Determination of Oil in Fried Potato Products by Differential Scanning Calorimetry

Jose M. Aguilera* and Hugo Gloria

Pontificia Universidad Católica de Chile, Santiago, Chile, and Nestle Research Centre, Vers-chez-les-Blanc, Lausanne, Switzerland

Differential scanning calorimetry (DSC) was used to determine the oil uptake of commercial frozen par-fried potatoes after frying at 180 °C in colza/soybean oil. The enthalpy and temperature range of the crystallization peak for the pure frying oil were 47.2 J/g and −44 to −50 °C, respectively. DSC was performed by cooling samples of crust and core of fried potatoes from 10 to −60 °C at 1 °C/min and the oil content calculated from the peak area. The crust contained almost 6 times as much oil as the central core (23.6% vs 4%, dry weight basis), as visualized by light microscopy. Only 87% of the oil in the intact crust can be removed by solvent extraction, the rest being extractable only after grinding. Deviation between DSC and Soxtec extraction methods was less than 3%. The DSC method is fast, specific, and reliable, does not use solvents, requires smaller samples (<100 mg) than conventional solvent extraction methods, and can also detect freezable water.

Keywords: *Differential scanning calorimetry; oil; frying; fried potatoes; microstructure*

INTRODUCTION

Deep-fat or immersion frying is an old method of cooking and a widespread commercial food operation. The process involves simultaneous heat and mass transfer resulting in a countercurrent flow of water and oil with a net oil uptake by the product (Singh, 1995). In French fries dehydration and oil uptake are necessary to produce a desirable crisp crust with a characteristic flavor and a mealy interior. Recently, nutritional and economic concerns have called for a reduction in the oil content of fried products (Saguy and Pinthus, 1995).

Among many foods of vegetable origin, potatoes absorb the least amount of oil during immersion frying (Makinson et al., 1987), yet French fries contain between 14% and 18% oil (Lamberg, 1990; Wills et al., 1981). Most oil uptake is concentrated in a thin crust, 0.5−1 mm thick, as revealed by low-magnification light microscopy (Keller et al., 1986). Oil distribution in the porous crust of a fried potato strip is uneven and depends on its microstructure (Gamble at al., 1987). Thus, it is necessary to quantify the frying oil in small portions of a French fry to study the mechanisms of oil uptake and its specific location and to generate concentration profiles for mass transfer studies (Baumann and Escher, 1995).

Determination of oil or fat uptake in fried potatoes is usually performed by solvent extraction in a Soxhlet or similar apparatus (Pinthus et al., 1995; Kozempel et al., 1991; Lamberg, 1990). Refractometry and gas chromatography (GC) after oil extraction in organic solvents have also been utilized (Baumann and Escher, 1995; Keller, 1988). All methods involving solvent extraction have the limitation of requiring a dried sample of several grams (e.g., 2−5 g) and size reduction to accomplish exhaustive removal of the oil. In particular, Soxhlet-type extraction methods use flammable solvents and are time consuming (taking several hours), and oil content is determined gravimetrically after solvent evaporation. The GC method also requires grinding, extraction with solvents (chloroform/methanol), filtration, and resuspension in organic solvents before introducing in the GC apparatus. Differential scanning calorimetry (DSC) has been used to investigate the thermal conductivity and specific heat of fried foods (Buhri and Singh, 1994), to investigate the melting and crystallization of pure edible oils and fats (Kaisersberger, 1989), and to determine the residual moisture content in seeds (Tomassetti et al., 1986).

The objective of this study was to use DSC as a method to determine the amount of frying oil in small samples from different locations in fried potato products.

MATERIALS AND METHODS

Materials. Commercial frozen par-fried potatoes (Findus, Switzerland) contained 7% of prefrying fat. Instructions for preparation were to finish frying in hot oil at 180−190 °C. Frozen par-fried potatoes were fried as described below and are referred to hereafter as FPFP(x,y), where x is the frying time (s) and y is the cooling time after frying and before sample preparation for analysis (min). Bintje potatoes (19.5% total solids) as well as colza/soybean, colza, soybean, and groundnut oils were purchased at a local supermarket in Lausanne, Switzerland.

