Supercritical Fluid Extraction of Encapsulated Oil Products

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ABSTRACT: Standard methods of oil analysis, for example, Soxhlet extraction and supercritical fluid extraction (SFE), were ineffective for recovering oil from encapsulated food products. Efforts were made to enhance SFE of the oil for these products. Samples were hydrated and heated, which helped to break down the encapsulating structure. In addition, extra diatomaceous earth was needed to absorb and disperse the added water. Optimal extraction conditions were established, and quantitative extraction of oil was achieved for various laboratory-prepared and commercially encapsulated food products.

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KEY WORDS: Diatomaceous earth, encapsulated oil, encapsulation, freeze-dry, oil extraction, spray-dry, supercritical fluid extraction.

Total oil content in food is normally determined by solvent extraction, and often the choice of solvent is critical for the analysis (1,2). The effectiveness of the extraction also depends to a degree on the processing characteristics of the sample. Sometimes, bound lipids in the sample may not be totally accessible to the solvent, and prior treatments, such as acid or heat hydrolysis, have been required to improve recovery (3,4). Generally, traditional extractions employing organic solvents are time consuming and the solvents are potential hazards to both users and the environment.

Supercritical fluid extraction (SFE) with carbon dioxide has become popular in recent years for small-scale oil extraction and as an analytical method. Carbon dioxide is nontoxic, noncombustible, easy to remove, and inexpensive. SFE is environmentally safe, timesaving, and can be automated (5). Fat recoveries for SFE and traditional solvent extractions are generally in good agreement (6), and the precision of analytical SFE is comparable to or better than that of the traditional methods (5).

A number of lipid-based products such as fish oil and vitamin A are unstable and easily oxidized. These products are often encapsulated by barrier materials in a network structure to prolong shelf life and enhance food-use functionality (7,8). However, encapsulation, commonly carried out by spray-drying, freeze-drying or extrusion, can also hinder the extractability of the lipid components, which may impede analysis and testing for quality control purposes. As a result, solvent or SFE recovery methods may need to be modified to ensure effective analysis for these samples.

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Here, we report our investigation of the SFE of encapsulated and stabilized oil samples prepared by freeze-drying or spray-drying. Results were compared with those obtained from the traditional Soxhlet method using petroleum ether. Effects of sample hydration and the presence of diatomaceous earth on the analysis were studied, and conditions were established for the enhancement of the analysis.

EXPERIMENTAL PROCEDURES

The encapsulation of rice oil was conducted as follows: Dissolve 1 g co-dried blend of microcrystalline cellulose and carboxymethylcellulose (Avicel; FMC Corporation, Newark, DE), in 50 mL water, and add 4 g lecithin (MC Thin HL66; Lucas Meyer, Decatur, IL), with good agitation. Slowly add 30 g rice bran oil (100% pure, Loriva Supreme Foods, Ronkonkoma, NY) in a thin stream while homogenizing at 24,000 rpm with a 25 GM-25F homogenizer probe (IKA, Wilmington, NC) for 2 min after all of the oil has been added. Dissolve 20 g gelatin (GP6 gelatin 200 bloom, Hormel Foods, Austin, MN) in 50 mL water at 60°C. Slowly add the gelatin solution to the rice oil emulsion and homogenize the mixture. Dissolve 20 g sodium caseinate (Sigma Chemical, St. Louis, MO) and 20 g maltodextrin (Maltrin M-100; Grain Processing Corp., Muscatine, IA) in 160 mL water at 50°C. Slowly add the rice oil mixture to this solution, again homogenizing for 5 min.

Emulsified oil samples were spray-dried or freeze-dried. Spray-drying was conducted using a Yamato Pulvis GB22 spray dryer (Yamato Inc., Orangeburg, NY) at 160°C inlet temperature, 80–82°C outlet temperature, 1.4 kg/cm^2 atomizing air pressure, and 0.4 m^3/min drying air flow rate. The sample flow rate was adjusted from 12–18 mL/min to obtain the desired outlet temperature. Freeze-drying was conducted using a Virtis 20 SRC-X Freeze Dryer (Gardiner, NY).

Oil was analyzed by Soxhlet and SFE methods. In the Soxhlet extraction, powdered sample (1.5 g) was placed in a thimble and extracted continuously for 4 h with the condensate of 100 mL boiling petroleum ether through the Soxhlet recycling system. The petroleum ether was removed with a Rotovap (Büchi, Westbury, NJ), and the flask with oil was heated to 110°C for 30 min and cooled to room temperature in a desiccator for 30 min. The flask was then weighed to determine the oil in the sample.

