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A RAPID SCREENING TECHNIQUE FOR VEGETABLE OIL IDENTITY BY SUB-AMBIENT DSC *

SUSAN M. DYSZEL

U.S. Customs Service, 1301 Constitution Ave. N.W., Washington, DC 20229 (U.S.A.)

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ABSTRACT

Vegetable oils are widely used in the food industry. Labeling requirements have alerted the consuming public to the presence of vegetable oils and to the wide variety of oils used. Vegetable oils are selected commercially for their physical properties, price and availability, and many ingredient labels contain the 'and/or' clause reflecting the interchangeability of food grade vegetable oils.

A 'fingerprinting' method has been developed utilizing the characteristic sub-ambient liquid–solid and solid–solid transitions of vegetable oils. The DSC was used in the temperature range 320 to 220 K. The cooling curves and their first derivatives were recorded for a pattern recognition library of pure vegetable oils, mixtures of oils, and oils present in standard cookie dough. This pattern library will serve as the basis for rapid verification of identity for vegetable oils, mixtures of oils and oils in commercially prepared food products.

INTRODUCTION

Vegetable oils are commercially important. They are used as food products, lubricants, paint vehicles, and stocks for soaps and detergents. The U.S. Customs Service analyzes vegetable oils to verify the claimed identity, and to determine whether there are mixtures of oils or further processing such as hydrogenation. Additionally, the detection of vegetable oil in packed or prepared foods can pose a major problem for analysis.

For the calendar year 1979, the U.S. imported 870 million lb. of coconut oil, 295 million lb. of palm oil and 148 million lb. of palm kernel oil. Other vegetable oils were imported in smaller quantities. For the same time period, domestic soybean oil usage was estimated at 9.27 billion lb. and soybean oil exports at 2.4 billion lb. Part of this total oil was consumed as food fats. In 1979, the annual domestic U.S. consumption of food fats (including animal

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and vegetable fats) was 57.7 lb./person visible fats and 77.6 lb./person invisible. The FDA has required that ingredient labels for prepared foods list these invisible fats [1]. Many ingredient labels now include the designation 'vegetable shortening (may include soybean and/or palm, and/or...etc)'.

The volume of vegetable oils used in industry has necessitated the development of several methods of analysis. The AOAC Methods for pure oils depend on observing the melting point of a solidified sample [2]. Gas chromatographic methods have been developed to characterize the fatty acid distribution in vegetable oils [3]. Thin layer chromatography [4] and fractionation techniques have also been used [5].

Thermal analysis has been applied to the study of vegetable oils and fractions of oils. Examples include fat solids [6], triglycerides [7–9], whole oils [10–15], and mixtures of fats and oils [16,17]. This study was attempted to develop a rapid thermoanalytical method to identify vegetable oils and to detect their presence in a food product.

EXPERIMENTAL

Subambient Differential Scanning Calorimetry (DSC) was chosen as the desired technique along with the use of a First Derivative Computer (FDC). All comparisons of cooling behavior of the oils and oil-containing samples were based on the FDC curves. Instrumentation was the Perkin-Elmer DSC-2 with Model FDC-1 First Derivative Computer and a Fisher Recordall 3-pen recorder (Fig. 1). A two stage freon-based mechanical cooler (Perkin Elmer Intracooler II) was used to cool the cell block of the DSC. Weighed samples were placed in the DSC and allowed to equilibrate for two minutes at 320 K. The cooling curves were generated at a cooling rate of 10° min^{-1} from 320 to 220 K. The cooling rate was linear from 320 to 235 K. However, from 235 to 220 K, the cooling rate was no longer linear due to an insufficient temperature gradient between the sample holder and the thermostated heat sink. The non-linear portion of the curve was reproducible over a

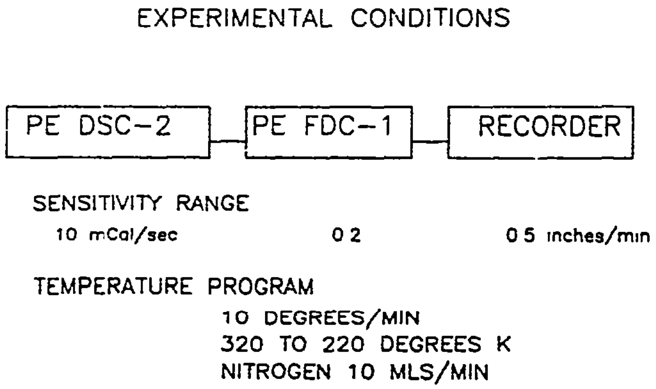

Fig 1. Instrumentation conditions.

series of runs. The DSC was allowed to equilibrate at 220 K and the sample was held at this temperature for five minutes.

Both the DSC and FDC signals were recorded during the cooling run. The sensitivity for the DSC was 10 mcal sec^{-1}. The FDC was operated at a range setting of 0.2 mcal sec^{-1} sec^{-1} for oils in a matrix and 1.0 mcal sec^{-1} sec^{-1} for pure oils. The temperature range for the DSC was calibrated using the ICTA standards of 1.2-dichloroethane (241.6 K) and cyclohexane (280.2 K).

