0 to 8.4 equation (2) gives:

$$M_{8\cdot4} = M_{8\cdot0}\left(1 - \frac{1.2}{8000}\right) / \left(1 - \frac{1.2}{8390.9}\right)$$

$$= (0.999\ 993\ 01)M_{8.0}$$

where: 8390.9 $kg.m^{-3}$ is the density of brass at 20° C; the density at 0° C is 8400 $kg.m^{-3}$.

Thus in high precision weighing, where air buoyancy corrections must be applied, they should be calculated on the basis that the density of the masses is 8000 $kg.m^{-3}$ and the actual value of the density of the air in the balance case, or the room, should be used.

DESIRABLE FEATURES OF AN ANALYTICAL BALANCE

By 'analytical balance' is meant a balance with a resolution of at least two parts in 10^6 and with an enclosed weighing chamber. The pan traditionally, but not always, hangs below the weighing mechanism.

1. The weighing compartment should be enclosed with access to the pan via sliding doors.
2. A level bubble and a means of levelling the balance should be provided.
3. The balance should have a resolution (or discrimination) of at least two parts in 10^6.
4. The standard deviation of the repeatability of reading should be no more than twice the resolution.
5. The departure from nominal value of the reading (linearity) should not be larger than five times the standard deviation.
6. The display should be stable and not change by more than ±1 digit when the balance is not being disturbed.
7. The calibration should be stable i.e. the scale value should not change by more than three times the standard deviation in any one month.
8. The balance should have either:
   (a) a calibration mass built-in; or
   (b) a calibrated mass provided with the balance so that the scale value can be checked.
9. The effects of off-centre loading and hysteresis should be less than three times the standard deviation.
10. The reading should stabilise within ten seconds.
11. The change of reading with change in temperature should be less than one part in 10^6 per °C.

CHAPTER IV

DENSIMETRIC METHODS OF ANALYSIS

The quantity of mass in unit volume of a substance is known as the density of that substance, and is expressed in such units as kilograms per cubic metre or grams per millilitre. Mathematically $d = \frac{m}{v}$ where d is the density, m the mass and v the volume of the substance. The volume of a given mass may, and almost invariably does, vary with temperature and pressure. For liquids and solids the change of volume with temperature is quite significant, but the effect of variation in pressure is usually negligible, so that it suffices to specify the temperature to which any statement of density is related. In the Queensland sugar industry the accepted standard temperature is 20 °C.

At any given place the mass of any body is proportional to its weight in vacuo. The ratio of the masses (weights in vacuo) of equal volumes of a substance and some standard material is known as the relative density of the substance. Customarily, when the standard material is water, the ratio is known as specific gravity, so that specific gravity (s.g.) may be defined as a number which indicates how much heavier or lighter a material is than water.

The derivation of specific gravity involves two densities each of which must be qualified by a temperature and so the ratio

$$\frac{\text{density of a substance at } t_s \ (D^{t}s)}{\text{density of water at } t_w \ (D^{t}w)}$$

is expressed as s.g. $\frac{t_s}{t_w}$

The relationship between two masses is correctly expressed by the ratio of their weights in vacuo. When a weighing operation is conducted under normal laboratory conditions, the buoyant effect of the atmosphere is exerted on both the sample and the weights, and as these usually differ in volume, the resultant force creates a difference between the weight of the sample in air and its weight in vacuo. A weight 'in air, with stainless steel' is convertible to the weight in vacuo if the density of the test sample is known. Hence, densities and specific gravities may be expressed in terms of weight in air with stainless steel, and as most weighings are conducted under these conditions, tables of density on this basis have great practical value. Great care should be taken to avoid confusion between density figures based on weight in vacuo and those based on weight in air with stainless steel.

The determination of specific gravity is one of considerable importance in sugar analyses. This is due to the interesting fact that solutions of different sugars of equal concentrations (w/w) have almost identical specific gravities. The following values for 10% solutions of nine distinct sugars illustrate this fact:

	s.g. $\frac{20}{4}$°C
Arabinose	1.037 9
Glucose	1.038 1
Fructose	1.038 5
Galactose	1.037 9
Sorbose	1.038 1
Sucrose	1.038 1
Maltose	1.038 6
Lactose	1.037 6
Raffinose	1.037 5
Mean	1.038 03

Further, the mean value for all sugars approximates closely to that for sucrose. It is possible, therefore, to determine very closely the percentage of dissolved substance in any solution of sugar or mixture of sugars simply by determining its specific gravity.

While the application of specific gravity tables established for sucrose may be applied with reasonable accuracy for the estimation of dissolved substance in a solution of mixed sugars, this is not the case where other dissolved substances are present. The errors resulting from this cause are at times very great as, for example, with final molasses. The influence of the salts present in such a solution may be gauged from the following data showing the concentration of solutions of sodium-potassium tartrate and potassium carbonate in comparison with sucrose solutions of equal specific gravity. For example, a 9% potassium carbonate solution has the same specific gravity as a 20% sucrose solution. Therefore if the dissolved solids content of a solution is estimated from the specific gravity and the relationship between specific gravity and sucrose concentration, it is obvious that the dissolved solids content would be grossly overestimated in the case of these salt solutions:

Specific gravity $\frac{15}{15}$°C	Sucrose %	Na-K tartrate %	K_2CO_3 %
1.0039	1	0.57	0.43
1.0197	5	2.87	2.15
1.0402	10	5.87	4.40
1.0833	20	12.16	9.00

When the specific gravity of such solutions is determined after dilution with water, the error is still further intensified, owing to more effective assimilation of the salt than sugar by the solution. This is related in part to stronger attractive interactions between the dissociated salts and the water molecules. This effect is illustrated in the above table. Concentrations determined by this method for other than pure sugar solutions must, therefore, be regarded as rough estimates only.

THE PYCNOMETER

A highly accurate instrument for the determination of specific gravity is the pycnometer or specific gravity bottle (Figure IV-1).

It is simply a glass vessel which is designed to contain an accurately reproducible volume of liquid at any particular temperature. The best pycnometers are vacuum jacketed for thermal insulation, and are fitted with a thermometer. By weighing the bottle filled first with water and then the given solution at constant temperature the weights of equal volumes of the two fluids may be determined, and hence the specific gravity of the test solution.

The pycnometer has been mainly used in the sugar mill laboratory for the determination of the brix of dilute sugar solutions extracted in the analysis of cane or bagasse. Except for the most precise work it is now replaced by the precision refractometer.

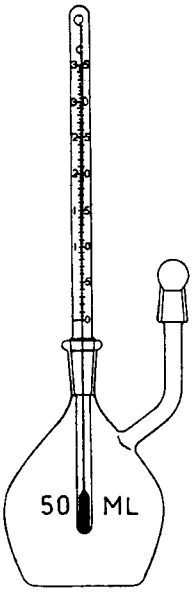


Fig. IV-1—Illustrating a type of pycnometer in use in Queensland.

Using the pycnometer

The bottle must be thoroughly cleansed and dried before weighing. This is done using in turn glass cleaning solution, water and alcohol. It is then dried in a stream of dry air and allowed to cool if warm air is used. After weighing, the bottle is filled with the required liquid at a temperature 2 to 3 °C above ambient. The stopper is inserted*, care being taken to prevent the introduction of air bubbles, and any excess liquid carefully removed by means of a filter paper (from the stopper and also from the capillary in the side-arm type).

The pycnometer is then placed in a water bath at a temperature lower than that of the water employed to fill the bottle (ambient or preferably a lower temperature). The liquid meniscus is thus drawn down the ground glass joint or the capillary depending on the type of pycnometer used. The pycnometer is then wiped dry and weighed.

In drying the surface considerable care must be taken and the following technique is recommended. The outside is first wiped thoroughly with a piece of clean, damp flannel, then the damp surface is dried with a clean chamois, after which a final rub is given with a second chamois. During these manipulations and the subsequent weighing the pycnometer must not come into contact with the fingers.

To determine the density of a liquid

To measure the density of a liquid using the pycnometer, three weighings are necessary. The cleaned and dried pycnometer is weighed empty. Following the procedure given above, the pycnometer is filled with cooled, recently-boiled distilled water (to expel dissolved air) and reweighed. After cleaning and drying the pycnometer is finally filled with the test liquid and weighed for the third time. The temperature of the water (t_w) and of the test liquid (t_l) is recorded and the conditions under which the weighings are made (density of air, density of weights) are also noted.

Let:

M_g = mass of pycnometer
M_w = mass of water to fill pycnometer
M_l = mass of liquid to fill pycnometer
V = internal volume of pycnometer at temperature of test liquid
W_g = weight of pycnometer (mass of the weights used to counterpoise the pycnometer on the balance)
W_w = weight of pycnometer plus water
W_l = weight of pycnometer plus liquid
W_g, W_w and W_l are the actual figures obtained from the balance or weighing operations
g = density of glass
ρ_w = density of water at temperature t_w
ρ_l = density of liquid at temperature t_l
σ = density of air
d = density of weights
γ = dilatation of glass of which pycnometer is made
t_w = temperature of water
t_l = temperature of liquid

The density of the test liquid at temperature t_l is calculated by dividing the mass of liquid to fill pycnometer (M_l) by the internal volume at temperature t_l i.e. V. The relationship for this density can be derived from the following equations which describe the equilibrium conditions when the three weighings are made. The equations take into account the air buoyancy on the object being weighted and on the weights used.

Weighing the empty pycnometer in air of density σ_1:

$$M_g\left(1 - \frac{\sigma_1}{g}\right) = W_g\left(1 - \frac{\sigma_1}{d}\right) \quad (1)$$

Weighing the water-filled pycnometer in air of density σ_2:

$$M_g\left(1 - \frac{\sigma_2}{g}\right) + M_w\left(1 - \frac{\sigma_2}{\rho_w}\right) = W_w\left(1 - \frac{\sigma_2}{d}\right) \quad (2)$$

Weighing the liquid-filled pycnometer in air of density σ_3:

$$M_g\left(1 - \frac{\sigma_3}{g}\right) + M_l\left(1 - \frac{\sigma_3}{\rho_l}\right) = W_l\left(1 - \frac{\sigma_3}{d}\right) \quad (3)$$

The liquid density is

$$\rho_l = \frac{M_l}{V}$$

* The temperature of the solution must be determined (to 0.1 °C) at the instant the stopper is fully inserted. Where a thermometer is incorporated in the stopper, the stopper is lightly set in place and the thermometer allowed to come to reading; where a stopper only is provided a thermometer is inserted first, read and withdrawn. The stopper is inserted immediately.

Now the internal volume of the pycnometer at the temperature of the water (t_w) may be determined as the mass of the water divided by the density of water i.e. M_w/ρ_w. Therefore, the internal volume V at temperature t_l is given by

$$V = \frac{M_w}{\rho_w}[1 + \gamma(t_l - t_w)]$$

$$\text{Therefore } \rho_l = \frac{M_l \times \rho_w}{M_w[1 + \gamma(t_l - t_w)]}$$

From equations 1, 2, 3 it follows that

$$\rho_l = \frac{\left[W_l\left(1 - \frac{\sigma_3}{d}\right) - W_g\left(\frac{1 - \sigma_1/d}{1 - \sigma_1/g}\right)\left(1 - \frac{\sigma_3}{g}\right)\right](\rho_w - \sigma_2)}{\left[W_w\left(1 - \frac{\sigma_2}{d}\right) - W_g\left(\frac{1 - \sigma_1/d}{1 - \sigma_1/g}\right)\left(1 - \frac{\sigma_2}{g}\right)\right][1 + \gamma(t_l - t_w)]} + \sigma_3$$

If $$\frac{1 - \sigma_3/g}{1 - \sigma_1/g} = \frac{1 - \sigma_2/g}{1 - \sigma_1/g} = 1$$

then $$\rho_l = \frac{\left[W_l\left(1 - \frac{\sigma_3}{d}\right) - W_g\left(1 - \frac{\sigma_1}{d}\right)\right](\rho_w - \sigma_2)}{\left[W_w\left(1 - \frac{\sigma_2}{d}\right) - W_g\left(1 - \frac{\sigma_1}{d}\right)\right][1 + \gamma(t_l - t_w)]} + \sigma_3$$

Assuming the air density is constant for all weighings, then

$$\rho_l = \frac{(W_l - W_g)(\rho_w - \sigma)}{(W_w - W_g)[1 + \gamma(t_l - t_w)]} + \sigma \qquad (4)$$

Thus the density of the test liquid at temperature t_l is obtained from the three weighings W_g, W_w, W_l, the density of water at temperature t_w, the air density σ, and the dilatation (coefficient of expansion) of the glass γ. Under usual laboratory conditions the density of air can be taken as 1.20 $kg.m^{-3}$ (refer to Chapter III). The dilatation of the glass will be taken as 0.000 025 per 1 °C rise in temperature.

Example:

Weight of empty pycnometer	= 57.645 5 g
Weight of pycnometer + water at 23.7 °C	= 82.529 7 g
Weight of pycnometer + liquid at 25 °C	= 82.958 1 g
Coefficient of expansion of glass	= 0.000 025 per °C
Density of water at 23.7 °C (from Table XXII)	= 997.37 $kg.m^{-3}$
Density of air	= 1.20 $kg.m^{-3}$

By using formula 4 above

$$\text{Density of liquid} = \frac{(82.958\,1 - 57.645\,5)(997.37 - 1.20)}{(82.529\,7 - 57.645\,5)[1 + 0.000\,025\,(25 - 23.7)]} + 1.20$$

$$= 1\,014.49 \text{ kg.m}^{-3}$$

Having determined the density at 25 °C the specific gravity at 25 °C can then be calculated from this density and the density of water at 25 °C. From Table XXII the density of water at 25 °C is 997.05. Hence specific gravity $\frac{25}{25}$ °C is 1.017 49.

This specific gravity may be converted to a specific gravity at any other reference temperature for the water, but, without tables applying specifically to the density of the solution, the reference temperature at 25 °C for the solution may not be altered. If a value for density at a selected temperature t is required, a density determination must be conducted at that temperature. This does not apply to sugar solutions for which temperature correction tables are available.

Determination of brix

In using the pycnometer for the determination of the brix of sugar solutions, a modified procedure is adopted for simplicity. If the true mass of the contents of the pycnometer at temperature t_l be divided by the volume of the pycnometer at some reference temperature T, the result derived is known as the observed density at temperature t_l. Let V_T be the internal volume of the pycnometer at reference temperature T, and all other symbols have the same meaning as before. Then:

$$\text{Observed density at } t_l = \frac{M_l}{V_T}$$

$$= \frac{M_l}{\frac{M_w}{\rho_w}[1 + \gamma(T - t_w)]}$$

Assuming the air density is constant for all weighings, then the following formula may be derived.

$$\text{Observed density at } t_l = \left[\frac{(W_l - W_g)(\rho_w - \sigma)}{(W_w - W_g)[1 + \gamma(t_l - t_w)]} + \sigma\right] \frac{[1 + \gamma(t_l - t_w)]}{[1 + \gamma(T - t_w)]}$$

The observed density at t_l is the value which would be read by taking a glass hydrometer calibrated to read correctly at the standard temperature T and immersing it in the test solution at t_l. A brix hydrometer is calibrated to read correctly at a standard temperature T, and, if used at another temperature t_l, will give a reading which differs from the actual brix. If the observed density at t_l, referred to above, be converted to brix by using the standard tables for conversion at temperature T, the value derived will coincide with the actual reading of the brix hydrometer at t_l.

Thus, in the determination of brix, the observed density is first derived. This observed density is converted to 'observed' brix, using the standard table, and the observed brix is then corrected for temperature according to the normal method for the brix hydrometer.

Example:

Weight of empty pycnometer	= 57.645 5 g
Weight of pycnometer + water	= 82.529 7 g
Temperature of water	= 23.7 °C
Weight of pycnometer + sugar solution	= 82.850 2 g
Temperature of solution	= 24.3 °C
Density of water at 23.7 °C	= 997.37 $kg.m^{-3}$
Density of air	= 1.20 $kg.m^{-3}$
Coefficient of expansion of glass	= 0.000 025 per °C

$$\therefore \text{Observed density at } 24.3\,^{\circ}C = \left[\frac{(82.850\,2 - 57.645\,5)(997.37 - 1.20)}{(82.529\,7 - 57.645\,5)[1 + 0.000\,025\,(24.3 - 23.7)]} + 1.20\right] \times \left[\frac{1 + 0.000\,025\,(24.3 - 23.7)}{1 + 0.000\,025\,(20 - 23.7)}\right] kg.m^{-3}$$

$$= (1\,010.185)\,(1.000\,107\,5)\ kg.m^{-3}$$

$$= 1\,010.29\ kg.m^{-3}$$

'Observed' brix from Table XV	= 3.10
Brix correction for 24.3 °C (Table I)	= +0.24
Brix	= 3.34

The coefficient of expansion of glass has been taken as fixed at 0.000 025 per degree Celsius. It is recognised that this coefficient may change with temperature as well as with the nature of the glass and for general scientific work it would be desirable to use the actual coefficient of the glass under the conditions of measurement. However, in the sugar mill laboratory the pycnometer is used almost exclusively for the determination of brix, in the course of which reference is made to Table I. This table incorporates an allowance of 0.000 025 for the coefficient of expansion of glass.

HYDROMETERS

A second method of determining the specific gravity of solutions, and the one most commonly employed in sugar laboratories, is by means of the hydrometer. It provides by far the easiest and most direct method of determination of this factor.

In its usual form this instrument consists of a hollow glass body, cylindrical in shape, and terminating at its lower extremity in a bulb, which can be weighted with mercury or lead shot and at its upper extremity is a slender, hollow stem within which a paper scale is sealed. If this instrument be allowed to float in a solution, the weight of liquid displaced is equal to the weight of the hydrometer. If placed in solutions of different specific gravity the instrument will sink to varying depths; and the scale is so graduated that the point on the stem which corresponds with the liquid surface indicates the density or percentage of dissolved substance for the given temperature.

In practice the hydrometer scale is standardised at a few points only, and the intermediate divisions are determined by interpolation. The density of a solution is equal to the weight W of the hydrometer divided by the volume V of the portion submerged.

Then $V = \frac{W}{\rho}$

The difference between the volume submerged for any two divisions v is:

$v = \pi r^2 d$

Where d = distance between divisions

and r = the radius of the stem.

The following table shows the relationship between the stem divisions of a hydrometer weighing 75 g and with a cross-sectional area of stem (πr^2) equal to 20 mm^2.

Density (ρ)	Vol. of part submerged $\left(\frac{75}{\rho}\right)$	Vol. between divisions (v)	Distance between divisions $\left(\frac{v}{20} \times 1000\right)$
g. mL^{-1}	mL	mL	mm
1.00	75.000		
		6.818	340.9
1.10	68.182		
		5.682	284.1
1.20	62.500		
		4.808	240.4
1.30	57.692		

It is clear that as the density increases the distance between scale divisions decreases. To effect this progressive reduction it is customary, in practice, to employ a dividing engine.

In the graduation of a hydrometer scale for indicating direct percentages of sugar (brix) the distance between scale divisions is more uniform, due to the partial compensating effect of the non-linear relationship between brix and density. At 20 °C the change in density from 0 to 10 ° brix is 0.039 91 g per mL, whilst the corresponding change from 50 to 60 ° brix is 0.056 89 g per mL. This effect is illustrated in the following table, where the dimensions of the hydrometer are the same as before.

Percentage sugar	Density at 20 °C (ρ)	Vol. of part submerged $\left(\frac{75}{\rho}\right)$	Vol. between divisions (v)	Distance between divisions $\left(\frac{v}{20} \times 1000\right)$
	g.mL^{-1}	mL	mL	mm
0.00	0.998 20	75.135		
			2.888	144.4
10.00	1.038 11	72.247		
			2.862	143.1
20.00	1.080 93	69.385		
			2.834	141.7
30.00	1.126 95	66.551		
			2.798	139.9
40.00	1.176 41	63.753		
			2.754	137.7
50.00	1.229 53	60.999		
			2.698	134.9
60.00	1.286 42	58.301		

It is, therefore, customary in graduating hydrometers which read direct percentages of sugar, to calibrate at, say, three points, and then divide the intervals between these points into equal subdivisions. Though not absolutely accurate, the error introduced is probably less than the errors of observation.

Brix hydrometer

The construction of the hydrometer which reads direct percentages of cane sugar is due to Balling. The scale as later recalculated by Brix constitutes the form at present in general use. The divisions of the scale are called degrees brix, and express weight per cent of sugar; that is, a sucrose solution of 20 ° brix is composed of 20 g of pure sucrose dissolved in 80 g of pure water. It should be observed that there is no reference in this definition to volume. A solution of 20 ° brix at 20 °C is still a 20 ° brix solution at 80 °C.

The confusion which frequently arises in this connection is due to the fact that the brix hydrometer responds primarily to the density of the solution tested, which varies with temperature. As the glass of which the hydrometer is made has a much lower temperature coefficient of volume than sugar solutions, it follows that, with increasing temperature, the hydrometer will sink deeper and yield lower readings. The brix scale marked on the hydrometer is

related to the density of the solution at the standard temperature (20 °C). Hence, at any other temperature, whilst the equilibrium position of the hydrometer is closely related to the actual density of the solution, the reading cannot be interpreted directly as brix. A correction must be applied to the observed reading to compensate for the change in reading which would result from bringing the temperature of the solution to 20 °C. In the derivation of temperature correction tables it is assumed that a hydrometer of a standard type of glass is immersed in a solution of sucrose in water.

One type of hydrometer which is used in Queensland mills is illustrated in Figure IV-2. The approximate dimensions are:

Overall length	360	mm
Length of scale	150	mm
Diameter of cylindrical bulb	30	mm
Diameter of upper tube	5	mm
Length of scale division (0.1 ° brix)	1.5	mm

The following ranges have been specified as the most convenient for sugar mill laboratory use:

0–10 °, 10–20 °, 15–25 °, 20–30 °, 30–40 °, 40–50 °, 50–60 °, 60–70 °, 60–85 °.

DIGITAL DENSITY METER

A more recent instrument for measuring the density of fluids is the Digital Density Meter (Mettler/Paar DMA45). The measuring principle is based on the change of the natural frequency of a hollow oscillator when filled with different fluids. The oscillator is a U-shaped borosilicate glass tube mounted in the centre of a thermostated double-walled glass cylinder. The space between the sample tube and the inner wall of the cylinder is filled with a gas of high thermal conductivity to give the sensor good temperature response and so minimise the time to reach temperature equilibrium. The glass tube is electronically excited in an undamped harmonic fashion and the period of vibration is measured. The introduction of a liquid or gas changes the natural frequency of the oscillator due to the change in mass. There is, however, no need to measure the mass or volume of the sample.

The density is calculated from the formula

$$\text{Density} = \frac{1}{A}(T^2 - B)$$

where T is the period of vibration, and A and B are temperature dependent apparatus constants which effectively account for the volume, spring constant and mass of the vibrating system. The constants A and B are determined from two calibration measurements on samples of known density, usually air and water but other fluids could be used to set a different measuring range for the instrument.

Once the apparatus constants are determined they are entered into the memory of the instrument by setting the appropriate decimal coded numerical switches. The instrument then performs all the necessary arithmetic processing, calculating the density according to the above equation and displaying the results digitally. A digital output to a printer or computer is also provided.

Since the apparatus constants are temperature dependent, accurate temperature control (± 0.05 °C) is necessary. Some instruments have a built-in electronic Peltier-effect thermostat and therefore no cooling water is required.

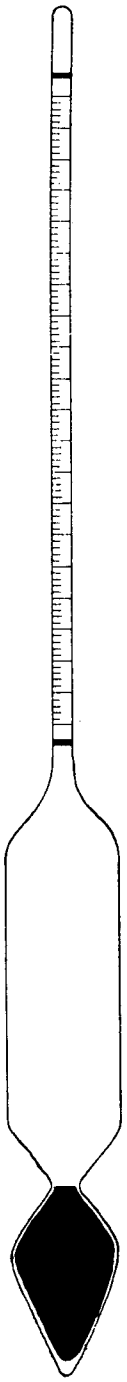


Fig. IV-2—Illustrating a Brix hydrometer.

To measure density at different temperature, the constants A and B must be measured for each temperature selected and set into the instrument memory as required.

The instrument can be set to measure and display directly the density dependent values, for example, brix. However, the range of brix over which this can be done accurately is limited since a linear relationship must exist between density and the desired density dependent value (brix). (The maximum and minimum brix are chosen such that the deviation from linearity of the density-brix relation is negligible for the desired accuracy.) In practice, the constants are set to operate over the selected range of brix measurement, with different constants being necessary to operate over other ranges of brix.

The oscillating U-tube is the heart of the instrument and it must be kept clean at all times. Build-up of foreign matter and the growth of micro-organisms on the inside wall must be prevented. The tube should be regularly rinsed with distilled water and then alcohol, and finally dried using the built-in air pump supplied for this purpose.

Samples must be injected in such a way that air is not introduced into the oscillator, and the tube is completely filled. Overfilling has no detrimental effect. An inside light can be used to observe the introduction of the sample into the tube but this light should be switched off when readings are being taken.

This type of instrument has been tested and found to give an accurate and precise measurement of density of sugar solutions. The instrument reads to 0.1 $kg.m^{-3}$ and has a precision of 0.1 $kg.m^{-3}$.

CHAPTER V

VOLUMETRIC EQUIPMENT

THE UNIT OF VOLUME

The SI unit of volume is the cubic metre, that is a volume based on a unit of length. However, the litre is still used as a unit of volume in Australia and is defined as exactly equivalent to one cubic decimetre. Therefore the terms cubic centimetre and millilitre are also equivalent.

The 'old' litre (pre 1964) was based on units of mass and the two are not precisely equivalent. To convert from 'old' to 'new' litres, multiply by 1.000 028. For most practical purposes the difference can be ignored. Tables in this manual are based on the cubic metre as a unit of volume so that mL and cm^3 are equal. In this manual volumes will be expressed in litres and millilitres.

VOLUMETRIC GLASSWARE

Volumetric glassware used in sugar mill laboratories includes flasks, burettes, pipettes and measuring cylinders. For general use glassware of class B standard is satisfactory with class A reserved for high accuracy work. Specifications for class A and class B volumetric glassware may be found in the relevant publications of the British Standard Institution or the Standards Association of Australia.

