Quantitative Analysis of Oil Removal from Cotton Fabrics Through the *in situ* Formation of Microemulsions by Solid-State Nuclear Magnetic Resonance

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ABSTRACT: Solubilization and subsequent removal of soybean oil from cotton fabrics through the *in situ* formation of microemulsions were evaluated by solid-state nuclear magnetic resonance (NMR) spectrometry. Regions of water-in-oil and oil-in-water microemulsions were identified for systems that contained polyoxyethylene (60) sorbitol hexaoleate, soybean oil, and an aqueous phase composed of water/ethanol or isopropanol (80:20 wt%) at 25°C. The amount of oil removed from the cotton fabrics was determined by solid-state NMR after constructing a calibration curve relating the intensity of camphor/oil NMR signals (I_c/I_0) to their molar ratio (M_c/M_0). A precision Crockmeter (Mul-Tech Industries, New York, NY) was used to reproducibly remove soybean oil stain from cotton fabric, which was subsequently analyzed by NMR. Typically, more than 90% of the oil stain was removed after 200 revolutions of the Crockmeter finger with 2 wt% surfactant at 25°C. Increasing the amount of surfactant to 6 wt% improved soybean oil removal from the fabric to 99 wt%.

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KEY WORDS: Cotton fabric, microemulsion, oil removal, phase diagram, solid-state NMR.

Removal of oil stains from surfaces occurs through three different mechanisms—rollback, direct emulsification, and oil solubilization (1–3). Rollback is the mechanism by which droplets of soil and aqueous surfactant are formed and either detached spontaneously or washed from the surface. The second is direct emulsification of the oil, which can be removed spontaneously or, if necessary, by applying additional energy. The third is based on oil solubilization into surfactant micelles or the formation of an intermediate phase, which contains oil, surfactant, and water and is more easily removed than in their absence.

Many investigators (4–7) have concluded that optimum detergency occurs near or at the phase inversion temperature (PIT) of the oil–water–surfactant, and thus depends on the composition of both surfactant and oil. The patent literature described different methods and compositions for the removal of stains. Joubran and Parris (8) described a process for the removal of oil stains through the generation of microemulsions. Swered and Girard (9) studied the synergistic activity of compositions containing polyoxyethylene sorbitol hexaoleate and 1,3-dichloroacetone oxime acetate against microorganisms. Others have described a novel process for the treatment of textile materials, as well as a stable isotropic liquid detergent that contained a particular silicone suds-controlling agent (10,11).

A number of different methods for detecting the removal of oil stains have been used. The American Society for Testing and Materials (ASTM) Method D-4265-83 (12) provides guidance for the selection, preparation, application, and examination of various types of stains on test fabrics. Other methods describe the use of electron microscopy (13,14), radiotracer analysis, Geiger and liquid scintillation counting (15), reflectometry (16), and nuclear magnetic resonance (NMR) (5) for measuring and reporting stain removal effectiveness. In this report, a procedure for the removal of a triglyceride, soybean oil, through the *in situ* generation of microemulsions is described. The removal of the oil stain is quantitated by solid-state NMR.

EXPERIMENTAL PROCEDURES

Materials. Cotton fabric, Birdseye, was obtained from Testfabrics, Inc. (Middlesex, NJ). Soybean oil was from Central Soya (Philadelphia, PA); ethanol, The Warner-Graham Co. (Cockeysville, MD); toluene and isopropanol, J.T. Baker Chemical Co. (Philipsburg, NJ); osmium tetroxide, Electron Microscopy Sciences (Fort Washington, PA); propyleneglycol, Sigma (St. Louis, MO); and polyoxyethylene (60) sorbitol hexaoleate, Henkel (Mauldin, SC); all were used as supplied.

Methods. To identify microemulsion regions, phase diagrams were constructed by titrating either soybean oil–surfactant or aqueous phase–surfactant mixtures with water–ethanol solutions or soybean oil, respectively, at 25°C. The phase boundaries of the microemulsion regions were found by vi-

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sual observation of the change from turbidity to transparency and were checked for anisotropy under polarized light as reported previously (17).

Staining of fabric. To ensure the homogeneity of oil on the fabric surface, a cotton fabric (4 × 4″) was immersed in a soybean oil (10 wt%) toluene solution, then mounted horizontally to dry overnight.