Samples of pure oils* ranged from 0.5 to 10 mg with 1.0 to 2.0 mg producing the most consistently on-scale data. Cookie samples weighed in the range of 15 to 30 mg. Pure oils were obtained from a variety of sources and stored in the dark at room temperature. Cookies were prepared in the laboratory from two recipes; the AACC standard recipe [18], and an oatmeal cinnamon recipe. Commercial cookie samples were also obtained.

RESULTS AND DISCUSSION

To provide a reference library of FDC cooling curves for pattern matching, a series of individual vegetable oils was run. The curves for these oils are shown as Figs. 2–6. Table 1 lists the FDC peak temperatures obtained from these curves. Three non-numerical indicators are used in this table: hold, less than 240 K and greater than 220 K. As noted before, the selected rate of cooling was more rapid than the instrument's cooling system could handle. Thus, precise temperature measurement was unobtainable under these experimental conditions for part of the temperature curve. The 240 K point was selected as the last precisely measured temperature before the non-linear

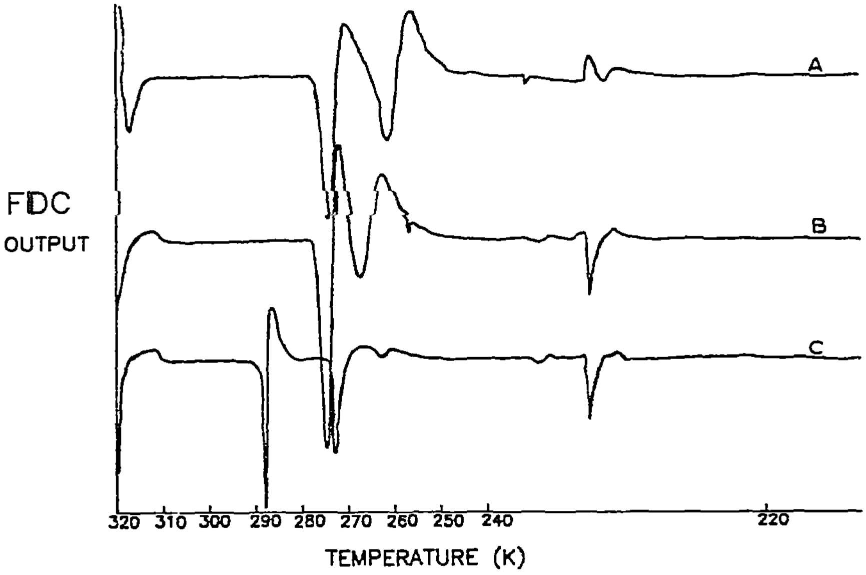

Fig. 2. Vegetable oil cooling curves. A, coconut; B, palm kernel; C, palm.

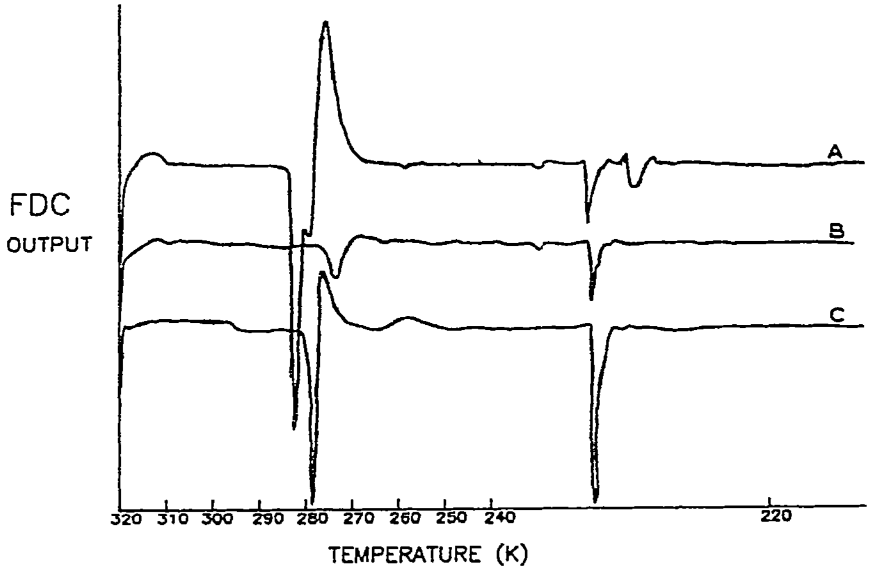

Fig 3 Vegetable oil cooling curves. A, palm kernel stearin; B, palm stearin; C, tucum.

cooling ramp. The 220 K point was determined by the indicator light showing that the instrument was back in control of the temperature. The hold region is indicative of the temperature region after the DSC had reached 220 K and had equilibrated at that temperature. Therefore, the greater than (>) and less than (<) indicators reflect the relative position of the peak of interest along the cooling curve. It must be noted that almost all vegetable oil samples had some FDC peaks in this non-linear region. The general peak cluster was consistent through several runs, but was not considered in the pattern identification process.

