Evaluation of Mettler Automatic Dropping Point Apparatus and Statistical Comparison with Wiley Melting Point Method[1]

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ABSTRACT

The Mettler FP5/53 automatic thermal analysis system was used to obtain dropping point data on a series of soybean, cottonseed, palm, palm kernel, coconut, and rapeseed oils after conditioning for 30 min at freezer temperature. Wiley mp were determined simultaneously on the same samples. A linear correlation was observed between the dropping point and Wiley mp data over a temperature range of 33-50 C. Meaningful data also were obtained on various fat blends and on samples outside this temperature range. The dropping point technique was found to be more reproducible and less time consuming than the Wiley method, while offering the added advantage of automatic endpoint detection. The technique has been used successfully in our laboratories for quality control and as a means of monitoring hydrogenation studies. Although the dropping point method can be related to the Wiley mp determination, it has developed into a meaningful independent measure of the melting characteristics of fats and oils.

INTRODUCTION

Alteration of the melting characteristics of fats and oils represents one of the more important modifications of physical properties associated with hydrogenation studies. Of the variety of techniques employed for the quantification of the melting process, one of the more routinely applied methods is the Wiley mp determination. This method is recognized as an official procedure by AOCS and, as such, is used extensively in the control laboratories of fat and oils processing plants.

The Wiley mp determination, as it is outlined in AOCS Method Cc 2-38 (1), is a tedious and time consuming analysis not suited for use as a control technique. Adherence to the official procedure requires an elapsed time of ca. 3 hr and an operator time of at least 1 hr for a single determination. As a result of the subjective nature of the endpoint, duplicate analyses are required to reduce the inherent variability of the method.

Introduction of the Mettler automatic thermal analysis system has renewed interest in a means of providing information comparable to that obtained by the Wiley method but devoid of its subjectivity and inefficiency. Recently, Mertens and DeMan (2) observed a meaningful relationship between dropping points obtained with the Mettler FP5/53 Thermo Analysis System and Wiley mp obtained on a series of Smalley check samples. The reproducibility of the dropping point instrument also was reported to be ca. 0.3 C.

The following investigation was undertaken to establish the nature of the relationship between the Mettler dropping point and the Wiley mp for a variety of industrial fats and oils. Evaluation of the technique for use as an in-plant control method and for the analysis of samples beyond the scope of the Wiley method also was undertaken.

INSTRUMENTATION

The Mettler Thermo Analysis System, consisting of the Mettler FP5 control unit, the FP53 softening and dropping point furnace and accessories, and sample cups (Mettler part no. 18712), with a lower orifice of 0.11 in., was used in this study.

The principle of operation for the dropping point instrument involves placing a sample cup containing the solid fat in a temperature controlled furnace which is heated at a constant rate. As the sample begins to melt, it flows through the lower orifice of the cup and interrupts a light beam resulting in an automatic display of the dropping temperature on the display board of the control unit.

EXPERIMENTAL PROCEDURE

Sample cups were placed on a clean glass plate and held in a freezer at -30 C for at least 10 min prior to filling. The samples were melted on a steam bath until free of solids and mixed thoroughly. A preconditioned sample cup then was filled with melted fat and conditioned in the freezer for 30 min at -30 C. After this tempering period, it was placed in a preheated FP53 furnace, equilibrated for 1 min at 31 C, and then heated at a rate of 1 C/min. The dropping point temperature was read directly from the display panel

