The Measurement of Fatty Solids by Differential Scanning Calorimetry

W. J. MILLER, W. H. KOESTER and F. E. FREEBERG,
The Procter & Gamble Co., Cincinnati, Ohio 45224

Abstract

A method has been developed for the measurement of the solids content of vegetable and animal fats by differential scanning calorimetry. Although precision is about half that of existing dilatometric methods, this is a rapid procedure, designed for hydrogenation control. Elapsed analysis time for the determination of solids at two temperatures is about 40 min, compared with 3 to 4 hr by dilatometry. Procedures are outlined employing either of two commercially available instruments.

Introduction

For many years, attempts have been made to replace or modify the time-consuming dilatometric methods for the determination of fatty solids. For plant control, it is costly to hold partially hydrogenated stocks for several hours until analyses are available to provide blending information. Measurement of the heat of fusion of fat, rather than its thermal expansion, appeared to offer promise as a means of control, providing needed information in a matter of minutes, rather than hours.

The use of differential scanning calorimetry (DSC) for the measurement of fatty solids was the subject of a report given by A. P. Bentz of General Foods, at the 1967 AOCS Spring meeting. The procedure described was a modification and extension of similar work reported by J. I. Justin of Perkin-Elmer, at the 1966 AOCS Fall meeting.

Briefly, the method is simply the measurement of the heat of fusion of a frozen, completely solid sample of fat. The area under the melting curve, presented on a strip chart, is measured, then selected partial areas are measured as a percentage of the whole. The temperatures selected for partial area measurements are normally those employed for the dilatometric solids analysis.

During the past two and a half years, we have investigated a number of procedures for the measurement of fatty solids. The total area technique, described above, was included in these studies, but was found to be much less precise than desired (in the order of ±10%).

The purpose of this communication is to describe a somewhat different technique for the same determination. Very briefly, after freezing the sample at −30 C to insure the existence of solid fat in excess of that to be measured, the temperature is raised to a pre-selected level, normally that employed for a dilatometric measurement, and held for a short time. This requires an instrument that will reach this temperature rapidly and reproducibly and maintain it with high precision. After holding the sample at this temperature for sufficient time to allow partial melting and to insure that only those solids remain which are to be measured, melting is allowed to proceed at a closely controlled rate and a melting curve is recorded, from which the partial heat of fusion may be obtained. If the same measurement is required for another temperature, the sample is again frozen, and the operation is repeated for the new temperature.

For production control, it is necessary much of the time to know the solids content only at a single temperature. Such a measurement may be made in about 20 min, depending upon the instrument employed. In normal day-to-day production control, 18 to 20 samples per shift may be analyzed for solids at all temperatures required for process control.

Both the DuPont 900 Differential Thermal Analyzer, with the Differential Scanning Calorimeter Cell attachment (Part No. 900600) and the Perkin-Elmer Model DSC-1B Differential Scanning Calorimeter were used in these studies. It was our experience that the DuPont instrument gave somewhat better precision, and was the preferred instrument for this application.

Experimental Procedures

The amount of sample used for the test was controlled between 9 and 10 mg, and all weighings were made to ±0.01 mg. Most of the weighings were made with a Brinkmann Micro Torque balance, 0–10 mg range; a Cahn Electrobalance may also be used but is not as convenient. Transfer of the sample was made with a plunger from a Hamilton 50 μl syringe, sharpened to a point. It is important that the metal be at or above the melted sample temperature, especially in the case of hard fats, to insure uniform sampling. Fat must never be removed from the sample pan, in the event of overweighing, except in the case of very soft fats. An empty pan containing 7–8 mg of aluminum was used on the reference side of the cell.

A dry ice-acetone slurry was used in the cooling accessories supplied with the instrument. To obtain the most rapid and reproducible cooling, only fresh dry ice should be used to slurry with the acetone. It should be kept in a closed container to prevent atmospheric moisture condensation, then crushed before use in an electric ice crusher and stored in a covered Dewar flask.