Frying Procedure. Frying was performed in a 500 mL glass beaker holding colza/soybean oil previously heated to 180 °C for 30 min over an electrically heated plate. The cc oil/g potato ratio was kept at 50 to achieve less than a 5 °C temperature drop during frying. Standard frying conditions were 150 s of frying time followed by 10 min of cooling/drainage. However, 30 s of frying time, zero cooling time, and blotting in a paper tissue immediately after frying were also studied. Crust and core were separated by sectioning a potato strip with a razor blade and scraping out the mealy interior from the crust with a fine spatula.

DSC Runs. A differential scanning calorimeter (Mettler DSC 820, Mettler Instrument AG, Volkestwil, Switzerland) was calibrated so that the onset of melting of pure ice occurred at 0 °C. Between 20 and 25 mg of frying oils (colza/soybean, soybean, groundnut, and colza) or 40−100 mg of fried material were weighed directly in medium pressure crucibles of 120 mL capacity. Samples of core material were placed directly in DSC

* To whom correspondence should be addressed [telephone, (562) 686-4254; fax, (562) 686-5803; e-mail, jmaguile@ing.puc.cl].

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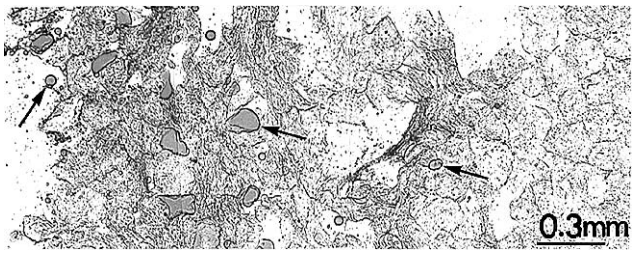

Figure 1. Photomicrograph of a thin cross section of a fried commercial par-fried potato. Crust is to the left, and oil droplets stained dark are pointed by arrows.

pans, while those from the crust were cut into small pieces (at least four) with a new razor blade so that no oil was lost during cutting (minute amounts of oil may adhere to the razor blade during cutting). DSC runs were performed on triplicate samples within the temperature range of 10 to −80 °C for oils and 10 to −60 °C for potato samples at a cooling rate of 1 °C/min using an empty pan as reference. Oil in fried potato products was calculated by dividing the integrated area under the exothermal peak corresponding to the oil (determined using the TAS810 Mettler datastation) by the crystallization enthalpy of the frying oil.

Analyses. Determination of oil by solvent extraction was performed in triplicate samples of ca. 3−4 g in a Soxtec apparatus (Tecator AB, Hoganas, Sweden) using extrapure hexane (Merck, Darmstadt, Germany) as solvent. Oil content was expressed on a dry matter (% db) basis. Total water (TW) was determined in three separate samples after the DSC runs and expressed on a wet basis (wb). Perforated pans having four small holes in their lids were placed in an oven at 105 °C overnight, cooled in a desiccator with P_2O_5, and weighed.

Residual Oil after Solvent Extraction. The effect of grinding in the residual oil in the crust of FPFP after solvent extraction was also assessed by DSC. Approximately 2−3 g of intact and ground crust (milled in a coffee grinder) was extracted three times for 15 min under agitation with 10 mL of extrapure hexane (Merck, Darmstadt, Germany), rinsed, and desolventized at room temperature.

Comparison of DSC and Soxtec Methods. Comparison of DSC and the Soxtec solvent extraction method was performed on the crust of strips (1 × 1 × 5 cm) of Bintje potatoes fried for 6 min at 180 °C and FPFP fried under standard conditions. Samples were ground in a coffee mill to achieve good homogenization and transferred to the DSC pans. Samples used in Soxtec analysis were dried in a vacuum oven for 6 h previous to extraction.

Determination of Accuracy and Sensitivity. Accuracy and sensitivity of the DSC method was assessed by DSC runs on control samples prepared by weighing directly into the pans known quantities of colza/soybean oil (1.2−22.2 mg), distilled water (5−45 mg), and lyophilized Bintje potato solids (40−70 mg).

Microscopy. Cross sections from FPFP(150,10) were rapidly frozen to −15 °C in the freezing stage of a Cryoset HM 500 microtome (Microm, Heidelberg, Germany) and cut into thin sections (12−15 mm thickness). Sections were picked up on gelatin-coated glass slides, dehydrated at room temperature for 6 h, exposed several times to a saturated solution of Sudan III in 65% ethanol at 60 °C, cooled over ice, and rinsed with distilled water. Stained sections were examined in a bright field microscope (Leitz, Ortoplan) and photographed.

