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Direct Analysis of Dimethicone in Aqueous Emulsions by Infrared Spectroscopy

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Synopsis

Dimethicone is a mixture of fully methylated linear siloxane polymers of various molecular weights. This water-insoluble ingredient provides exceptional skin protection and lubrication when incorporated into skin and hair care products. Quantitative analysis of dimethicone is often required to support quality assurance testing of finished products. We report a new, rapid analytical method based on Fourier transform infrared spectrometry, using a special attenuated total reflectance cell to determine concentrations of dimethicone directly in aqueous emulsions present in personal care products. This rapid, simplified method eliminates sample preparation to remove water, while providing reliable results across a wide range of dimethicone concentrations.

INTRODUCTION

Dimethicone, polydimethylsiloxane [-$(CH_3)_2SiO$-$)_n$], is the most widely used silicon-based organic polymer, finding diverse applications ranging from industrial products to health care. It is a common ingredient in cosmetics (1), hair care products (2), and pharmaceuticals. Pure dimethicone is a highly effective pediculicide for treating head lice (3,4). The US Food and Drug Administration allows certain skin protection claims for over-the-counter (OTC) drug products containing concentrations of 1–30% (5).

Rapid, robust analytical methods are needed to support quality assurance during manufacturing. Dimethicone is no exception, especially when it is the active ingredient in drug products. This clear, water-insoluble polymer is often incorporated into personal care products as an aqueous emulsion. Commercially available dimethicone emulsions contain a variety of surfactants and preservatives. During compounding, more ingredients are added to create final products. These additives and dimethicone's relatively low concentration in such aqueous emulsions can complicate its analysis. Sample preparations often focus on separating the dimethicone from water and other excipients before analysis.

Many different types of instrumental techniques for analyzing dimethicone have been reported, including gas chromatography (6), gel permeation chromatography (7),

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high-pressure chromatography (HPLC), (8–11), X-ray fluorescence (12,13), inductively coupled plasma optical emission spectroscopy (13), atomic absorption (14), and Fourier transform infrared (FTIR) spectroscopy (15–17). FTIR spectroscopy has been a particularly useful technique in quality testing laboratories for many applications over the past two decades due to its relatively low cost and ease of use (18,19). An identification and quantitative method of analysis for pure dimethicone is described in the U.S. Pharmacopeia (20) that uses infrared spectroscopy.

Sabo et al. (15) described in this journal the application of FTIR spectroscopy with a fixed-length transmission cell to the quantitation of dimethicone in lotions, following extraction into an organic solvent. In fact, all of the published FTIR methods we have reviewed describe the extraction of emulsified dimethicone into a variety of organic solvents, including methylene chloride (15), toluene (16), carbon tetrachloride (17,20), and hexane (21), before analysis. Solvent extraction is often followed by additional steps to dry the solvent and filter out insoluble particulates, all of which increase sample preparation times and escalate the potential for errors. Some extraction solvents exhibit infrared absorption frequencies similar to dimethicone, requiring spectral subtraction to overcome these interferences (15).

The primary purpose of these solvent extractions is to remove water before FTIR analysis. Aqueous solutions and emulsions typically cause problems with FTIR analysis because water's intense, broad absorption spectrum overpowers most other analytes. Even small percentages of water in samples or high humidity can distort infrared spectra.

