J. Cosmet. Sci., **68,** 133–136 (January/February 2017)

Review of innovations to improve fragrance bloom, release, and retention on skin from surfactant-rich cosmetics

VETHAMUTHU, M., LIRA, S., DIANTONIO, E., and FARES, H.,
Ashland Specialty Ingredients, Bridgewater NJ 08807.

INTRODUCTION

Fragrance molecules are small, highly volatile, and amphiphilic to different extents all of which makes them a challenging composition to efficiently encapsulate, retain in microcapsules, or a polymer matrix, and deposit them on a substrate such as skin or hair. This is particularly true when trying to do so from surfactant-rich cosmetic rinse-off product (1–3). Since volatility is an inherent fragrance attribute that leads to reduced sensory perception over time, a number of fragrance encapsulation technologies have been developed to address this issue. These include fragrance-encapsulated polymeric microspheres (4), complex coacervation with various macromolecules (5), molecular inclusions into a host, such as cyclodextrin (6), and incorporation into solid lipid nanoparticles using appropriate lipids and surfactants (1,2,7). There are many challenges associated with these approaches, mainly due to the partial solubility in water of the many essential oil fragrance components, causing hydrolytic instability in the microencapsulation process by interfacial reactions. In addition, side reactions could also lead to alteration of the encapsulated "fragrance oils" which may limit its application in personal care products.

This presentation will provide an overview of innovations and current challenges that address stability of fragrance encapsulates alone and in surfactant-rich formulations specifically from leakage kinetics (integrity of microcapsule and its cargo). Next, technologies that provide improved fragrance delivery and long-lasting fragrance perception on skin will be discussed.

MATERIALS AND METHODS

INSTRUMENTATION

Analyses were performed on a 7890A GC combined with a 5975C Inert XL MSD with triple axis detector (Agilent Technologies). The gas chromatography mass spectrometry

Address all correspondence to Martin Vethamuthu at MSVethamuthu@ashland.com.

(GC–MS) system was configured with a Cooled Injection System (CIS 4) PTV-type inlet, thermal desorption unit (TDU), and multipurpose sampler with 10 µl ATEX syringe.

ANALYSIS CONDITIONS:

TDU: Splitless, 40°C, 720 °C/min, 230°C (5 min)

PTV: Solvent vent (70 ml/min); splitless; -120°C, 12°C/s, 270°C (3 min)

Column: 60 m DB-624 (Agilent J&W), di = 0.25 mm df = 1.4 µm

Pneumatics: He, constant flow (1.0 ml/min)

Oven: 40°C, 5°C/min, 230°C (17 min)

MSD: Full scan, 20–550 amu

SAMPLE PREPARATION

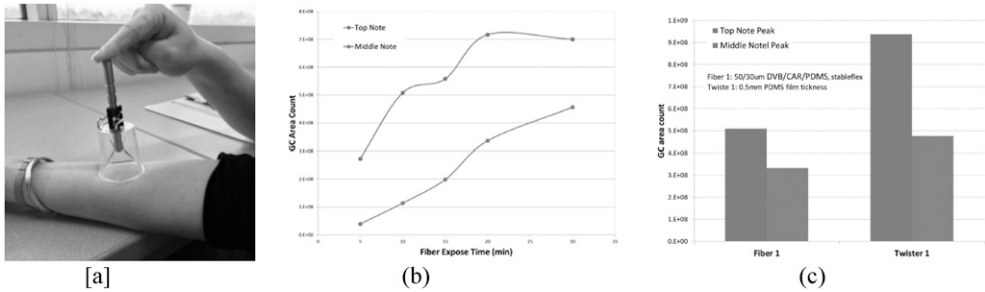
An area of 18 cm^2 of the inside arm was washed with 3.3 mg/cm^2 of a shower gel formulation and rinsed with tap water for 30 s and dried. Subsequently, the area of the arm was exposed to the twister bar for 15 min (Figure 1). This step was repeated at intervals of 1 h for a total time of 2 h. After extraction the twister bar was removed and placed into a clean glass thermal desorption tube for GC–MS analysis.

GC–MS ANALYSIS

All samples were run in triplicate, areas of the peaks selected in the GC–MS chromatographs were manually integrated and average areas obtained from the three runs were graphically represented.

SOLID PHASE MICROEXTRACTION FIBERS VERSUS TWISTER BAR

Twister bar presents a larger surface area than the fiber, increasing the sensitivity of the twister bar by over 1000 times with respect to the fibers. They are also much easier to handle, especially when you have to complete the sampling over an extended period of time.



[a] (b) (c)

Figure 1. (A) Sampling, (B) analysis, and (C) fiber versus twister bar.

Test formulations containing either encapsulated fragrance or neat fragrance or a mixture of both neat and encapsulated fragrance is shown in Table I. The primary objective was to confirm that encapsulated fragrance oils provided an increase in odor perception over time compared to the neat fragrance control formulation 2.

Formulation procedure:

1. In main beaker combine ingredients in Phase A one at a time, in order, mixing to uniformity before adding the next
2. Add sodium hydroxide of Phase B to main beaker slowly, with mixing, measure pH, adjust to ~6.4
3. Add cocamidopropyl betaine of Phase C to main beaker with mixing, mix until uniform
4. Add ingredients of Phase D to main beaker, one at a time, in order with mixing, waiting for uniformity before adding the next
5. Add ingredients of Phase E to the main beaker and slowly mix until uniform. Measure final pH and adjust to pH ~6.5 as appropriate

RESULTS

Based on the results presented in Figure 2, it appears initially that formulation 3, containing 20% of the encapsulated fragrance and 80% neat fragrance, gives a higher GC count. After 1 h we also see not only the 20% encapsulate/80%neat fragrance formulation with a higher count, but also that formulation 4 with 50% encapsulate/50% neat fragrance has an even higher GC count. Results of these instrumental experiments will be confirmed through expert evaluation.