The volume contained, or delivered, by a glass vessel depends appreciably on the thoroughness with which the vessel has been cleaned. In vessels graduated 'to contain', any foreign matter left on the wall after cleaning tends to rise with and contaminate the surface of the liquid whose volume is to be measured. This leads to a decrease in the surface tension at the liquid surface and a consequent change in shape and volume of the meniscus, i.e. the concave (or convex) liquid surface in the vessel. Vessels graduated 'to deliver' are also affected in this way, but in addition, erroneous readings may be obtained if, as a result of imperfect cleaning, the film of liquid left on the wall is not regularly distributed.

To ascertain whether a piece of glass apparatus is satisfactorily clean it should be observed during filling. A vessel graduated 'to deliver' should preferably be filled from below the meniscus. The rising liquid meniscus should not change shape, e.g. it should not crinkle at its edges. After overfilling and withdrawing a little liquid (through the jet if a delivery vessel, and by means of a drawn-down glass tube if a content vessel) the surface of the glass above should remain uniformly wetted and the meniscus should not crinkle at its edges but should merge gradually onto the wall of the vessel. With experience, an observer is able to recognise the shape of a contaminated meniscus in relation to its diameter.

Obvious loose contamination should be removed mechanically from the glass vessel, e.g. by brushing or shaking with water. Oil or grease can be removed by the use of suitable solvents. The vessel should be nearly filled with an aqueous solution of a soapless detergent, and shaken vigorously. It should then be repeatedly rinsed with distilled water until all traces of detergent are removed. If the vessel is not sufficiently clean after this treatment it should be filled with chromic acid cleaning solution, allowed to stand overnight if possible and then repeatedly rinsed with distilled water.

The heating of glass vessels to temperatures above 100 °C, either by direct heat or by filling with a hot liquid, should be avoided, as the vessel may undergo permanent changes in volume if heated above this temperature.

The capacity of a graduated glass vessel is defined as the nominal volume of water (or mercury) contained, or delivered by an article of volumetric glassware, at its reference temperature when the meniscus is brought to the graduation line in the specified manner. In the case of a water meniscus the top edge of the graduation line is set tangentially to the lowest point of the meniscus. To make a precise setting of the meniscus, the lighting should be so arranged that the meniscus appears dark and distinct in outline; it should therefore be viewed against a white background and shaded from undesirable illumination. This effect can be achieved by securing a suitable strip of black paper around the vessel, not more than 1 mm below the level of the meniscus. This paper shall have a straight edge nearest the meniscus and can be held in place by means of a paper clip. The width of the paper strip shall be at least equal to the diameter of the vessel at the point where the meniscus is located.

Volumetric apparatus is graduated either to contain or to deliver a particular volume. This is usually indicated on apparatus made to British or Australian specifications

by the inscription 'In' or 'C' to indicate the vessel is graduated to contain, and 'D' or 'Ex' to indicate to deliver.

Since the capacity of a glass vessel varies with change in temperature, any given vessel can be correct at only one temperature. The particular temperature at which a vessel is intended to contain or deliver its nominal capacity is the 'reference temperature' of the vessel which in Australia is 20 °C.

FLASKS

A volumetric flask is a vessel designed to contain a known volume of liquid. It should be sufficiently robust in construction to withstand normal usage, and the wall thickness should show no gross departures from uniformity. The body of the flask should preferably be pear-shaped so as to provide a large base on which the flask can stand vertically without rocking or spinning. The base may be lightly ground in order to ensure adequate stability. The most important single factor affecting the accuracy of any item of volumetric glassware is the internal diameter in the plane of the graduation line. For this reason the neck of a flask is made cylindrical, with no undue variation in internal diameter or wall thickness, and as narrow as is practically possible.

When determining the capacity of a flask it is first thoroughly cleaned and dried, as discussed previously, remembering that if warm air is used to accelerate drying care must be taken that the flask settles down to room temperature before testing. The clean dry flask is weighed empty and then filled with distilled water to a few millimetres above the graduation line, care being taken to avoid wetting the neck of the flask above the water surface and also to avoid trapping any air bubbles on the walls of the flask below the neck. The meniscus is then adjusted to the graduation line as discussed earlier by withdrawing small amounts of water by means of a glass tube drawn out to a jet at its lower end. The flask plus water is then weighed and the weight of water determined. The temperature is recorded immediately after completion of the last weighing. The weight of water may then be converted to the volume at 20 °C by adding or subtracting corrections from Tables XXIII and XXIV which allow for the current density of the liquid, the change of capacity of the vessel with temperature, and the buoyancy of the air during the weighing.

Table XXIII converts the observed weight of water, in grams, in air of average density, at a known temperature, to the capacity of the vessel at 20 °C. Table XXIV corrects for departure of the effective air density from the average air density assumed in Table XXIII. The latter correction is negligible for most flasks used in sugar laboratories. The tables apply to a unit volume of 1000 mL and for other volumes the corrections must be adjusted in the ratio of the volumes.

The following is an example for a 100 mL flask filled with water at a temperature of 23 °C and an atmospheric pressure of 755 mm of mercury.

Weight of empty flask	=	42.000 g
Weight of flask + water	=	141.650 g
Weight of water	=	99.650 g
Correction for 100 cm^3 at 23 °C (Table XXIII)	=	+0.343 g
Correction for 755 mm pressure (Table XXIV)	=	−0.002 g
Capacity of flask at 20 °C	=	99.991 mL

The tolerances permitted for class B flasks are specified in Table XXV.

BURETTES

The burette is used either to deliver a measured volume of liquid or to measure a volume of liquid delivered. The most common burette consists of a cylindrical tube of capacity 25 or 50 mL graduated in 0.1 mL fitted at the bottom with a single or double bore stopcock. For class A burettes it is mandatory that the stopcock and jet be an integral part of the burette and while it is recommended that this apply to class B burettes, alternative designs are permitted provided that they may be attached to the graduated tube in a satisfactory manner. For class B burettes only, a further alternative is permitted. Instead of having a stopcock the burette may be provided with a pinchclip and jet attached to the burette tube by rubber or certain grades of PVC tubing. In this case the lower end of the burette shall be constricted to a nipple suitable for attaching the tubing.

In testing a burette it is first checked for leakage. A stopcock of conventional design made solely of glass or intended for use greased is tested for leakage with the burette clamped in a vertical position, the stopcock free from grease, the barrel and key wetted with water, and the burette filled initially to the zero line with water. The rate of leakage, with the key in either of the fully shut-off positions, shall not exceed one half of one scale subdivision in ten minutes in the case of class A burettes or one scale subdivision in ten minutes in the case of class B burettes, the test being continued for at least 20 minutes.

The accuracy of a burette is also a function of its rate of delivery. The delivery time is the time occupied by the descent of the water meniscus from the zero line to the lowest graduation line. This is determined with the stopcock fully open and with the jet **NOT** in contact with the side of the receiving vessel.

For calibration, the burette is clamped in a vertical position and filled through the jet to a few millimetres above the zero line and then zeroed. It is usual to test at five points on the scale, starting from zero each time. Delivery is made into a tared weighing vessel, the outflow being unrestricted until the meniscus is approximately 10 mm above the graduation line of the test point. The rate of flow is then reduced to allow the final setting to be made with no period allowed for drainage time. The drop adhering to the jet of the burette is removed by bringing the side of the weighing vessel in contact with the tip of the burette. The weighing vessel is then weighed and the temperature of water recorded. The volume delivered at 20 °C is then calculated from Tables XXIII and XXIV.

The tolerances on capacity and delivery time for class B burettes are shown in Table XXV.

NOTE: The tolerance on capacity represents the maximum error allowed at any point and also the maximum difference allowed between the errors at any two points. For example, a class B 50 mL burette may be in error by ±0.10 mL at any point, provided that the difference between the errors at any two points does not exceed 0.10 mL.

Automatic burettes are convenient for repetitive volumetric work and for applications where the reagents require some protection from contamination from the air. They are also used to minimise direct contact by the analyst with toxic reagents. The procedures detailed for the use of burettes apply, with the additional requirement to check that the filling operation does satisfactorily top up the burette to the zero mark in a reproducible manner. Besides Australian Standard 2165:1978, the British Standard 1428:Part D1:1965, 'Burettes with pressure filling device and automatic zero', is especially applicable. Routine replenishment of absorbents in the guard tubes is important to prevent formation of solids, which may affect the accuracy of the dispensed volume, or changes in the strength of the reagent. Regular cleaning is still necessary to remove the inevitable deposits that form over a period of time with reagents such as wet lead.

BULB PIPETTES

The function of the bulb pipette is to deliver a particular volume of liquid. In construction, the pipette consists of a suction tube above the bulb and delivery tube below, all three portions being straight and coaxial. The top of the pipette should be finished square with the axis of the tube and be free of any blemishes which might interfere with the accurate finger control required. The end should be lightly fire-polished or smoothly ground with a slight bevel on the outside. The graduation line should be a clearly visible permanent uniform line of thickness not exceeding 0.3 mm and completely encircling the tube in a plane at right angles to the longitudinal axis of the pipette. The delivery tube should terminate in a jet having a gradual taper without any constriction at the orifice. The end of the jet should be preferably ground smooth at right angles to the axis and slightly bevelled on the outside.

The delivery time is the time occupied by the descent of the water meniscus from the graduation line to the point at which it appears to come to rest in the jet. The delivery time is determined with the pipette in a vertical position and the jet in contact with the side of the receiving vessel, which is supported in a sloping position. When determining the capacity of a one-mark pipette the following procedure is to be observed, the pipette having first been thoroughly cleaned.

The pipette is clamped in a vertical position with the jet downwards and filled with distilled water to a short distance above the graduation mark, the water being retained in the pipette by pressing a finger on to the top of the suction tube. The outside of the delivery jet is wiped free from water with a cloth. By reducing the pressure of the finger, water is allowed to run out slowly. As the descending water surface approaches the graduation mark the pressure of the finger is increased so that the water surface is brought to rest with the lowest point of the meniscus in the horizontal plane containing the top edge of the graduation mark. The drop of water then adhering to the jet is removed by bringing the inside of a glass vessel, e.g. a beaker, into contact with the jet and detaching the drop on to the side of the vessel. A clean weighed glass beaker, or other convenient vessel, is placed beneath the pipette and inclined slightly so that the tip of the jet of the pipette is in contact with the inside of the vessel. The finger on the top of the pipette is then removed and the pipette allowed to empty. In order to ensure delivery of the true capacity, the tip of the pipette is kept in contact with the inside of the receiving vessel for approximately three seconds after movement of the meniscus appears to have ceased. The small quantity of water remaining in the jet is not expelled, nor the natural rate of delivery of the pipette under the conditions specified influenced in any way, for example by the application of a pressure other than atmospheric to the top of the pipette.

The weight of the water thus delivered is determined.

All operations are to be carried out at room temperature. The volume of water delivered by the pipette at 20 °C is calculated from the weight thus determined, by applying corrections from Table XXIII and XXIV. The tolerances for capacity and delivery time for pipettes are specified in Table XXV.

The method of delivery described above leaves a small quantity of water remaining in the jet of the pipette and, when using the pipette, no method of emptying, such as blowing out, should be used which expels liquid completely from the jet or increases the natural rate of delivery.

GRADUATED PIPETTES

Two types of graduated pipettes are of interest:

Type 1 pipettes which are calibrated for delivery from the zero line down to any graduation line (Figure V-1).

Type 2 pipettes calibrated for delivery from any graduation line down to the jet (Figure V-2).

The capacity of a type 1 pipette corresponding to any graduation line is defined as the volume of water at 20 °C delivered by the pipette at 20 °C when emptied from the zero line to that graduation line.

The capacity of a type 2 pipette corresponding to any graduation line is defined as the volume of water at 20 °C delivered by the pipette at 20 °C when emptied from the graduation line to the jet.

The top and jet of a graduated pipette should be constructed in the same manner as for a bulb pipette.

The delivery time is the time occupied by the free descent of the water meniscus from the highest graduation line to the lowest graduation line for type 1 pipettes or to the point at which it appears to come to rest in the jet for type 2 pipettes, the pipette being vertical and the tip of the jet being in contact with the side of the receiving vessel which is supported in a sloping position.

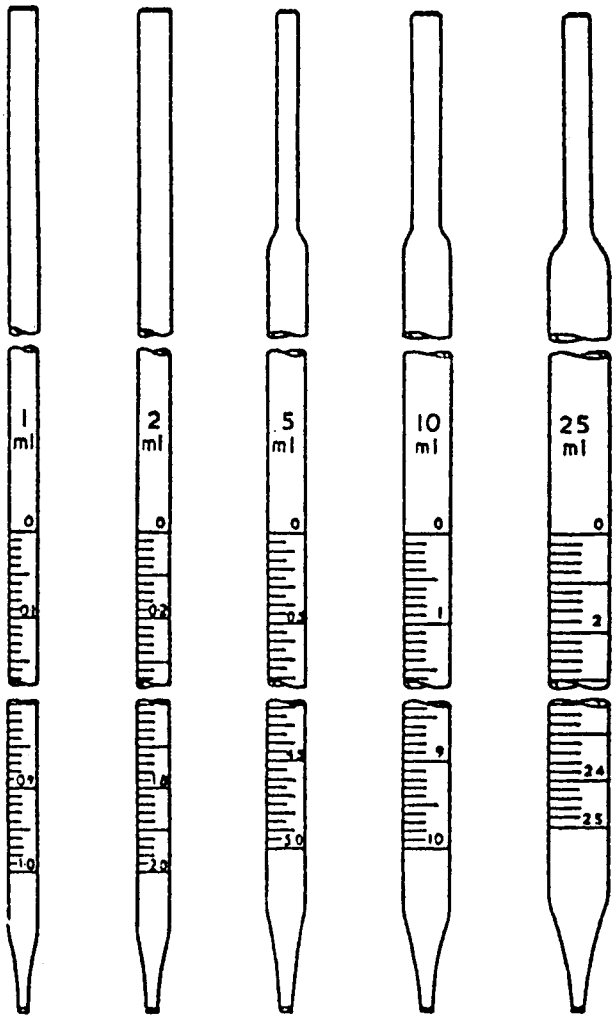


Fig. V-1—Type 1 graduated pipettes (calibrated for delivery from zero line to a graduation line).

When determining the capacity of a pipette calibrated for delivery the following procedure is to be observed, the pipette having first been thoroughly cleaned.

The pipette is clamped in a vertical position with the jet downwards, and filled with distilled water to a short distance above the graduation line, the water being retained in the pipette by pressing a finger on the top of the suction tube. Any water remaining on the outside of the delivery jet is removed. By reducing the pressure of the finger water is allowed to run out slowly. As the descending water surface approaches the zero line (type 1) or the graduation line to be tested (type 2), the pressure of the finger is increased so that the water surface is brought to rest with the lowest point of the meniscus in the horizontal plane containing the top edge of the graduation line. The drop of water then adhering to the jet is removed by bringing the inside of a suitable vessel, e.g. a beaker, into contact with the jet and detaching the drop on to the side of the vessel. A clean tared weighing bottle or other convenient vessel is placed beneath the pipette, inclined slightly so that the tip of the jet of the pipette is in contact with the inside of the vessel.

The finger is removed from contact with the top of the pipette to allow free delivery of the water into the receiving vessel. The procedures described below are followed for type 1 and 2 pipettes respectively.

Type 1

Free delivery of the water into the receiving vessel is allowed until the water surface is within about 10 mm of the graduation line to be tested. The rate of outflow is then reduced by pressing the finger on the top of the pipette, thus bringing the water surface under control so that an accurate setting can be made on the top edge of the graduation line. The receiving vessel is withdrawn without allowing any drainage period after making this setting.

Type 2

Free delivery of the water into the receiving vessel is allowed without restricting the rate of outflow. The receiving vessel is withdrawn after a waiting period of approximately three seconds which starts at the instant at which visible outflow ceases, i.e. at the instant at which the meniscus comes to rest slightly above the lower end of the jet.

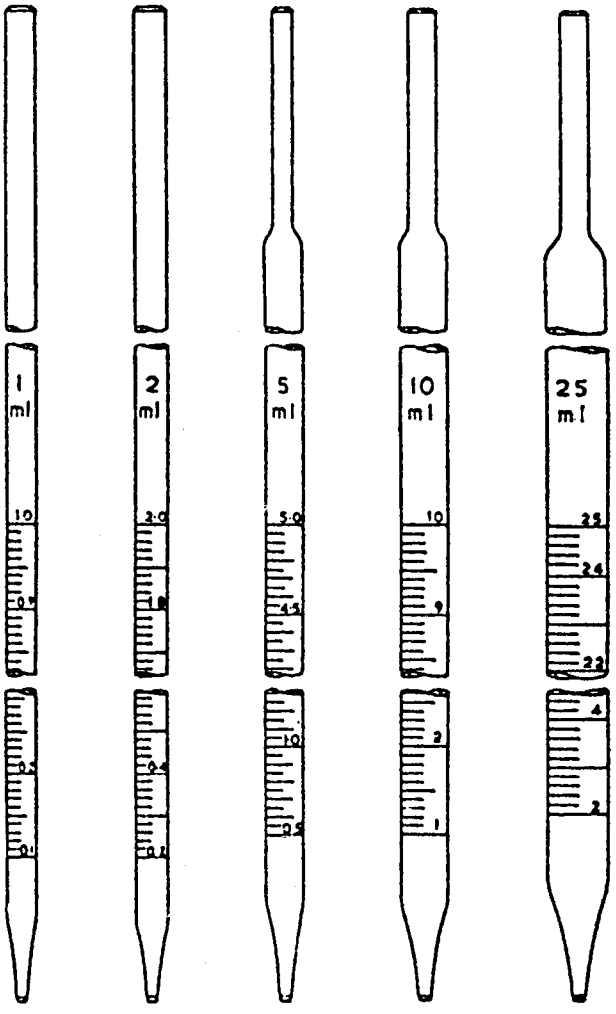


Fig. V-2—Type 2 graduated pipettes (calibrated for delivery down to jet).

NOTE: The small quantity of water left in the jet by the method of delivery described for type 2 pipettes is not to be expelled nor is the natural rate of delivery of the pipette under the conditions specified to be influenced in any way, for example by the application of a pressure other than atmospheric to the top of the pipette.

All operations are carried out at room temperature. The weight of water contained in the receiving vessel is determined and the volume of water delivered by the pipette at 20 °C corresponding to the graduation line tested is calculated by applying corrections from Tables XXIII and XXIV. The tolerances allowed for graduated pipettes are shown in Table XXV.

AUTOMATIC PIPETTES

A variety of automatic pipettes is currently available. These are useful when repetitive work is being performed. They should be used as directed by the manufacturer, and the pipette should be selected to suit the accuracy of the analytical method being employed.

MEASURING CYLINDERS

Measuring cylinders are used for rapid approximate estimation of liquid volumes but cannot be employed for accurate work. They may be standardised by the usual method of weighing the water which they contain or deliver.

THERMOMETERS

Although not a volumetric instrument, the thermometer is so often closely associated with volumetric determinations it is thought appropriate to include it in this chapter.

Mercury in glass type

In the range −80 °C to 500 °C, temperature is most easily measured by using the expansion, relative to glass, of a thermometric liquid. Mercury is the most suitable liquid in the range −38.9 °C to 500 °C (if suitable gas pressure is used) as its coefficient of thermal expansion is uniform and fairly large compared with that of glass. It is also clearly seen and does not wet glass.

The bulb of a good thermometer is made of approved thermometric glass, that is glass which is as stable as possible with respect to time and to heating. The bulb is more important in this respect than the stem as the ratio of bulb area to capiliary area is of the order of 1000:1 so that very small changes in bulb volume are significant. The stem is usually made of lead glass (low softening point) which is easily etched and will take an enamel backing. Most thermometers are filled with nitrogen, an inert gas, above the mercury column. This prevents the mercury column from breaking easily and raises the boiling point of mercury (356.6 °C at atmospheric pressure).

The accuracy obtainable from a calibrated thermometer depends on the fineness of graduation, frequency of pointing marks (marks made by the manufacturer at fixed temperatures, the graduations between the pointing marks being made on a dividing machine) and the thermal properties of the glass used. The latter vary with the particular batch of glass used and account for most of the sources of error and change in the calibration of a thermometer.

Glass acts somewhat like a supercooled liquid in that its molecules are comparatively free to move, even at room temperature. When glass is heated it expands. On cooling it does not contract completely to its original volume for some time. This means that when a thermometer is heated, the bulb expands and a subsequent reading will be lower than it was before heating. The magnitude of this effect is approximately 0.004 °C per 10 °C rise in temperature and occurs each time the thermometer is used. It is called the 'temporary depression of zero'. At the same time the bulb is recovering from manufacture when the glass was heated to 500-600 °C and allowed to cool fairly rapidly from being in a plastic state. This means that considerable strain is introduced and the first time such a thermometer is used it will show a large rise in zero (which may amount to 20 °C). In a good thermometer this strain is relieved by annealing before the thermometer is graduated, i.e. heating towards the softening point of glass and allowing to cool slowly. After the thermometer has been annealed, its bulb continues to recover indefinitely. The recovery is large during the first year then steadies off to about 0.001 °C per year. This phenomenom is known as 'secular change'. If 0 °C appears on a thermometer, the thermometer is tested at the melting point of ice, whether or not this is in the required test range. This is done as a check on permanent changes in bulb volume.

Thermometers which are marked 'Total Immersion', 'Full Immersion' or which are unmarked are intended to be immersed vertically to the reading. 'Complete Immersion' means that the whole instrument is immersed in the medium. Partial immersion is indicated by an etch mark around the stem or an inscription such as '100 mm Imm.'. The thermometer should be immersed vertically and close to the etched mark, or to 100 mm above the bottom of the bulb, as the case may be.

If in practice the thermometer is used under conditions in which the temperature of its liquid column differs from that pertaining at the time of calibration, it may be necessary to apply a further correction for the expansion (or contraction) of the liquid column. The correction to be applied depends on the expansion of the liquid compared with that of glass, the length of liquid in the glass column exposed and the change in temperature. The increase 'δ' in the reading of a thermometer, due to an increase in temperature of the exposed column, may be expressed by the formula:

$$\delta = Knt$$

where
- K = a constant for the expansion of mercury relative to glass and is 0.000 16 per Celsius degree
- n = length of exposed column in Celsius degrees
- t = the change in the mean temperature of the exposed column.

Digital thermometers

In recent times a large and ever-increasing number of digital thermometers has become available. These depend upon the electrical signal generated from thermocouples, thermistors or from diode, transistor or integrated circuit sensors. There is a temptation to accept the digital readings as being exact but in fact these devices may be as subject to errors as are the solid stem glass thermometers. Some have built-in calibration checks to test their circuitry but all such devices should be checked regularly by the measurement of a standard temperature such as the ice point. This is the temperature of a mixture of ice and air-saturated water at a pressure of one standard atmosphere. Simple checks in an ice-water mixture will show up obvious measurement errors but a more stringent procedure is required if the accuracy is to be determined with less than 0.1 °C uncertainty.

CHAPTER VI

THE BSES STANDARDISATION LABORATORY

BSES provides a calibration service for apparatus used in sugar mill laboratories. Regulation 57 of 'The Regulation of Sugar Cane Prices Act 1962-1981' states: 'Only such measuring instruments as are certified by the Bureau of Sugar Experiment Stations to be within the required limits of accuracy shall be used in the determination of brix, pol and fibre for cane payment purposes. Certification shall be done at least once every five (5) years and at such time or times as may be directed by the Senior Inspecting Cane Tester.'

Included in this category are brix hydrometers, polarimeters or saccharimeters, polarimeter tubes, refractometers, balances, weights, thermometers and volumetric glassware.

The laboratory is registered with the National Association of Testing Authorities, Australia (NATA) in three fields of measurements viz. metrology, heat and temperature measurement, and optics and photometry. These three fields cover all calibrations performed on the abovementioned apparatus. Standard equipment used in the laboratory is certified at predetermined intervals by the CSIRO National Measurement Laboratory (NML), Sydney or other laboratories nominated by NATA. Regular inspections by NATA and NML personnel ensure that proper laboratory procedures are maintained.

Equipment is either tested for compliance with a specific standard to which it is purportedly manufactured or else for compliance with the specifications for apparatus used in the analysis of cane for payment purposes as outlined in Table XXV in Volume 2.

Reports are issued for all apparatus tested. Those tests covered by NATA registration are endorsed accordingly. Certificates issued for apparatus approved for use in the analysis of cane for payment purposes are endorsed to this effect.

THERMOMETERS

BSES may calibrate mercury-in-glass thermometers in the range 0 to 110 °C. They are calibrated for use in the vertical position by comparison with mercury-in-glass thermometers standardised by the National Measurement Laboratory. A best accuracy of 0.1 °C can be quoted, but this depends on the particular thermometer being tested. Two types of thermometer are available, partial immersion or full immersion, and care should be exercised that they are used accordingly. Should a thermometer not be used as specified then errors occur, as discussed in Chapter V. Thermometers are normally tested at the icepoint (0 °C), the highest graduation mark, and three or four intermediate points.

BRIX HYDROMETERS

Hydrometers within the range 0 to 70° brix may be tested with an accuracy of ±0.05° brix.

Standardisation is carried out by comparing the test hydrometer readings with those of a standard hydrometer with known corrections. The hydrometers are immersed in solutions of sulfuric acid in rectangular perspex containers of sufficient size to allow both hydrometers to float freely side by side. As both the test and standard hydrometers are under identical conditions, this method is independent of temperature. The reading of each hydrometer is obtained by viewing, from below the liquid surface, the point where the level of the liquid surface intersects the stem of the hydrometer. This point is clearly defined when a screen painted with the top section white and the lower section black is placed behind the perspex container with the junction of the black and white sections slightly below the surface of the solution when both hydrometers are immersed. This screen provides a dark elipse around the stem of the hydrometer. This elipse becomes a thin straight line as the head is raised to bring the eye to a position exactly level with the liquid surface. Both hydrometers are read in this manner under identical conditions.

The scale is checked at each end of the range and at a third point approximately in the middle.

POLARIMETER TUBES

A comparator incorporating two dial gauges is used to determine the length of polarimeter tubes. The tube is compared with a standard bar of known length, the dial

gauge measuring the difference in length between the tube and the standard bar to an accuracy better than 0.01 mm. The length is checked on two gauges, thus providing a check on the accuracy of the individual gauges.