RESULTS AND DISCUSSION

Oil Location. FPFP consist of two distinctive structures: an outer crust (ca. 1.2 mm thick) formed by dehydrated cells containing most of the oil and a core of round hydrated cells extending over 85% of the thickness of the strip (Figure 1). Most of the oil in the crust is held as drops (50−100 μm in size) in voids or blisters. Fewer and smaller oil droplets, generally positioned between intact cells, are observed toward the interior, giving a sharp inward gradient of oil in the cross section. The core of a FPFP is formed by tightly packed intact cells resembling those of a cooked potato (Spiruta and Mackey, 1961).

DSC Tracings of Pure Oils. Preliminary experiments (not reported) showed that lowering the cooling rate to 1 °C/min led to sharper crystallization peaks for oils (Figure 2). The crystallization peak of the colza/soybean oil (−47 °C) was intermediate between that of pure soybean (−59 °C) and colza oils (−45 °C). Crystallization was chosen over melting because the peak was narrower and farther removed from the freezing point of water, which is important to avoid interference in the case of hydrated samples (Figure 2). Complete crystallization of pure and extracted colza/soybean oil between −44 and −50 °C was confirmed by the absence of other peaks when cooling down to −110 °C. An enthalpy of crystallization of 47.2 J/g calculated by integration of the peak area under the DSC tracing was used later to determine oil contents in fried samples. Linearity of the peak area versus oil sample size extended in the range of 1 and 25 mg of oil. As discussed by Kaiserberger (1989), the range and peak shape of crystallization/melting transitions for oils are the result of overlapping effects from fatty acid composition, polymorphism, and thermal history. The uniqueness and sharpness of peaks shown in Figure 2 assure that the DSC technique can be used safely for several frying oils.

DSC Tracings of FPFP. The crust was easily isolated by scraping out the wet and mealy central part or core from a FPFP. As there is no exact boundary between crust and core, their composition and relative weights depend on the sample separation process. DSC tracings (Figure 3) of the crust and core of FPFP(150,10) show peaks corresponding to the freezable water, FW (around −24 °C), and oil (−46 to −50°C). The area under the oil peaks for crust and core, which is proportional to the oil content and the sample, resulted in calculated oil contents of 23.6% and 4%, respectively (Table 1). The peak representing oil held in the crust is slightly wider that of the pure oil (Figure 1). This difference may be attributed either to the presence of oil in a porous and dehydrated matrix (crust) or to differences in heat transfer from the instrument to irregular pieces of crust inside the crucibles. As expected, the crystallization peak for water at −20 °C was broader than that of pure ice as water is known to interact with starch (Liu and Lelievre, 1992), and the baseline remained constant below the FW peak. The calculated enthalpy of phase change for the peak of distilled water was 324 J/g, which compares well with the value of 334 J/g reported by Raemy and Lambelet (1991).

Oil and Water Content. Table 1 shows the oil content, total water (TW), and fraction of TW as freezable water (FW) of different samples of FPFP. The average oil contents of the crust and the core of FPFP-(150,10) were 23.6% and 4%, respectively. When the crust was blotted in paper tissue immediately after frying, a practice utilized in most frying studies, the oil content in the crust fell to 19.2%. Blotting is difficult to standardize as part of an analytical procedure, although it is effective in removing nearly one-fifth of the oil held superficially in the crust. Oil in the crust of FPFP(30,10) was already 22.8%, suggesting that under this condition oil uptake is due to wetting of the outer surface (Gamble et al., 1987).