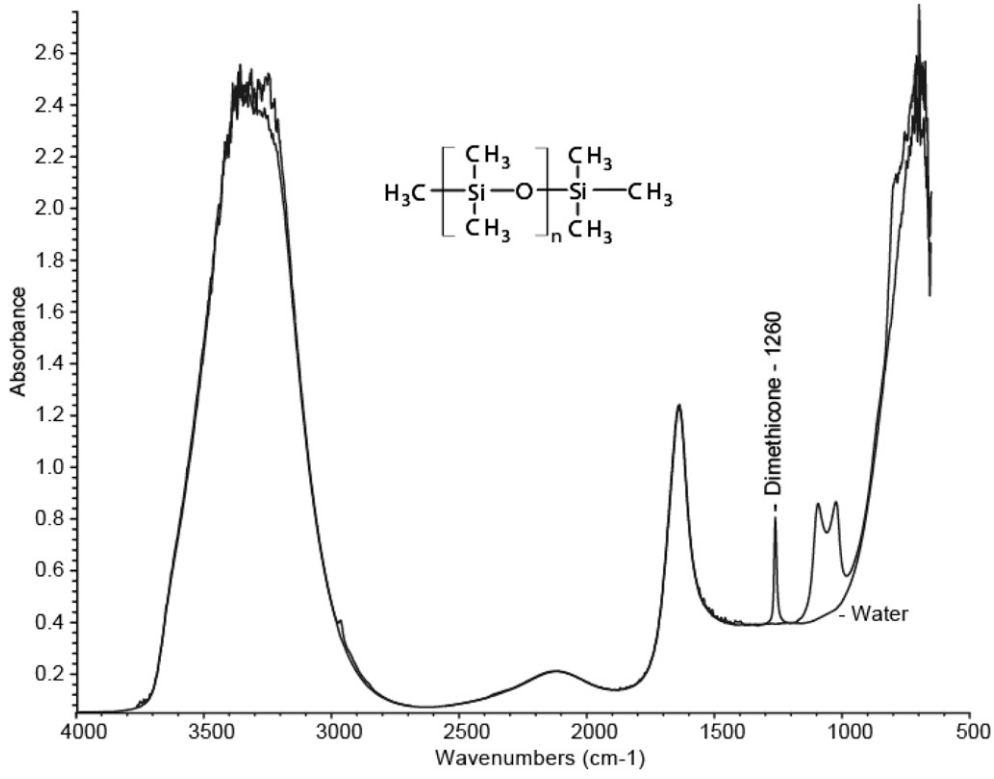

Figure 1. FTIR-ATR absorption spectra for water and aqueous emulsified dimethicone.

Surprisingly, dimethicone is an exception: three of its absorption peaks at 1,260, 1,072, and 1,007 cm^{-1} rise above the water's relatively low absorption at these frequencies, as seen in Figure 1. The single, well-defined peak at 1,260 cm^{-1} is due to the symmetric deformation vibration of the methyl groups attached to the silicon atom. This unique absorption peak of dimethicone is the basis for quantitative testing for pure dimethicone (20) and for dimethicone solutions in some organic solvents (16,17), whereas the double peaks at 1,072 and 1,007 cm^{-1} are preferred in methylene chloride (15). The single peak maximum at about 1,260 cm^{-1} differs slightly among previously published methods, ranging from 1,258 to 1,262 cm^{-1}. These differences are caused by spectral shifts in solvents of differing polarities and instrumental differences such as transmission and attenuated total reflectance (ATR). Infrared absorption frequencies for dimethicone are well characterized (22) and listed in Table I.

We have exploited the use of an ATR cell with a long contact surface path length to measure the concentration of dimethicone in aqueous emulsions by integration of peak areas at 1,260 cm^{-1}. Neat samples were analyzed without any sample preparation in the concentration ranges of 1–35% (g/100 g).

EXPERIMENTAL

REAGENTS

Dimethicone reference standards, Belsil® DM 350 (pure oil), and DM 5102E and DM 5700E (50% aqueous emulsions with different emulsifying surfactants), were from Wacker Chemie AG (Munich, Germany). ACS reagent-grade hexane and anhydrous ethanol were purchased from Fisher Scientific (Hampton, NH). PEG-100 stearate, sorbitan laurate, PPG-15 stearyl ether, Triton X-100, Tween 20, Tween 80, phenoxyethanol, DMDM hydantoin, sodium benzoate, methyl paraben, and propyl paraben were purchased from MilliporeSigma, Burlington, MA; laureth-23 and laureth-4 were obtained from Rita Corporation, Crystal Lake, IL; PPG-15 stearyl ether was purchased from Jeen International, Fairfield, NJ; and Kathon was purchased from Rohm and Haas, Philadelphia, PA.