In a regular SFE extraction, the oil analysis was conducted using an ISCO SFX 2-10 Supercritical Fluid Extraction System (ISCO, Lincoln, NE). The extraction cartridge was filled sequentially with 2 g sand, 1.5 g diatomaceous earth (Sigma Chemical), 1.5–2.0 g of the dried sample powder, and then

diatomaceous earth to the top. The sample was held statically at 100°C, 7500 psi carbon dioxide for 10 min and extracted dynamically at a flow rate of 2.7 mL/min for 24 min. Oil was collected on glass wool through coaxially heated restrictors at 140°C and weighed after cooling to constant weight.

In a modified SFE extraction, the dried sample was first hydrated in a 20–30% aqueous suspension. The mixture was heated at 90°C for 30 min. Diatomaceous earth was then added to the hydrated and heated sample at w/w ratios of 1:2, 1:1, 2:1, and 5:1 to a total weight of 1.5–2.5 g for the mixture. Oil analysis was subsequently conducted at the 2:1 ratio of diatomaceous earth to hydrated and heated sample following the procedure described above in a regular SFE analysis.

Oil analyses were also conducted using the modified SFE method for commercially encapsulated oil products including oil-based flavor products of Kraft Fried Flavor and Kraft Richmix 50 (Kraft Food Ingredients, Memphis, TN). According to the manufacturer, Kraft Fried Flavor is used for fried foods and Kraft Richmix is for coffee creamers.

Oil analysis was done in triplicate. Values are reported as the mean ± standard deviation, determined in MS Excel (vs. 9) (Redmond, WA).

RESULTS AND DISCUSSION

Effectiveness of oil extractions. As shown in Table 1, neither the SFE method using carbon dioxide as the extracting agent nor the Soxhlet method using petroleum ether is capable of extracting oil effectively from the freeze-dried or spray-dried samples. The reason is that the samples are prepared by encapsulating nonpolar oil in polar carbohydrate and protein-based materials. Compressed carbon dioxide fluid and petroleum ether can easily extract oil from nonencapsulated products as evidenced by the nearly quantitative recovery of oil from the control. However, these solvents have difficulty penetrating the encapsulating network and are not effective in extracting the encapsulated oil. Of the two methods, SFE appears to be more effective than the Soxhlet method. However, even the SFE method recovers only slightly more than half the oil present in the freeze-dried sample and only about 20% in the spray-dried sample.

Modified SFE extraction. Efforts were made to improve the SFE for the analysis of oil in encapsulated environments.

TABLE 1
Effectiveness of Oil Extraction by Regular Methods

Sample	SFE (% oil)	Soxhlet (% oil)
Freeze-dried	54.5 ± 2.3	26.5 ± 0.4
Spray-dried	20.1 ± 1.6	4.7 ± 0.4
Reference[a]	99.6 ± 2.9	101 ± 1.8
Freeze-dried and treated[b]	99.8 ± 2.7	32.3 ± 0.9

[a]Reference sample was prepared by simple mixing of oil and ingredients as used in the freeze-dried or spray-dried sample.
[b]Sample was freeze-dried and hydrated in diatomaceous earth under modified conditions as described in the Experimental Procedures section. SFE, supercritical fluid extraction.

Normally, water has a negative effect on lipid extraction. The removal of moisture prior to the extraction has been reported to enhance the SFE of foods (9). Absorbents such as diatomaceous earth are generally added to regular SFE to absorb and reduce the amount of water. However, as compressed liquid carbon dioxide is a poor solvent for polar materials, polar compounds such as water may be useful for breaking down the encapsulating network of polar materials so that the oil is accessible for extraction (10).

Experiments were designed to study the effects of hydration and heating, extra diatomaceous earth, and amount of sample on the SFE oil analysis. Essentially, as a pretreatment, samples were hydrated and heated to ensure the breakdown of the encapsulating network. Diatomaceous earth was then added at various ratios, and the mixture was analyzed following the regular SFE procedure. Figure 1 shows the change in the percentage of oil extracted for the freeze-dried sample as a function of the w/w ratio of diatomaceous earth to hydrated and heated sample. The effectiveness of oil extraction increased as the ratio of diatomaceous earth to hydrated and heated sample increased. At the 1:2 ratio, only 44.8% of oil was recovered, whereas at the 2:1 ratio and beyond, it was 99.8%.