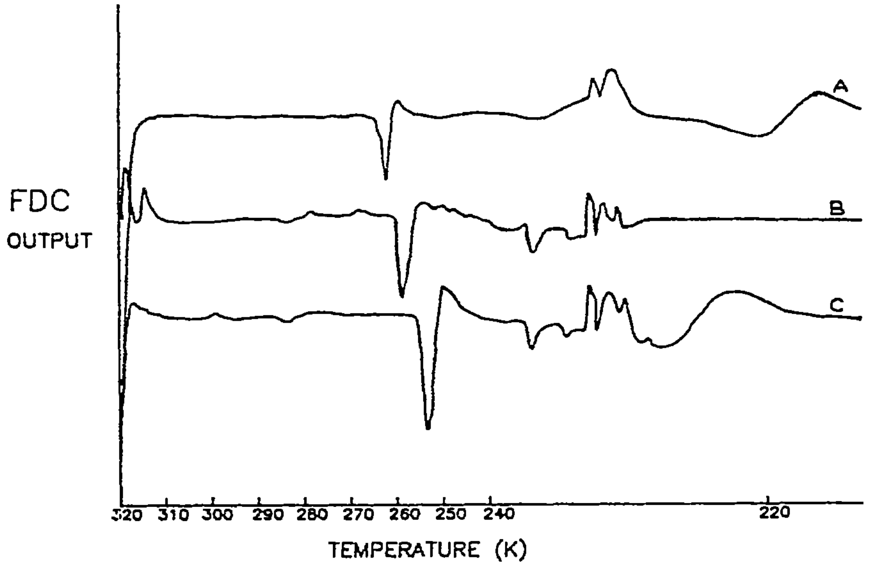

Fig. 4. Vegetable oil cooling curves. A, peanut, B, cotton seed; C, ph soybean.

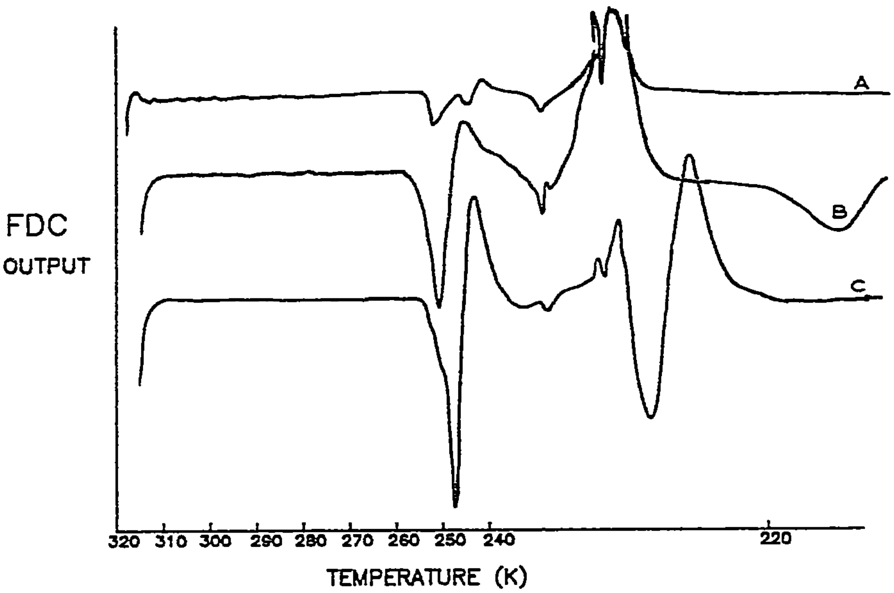

Fig 5. Vegetable oil coolıng curves A, sunflower; B, corn; C. olıve

While in some cases, there were similarities in the FDC curves for members of a group of related oils, such as the lauric acid oils (palm, palm kernel, coconut and tucum), there were sufficient differences to distinguish them. Based on the varieties of oils sampled in this study, if two oils have one FDC peak temperature in common, one will have a second peak by which it can be distinguished from the other.

Figure 7 shows that four different samples of coconut oils gave essentially

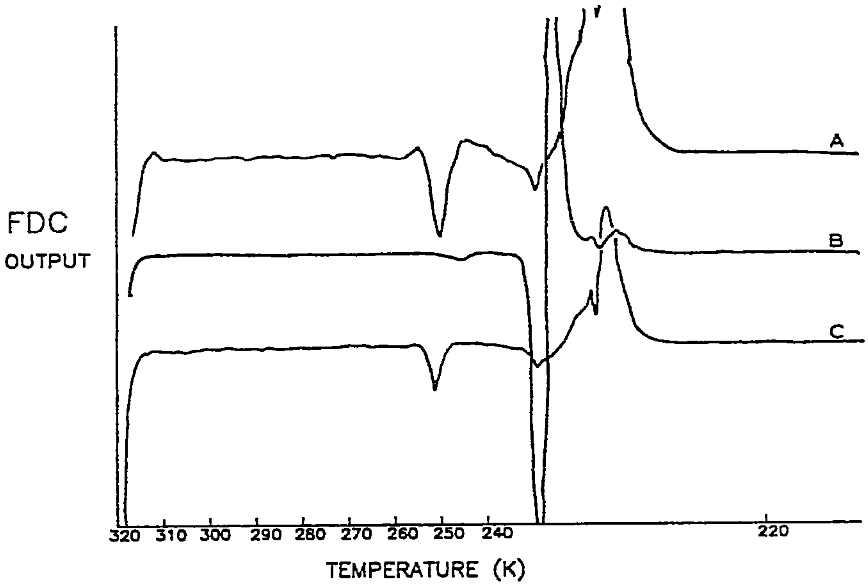

Fig. 6. Vegetable oıl coolıng curves. A, safflower; B, rapeseed; C, sesame.