INSTRUMENTATION

Analyses were performed using a Nicolet Avatar 470 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA) fitted with a Smart Ark horizontal ZnSe ATR 45° multi-bounce

Table I
Dimethicone IR Absorption Frequencies (22)

Frequency (cm^{-1})	Description
2,965	CH_3 asymmetrical stretch
2,906	CH_3 symmetrical stretch
1,410	CH_3 asymmetrical bend
1,258	CH_3 symmetrical bend
1,072	Si-O-Si asymmetrical bend
1,007	Si-O-Si asymmetrical stretch
864	Si-CH_3 asymmetrical rock

trough plate and controlled with OMNIC software (Thermo Fisher Scientific). This cell is much longer (approximately 72 mm in length with multi-bounce optics) than typical ATR cells (only 1.5 mm diameter with single bounce). This longer ATR plate yields enhanced sensitivity compared to those with shorter path lengths. The sample cell for transmission measurements was a demountable liquid cell with CaF_2 windows and a 0.1-mm PTFE spacer. Quantitative scans for both ATR and transmission were limited to the expanded region of 1,239–1,279 cm^{-1} in the absorbance mode (Figure 2). Integrated peak areas for the absorption band centered at 1,260 cm^{-1} were then plotted as a function of dimethicone concentration to calibrate the instrument and to measure samples.

METHOD 1: FTIR TRANSMISSION

Pure dimethicone standards were prepared by dissolution in hexane at concentrations of 0.3–1.5 g/100 mL. Dimethicone emulsions were analyzed by extraction into hexane before FTIR scanning in transmission mode. Depending on the dimethicone concentration, between 0.20 and 2.0 g samples of each liquid emulsion (carefully weighed to 0.001 g) were placed in separate 60-mL wide-mouth jars. The open jars were heated in an oven at 115°C