Sample hydration and heating, followed by diatomaceous earth dehydration, were effective in enhancing the SFE of encapsulated oil samples but were less effective in enhancing the Soxhlet extraction (Table 1). For the SFE analysis, hydration and heat treatment appeared to make the encapsulated oil more accessible, probably by loosening the encapsulating structure prior to the extraction. The addition of diatomaceous earth most likely controlled and lowered the water content and facilitated sample dispersion. The results indicate that a

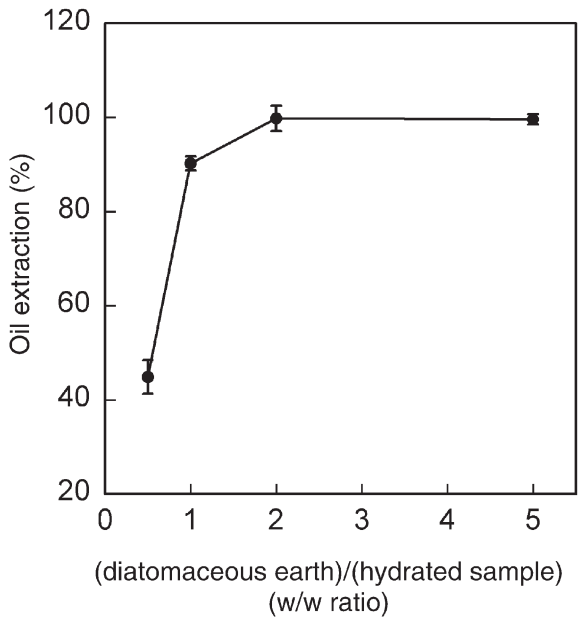

FIG. 1. Effect of extraction conditions on oil analysis. Diatomaceous earth was added to the hydrated sample at w/w ratios from 1:2 to 5:1, and the oil content was analyzed by the modified supercritical fluid extraction method.

TABLE 2
Analysis of Encapsulated Oil Products by the Modified SFE

Sample	Treatment	Total oil reported (%)	Total oil recovered (%)[e]	Oil encapsulated (%)[e]
Rice oil	Spray-dried	31.6[c]	101 ± 2.2	92.5 ± 1.9
Rice oil	Freeze-dried	31.6[c]	99.8 ± 2.7	92.1 ± 3.1
Flavor oil	Spray-dried[a]	40.0[d]	95.6 ± 0.6	93.0 ± 1.8
Flavor oil	Spray-dried[b]	49.9[d]	95.6 ± 1.5	98.4 ± 6.3

[a]Commercially encapsulated flavor oil (Kraft Fried Flavor; Kraft Food Ingredients, Memphis, TN).
[b]Commercially encapsulated flavor oil (Kraft Richmix 50; Kraft Food Ingredients).
[c]Calculated from the ingredient formulation.
[d]Reported by the manufacturer.
[e]Based on total oil reported as 100%.

2:1 ratio of diatomaceous earth to hydrated sample would be most suitable for the SFE analysis of the encapsulated oil.

Analysis of encapsulated oil. The amount of oil encapsulated in laboratory-prepared and commercial products was determined. Samples, with and without prior washing with hexane, were analyzed by the modified SFE method. Amounts of encapsulated oil were obtained from the washed samples, whereas differences between the washed and unwashed samples were used to determine the free or unencapsulated oil. Table 2 shows data from analysis of oil products encapsulated by various materials and methods. The first two samples were laboratory-prepared rice oil products encapsulated, using carbohydrate and protein-based materials, by spray-drying and freeze-drying. Under conditions as described earlier, the modified SFE procedure quantitatively recovered the oil in the unwashed sample. Extraction of the hexane-washed sample showed that 92% of the total oil was encapsulated for both samples. Both spray-drying and freeze-drying appeared to be effective for the rice oil encapsulation, and the modified SFE was an effective method of oil analysis for the products. The flavor oil samples were spray-dried commercial products. Again, the modified SFE procedure appeared to be successful in confirming the oil content, as reported by the manufacturer in the unwashed sample. The total oil extracted in the unwashed sample was about 96% for both samples, and the encapsulated oil was 93 and 98% for flavor oil samples *a* and *b*, respectively.

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