After the sample had been placed in the instrument, the cell temperature was raised to 60 C and held there for 2 min to insure that all solids present in the sample had melted. This insured that each sample would have the same thermal history. Then the cell temperature was lowered to −30 C and held at this point for 1 min. The cell temperature then was adjusted to the temperature at which a solids value was desired. Care was exercised to insure that this temperature was not overshot and the cell was maintained at this temperature for 4 min. This time was found to be necessary to allow the solids present in the sample to equilibrate. At this point a melting curve was recorded. With the DuPont instrument a heating rate of 10 C/min and a temperature differential scale (ΔT) sensitivity of 0.2 C/in. were used. A heating rate of 20 K/min and a sensitivity setting of 8X (8 millicalories full scale)

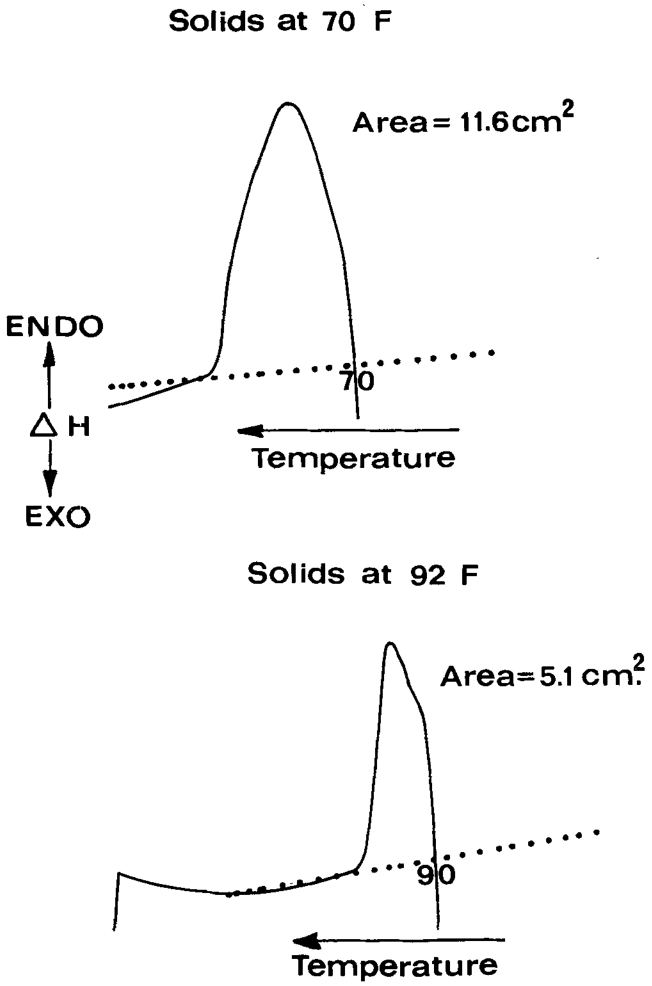

FIG. 1. Typical partial heat of fusion curves for a hydrogenated soybean oil obtained with Perkin-Elmer instrument.

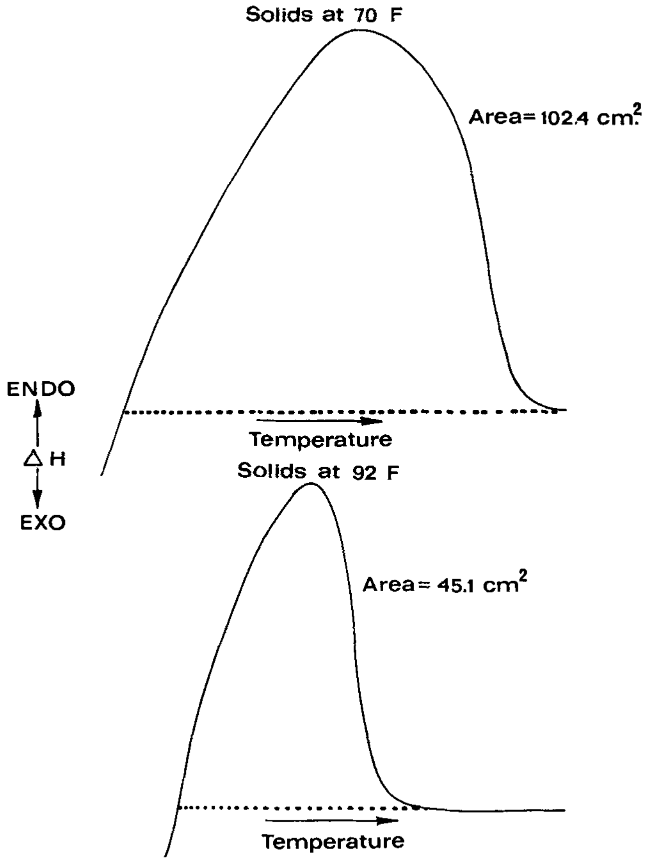

FIG. 2. Typical partial heat of fusion curves for a hydrogenated soybean oil obtained with DuPont instrument.

