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Laboratory Experiment

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Integrating Elemental Analysis and Chromatography Techniques by Analyzing Metal Oxide and Organic UV Absorbers in Commercial Sunscreens

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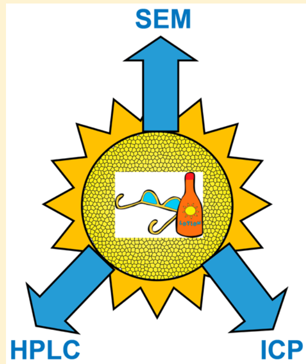
Supporting Information

ABSTRACT: A series of undergraduate laboratory experiments that utilize reversed-phase HPLC separation, inductively coupled plasma spectroscopy (ICP), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) are described for the analysis of commercial sunscreens. The active ingredients of many sunscreen brands include zinc or titanium oxide in addition to organic acids. Students determine the zinc content using ICP, and the chemical composition as well as particle sizes using SEM-EDS. The organic UV absorbers octocrylene and oxybenzone are quantified using HPLC. With the incorporation of these interesting characterization techniques in second or fourth-year chemistry courses, and by having students analyze sunscreen samples that are medically relevant in terms of health effects, students engage in timely research and at the same time gain exposure to a variety of instruments in the analysis of a familiar household product.



KEYWORDS: *Second-Year Undergraduate, Upper-Division Undergraduate, Analytical Chemistry, Hands-On Learning/Manipulatives, Atomic Spectroscopy, Chromatography, Instrumental Methods, Nanotechnology, Quantitative Analysis*

BACKGROUND

Growing concern toward melanoma and other phototoxic effects has led to increased use of sunscreen within recent years.[1−3] Dermatologists often recommend sunscreen usage for protection against harmful UVA (λ = 320−400 nm) and UVB (λ = 290−320 nm) radiation from the sun. Sun Protection Factors (SPFs) are written on sunscreen packaging and indicate the product's ability to screen or block the sun's burning rays. SPF values can range from 2 to 100, and are assigned by manufacturers as the ratio of the energy required to produce minimal sunburn in the presence of a sunscreen to the energy required to produce the same effect in the absence of a sunscreen. Ideally, the higher the SPF value, the longer a person can safely spend in the sun.[4] SPF ratings are determined by the content of the active ingredient in the sunscreen, which are usually either organic acids or metal oxides. The active ingredients can absorb, scatter, or reflect sunlight off the epidermis, thereby minimizing exposure to damaging rays. Traditional organic UV-absorbers include oxybenzone (benzophenone-3), avobenzone, octinoxate (octyl methoxycinnamate), octisalate (octylsalicylate), homosalate, and octocrylene. Titanium dioxide (TiO_2) and zinc oxide (ZnO) nanoparticles are common metal oxides in sunscreen as they are cheap, thermally stable, and scatter UV light in the range of 200−500 nm.[5−7] A recent goal is to decrease the particle sizes to 10−50 nm in order to reduce the scattering of visible light while maintaining the scatter of UV light.[5] Decreasing the particle size, however, results in agglomeration of the metal oxide nanoparticles, which may reduce the efficiency of scattering the UV light.[8] This agglomeration can be detected by using a scanning electron microscope (SEM). Such an issue is of especial concern with the higher concentrations found in higher SPF values.[6,8]

Despite the effectiveness of sunscreens, questions exist regarding potential health impacts of exposure to some of the active ingredients. A study conducted by Gulson et al. showed that subjects using sunscreen with ZnO nanoparticles have increased zinc levels in their blood and urine after use.[7] This may cause some anxiety given that ZnO nanoparticles have been known to be toxic for aquatic organisms.[1] Furthermore, organic UV absorbers in the sunscreen formulation, in particular oxybenzone, must be monitored due to side effects such as photoallergic contact dermatitis which is skin hypersensitivity resulting from an allergen exposed to light.[9] Despite possible health concerns, the Food and Drug Administration (FDA) currently provides little to no regulation

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Table 1. Comparison of Sunscreens' Active Ingredients by SPF Rating, Label Claims, and As Measured