COVER GLASSES

Cover glasses for polarimeter tubes are checked for strain by means of a strain viewer. The surfaces may be checked for plane parallelism using an optical flat. The surfaces are also checked for scratches, chips and other defects.

SUGAR POLARIMETERS

Sugar polarimeter scales are calibrated with a best accuracy of ± 0.03 °S using five quartz plates ranging from -25 °S to $+100$ °S.

QUARTZ PLATES

Quartz control plates are tested in a Bates Fric saccharimeter for °S rotation. A best accuracy of ± 0.03 °S is quoted. The rotation in angular degrees for subsequent conversion to °S may also be determined in a Schmidt & Haensch polarimeter using the sodium yellow 589.4 nm or the mercury green 546.2 nm wavelengths of light. Quartz plates are also tested for correct mounting.

REFRACTOMETERS

Abbe refractometers are tested against calibrated liquid and solid standards in the range 1.33 to 1.52 refractive index with an accuracy of ± 0.0002 R.I. Hand refractometers are also calibrated using refined sugar solutions of varying brix, but NATA certification does not apply to this calibration.

BALANCES

Balances up to a maximum capacity of 5 kg are tested according to the principles set out in Chapter III.

WEIGHTS

Weights to a maximum of 100 g are standardised with a best accuracy of 5 in 10^6 or 100 μg (whichever is the greater). The standardisation is based on weighings made in air of density 0.001 20 $g.cm^{-3}$ against standard weights of density 8.0 $g.cm^{-3}$. The method of double weighing is used.

VOLUMETRIC GLASSWARE

Calibration of volumetric glassware is determined according to the method set out in Chapter V for each item of glassware.

CHAPTER VII

ADVANCED ANALYTICAL TECHNIQUES

Improvements in instrument technology and increasing demands on quality control have led to the introduction of relatively advanced analytical techniques in the sugar industry. These techniques, which are mainly of use in a research environment, are often mentioned in reports, at technical sessions and in current literature. Therefore, an outline of the principles involved and the potential use of these techniques in analysis are described below.

CHROMATOGRAPHIC METHODS

All forms of chromatography may be defined as differential migratory processes in which the components of a mixture can be separated. The mixture, which is contained in a mobile phase (gas or liquid), percolates through a stationary phase (solid, or liquid retained on an inert mount) where separation of the components is effected through their differing interactions with the latter phase. Ideally, this results in the components passing out of the stationary phase to be detected by a monitor at different and characteristic times. The magnitude of the detector response is proportional to the component concentration, which is quantified by comparison with the response of standard concentrations of each component.

Chromatographic techniques in common use include paper chromatography, thin layer chromatography, electrophoresis, gas chromatography and liquid chromatography. Gas chromatography and liquid chromatography (including ion chromatography) have particular relevance to the sugar industry and are discussed here.

Gas chromatography (GC)

In GC the sample is volatilised into a gaseous mobile phase which then passes through a column containing the stationary phase. The latter phase may be an adsorptive solid (gas-solid chromatography) or more commonly a relatively non-volatile liquid spread as a thin film over an inert solid (gas-liquid chromatography). A high-pressure gas cylinder and pressure regulator provide inert carrier gas (mobile phase) of uniform pressure to the column inlet. This provides a uniform flow rate through the column so that, at a given temperature, molecules introduced into the gas stream via the sample injection port will elute after a characteristic period of time (retention time). Commonly used carrier gases are nitrogen, helium and hydrogen. A GC system is illustrated in Figure VII-1.

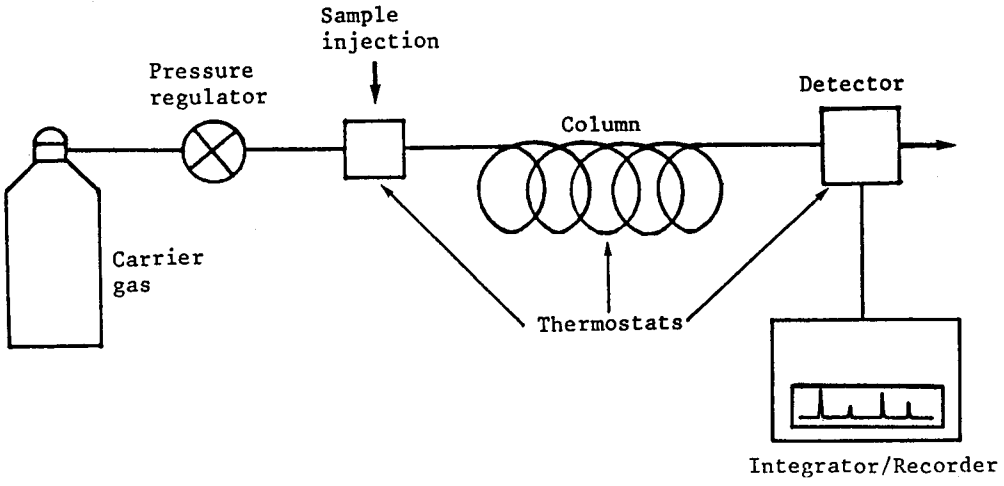


Fig. VII-1—Gas chromatography system.

Columns are usually made from stainless steel or glass in straight, bent or coiled form and may vary in length from 0.5 to 50 metres. External column diameters of 1.5, 3 or 6 mm are usual. In gas-solid chromatography, commonly used column packings are silica gel, molecular sieve and charcoal. In gas-liquid chromatography, a wide range of liquids may be used as the stationary phase, the choice depending on the separations required. The higher the solubility of a component in the liquid, the more its passage through the column is retarded and the later it will elute. The solid support for the liquid should have a large surface area for maximum contact of the liquid with the carrier gas and regularly shaped particles for efficient packing of the column. It should also be inert with respect to the sample. Diatomaceous silica is usually used for this purpose. Alternatively, the liquid may be contained on the inner surface of a long, narrow capillary column.

Thermal conductivity and flame ionisation detectors are commonly used due to their high sensitivity, low noise level, wide linearity of response and universal response to all types of compounds. Thermal conductivity detectors employ a tungsten filament through which a constant current is passed. The heat produced is dissipated at a constant rate by the carrier gas which passes over it. When sample molecules mixed with carrier gas pass over the hot filament, the rate of heat loss is reduced and the resistance of the filament increases. The increase appears as a peak in the recorder signal. In flame ionisation detectors, the effluent gas is mixed with hydrogen and burned in air or oxygen. An electrode with a DC potential applied is situated above the flame to measure the conductivity, which increases as emerging organic compounds undergo combustion.

The temperature of the sample injection port, column and detector must be high enough to keep the sample vaporised but below that at which thermal decomposition occurs. In the analysis of carbohydrates successful vaporisation requires prior conversion to suitable chemical derivatives, for example trimethylsilyl ethers.

Liquid chromatography (LC)

In liquid chromatography, the sample is introduced into a liquid mobile phase which is then passed through a liquid or solid stationary phase where separation of the sample components occurs. High performance liquid chromatography (HPLC) has resulted from the development of instrumentation with high separation efficiency. The improved performance over earlier liquid chromatographs has resulted mainly from the development of column packings having uniform particles of less than ten microns in size and hence more efficient packing properties. However, this has led to increased resistance to solvent (mobile phase) flow through the column, a disadvantage overcome by the parallel development of high-pressure pumps with precision flow control.

HPLC can be regarded as a complementary technique to GC since it is able to separate substances that cannot be readily volatilised. The sample preparation is usually simpler. Often a filtration step using a microfilter membrane is sufficient, provided that the main separation column is protected by a guard column. The latter removes any contaminants which may affect the life of the analytical column. Figure VII-2 shows a schematic diagram outlining the various components of a liquid chromatograph.

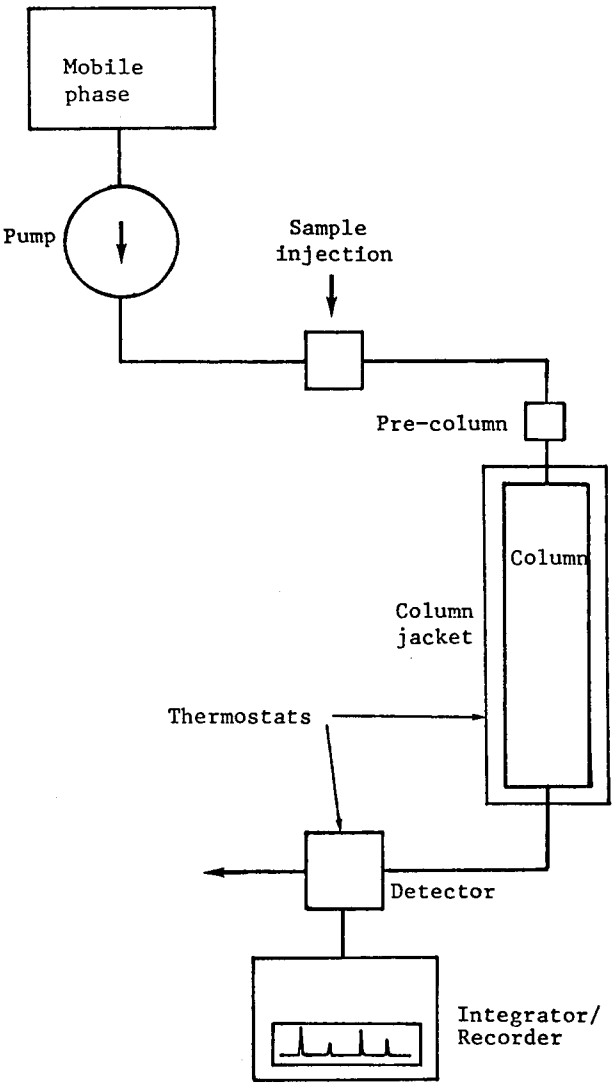


Fig. VII-2—High performance liquid chromatography system.

Commonly used detectors are differential refractometers and light absorption detectors. Both types supply an output signal related to the concentration of the sample component in the column effluent. Carbohydrates are usually monitored by refractometry. This is a convenient and reliable method although it is affected by temperature variations and has only modest sensitivity. Light absorption detectors are used where components absorb radiation at a characteristic wavelength without interference from other substances in the sample. Where necessary, post column derivatisation can be used to produce a characteristic light absorbing derivative of a particular component. This technique, which is achieved by mixing a specifically reactive chemical with the column effluent, often results in greater sensitivity of detection.

There are a number of separation systems available which are suitable for the HPLC analysis of carbohydrates in process materials. Each has its own particular advantages and disadvantages. A brief summary of these systems is given below.

One system in common use employs a sulfonated polystyrene, divinylbenzene-crosslinked resin in a suitable cationic form as the stationary phase and water as the mobile phase. The separation mechanism is probably a combination of ligand exchange and size exclusion effects. Ligand exchange involves the temporary replacement of some of the water molecules of the hydration sphere of the sulfonate-bound cations with components of the sample. In the case of carbohydrates, the exchange is due mainly to electrostatic attraction between the cations and the electronegative oxygen atoms of the hydroxyl groups. Size exclusion is the sorting of molecules according to their size and results from the increased difficulty experienced by relatively large molecules in entering the highly porous resin beads. This has the effect of causing molecules to be eluted in decreasing order of size.

Figure VII-3 shows the chromatogram of a final molasses sample obtained using a polystyrene-divinylbenzene resin. Good separations are apparent for polysaccharides and salts, trisaccharides, sucrose, glucose, fructose and a substance believed to be glycerol. Minor constituents such as mannose, galactose and mannitol have retention times similar to those of glucose and fructose. However, interference by the minor constituents in the determination of glucose and fructose is minimised by the use of peak height rather than peak area quantification. Elevated column temperatures (40 to 90 °C) are normally required to obtain good separations when polystyrene-divinylbenzene resins are used.

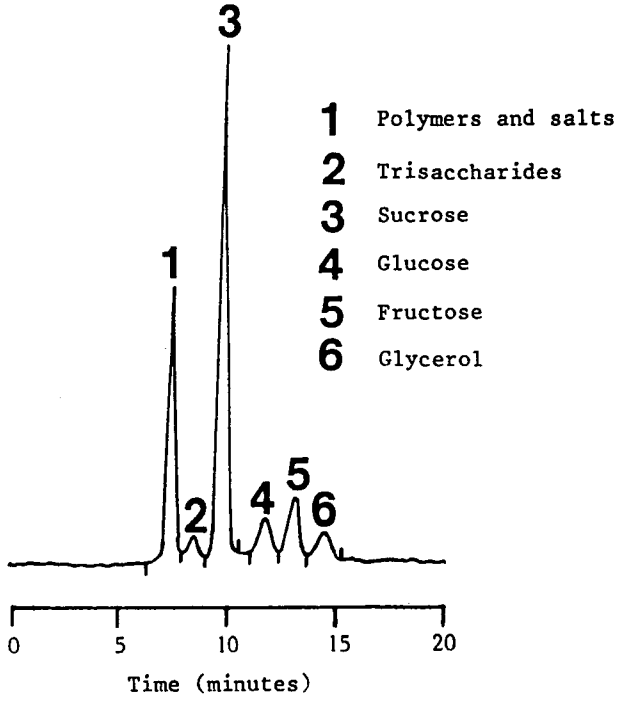


Fig. VII-3—High performance liquid chromatogram of final molasses using a column of sulfonated polystyrene, divinylbenzene-crosslinked resin in the sodium form (Shodex S-801/S) at 50 °C. Distilled water mobile phase; flow rate 0.5 mL.min^{-1}, Refractomonitor-LDC detector, 20 μ L injection.

Another common HPLC system is that which employs silica with bonded aminoalkyl groups to effect separation. The mobile phase in this case is aqueous acetonitrile (ca. 20% water). Separations are believed to result from electrostatic interactions between the amine groups and, for example, the hydroxyl groups of sugars. This system provides more rapid separations than those employing polystyrene-divinylbenzene resins and can be operated satisfactorily at ambient temperature. However, molecules containing aldehydic or ketonic groups, for example monosaccharides, may react with the amine groups and eventually modify the surface properties of the column. Separations similar to those obtained using aminoalkyl bonded systems may be obtained using conventional silica columns treated with amine modifiers contained in the mobile phase of aqueous acetonitrile. This dynamic amine modification apparently stabilises the surface characteristics of the column packing. Amine systems achieve good monosaccharide and sucrose separation but have the disadvantage that the acetonitrile solvent is relatively expensive and toxic.

Another approach uses silica particles with long chain C_{18} aliphatic groups bonded to their surface as the stationary phase and water as the mobile phase. This system, which is effective at room temperature, separates carbohydrates which differ significantly in molecular weight. Its ability to separate sugars of similar size (e.g. glucose and fructose) is poor. However, the absence of significant concentrations of other disaccharides in cane sugar process materials makes this approach particularly suitable for sucrose analysis. A typical chromatogram obtained for a final molasses sample on a C_{18} bonded phase column is shown in Figure VII-4.

Ion chromatography (IC)

In ion chromatography, which is a form of liquid chromatography, the sample is introduced into a liquid mobile phase containing ions which compete with those of the sample for sites of opposite charge on a stationary phase of low capacity ion exchange resin. In this way the sample ions are reversibly adsorbed and have retention times which depend on their individual affinities for the stationary phase and on the concentration of the competing ions in the mobile phase.

In most systems the separated ions are detected by electrical conductivity. This method is highly sensitive and is responsive to all ionic species. In order to overcome the practical problems associated with a relatively high background (mobile phase) conductivity, the Dionex Corporation has introduced a suppressor system which converts the mobile phase into a medium of low conductivity and the sample ions into a common form with high conductivity (strong acid or strong base). The latter system may consist of a column of high capacity ion exchange resin or a hollow fibre ion exchanger.

A number of non-suppressed systems are available which, although simpler and cheaper, may suffer from inaccuracy of measurement due to matrix effects. Relatively high baseline noise levels and temperature sensitivity may also be present.

Ion chromatography is particularly useful in that the method is rapid and allows several elements to be determined simultaneously. For example, the major inorganic anions present in sugarcane products viz. chloride, phosphate, nitrate, sulfate and oxalate may be separated and determined together (Figure VII-5), as may the major group I elements sodium and potassium and the major group II elements calcium and magnesium.

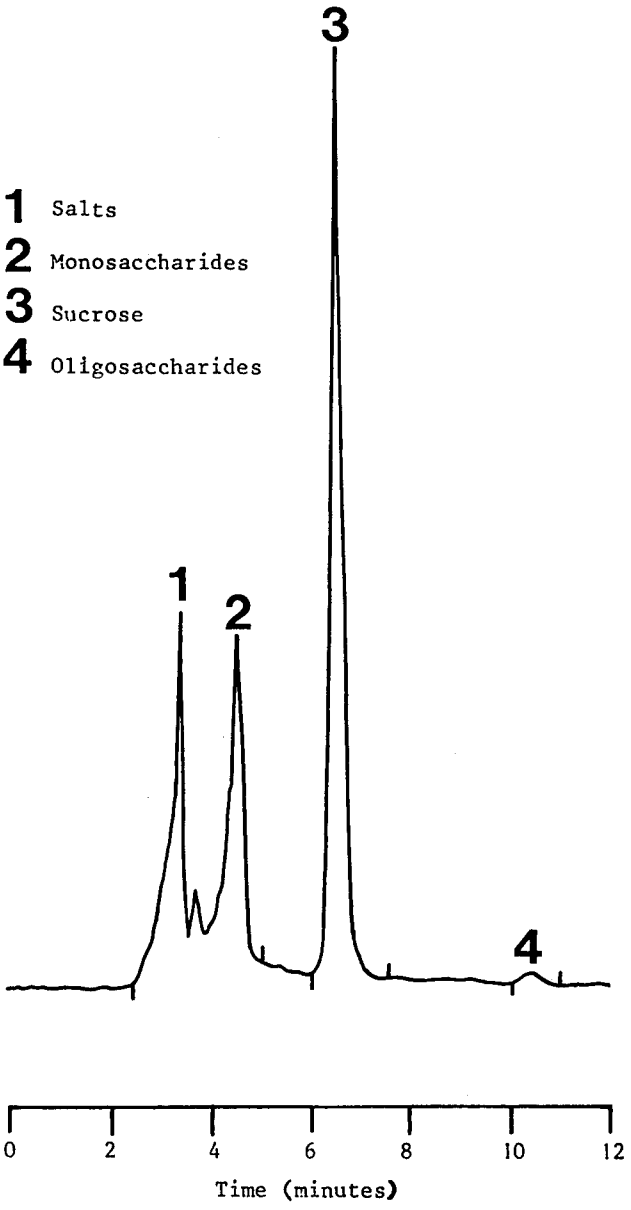


Fig. VII-4—High performance liquid chromatogram of final molasses using a C_{18} bonded phase column (Radially Compressed Dextro PAK) at ambient temperature. Distilled water mobile phase; flow rate 0.7 mL.min^{-1}, R401 differential refractive index monitor, 10 μ L injection.

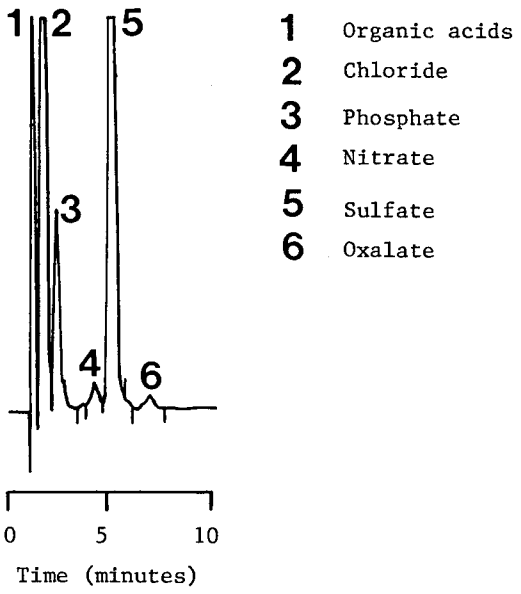


Fig. VII-5—Anion chromatogram of mixed juice using a Dionex 2010i system. HPIC—AS4 separator column; Carbonate/bicarbonate eluent; Hollow fibre suppressor; flow rate 2 mL.min^{-1}; Conductimetric detector (30 microsiemens full-scale).

ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Since the introduction of atomic absorption instruments, the analytical scope of the technique has been extended to cover 67 elements. Most of these can be detected at trace levels even in the presence of other elements at much higher concentrations. Solutions of the samples are nebulised into a flame formed from a mixture of gases e.g. acetylene and air where desolvation, compound decomposition and atom formation take place.

Atomic absorption methods rely on the absorption of characteristic radiation by atoms in the ground state causing a change in their electronic state. Sodium atoms, for example, absorb light very strongly at 589.0 nm, because light at this wavelength has exactly the right energy to transform the sodium atom to another electronic state. This electronic transition is quite specific for sodium; atoms of any other element are different, so their energy requirements are different and they cannot absorb light at this wavelength. The magnitude of radiation energy absorbed is proportional to the number of atoms and therefore the concentration of the element in the flame.

In practice, the characteristic radiation is produced by a hollow cathode lamp designed to be specific for up to four separate elements. The radiation is passed through the flame and transmittance differences before and after nebulisation of the sample solution are measured by a monochromator and related to those from standard concentrations of solutions containing the relevant element.

Ionised species cause some interference in the flame by changing the number of free atoms available for the characteristic absorption. Compound formation also affects free atom availability but is avoided by the use of

high temperature flames or releasing agents. High temperature flames may of course cause an increase in the extent of ionisation. The AAS technique is useful for the analysis of soils, deposits, waters and condensates in sugar mills.

Electrothermal atomisation is a related technique which uses a high temperature furnace instead of a flame to produce the required population of free atoms. Carbon rods, tubes or cups are held between two electrodes. The temperature is programmed so that the sample solution, introduced by a micropipette is dried, ashed and atomised in optimised steps to suit the element and its matrix or type of sample.

Sensitivity improvements of several orders of magnitude are gained over conventional flame atomic absorption. Very small samples in sample-limited applications can be used and samples containing organic matter may be analysed without any pretreatment. However, there are some spectral and chemical interferences, and a high analytical skill is required.

Inductively coupled plasma atomic emission spectroscopy (ICP) is rapidly replacing conventional atomic absorption where high numbers of multi-element analyses are required. In general, ICP has better precision and sensitivity than AAS. It differs from AAS in that it uses a highly ionised, very hot gas known as a plasma to energise the atoms to their excited state. Characteristic radiation is emitted from the atoms as they revert to their ground state. The sample solutions are nebulised and transported to the plasma in a carrier gas.

A more versatile spectrophotometer can be used to allow measurement of the various wavelengths and their intensities under the control of a microprocessor. Up to 60 elements per minute can be determined on a single sample with interferences automatically corrected by reference to data held within the microprocessor memory.

ENZYMATIC ANALYSIS

There are many different enzymes in existence, each being a unique polymer of amino acids with a characteristic catalytic action in a specific chemical reaction, usually involving organic compounds. Enzymes have been used in analytical procedures for many years in the sugar industry. For example, the enzyme invertase (β-Fructosidase) may be used to catalyse or speed up the rate of hydrolysis of sucrose into fructose and glucose in place of the hydrochloric acid often used in double polarisation procedures. Indeed, investigations by ICUMSA have indicated that enzymatic hydrolysis produces a more accurate result than is obtained with the acid.

Most enzymatic methods applicable to the sugar industry depend upon their use with other reagents which undergo a change in spectrophotometer optical density proportional to the concentration of the substance being measured. The procedures involve the addition of reagents directly into the spectrophotometer cuvette with the aid of micropipettes. The reaction is then followed by absorbance measurements with due allowance for blank or reagent corrections. The utmost cleanliness is essential to ensure freedom from interferences by contamination.

Enzymatic analysis of sucrose, glucose, fructose, mannose, total fermentable sugars and lactic acid are examples of procedures that have been carried out on sugar process materials or by-products.

Enzymatic reagents have a limited shelf life and must be stored at about 4 °C. Reagents are brought to room temperature before being used for the assay. The activity and purity of enzymes and coenzymes are usually checked by the enzymatic assay of a standard. A reasonable degree of analytical skill is required in the mixing and timing of the reactions. Overall, enzymatic analysis is specific, relatively cheap in equipment costs but slower and less precise than HPLC.

CHAPTER VIII

SAMPLING OF SUGAR MILL PRODUCTS

Throughout the sugar factory there are various process streams or unit batch operations which require monitoring in order to obtain a picture of the variability of the composition of the product over time.

In all cases, whether for the analysis of various parcels of cane for payment purposes or to determine if the process is within the desired control limits, the 'most valid estimate' of the true value is required.

There are two main sources of error in achieving this 'most valid estimate' and these are errors due firstly to sampling and secondly to analysis.

It is of no use to improve the accuracy and precision of the analytical procedure if due regard is not paid to sampling. In fact, sampling should be regarded as part of the analysis, and sampling errors resulting from the variability of the product must also be considered.

The derivation of the best sampling strategy as to the frequency and method will largely depend on knowledge accumulated from past experience through the analysis of many samples from similar sample streams.

Due regard to these aspects is included in the sampling procedures recommended here. The precision and accuracy of analytical techniques is covered elsewhere but should be considered in conjunction with this chapter.

CANE AND JUICE FOR C.C.S. DETERMINATION

The procedures for weighing, sampling and analysis of cane and juice for calculation of commercial cane sugar are to be carried out in accordance with the current Regulations 58 to 63 of the Regulation of Sugar Cane Prices Act 1962 to 1981 and also as approved by personnel authorised under those regulations.

Cane sampling

Cane for fibre determination is sampled in the prepared state prior to milling from the prepared cane elevator by means of a sliding hatch or other approved device. Such devices are usually installed, for practical purposes, at the higher end of the elevator, and must be arranged so as to sample at least three-quarters of the width, and the full depth of the bed of prepared cane.

For fibre determination, cane is sampled on the basis of classes such as major, minor, hard, soft, standover etc. Each class of cane should be sampled at least four (4) times a shift by discharging from the cane elevator a primary sample of not less than 4 kg of cane onto a table and subsampling manually by levelling and taking three double handfuls through the depth of the material without any prior mixing.

The subsamples of not less than 2 kg of cane are composited and stored in closed, labelled containers, a separate container for each class.

The regulations also provide for fibre determination on the basis of individual deliveries of cane or cane from individual canegrowers. These categories are no longer in general use.

The composite sample for fibre determination should be collected over not less than two shifts and not more than 36 hours.