were used with the Perkin-Elmer instrument. The heating rate of 20/min was used in order to obtain easily integratable areas and our studies showed no differences when a slower rate was used. The sensitivity scale of the DSC-1B was calibrated using indium and tin standards. Temperature calibration checks for the DSC were made using water and stearic acid. The recommendations of the Perkin-Elmer Co. were followed for both of these calibration checks. Additional details on the procedures used to analyze samples or calibrate instruments may be obtained from the authors.

Standard curves of partial ΔH vs. dilatometric solids (SFI-SCI) values at 50, 70, and 92 F were established for various types of fats using samples having known solids values. These curves were then used to determine solids values on unknown samples.

Discussion

Typical partial heat of fusion curves for a hydrogenated soybean oil, obtained with the Perkin-Elmer instrument are shown in Figure 1. The SCI (SFI) values for this sample at 70 and 92 F were 43.8 and 19.6, respectively. The 70 and 92 F solids in the same sample, as measured with the DuPont instrument, are shown in Figure 2.

DSC-SCI (SFI) correlation curves developed with the Perkin-Elmer instrument were not linear over a wide range of solids (Fig. 3). Melting areas became comparatively smaller as the solids content increased. There are two possible explanations.

First, the assumptions that the specific heat of a fat increased, linearly, 20% over 100 C, and that there were no discontinuities in the specific heat-temperature curve might not be entirely valid. Perhaps a better explanation is one not recognized until our studies with the DuPont instrument.

When the Perkin-Elmer cell is advanced manually to the pre-selected temperature for solids measurement, say 70 F, the instrument attempts to reach this temperature rapidly and the average tempera-

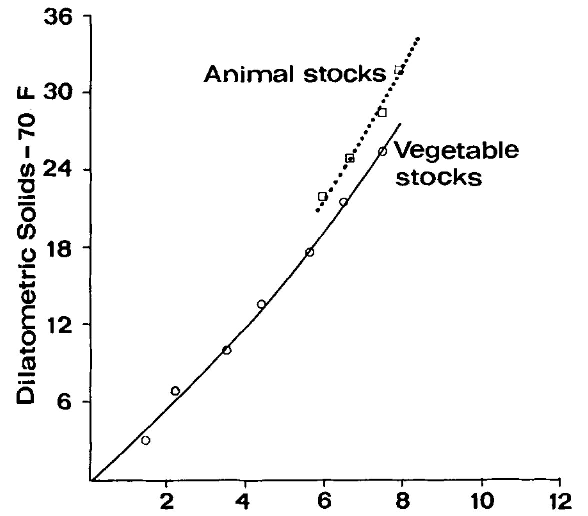

FIG. 3. DSC-dilatometric solids correlation curves developed with Perkin-Elmer instrument.