Sunscreen	SPF Rating	Active Ingredient	Label (wt %)	Measured (wt %)[a]
Coppertone Ultra Guard	15	Avobenzone	2	—[b]
		Homosalate	10	—[b]
		Octisalate	5	—[b]
		Octocrylene	5	5.9 ± 0.7 (n = 18)
Blue Lizard−Sport	30+	Octinoxate	4.7	—[b]
		Octocrylene	2	1.5 ± 0.7 (n = 48)
		Oxybenzone	3	2.9 ± 1.0
		Zinc Oxide	6	5.0 ± 1.3
Nature's Gate Aqua Water Sports	50	Octinoxate	7.5	—[b]
		Octisalate	5	—[b]
		Octocrylene	7	4.8 ± 1.4 (n = 24)
		Zinc Oxide	6.9	4.8 ± 1.0
Safe Harbor Natural Suncare Sensitive Lotion	50	Zinc Oxide	4.0	3.7 ± 0.6 (n = 21)
		Titanium Oxide	10.5	—[b]
Coppertone Ultra Guard	50	Avobenzone	3	—[b]
		Homosalate	13	—[b]
		Octisalate	5	—[b]
		Octocrylene	7	5.9 ± 0.7 (n = 12)
		Oxybenzone	4	4.2 ± 0.8
Walgreens Clear Zinc Sunscreen Broad Spectrum	50+	Octocrylene	4.0	2.4 ± 0.1 (n = 18)
		Zinc Oxide	5.0	4.0 ± 0.5
Neutrogena Sensitive Skin	60+	Titanium Oxide	4.9	—[b]
		Zinc Oxide	4.7	2.4 ± 0.3 (n = 9)
Walgreens Sunscreen Zinc Oxide	70	Octocrylene	5	2.9 ± 1.4 (n = 33)
		Oxybenzone	2	1.5 ± 0.3
		Zinc Oxide	3.9	3.1 ± 1.0
Solar Sense Clear Zinc	70+	Octinoxate	4.5	—[b]
		Octocrylene	8	7.8 ± 2.4 (n = 30)
		Zinc Oxide	8	6.0 ± 2.0

[a]Average ± standard deviation values calculated using data measurements from ICP and HPLC. [b]Not measured.

on metal oxides in sunscreens, and even though organic UV absorbers are monitored, it is difficult to correlate the SPF values and concentration.[6,9,10]

Most of the laboratory sunscreen experiments reported in this *Journal* focus on overall effectiveness by using either UV−vis spectroscopy[4,11−15] or UV beads.[16,17] An exception is an experiment in which liquid chromatography is used to analyze some of the organic components while another consists of synthesizing ZnO to make homemade sunscreen.[18,19] The experiments described in this paper, however, examine both the metal oxide and organic active ingredients found in a variety of sunscreens. Undergraduate students measure the amount of zinc using inductively coupled plasma spectroscopy (ICP) and by generating a calibration curve. Scanning electron microscopy is then employed to determine the metal oxide particle size distribution and morphology as well as the elements present through energy dispersive spectroscopy (SEM-EDS). Octocrylene and oxybenzone organic absorbers are quantified using high performance liquid chromatography (HPLC) and an internal standard.

These experiments have been implemented in both lower-level analytical and upper-level instrumentation courses. The laboratory sections are taught by professors, with 15−18 students present during a lab period. Students work in pairs for the sunscreen analyses. In addition, one student lab assistant is typically present to help with reagent preparation, and to assist with instrument use. The experiments are designed such that each could be implemented in a second-year analytical course or an upper-level instrumental analysis lab. Second-year and fourth-year analytical students at Washington & Jefferson College performed both the ICP and HPLC protocols. Students at Marshall University completed ICP, HPLC, and SEM-EDS analyses. The following topics are thus emphasized in this publication:

(1) chromatography and atomic spectroscopy
(2) sample preparation using an internal standard and calibration curve
(3) chemical composition and morphological differences in the shape and size distribution analysis based on SEM imaging and EDS measurements
(4) method validation using statistics

These laboratory experiments thus expose students to atomic spectroscopy phenomena in an engaging context with medical and environmental relevance. Furthermore, students are introduced to chromatography and chromatographic parameter quantity calculations, taking them beyond standard univariate analyses. Students also visualize particles through microscopy measurements.