Juice sampling

The first expressed juice is sampled for cane payment purposes in accordance with one of the three systems known as 'spot', 'semicontinuous' and 'continuous sampling'. These are defined under the above-mentioned regulations. Spot sampling has been phased out and most mills are now operating the continuous sampling system in which all cane supplied by one grower in a group of consecutive bins constitutes a single sample.

Tracking of samples of cane from the tipping point in the carrier, through the preparatory devices, the carrier and elevator to first mill and pumping of sample juice to the laboratory is performed by electronic trackers or computers. The tracking of each sample is initiated at the weighbridge or tippler and the progress of cane is monitored by tracking units which are actuated by pulses generated by movement of the carrier or elevator drive shaft. The pumping time from the intake vessel at first mill to the receiving vessel in the laboratory is timed by clock pulses.

At the first mill the juice is collected on a tray and trough located under the feed roller of the mill. All the juice flows through a central hole in this trough and spills over the conical screen on top of the intake vessel from which it is pumped to a sample vessel in the laboratory. Figure VIII-1 shows juice collection equipment under the first mill.

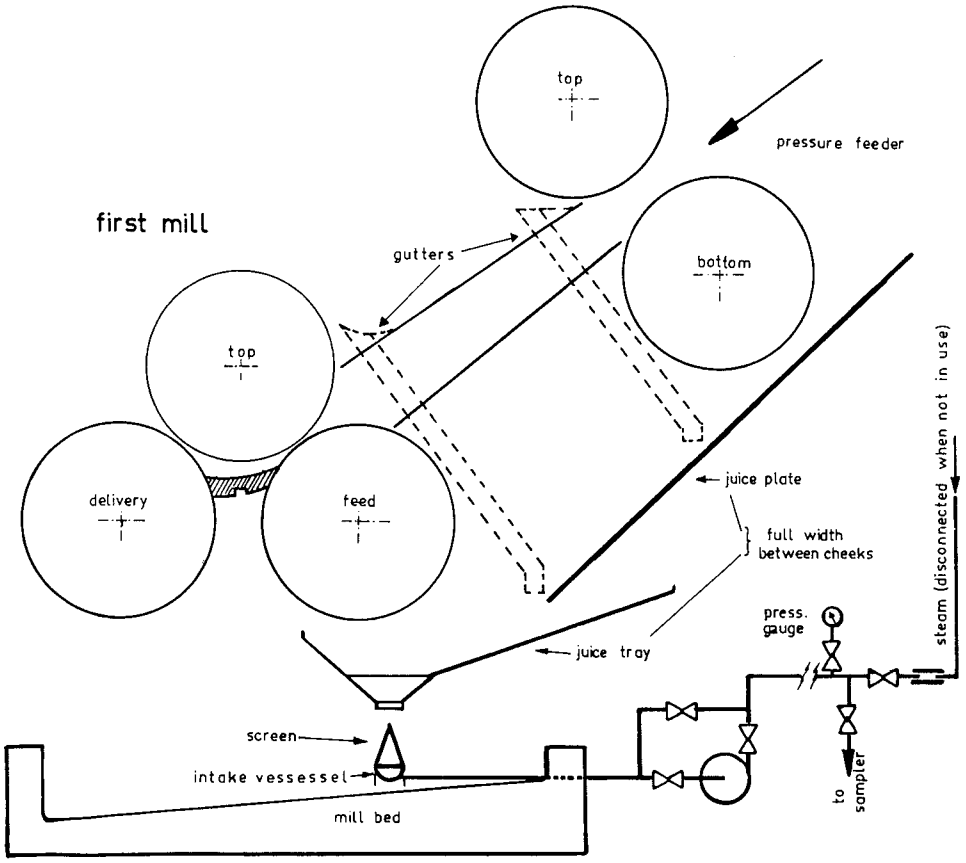


Fig. VIII-1—Equipment for collection of juice at the first mill.

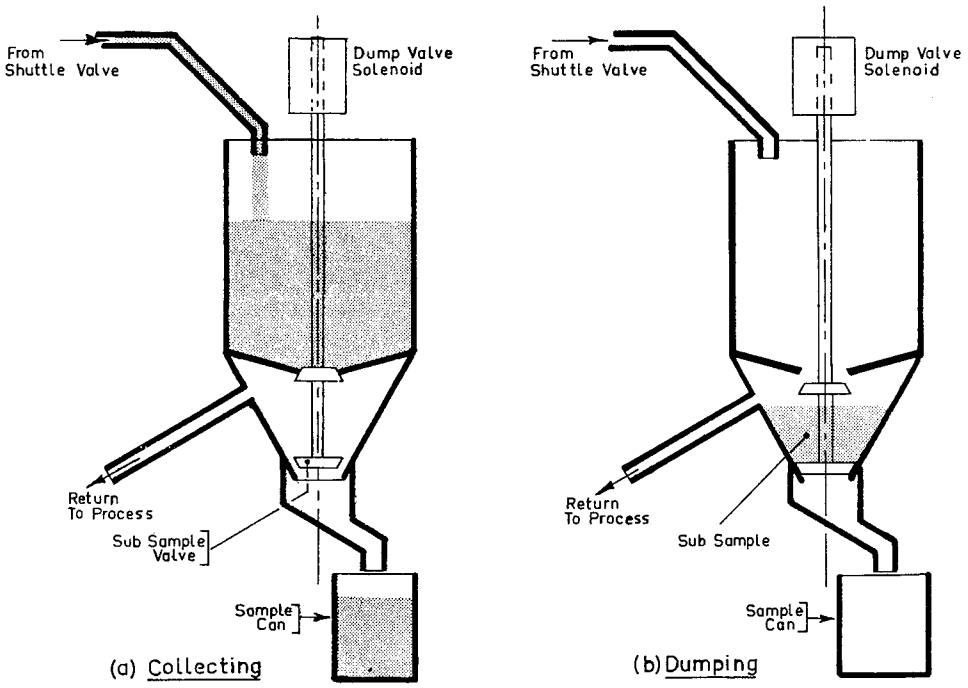


Fig. VIII-2—The operation of the sample receiving vessel.

In the laboratory, juice is collected with the assistance of a proportioning device into a receiving vessel and subsequently subsampled into a sample can of not less than one litre capacity. Figure VIII-2 shows a standard type of sample receiving vessel. The proportioning device is controlled by the electronic tracker or computer which preselects a rate of flow commensurate with the amount of cane to be sampled, in order that sufficient quantity of juice is collected without overflowing the collecting vessel.

Normally, sample cans are automatically positioned to receive the subsample. They are numbered for sample identification purposes.

Juice samples must be analysed within an hour of collection.

NORMAL MILL AND FACTORY JUICES

Sampling from juice gutters presents some difficulties.

The best device for this purpose is a small undershot water wheel. One of the spokes is made hollow and terminates in a spoon-shaped blade. This spoon takes up a little of the juice, which flows down the spoke to the hollow axle which is provided, and then into the container. The main objection to this type is that the small pipes are liable to become choked, after which sampling will cease. In order to ensure a true average sample, small baffles should be fitted in the trough upstream from the wheel to effect a thorough mixing of the juice.

Sampling of mixed juice, particularly where insoluble solids determinations are to be carried out on the juice, is best accomplished by means of a pitot-tube type sampler placed in the delivery pipe from the mixed juice pump. In this way, a sample of the juice is taken before the suspended solids have had a chance to settle, and a reasonably accurate sample can be obtained. A moving receiving tube which passes at regular intervals through the juice flowing from the sampling tube comprises an efficient method of subsampling the main sample flow.

Clarified juice is less troublesome and a continuous sample could be collected in a container provided with a conical lid and adaptor in which a small hole has been drilled. A portion of the main clarified juice stream is diverted to flow over the orifice on the top of the sample collector. The size of the orifice is adjusted to give a reasonable volume of sample for analysis in the sampling time (say four hours).

SYRUP

Continuous sampling of syrup may be effectively carried out by diverting portion of the syrup from the pump delivery line and subsampling this smaller flow by means of a sample splitter. One simple and inexpensive method of sampling is illustrated in Figure VIII-3. The sampler consists essentially of a steel rod about 6 mm in diameter and 300 mm long clamped in a pipe welded to an adjustable arm. When the rod is clamped in a stream of syrup at an angle to the vertical (normally about 60 degrees) some of the syrup trickles along the rod and falls off the tip into a sample container placed below the end

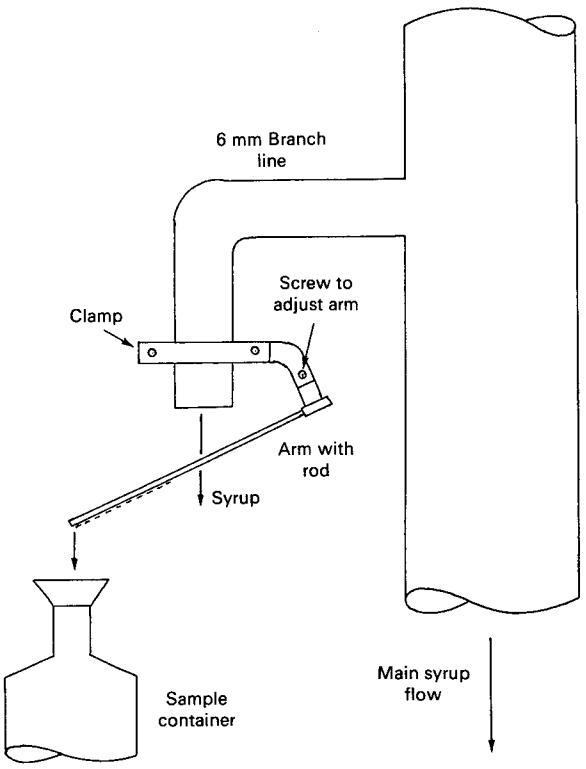


Fig. VIII-3—Continuous sampler for syrup.

of the rod. The sampling rate may be altered by adjusting the angle of inclination of the rod in the stream of syrup. The only cleaning necessary is a quick wipe down with a rag at the end of each shift when the sample is collected.

If continuous sampling is not practised, syrup may be snap sampled at regular intervals and these samples composited over a period. Preservation is not required for syrup, massecuite or molasses samples.

MASSECUITES AND MOLASSES

The composition of massecuite varies from point to point throughout a pan due to imperfect circulation, and therefore sampling is normally carried out as the massecuite is being discharged into the receiver. For routine control purposes a snap sample is usually adequate, though it is preferable that three such samples be taken and composited for each strike. These should be taken at regular intervals as the massecuite is discharged, but care should be taken that the initial sample is not taken from the first flow of massecuite. In compositing samples of massecuite, it should be ensured that the respective portions are proportional to the quantity of massecuite which each represents.

Sampling of molasses is carried out in a similar manner to that outlined for syrup. It is preferable to obtain a continuous sample of final molasses. A convenient sampler for those mills using molasses scales consists of a small pipe leading from the receiving tank to a sample container. Each time the weighing tank discharges, the inlet to the sample pipe is submerged to a similar depth and a uniform quantity of molasses is transferred to the sample container.

BAGASSE

Purpose of sampling

Bagasse is sampled and analysed for two different purposes, each requiring a rather different approach. Final bagasse is sampled for factory control purposes, to determine the amount of sugar lost in bagasse. Bagasse from all mills in the train is sampled to determine the extraction performance of the milling train.

For factory control, it is important that the sample analysed should represent the operation of the milling train over a complete shift. The sample should therefore be composited from subsamples collected at regular intervals during the shift. These intervals should be, at most, hourly, and less for a mill with a wide range of varieties in the cane supply. The schedule of sampling should be rigidly adhered to, regardless of the conditions pertaining at the sample time, provided that the mill is actually crushing at that time.

The analysis of milling train performance should be performed regularly, usually daily, so that a check can be kept on performance and mill adjustments. It is important for this analysis that associated mill parameters be measured at the same time as the sample is collected. For accurate measurement of mill parameters an extended test period is required. The sampling and measurement of milling parameters should therefore be scheduled for a period of about 30 minutes. Care should be taken to time the collection of samples down the train so that the same parcel of cane is sampled as it passes through each mill.

Sampling procedure

The accurate sampling of bagasse is a very difficult problem. No satisfactory continuous samplers have been devised and hand sampling is necessary. The most efficient method of withdrawing samples of bagasse from intermediate mills along the train is by the use of long-handled tongs which are able to fully penetrate the discharge blanket. It is also necessary to sample from points across the full width of the mill to gain a representative sample.

Access to the discharge side of the final mill is usually difficult and necessitates the use of a shovel thrust through a falling curtain of bagasse or scooped directly from the conveyor belt at a point as close as practicable to the exit from the mill. As before, the aim is to gather a sample representative of the throughput for the test period. Factors which could lead to a bias in the collected bagasse sample should always be recognised and overcome. These could be such things as segregation of particle sizes while moving down a chute or falling to a conveyor belt, evaporation of moisture or contamination from maceration liquids applied close to the point of collection.

In general the analyses of final bagasse samples are seldom considered individually, but only with references to their average value, which is used for control purposes. The compositing and preservation of samples taken at short intervals and the subsequent analysis of the well-mixed sample is strongly recommended in preference to the taking of snap samples once or twice per shift.

Analyses of samples from earlier mills in the train are usually intended to supply the engineer with specific information and, as stated earlier, samples should be taken from each mill in sequence, as far as possible from the same parcel of cane as it moves down the milling train. Reliable milling performance information may be obtained from this test, only if its duration is for a period of 30 minutes or more. The bagasse from each mill should be composited in a suitably sealed container with preservative. At the completion of the final sampling, each mill's composite should be thoroughly mixed prior to analysis.

Preservation

Samples of final bagasse may be preserved for long periods using either of two recommended procedures. For periods up to 24 hours, toluene can be added at the rate of 1 mL per kg sample and the sample stored in a plastic bag at a maximum temperature of 4 °C. Alternatively, the sample, sized so that the thickness of the bagasse is not greater than about 80 mm, should be quickly frozen within a sealed plastic bag. Samples in thick over-filled bags take too long to both freeze and defrost and then may suffer localised deterioration. Special care should be taken to bring the sealed samples back quickly to ambient temperature prior to mixing together of the subsamples to obtain the composite for the period tested. If this procedure is not followed, deterioration and condensation can affect the analysis. Manipulation of the sample within the sealed bag will be necessary at regular intervals during the defrost period to break up lumps and help heat transfer.

Preparation and mixing

The possibility of obtaining some separation of large or small particles during collection or mixing must be recognised and suitable techniques must be employed to avoid any bias.

Bagasse samples do not require further preparation before disintegration.

Shredded cane is generally sufficiently well broken and divided to require little further attention but any long fibrous pieces or whole stick portions may be cut up with a cane knife. Sections of whole stick which have come through the shredder unbroken may be rejected if they comprise not more than 5% of the total sample weight.

Mixing of the collected sample is best achieved by halving and heaping at least three times. Two people are required for this operation. It must be carried out on a clean, non-absorbing surface in a sheltered, draught-free area. A subsample for analysis is finally taken from the mixed sample and again care is taken that there is no bias towards selection of fine or coarse particles.

FILTER CAKE

It is suggested that full depth samples be collected off the final mud belt. Filtrate spillage from the drum should be included as it also represents a sugar loss.

If it is not possible to sample off the final mud belt it is suggested that the sample be collected from across the face of *EACH* filter using a thin scoop to catch the cake *LEAVING* the drum. The number of samples taken off each filter should be in proportion to the discharged cake weights from each filter. Every endeavour should be made to include filtrate spillages in the sample.

The following procedure is recommended:

(a) Samples are collected hourly from the final mud belt, taking a full depth sample with a scoop, and composited on a four-hourly basis in a suitably sealed container.

(b) Each four hours a subsample is taken by carefully mixing and sampling, or by means of a tubular probe, portion of which is analysed for pol.

(c) A fixed weight of each four-hour sample is set aside and refrigerated immediately. Using this procedure a 24-hour sample is obtained from the four-hour composites.

It is suggested that three 24-hour composites be collected on Tuesday, Wednesday and Thursday so that fibre and moisture analyses can be performed on each sample on the following day. The calculated mud solids figures can then be averaged to produce the weekly result.

It should be noted that experiments have shown that deterioration of sample will occur after four hours, and hence the four-hourly composite is recommended for pol determination.

RAW SUGAR

The following general rules apply to raw sugar sampling:

- Subsamples should be drawn in proportion to weight.
- Sampling equipment should be clean, dry and in satisfactory condition.
- Incomplete samples should be carefully protected from contamination and the absorbtion of moisture from the atmosphere.
- Precautions should be taken when compositing, handling or mixing to avoid possible changes in water content by minimising exposure to atmosphere. Contamination from sugar dust or other material should be avoided.
- The mixed sample should be stored in a sealed container or a new heavy-quality plastic bag.

A method of periodic systematic sampling on a mass basis is recommended.

The most convenient sampling point is from a falling curtain of sugar at some transfer point between the drier and the bin. The simplest situation would be in the case where a Servo Balans weigher is in use. Here a fixed volume of sugar could be extracted from each dump. In other situations a sampling device taking a fixed cut at a transfer point or at the drier exit would be suitable.

A type of sample collector as illustrated in Figure VIII-4 could be suitable for collecting a regular sample. This collector should deposit its sample in a sealed collecting device which is composited and subsampled on a regular basis. Compositing on a four-hourly basis is recommended. The importance of this sample as a quality check on production is strongly emphasised and warrants a degree of sophistication in designing the sampling device to eliminate contamination and to ensure the sample as collected is representative of production.

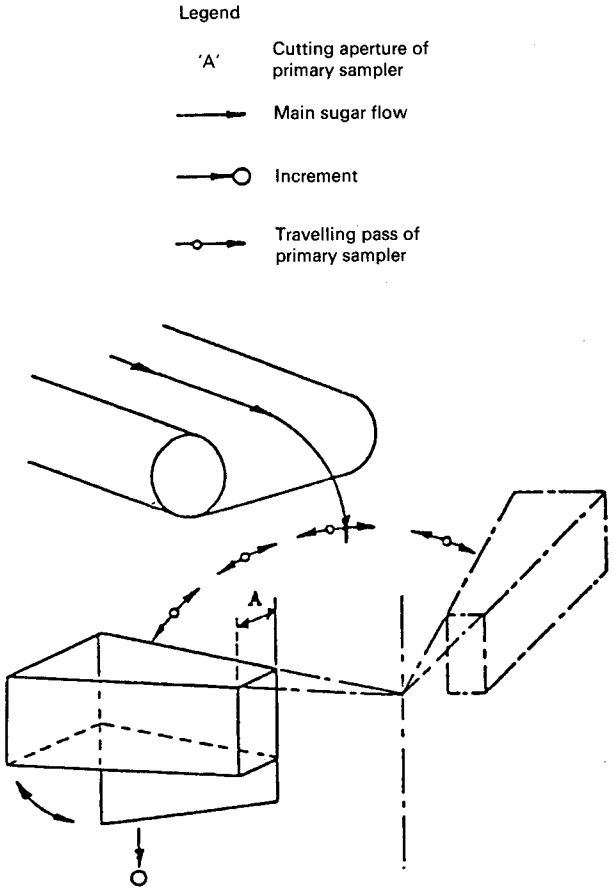


Fig. VIII-4—Swing arm type sampler.

CARE OF SAMPLERS AND CONTAINERS

All sugar-mill products are susceptible to rapid deterioration due to bacterial activity; it is therefore imperative that all sample containers be maintained in a thoroughly clean condition and be subjected to frequent sterilisation. Sample jars should be washed with hot water after each usage and thoroughly dried. Metal containers (preferably of stainless steel) should be frequently washed and steamed.

CHAPTER IX

THE DETERMINATION OF pH

Hydrogen ion concentration

Pure water exhibits a very high resistance to the passage of an electric current, but its conductivity is markedly increased when substances known as *electrolytes* are dissolved in it; electrolytes include all acids, bases and salts, whereas substances such as sugars, alcohols and ketones are without influence on the conductivity of the solution and are known as *non-electrolytes*. An attempt to explain the effect of electrolytes led Arrhenius in 1887 to propound his Electrolytic Dissociation Theory. He postulated that when an electrolyte is dissolved in water, some of the molecules of the substance dissociate into electrically charged particles, which are known as ions. Thus a molecule of hydrochloric acid gives in solution a positively charged hydrogen ion H^+, and a negatively charged chloride ion Cl^-. In all cases, the sum of ionic charges must be zero, for the molecule is electrically neutral.

The molecules of all electrolytes are not dissociated to the same degree. For example, a normal solution of hydrochloric acid is essentially completely dissociated, while a solution of acetic acid of similar concentration possesses but 0.43% of its molecules in the ionised form. Electrolytes which are fully dissociated in solution are known as *strong* electrolytes. Those which are but slightly dissociated are called *weak* electrolytes, for which the degree of dissociation is a function of the concentration of the solution; the more dilute the solution the higher the percentage of dissociation.

Pure water does conduct an electric current to a slight degree, and is therefore itself a weak electrolyte. The equation for the electrolytic dissociation of water may be represented as:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

for which the equilibrium constant is given by

$$K = \frac{{}^{a}H_3O^+ \times {}^{a}OH^-}{{}^{a^2}H_2O}$$

where a is activity.

If the solution is dilute the activity of water may be taken as unity so that

$$K_W = {}^{a}H_3O^+ \times {}^{a}OH^-$$

where the constant K_W is known as the ionic product of water. For moderately dilute solutions, the activities may be replaced by concentrations so that, to a good approximation

$$K_W \simeq [H_3O^+]\,[OH^-]$$

Careful measurements have demonstrated that at 22 °C, pure water possesses a concentration of hydrogen ions equal to 10^{-7} gram ion per litre. It contains also an equal ionic concentration of hydroxyl ions. Thus at 22 °C the dissociation constant of water is equal to $10^{-7} \times 10^{-7}$ or 10^{-14}. It should be observed, also, that *in dilute aqueous solution the product of the concentrations of* H^+ *and* OH^- *is for practical purposes a constant at constant temperature*, and equals 10^{-14} at 22 °C.

As the concentration of hydrogen ions often has a very low value, in order to avoid the nuisance of writing a long decimal expression to describe it, it has been found useful to use an exponential notation. The term pH, first proposed by Sorensen in 1909, is widely used today. It is defined as the negative logarithm of the hydrogen ion concentration.

Thus,

$$pH = -\log_{10}[H^+]$$

For pure water at 22 °C, $[H^+]$ equals 10^{-7}grams per litre, therefore the pH is 7.

An acid solution may be defined as one in which the concentration of the H^+ exceeds that of OH^-; and conversely, an alkaline solution is one which possesses an excess of OH^- over H^+. A solution of pH 7.0 is, therefore, regarded as a neutral solution; pH values less than 7.0 indicate an acid solution, while values above 7.0 are characteristic of alkaline solutions. In employing this convention, it must be remembered always that pH is a *logarithmic* function; and therefore a solution of pH 6.0 has a H^+ concentration ten times that of a solution of pH 7.0.

It will be observed that the value of pH for water at 22 °C is 7.0. This value does vary with the temperature in quite a marked degree, as is shown by the following table for pure water:

Temperature °C	pH
16	7.10
20	7.03
22	7.00
25	6.95
40	6.71
100	6.12

The importance of temperature control must be borne in mind when carrying out pH determinations; strictly these should be made at a constant temperature, so as to be comparable with one another.

BUFFERS

Aqueous solutions of salts, e.g. sodium chloride, ammonium acetate, usually have a pH of about 7, but the addition of 1 cm^3 of 0.1 molar hydrochloric acid to 1 litre alters the pH to 4 in the former solution, although it hardly affects the pH of the latter. The addition of an equivalent quantity of sodium hydroxide would likewise change the pH of sodium chloride solution from 7 to 10, but it would not appreciably alter that of the ammonium acetate solution. The solution of ammonium acetate thus has the property of resisting change of pH when acid or alkali is added, and this property is known as buffer action. In general, a buffer solution is *one which is resistant to change of* pH *upon the addition of acid or alkali.* Such solutions usually consist of a mixture of a weak acid and its salt or of a weak base and its salt; a salt of a weak acid and a weak base, such as ammonium acetate, also has some buffer action, as indicated above.

The buffer action of a solution of a weak acid and its highly ionised salt is explained by the 'neutralisation' of added hydrogen ions by the anions acting as a base. If hydroxyl ions are added, they are removed by reaction with acid in the solution.

In view of these reactions it can be understood why a buffer solution of the type described resists change of pH when acid (H^+ ions) or alkali (OH^- ions) is added.

Buffer solutions of definitely known pH are of great value in various aspects of chemistry, and the problem of preparing such solutions is of interest. The hydrogen ion concentration of a buffer solution, consisting of a weak acid and its salt, is given with fair approximation, in the pH range of 4 to 10, by the equation

$$pH \simeq pK_a + \log \frac{[salt]}{[acid]}$$

Where $pK_a = -\log K_a$

And K_a = dissociation constant of the acid.

By means of this equation, known as the Henderson-Hasselbalch equation, it is possible to calculate the pH of a buffer solution of known concentration; alternatively, it may be employed to prepare a buffer solution of definite pH.

In general, the resistance to change in the [salt]/[acid] ratio, and hence in the pH of the solution, upon the addition of acid or alkali, is greatest when the ratio is unity. The buffer capacity is therefore a maximum in a solution containing equivalent amounts of a weak acid and its salt; it falls off as the ratio of salt to acid changes in either direction. Although it is difficult to give an exact limit, it is generally accepted that a solution has useful buffer capacity provided the value of [salt]/[acid] lies within the range 10 to 0.1, i.e. 10 parts of salt to 1 of acid, at one extreme, to 1 part of salt to 10 of acid, at the other extreme. It follows, therefore, that a particular acid can be employed for making useful buffer solutions of pH lying within the range of $[pK_a - 1]$ to $[pK_a + 1]$. Acetic acid, for example, has a pK of 4.76 at 25 °C; hence mixtures of sodium acetate and acetic acid can be used for preparing buffer solutions whose pHs are roughly in the range of 3.75 to 5.75. Outside this range the buffer capacity of the sodium acetate-acetic acid system is too small to be of practical value.

Any given weak acid can be used for the preparation of buffer solutions over a limited range of pH only; hence, a number of different acids, and their salts, are required to cover the useful range of pH from about 2 to 12. Some of the recommended mixtures and their effective ranges are given in the accompanying table; the pH values have been obtained by experimental determinations with the hydrogen electrode. By following the directions given in the literature a solution of any desired pH value can be prepared with rapidity and precision.

