Determination of Solid Fat Index of Fats and Oils Using the Anton Paar Density Meter

B.L. MILLS[1] and **F.R. van de VOORT**, Department of Food Sceince, University of Guelph, Guelph, Ontario, Canada

ABSTRACT

The Anton Paar Density Meter was investigated for its potential use in the determination of Solid Fat Index (SFI) of fats and oils. By deriving equations for the behavior of instrument constants as a function of temperature, the specific volume of a fat could be determined as it underwent heating at a controlled rate of 2 C/min. The specific volume data obtained as a function of temperature could be converted into SFI data by minor modifications to the AOCS dilatometry equations, and hence provide a smooth SFI curve for fats and oils. The method was capable of providing more detailed dilation data in a shorter period of time and the SFI values determined related well to the conventional dilatometric technique.

INTRODUCTION

The determination of solids content in fats is essential in establishing parameters for process control and formulation in the fats and oils industry. Dilation is the basis of the most widely used method for determination of the solid content of fats. The American Oil Chemists' Society (AOCS) dilatometric Solid Fat Index (SFI) determination is a tedious and a time-consuming technique, but it does give reproducible results and works well, considering its empirical nature. A number of methods, e.g., nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and ultracentrifugation have been used over the years in an attempt to simplify measurement of solid fat content, but of these, dilatometry remains the most generally accepted technique. Because dilatometric measurements are based on specific volume, the inverse of density, it would appear that an instrument which provides rapid and accurate density measurements could be used for SFI determinations.

A major advance in density measurements has been made with the introduction of the Anton Paar Density Meter which, in contrast to pycnometry, the Westphal balance and hydrometry, makes density-related measurements simple and accurate. In this work, the density meter has been investigated as a potential alternative to the standard dilatometric method for fat characterization.

THEORY

The electronic density meter, manufactured by Anton Paar (Graz, Austria), was first described in 1969 by Kratky et al. (1). The measurement of density is based on the change in the natural frequency of a hollow oscillator when filled with liquids of different mass. The oscillator cell is a U-shaped borosilicate glass tube which is electronically excited and oscillates in an undamped harmonic fashion within the elastic range of the glass. The natural frequency of this system can be expressed as:

$$f = 1/2\pi [c/(m + \rho v)]^{1/2} \quad [I]$$

where f = the frequency of the oscillator; c = the coefficient of elasticity; m = the mass of the oscillator; ρ = the density of the sample; v = the volume of the hollow oscillator.

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The inverse of the frequency is the period (T) and the equation reformulated on this basis becomes:

$$T = 2\pi [(m + \rho v)/c]^{1/2} \quad [II]$$

Rearrangement of Equation II yields the following expression for the density at a specific temperature:

$$\rho(t) = (T^2 - B)/A \quad [III]$$

Equation III is the fundamental relation used to calculate density. Because A contains the volume of the oscillator (v), and B, the mass of the oscillator (m), and both A and B contain the coefficient of elasticity (c), these terms can be considered to be instrument constants at a given temperature (t). By substitution and the use of simultaneous equations, Equations IV and V can be derived using tabulated density values for air (ρ_1) and water (ρ_2):

$$A(t) = (T_2^2 - T_1^2)/(\rho_2 - \rho_1) \quad [IV]$$

$$B(t) = T_2^2 - A\rho_2 \quad [V]$$

Once the constants have been determined and the period measured at a specific temperature, the density can be calculated using Equation III.

MATERIALS AND METHODS

Density Meter

Apparatus. A DMA 40 digital density meter was used in this study. This model consists basically of a measuring cell, built-in air pump and digital readout which displays the period (T) of oscillation. (Models are available which display density directly, but were of no advantage for this investigation.) The oscillator tube is mounted in the center of a double-walled glass cylinder and the space between the sample tube and the inner wall of the cylinder is filled with hydrogen gas (Fig. 1). Hydrogen gas is used as a medium of high thermal conductivity and permits thermal equilibrium to be obtained in the shortest possible time. A thermostated liquid is circulated between the outer and inner wall of the glass cylinder by a Haake Model F2 circulating bath. For this work, a Haake PG 10 temperature programmer was coupled to the circulating bath to permit heating of the sample at a controlled rate. The cooling capa-
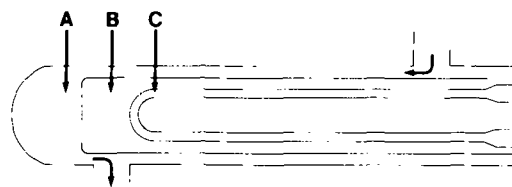