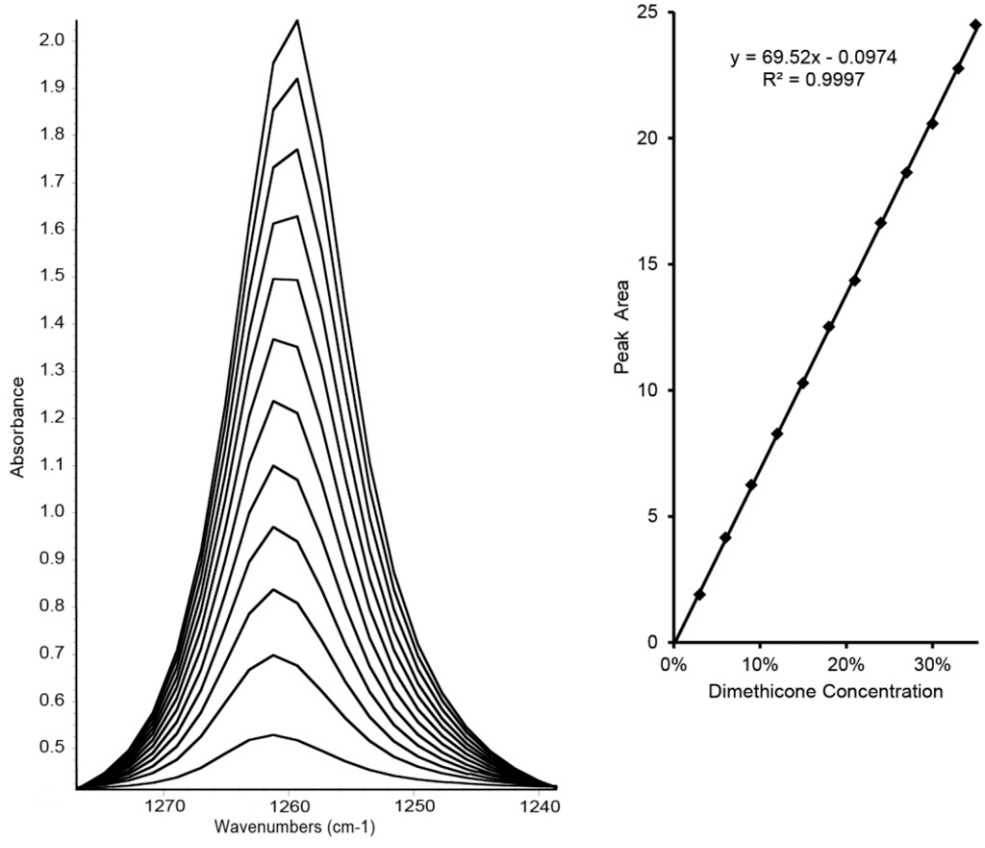

Figure 2. Emulsified dimethicone calibration standards.

for 1 h or until all the water evaporated. After cooling to room temperature, 5.0 mL of anhydrous ethanol was added and mixed well. The open jars were returned to the oven and heated again at 115°C to evaporate the ethanol and any remaining water by azeotropic evaporation. Following evaporation, the jars were cooled to room temperature and 25.00 mL of hexane was pipetted into each jar. The jars were then capped and sonicated for 1 min. After settling for 2 h, 15–20 mL of the upper solution was transferred to clean, capped vials and stored at room temperature until analyzed by FTIR in transmission mode.

METHOD 2: FTIR-ATR

Two different commercially available dimethicone emulsions were compared. Both DM 5102E and DM 5700E contained 50% dimethicone but different emulsifying surfactants. No differences were observed in the FTIR-ATR absorption spectra of these two different emulsions at any dilution. DM 5102E was used as the primary standard for calibration. After its concentration was verified by Method 1 (transmission FTIR of the hexane extract), portions of this DM 5102E emulsion were diluted by mixing with distilled water to prepare a series of secondary calibration standards in the range of 0–35.0% (g/100 g). These aqueous emulsion standards were analyzed directly by FTIR-ATR. Liquids from five different retail skin-protection wipe products were squeezed from the wipes and analyzed directly by FTIR-ATR without any further preparation. Dimethicone concentrations of each sample were calculated by comparing the integrated peak areas with the primary calibration standards.

METHOD 3: FTIR-ATR STANDARD ADDITION

Each of the retail skin protection wipe products was analyzed again by Method 2 following standard addition. The primary standard was added to each sample, increasing its dimethicone concentration by 50%. After mixing to ensure homogeneity, each spiked sample was again analyzed directly by FTIR-ATR without any further preparation. The increased absorbance of each sample was used to calculate its original dimethicone concentration, rather than the external calibration in Method 2.

POTENTIAL INTERFERENCES

To examine potential matrix interference, a series of 3% dimethicone emulsions containing various surfactants and preservatives were prepared and analyzed. A 20% dimethicone emulsion was prepared by blending 200 g of pure dimethicone oil (Belsil® DM 350), 10 g of Tween 20, and 10 g of Tween 80. Then, 780 g of DI water was added slowly with vigorous stirring at 80°C.

The resulting mixture was homogenized with a Silverson homogenizer for 10 min at medium speed. The resulting 20% stock solution was then mixed with deionized water and individual surfactants or preservatives at levels typically present in personal care products, such that the final dimethicone of each sample was 3.00%. Triplicate samples of each surfactant and preservative were prepared and analyzed by all three methods.