TABLE 1

Representative FDC peak temperatures

Oil	1st Peak (K)	2nd Peak (K)
Olive	247	>220
Rapeseed	250	
Safflower	250	<240
Corn	250	220 hold
Sunflower	252	242
Sesame	253	
Soybean (ph)	255	>220
Cottonseed	259	
Peanut	262	220 hold
Palm stearin	274	
Coconut	275	261
Palm kernel	275	268
Tucum	278	
Palm kernel stearin	282	280
Palm	288	272

the same FDC curves, illustrating the consistency of response from one sample to another of the same oil variety. However, the age and previous chemical processing of an oil can influence the FDC pattern as demonstrated by Fig. 8. In this case, old soybean oil is compared with newly purchased soybean and partially hydrogenated soybean oils. The aged oil had been stored at room temperature for at least 3 years. Hydrogenation

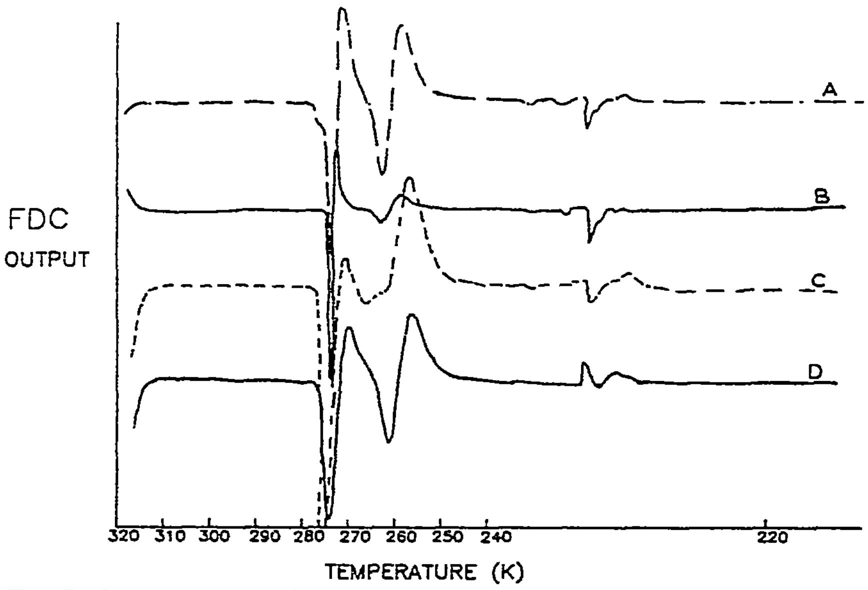

Fig. 7. Coconut oil cooling curves.

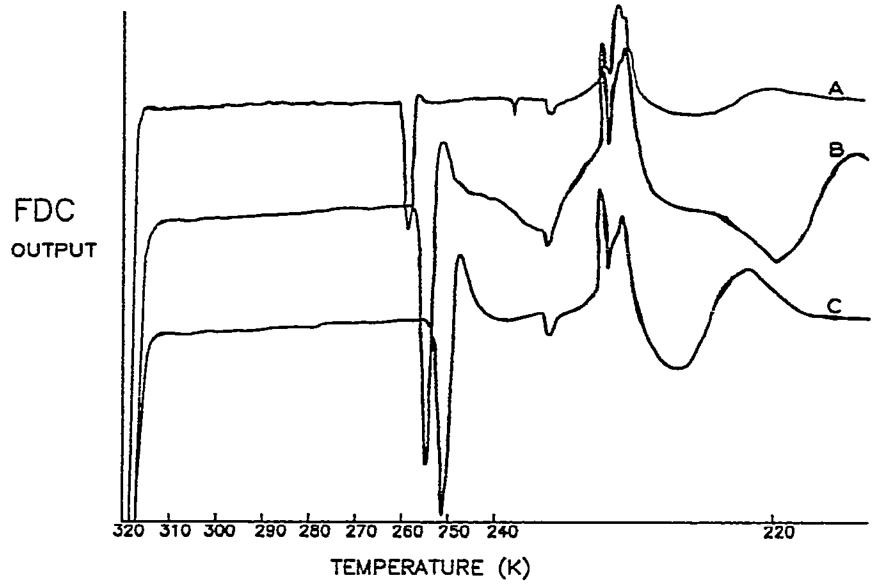

Fig. 8. Various soybean oils. A, 'old'; B, 'new'; C, partially hydrogenated.