Buffer mixtures

Constituents	pH range
Glycine and glycine hydrochloride	1.0–3.7
Phthalic acid and potassium acid phthalate	2.2–3.8
Acetic acid and sodium acetate	3.7–5.6
Disodium citrate and trisodium citrate	5.0–6.3
Monosodium phosphate and disodium phosphate	5.8–8.0
Boric acid and borax	6.8–9.2
Borax and sodium hydroxide	9.2–11.0
Disodium phosphate and trisodium phosphate	11.0–12.0

MEASUREMENT OF pH

Two general methods are employed in the deter mination of pH, the colorimetric method and the electrometric method. Each possesses its advantages and disadvantages; the latter requires a pH meter and is more accurate, while the former requires less sophisticated apparatus.

Colorimetric method

Certain chemical compounds have the ability to change colour when the pH of the solution, in which they are dissolved, changes over certain ranges. These compounds are known as indicators. Compounds of this nature behave as weak acids or bases, the neutral

molecules of which are able to absorb light of a definite spectral band. An acid indicator at low pH values will exhibit the colour characteristics of the undissociated molecules, while the neutralisation of the acid by the addition of a base results in the production of a highly dissociated salt (since all salts are highly dissociated) and the solution exhibits the colour of the ions. Indicators are usually utilised in the measurement of the pH of solutions by means of test papers or a colour comparator.

Test papers

There are numerous different types of test papers available commercially for the estimation of pH. 'Universal' test papers cover the range 1.0 to 11.0 pH in steps of 1.0 pH; the colour change chart for these papers is printed on the inside of the cover. Another useful type for sugar mill application is the 'Hydrion' short range pH test paper covering the range 6.0 to 8.0 in half unit steps. Short range papers are available in smaller steps and for other ranges if required. These test papers are portable and speedy but not extremely accurate.

Comparator

The Lovibond or Hellige comparator comprises a plastic housing into which can be fitted a disc of permanent colour standards together with two glass containers, one for the specimen under test and the other for a blank (to compensate for inherent colour in the sample).

Each particular test requires the use of the appropriate disc which contains a number of permanent glass colour standards (usually nine) representing the range of colours produced by different concentrations of the material which is the subject of the test. The discs for pH determinations are usually supplied complete with the appropriate indicator. A useful disc for sugar mill work is the Bromothymol blue disc, containing nine steps of 0.2 pH over the range of 6.0 to 7.6. The comparator can only be used for fairly clear solutions. It is slower than the test papers but more accurate.

Electrometric method

Electrometric methods are based upon the principle of measuring the electromotive force generated, as a function of the hydrogen ion concentration (and temperature), between electrodes of various types immersed in a solution to be tested (measuring electrode) and in a solution of known and definite characteristics joined thereto by a liquid junction (reference electrode). The standard and classical electrometric method employs the hydrogen electrode and while, because of the many difficulties involved in its use, the hydrogen electrode has found no direct application in the sugar industry, an understanding of its operation is useful to give a clear picture of the method.

MEASURING ELECTRODES

Hydrogen electrode

The hydrogen electrode consists of a platimum or gold foil carefully coated with a porous layer of platinum, palladium, or iridium, and immersed in the solution being tested, which is saturated to equilibrium with purified hydrogen gas. The hydrogen is bubbled through the solution surrounding the electrode. In order to measure the electric potential of the solution in which the hydrogen electrode is placed, it is brought in contact by liquid junction with another electrode or half-cell, which may be a similar hydrogen electrode, or it may be one of the other types of standard half-cells, such as one of the calomel electrodes. Thus, if two hydrogen electrodes are placed in solutions containing different hydrogen ion concentrations, but joined by a liquid junction, then the potential difference is given by the equation

$$E = \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

where E = potential difference
R = gas constant
T = absolute temperature
n = valency of hydrogen
F = quantity of electricity required to neutralise the charge carried by one gram-equivalent of ions
C_1 and C_2 = concentration of hydrogen ions
ln = natural logarithm

thus
$$E = 2.303 \frac{RT}{F} \left(\log \frac{1}{C_2} - \log \frac{1}{C_1} \right) \text{ since } n = 1$$

$$= 2.303 \frac{RT}{F} \left(pH_2 - pH_1 \right)$$

and therefore the potential difference is proportional to the difference in pH between the two solutions. If E is measured, and one pH is known, the unknown pH may be evaluated.

The electrochemical effects of ions in solution are influenced not only by the concentration of the ions but also by the 'activity coefficient', and strictly speaking the pH is a function of both the concentration and the activity coefficient of hydrogen ions. However, for practical purposes the pH is accepted and interpreted as being related to the hydrogen ion concentration.

As previously mentioned, it is not practicable to measure the pH of a solution by means of hydrogen electrodes. It can, however, be measured by a combination of two other electrodes (half-cells) such as the calomel electrode and the glass electrode.

Glass electrode

The glass electrode, as the name implies, is a bulb of thin-walled glass of special composition blown on the end of a glass tube. Inside this tube is an electrode of some type, such as a silver-silver chloride electrode in a hydrochloric acid solution or a buffered chloride solution. A typical glass electrode is shown in Figure IX-1(a). It is believed that an actual transfer of hydrogen ions takes place through the bulb, which makes it behave like a hydrogen electrode, and like the hydrogen electrode it needs a reference electrode and salt bridge to complete the hydrogen ion cell.

In many respects the glass electrode is considered ideal, in that nothing has to be added to the solution which might alter its hydrogen ion concentration; also the electrode cannot become poisoned, and it can be used

for measuring the pH of all kinds of materials, including those which are semi-solid in consistency and those which contain active reducing or oxidising substances. The range of application is normally from about 1 to 13 pH. Although errors may be introduced in alkaline solutions containing appreciable amounts of sodium salts, corrections can be made for this error. With frequent and proper calibration a limit of error of about 0.02 pH is attainable with the glass electrode.

Before use, all glass electrodes should be immersed in distilled water for at least 24 hours. When not in use, the glass electrode should be stored in distilled water, as repeated wetting and drying impairs the action of the glass membrane. Several makes of pH equipment using glass electrodes are on the market, all of which operate on more or less similar principles, the main differences between them being in structural detail.

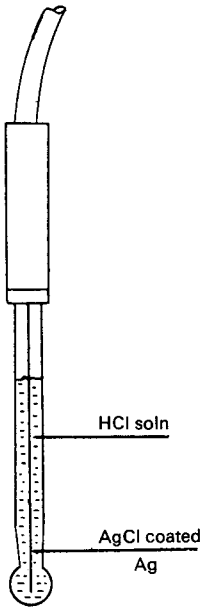
REFERENCE ELECTRODES

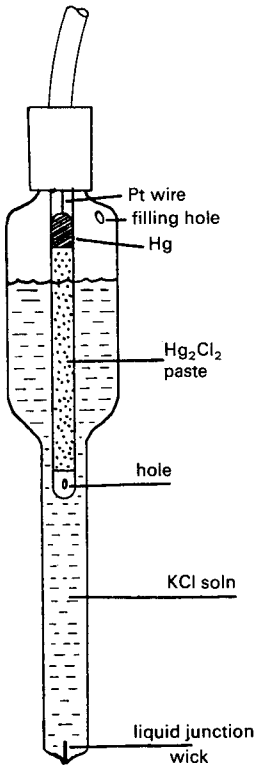
Calomel electrode

The calomel electrode is composed of mercury and calomel (mercurous chloride) in an aqueous solution of potassium chloride. These materials are contained in a glass vessel of a suitable design. One such design is shown in Figure IX-1(b). Provision is made in some manner to protect the electrode from contamination caused by diffusion of the solution being tested through the liquid junction. This is normally achieved by maintaining the solution inside the cell at a higher level than the test solution. Electrical contact to the calomel cell is obtained through the mercury by means of a platinum wire, sealed through the bottom of the calomel electrode, or fed through the top opening of the vessel into the mercury. The potential of a calomel electrode is dependent upon the concentration of the potassium chloride solution in contact with the calomel and mercury. One of three concentrations may be used, namely, 0.1 normal, 1.0 normal, or saturated. The last is used most widely in practice because it is easily prepared. Because the solubility of mercurous chloride in potassium chloride is appreciable at elevated temperatures, calomel electrodes are usually restricted to temperatures below 50 °C although some are available which can be used up to 90 °C. However, prolonged use at high temperatures reduces the life of the electrode.

Silver-silver chloride electrode

The silver-silver chloride electrode usually consists of a silver wire coated with a layer of silver chloride in an aqueous solution of potassium chloride saturated with silver chloride. These materials are contained in a glass vessel similar to those used for the calomel electrode. A typical electrode is shown in Figure IX-1(c). As with the calomel electrode, contamination is prevented by keeping the liquid junction flushed with potassium chloride.





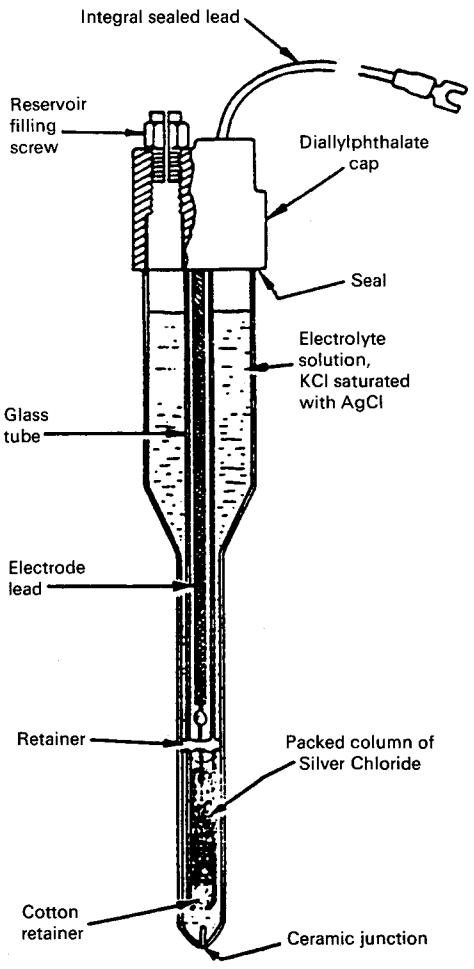


Fig. IX-1—(a) Glass electrode. (b) Calomel electrode. (c) Silver/silver chloride electrode.

The potential of the electrode is also dependent on the concentration of the potassium chloride solution. Saturated solutions are normally used for laboratory electrodes but industrial electrodes use a 4 normal solution. Silver-silver chloride electrodes can be used at temperatures up to 100 °C if required without markedly affecting the electrode life, provided the internal solution has been saturated with silver chloride.

pH Meters

Modern pH meters usually utilise the glass electrode-calomel electrode combination. A typical modern pH meter is illustrated in Figure IX-2. Because the conductivity of glass is very low, and even a thin membrane exhibits very high resistance (10^8 ohms), it is necessary to amplify the potential difference across the two electrodes, and to measure the voltage directly with a calibrated galvanometer.

The overall potential developed by the complete electrode assembly is of the form

$$E = K\,pH + Eo$$

where E = overall measured potential
K = a thermodynamic constant varying with temperature
Eo = the result of a group of fixed potentials — half cell potentials, asymmetry potential, liquid junction potentials, etc. This also varies with temperature.

For normal mill products, buffers of pH 4 and pH 9 are adequate. The electrodes are first immersed in the buffer of higher pH. If the instrument does not have automatic temperature compensation, the temperature compensation dial must be adjusted to the temperature of the buffer. The 'standardise' control is used to adjust the meter reading to the pH of the buffer. The value of Eo in the above equation is then established. After rinsing with distilled water the electrodes are immersed in the second buffer and the meter adjusted to the correct reading using the 'slope' control. This establishes the value of K in the equation. The meter should then read correctly the pH of the unknown solution. With proper calibration accuracies of ±0.01 pH unit can be obtained on a 0-14 scale, and ±0.002 on expanded scales.

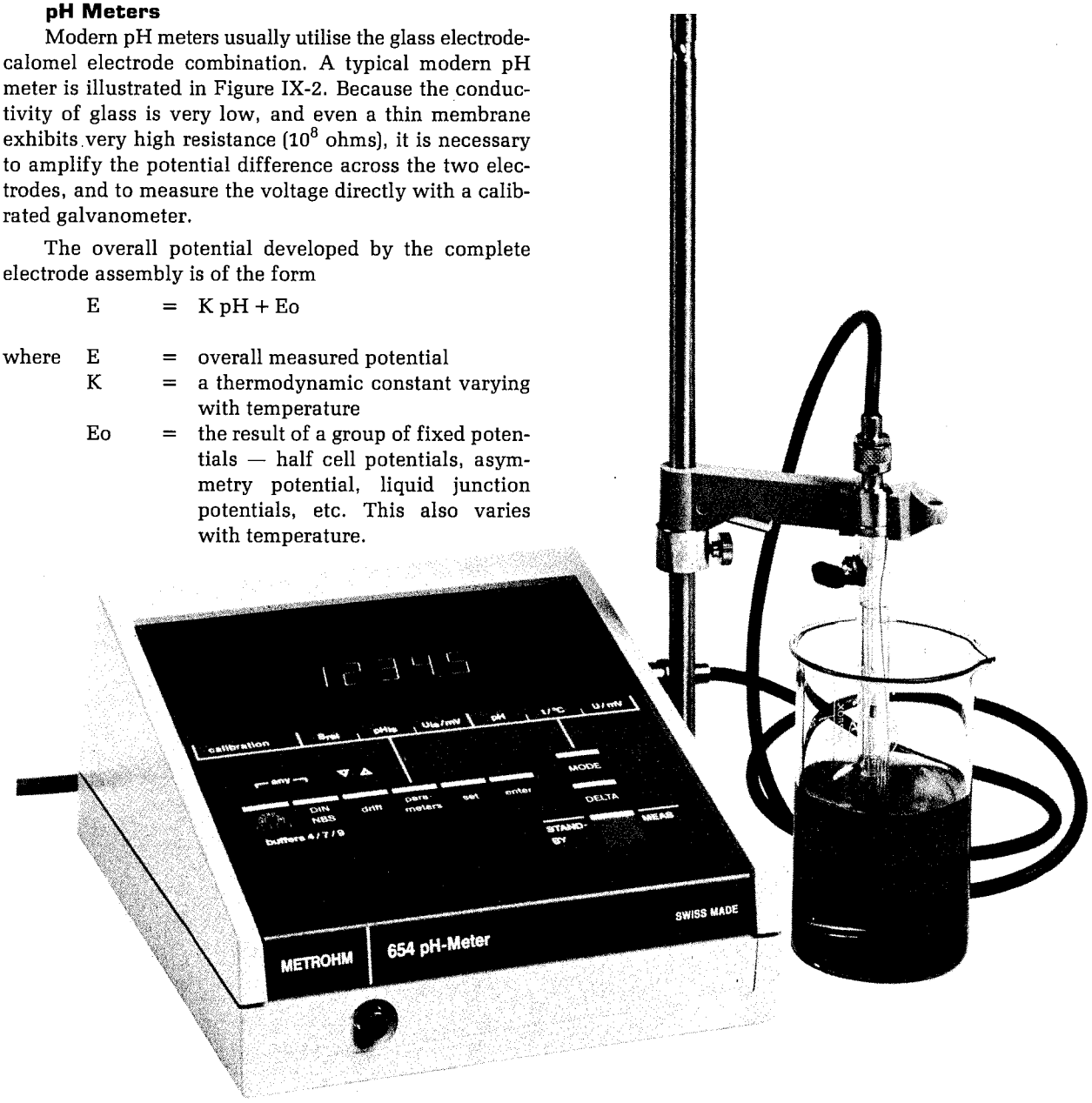


Fig. IX-2—A typical modern pH meter.

Standardisation

Due to the fact that the fixed potentials will vary from electrode to electrode and from time to time, the pH meter must be standardised before being used to measure the pH of an unknown solution. Most modern pH meters have provision to adjust both the slope and the fixed potentials and are best standardised using two buffers of known pH covering the expected range of the unknowns.

Many of the simpler instruments do not have provision for slope control and can only be standardised with a single buffer. The pH of the buffer used in standardisation should therefore be as close as possible to the pH of the unknown. The accuracy of measurement will depend on the difference between the sample and buffer pH's but is of the order of ± 0.1 unit for many instruments. While this may be adequate for general process control, laboratory analytical work requires accuracies generally provided only by instruments with both slope and standardisation controls.

Values of pH obtained at one temperature cannot be converted to another temperature unless the pH—temperature relationship of the solution is known. For strict accuracy, the buffer solutions and test solutions should be at the same temperature so that the results obtained will then correspond to pH at that temperature.

Determination of pH values of sugar mill products

The most important aspect of pH measurement in a sugar mill is its use for the control of the clarification process. All mills have now installed automatic equipment for the addition of lime to mixed juice, and this addition of lime is controlled by pH measurements made on the limed juice. This pH measurement is continuous and utilises an industrial glass electrode, which will operate at high temperature and withstand erosion, together with an industrial reference electrode, which maintains a slight pressure on the potassium chloride solution to ensure that the liquid junction is not fouled. Silver-silver chloride electrodes are preferred for process control use because of their better temperature characteristics. The pH of limed juice determines the final pH of clarified juice, and the set point of the pH controller is altered up or down according to the value determined on the clarified juice. The pH of limed juice is the most important pH measurement in the factory, and this quantity should be measured continuously using a pH recorder. Periodic laboratory pH determinations should be carried out to determine the pH of clarified juice and to check the accuracy of the recorder.

These determinations should be carried out with an accurate laboratory pH meter, which is a most useful instrument for general laboratory work and for measurements of pH on other factory products. Laboratory pH measurements are best carried out at ambient temperature in the following manner:

Check and restandardise the instrument at least once per shift with standard buffer solution as described previously.

Cool the solution to room temperature or to the temperature at which the instrument was restandardised.

Rinse the electrodes with a portion of the test solution prior to carrying out the determination.

Fill the beaker or receptacle with test solution to a level which will ensure that the electrodes and thermometer bulb are well covered.

Read the temperature of the solution and adjust the instrument temperature compensator to the desired setting. (Reference tables may have to be used on older model pH meters.)

Allow sufficient time for the system to come to equilibrium, and determine the pH.

After the determination is completed, thoroughly wash the electrodes with distilled water and keep them immersed in distilled water when not in use.

N.B. — Glass electrodes are fragile and susceptible to breakage. Extreme care should be taken when handling these electrodes.

CHAPTER X

CALCULATIONS INVOLVED WITH CHEMICAL CONTROL IN THE FACTORY

INTRODUCTION

The factory operates to process a known quantity of cane and from it produces sugar, molasses, mud and bagasse.

A method of chemical control has been evolved to index the recovery of sugar, to provide an accurate assessment of the known losses of pol in the process and to give a quantitative control of the unit operations involved in the overall operation of the factory.

Factory chemical control is really in the realm of the factory chemist but there is no reason why people of other disciplines cannot follow and understand the principles involved. An endeavour will be made to explain these where possible in non-technical terms and to build a rationale which may be easily followed.

Each section of the process is monitored by the collection and analysis of samples from the process stream. Obviously the knowledge so obtained is only as good as the sample on which it is based and one assumes that representative sampling techniques apply.

We are interested in three aspects:

(a) The overall factory pol balance which involves an estimate of the pol entering in cane, the percentage recovered and the losses sustained in mud, bagasse, molasses and waste water;

(b) The efficiency of the unit operation involved e.g. milling, evaporation, filtering, crystallisation, etc.;

(c) Chemical analysis required to ascertain (a) or (b).

To some extent there are known shortcomings in the method of chemical control presented below. Compromises are accepted in lieu of fundamental data e.g. pol is a substitute for sucrose, brix is used instead of total soluble solids and various other empirical formulas apply, the most noteworthy being for cane analysis. These are known and currently accepted by the industry and taken into consideration where necessary.

POL BALANCE

The weekly operation involves the processing of a certain tonnage of cane. This weight is accurately determined at the weighbridge and from an analysis of the first expressed juice an estimate is made of the pol in cane and hence the tonnes of pol entering the factory. An independent determination of fibre in cane is made. The c.c.s. content of cane for payment purposes is determined from the analyses for pol, brix and fibre.

The cane is crushed as it passes through the milling train and the juice thus extracted, diluted by added maceration water, is passed on to process.

Bagasse from the last mill passes as fuel to the boiler station and carries with it a quantity of the original pol entering the factory. From an analysis of the final bagasse combined with the fibre content in cane, the pol extraction by the milling process and the pol lost in bagasse are determined.

The other product streams are sugar, mud and molasses. Each of these should be measured and respective samples analysed for pol to achieve an accurate accounting of factory performance and pol lost in these streams.

Not all the pol entering in a given period leaves in the various products produced in that period. Some remains in process as a carry-over into the next period. Thus an accurate estimate of recoverable pol in stock at the beginning and end of the period is necessary. Stock measurement is an important aspect of factory control.

In arriving at a pol balance the following determinations and calculations are made:

$$\text{Tonnes pol in cane} = \text{tonnes cane} \times \frac{\text{pol \% cane}}{100}$$

$$\text{Pol \% cane} = \text{pol 1st exp. juice} \times \frac{100 - (F + 5)}{100}$$

where F is the fibre % cane

$$\text{\% pol loss in bagasse} = 100 - \text{pol extraction}$$

$$\text{\% pol loss in mud} = \frac{\text{tonnes mud} \times \text{pol \% mud}}{\text{tonnes pol in cane}}$$

$$\text{\% pol loss in molasses} = \frac{\left[\text{tonnes molasses} \times \left(\frac{\text{pol \% molasses}}{100}\right) \pm \text{stock difference}\right]}{\text{tonnes pol in cane}} \times 100$$

$$\text{\% pol in sugar (\% recovery)} = \frac{\left[\text{tonnes sugar} \times \left(\frac{\text{pol \% sugar}}{100}\right) \pm \text{stock difference}\right]}{\text{tonnes pol in cane}} \times 100$$

Undetermined loss—This is a residual calculated by difference (100 — recovery — other losses) and represents waste water losses plus other losses.

As mentioned the above pol balance depends on the empirical relationship between pol in first expressed juice and pol in cane.

A direct analysis of cane using the wet disintegrator method is an alternative technique for determining the pol in cane. Here again the accuracy of this system depends on the adequacy of sampling techniques plus strict adherence to good analytical techniques.

COEFFICIENT OF WORK

As stated in the definitions,

$$\text{Coefficient of work} = \frac{\text{tonnes 94 n.t. sugar}}{\text{tonnes c.c.s. in cane}} \times 100$$

Irrespective of its merits as a criterion of factory performance, the coefficient of work is the most important figure in mill control in Queensland since it relates the sugar made to the cane crushed in terms of the basis on which these commodities are bought and sold. Hence the figure has high significance financially. As a measure of factory performance the coefficient of work embodies the deficiencies of the c.c.s. and net titre formulas and must be accepted with caution.

As stated earlier, the c.c.s. formula postulates a standard loss of sucrose in process. Working to this standard, a mill treating 100 tonnes of c.c.s. would yield 100 tonnes of cane sugar, which would be equivalent to nearly 106.4 tonnes of 94 n.t. sugar. The coefficient of work would be nearly 106.4. This is sometimes regarded as the upper limit of the coefficient of work. The ideas that (1) the upper limit of coefficient of work is 100, and (2) the upper limit is about 106.4 are both erroneous. The upper limit is variable, but represents a performance in which *all* the sucrose in the cane is recovered as pure sugar. It would be much higher than 106.4.

CHEMICAL CONTROL—MILLING

Extraction

Extraction is of prime importance in monitoring the milling train performance.

It is defined as the quantity of pol removed by the milling plant compared to the original pol present i.e. pol extracted % original pol.

Extraction is calculated from the analysis of cane and bagasse as follows:

Suppose P_c = pol % cane
F_c = fibre % cane
P_b = pol % bagasse
B_b = brix % bagasse
W = moisture % bagasse
F_b = fibre % bagasse

Auxiliary formula

$$F_b = 100 - (B_b + W)$$

(Brix in bagasse can be estimated as pol % bagasse divided by purity ratio of last expressed juice, or directly by pycnometer or precision refractometer on wet disintegrator extract.)

$$\text{Bagasse \% cane} = 100 \times \frac{F_c}{F_b}$$

$$\text{Pol lost in bagasse/100 cane} = 100 \times \frac{F_c}{F_b} \times \frac{P_b}{100} = \frac{F_c}{F_b} \times P_b$$

$$\text{Pol extracted/100 cane} = P_c - \frac{F_c}{F_b} \times P_b$$

$$\text{Pol extracted \% pol in cane} = \frac{\left(P_c - \frac{F_c}{F_b} \times P_b\right) \times 100}{P_c} = \left(1 - \frac{F_c \times P_b}{F_b \times P_c}\right) \times 100$$

By assuming the same fibre is common to cane and bagasse the extraction concept may also be described as the pol/fibre ratio in cane minus pol/fibre ratio in bagasse compared with the original pol/fibre in cane.

$$\text{i.e.} \quad \text{Extraction} = \left[\frac{\frac{P_c}{F_c} - \frac{P_b}{F_b}}{\frac{P_c}{F_c}}\right] \times 100$$

$$= \left(1 - \frac{F_c \times P_b}{F_b \times P_c}\right) \times 100$$

Individual mill extraction

The extraction obtained by individual mills subsequent to No. 1 mill can also be calculated as a percentage of the pol in the bagasse from the previous mill in the following manner:

$$e_n = \left(\frac{E_n - E_{n-1}}{100 - E_{n-1}}\right) \times 100$$

where e_n = pol extraction at the nth mill expressed as a percentage of pol in the bagasse from the previous (n — 1) mill

E_n = pol extracted % pol in cane for n mills of the train

E_{n-1} = pol extracted % pol in cane for n—1 mills of the train.

For example—Consider the following list of pol extractions % pol in cane.

No. 1 mill—75.0 No. 3 mill—92.0

No. 2 mill—85.0 No. 4 mill—96.0

Then extraction by number three mill, expressed as a percentage of the pol in number two mill bagasse:

$$e_3 = \left(\frac{92.0 - 85.0}{100 - 85.0}\right) \times 100 = 46.7\%$$

The extraction obtained by each individual mill expressed as a percentage of the pol in the feed to the mill can be calculated by carrying out a materials balance over the milling train.