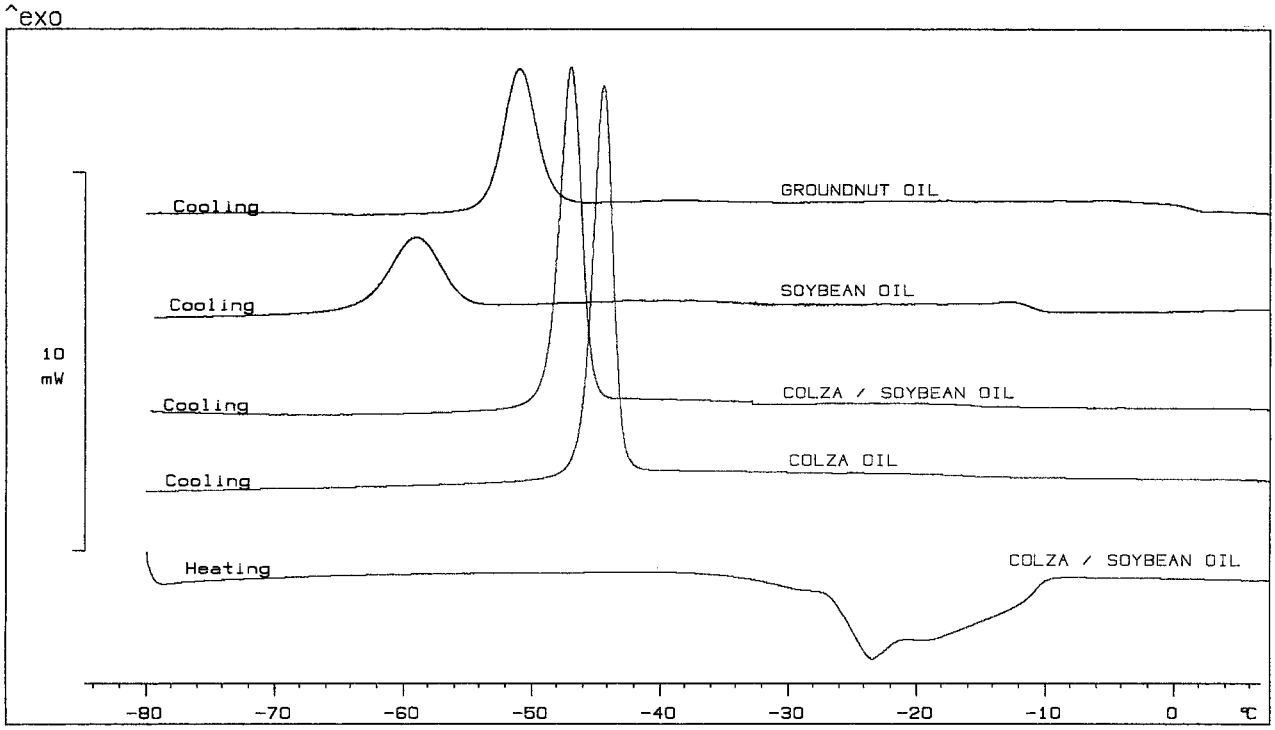

Figure 2. DSC tracings of a cooling/heating cycle of colza/soybean oil and for cooling of other frying oils (soybean, colza, and groundnut).