shifted the FDC peak to a lower temperature while aging had the reverse effect on the peak temperature. The shift in DSC–FDC peaks to lower temperatures with increasing degree of hydrogenation is in general agreement with the findings of Rossell for a series of palm oils with varying iodine values [19]. The effect of aging on the DSC-FDC peak in the cooling mode suggests a possible alternative approach to the well known oxidative stability test by DSC [20–23] for determining the shelf life of fats and oils. The

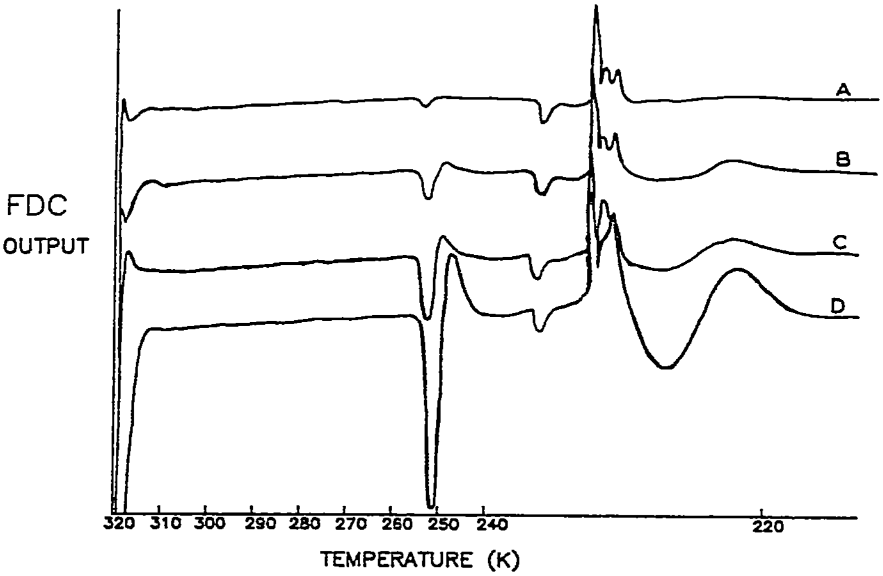

Fig. 9. Concentration effect. A, 0.22 mg; B, 0.78 mg; C, 1.34 mg; D, 4.60 mg.

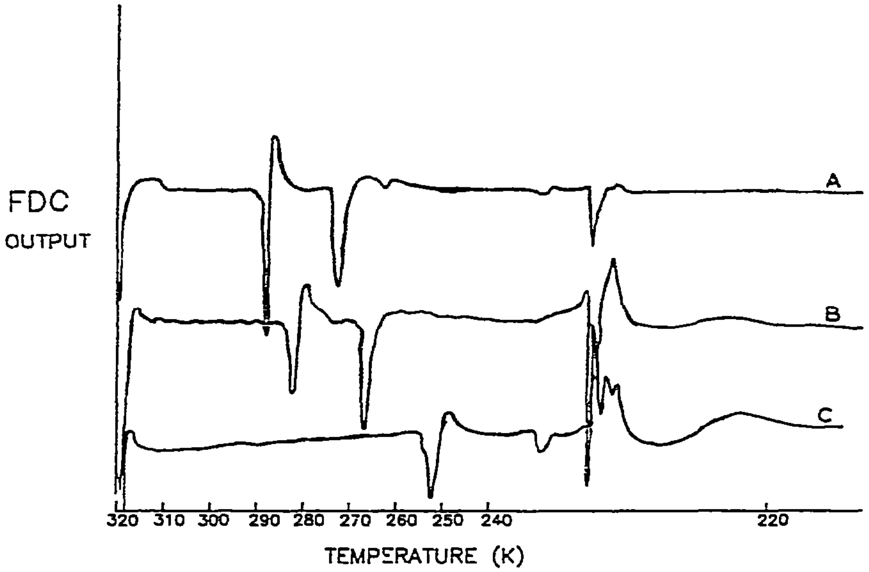

Fig. 10. Palm–ph soybean oil mixture. A, palm; B, palm–ph soybean 50/50 by weight; C, ph soybean

magnitude of the FDC peak was seen to vary directly with the sample mass, as shown in Fig. 9.

Having established that individual vegetable oils have characteristic FDC curves, the next step was to determine the subambient thermal behavior of mixtures of oils. It was hoped that the individual oils would retain their cooling characteristics and the resulting scan of the mixture would be equivalent to the overlaying of two individual scans. This was not the case. Figure 10 shows the FDC scans of soybean, palm and a 50/50 blend of soybean and palm oils. This mixture produced not three transitions (two from the palm oil and one from the soybean oil) but two peaks, characteristically spaced, of palm oil shifted down to lower temperatures intermediate between the palm and soybean transition temperatures. The polymorphism of vegetable oils is a well known phenomenon. Mixtures of fats or oils

TABLE 2

AACC standard cookie

Ingredient	Weight (%)
Flour	46 8
Sugar	27.5
Shortening	13.5
Water	11.1
Leavening	1.1