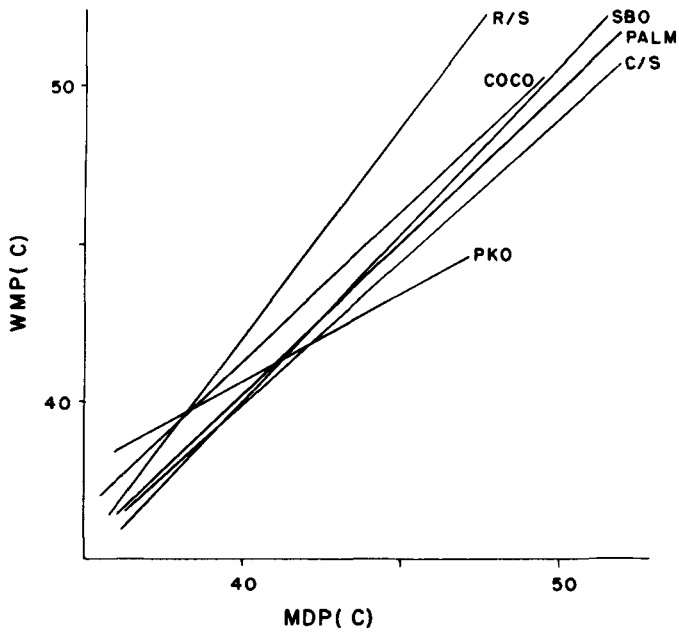

FIG. 1. Extrapolated regression lines derived for each oil. WMP = Wiley mp, MDP = Mettler dropping point, R/S = rapeseed oil, SBO = soybean oil, PKO = palm kernel oil, and C/S = cottonseed oil.

[1]Presented at the AOCS Fall Meeting, Chicago, October 1973.

TABLE I

Linear Regression Analysis

Hydrogenated oil	Correlation coefficient	95% Confidence limits (±2 σ)
Coconut	0.971	1.80 C
Cottonseed	0.990	0.86
Palm	0.996	1.36
Palm kernel	0.589	1.14
Rapeseed	0.976	1.30
Soybean	0.992	1.14

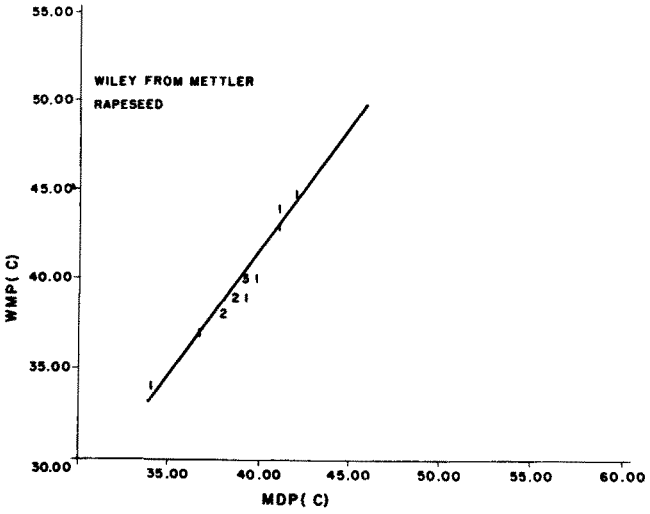

FIG. 2. Plot of Wiley mp (WMP) vs Mettler dropping point (MDP) and regression line for hydrogenated rapeseed oil.

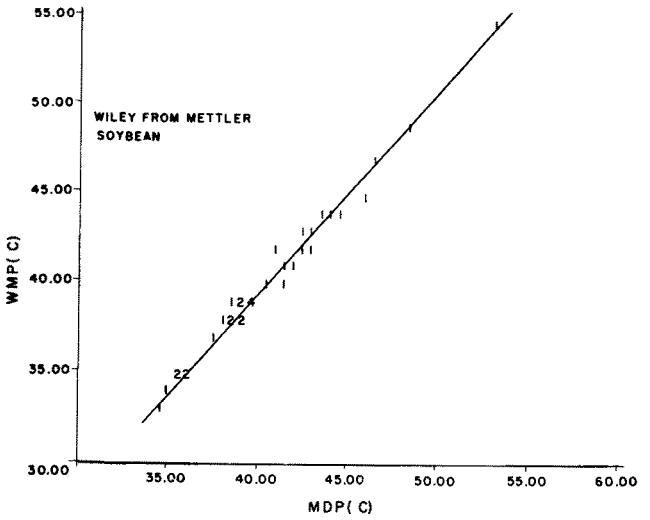

FIG. 3. Plot of Wiley mp (WMP) vs Mettler dropping point (MDP) and regression line for hydrogenated soybean oil.