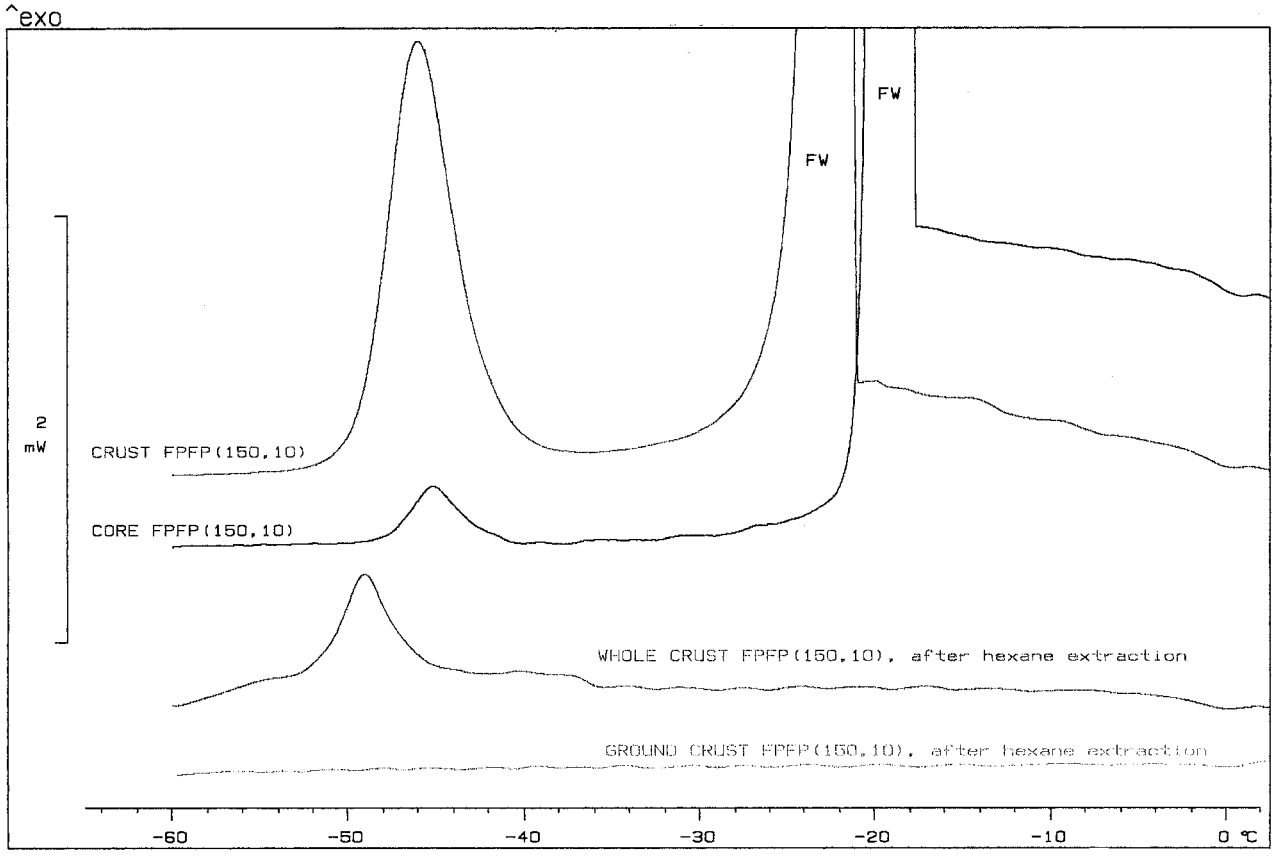

Figure 3. DSC tracings of the crust and core of a fried commercial par-fried potato showing peaks for oil and freezable water (FW). At bottom, curves for crust solvent extracted whole and ground.

DSC was particularly adequate to determine the residual oil content after hexane extraction of intact and ground crust of FPFP(150,10). Only 87% of the total oil could be removed from the intact crust (residual oil 3.1%, Table 1), suggesting that this fraction is accessible to the solvent while the rest is physically occluded between or inside cells. However, the extracted ground sample presented no oil peak in the thermogram meaning that all the oil was removed during extraction (Figure 3). Absence of the freezable water peak in hexane-extracted samples (bottom of Figure 3) is due to drying previous to extraction. Avoidance of grinding