Table II
Replicate FTIR-ATR Assays of Standards

Dimethicone conc. (%)	Average ($n = 6$)	RSD (%)
3.00	3.01%	0.27
12.00	12.00%	0.15
21.00	21.00%	0.18
30.00	30.03%	0.26

RESULTS

Calibration of FTIR-ATR for aqueous emulsifications of dimethicone yielded outstanding linearity for a 12-level series of standards up to 35% ($r^2 = 0.9997$) as shown in Figure 2. The excellent precision of the FTIR-ATR method was demonstrated by repeated analysis of selected calibration standards, yielding relative standard deviations of less than 0.3% (Table II).

Five different retail OTC wipe products with label claims in the range of 3–5% emulsified dimethicone were analyzed. Analytical results from all three methods (Table III) compared favorably with label claims and with each other. The agreement between standard addition and external calibration (Methods 2 and 3) for five different wipe products is a strong indication that there is no matrix interference with this method. This was further verified by the dimethicone test results in the presence of various surfactants and preservatives shown in Table IV. No statistically significant interference was observed for any of the ingredients tested.

CONCLUSIONS

Direct testing of dimethicone in aqueous emulsions by FTIR-ATR is a viable method that has been ignored in the past. Dimethicone is a rare analyte that may be analyzed by FTIR-ATR in the presence of large quantities of water because of its unique absorption frequency at 1,260 cm^{-1}. It may, in fact, be accurately measured across a wide range of

Table III
Results of Three Analytical Methods—% Dimethicone (g/100 g)

Wipe samples		Method 1 ($n = 6$)		Method 2 ($n = 6$)		Method 3 ($n = 6$)	
Product	Claim (%)	Average (%)	RSD (%)	Average (%)	RSD (%)	Average (%)	RSD (%)
A	3.2	3.31	3.29	3.26	0.30	3.12	11.7
B	3.6	3.65	4.71	3.70	0.37	3.74	9.26
C	3.0	3.19	5.85	3.05	0.27	3.09	15.7
D	3.0	3.25	5.17	3.14	0.24	3.30	13.1
E	5.0	5.20	3.71	5.23	0.23	5.50	7.08

Six separate replicates of each product were tested by the three methods:
Method 1: Extraction in hexane; FTIR transmission.
Method 2: Emulsion (no extraction), FTIR-ATR, external calibration.
Method 3: Emulsion (no extraction), FTIR-ATR, standard addition.

Table IV
Effect of Various Excipients on Method 2 Assay Results

Excipient added	Excipient conc. (%)	Dimethicone % average[a] (n = 3)	RSD (%)
Control	0.00	3.01	0.51
Laureth-4	0.30	2.96	1.60
	0.60	3.02	2.32
Laureth-23	0.30	3.05	1.68
	0.60	3.06	1.68
Triton X-100	0.30	2.95	1.55
	0.60	3.03	2.70
PPG-15 stearyl ether	0.30	3.00	2.03
	0.60	3.01	2.03
PEG-100 stearate	0.30	3.01	2.82
	0.60	2.95	1.74
Sorbitan laurate	0.30	3.02	2.82
	0.60	2.95	1.60
Methylparaben	0.05	2.99	1.65
	0.10	2.99	0.84
Propylparaben	0.05	3.01	0.96
	0.10	3.00	1.17
Phenoxyethanol	0.05	2.99	0.67
	0.10	3.00	1.07
DMDM hydantoin	0.01	3.00	1.68
	0.02	3.02	1.15
Kathon	0.0050	2.97	0.19
	0.0100	3.00	1.39
Sodium benzoate	0.05	3.01	1.45
	0.10	3.00	1.15

[a]Actual dimethicone concentration in all samples = 3.00% (g/100 g).

concentrations while still in aqueous emulsions. This rapid method of analysis will be helpful in quality testing to support manufacturing and stability testing of products that contain dimethicone emulsions. Direct analysis of samples without sample preparation is appealing compared with more lengthy, complex methods. Of course, as with all new analytical procedures, this method should be validated on a product-by-product basis because other ingredients and excipients could potentially interfere with this procedure.

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