■ EXPERIMENTAL SECTION

Reagents

Concentrated nitric acid (TraceMetal grade), *trans*-cinnamic acid (≥99%), octocrylene (2-ethylhexyl 2-cyano-3,3-diphenyl acrylate), oxybenzone (2-hydroxy-4-methoxybenzophenone), methanol (HPLC grade), and concentrated sulfuric acid were purchased from Fisher Scientific. Ethanol (200 proof) was obtained from Pharmco−Aaper. A 1000 mg/L zinc standard for

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ICP (prepared from high purity Zn metal in 2% nitric acid) was purchased from Sigma-Aldrich.

Sunscreens

A variety of commercial sunscreen products were purchased and analyzed. Table 1 summarizes the commercial sunscreens including their active ingredients and SPF values. Students, working in pairs, were assigned a sunscreen with at least three pairs testing a given sunscreen to allow for statistical analysis.

Apparatus

Instruments used in these experiments as well as parameters can be found in Supporting Information.

Sample Preparation

ICP Sample Preparation. For metal oxide analysis, 100–150 mg (to the nearest 0.1 mg) of sunscreen is dissolved in 15 mL of concentrated nitric acid and the mixture is stirred for 2 h at 55 °C. The sample is then quantitatively transferred to a 100 mL volumetric flask and diluted to the mark with deionized water. The process is repeated twice, yielding a total of 3 samples for one sunscreen brand. A blank is prepared in a similar manner, with the sunscreen excluded. All samples are then filtered using filter paper prior to ICP analysis and stored in Erlenmeyer flasks.

HPLC Sample Preparation. Organic analysis consists of 100–150 mg (to the nearest 0.1 mg) of sunscreen mixed with 2 mL of 6 M sulfuric acid and 20 mL of methanol. The solution is ultrasonicated for 30–35 min at 45 °C, and then centrifuged at 1000*g* for 10–15 min. The sample is quantitatively transferred to a 100 mL volumetric flask. A 10 mL aliquot of 2000 ppm *trans*-cinnamic acid in methanol is then added as an internal standard and diluted to the mark with methanol. The process is repeated twice, yielding a total of 3 samples for one sunscreen brand. A blank is prepared in a similar manner, but with the sunscreen excluded. All samples are filtered using 0.2 μm syringe filters and stored in Erlenmeyer flasks.

Standard Solutions. For both experiments, students work in groups of four to prepare a series of four standards consisting of 1–250 ppm zinc and another four standards consisting of 1–250 mg/L octocrylene and oxybenzone by diluting stock solutions using appropriate volumetric flasks and volumetric pipettes. An aliquot of 2000 ppm *trans*-cinnamic acid (internal standard) is added to each HPLC standard such that a concentration of 158 mg/L is achieved.

SEM Sample Preparation. To assess metal oxide content and particle size, 50 mg of sunscreen is suspended in 5 mL of ethanol, and the mixture is ultrasonicated for 10–15 min at room temperature. The solvent is then evaporated from a small drop of the resulting suspension on a clean surface, and spectrally pure carbon tape is used to transfer the dried particles for further analysis.

■ HAZARDS

Normal laboratory precautions are called for, including adequate ventilation and the use of proper eye protection. *Trans*-cinnamic acid, octocrylene, and oxybenzone are harmful if swallowed. Nitric acid and sulfuric acid are extremely acidic/corrosive and should be handled with caution. Acid-resistant gloves are a necessity when working with strong acids. Methanol is flammable, harmful if swallowed, and is a skin and eye irritant. Sunscreen sample solutions should thus be prepared in fume hoods.

■ RESULTS AND DISCUSSION

These experiments have been successfully implemented into undergraduate analytical laboratory and upper division instrumentation courses for three years involving a total of 127 students. The experiment is designed to cover five, 3 h laboratory periods, but could be shortened or expanded to accommodate alternative schedules. A suggested timeline is available in the Supporting Information. In general, sample preparation occupies two lab periods and instrumental analysis requires three additional periods.

Using the ICP instrument, students analyze standards, blanks, and samples by detecting zinc at a wavelength of 213.9 nm. Figure 1 shows a calibration curve produced by students, with intensity or "counts" of the zinc standard against concentration in ppm.