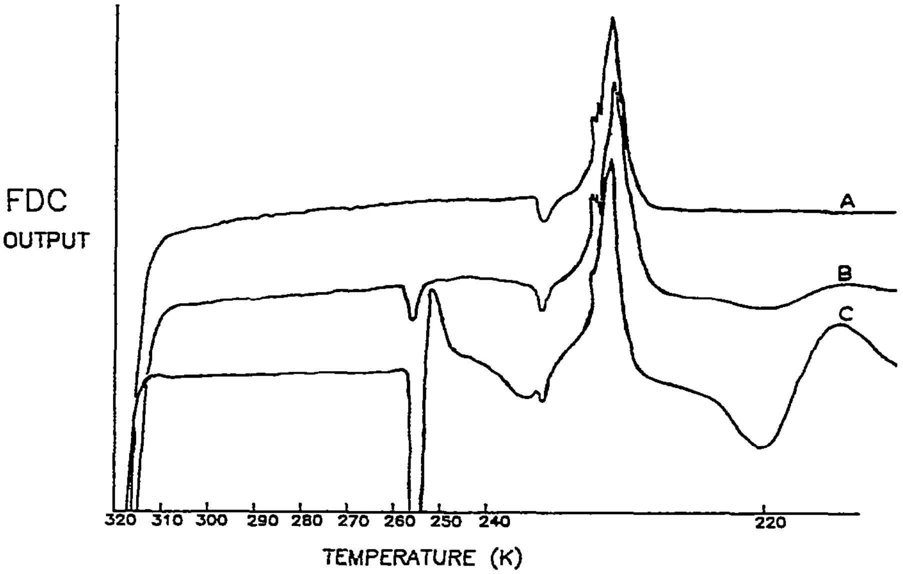

Fig. 11. Standard cookie. A, no oil dough; B, soybean oil cookie; C, soybean oil.

appear to behave as solutions rather than physical mixtures. Additionally, the FDC peaks are broadened by the presence of other polymorphic crystalline shapes. This broadening and temperature shifting of FDC peaks has been observed for other binary oil mixtures.

Standard cookies were prepared using the recipe shown in Table 2. Figure 11 illustrates the type of scans obtained from the standard cookie dough prepared with and without soybean oil. A scan of the soybean oil used in the preparation is included for comparison. It is noted that the cookie dough without oil has essentially no FDC features in its scan and that microwave baking of the dough does not change the thermal behavior of the oil to any significant degree. Figure 12 provides evidence that in a baked cookie dough cottonseed oil behaves in a manner similar to soybean.

TABLE 3

Oatmeal cinnamon cookie

Ingredient	Weight (%)
Flour	28.4
Oats, rolled	28.2
Shortening	22.0
Sugar	14.8
Water	5.5
Leavening	0.6
Cinnamon	0.5

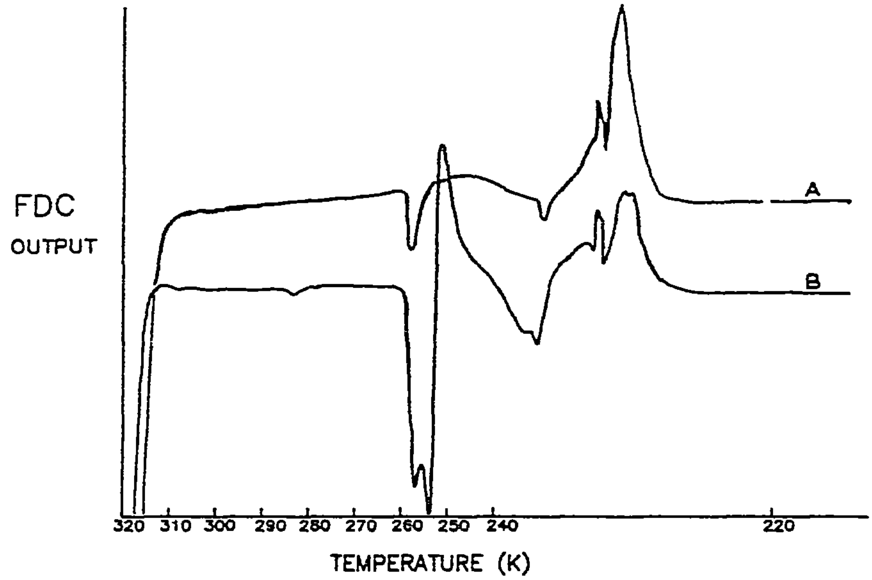

Fig. 12. Standard cookie. A, cottonseed oil cookie; B, cottonseed oil.

Reproducibility of response is demonstrated by the FDC curves of two separate but compositionally identical batches of standard cookies (Fig. 13). The oatmeal cookies recipe (Table 3) was used for both single and mixed oil cookie batches. Figure 14 shows the effect of mixed oils (peak shifting) and the effect of oil added to the baked cookie (peak broadening and shifting). The addition of other ingredients such as oatmeal and flavoring had no apparent effect on the thermal behavior of the oil or oil mixtures.