FIG. 1. Cross section of the entire measuring cell, showing the circulation jacket (A), the hydrogen gas envelope (B) and the oscillator tube (C).

city of the circulator was supplemented by an alcohol/Dry Ice bath, which allowed rapid cooling of the system between runs.

In order to calibrate the PG 10 programmer, the temperature of the sample and of the circulating bath was monitored by copper-constantan thermocouples. The signal from the thermocouples was sent to a dual pen stripchart recorder calibrated to read temperature (C) directly. The recorder allowed visual presentation of time and temperature and was used to check linearity and the actual heating rate of the programmer. After programmer calibration, sample temperature was monitored using a thermistor-based digital thermometer, the probe of which was inserted into the cell entrance.

The entire apparatus, i.e., cooling bath, density meter, programmer and stripchart recorder is shown in Fig. 2. Horizontal positioning of the density meter is not necessary to ensure accuracy, and for practical purposes, the instrument can be placed on its side for filling and measurement.

Determination of instrument constants. Before any density measurements can be made, the instrument constants A and B have to be determined. Both constants are temperature-dependent and, according to the original design of the instrument, have to be determined for each temperature at which measurements are to be made. For this work, it was imperative that the constants be evaluated as a function of temperature. This procedure involved the measurement of the period of water and air in stepwise temperature increments. The period of distilled deionized water was measured first; the water was removed by rinsing the cell with absolute ethanol followed by evaporation with a stream of dry air. The period of dry air was then measured and the entire procedure repeated many times over the range of 2-74 C.

The constants A and B were calculated using Equations IV and V with the density values of water being taken from Critical Tables (2) and the density of air calculated (3) using the following equation:

$$\rho = (P/760)[0.001293/(1 + 0.003670)t] \qquad [VI]$$

where: P = the barometric pressure; t = temperature.

Although Equation VI indicates barometric pressure to be a variable, a constant value of 760 mm Hg was used, since the density differences in the normal range of atmospheric pressures are outside the range of detection by the DMA 40.

Sample measurement. The sample under investigation was heated to 80 C and dearated for a minimum of 5 min. The molten fat was injected into the tube using a plastic-tipped, disposable syringe until the sample overflowed. Overfilling does not affect the measurements and provides a reservoir for the expansion and contraction of the fat as the temperature of the cell changes. For density measurements, the temperature was lowered to 0 C and programmed to increase at 2 C/min to 70 C, and the period was recorded every minute. After the measurements were made, the fat sample was removed using petroleum ether, followed by rinsing with absolute ethanol and air drying.

Dilatometry

The fat samples were deaerated in the same manner as described for density measurements. Pyrex dilatometers constructed in accordance with specifications given in the *AOCS Official Methods* were used (4). However, hollow dilatometer stoppers of the type described by Teasdale and Svardal (5) were substituted. This stopper design increases
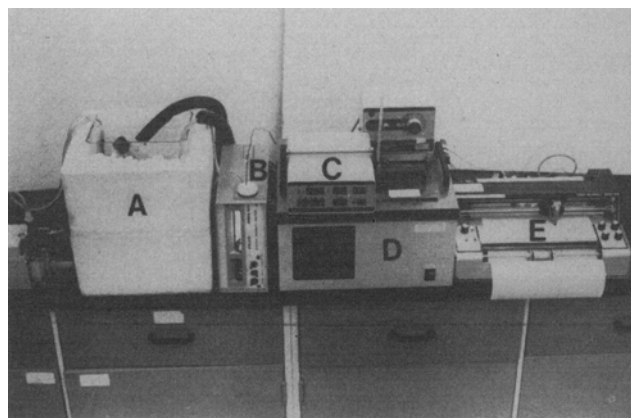
the dilatometer surface area, thus reducing the time required to obtain temperature equilibrium. Two ml of potassium dichromate indicator solution was overlaid with molten sample, the dilatometer rinsed with petroleum ether and reweighed. The dilatometer was immersed successively in constant temperature baths and the general procedure outlined by the official AOCS method was followed (i.e., conditioning at 0 C for 15 min. before and after tempering at 26.7 C for 30 min. Volume readings were recorded at fixed temperature intervals after allowing 30 min for temperature equilibration.