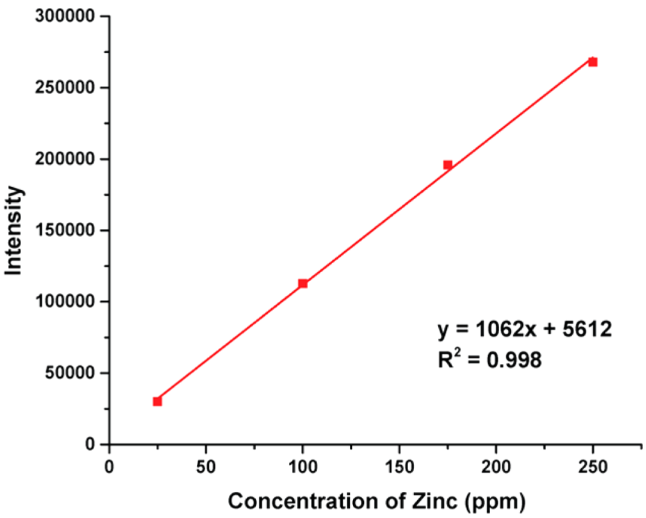

Figure 1. Maximum Intensity or "counts" measured by ICP vs zinc standard concentration in ppm units. This calibration curve was obtained by a group of students.

On the basis of the calibration curve, the concentration of Zn (ppm) is calculated for each of the three sunscreen samples and then converted to weight percent (wt %) of ZnO. Students compare their weight percent with the percent reported on their sunscreen bottle (Table 1). Using a 95% confidence interval (CI) around the mean value, students determine whether their measured values are significantly similar to or different from the reported value (see Supporting Information for details). As an additional exercise, students calculate the percent error and percent relative standard deviation (RSD) as shown in Table 2.

Students determine the calibration sensitivity, analytical sensitivity, and detection limit of their instrument as shown in Table 3. More specific details for these calculations can be found in the Supporting Information. Measuring such parameters provides the opportunity to teach students about the limitations of a particular technique. A search of this *Journal* reveals a few experiments that describe, or determine, the sensitivity and detection limits of instrumental measurements.[20,21] In particular, such limitations are calculated when students build a new instrument.[20,22,23] It is important for students to not only understand the concept behind individual figures of merit, but to determine them on their own from data they generate.[21]

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Table 2. ICP−AES Data and Calculations To Find Weight Percent of ZnO in Two Different Sunscreens

Sunscreen	Concentration Zn, ppm	ZnO, wt %	ZnO, Average wt %	SD[a]	CI[b]	RSD, %	Error, %[c]
Blue Lizard (SPF 30)	149.1	6.0	5.80	0.20	±0.4	2.7	0.3
	147.0	5.9					
	142.1	5.7					
Walgreens (SPF 70)	101.7	4.1	4.03	0.08	±0.2	2.0	0.3
	102.0	4.1					
	98.2	3.9					

[a]SD indicates the standard deviation. [b]CI indicates the confidence interval. [c]Data for n = 3 are shown in this table.

Table 3. Summary of Calculated Percent RSD, Calibration Sensitivity, Analytical Sensitivity, and Detection Limit for the Standard Concentrations Used for ICP−AES

Concentration (ppm)	RSD, %	Analytical Sensitivity[a]
0	6.205	—
25.0	7.463	0.506
100.0	0.962	0.972
175.0	3.421	0.163
250.0	2.919	0.139

[a]Calibration sensitivity = 1062; detection limit =75 ppb; data for n = 6 are shown in this table.

It is known that suboptimal dispersion of metal oxide particles may lead to agglomeration which decreases sunblock properties.[5,6] This concern is acknowledged by having students obtain images of the particles and measure their size using a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) (Figures 2, S1 and S2). In this *Journal*, there are some publications using the SEM-EDS to introduce students to this technique, but only a few of them discuss particle size distribution and/or agglomeration.[24−27] The majority of these publications focus on the collection of images and exploration of the chemical composition and properties of new synthetic materials such as graphene, silicon oxide spheres, and birnessite.[28−30] In the case of sunscreen, particle size can be difficult to measure since agglomeration occurs during sample preparation. Figure 2 shows EDS and SEM results from a single sunscreen product containing both Ti and Zn nanoparticles. Individual metal oxide particles in the sunscreen sample clumped together, but in this image are still discernible as nanoparticles. This is not always the case as some preparations yielded large (multimicrometer) agglomerations with no visible individual nanoparticles; the limitations of this technique are thus noted by students. SEM-EDS is also used to identify elements that are present. Students are able to see that inactive ingredients (often ignored on consumer product labels) are present and account for additional (and surprising) materials found in the sunscreens (such as the large Si containing particles seen in Figures 2a and S1). Particles seen in Figure 2a were further analyzed as shown in the particle size histogram in Figure 2c. This chart emphasizes the presence of both small Zn and Ti particles and larger, 300−400 nm, spheroid particles presumed to be the silicate listed on the sunscreen package (evidence in X-ray maps in Figure S1).