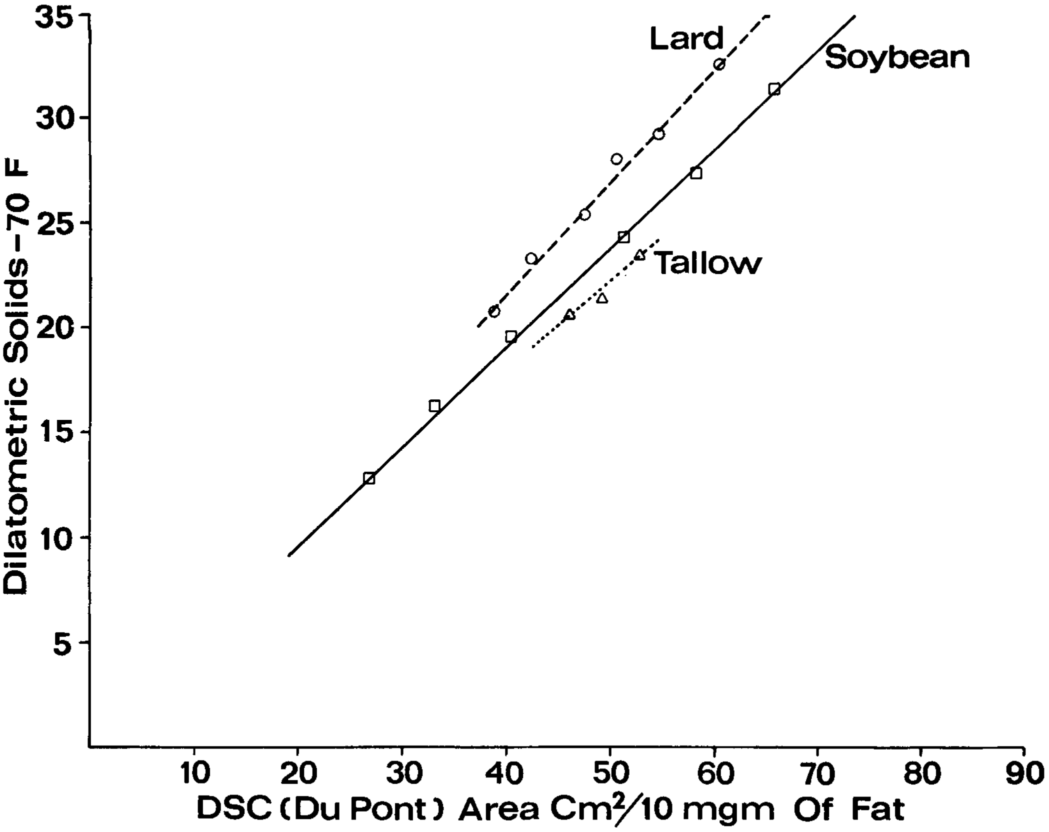

FIG. 4. DSC-dilatometric solids correlation curves developed with DuPont instrument.

ture light comes on to indicate that the temperature has been reached. However, there is no way of knowing whether or not there has been a temperature overshoot. If there is an overshoot, some of the solids to be measured melt, and normally may not completely solidify within the hold time during which the temperature will return to that selected. This phenomenon was seen quite dramatically on an early model of the DuPont instrument employed in these studies.

The DuPont system uses an X-Y recorder, and the cell temperature may be monitored at all times on the X-axis. When the temperature was advanced manually, there was as much as a 5 C overshoot; return to the selected temperature required about a minute. Experience has shown that solids melting during the temperature overshoot do not resolidify rapidly enough for good reproducibility. Although there is no way of seeing this on the Perkin-Elmer instrument, the behavior of certain samples indicated that it did happen. A modification of the DuPont instrument has prevented more than about 0.5 C overshoot, and this is eliminated entirely by approaching the starting temperature in two steps.

Correlation curves developed with the DuPont instrument were linear over a wide range of solids for a given type of oil. Typical curves for various vegetable and animal stocks are shown in Figure 4. Our studies indicated that for eventual production control, better accuracy would be obtained if narrow range curves for each of the separate stocks were employed.

Although the correlations appear good with both instruments, it can never be truly determined since comparison is being made with a procedure that is empirical and has its own errors. There are no absolute standards.

Reproducibility studies indicate that the standard deviation for the test using the Perkin-Elmer instrument is about ±0.4 SCI (SFI) units at any solids level, i.e., a constant error suggesting the system to be limiting. The standard deviation for the DuPont instrument calculated from duplicate analyses by the same analyst varied from 1.1% to 2.2% relative and averaged 1.6%. Typical data on samples ranging in solids from 5 to 43 are shown in Table I.

We have concluded that effective control of fatty solids can be attained with thermal analysis. Precision is slightly poorer than with the dilatometric technique with instruments currently available. However, we feel the reduced elapsed time for the analysis more than compensates for this disadvantage in many situations where the results are needed quickly. The direct use of thermal analysis values would logically be expected to supplant the use of calibration curves for conversion to equivalent dilatometric values.

TABLE I
Reproducibility Data—DuPont Instrument

SCI Range	Average SCI	Number of Duplicates	Sigma for Duplicates	Reproducibility-% (Sigma/ Avg. SCI)
5–19.9	10.6	45	.23	2.2
20.0–29.9	22.2	37	.30	1.4
30.0–43.0	35.0	11	.39	1.1
Overall	18.1		.28	1.6

[Received June 25, 1968]