Reduced extraction

In the extraction formula it may be seen that, for constant values of pol in cane and pol and fibre in bagasse, the higher the fibre in cane, the lower the extraction. Accepting this as true in practice, the reduced extraction formula sets out to eliminate the effect of variations due to fibre % cane by 'reducing' this figure to a standard 12.5%.

The formula was derived by Deerr, who argued along the following lines:

If E is the actual extraction, and F_c the fibre % cane, then v the absolute juice % fibre in bagasse is given by the expression

$$v = \frac{(100 - E)(100 - F_c)}{F_c}$$

Solving for E

$$E = 100 - \frac{vF_c}{100 - F_c}$$

When $F_c = 12.5$ this reduces to

$$E_m = 100 - \frac{v}{7}$$

Where E_m = reduced extraction.

Substituting for v

$$E_m = 100 - \frac{(100 - E)(100 - F_c)}{7F_c}$$

In this formula the assumption that

$$v = \frac{(100 - E)(100 - F_j)}{F_c}$$

is open to criticism for it implies that the pol of the absolute juice is uniform throughout the cross-section of the cane stalk.

The main weakness of the formula is the implicit assumption that the higher the fibre content of the cane, the lower the extraction. If the higher fibred canes display improved response to milling and maceration the relationship may actually be reversed. The reduced extraction formula would then become even worse than pol extraction as a measure of milling efficiency.

Maceration

The quantity of maceration is logically considered as a percentage of fibre. *It is strongly recommended that the maceration water be weighed or measured, since this gives an accurate figure for the water used,* which moreover is immediately available as a guide to the correct regulation of the added water. The maceration water % fibre for any period is then readily calculated from the weight of water, weight of cane and average fibre in cane for the period.

The proportion of water added is often conveniently reported in terms of 'dilution', i.e. the portion of the maceration water which passes into the mixed juice. This may be expressed as a percentage of undiluted juice or as a percentage of fibre in cane.

Dilution % undiluted juice—This is calculated by a brix balance, since the added water introduces no solids and the quantity of brix in the diluted juice is identical with that in the undiluted juice.

Let 100 = weight of undiluted juice
B = brix of undiluted juice
b = brix of diluted juice
X = weight of maceration water in diluted juice
and 100 + X = weight of diluted juice (mixed or clarified juice).
Then 100 B = (100 + X)b
and $X = \frac{(B - b)}{b} \times 100$
= dilution % first expressed juice.
Similarly $\frac{(B - b)}{B} \times 100$ = dilution % mixed or clarified juice.

This figure is subject to significant error as an indication of maceration quantity, due to dilution from sources other than maceration e.g. filtrate, polyelectrolyte, hosing etc.

CHEMICAL CONTROL—CLARIFICATION

Clarified juice

The quantity of clarified juice % cane is a useful figure in some calculations and factory comparisons. It gives a combined effect of juice extraction, maceration, filter wash water, plus other dilution.

It is obtained by means of a pol balance as follows:

Tonnes pol in clarified juice = tonnes pol in cane
+ tonnes pol in syrup saccharate
— tonnes pol in bagasse
— tonnes pol in mud

Tonnes clarified juice $= \frac{\text{tonnes pol in clarified juice}}{\text{pol \% clarified juice}} \times 100$

and Clarified juice % cane $= \frac{\text{tonnes clarified juice}}{\text{tonnes cane}} \times 100$

CHEMICAL CONTROL—EFFETS

Water evaporated

It is often necessary to determine the quantity of water removed in the effets.

This is calculated as follows:

Let 100 = weight of original juice
b = brix of original juice
B = brix of final product
X = water evaporated, as percentage by weight of original juice.

Then $100\ b = (100 - X)B$

and $X = \frac{(B - b)}{B} \times 100$

Overall evaporation coefficient of effets

This estimate is required to check the efficiency of the heating surface in the effets and represents the weight of water in kilograms evaporated per hour per unit area of heating surface. It is calculated with the aid of the two preceding formulas as follows:

$$\frac{\text{tonnes clarified juice} \times 1000 \times X}{\text{heating surface in m}^2 \times \text{hours boiling} \times 100}$$

N.B. The calculation of heating surface area for effets or other vessels must be clearly defined if comparisons are to be made. The SAA code lays down:

'Evaporators, vacuum pans etc.—For evaporators, vacuum pans, heaters and other similar unfired vessels, the heating surface shall include the total area of tubes, including circulating tubes (if any), the tube plates excluding the area of the tube holes, and in the case of basket calandrias, the area of the shell.

For this purpose the area of the tubes shall be based on the external diameter of the tubes and their length between the outer surfaces of the tube plates. The net tube plate area shall be the total area of the tube plate, calculated on the external diameter of the calandria, minus the area of the tube holes. In the case of basket calandrias the upper tube plate, minus the tube holes, and the area of the steam inlet shall be measured, and also, in the basket type, the area of the shell shall be based on the outside diameter and the length between the outer surfaces of the tube plates. In the case of evaporators with coils, heating surface shall be based on the external diameter of the coil and the coil length between the inlet and tail pipe.'

CHEMICAL CONTROL—MUD FILTERS

Mud solids

The following analysis and calculations are of importance in assessing filter performance. An analysis of a composite sample of filter cake in conjunction with the weight of cake produced is necessary. The % moisture, % pol and % fibre are determined directly by actual cake analysis.

The juice purity in cake is assumed to be 80% so that % soluble solids is % pol divided by 0.80. As filter cake consists of fibre, moisture, mud solids and soluble solids, the % mud solids can be determined by difference.

Note: Soluble solids $= \frac{\text{pol \% cake}}{0.8}$

$= 1.25\ P$

Mud solids $= 100 - M - F - 1.25\ P$

The expected range of results is

Pol in filter cake (P)	0.5— 5.0%
Moisture in filter cake (M)	70 —80 %
Fibre in filter cake (F)	4 — 8 %
Mud solids in filter cake	8 —20 %

Water added at filter stage

Mills should possess accurate flow metering facilities to permit either potential wash water or total water quantities to be calculated. Potential wash water is that applied to the filter cake whilst total water includes wash water and dilution water which may result from the following sources.

(a) Transport water to assist gravity flow between the subsider and the mud mixer.

(b) Dilution water added to the mud tank or mud mixer.

(c) Filter flocculant dilution water.

Either wash water or total water should be expressed in terms of mud solids treated.

e.g. Wash water % mud solids $= \frac{\text{tonnes wash water used}}{\text{tonnes mud solids produced}} \times 100$

$$= \left(\frac{\text{tonnes wash water used}}{\text{tonnes filter cake produced} \times \frac{\text{mud solids \% cake}}{100}} \right) \times 100$$

Pol % mud solids

This is a useful index of filter performance. It can be derived from the analyses of filter cake.

Pol % mud solids $= \frac{\text{pol \% cake}}{\text{mud solids \% cake}} \times 100$

Mud solids % cane

Mud solids % cane enables the actual mud solids loading imposed on the filter station to be calculated.

$$\text{Mud solids \% cane} = \frac{\text{mud solids \% cake} \times \text{cake \% cane}}{100}$$

Fibre ratio in filter feed

This parameter affects both mud solids retention and cake permeability. It is calculated from the analysis of filter feed.

$$\text{Fibre ratio in filter feed} = \frac{\text{fibre \% filter feed}}{\text{mud solids \% filter feed}}$$

Mud solids retention

High accuracies are not required for this determination, the aim being to establish the operating range. Broadly, these ranges can be categorised as follows:

Low : 50%— 70%
Intermediate : 70%— 85%
High : 85%—100%

Thus retentions within 5% of the true value would generally be acceptable.

Three methods are presented.

(i) Fibre ratio method

This calculation is based on the assumption that all fibre (bagacillo) in filter feed is retained in the cake. The retention can be computed from the analysis of filter feed and cake.

$$\text{\% retention} = \frac{\text{fibre ratio in filter feed}}{\text{fibre ratio in cake}} \times 100$$

$$= \left(\frac{\text{fibre \% filter feed}}{\text{mud solids \% filter feed}} \times \frac{\text{mud solids \% cake}}{\text{fibre \% cake}}\right) \times 100$$

Whilst this method is fairly straightforward, involving analyses only, erroneous results viz. values greater than 100%, may occur if representative sampling is not performed.

(ii) Filtrate and cake measurement and analyses

Provided the pickup and wash filtrates are combined and the filtrate flow rate can be measured or estimated, the following calculation is applicable and will always yield a retention figure below 100%. Mud solids determinations are carried out on cake and filtrate.

$$\text{\% retention} = \left(\frac{\text{weight mud solids in cake}}{\text{weight mud solids in cake} + \text{weight mud solids in filtrate}}\right) \times 100$$

$$= \left(\frac{\text{cake weight} \times \text{mud solids \% cake}}{\text{cake weight} \times \text{mud solids \% cake} + \text{filtrate weight} \times \text{mud solids \% filtrate}}\right) \times 100$$

(iii) Analysis of filter feed and filtrate

If the filtrate flow cannot be measured or estimated, the following gives a reasonably accurate estimate of retention provided the pickup and wash filtrates are combined. It involves mud solids determinations on filter feed and filtrate. Also the brixes of the liquid in filter feed and filtrate are determined, after centrifuging to remove insoluble solids.

Retention is derived from the relation:

$$\text{\% retention} = \left(\frac{\text{weight mud solids in filter feed} - \text{weight mud solids in filtrate}}{\text{weight mud solids in filter feed}}\right) \times 100$$

Assuming the soluble solids in cake are negligible compared to soluble solids in filter feed, the above expression converts to:

$$\text{\% retention} = 100 - \left(\frac{\text{mud solids \% filtrate}}{\text{mud solids \% filter feed}} \times \frac{\text{brix filter feed}}{\text{brix filtrate}}\right) \times 100$$

CHEMICAL CONTROL—PAN STAGE

Massecuite composition

The control of pan stage operation is virtually based on control of massecuite purities and the number of strikes e.g. three strike formula with

A mass = 85
B mass = 75
C mass = 60

In order to determine the relative quantities of syrup and molasses required to produce a massecuite of a definite purity, the following formula gives a close approximation. It is based on the assumption that the brix values of both syrup and molasses are equal, an approximation which is usually experienced in practice, particularly when the quantities are measured in terms of the volumes of massecuite boiled on the respective materials.

Let p = purity of molasses
P = purity of syrup
M = purity of massecuite
x = percentage of strike derived from molasses
y = $100 - x$ = percentage of strike derived from syrup.

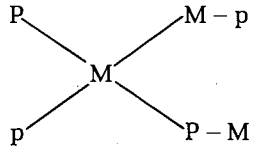
Assuming uniform brix

$$100\,M = xp + (100 - x)P$$

whence $$x = \left(\frac{P - M}{P - p}\right) \times 100$$

and $$y = 100 - x = \left(\frac{M - p}{P - p}\right) \times 100$$

These formulas can be applied to any mixture of materials of different purities, and the calculation is often conveniently carried out by using the 'cross' method as follows:



call this C.

call this D.

Then $$x = \frac{100\,D}{C + D}$$

$$y = \frac{100\,C}{C + D}$$

When it is desired to know the actual quantities of molasses and syrup necessary to give the strike, the following procedure should be followed:

Let B = brix of massecuite
b = brix of syrup and molasses
X = quantity of molasses used per 100 massecuite
Y = quantity of syrup used per 100 massecuite.

Then $$X = \frac{xB}{b} = \left(\frac{P - M}{P - p}\right) \times 100 \times \frac{B}{b}$$

and $$Y = \frac{(100 - x)B}{b} = \left(\frac{M - p}{P - p}\right) \times 100 \times \frac{B}{b}$$

Crystal content of massecuites

The crystal content of a massecuite may be calculated from the analyses of the massecuite and the mother liquor of the massecuite. For the purposes of deriving formulae for crystal content it is assumed that the 'crystal' consists of pure sucrose. The amount of crystalline material present may be expressed as crystal per 100 parts of massecuite. From material balances, formulae may be derived in terms of sucrose content, dry substance or true purity.

With sucrose content as the basis for calculation the formula is:

$$\text{Crystal content \% massecuite} = \left(\frac{\text{S mass} - \text{S mol}}{100 - \text{S mol}}\right) \times 100$$

where S mass is the sucrose content of the massecuite and S mol is the sucrose content of the mother liquor.

The expression involving dry substance will be of the same form, with dry substance in place of sucrose.

With purity as the basis of calculation the expressions for crystal content are:

$$\text{Crystal content \% massecuite} = \left(\frac{\text{P mass} - \text{P mol}}{100 - \text{P mol}}\right) \times \text{DS mass}$$

and $$\text{Crystal content \% total solids} = \left(\frac{\text{P mass} - \text{P mol}}{100 - \text{P mol}}\right) \times 100$$

where P mass and P mol are the purities of the massecuite and mother liquor respectively, and DS mass is the dry substance of the massecuite.

The crystal content per 100 parts total solids (dry substance) in the massecuite is a useful figure, particularly as it may be calculated using only purity figures, which are the most commonly available for pan products. The crystal contents set out in Table XIX are calculated by this formula.

Analogous formulae to those above also exist if the analyses are in terms of pol, brix and apparent purity.

There are then three formulae for calculating crystal content % massecuite from true analysis and a similar three formulae on the basis of apparent analysis. The question arises as to the order of the merit of the various formulae in practice. Sucrose and true purity provide the best basis of calculation; pol and apparent purity figures yield results sufficiently accurate for routine work; dry substance gives reasonably satisfactory results; brix gives unreliable results and should not be used to calculate crystal contents. *If the method of separation of the mother liquid from the massecuite involves any significant degree of concentration or dilution, crystal content calculations must be based on purity.*

Expected purity: final molasses

A formula derived statistically by the staff of Sugar Research Institute is designed to give a target purity which is the lowest purity of molasses which could normally be expected to be attained from the material being processed. The expected true purity is calculated from the reducing sugar to ash ratio of the molasses in the following manner:

$$\text{Expected purity} = 40.67 - 17.80 \log X$$

where X = reducing sugar/ash ratio

Molasses in stock

The estimation of molasses in stock follows simply from the calculation of recoverable pol, for:

Tonnes pol in molasses = tonnes pol in stock − tonnes recoverable pol.

The figure for pol in molasses thus derived may be used directly in the calculation of the pol balance. If it be desired to express the quantity as molasses, then

$$\text{Tonnes molasses} = \frac{\text{tonnes pol in balance}}{\text{pol \% molasses}} \times 100$$

Recovery formula

This section should be read in conjunction with estimate of stock. The main recovery formula currently in use to estimate the percentage of recoverable pol in syrup molasses or massecuites is the S.J.M. formula.

This is derived as follows:

Let 100 = weight of primary product
J = purity of primary product
P = pol of primary product
S = purity of sugar produced
M = purity of final molasses
X = recovery of pol % pol in primary product

$$\text{The pol in sugar} = \frac{XP}{100}$$

$$\text{Pol in final molasses} = P - \frac{XP}{100} = P\left(1 - \frac{X}{100}\right)$$

$$\text{Brix in original material} = \frac{P}{J} \times 100$$

$$\text{Brix in sugar} = \frac{XP}{100\,S} \times 100$$

$$\text{and Brix in final molasses} = \frac{P\left(1 - \frac{X}{100}\right)}{M} \times 100$$

$$\text{From brix balance} \quad \frac{P}{J} = \frac{XP}{100\,S} + \frac{P\left(1 - \frac{X}{100}\right)}{M}$$

$$\text{hence } \frac{1}{J} = \frac{X}{100\,S} + \frac{1}{M} - \frac{X}{100\,M}$$

$$\frac{X}{100}\left(\frac{1}{M} - \frac{1}{S}\right) = \frac{1}{M} - \frac{1}{J}$$

$$\frac{X}{100} \times \frac{S-M}{MS} = \frac{J-M}{JM}$$

$$\text{and} \quad X = \frac{S(J-M)}{J(S-M)} \times 100 \text{ (S.J.M. formula).}$$

Example

Given 130 tonnes of massecuite of brix 95 and pol 66.5—hence 70% purity, calculate the quantity of sugar recoverable.

S.J.M. formula—assuming 100 purity for sugar, and molasses purity of 35—

$$X = \frac{100(70-35)}{70(100-35)} \times 100 = 77\%$$

$$\text{and Recoverable sugar} = \frac{77}{100} \times \frac{130}{1} \times \frac{66.5}{100} = 66.6 \text{ tonnes.}$$

RECOVERABLE POL IN STOCK

Accuracy

Where it is normal to cease production at weekends for maintenance etc. the practice is to boil-off and reduce stock to a level at which the remaining material can be stored with safety. This means running down levels in clarifiers, and emptying the effets and certain pans.

The stock in process expressed as tonnes of recoverable pol will vary from one shut-down period to the next and it is the change in stock level which has to be ascertained determining the quantity of sugar made and estimated from the cane crushed in the period.

If an accuracy of 0.1% is required in the estimate of recovery the allowable error in a normal factory producing say 8000 tonnes sugar per week would be eight tonnes. Therefore a reasonably accurate estimate of stock is necessary.

Taking stock

All pans, tanks and other holding vessels should be calibrated in cubic metres so that the volume of stock can be readily recorded on the stock sheet.

Most factory chemists keep a well-documented list of vessels and their respective calibrations. This list is built up over time and each new vessel introduced to the factory should be calibrated and added to the list. The stock can be readily recorded by reference to the calibration marks or by dipping with a calibrated dip stick.

Once the stock is recorded as cubic metres of the various components it is necessary to convert this to tonnes of recoverable pol. The most convenient method is to convert each product volume to the tonnes of brix and pol and then find the total tonnes of brix and pol in stock. The average purity of the stock is the ratio of tonnes pol to tonnes brix. The recoverable pol is calculated by means of the S.J.M. formula using the purity so calculated for J and the current molasses purity for M.

The following is an example of the calculation of weights of brix and pol in a given tank.

Suppose there is a stock of 500 cubic metres of syrup. From the previous shift analysis the brix was 70, purity 90 and the temperature 45 °C.

Apparent brix at 45 °C (Table I) $= 70 - 2.08$

$\simeq 68$

Apparent density (Table XVI) $= 1.333\,71 \text{ tonnes.m}^{-3}$

Wt of syrup $= 500 \times 1.333\,71 = 667$ tonnes

Wt of brix $= 667 \times \frac{70}{100}$

$= 467$ tonnes

Wt of pol $= 467 \times \frac{90}{100}$

$= 420$ tonnes

Special cases

Special considerations should be given to determining the stock of sugar and final molasses.

With the trend to larger bulk sugar storage bins it is becoming increasingly difficult to estimate with any degree of accuracy the bin contents. Several alternatives are available. Sugar could be weighed prior to storage either with a Servo Balans type weigher or a belt weigher. The former is the more accurate. A belt weigher needs regular re-calibration. The third alternative is to mount the bin on load cells and read directly the weight of sugar in the bin. Sugar dispatched to bulk terminals is weighed accurately on reaching the terminal. The weekly sugar make is thus the sum of sugar dispatched (terminal receipts) plus the difference in bin stock at the beginning and end of the week.

Final molasses is usually aerated and the volume measured is an inaccurate estimate of the true volume. Molasses output can be measured by means of Servo Balans type weigher or the tank contents measured by means of a differential pressure cell. The dP cell will measure the force per unit area at the bottom of the tank and from the area of cross-section the total weight of molasses can be calculated. Alternatively the instrument could be calibrated to measure tonnes molasses directly.

CHAPTER XI

THE BOILER STATION

INTRODUCTION

The large quantity of steam required by the factory for electrical power generation, prime mover and heating purposes is supplied by the boiler station. Chemical energy stored in the bagasse is released during combustion in the furnace space and subsequently transferred by radiation and convection to the water circuit where steam is generated. In this way steam is a flexible medium for supplying energy and power wherever it may be required in the factory.

The efficiency of the boiler station is selected such that a balance exists between the factory energy requirements and the energy available in the bagasse. This balance minimises the need for supplementary fuels such as coal, wood or oil and eliminates the disposal of bagasse by cartage and dumping. Because of the variations in cane fibre content and factory operating practices, variable efficiency of the boiler station is generally required.

DESCRIPTION OF PLANT

Two basic types of boilers are utilised in the sugar industry:

(1) stepped-grate boilers which burn bagasse as a moving sloping bed and have no suspension firing, and

(2) suspension fired boilers in which bagasse is distributed pneumatically and burns in suspension.

Stepped-grate boilers were developed for bagasse combustion early this century and were the principal means of steam production for many years. They were limited in size to approximately 50 000 $kg.h^{-1}$ Since the 1960s, suspension fired boilers have been installed exclusively and currently range in size from 50 000 $kg.h^{-1}$ to 270 000 $kg.h^{-1}$. A limited number of stepped-grate boilers remain in operation. Larger unit capacity and economy of scale, operational flexibility and reduced maintenance costs were the principal reasons for the adoption of suspension firing as a standard.

Stepped-grate boilers and modern boilers utilising suspension firing of bagasse consist of four basic sections:

(a) furnace chamber,
(b) convection bank,
(c) heat recovery section,
(d) dust collection section.

The *furnace chamber* is physically the largest component of a boiler structure and complete combustion of the bagasse occurs in this section. Stepped-grate boilers have a brick/refractory furnace with no water-cooled heat transfer surfaces. In suspension fired designs the furnace chamber consists of four vertical walls, each wall constructed of a single row of metal tubes closely spaced and through which water circulates. A layer of refractory tiles is placed on the outside of the tube walls to minimise energy losses from the chamber. Air for combustion is supplied as a low velocity bulk flow (2 to 4 $m.s^{-1}$) through a horizontal grate which is located at the bottom of the furnace. The grate can be of the moving, dumping or water-cooled type and acts as a support bed for the combustion of large bagasse particles which do not remain in suspension. The largest ash particles (typically 15% of the total bagasse ash content) are collected on the grate and are discharged into a wet sluice hopper beneath the grate for subsequent disposal.

The supply of bagasse for combustion in suspension fired boilers is regulated by mechanical feeders which are controlled by the steam demand of the factory. The bagasse is fed to the furnace under gravity and is pneumatically distributed as a dispersed cloud in the lower region of the furnace chamber. In excess of 95% of the bagasse input is burnt in suspension remote from the grate. The combustion of bagasse involves the sequential processes of drying, volatile release and residual char burnout. Stability of the combustion process demands a balance between the amount of energy required to dry and heat the bagasse particles to ignition temperature and the amount of energy absorbed by the waterwalls of the furnace chamber. The size of the furnace chamber is thus restricted within certain limits for a given bagasse consumption rate.

Furnace size is also influenced by the requirement for a minimum residence time to ensure maximum burnout of the residual char. In general, greater than 98% of the chemical energy content of the bagasse is released in the furnace during combustion and 25 to 40% of this energy is absorbed by the furnace waterwalls depending on the boiler design. Radiation is the principal form of energy transfer in the furnace and less than 5%

of the total furnace absorption occurs by convection at the waterwall surfaces. The flue gas temperature leaving the furnace chamber varies from approximately 900 to 1050 °C. Combustion air is usually preheated to approximately 200 to 240 °C to improve ignition stability. Undergrate air temperatures are limited to less than 285 °C to prevent grate damage. A layer of refractory may be placed over the waterwall tubes in the lower region of the furnace above the grate to increase gas temperatures and improve bagasse drying, especially during periods of abnormally high bagasse moisture content when ignition stability deteriorates. Secondary air in the form of high velocity jets (typically 10% of the total combustion air) is injected into the furnace at a number of locations to enhance mixing and provide additional oxygen to remove unburnt combustible gases and reduce smoke emission.

The furnace chamber is operated at slightly less than atmospheric pressure under a balanced draft system. A single electric or turbine-driven forced draft fan supplies undergrate air, and secondary air is supplied by an independent high-pressure fan. One or two turbine-driven induced draft fans remove the combustion gases from the boiler and control the furnace chamber pressure at a predetermined level.

The *convection bank* section of a boiler receives the hot gases leaving the furnace chamber and transfers the gas sensible energy to the water-steam circuit, predominantly by convection. The convection bank consists of multiple rows of spaced tubes across which the hot flue gases pass. Two drums act as termination points for the multiple tube arrays. The lower, or mud drum, distributes preheated water to the furnace waterwalls and steam generating convection bank tube rows. The upper, or steam drum, receives steam/water mixtures from all of the furnace wall tubes and convection bank tubes by natural circulation. Water separation from the steam flow occurs in the steam drum by louvre or cyclone separators and the water is recycled to the mud drum through the convection bank downcomer tubes for redistribution. Steam from the steam drum may be discharged direct to the factory or undergo further heating (typically 50 to 100 °C superheat) in a superheater stage located upstream of the convection bank array in the flue gas pass.

Feedwater supply to the boiler occurs through the steam drum and is regulated to maintain the water level in the drum to within narrow limits. During normal operation the steam drum is approximately half full of water. Chemical injection, which is necessary for boiler water treatment, occurs in the steam drum or in the feedwater supply line to the steam drum.

The physical arrangement of the convection bank influences the design of the boiler support structure and two basic configurations of the convection bank have been developed. These are termed the 'baffleless' and 'baffled' boiler and typical designs are illustrated in Figure XI-1. The baffled convection bank is usually bottom supported and has wide tube spacing. The hot gas path is long and includes several sharp flow-directional changes. This design has given rise to high localised gas velocities and excessive tube erosion due to ash particle abrasion. The baffleless design was developed to overcome the problem of abnormal velocity distribution and high tube wear. The convection bank is roof supported and only a single gas pass occurs with no severe directional changes. Similar convection bank heating surface areas are maintained by the inclusion of additional tube rows and a reduction in tube spacing. To minimise tube wear, gas velocities are limited to 15 $m.s^{-1}$ in both boiler types. The baffleless boiler is more expensive due to the additional supporting structure required. Gas temperatures leaving the convection bank typically lie in the range 350 °C and 600 °C.

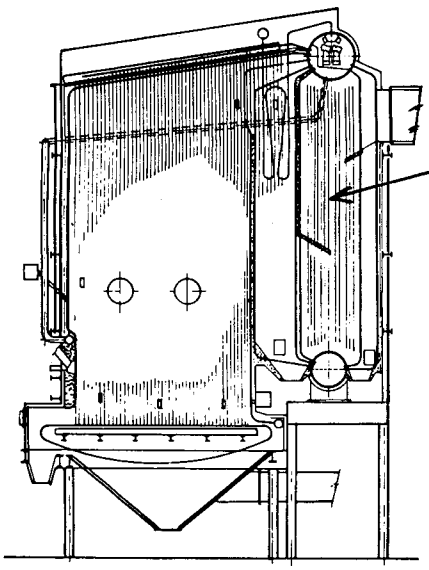


Fig. XI-1(a)—Baffled Boiler, (not to scale).