Organic active ingredients are assessed using HPLC. From chromatograms, students prepare calibration curves of either oxybenzone or octocrylene, plotting the analyte to internal standard (*trans*-cinnamic acid) peak area ratio versus analyte concentration (Figure 3). The calibration curves are then used to calculate the mass fraction of analyte in all three samples of the same commercial sunscreen (Table 1). Students thus acquire two different types of graphs to calculate their sunscreen unknown. It should be noted that the use of an

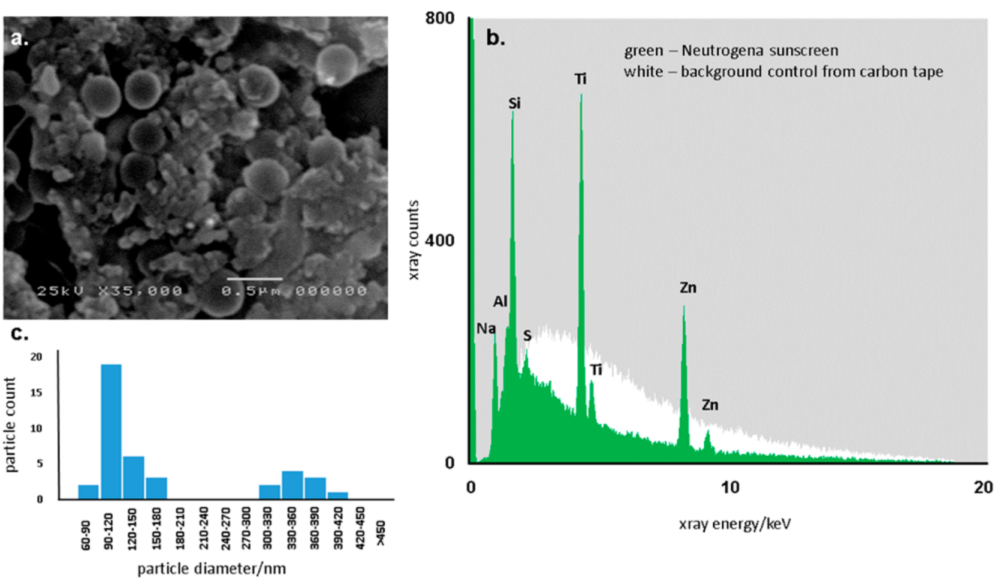

Figure 2. SEM image (a) and EDS spectrum with background control (b) of example sunscreen product nominally containing both Zn and Ti oxides. (c) Particle size histogram of image in (a) (reproduced with permission of MU student Kelsey Longe) showing a bimodal distribution of particle diameters.

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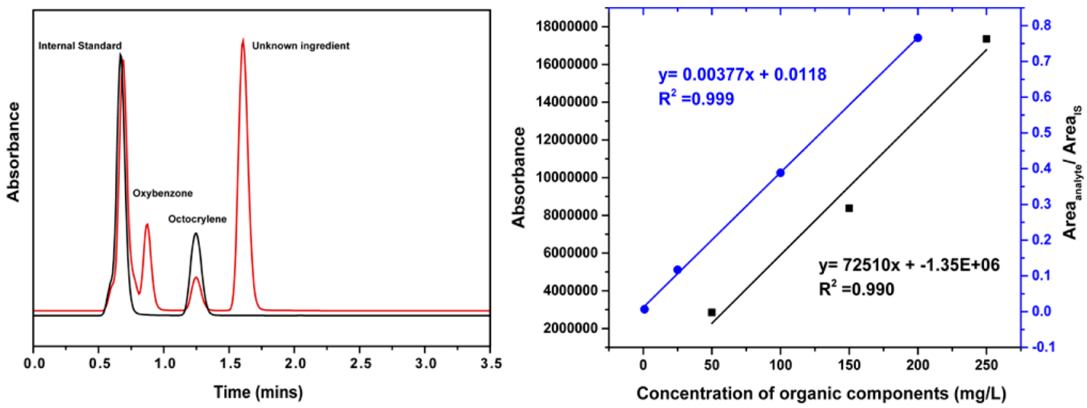