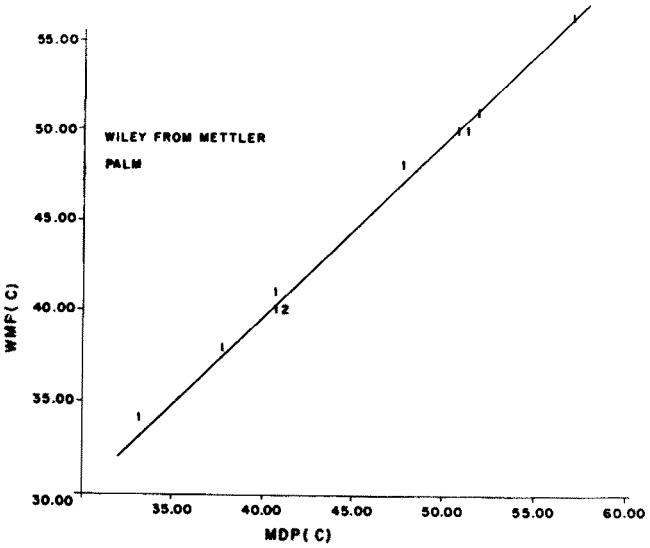

FIG. 4. Plot of Wiley mp (WMP) vs Mettler dropping point (MDP) and regression line for hydrogenated palm oil.

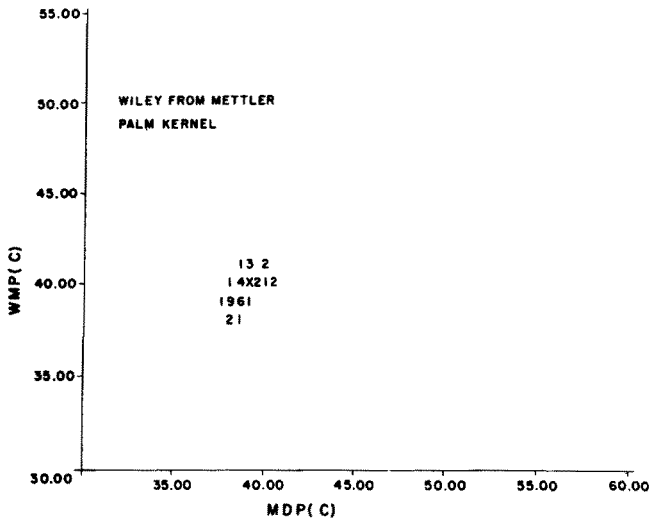

FIG. 5. Plot of Wiley mp (WMP) vs Mettler dropping point (MDP) for hydrogenated palm kernel oil. (X = more than 10 observations.)

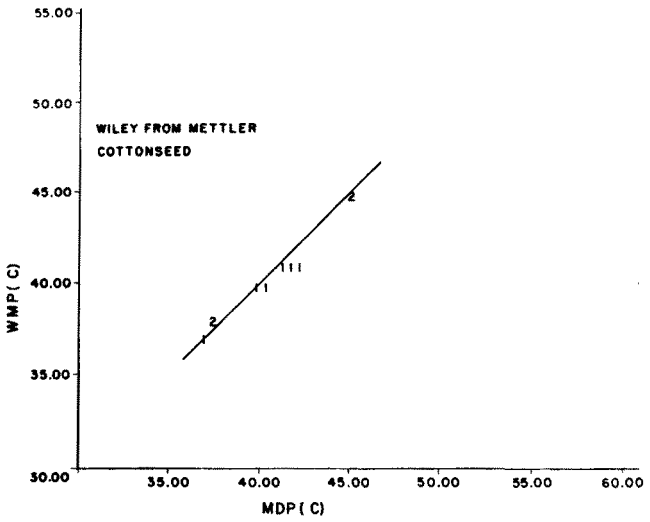

FIG. 6. Plot of Wiley mp (WMP) vs Mettler dropping point (MDP) and regression line for hydrogenated cottonseed oil.