Solid-state NMR. All ^{13}C NMR spectra were obtained on a Bruker MSL-300 (Bruker, Karlsrube, Germany), operating at 75.5 MHz and equipped with a Doty Scientific CPMAS (Cross-Polarized Magic Angle Spinning; Doty Scientific, Columbia, SC) NMR probe. A 1.9-μs (45 pw) carbon pulse width was used. The spectra were collected with a gated decoupled sequence and a 12-Gauss decoupled field. A 15-s recycle time was used to eliminate any nuclear overhauser effect buildup. Samples, approximately 60 × 10 mm, 0.3 g, were placed in 0.5-mL zirconium oxide tubes (Doty Scientific). The samples were spun at the magic angle at a rate of approximately 500 Hz to eliminate any line broadening caused by anisotropic motion of the lipid. Transients (1,024) were collected and Fourier-transformed with a 10-Hz broadening factor. A piece of cotton fabric was cut and weighed (0.0500–0.0700 g); then, different ratios of oil/camphor were weighed into NMR tubes, which were later sealed. The molar ratios (M_c/M_0) were calculated and used for constructing the calibration curve vs. the intensity ratios (I_c/I_0).

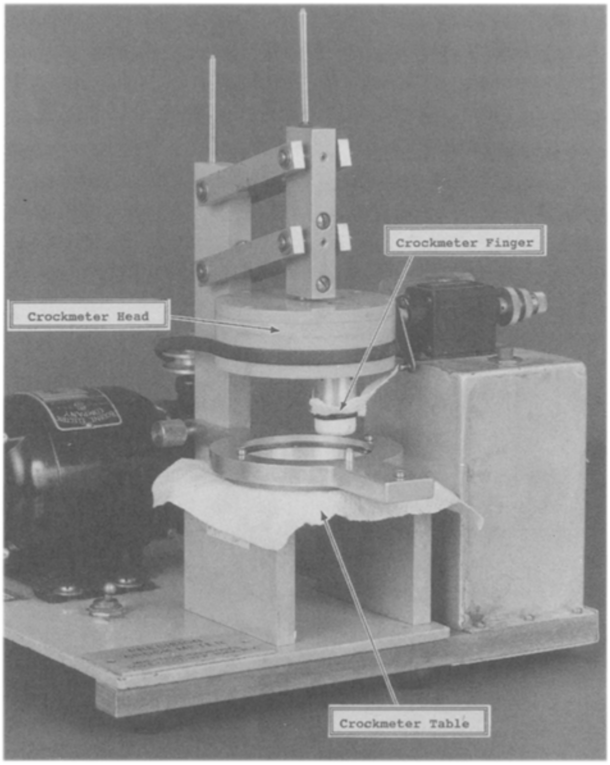

FIG. 1. Photograph of Precision Crockmeter (Mul-Tech Industries, New York, NY).

Removal of oil stain. Oil was removed by washing stained fabric with a surfactant/aqueous phase mixture to generate the microemulsion *in situ*. To simulate the cloth-to-cloth rubbing action of the stained fabric, a Precision Crockmeter (Mul-Tech Industries, New York, NY) was used. The cloth is placed on the surface of the Crockmeter table (Fig. 1), and a head carrying the Crockmeter finger, with a piece of the same cloth mounted over the finger, is lowered onto the surface. A mixture of 5 g surfactant/aqueous phase was applied to the cloth, and the Crockmeter head was allowed to rotate for a specific number of revolutions on the sample fabric. The crock finger also rotates slowly in relation to the head, thus producing a sliding–rubbing action on the cloth. The cloth was removed and rinsed under tap water for two minutes. The amount of soybean oil removed from the washed (the term "washed" is used to indicate treatment with surfactant and crocking process) portion of the fabric (sample) was then quantitated by solid-state NMR. The amount of oil on the unwashed portion of the same fabric (blank) was also quantitated by the same technique. M_0 was determined from the calibration curve (Fig. 2), and grams of soybean oil were calculated and normalized for one square meter of fabric. The removal of soybean oil from fabrics was expressed as the weight percent of oil removed compared to the unwashed fabric according to the following equation:

$$\text{wt\% oil removed} = [(\text{grams of oil})_{\text{blank}} - (\text{grams of oil})_{\text{sample}}] \div (\text{grams of oil})_{\text{blank}} \times 100 \qquad [1]$$

where the sample was the washed portion of fabric; and the blank was the unwashed portion of fabric.