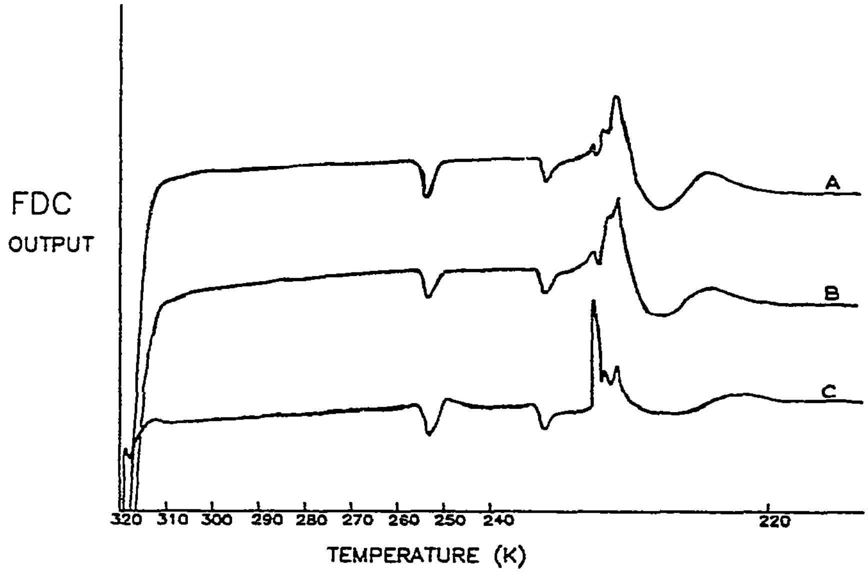

Fig. 13. Reproducibility. A, batch 1 ph soybean oil cookie; B, batch 2 ph soybean oil cookie; C, ph soybean oil.

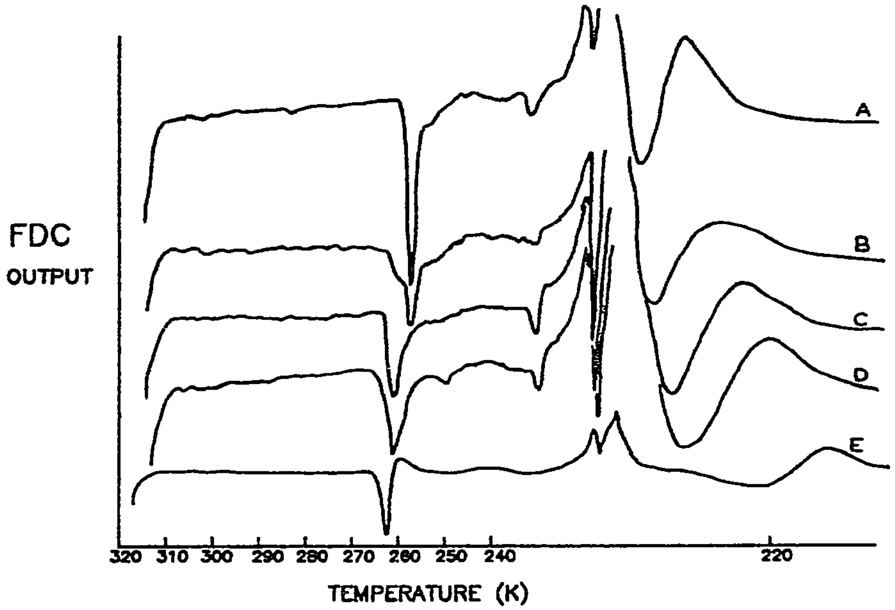

Fig 14. Oatmeal cookie. A, soybean; B, soybean and 10% peanut; C, soybean/peanut 50/50, D, soybean/peanut and 10% peanut; E, peanut.

The remaining figures (Figs. 15–17) show three examples of the application of the subambient DSC–FDC technique to commercially baked cookies. Each scan is shown with the oil or mixture of oils which best matched the FDC pattern. The ingredient label for each cookie was used to assess the probability of success for each match.

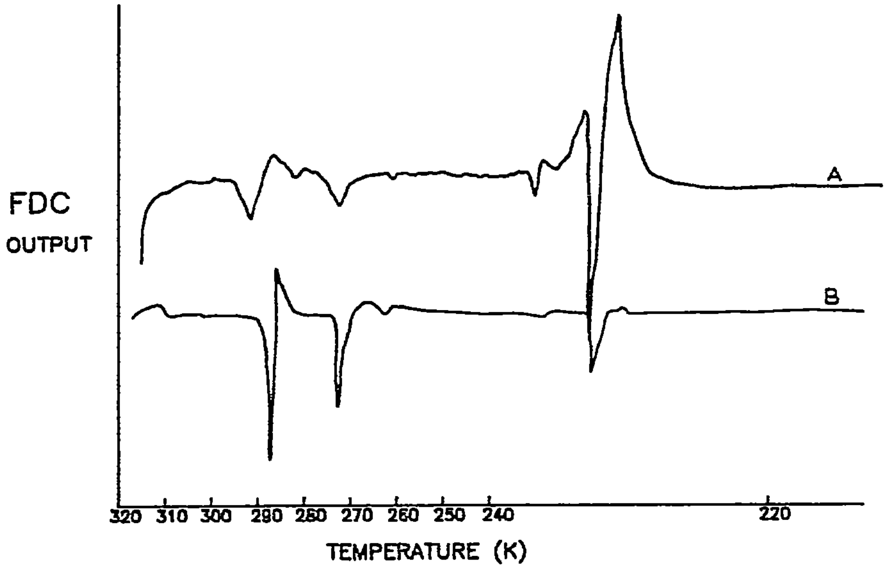

Fig. 15. Commercial cookie. A, spice cookie; B, palm oil.