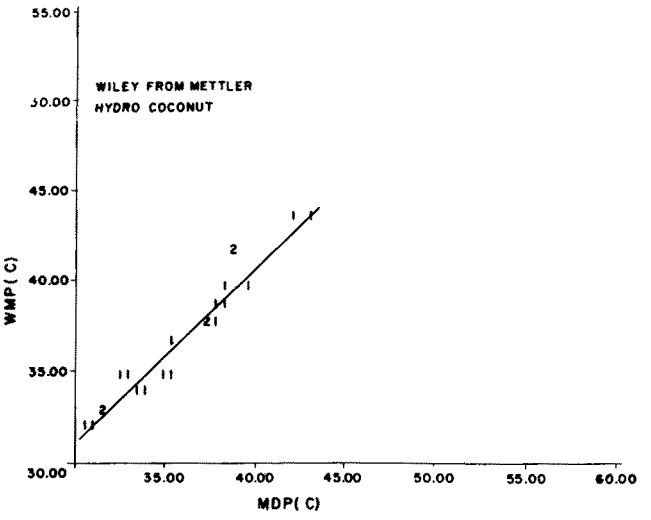

FIG. 7. Plot of Wiley mp (WMP) vs Mettler dropping point (MDP) and regression line for hydrogenated coconut oil.

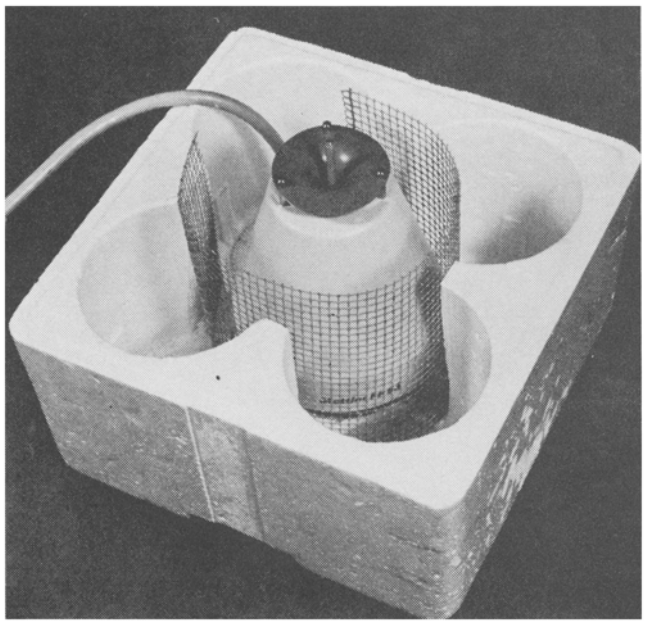

FIG. 8. Styrofoam cold box for low temperature dropping points.

TABLE II

Hydrogenation Studies

	Wiley mp (C)	Mettler dp[a] (C)
Soybean/cottonseed 1	34.8	35.0
Soybean/cottonseed 2	36.8	37.4
Soybean/cottonseed 3	38.0	38.1
Soybean/cottonseed 4	38.9	39.0
Soybean 1	33.4	33.1
Soybean 2	35.0	35.0
Soybean 3	35.4	35.5

[a]dp = Dropping point.

of the control unit. On completing a run, the furnace was returned to 31 C in preparation for the next analysis. The recovery time for the furnace was ca. 2 min. Wiley mp were determined simultaneously on the same samples.

RESULTS AND DISCUSSION

Hydrogenated Oils

The conditioning sequence used in this investigation was arrived at after data obtained on samples conditioned for 1/2, 1, 2, 4, and 24 hr at -30 C and 1, 2, 4, and 24 hr at +5 C all were found to be within the limits of reproducibility of the dropping point technique. A general trend, however, toward lower values with increasing conditioning times was observed.

The Wiley mp and Mettler dropping point data obtained on a variety of hydrogenated oils were evaluated using linear regression analysis to determine if a correlation exists and, if so, to define the relationship mathematically. Table I presents the correlation coefficients and 95% confidence limits for each oil studied.