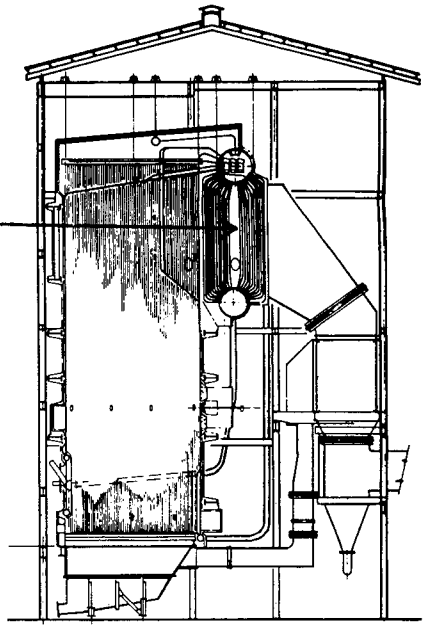


Fig. XI-1(b)—Baffleless Boiler, (not to scale).

The *heat recovery* section, which is downstream of the convection bank, transfers sensible energy by convection from the gas flow in accordance with the designed efficiency rating of the boiler. An airheater, and in some cases an economiser, may be included for heat recovery. The airheater consists of banks of tubes through which the hot flue gases flow. Combustion air flows across the tube banks in one or two passes. The size of an airheater is limited by the temperature of the inlet gas flow and the increasing capital cost associated with small increases in heat recovery. The economiser is usually installed upstream of the airheater to take advantage of the high gas temperature at the convection bank exit and thus minimise the size of the unit. The economiser consists of several rows of finned tubes in which the feedwater from the boiler feed pumps is preheated prior to entry into the steam drum. In general the size of the economiser is restricted so that steaming does not occur. The flue gas temperature at the exit of the heat recovery section determines the overall boiler efficiency and values range from 160 °C to over 300 °C.

Flue gas *dust collection* is necessary to minimise dust emission into the surrounding environment. Dust collection systems utilised include dry cyclones and swirl vane units, wetted louvres, water sprays and liquid film interception. Dry multicyclone types (cyclones 230 to 280 mm diameter, 1000 to 1500 mm high, rated from 15 to 30 $m^3 .min^{-1}$) operate with a pressure drop of 75 to 100 mm water and an efficiency of approximately 90 to 93%. The collected dust falls into a common hopper or sluice channel for disposal. Care must be exercised in the design to ensure that re-entrainment of the dust by leaks and poor air distribution does not occur. The very fine particles are the most difficult to collect. Negligible flue gas temperature decrease occurs across dry collectors.

Wet collectors function by contacting the flue gas with water, either as a reservoir, free-falling film or wetted surface. They are generally modular in design and have a high collection efficiency (99%). However, a significant water loss through evaporation (up to 15% of boiler rating) occurs in the collectors and they can be utilised to concentrate and reduce effluent discharge. The flue gas pressure drop is similar to that for dry collectors.

The principal disadvantage of wet collection is that the ducting, induced draft fans and stack are subject to corrosion where condensation occurs. Water circulation, ash separation and lime addition to control pH also increase the operational complexity of wet collectors.

Special consideration has to be given to the design of the induced draft fans to ensure satisfactory long term operation under the dust concentration and moisture conditions produced by the dust collection equipment.

High dust loadings in the gas flow to the boiler dust collectors are generally caused by carryover from the furnace chamber due to high boiler load, high excess air levels and poor combustion conditions.

Ash which has been collected from the furnace grate and the dust collectors is transported to a central location for dewatering and subsequent disposal. Where dry dust removal occurs, this material is carried by conveyor to a storage hopper for disposal.

BOILER EFFICIENCY VARIATION

The efficiency of the boiler station is generally variable so that the bagasse demand of the boilers is matched to the bagasse availability from the milling train. Several techniques have been developed for this purpose.

(a) Convection bank flue gas bypass—hot gas from the furnace chamber exit bypasses the convection bank and airheater through a damper-controlled bypass duct in which water quenching occurs to reduce the gas temperature to below the limit demanded by the induced draft fans. The bypass flow rejoins the main flow upstream of the dust collectors. Typical efficiency range 51 to 65%. This corresponds to an increase in bagasse consumption of from 61.9 $t.h^{-1}$ to 78.8 $t.h^{-1}$ for a nominal 150 $t.h^{-1}$ rated boiler.

(b) Economiser flue gas bypass—efficiency range 43 to 55%.

(c) Airheater air bypass—cold air is supplied direct to the furnace chamber. Airheater gas bypass is not practised as condensation can occur on the gas side surfaces of the tubes and severe metal corrosion results. Typical efficiency range 59 to 67%.

(d) Airheater hot air water quench—the hot air temperature is reduced by water sprays prior to entry into the furnace. Energy is lost from the boiler principally as latent heat of the additional water.

(e) Dump condenser—the efficiency of the boiler is not altered but bagasse consumption is increased by the generation of excess steam which is retrieved as condensate from an air-cooled steam condenser located on top of or adjacent to the boiler station. The steam capacity of a condenser can range from 30 to 70 tonnes steam per hour. For a 150 $t.h^{-1}$ boiler fitted with a 60 $t.h^{-1}$ steam condenser, bagasse consumption would be increased by 40% at full load.

The type of variable efficiency method adopted for a boiler station depends on the range of efficiency required and the high and low efficiency levels. The variation in cost between the different methods can be considerable. Techniques (a), (b) and (c) have been widely adopted in the industry. The use of dump condensers is increasing due to their simplicity of operation and the fact that they also increase the supply of clean boiler feedwater. Types (b) and (c) have been applied simultaneously.

BAGASSE AS A FUEL

Bagasse, the solid residue from the milling process, consists of lignocellulose, water, insoluble inorganic matter (ash) and water soluble material (brix). A typical analysis of bagasse is shown in Table I.

TABLE I
Analysis of bagasse

	Proximate (%)	Ultimate (%)
Ash	4.0	
Carbon		48.43
Hydrogen		5.83
Oxygen		45.40
Nitrogen		0.31
Sulfur		0.03
Volatiles	83.7	
Fixed carbon	12.3	
Gross calorific value	19 400 kJ.kg^{-1} dry ash free	
Moisture as fired	45 to 53%	
Brix as fired	2 to 4%	

During the combustion of a fuel the chemical energy inherent in the material structure is released in the form of heat. The quantity of heat produced per unit weight of fuel is termed the calorific value. Most fuels contain hydrogen which is converted to water in vapour form during combustion; furthermore, any water originally present in the fuel is also converted to vapour. This water vapour contains latent heat which can only be recovered if the vapour is condensed to the liquid form in the combustion device. The calorific value which includes the latent heat of vaporisation of the water vapour produced during combustion is called the gross calorific value (GCV). The heat released per unit weight of fuel, not including the latent heat of water vapour, is termed the net calorific value (NCV).

All boilers, whether fired by bagasse, coal, oil or gas, do not recover the latent heat of water vapour. However, it is usual practice to base all boiler calculations on gross calorific value. The GCV of dry ash-free bagasse has been found to be uniform and not vary significantly between cane varieties or growing districts.

The GCV (kJ.kg^{-1} bagasse) can be estimated by the equation:

$$GCV = 19\,574 - 38.177P - 195.74(W + A)^* \quad (1)$$

where P = % pol in bagasse
W = % water in bagasse
A = % ash in bagasse

The accuracy of the GCV determined by Equation (1) is better than 2%. In general, ash is determined as a percentage of dry fibre, in which case,

$$A = A'(1 - 0.01W) \quad (2)$$

and A' = % ash in dry fibre.

The GCV is very dependent on the water content of the bagasse and can therefore vary appreciably with the operating conditions of the milling train. When samples of bagasse are collected for analysis in relation to the boiler station, sampling should be carried out as close as possible to the boiler and preferably from the bagasse chute at the inlet of the bagasse feeders. It is possible for the moisture content to decrease by up to 2% during transit from the final mill to the boiler. Bagasse samples analysed for moisture content should be not less than 500 g to give acceptable accuracy of measurement.

Table II shows the quantities of air required for the combustion of unit mass of combustibles (C) and the mass of flue gas produced. The mass of combustibles per unit mass of bagasse is determined as:

$$C = 1 - \frac{W}{100} - \frac{A}{100} \quad (3)$$

The water/combustibles ratio $(\frac{W}{C})$ is a measure of the combustion quality of the bagasse. Bagasse with a $(\frac{W}{C})$ ratio of less than 0.9 is considered to be a good fuel and a $(\frac{W}{C})$ ratio of greater than 1.2 indicates a poor fuel.

* Based on Frew, R. & James, P. J. (1977) Combustion calculations for high ash content bagasse. Proc. Qd Soc. Sugar Cane Technol., 327-334.

TABLE II
Air and gas quantities for the combustion of one kilogram of combustibles

Gas	Quantity of gas with no excess air		Added quantity for each 10% excess air	
	Mass kg	Volume @ STP m^3	Mass kg	Vol. @ STP m^3
Flue gas				
Dry gas	6.316	4.493	0.593	0.459
H_20 (Note 1)	$0.617 + \frac{W}{C}$	$0.766 + 1.2416\frac{W}{C}$	0.006	0.007
Total (Note 2)	$6.933 + \frac{W}{C}$	$5.259 + 1.2416\frac{W}{C}$	0.599	0.466
Air required for combustion (dry)	5.933	4.591	0.593	0.459

Note 1: 0.617 kg of H_20 represents 0.558 kg of H_2O resulting from the chemical reaction of hydrogen in the fuel + 0.059 H_20 in combustion air.

Note 2: Total flue gas quantity equals combustibles in bagasse + H_20 in bagasse + air required for combustion + excess air.

Note 3: STP = standard temperature (O °C) and pressure (1 atm).

A number of supplementary fuels are often used during lightup and when fibre content is low. The mass equivalents of these fuels, listed below, are based on an equivalent bagasse containing 48% moisture, 2% pol, 3% ash and a GCV of 9510 kJ.kg^{-1}.

Wood—The GCV of wood depends mainly on its condition, i.e. how much moisture it contains. An average value is 20 500 kJ.kg^{-1} dry wood, so that for air-dried wood containing 10-20% moisture the mean GCV would be 17 425 kJ.kg^{-1}.

Fuel oil and diesel fuel—The average GCV of these fuels can be taken as 43 500 and 44 650 kJ.kg^{-1} respectively.

Coal—The GCV of coal varies considerably depending on the coal rank and ash and moisture contents. Bituminous coal is most readily available to sugar mills and the GCV is typically 26 000 kJ.kg^{-1}.

The supplementary fuels are calculated to equivalent bagasse from the following formulas. Corrections have been applied to take account of the increase in boiler efficiency when firing oil or coal in particular, due to the reduced moisture content of these fuels.

tonnes equivalent bagasse = 2.04 × tonnes wood
tonnes equivalent bagasse = 5.88 × tonnes fuel oil
tonnes equivalent bagasse = 3.45 × tonnes coal

BAGASSE AVAILABILITY

The calculation of the mass of bagasse available as fuel for the boiler station requires consideration of the crushing rate, cane fibre content, bagacillo offtake and fibre removal in the milling train. When the weight of insoluble solids removed is not measured, an approximate estimate of net bagasse available is given by:

$$E = \frac{0.95 \times Q \times F}{(100 - W - B)} \quad (4)$$

where E = bagasse rate t.h^{-1}
Q = crushing rate t.h^{-1}
F = % fibre in cane
W = % moisture in bagasse
B = % brix in bagasse.

In factories where bagacillo additions are minimal, the actual quantity of fibre in bagasse can be calculated from the insoluble solids in mixed juice by the relation:

$$E = \frac{(Q \times F - I \times J)}{(100 - W - B)} \quad (5)$$

where I = % suspended solids in mixed juice
J = mixed juice rate t.h^{-1}.

Where intermediate storage and recycling of bagasse occurs from the bagasse shed, allowance must be made for a change in the quantity of stored bagasse when estimating boiler consumption. The density of bagasse varies considerably and is affected by preparation, moisture and compaction. The density can range from 110 to 190 kg.m^{-3} and therefore it is difficult to estimate bagasse quantities accurately. It is suggested that such quantities may be determined with reasonable accuracy by volume measurement allowing a density of 160 kg.m^{-3} for piled bagasse.

BOILER EFFICIENCY DETERMINATION

It should be the aim in every factory to operate the boiler station at an efficiency which enables all steam requirements to be met by burning only the bagasse fuel which is available from the milling process. In the future the use of bagasse for by-product manufacture may mean that the boiler station will have to be operated at the highest possible efficiency such that the amount of surplus bagasse will be maximised. The boiler efficiency for any period of time may be stated as:

$$\frac{\text{kilogram of steam produced} \times \text{heat content per kilogram steam}}{\text{kilogram of bagasse used} \times \text{calorific value per kilogram bagasse}} \times 100$$

Direct method

Determination of the boiler efficiency by the direct method requires measurement of the quantities of steam produced and bagasse consumed during the period of the test, as well as the mean calorific value of the fuel. Boiler steam flow can be measured with high accuracy by an orifice plate device and suitably designed pipework. Likewise the unit heat content of the steam can be accurately determined by measurement of the temperature and pressure of the inlet feedwater and the temperature and pressure of the steam at boiler discharge. These parameters must remain quite steady during the period of a properly run test. Where a superheater is not installed, steam sampling with a throttling calorimeter will be necessary to determine the degree of steam dryness.

However, the accurate measurement of bagasse quantity and calorific value is very difficult. Special mechanical or nuclear belt weighers have to be installed, and in general two are necessary where bagasse recycling from storage occurs. The total bagasse consumption can thus be measured with reasonable accuracy. Another source of error in the direct method arises in the estimation of calorific value. Bagasse samples have to be taken from the conveyor belt at regular intervals during the test period. Non-uniform distribution and segregation occur on the belt during transport and also during stacking and reclaiming at storage. The greatest difficulty lies in preserving the bagasse moisture content during the sampling and intermediate storage and handling prior to sample analysis, as this variable alone has the largest influence on bagasse calorific value. For these reasons boiler efficiency determination by the indirect method has now become standard for all solid fuel boiler plant.

Indirect method

A certain proportion of the theoretical heat available from the bagasse fed into a furnace is used to generate steam while the remainder is absorbed by various losses. It is possible to calculate the major losses quite accurately without the need to weigh total quantities of bagasse and ash and dust. A reasonable estimate of the minor losses can be made from specific tests and results obtained in previous tests on boilers of a similar type. All losses are expressed as a percentage of the GCV of the bagasse, so that boiler efficiency = 100 − losses.

For a particular boiler the losses which are estimated will, under normal working conditions, remain constant while the losses which are calculated include those under the operator's control. The method gives an accurate guide as to how efficiently a boiler is operating. The limitation of the method remains the determination of the gross calorific value of the bagasse.

Major losses

(1) dry gas loss
(2) combustion moisture loss
(3) fuel moisture loss
(4) unburnt carbon loss

Minor losses

(1) moisture in air loss
(2) unburnt carbon monoxide loss
(3) external radiation and convection loss
(4) sensible energy loss in ash and dust

The measurement and calculation of the major and minor losses is set out in detail in B.S. 2885: "Code for acceptance tests for steam generating units." The losses of consequence in bagasse suspension boilers can be determined from the following equations. The concentration of carbon monoxide in the flue gas is assumed to be negligible (*<0.05%*).

Dry gas loss (%)

$$L_1 = 1.01 \frac{C}{GCV} (T - Ta)(6.316 + 0.0593\ S) \quad (6)$$

where

T = stack flue gas temperature (°C)
Ta = ambient temperature (°C)
S = % excess air.

The bagasse gross calorific value (GCV) and combustible content (C) are calculated from equations (1) and (3) respectively. The excess air level (S) is estimated by reference to Figure XI-2 for a measured flue gas oxygen content. Curves are shown for oxygen concentration based on wet and dry gas analysers.

Combustion moisture loss (%)

$$L_2 = 0.558 \frac{C}{GCV} (2476 + 2.01\ T - 4.195\ Ta) \quad (7)$$

Fuel moisture loss (%)

$$L_3 = \frac{W}{GCV} (2476 + 2.01\ T - 4.195\ Ta) \quad (8)$$

Unburnt carbon loss (%)

$$L = \frac{32\,790}{GCV} \left(\frac{R}{100 - R}\right) \frac{0.85\ A}{100} \quad (9)$$

where

R = % combustible in fly ash

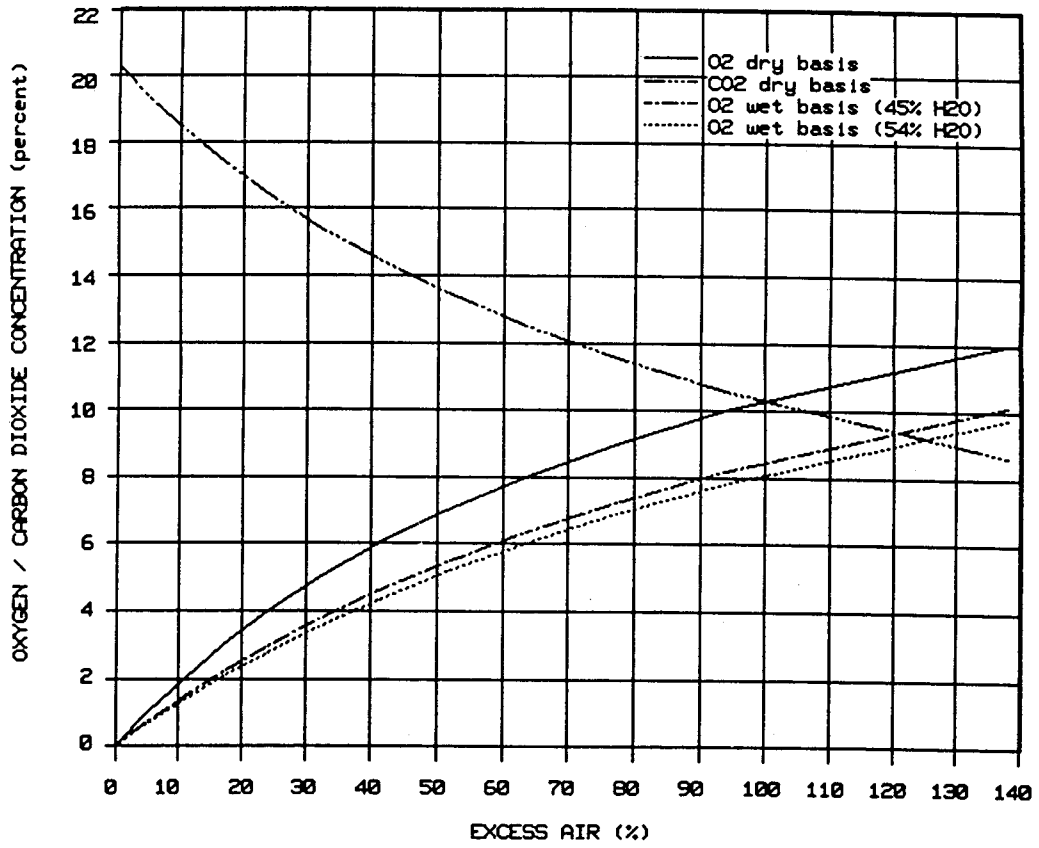


Fig. XI-2—Variation of flue gas oxygen and carbon dioxide conventration with excess air level for dry and wet gas analysis. Oxygen concentrations (wet) for two levels of bagasse moisture content are shown. O_2 (dry basis) curve applies with reasonable accuracy for wood, coal and oil firing.

Bagasse ash deposition in modern boilers occurs as grate ash and dust collector fly ash. The relative distribution of ash has been estimated as 15% to the grate hopper and 85% to the dust collectors, assuming negligible loss to stack emission. Numerous tests have shown that when a boiler is operated satisfactorily with no excessive bagasse deposition on the grate, the level of combustibles in grate ash is small and therefore only an analysis of dust collector ash need be considered in equation (9), with negligible loss of accuracy.

Moisture in air loss is small and can be taken as 0.22% for normal humidity and excess air levels. Radiation and convection losses from external surfaces have been estimated to vary between 0.3% for a 250 000 $kg.h^{-1}$ boiler and 0.42% for a 100 000 $kg.h^{-1}$ boiler. Unburnt carbon monoxide levels in modern suspension boilers have been measured at less than 0.02% during normal operation and the efficiency loss from this source is generally less than 0.09%. For carbon monoxide levels of 0.1% and 0.4% the efficiency loss is approximately 0.4% and 1.5% respectively. The sensible energy loss in the ash and dust is small and can be neglected.

Overall boiler efficiency is then determined as:

$$\eta = 100 - (L_1 + L_2 + L_3 + L_4 + 0.56) \quad (10)$$

FLY ASH EMISSION

The concentration of particulate matter (dust) in the boiler flue gas has to be reduced to the statutory level before discharge to atmosphere can take place. Typical emissions from bagasse suspension boilers are less than 500 $mg.m^{-3}$ but considerable variation occurs due to bagasse quality, boiler load and operating conditions.

The Clean Air Act of 1971-73 and its Regulations (1982) specify a maximum emission level of 800 $mg.m^{-3}$ for plant existing at the time of introduction of the Act and 690 $mg.m^{-3}$ for new plant. Thus a collector efficiency of typically 90% or higher would be required. The Act and Regulations also specify a minimum stack height of twice the maximum height of the surrounding buildings and an efflux velocity of greater than 15 $m.s^{-1}$. Smoke opacity is not to exceed scale 2 on the Ringlemann Chart except for small time periods as allowed in the Act. Both dry and wet collector systems are used to meet emission requirements.

Measurement of the flue gas dust concentration is carried out in the stack or at a suitable location in the ductwork where the flow distribution is reasonably uniform. Dust samples are taken from numerous positions in the duct and the sampling velocity is continuously adjusted so that it equals the local flue gas velocity (i.e. isokinetic sampling). In this way no bypassing of the sample probe by the smaller particles occurs.

BOILER WATER TREATMENT

The problems of boiler water treatment have become magnified in recent years with the advent of modern, water-walled, high capacity boilers in the industry. Such boilers are particularly prone to damage from overloading and inadequate water conditioning, and it is false economy to run the risk of ruining or damaging an investment worth millions of dollars for the sake of a small outlay on boiler feedwater treatment.

The sugar industry is fortunate in that more condensate is formed from the evaporative process than is usually required for feedwater in steam production. If sufficient storage is available and condensate quality is satisfactory, the mill becomes independent of raw water make-up quality, except in prolonged periods of unsettled milling. A storage capacity of four hours feedwater supply has generally been found adequate. Providing raw water usage is not excessive, an internal chemical treatment of feedwater is sufficient to prevent scale formation within the boiler.

There are a number of reputable commercial firms with long experience in this field, and, providing their recommendations are within the limits prescribed by British Standard 2486:1978, the advice of such firms can be profitably followed. The indiscriminate addition of boiler water additives whose composition is not specified by the manufacturer should, however, be avoided.

The objects of boiler water treatment are threefold, namely:

1. The prevention of scale on heating surfaces
2. The prevention of corrosion and caustic embrittlement
3. The production of clean steam free from entrained water or solids.

These criteria will now be discussed separately.

The prevention of scale on heating surfaces

The avoidance of scale on internal heating surfaces is most important, for, as well as reducing the efficiency of heat transfer to a boiler, heavy scale will cause overheating of the tube metal which, if sufficiently severe, can cause tube failure.

Scale is normally a hard adherent deposit on heating surfaces and is caused chiefly by the presence of substances in the water such as salts of calcium and magnesium and silicates.

There have also been a few deposits found in boiler feedwater tanks, boiler drums and feeders which contained appreciable percentages of iron, zinc or copper indicating that some corrosion must have taken place in the feed supply or condensate lines. These corrosion products can form particularly intractable scales on high heat transfer surfaces but are not normally a serious problem in the sugar industry.

The ideal answer to the problem is not to introduce water containing scale forming compounds in the boiler. This can be done by returning only clean condensed steam from heaters, pans and evaporators. This practice reduces the usage of raw water, i.e. untreated water from outside the steam-condensate cycle, as far as possible.

The use of clean condensate is the greatest single factor in the avoidance of boiler feed treatment pro-

blems. Where raw water make-up containing scale-forming constituents must be added, the water must be treated by distillation, external water treatment (softening or ion exchange), or by internal water treatment.

The installation of special process or continuous external water treatment systems is uneconomical under sugar industry conditions. It is much better to install condensate storage vessels with at least four hours feedwater capacity together with condensate conductivity monitoring and dumping facilities.

Sometimes a simple sodium base cation exchanger is used to lower the hardness of the occasional raw water make-up to acceptable levels. However, this does not treat the natural alkalinity and there may still be problems with the internal boiler water alkalinity control.

There are two main types of internal boiler water treatment practised in the Australian sugar industry: one based on the addition of caustic soda, phosphates and dispersants; and one based on the addition of a chelant and polymers. These affect solids dispersion, crystal formation and metal surface characteristics.

(a) Alkali-phosphate treatments

These entail the chemical treatment of the boiler water in such a manner that the scale-forming substances are not deposited on the heating surface as scale, but precipitated as a mobile sludge which flows to the lowest point in the boiler and is removed in the blowdown. This is usually achieved by adding phosphate to the boiler water and maintaining an excess of alkalinity, by the addition of caustic soda. Under the alkaline conditions prevailing, the phosphate precipitates any calcium present as calcium phosphate sludge. The caustic alkalinity precipitates magnesium salts as magnesium hydroxide, also a mobile sludge. Any silica present will normally be absorbed on the magnesium hydroxide precipitate and removed, or may co-precipitate with magnesium as magnesium silicate. Thus harmful concentrations of scale-forming compounds can be removed from the boiler in the blowdown, provided the correct concentrations of phosphate and alkalinity are maintained at all times.

The use of polymer dispersants is routine and most necessary to improve sludge characteristics and facilitate transport of solids from the boiler via the blowdown.

The majority of sugar mill boilers receive this type of treatment and the cleanliness of most boilers attests to its effectiveness. Any problems with the treatment can be directly attributed to excessive raw water make-up, contaminated return condensate or inefficient chemical treatment.

