Analysis and Monitoring of *Trans*-Isomerization by IR Attenuated Total Reflectance Spectrophotometry

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ABSTRACT

Attenuated total reflectance for IR determination of *trans*-isomers in fats appears to have distinct advantages over procedures currently used. The AOCS standard method CD 14-61 requires weighing and quantitative dilution of a sample with carbon disulfide before spectrophotometric analysis at 10.3 μm. In contrast, according to the attenuated total reflectance analytical procedure, one neither weighs nor dilutes but merely fills the cell with oil and reads at 10.3 μm. In addition to analyses for *trans*-isomers in liquid oils, margarines and shortenings, attenuated total reflectance enables one to monitor *trans*-development continuously during hydrogenation. The presence of catalyst in unfiltered hydrogenated oils does not interfere with attenuated total reflectance measurements in contrast to classical transmission measurements. Unfiltered oil from the hydrogenator can be circulated through the attenuated total reflectance cell to record *trans*-isomerization during the reaction.

INTRODUCTION

Need exists for improved, rapid, facile procedures of *trans*-analysis in fat products. Currently, *trans*-contents of fats are determined by the AOCS Tentative Method No. Cd-14-61–Isolated *trans*-Isomers-Infrared Spectrophotometric Methods (1). The AOCS Spectroscopy Committee is studying Allen's (2,3) procedure requiring only dilution with carbon disulfide and determination of absorbance at 8.6 and 10.3 μm. Because the attenuated total reflectance (ATR) procedure has such distinct advantages, lipid chemists should become more aware of the analytical potentialities of this simple procedure.

EXPERIMENTAL PROCEDURES

ATR spectrophotometry first described in 1961 is a procedure of relatively recent development (4,5). The equipment of new design (Miran ATR) used in this study was made available by the Wilks Scientific Corp., S. Norwalk, Conn. Percentage transmissions at 10.3 μm are converted directly to percentage *trans*-isomers by reading from a calibration curve. The curves in Figure 1 represent methyl elaidate diluted with refined soybean oil and analyses according to the American Oil Chemists' Society Method Cd-14-61 for methyl esters on a variety of samples.

The ATR cell with its KSR (potassium thallium bromide) reflecting crystal was redesigned for low dead volume (2 cc) and has 1/8 in. tubing entry, heater, and magnetic stirrer. At 12.5 cc/min flow and 150 C, the magnetically stirred cell attained equilibrium from sample to sample in ca. 15 sec as compared to ca. 1 min for the unstirred cell. A second prototype cell supplied by the equipment manufacturer also provides for heating the cell and has 1/4 in. inlets for large volume flows.

Fat products were purchased at a local grocery store: two unhdyrogenated vegetable oils, three liquid hydrogenated winterized vegetable oils, and three plastic shortenings of vegetable oil origin. Analyses of these samples by the ATR procedure and by the AOCS Method are given in Table I.

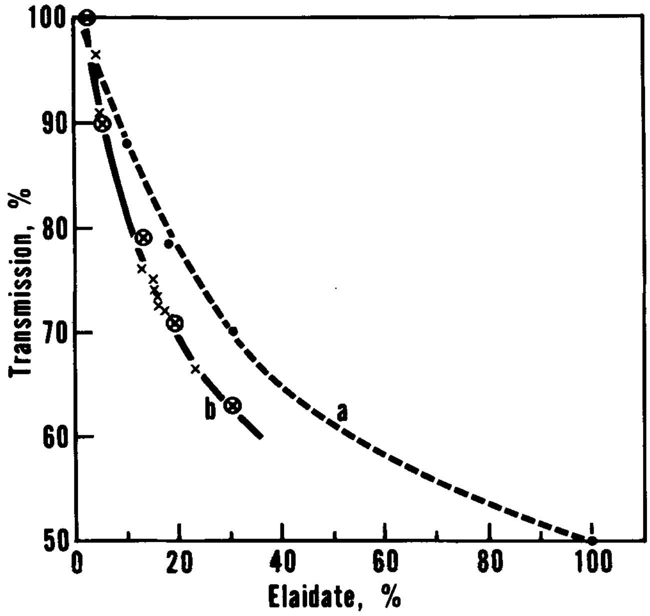

FIG. 1. Calibration curve for a magnetically stirred continuous flow cell: (a) methyl elaidate diluted with soybean oil and (b) AOCS Standard Method Cd-14-61 to determine the *trans*-content.

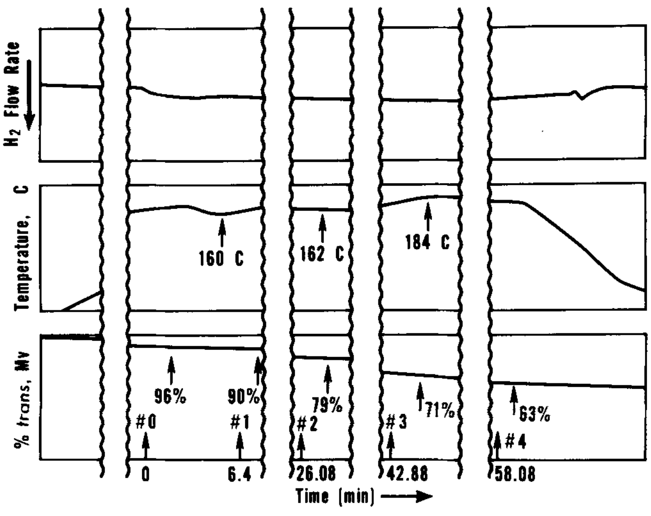

FIG. 2. Time course of the hydrogenation reaction displaying (a) hydrogen flow, (b) temperature of the reactor, and (c) percentage transmission of the Miran attenuated total reflectance (ATR) spectrophotometer.

Applicability of the ATR cell for continuous flow was demonstrated by incorporating it into a hydrogenation system. The reaction mixture of oil and catalyst from a laboratory stirred hydrogenator (Parr Instrument Co., Moline, Ill.) was circulated by means of a diaphram pump at 12.5 ml/min through the ATR cell and back into the reactor. The reaction whose time course is shown in Figure 2 was for soybean oil hydrogenated with Girdler's (G-15) nickel catalyst at 0.1% and 14.7 psi hydrogen. As shown in

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11 internal reflections appears to give a useful range of percentage transmissions, i.e. 100 to 60%), for determining *trans*-contents of hydrogenated products. Sensitivity of the existing cell, of course, could be doubled if desired by using both sides of the crystal for oil contact rather than one side as was done here. The shape of the calibration curve reveals that the lower the *trans*-content the greater is the sensitivity of analysis. Increasing the sensitivity of the AOCS Method by differential IR spectrophotometry is also under study by the AOCS Spectroscopy Committee (3,9).

It is well known that the Beers-Lambert law is not obeyed by ATR procedures, except over narrow concentration ranges (5). However, the use of a calibration curve of percentage transmission vs percentage elaidate (Fig. 1) poses no problem for the analyst. At the Northern Laboratory, the calibration will reside in a computer as a polynomial fit curve, and percentage *trans*-value corresponding to the percentage transmission read will be returned to the analyst via teletype. As a simple alternative to computer calibration, a scale on the meter of the spectrophotometer could be constructed to read out the percentage *trans* directly for a particular ATR cell. In such an instrument designed exclusively for the *trans*-content of fat products, a single wavelength band pass filter at 10.3 μm, rather than the present continuously variable filter, would be anticipated (10).

On the basis of the results and experience presented here, it would appear that further study and use of the ATR IR spectrophotometer for determining *trans*-isomers are justified.

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