Table I

INCI Name	Formulation 1	Formulation 2	Formulation 3	Formulation 4
Phase A				
Water	31.01	30.01	29.55	28.87
Glycerin	3.00	3.00	3.00	3.00
Disodium EDTA	0.10	0.10	0.10	0.10
Acatylate copolymer (and) water (30%)	6.67	6.67	6.67	6.67
Sodium laureth sulfate (25%)	48.00	48.00	48.00	48.00
Phase B				
Sodium hydroxide (10% aq)	1.20	1.20	1.20	1.20
Phase C				
Cocamidopropyl betaine (35%)	8.00	8.00	8.00	8.00
Phase D				
Sodium chloride	0.02	0.02	0.02	0.02
Sodium hydoxymethyglycinate (and) water	0.50	0.50	0.50	0.50
Phenoxyethanol (and) caprylyl glycol	1.00	1.00	1.00	1.00
Phase E				
Fragrance	0.00	1.00	0.80	0.50
Encapsulate EN C-623 (30.5%)	0.00	0.00	0.66	1.64
Styrene/VP copolymer	0.50	0.50	0.50	0.50
Final pH	6.5	6.5	6.5	6.5
Level fragrance: encapsulate (active)	0%/0%	1.00%/0.00%	0.80%/0.20%	0.50%/0.5%

INCI: International Nomenclature of Cosmetic Ingredients; EDTA: ethylenediaminetetraacetic acid.

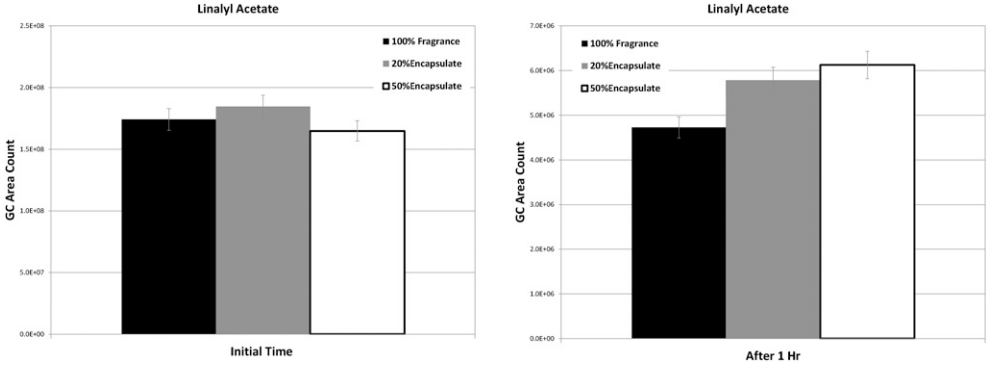


Figure 2. GC Area count of linalyl acetate after sample application (A) Initial and (B) after 1h.

CONCLUSION

The headspace GC instrumentation coupled with the appropriate solid phase microextraction fiber or twister bar is very capable of monitoring time-dependent release/retention profiles of fragrance ingredients from the substrate. The results from this study show that a method exists that will be used to further demonstrate the benefits of other polymeric ingredients incorporated as foam boosting or deposition aids in surfactant-rich cleansing compositions that can enhance fragrance bloom, release, and retention on skin during the cleansing process. Finally, the presentation will demonstrate that polymeric technology, when combined with microencapsulation routes, will provide the best approach to significantly improve fragrance delivery from rinse-off cosmetics.

ACKNOWLEDGMENTS

The authors would like to thank Robertet team for design of fragrances used in this study.

REFERENCES

(1) A. Sansukcharearnpon, S. Wanichwecharungruang, N. Leepipatpaiboon, T. Kerdcharoen, and S. Arayachukeat, High loading fragrance encapsulation based on a polymer-blend: Preparation and release behavior, *Int. J. Pharm.,* **391,** 267–273 (2010).
(2) I. Hofmeister, K. Landfester, and A. Taden, pH-Sensitive Nanocapsules with Barrier Properties: Fragrance Encapsulation and Controlled Release *Macromolecules* **47(16),** 5768–5773 (2014).
(3) T. Lukowicz, R. C. Maldonado, V. Molinier, J-M. Aubry, and V. Nardello-Rataj, Fragrance solubilization in temperature insensitive aqueous microemulsions based on synergistic mixtures of nonionic and anionic surfactants, *Colloids Surf A Physicochem Eng Asp* **458,** 85–95 (2014).
(4) B. Jean-Pierre, J. Richard, and C. Thies, Method for preparing microcapsules of active substances coated with a polymer and novel microcapsules in particular resulting from the method. WO 98/13138 A1.
(5) A. Bachtsi and C. Kiparissides, Synthesis and release studies of oil-containing poly(vinyl alcohol) microcapsules created by coacervation, J. Control Release **38,** 49–58 (1996).
(6) Wang, C. et al. Fragrance release property of β-cyclodextrin inclusion compounds and their application in aromatherapy, *J. Ind. Text,* **34,** 157–166 (2005).
(7) F. Lai, S. A. Wissing, R. H. Müller, and A.M. Fadda, *Artemisia arborescens* L essential oil-loaded solid lipid nanoparticles for potential agricultural applications, *AAPS PharmSciTech,* **7(1),** E2 (2006).