(b) Sequestering agent—polymer treatment

A sequestering agent is a compound which suppresses certain properties of a metal ion without removing it from the system. Thus, in boiler waters, the precipitation of hardness salts can be suppressed and the concentration of suspended soilids controlled to maintain cleaner water side internals.

Sequestering action in boiler water is usually achieved either by chelation or by the 'threshold effect'. Chelation controls precipitation by the formation of stable, soluble complexes between metal ions and organic compounds such as ethylene diamine tetraacetic acid (EDTA) or, more commonly, nitrilotriacetic acid (NTA). This form of treatment is not used now, not only because it is expensive but also because excessive concentrations of chelants may attack the steel of boiler internals. Threshold agents act as precipitation inhibitors by preventing the formation of stable crystal nuclei. Only very small amounts are needed to inhibit precipitation well beyond normal supersaturation levels, without evident precipitation or scaling. Polyphosphates, chemically modified lignins and synthetic polymers such as phosphonates and polyacrylates are all threshold inhibitors.

Sequestrants may be used with or without some phosphate treatment, the latter being mainly for protection against accidental introduction of hardness salts.

Sufficient caustic alkalinity is still required to precipitate excess magnesium, for pH and corrosion control, and also to solubilise silica entering the feedwater. Polymer dispersants are necessary in order to control the deposition of tramp-suspended solids, such as silt, iron oxide, etc. returning in the condensate to the feedwater. Chemically modified lignins and anionic carboxylates are generally used.

The sequesterant-polymer approach should only be selected if feedwater quality and chemical dosing and monitoring are of a consistently high standard, and alkali-phosphate treatment has proven unsatisfactory in the given circumstances.

The consumption of treatment chemicals depends on the quantity of scale-forming compounds fed to the boiler, the target concentrations of these chemicals and the rate of blowdown. Therefore to keep treatment costs low it is important that the maximum possible amount of clean condensate be returned to the boiler and the minimum of poor quality water added.

There is also the secondary reason for the avoidance of feed contamination by scale-forming materials. Both the scale-forming materials and their associated treatment chemicals increase the total dissolved and suspended solids in the boiler water. The blowdown rate must then be increased to maintain a safe solids level, as will be discussed in a subsequent section, and this results in some of the treatment chemicals being lost. Chemical costs can become excessive unless blowdown is minimised by the maximum use of good quality condensate.

The prevention of corrosion and caustic embrittlement

Corrosion

Corrosion in a boiler arises chiefly from two causes: acidity and oxygen.

Acidic conditions are corrosive to iron and steel, so that the material of a boiler will be eaten away if acid

conditions are allowed to prevail for any length of time. The control of this problem is a relatively simple one. The boiler water must be kept alkaline at all times. This is in conformity with the internal method for the prevention of scale, as discussed in the previous section, and the provision of the correct alkalinity serves a dual purpose.

The presence of dissolved oxygen in a boiler can cause very severe corrosion. Corrosion from this source, and sometimes from acids as well, normally occurs in the form of pits in the boiler shell or as wasting away at the tube ends. The fact that the corrosion is concentrated in small areas and not evenly distributed over the whole surface means that the effects are more severe. In extreme cases of pitting, the boiler drum may become holed by pits which extend right through the metal. The theory of corrosion caused by the presence of oxygen is complex, but the process is an electrochemical reaction. Due to stresses in a boiler shell, and to lack of complete uniformity of metal composition, under operating conditions certain areas of a boiler become anodes (oxidation) while others become cathodes (reduction). A current will pass between the anodic and the cathodic areas and this will cause the removal of metal from the anodic areas. The metal removed forms an hydroxide under the alkaline conditions in the boiler, but in order to proceed, the galvanic action requires oxygen. If oxygen is present the action can continue indefinitely and the anodic areas can be continually denuded of metal. The anodic areas, once established, remain localised, and severe corrosion occurs at these localised points, giving the typical pitting of oxygen corrosion.

Obviously the answer to this problem is to ensure that the boiler water contains no dissolved oxygen. The oxygen enters the boiler in the feedwater and so conditions in the feed should be maintained so that a minimum amount of dissolved oxygen is present. The solubility of oxygen in water depends upon temperature and pressure. The solubility decreases with temperature, at a given pressure, so that it is obviously advantageous to maintain the boiler feedwater at as high a temperature as possible. It is also essential to provide venting to the atmosphere in the feed system so that any oxygen or other gases released from condensate or raw water make-up can be expelled. The vent should release a certain amount of vapour, in order that no atmospheric oxygen can enter the system. Condensate collection vessels and feed tanks should be covered, except for the venting, and pump glands maintained in good order for the same reason. The need for a maximum of steam condensate return is paramount, and for the purposes of oxygen content the condensate should be as hot as possible.

In large boiler plants feed de-aerators are sometimes used to remove oxygen before feed entry into the boiler. These units consist essentially of a combination heater and flash tank in which the boiler feed is heated and flashed, to allow dissolved oxygen to be released and removed. The residual oxygen left in the feed after the de-aerator is treated inside the boiler.

Whether de-aerators are used or not it is standard practice to remove any residual oxygen with sodium sulfite. The reaction takes some time and in certain problem cases the more expensive catalysed sodium sulfite is added to remove the oxygen more quickly.

Hydrazine, a compound of nitrogen and hydrogen, N_2H_4, is used in high-pressure installations where dis solved solids are a problem, because both products of the reaction are inert, one being water and the other nitrogen. The latter goes out in the steam and is vented through the non-condensible gas vents.

The sodium sulfate formed from sodium sulfite is not scale forming and is beneficial from the point of view of embrittlement control, as will be seen later. Sulfite, if added in the correct manner and in such quantities as to keep a reserve in the boiler at all times, can completely remove all significant oxygen corrosion and, coupled with alkalinity control, should result in the complete avoidance of boiler corrosion. Once again, as with scale-forming materials, the feeding of oxygen to the boiler should be avoided since this causes increased dosage of chemicals, with consequent higher dissolved solids, greater blowdown and resultant chemical wastage.

Caustic embrittlement

This can only occur under the following conditions:

(a) The water in the boiler must contain free hydroxide alkalinity.

(b) The caustic soda must become concentrated to an extent which is usually only possible in a joint or seam where evaporative leakage can take place.

(c) The tensional stress in the steel must be high at the point where the concentration of caustic soda is occurring.

Although not a problem in modern stress-relieved boilers, in older boilers embrittlement is kept under control with chemical additives. In phosphate-treated waters it has been found that the sodium triphosphate in the boiler water inhibits this type of corrosion. Additional additives such as sodium nitrate, sodium sulfate and certain organic materials such as lignins and tannins have also been found effective in combating caustic embrittlement. A typical treatment for older boilers maintains the sodium sulfate/sodium hydroxide ratio above 2.5.

The production of clean steam free from entrained water or solids

The prevention of priming, or carryover, in boilers depends upon three main factors:

(a) The dissolved solids concentration in the water;

(b) The presence of foam producing solids;

(c) The degree and severity of load fluctuations.

The boiler water containing a high solids content is more prone to foam than one with a low solids water, and to this end, the solids content of a boiler water must be kept under control. This is achieved by means of blowdown. All feedwater will contain some dissolved solids, and obviously if steam free from entrained solids is being produced, the solids will concentrate in the boiler water. To counteract this, some of the boiler water is blown down out of the boiler and replaced by low

solids feed. The amount of blowdown necessary will thus obviously depend upon the solids content of the feedwater and the acceptable solids level in the boiler. Blowdown should be kept to a minimum, as stressed before, to avoid chemical losses, and therefore the solids content of the feedwater should be kept to a minimum.

Contamination of the steam with boiler water solids can also be caused by inefficient mechanical separation of boiler water from steam in the separating equipment and by priming due to sudden load changes. This is especially so at maximum steaming rates with high levels of impurities in the boiler water.

The main foam producing conditions are sugar in feedwater, excessive alkalinity and the presence of oil. The problem of sugar contamination will be discussed further in a later section. Excessive alkalinity can be avoided by chemical control and the incidence of oil should be kept to a minimum by eliminating oil contamination of the steam as far as possible. Some of the oil unavoidably fed to a boiler will be carried down with the alkali-phosphate precipitate, but the remaining oil globules can attach themselves to the heating surfaces of the boiler. If this occurs over a period, the heat transfer resistance at this point increases markedly and the tube may overheat and fail. Anti-foam chemicals, usually complex polyamides, polyoxides or silicones are introduced into the boiler to reduce the danger of foaming but should not be regarded as a cure-all for high oil levels or high dissolved solids.

Blowdown from a boiler also serves to remove the alkali phosphate precipitate, so that blowdown points are placed at the lowest levels in the boiler. These points are opened at intervals, the frequency and interval of opening depending upon the amount of blowdown required. In some of the modern boilers a continuous blowdown is installed as well, usually in the top drum, to effect continuous removal of some of the high solids water.

Sampling, methods of analysis and chemical dosage

There are many standards and manufacturer's recommendations on the limits for boiler water composition which are related to the pressure at which the unit operates. A number of British Standards are available on the subject of water treatment: B.S. 2486 'Treatment of water for land boilers', B.S. 1427 'Routine control methods of testing water used in industry', B.S. 1328 'Methods of sampling water used in industry' and B.S. 2690 'Methods of testing water used in industry'. Table III (adapted from B.S. 2486) shows the requirements for boiler water at the two pressure ranges encountered in the Australian sugar industry.

The sample for analysis is generally taken from the top drum and water-cooled in a coil type cooler.

The sampling container should be a closed vessel, for accuracy of sulfite analysis, and it is essential that the water from the sampling point should be allowed to run for a sufficient time before the sampling commences, to ensure that a representative sample is obtained.

TABLE III
Recommended water characteristics for water tube boilers

	Operating pressure (kPa)	
	2000	4000
Phosphate ($mg.L^{-1}$) as PO_4	30-60	17-40
Caustic alkalinity ($mg.L^{-1}$) as $CaCO_3$ min.	300	150
Total alkalinity ($mg.L^{-1}$) as $CaCO_3$ max.	700	500
Sodium sulfite ($mg.L^{-1}$) as Na_2SO_3	30-50	20-40
Suspended solids ($mg.L^{-1}$)	200	50
Dissolved solids ($mg.L^{-1}$)	3000	2000
Silica ($mg.L^{-1}$) as SiO_2, max.	Less than 0.4 of the caustic alkalinity	

For good control it is recommended that the boiler water samples should be analysed, at least once a day, for:

Alkalinity, caustic [$P(BaCl_2)$]
Phosphate,
Sulfite,
Hardness,
Total dissolved solids.

Where carryover problems occur it is also desirable to monitor suspended solids and oil and grease content. Each shift, simple pH and total dissolved solids measurement should be carried out on each boiler to detect any abnormal trends. If sulfate is used for caustic embrittlement control, the sulfate to caustic alkali ratio should be determined periodically.

Feedwaters should be analysed for pH each shift after start-up, for hardness every shift and for sugar contamination at least daily. Cleaning solutions used in effets on the weekend may contaminate the condensate system through calandria leaks. This results in either acid or very alkaline condensates and the pH will lie outside the range of 6.0 to 9.5 normally obtained with clean condensates.

Hardness measurements will indicate over-use of raw water make-up and give advance warning of potential control problems with the internal boiler water chemical treatment. Likewise, regular measurements of sugar contamination using the phenol-sulfuric acid colorimetric procedure give useful information for adjustments of the conductivity controlled condensate dumping system and confirm the presence of abnormal levels.

The methods of carrying out these analyses and the levels recommended in the boiler may vary slightly between treatment systems. Detailed procedures are given in Volume 2 of this manual. However, a few additional comments on water treatment are given below.

Alkalinity

The most useful type of measurement of alkalinity in boiler waters is that of 'free hydroxide' or caustic alkalinity. This is necessary to maintain the correct con-

ditions for precipitation of impurities, prevention of corrosion and to solubilise any silica entering with the feedwater.

Caustic alkalinity in boiler waters should only be determined by the phenolphthalein end-point after barium chloride precipitation of interferents. This titration is represented symbolically as $P(BaCl_2)$. (P represents the titration obtained without the precipitation.)

Boiler manufacturers and standards also usually specify a maximum limit for: 'total' alkalinity. It is normal practice in other industries to take this as the end-point obtained with methyl orange or a mixed indicator which changes colour at about pH 4.5. However, in sugar mill boiler waters, it has been found by examination of potentiometric titrations that there is no abrupt change or meaningful end-point about pH 4.5 due to the presence of a number of organic salts which affect the shape of the titration curve. Therefore, it is difficult to determine a useful estimate of total alkalinity.

One term, total sodium alkalinity, determined by the formula $2P - P(BaCl_2)$, may be a useful measurement, but does not take into account all alkalinity contributions from the organic salts.

If the caustic alkalinity is kept in the range recommended for the boiler then it can be taken that the total alkalinity will be under control. The exception to this rule arises from the heavy process contamination of feedwater. In this case organic salt concentrations produced by degradation of sugars in the boiler will necessitate high dosage of caustic soda which leads to excessive total alkalinity, but this situation will first be indicated by a loss of control of caustic alkalinity and a marked drop in pH to below a value of 10.0. Total dissolved solids will also rise steeply.

Phosphate

Excess phosphate is not harmful except that it adds solids to the water and increases chemical costs.

Sulfite

Sulfite addition controls the residual dissolved oxygen after mechanical de-aeration or in condensate from vacuum vessels after venting. Too much sulfite may lead to the formation of acidic gases which can accelerate corrosion. This particularly applies with low alkalinity, and higher steam pressures than those normally used in sugar mill boilers.

Most mills control dissolved oxygen satisfactorily by maintaining sulfite in the range of 50 to 150 $mg.L^{-1}$, as $Na\ SO_3$, as recommended by their consultants. British Standard 2486:1978 indicates that levels nearer 30 to 50 $mg.L^{-1}$ as Na_2SO_3, should be satisfactory, but they really only apply if the feedwater is consistently de-aerated or consists largely of oxygen-free condensate.

The addition of a catalyst with the sodium sulfite oxygen scavenger is an added cost but should be considered if feedwaters are not de-aerated and temperatures are low. The increased cost of the catalyst could be offset by the use of the lower recommended target levels since its faster rate of reaction with oxygen provides a greater safety margin.

Hardness

If the alkalinity level and phosphate level are correct, boiler water hardness will always be zero. A soap method is sufficiently accurate for this determination, and it is merely used as a double-check for phosphate and alkalinity. The simple EDTA complexometric titration for hardness is subject to interferences in boiler waters but is usually satisfactory for feedwaters. If an accurate determination of hardness is required in boiler waters there is a procedure set out in British Standard 2690:Part 4:1968.

Total dissolved solids

This is most conveniently determined on a routine basis by using a special type of hydrometer. This method should be checked periodically by a laboratory method involving the evaporation of a sample of water and weighing the residue. The limits for total dissolved solids vary, as stated before, depending on the load. The manufacturer's recommendations for total dissolved solids should be followed whether antifoam is used or not.

Conductivity methods for the measurement of total dissolved solids are used successfully in some industries. In a sugar mill, however, the results from a conductivity meter must be treated with caution as the relationship between conductivity and TDS will vary with differing composition of contaminants.

Filming amines

Some mills use filming amines to minimise corrosion in the steam and condensate lines. Corrosion products entering the boiler feedwater via the condensates form adherent deposits on heat transfer surfaces and reduction of this effect is important. The amine normally used is octadecylamine, in the soluble acetate form, which is dosed continuously into the boiler feedwater at about one ppm on steam rate. Once in the boiler it volatilises and travels into the steam systems. Here it can form a non-wettable organic film on metallic surfaces to prevent contact with corrosive gases and condensates.

Although of proven value in other industries, filming amines have not been proven to be economic in the sugar industry. Sugar mill condensate has a pH about 8.0 due to traces of ammonia from process. At this pH, steel corrosion rates are at a minimum. This fact probably explains why comparative tests, with and without amine treatment, have not shown significant differences in corrosion rate.

Polymer additives

Various naturally-derived organic substances such as starches, tannins and lignin derivatives as well as synthetic polyacrylates and organic phosphonates may be used to affect the crystal growth of the precipitating solids and to disperse or flocculate them so that a non-adherent sludge tends to be formed rather than an adherent deposit. Dispersants, antifoams and crystal growth modifiers are an important adjunct to the basic alkali phosphate or chelant treatment.

The cost of these additives can constitute up to 50% of the total chemical treatment costs and therefore their use should be closely controlled.

The amount of chemical required does not appear to bear any fixed relationship to the amount of suspended solids in the boiler water and usually must be established empirically. A compromise then must be made between costs and effectiveness.

Methods of chemical dosage

Chemicals can be added to a boiler continuously or in slug doses. In order to maintain chemical concentration at an even level, continuous dosing is used wherever possible. Thus caustic soda, sodium sulfite and antifoam (where used) are normally dosed continuously. If the sodium sulfite is not used with catalyst, all three chemicals can be mixed together and added continuously after the feed vent. If catalyst is used, the sulfite should be added, by a separate dosing pump, as early in the system as possible, and caustic added just before the feed enters the boiler. The quantities added are calculated from the analyses of the water and based on estimated demand. Sufficient chemicals for the next 24 hours are usually mixed in a predetermined quantity of water, and the dosing pump set to deliver this volume in the 24-hour period.

Phosphate should not be added continuously to the feed lines, as under these circumstances calcium phosphate can be precipitated in the lines, thus gradually blocking them. A high-pressure slug-dosing pump, with *individual connections* to each boiler, is normally recommended in order to add phosphate according to each boiler's demand. This pump is also conveniently used to add caustic or sulfite to individual boilers to maintain balanced concentrations between boilers, if they vary due to varying load or feed conditions. Slug dosage once in 24 hours is normally sufficient, but if this is not so, a pH and total dissolved solids check can be taken once a shift to decide whether anything abnormal has occurred, and further action taken if required.

Problems of boiler feed treatment peculiar to the sugar industry

There are problems of boiler feed treatment which are peculiar to the sugar industry. As well as having to contend with the usual contaminants, such as scale-forming compounds and oxygen, contamination of condensates by the material being processed may be caused by leaking heater tubes and other faults. This results in sugar entering the feedwater and, from the point of view of boiler feed treatment, this is most undesirable.

As well as causing an increase in dissolved solids, sucrose and reducing sugars, under the influence of heat, break down in solution to form a series of organic acids. It has been stressed, in the section under corrosion, that acid conditions are most corrosive to steel. Sugar contamination to any extent can result in very acid conditions in the boiler, and this will cause serious corrosion.

To counteract the acidity from the sugar degradation more caustic soda must be added to the boiler, resulting in further increased and sometimes dangerously high solids level in the boiler. This can cause carryover of water and solids. Cases of serious turbine trouble, due to carbon and other products building up on the turbine blades, are not unknown. The elimination of sugar contamination is therefore most important. To this end checks for sugar must be made regularly on the feedwater and, if sugar in any significant concentration is found, the source must be located by further testing.

The most serious contamination can be obtained from a split juice heater tube, as the juice in the heater is under pressure, and this can lead to gross contamination of condensates. Leaking effet and pan tubes can also cause serious trouble when the effets or pan concerned are shut down.

With the advent of chemical cleaning agents such as aluminium sulfate, additional care must be taken to ensure that the reagents do not leak into the condensate systems returning to the boiler feedwater on start-up. Aluminium salts are particularly undesirable as they quickly form adherent scale deposits on heat transfer surfaces, in a similar manner to iron salts.

Condensate quality should be checked for carbohydrate contamination with the aid of the phenol-sulfuric acid colorimetric test. Immediately after start-up it is also useful to measure pH in effet condensates to ensure that cleaning solutions have not leaked through cracked tubes. Normal condensates have pH values in the range 8.0 to 9.5.

It is desirable to monitor condensate sugar contamination continuously. Various instruments using chemical methods are available but are expensive, slow in reaction and rather tedious to maintain.

Sugar contamination in a raw sugar factory is always in the form of impure solutions which carry other materials besides sugar. Many of these impurities are electrolytes; that is, they are ionised in solution, and are conductors of electric current. Thus the conductivity of a condensate can be a guide to its sugar content. Any significant contamination can be detected in this way, and the method can be used in conjunction with a multipoint conductivity recorder, which can monitor every source of boiler feed in rapid succession, and operate automatic valves to divert any contaminated condensate away from boiler feed.

If boiler water conditions are maintained correctly at all times, the incidence of corrosion should be negligible and the cleaning of boiler tubes completely avoided.

Blowdown requirements

The quantity of solids accumulated in the boiler water from the feed and chemical treatment is reduced by blowdown. This can be carried out on a continuous basis or intermittently (e.g. once per shift). Blowdown is taken from the steam or mud drum, or from the drum downcomer drains. Blowdown is not normally taken from the waterwall bottom header drains while the boiler is on load as water starvation and tube distortion can occur. A decrease of 25 mm in the steam drum water level is usually adequate for one blowdown.

Continuous blowdown is often employed and this occurs from the region of the water/steam separators in

the steam drum where the concentration of solids in the boiler water is greatest. The blowdown rate required is determined from the following relationship:

$$X = \frac{F \times Y}{Z} \quad (11)$$

where X = blowdown rate $t.h^{-1}$
F = feedwater rate $t.h^{-1}$
Y = ppm TDS of feedwater
Z = ppm TDS of boiler water permitted.

STEAM USE

In a sugar mill the energy required for juice heating and boiling is normally greater than the energy consumed in providing factory power, and consequently it is the low-pressure steam consumption which determines boiler requirements. Steam usage should be such that the demand of the process side exceeds that of the high-pressure side by an amount to cover fluctuations in steam flow as a result of batch operations at the pan stage. The difference is supplied from the high-pressure system by a make-up valve and is usually 10% to 20% of process requirements.

The approximate energy requirements per tonne of cane to provide power for a typical raw sugar factory are indicated in Table IV.

TABLE IV
Typical energy requirements at major work stations

Function	Energy per tonne of cane ($kW.h.t^{-1}$)
Shredding	4-8
Milling	4-8
Electricity generation	10-16
Boiler auxiliaries	2-4

To convert these to steam flow requirements, the following formula is applied to those units driven by steam engines or turbines.

$$SF = 360\ CR \times P/\Delta H\eta \quad (12)$$

Where SF = $t.h^{-1}$ steam flow
CR = $t.h^{-1}$ crushing rate
P = energy requirement per tonne of cane (Table IV)
ΔH = $kJ.kg^{-1}$ enthalpy drop from high-pressure side to low-pressure side
η = % turbine efficiency.

Where turbine steam consumption is to be calculated, the appropriate turbine efficiency should be determined from the manufacturer's curves. In the absence of such data, some estimates for the approximate efficiency ranges of the prime movers commonly encountered in a raw sugar factory are given in Table V. Milling train turbines generally operate off their design speed and their efficiencies have been acordingly discounted.

TABLE V
Efficiencies of prime movers in their principal applications

Function	Prime mover type (turbines)	Overall efficiency range (%)
Shredding	Compound impulse, Combination impulse-reaction	50-70
Milling	Simple impulse, Compound impulse	30-50
Electricity generation	Reaction, Combination impulse-reaction	50-70
Boiler auxiliaries	Simple impulse, Compound impulse	30-40

The low-pressure steam requirements can be approximately calculated in the following manner:

Juice heating

$$S1 = J \times Cp_j \times \Delta T/L_{S1} \quad (13)$$

where $S1$ = $t.h^{-1}$ of steam or vapour requirement
J = $t.h^{-1}$ juice flow
Cp_j = $kJ.kg^{-1}.K^{-1}$ specific heat of juice (typically 3.89 $kJ.kg^{-1}.K^{-1}$)
ΔT = °C temperature rise in juice
L_{S1} = $kJ.kg^{-1}$ latent heat of steam or vapour.

As a first approximation, the following formulas can be applied:

Primary heater requirement

$$S1' = 0.088 \times J\ t.h^{-1} \quad (14)$$

Secondary heater requirement

$$S1'' = 0.058 \times J\ t.h^{-1} \quad (15)$$

Total juice heating requirement

$$S1 = S1' + S1'' = 0.146\ J\ t.h^{-1} \quad (16)$$

Preheating

Preheat is the steam required to raise the juice from effet supply juice (ESJ) temperature to the temperature of the number 1 vessel.

$$S2 = J \times Cp_j \times (T1 - T_J) / L_{S1}\ t.h^{-1} \quad (17)$$

where $S2$ = $t.h^{-1}$ of steam
Cp_j = $kJ.kg^{-1}.K^{-1}$ specific heat of juice (typically 3.89 $kJ.kg^{-1}.K^{-1}$)
$T1$ = °C temperature of number 1 evaporator vessel
T_J = °C temperature of ESJ.

Preheating may be carried out by a preheater, pre-evaporator, or within the number 1 evaporator vessel itself.

Evaporation

The total water to be evaporated from juice (E $t.h^{-1}$) is given by the following relationship:

$$E = J \times (B - b) / B \; t.h^{-1} \quad (18)$$

where B = syrup brix
b = ESJ brix.

The steam consumption is then determined from the following relationship:

$$S3 = S2 + E/n + (V_{PE} + V_1) \times (n-1)/n + V_2 \times (n-2)/n \; t.h^{-1} \quad (19)$$

where
n = the number of evaporating vessels (excluding the pre-evaporator)
V_{PE} = $t.h^{-1}$ of vapour bled from the pre-evaporator
V_1 = $t.h^{-1}$ of vapour bled from the number 1 evaporator(s)
V_2 = $t.h^{-1}$ of vapour bled from the number 2 evaporator(s).

Pan stage

Pan stage steam and/or vapour consumption may be approximated by the following relationship:

$$S4 = 0.65 \times (J - E) \; t.h^{-1} \quad (20)$$

The value quoted for pan stage use is a first estimate. There are many variables affecting pan stage use: type of pan (coil, calandria, high grade, low grade, continuous), pan stage practice with respect to wash and movement water and use of vapour. Pan stage practice can significantly affect steam economy. For this reason, where condensates are returned to a central collecting tank before pumping to the condensate tank, flow measurement in this pump line can be useful in providing an estimate of pan stage consumption. If corrected for vapour use, low-pressure steam consumption may be determined.

The *total* low-pressure steam consumption is then given by the sum $S_1 + S_3 + S_4$—vapour bled to heaters and pans. It is usual to increase this total by about 5% to allow for steam losses, centrifugal steam, and some water heating.

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