Examination of the statistical analysis indicates that, with the exception of palm kernel oil, a highly significant correlation exists between the two techniques for each oil. The correlation coefficient for palm kernel oil is considerably lower than expected, stemming primarily from the very narrow range over which data was obtained.

The 95% confidence limits (ca. 2 standard deviations) for each oil fall within the range of 2σ limits reported for the Wiley method in a recent Smalley check sample study (3).

TABLE III

Low Temperature Analysis

	Wiley mp (C)	Mettler dp[a] (C)
Soybean 1	NA[b]	18.0
Soybean 2	NA	19.0
Soybean 3	25.8	25.1
Soybean 4	30.1	29.4
Soybean 5	33.8	33.0

[a]dp = Dropping point.
[b]NA = Not applicable.

TABLE IV

Oil Blend Analysis

	Wiley mp (C)	Mettler dp[a] (C)
Tallow/coconut 1	37.7	37.1
Tallow/coconut 2	39.6	38.8
Tallow/coconut 3	40.4	39.8
Coconut/palm kernel 1	37.5	35.1
Coconut/palm kernel 2	38.8	36.7
Coconut/palm kernel 3	40.2	38.3
Soybean/cottonseed 1	41.0	40.4
Soybean/cottonseed 2	42.0	41.0
Soybean/cottonseed 3	41.2	41.4

[a]dp = Dropping point.

It is obvious from a qualitative comparison of the extrapolated regression lines derived for each oil (Fig. 1) that the relationship between the two techniques is a direct function of the oil being analyzed. In the case of soybean, palm, and cottonseed oils, however, the regression lines are sufficiently close to that of a one for one relationship between the two techniques that the Mettler dropping point can be used interchangeably with the Wiley mp for most applications.

Figures 2-7 represent computer printouts of the observed data and the associated regression line for each oil investigated. The numbers printed correspond to the number of observations which fall within a given coordinate increment of the printer-plotter. Plots of this type currently are being used in our laboratories for the determination of Wiley mp from Mettler dropping points.

The data are sufficiently linear that multiple regression analysis employing second order relationships did not improve the standard error of prediction enough to justify its use.

The results of the linear regression analysis suggest that, for those oils investigated, the Mettler dropping point method can predict the Wiley mp within the limits of precision of the Wiley method.

Monitoring Hydrogenations

Because the elapsed time for the Mettler dropping point determination is ca. 40 min as compared with 180 min for the Wiley mp determination, this approach becomes a realistic one for monitoring hydrogenations in which uniform processing conditions are used.

Table II presents the Wiley mp and Mettler dropping point values obtained for two hydrogenation studies. In every instance, the two techniques are in satisfactory agreement.

Limited data suggest that conditioning the sample at -30 C for 15 min will yield dropping points which are identical to those obtained after 30 min conditioning. This effectively reduces the elapsed time for dropping point analysis to 25 min/sample, making this technique well suited for use at the control level.

Low Temperature Dropping Points

For samples melting below 33 C, the FP53 furnace was placed in a styrofoam cold box (Fig. 8) which was maintained at -5 to -10 C using dry ice. Samples were conditioned for 30 min at -30 C and then placed in the furnace which had been preheated to a temperature of 15 C. After equilibrating for 1 min, the sample was heated at a rate of 1 C/min.

Table III gives the results obtained on a series of hydrogenated soybean oils. Samples 1 and 2 could not be analyzed by the Wiley method, because the fat pellet would not release from the aluminum tempering block without deforming. However, agreement between the techniques for the remainder of the samples is considered acceptable.

Oil Blends

Limited data also have been obtained on blends of various oils. Table IV presents a comparison of Wiley mp and Mettler dropping points obtained on a number of different blends. At present, insufficient data are available to permit establishing a statistical correlation between the techniques for these blends, but it is apparent that, in some instances, the relationship is very nearly linear.

ACKNOWLEDGMENTS

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REFERENCES

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2. Mertens, W.G., and J.M. DeMan, JAOCS 49:366 (1972).
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