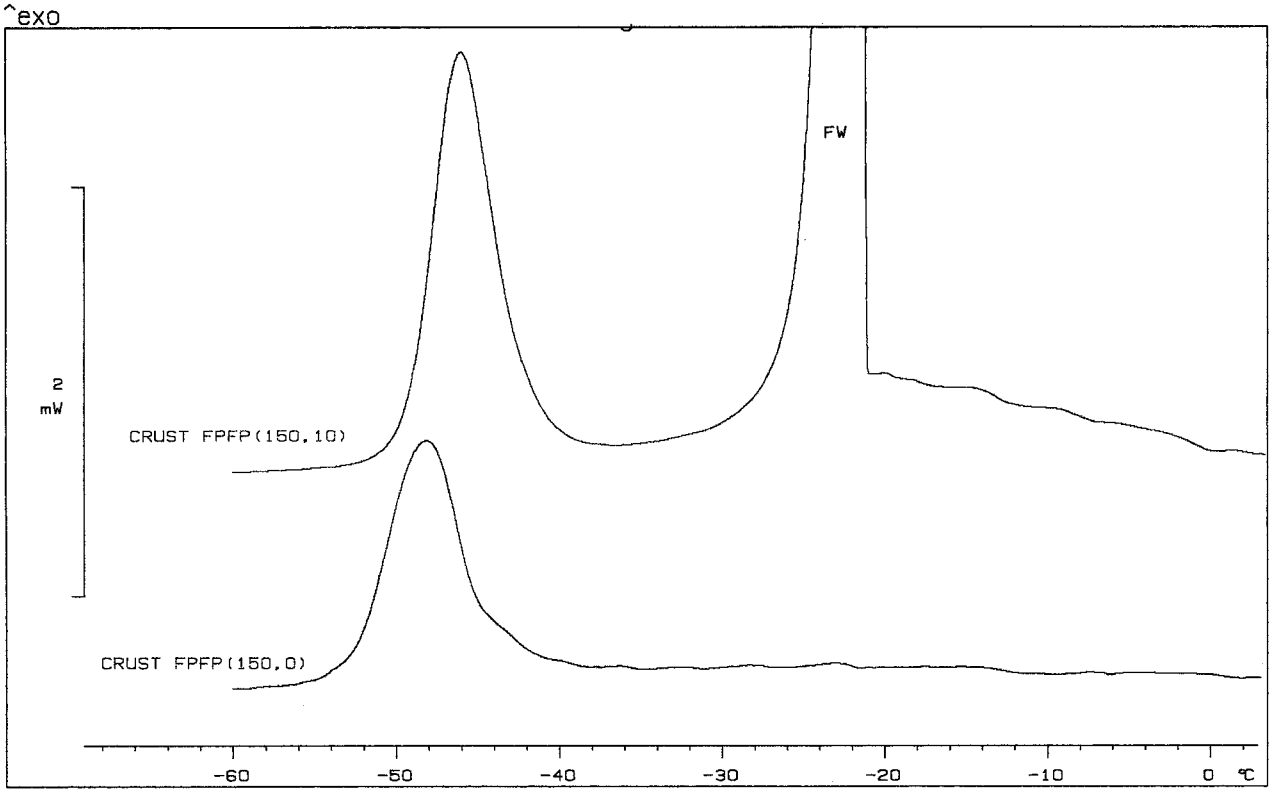

Figure 4. Effect of cooling time after removal of the potato strip from the fryer on the amount of freezable water (FW) in the crust.

Table 1. Oil, Total Water, and Fraction of Freezable Water in Core and Crust of FPFP As Detected by DSC[a]

sample	oil (% db)	total water (% wb)	fraction of FW
crust FPFP(30,10)	22.8 ± 0.5	45.7 ± 1.6	0.66
crust FPFP(150,0)	20.8 ± 1.9	16.5 ± 1.8	nd
crust FPFP(150,10)	23.6 ± 3.6	31.9 ± 1.7	0.40
crust FPFP(150,10), blotted	19.2 ± 2.6	27.2 ± 2.8	0.18
core FPFP(150,10)	4.0 ± 4.1	76.9 ± 1.6	0.89
crust FPFP(150,10), whole[b]	3.1 ± 1.5	27.8 ± 6.2	nd
crust FPFP(150,10), ground[b]	nd	22.1 ± 0.3	nd

[a] Numbers in parentheses represent frying time (s) and cooling time (min) before sample preparation for DSC. [b] After hexane extraction. nd = not detectable.

Table 2. Oil Content in FPFP and Fried Bintje Potato Strips As Determined by DSC and Soxtec Methods (% db)

sample[a]	DSC	Soxtec
fried Bintje potatoes	17.2 ± 0.78	16.7 ± 0.39
FPFP	23.9 ± 1.0	23.8 ± 0.9

[a] Ground crust.

is an advantage of the DSC method over all other methods currently reported since effective grinding requires a brittle sample (normally achieved by predrying) and releases oil which adheres to the interior of the mill. Breakdown of microstructure by physical means (grinding or flaking) is widely practiced in food analysis and by industry to achieve full oil extraction by solvents (Aguilera and Stanley, 1991).

As shown in Table 1 the TW in the core of FPFP(150,10), 76.9%, was similar to that of raw potato and much higher than the TW of the crust (31.9%). The crust of FPFP(30,10) had a TW content of 45.7%, revealing less dehydration than after 150 s of frying. When core and crust were separated immediately after frying, the TW of the crust of FPFP(150,0) was 16.5%, or almost one-half of that of FPFP(150,10). This difference in TW of crusts is due to water diffusion from the wet core during the 10 min cooling period before separating both parts. The phenomenon is well-known to fast-food processors because it leads to fries with a "limp" texture within minutes of frying (Weaver and Huxsoll, 1970). It can only be hypothesized at this time that this water plasticizes the amorphous starch in the dehydrated outer layer resulting in progressive textural changes from a crisp to a soggy and limp crust (Slade and Levine, 1991).