Scanning electron microscopy. Ten-mm square patches of each fabric sample were immersed in a 4% aqueous solution of osmium tetroxide for one hour at room temperature. Then, the patches were washed in distilled water and air-dried. Dry patches were mounted on specimen stubs with colloidal silver adhesive, then coated with a thin layer of gold by DC sputtering. Images of yarns in the fabric samples were made

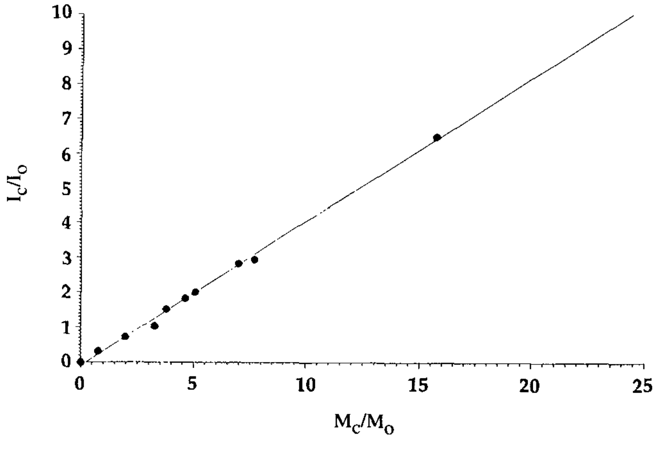

FIG. 2. Calibration curve of intensity ratio (I_c/I_0) of signals 43.7/128.6 vs. molar ratio (M_c/M_0) of camphor/oil in systems containing cotton fabric with known amounts of soybean oil and camphor.

in the secondary electron imaging mode with a JEOL 840A electron microscope (JEOL USA, Peabody, MA).

RESULTS AND DISCUSSION

Microemulsion systems have been suggested for the removal of oil stains from various fabrics; however, triglyceride molecules are more difficult to solubilize into microemulsion systems than hydrocarbons (18). Recently, however, a bicontinuous microemulsion region has been identified for systems that contained polyoxyethylene 40 sorbitol hexaoleate, soybean oil, and aqueous phase (water/ethanol, 80:20 wt%), which maximizes the solubility of the oil in aqueous systems (19). These microemulsion regions were maximized by changing the type and composition of both the surfactant and the aqueous phase. The preparation of triglyceride or alkane microemulsions and the effect of cosolvents, composition, and temperature have been reported (17–19). Figure 3 shows the phase diagram of systems that contained soybean oil, polyoxyethylene (60) sorbitol hexaoleate, and an aqueous phase composed of water/ethanol (80:20 wt%), water/ethanol/sucrose (70:20:10 wt%), and water/isopropanol (80:20 wt%). Figure 3A, which represents 80:20 wt% of water/ethanol, consists of two separated microemulsion regions: oil-in-water (L$_1$) and water-in-oil (L$_2$). Addition of sucrose (Fig. 3B) or replacing ethanol with isopropanol (Fig. 3C) results in the formation of a continuous microemulsion region from the oil–surfactant side to the aqueous corner of the phase diagram. The composition of the L$_1$ region (Fig. 3A) was used for removing oil stains from the cotton fabrics in this study.

Solid-state NMR was selected over other methods for the quantitation of oil removed because it is nondestructive and does not require extraction with various organic solvents. Figure 4 shows ^{13}C NMR spectra of cotton fabric (Fig. 4A) with soybean oil (Fig. 4B) and an internal standard, camphor (Fig. 4C). Because of the low signal-to-noise ratio of the cotton fabric (Fig. 4A), 16,384 transients were required to obtain a suitable spectra although all other spectra were from 1,024 transients. The signals at 43.7 and 128.6 ppm correspond to the methyl groups of the camphor and the double bonds of the soybean oil, respectively (Fig. 4D). After washing the fabric (Fig. 4E) with a solution containing 6 wt% of surfactant and 94 wt% of aqueous phase (80:20 wt% water/ethanol), the signal at 128.6 is no longer present, indicating that the soybean oil was removed from the fabric within limits of detection.

The removal of oil from stained, washed fabrics, observed in NMR spectra, was confirmed independently by examination of yarns by scanning electron microscopy of stained, washed, and control fabrics (Fig. 5). Fibers in yarns of the stained fabric were almost completely coated with oil, which filled the interfibrillar spaces. After washing, yarns contained distinct, separate, cotton fibers with surface features that compared with surfaces of fibers in unstained cotton fabric (control).