Figure 3. Representative chromatogram (left) for a sunscreen sample from student data (red line). Peaks are seen for internal standard, oxybenzone, octocrylene, and an unidentified peak. The commercial sunscreen is compared with an octocrylene standard and internal standard (*trans*-cinnamic acid, black line). Calibration curve (right) collected by students (black line) and calibration curve using internal standard method (blue line) for oxybenzone analysis.

internal standard with HPLC is not common with only a few publications appearing in this *Journal*.[31,32] Using an internal standard prevents variations in the injected volume and improves the accuracy of analyte extraction.[33] The ratio of the peak areas of the analyte to the internal standard ($A_{analyte}/A_{IS}$) was used to account for some of the student to student sample variation. Furthermore, the use of an internal standard provides a more correct quantitation as reported in the literature.[9,31−35] Students also determine the resolution value between the active ingredient and internal standard, percent recovery, and number of plates for their standards and their sunscreen samples as shown in Table 4. More specific details of these calculations can be found in the Supporting Information.

Table 4. Average Resolution Value between the Active Ingredient and Internal Standard, Number of Plates, and Percent Recovery for Each Standard Solution, and Resolution for Some Sunscreens Analyzed by HPLC

Concentration, mg/L	Resolution	Number of Plates (Standard)	Recovery, %[a]
50	1.6 ± 0.1	824 ± 11	123
100	1.2 ± 0.2	800 ± 86	103
150	1.6 ± 0.1	880 ± 94	113
250	1.6 ± 0.1	880 ± 104	103
Blue Lizard	1.8 ± 0.2	—[b]	—[c]
Coppertone	1.6 ± 0.3	—[b]	—[c]
Solar Sense	1.3 ± 0.2	—[b]	—[c]

[a]Data for n = 9 are shown in this table. [b]Not measured. [c]Not applicable.

Potential Variations

The sunscreen experiments were well received by students. Some of the feedback indicated these experiments were "enjoyable and informative" as students could "test and analyze an item used on a daily basis." Another commented that "being able to work with something with which I was in daily contact and had some knowledge about, peaked my interest." Students also appreciated being able to apply theoretical equations and statistical analysis to a practical application. One noted that the "in-depth and exhaustive analysis on the sunscreen chemical composition will influence my decision on what SPF and brand to pick in the future."

Consumer advocacy is indeed a possible extension of these experiments where the assignment could be modified to have students further consider the implications of results that differ significantly from reported values. Additional extensions include using other types of atomic spectroscopy instrumentation such as flame (FAAS), or graphite atomic absorption spectroscopy (GAAS), as shown in other lab experiments in this *Journal*.[21,36] Some preliminary laboratory experiments using FAAS in comparison with ICP were performed in an instrumentation methods laboratory course showing how the linear range of the calibration curve decreases in FAAS and therefore, further percent error can be calculated for the sunscreen samples. Experiments analogous to those described can also be performed where titanium is measured for sunscreens containing TiO_2 as the active ingredient. For the HPLC analysis, other active ingredients can be analyzed such as avobenzone, homosalate, and octisalate. Furthermore, students can investigate the effect of varying the mobile phase ratio (for example, 80:20, 70:30) and flow rate (0.5, 2.0 mL/min) and calculate the resolution and number of plates, deciding which of the parameters would improve the chromatogram.[37]

■ CONCLUSION

It is interesting to expose students to "real life" samples and to analyze their active ingredient content. The results of these experiments are important since there are no standardized methods that provide quality information for sunscreens. ICP and HPLC instruments are analytical tools that can be found in undergraduate institutions. There is a dearth of lab experiments in this *Journal* that combine both spectroscopy and chromatography methods specifically for analyzing the inorganic and organic components of sunscreens. SEM has become increasingly popular in undergraduate institutions due to the imaging capabilities, and particle size analysis and sunscreen provides an appropriate application for this technique. These experiments could be adapted to other commercial cosmetic formulations (e.g., calamine, hair care) that contain inorganic metal oxides and organic compounds as active ingredients.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00866.

Instructor's notes, lab experiment information, and student's notes (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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