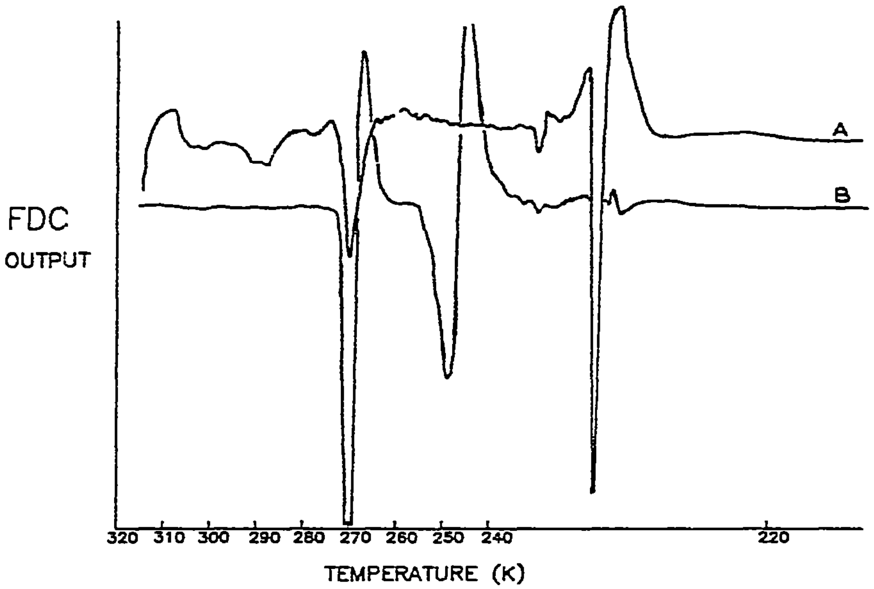

Fig. 16. Commercial cookie. A, wheat biscuit; B, ph soybean–coconut oil mix.

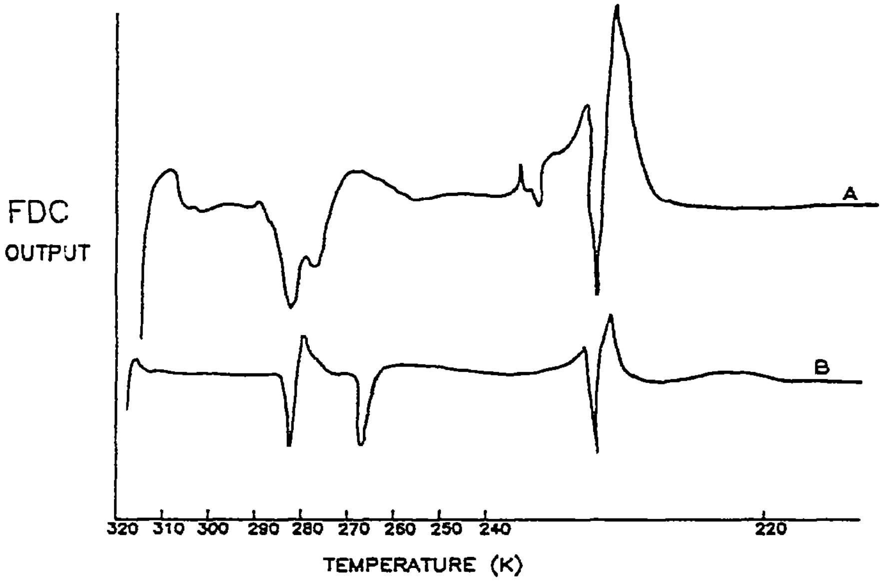

Fig. 17 Commercial cookie. A, shortbread cookie; B, ph soybean–palm oil mix.

CONCLUSIONS

A simple and rapid DSC–FDC method has been devised for verifying the identity of vegetable oils. The cooling rate was chosen to provide rapid scan times despite a loss of a portion of the FDC curves due to non-linear cooling. There proved to be sufficient, distinctive, FDC peaks outside of this non-linear region to provide adequate identity patterns or ‘finger-prints’. Variations of DSC–FDC behavior within an oil type due to geographical origin or plant strain must be considered before any positive identification of an oil can be made. This method however, can provide a library of curves against which the sample can be compared for rapid verification. Further, the method can be used to detect mixtures of oils and to verify the identity of a vegetable oil in a more complex food product matrix.

NOTE

The mention of any brand name does not constitute an endorsement by the U.S. Customs Service.

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