Quantitation of oil stain removal from the fabric was accomplished by constructing a calibration curve prepared with cotton fabric and known amounts of soybean oil and camphor (Fig. 2). Camphor was selected as the internal standard because its NMR signal does not overlap with the soybean oil signals (confirming Fig. 4D). The calibration curve compares the intensity ratio of the NMR signals for the camphor and oil (I$_c$/I$_0$) at 43.7 and 128.6 ppm, respectively, as well as their molar ratio (M$_c$/M$_0$).

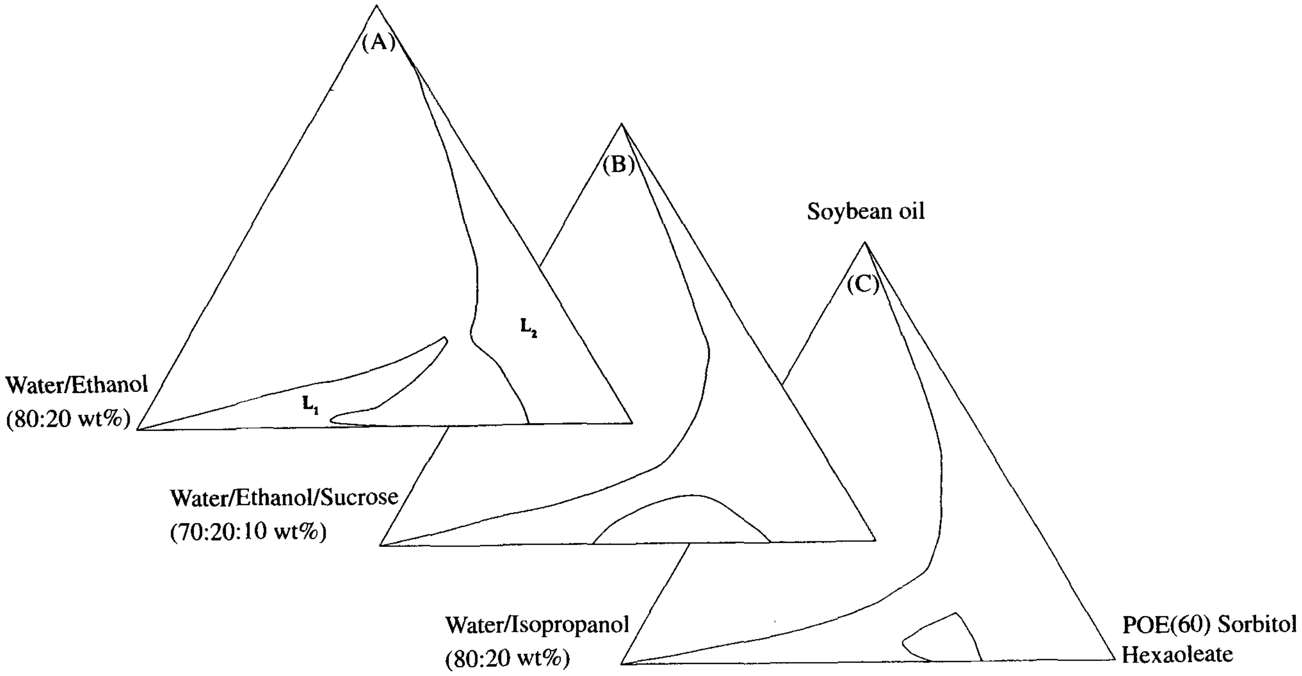

FIG. 3. Microemulsion regions (L$_1$ and L$_2$) in systems containing soybean oil, polyoxyethylene (POE) (60) sorbitol hexaoleate, and different aqueous phases: (A) water/ethanol (80:20 wt%); (B) water/ethanol/sucrose (70:20:10 wt%), and (C) water/isopropanol; (80:20 wt%) at 25°C.