The results of dilatometry are expressed as Solid Fat Index (SFI) and were calculated by the official AOCS method (4). The SFI was calculated from the change in specific volumes (vol. at 60 C minus the vol. at t C, divided by the weight) for various temperatures. Although the term "Solid Fat Index" implies solids content, it refers, in fact, to a volume change.

The SFI is often expressed as percent solids based on the assumption that the melting dilation observed due to a complete change of phase is 0.1 ml/g (6). Two other assumptions commonly made in the SFI calculation are: (a) that the thermal expansion of the fat in the solid state is equal to the thermal expansion of the fat in the liquid state, and (b) that the thermal expansion for different fats is constant. The thermal expansion value (TE) for most commercial fats generally lies in the range of 0.00081 to 0.00086 ml/g/C and determination of the actual slope of the liquid line is generally avoided by using an average value of 0.00084 ml/g/C. Due to these and other assumptions (6), the term "index" is appropriate, and the value should only be used as an indicator of the solids content, keeping in mind that it really represents dilation in ml/kg.

Attempts were made to use calculated slope values rather than using a constant TE value when calculating SFI. In the case of density meter data, the slope was obtained by linear regression of specific volume vs temperature data in the liquid line portion of the dilation curve, whereas in the case of dilatometry, the slope was obtained from only two points as recommended in the official method. In both cases, the slopes for a typical fat (e.g., margarine) fell into the prescribed range of slope values (0.00081-0.00086) but were quite variable, leading to significant differences in the SFI values between replicates. These results put into effect the less elegant, but more practical approach of using a single average slope, i.e., 0.00084 ml/g/C, for SFI calculations.

RESULTS

Calibration Curves

The experimentally determined A and B constants are presented graphically as a function of temperature in Figure 3. Both functions are quite smooth and show slight curvilinearity. Linear regression provides a reasonable approximation of the constants, and a linear equation could be used. However, a better fit to the data can be obtained with multiple regression using a cubic function. The best fit equations derived for the constants were:

$$A = 9.135 - 9.142E\text{-}4t - 1.722E\text{-}5t^2 + 1.788E\text{-}7t^3 \qquad [VII]$$

$$B = 11.264 - 1.717E\text{-}3t + 2.529E\text{-}6t^2 + 2.791E\text{-}8t^3 \qquad [VIII]$$

The correlation coefficients for Equations VII and VIII were 0.9994 and 0.9998, respectively, whereas the linear regression correlation coefficients were 0.9973 and 0.9961. Equations VII and VIII provide estimates of the instrument constants as a function of temperature, and in conjunction with the period of the sample, allow the density and its reciprocal, the specific volume, to be calculated. A program was written for a Texas Instruments (TI-59) programmable calculator to solve these equations.

In order to verify the regression equations for actual density determinations, the period of water was measured as a function of temperature. The density was calculated using the derived constants and the results compared with values tabulated in the Critical Tables (2). Using the absolute difference between calculated and tabulated values, the mean difference and standard deviation of the difference was found to be 0.00042 and 0.00057 g/cc, respectively. Because the values obtained with the density meter compared well with those published, it was concluded that the estimated constants were adequate.