FW represents the fraction of TW that becomes ice during cooling in the DSC. Almost 90% of the water in the core of FPFP(150,10) was "freezable", while, as expected, lower proportions of FW were found in the crusts (Table 1). A larger proportion of FW was found in the crust after 30 s of frying than after 150 s (0.66 versus 0.40). Apparently, blotting was effective in reducing the FW in the crust from 40% to 18% of the TW. No FW was detected in the thermogram of the crust of FPFP(150,0), while for FPFP(150,10) it amount to 40% of the TW (Figure 4 and Table 1). This result confirms that considerable moisture migrates from the core to the crust during cooling and shows up as FW.

In some cases large standard deviations were observed in Table 1 for oil and water contents. There are several sources for this variability: the heterogeneity of the potato tissue itself and of the oil distribution in the crust (Figure 1) and differences in the effectiveness of separation of crust and core.

Reliability of the DSC Method. Specificity, sensitivity, and accuracy are important characteristics of an analytical method (Pomeranz and Meloan, 1994). The specificity of the DSC method depends on the presence of thermal transitions of interfering substances in the temperature range where oil crystallization occurs. In our case the DSC baseline for a commercial par-fried potato did not show thermal transitions in the temper-

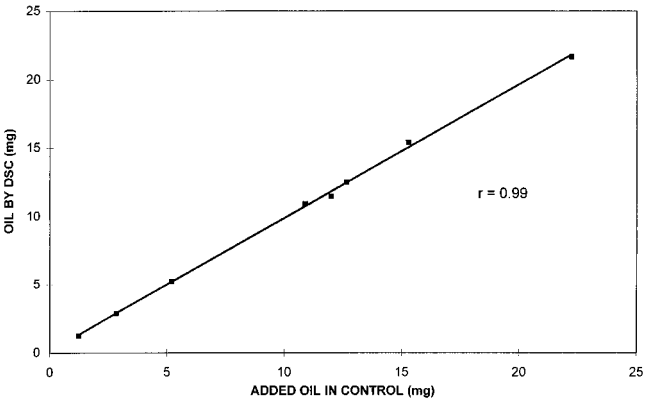

Figure 5. Relationships between amount of oil added in a prepared control and that determined by DSC.

ature range of −40 to −80 °C. Interference may arise if crystallization of the frying oil occurs at a temperature close to the solidifying point of water, which was not the case for the oils under study (Figures 2 and 3).

Average (standard deviation) oil contents determined by DSC and Soxtec extraction of ground samples of crust material from fried Bintje potato strips were 17.2% (±0.8) and 16.7% (±0.4). For ground FPFP(150,10) crust the oil contents were 23.9% (±1.0) and 23.8% (±0.9), respectively (Table 2). The deviation between the two methods was less than 3%. While the average sample weight for DSC was 0.069 g, that required for the Soxtec was at least 40 times larger (3 g). Since in the Soxtec method the oil content is quantified by gravimetry after extraction, it gains precision as the sample weight increases.

Accuracy, defined as the degree to which a mean estimate approaches a true value of the analyzed substance, was assessed by DSC of controls with known quantities of oil, water, and lyophilized Bintje potato. Figure 5 shows that a linear correlation existed (r^2 = 0.99) between oil content determined by DSC and the known weights of oil in controls. Sensitivity is the ratio between the magnitude of the instrumental response and the actual amount of the substance. Figure 5 also shows that the previous linear relationship extended to total oil contents as low as 1 mg.

CONCLUSIONS

DSC has been effective in quantifying the oil content of small samples (<100 mg) of fried potato products. Values are similar to those obtained by Soxtec solvent extraction, but the method is faster, uses no solvent, and requires less sample weight. DSC is particularly useful to quantify oil in small specimens of fried potato products and potentially to study oil uptake and location. It gives information on the freezable water as well. The method is specific, accurate, and sensitive to at least 1 mg of oil.

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