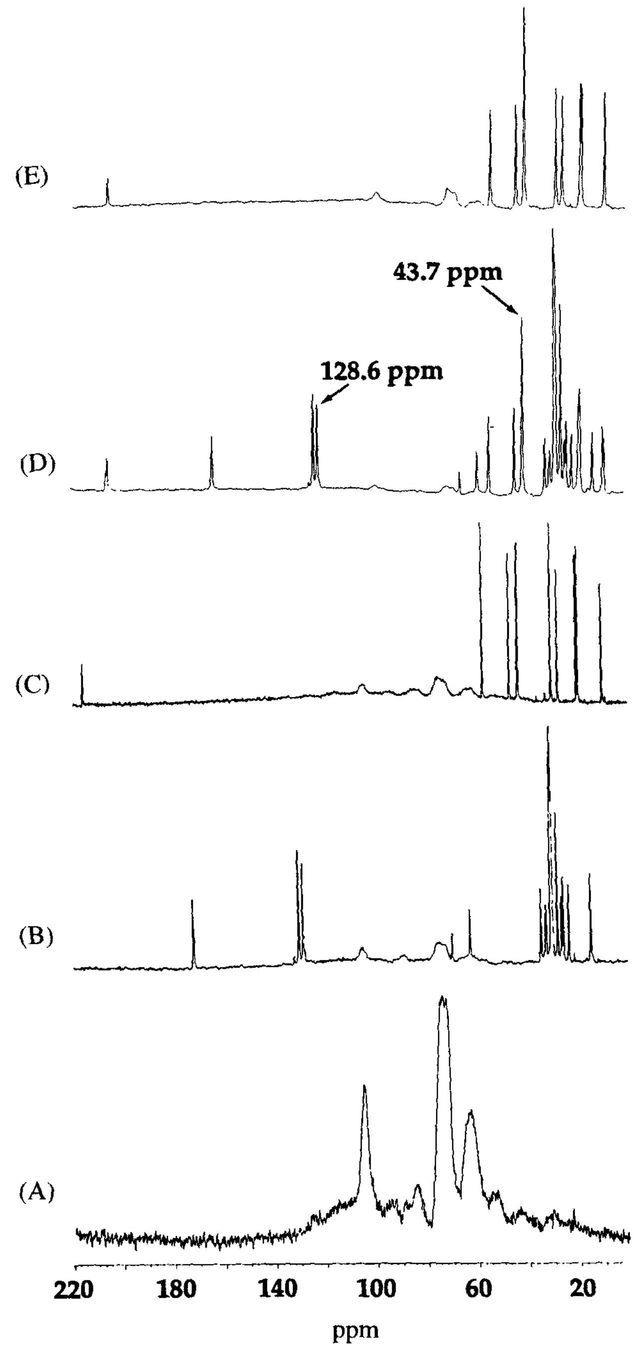

FIG. 4. ^{13}C solid-state magic angle spinning spectra of: (A) cotton fabric, (B) cotton fabric + soybean oil, (C) cotton fabric + camphor, (D) cotton fabric before washing + camphor, and (E) cotton fabric after washing + camphor. Spectrum A was from 19,384 transients, and all other spectra were from 1,024 transients. The peaks marked in spectrum D are from soybean oil (128.6 ppm) and camphor (43.7 ppm). These two peaks were used to determine I_c/I_0 for the calibration curve (abbreviation and calibration curve as in Figure 2).