Density Meter vs Dilatometry

In dilatometry, the change in volume is determined in a stepwise manner, allowing the fat to come to thermal equilibrium for 30 min at each temperature. In the density meter, a dynamic approach was attempted to save time and obtain more data. No significant difference was observed between the specific volume curves obtained when the density meter was first run in the static stepwise manner and then run in the dynamic programmed way (<2 C/min). Rapid heat transfer is possible in the density meter due to the small sample size (0.7 ml) and relatively large surface
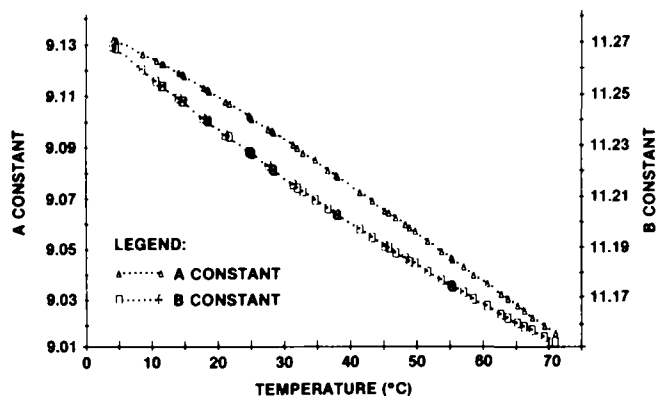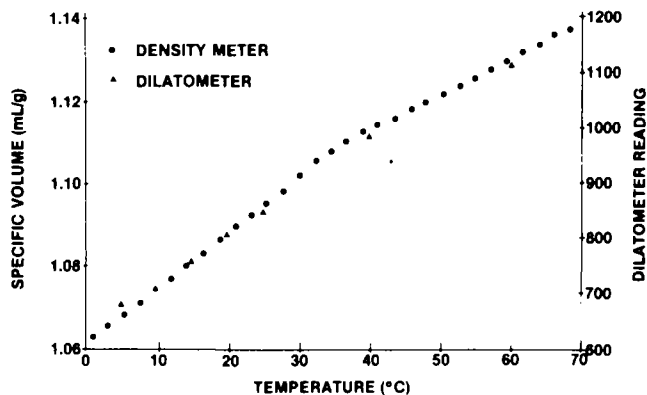
FIG. 4. A comparative plot of dilation as a function temperature measured by the density meter and the dilatometer.

area of the oscillator tube.

Some insight into the relationship between the dilatometric and the density meter methods may be gained from comparing melting dilation curves (Fig. 4). One can appreciate the advantage of the density meter over dilatometry; in contrast to the density meter curve, it is difficult to properly define the shape of the dilatometric curve. For a valid appraisal of a fat's behavior, including polymorphic effects, it is desirable to have a well-defined curve such as that available from the density meter.

Confidence in dilatometry over the years stems from its ability to provide reproducible results, hence, reproducibility is an important criterion in evaluating the reliability of this new approach. Figure 5 shows the means and standard deviations for three replicate experiments on two fats performed on separate occasions using the density meter. The plots show that high precision is possible when using the density meter for characterization of fats.

The data obtained with the density meter can be used to calculate the SFI according to the AOCS equations in the same way as the data obtained by dilatometry. The volume correction, however, is not included, because it is accounted for by the instrument constants. Figure 6 presents the SFI values determined for margarine using the density meter, compared with the three-point SFI determination used by industry.

DISCUSSION

Dilatometry has been used as an analytical tool by some margarine manufacturing establishments since the early

FIG. 3. A plot of the A and B instrument constants as a function of temperature.
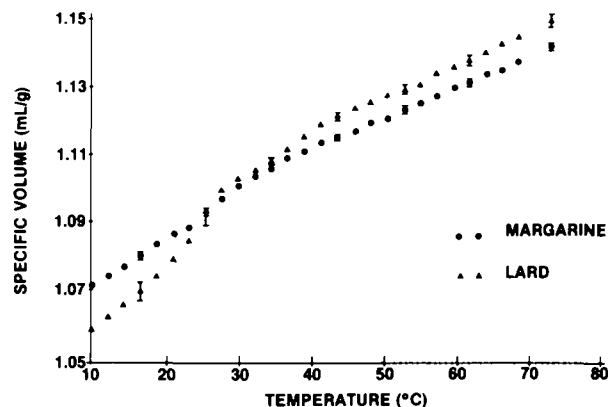
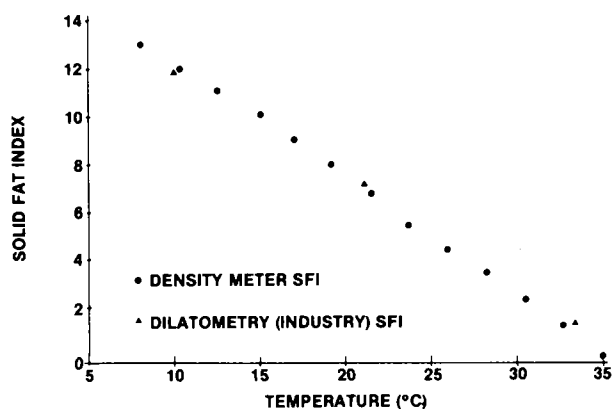FIG. 5. A plot of specific volume as a function of temperature for two different fats, margarine and lard.