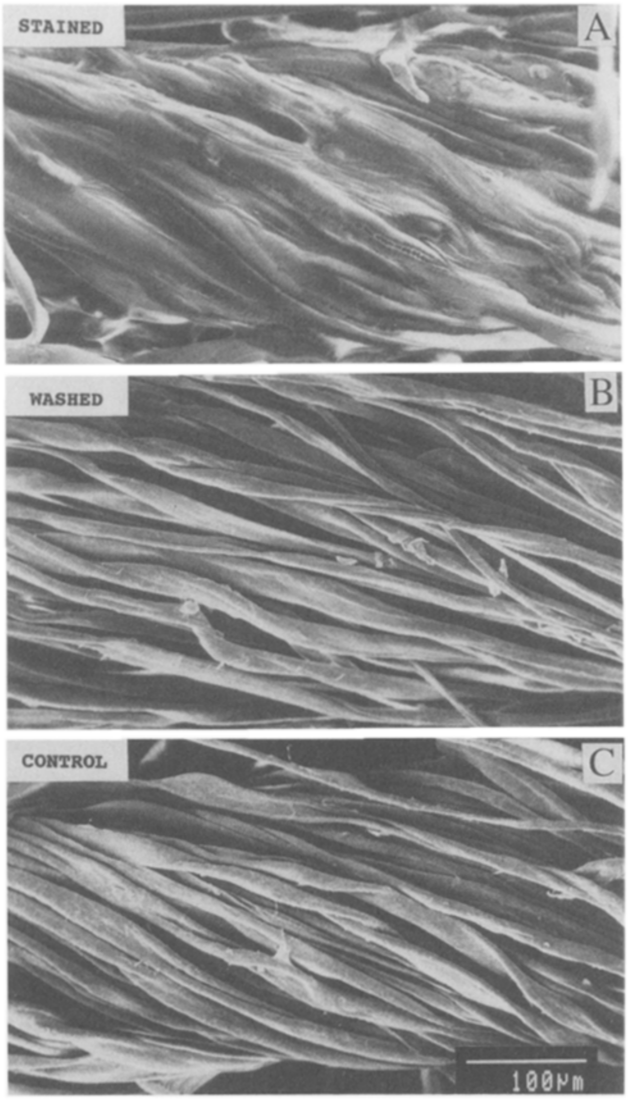

FIG. 5. Secondary electron images of yarns in cotton fabric that were immersed in a 4% osmium tetroxide solution and rinsed with distilled water, after experimental treatment. (A) Yarn stained with soybean oil, (B) matching yarn from fabric after washing, and (C) control (cotton fabric). Magnification: 250×.

The removal of soybean oil from the cotton fabric depended on the number of revolutions of the Crockmeter finger on the fabric surface. Washing prestained fabrics with 5-g solutions, containing 2 wt% surfactant, at room temperature and varying the number of revolutions of the finger indicated that 150 revolutions were required to remove more than 90 wt% of the oil (Fig. 6). In addition, oil removal is dependent on the concentration of surfactant (Fig. 7). For example, in order to remove 90 wt% of soybean oil, the fabric must be washed with a solution containing 2 wt% surfactant. Solutions containing 6 wt% of surfactant were required for complete removal of soybean oil. Raney *et al.* (4) reported that optimum detergency occurs at temperatures near the PIT of the oil–water–surfactant system, and, therefore, changing either the surfactant and/or oil composition will change the PIT of the system and thus affect stain removal performance (20).

In conclusion, aqueous microemulsion regions were identified and used for the removal of soybean oil stains from cotton fabric. Solid-state NMR is a suitable technique for quantitating the removal of triglycerides from cotton fabrics and

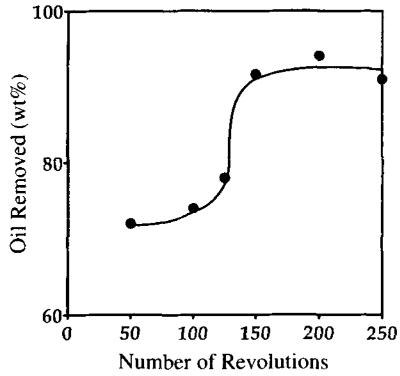

FIG. 6. Effect of revolutions of Crockmeter finger on the removal of soybean oil from cotton fabrics washed with a 5-g solution that contained 2 wt% surfactant at room temperature. Company source as in Figure 1.

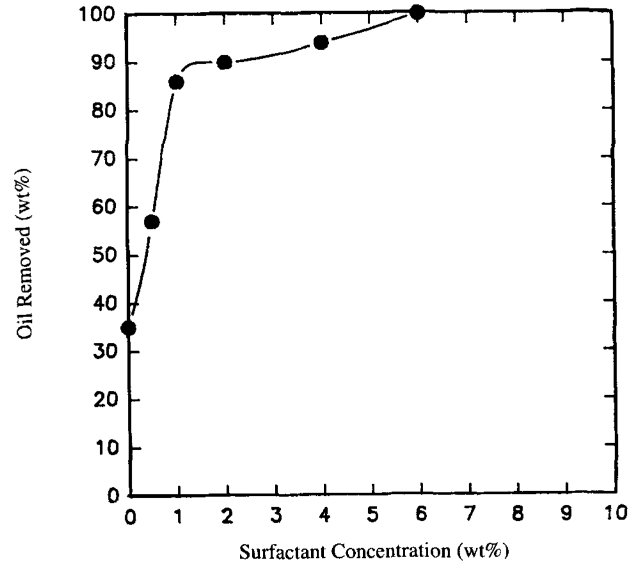

FIG. 7. Effect of surfactant concentration on soybean oil removal from cotton fabrics using 5 g of wash solution that contained various amounts of surfactant after 250 revolutions of Crockmeter finger at room temperature. Company source as in Figure 1.

requires significantly less sample preparation time than traditional methods. The method is rapid, nondestructive, and does not incur the sample-handling problems associated with other techniques, such as radiotracers (15) and erroneous soil removal values associated with reflectance measurements (21).

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