FIG. 6. A comparative plot of Solid Fat Index as a function of temperature by the density meter and by the three-point industrial method.

FIG. 7. Illustration of the erratic behavior (between 0 and -10 C) sometimes observed in the dilation curve at lower temperatures.

1920s. The dilatometric procedure includes many manipulations which require dexterity and exactness, e.g., filling the dilatometer, weighing, and reading the scale on the capillary. A certain apprenticeship is necessary for the experimenter to acquire good technique and obtain reproducible results. Although the initial investment in a dilatometer is minimal when compared with that in a density meter, the replacement costs due to breakage can become important. In addition, a number of thermostated water baths are required, one for each data point on the SFI curve. Basically, dilatometry is a cumbersome, time- and space-consuming analytical procedure.

In contrast to dilatometry, the density meter is a rapid and convenient analytical instrument. A minimal amount of operator skill and knowledge is required and no weighing is necessary. The single most important advantage of the density meter is necessarily its ability to provide a continuous profile of the fat's behavior as a function of temperature. At this time however, measurement of solid fat with the density meter over the temperature range recommended by the official dilatometric method is limited to fats such as margarine or fats with a fine crystal structure such as interesterified lard. Fats of relatively high solids content (SFI>35) may create some difficulty when the density meter is used at low temperatures since there is a tendency for these fats to contract or pull away from the inner wall of the sample tube. When there is cracking or vacuole formation, the instrument may give erratic values at lower temperatures as is shown in the case of a shortening and a soya fraction (Fig. 7). This problem was persistent in the soya hydrofraction which had a high solids content (SFI>40), but was intermittent in the case of shortening. In both cases, the SFI values were quite reliable from 15 C upward. It is possible that the use of microcells (0.1 ml) might reduce vacuole formation and other problems caused by contraction of the sample.
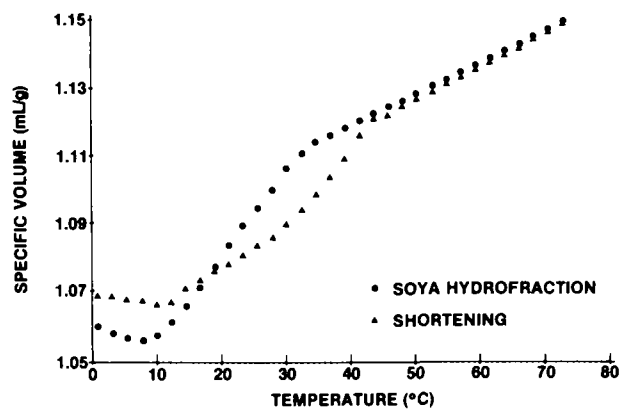
The time required to process a sample with the density meter is ca. 30 min. This time could be improved through the use of multiple external cells for simultaneous analyses and the use of microcells for increased heat transfer (7). Microprocessor multiplexing, sampling and processing of temperature and period data from each cell would allow a smooth dilation or SFI curve to be plotted. Technically, the integration of a microprocessor, multiple cells and plotter should be possible, but would be beyond the scope of this work. We suggest that such a system could be put together specifically for the determination of Solid Fat Indices. The density meter also offers interesting possibilities in processes such as hydrogenation, interesterification and winterization, where continuous monitoring might be useful.

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