APPLICATION NOTE

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Advancing Sunscreen Studies with non dilution and fast Zeta potential

Introduction/Context

Controlling zeta potential is crucial for sunscreen sprays, as it affects particle stability and dispersibility. Maintaining an optimal zeta potential prevents aggregation, ensuring even skin coverage, improved stability, and effective sun protection. This enhances product quality, reliability, and consumer safety. Besides the zeta potential, polyelectrolyte (PE) titration to find the zero point of charge (zeta potential = 0) is another important parameter as it determines charge density, total charges, the number of active ingredients, and the type of charge in cosmetic samples.

Importance of Zeta Potential in Sunscreen Spray:

- Higher zeta potential values generally indicate better stability of the sample.
- The skin's zeta potential is around -20 mV, so maintaining an optimal range for cosmetics is essential:
  - **Positive Zeta Potential**: the product may be hard to wash off the skin.
  - **Negative Zeta Potential:** If too negative, the product may not adhere well to the skin.

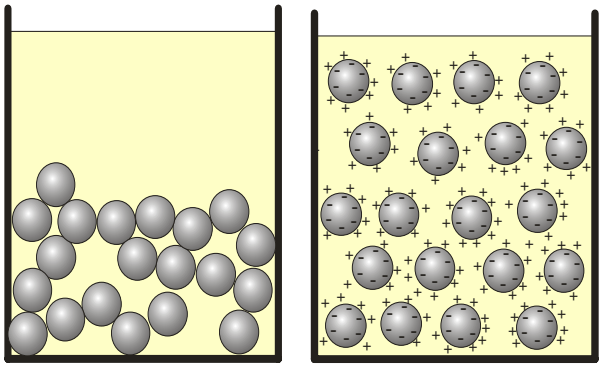

Figure 1: Samples without zeta potential sediment quickly, while those with high zeta potential stay suspended longer.

In this application note, we demonstrate the use of zeta potential and polyelectrolyte titration to monitor the destabilization of cosmetic samples. Specifically, we analyzed sunscreen sprays of the same brand with different expiration dates by measuring their zeta potential and performing polyelectrolyte titration to determine charge concentration. A correlation between these two

parameters was observed, which can be used to determine the destabilization of the cosmetics.

Figure. 2: Stabino Zeta

Unique Features of STABINO-ZETA

- The Stabino Zeta features a unique streaming potential technique for measuring the zeta potential of any suspensions. This approach provides consistent measurements, even at high concentrations.
  More info: STABINO ZETA - Zeta Potential Analyzer | MICROTRAC
- It accommodates particle sizes ranging from 0.3 nm to 300 µm, without requiring prior knowledge of the sample.
- Stabino Zeta offers a unique combination of polyelectrolyte titration and pH auto-titration features enabling rapid determination of the **zero point of charge** and the **isoelectric point**.
- **pH titration** identifies the isoelectric point (IEP), which is very crucial for determining the pH at which a sample has the best stability.
- **Polyelectrolyte titration** determines charge density, a key factor for assessing stability, total charge, the amount of active ingredients, and the type of charge in samples.

Experimental

In this study, three sunscreen samples were selected for comparative analysis of zeta potential, zero point of charge, and charge concentration to monitor the destabilization of sunscreen spray with 50 SPF. The samples included:

1. **Expired Sample:** A generic sunscreen product, 13 months past expiration, referred to as a "Generic Expired Sample".
2. **About-to-Expire Sample**: Same sunscreen product with 3 months until expiration, labeled as "Generic Sunscreen 3 months exp."
3. **Long-Shelf-Life Sample**: Same sunscreen spray with 24 months until expiration, named "Generic Sunscreen Spray.

These samples were analyzed to evaluate the changes in surface charge related to the expiration date.

To measure the zeta potential of all samples, a 400 µm piston was used, and the samples were pre-mixed for 120 seconds before each measurement. Data were collected for 120 seconds and repeated three times. For polyelectrolyte titration, a cationic surfactant solution of 0.0025 M Poly-(diallyldimethylammonium chloride) (p-DADMAC) was used as a titrant.

Results:

Initially, zeta potential data is collected for the three samples in triplicate, and the results are presented in Figure 3.

Sample Name	Average Zeta potential [mV]	pH Averag	Average Conductance [S/cm]	Temperature Average [Deg C]
Generic Expired Sample	-1.9	5.9	14.6 u	21.3
Generic Expired Sample	-1.9	5.9	14.6 u	21.5
Generic Expired Sample	-1.9	5.9	14.6 u	21.8
Generic Sunscreen 3 months ex	-4.9	6.6	38.4 u	23.6
Generic Sunscreen 3 months ex	-4.8	6.6	40.5 u	23.6
Generic Sunscreen 3 months ex	-4.7	6.6	41.6 u	23.6
Generic Sunscreen Spray	-9.6	6.8	39.7 u	25.5
Generic Sunscreen Spray	-9.6	6.8	39.5 u	25.4
Generic Sunscreen Spray	-9.6	6.8	39.8 u	25.3

Figure 3: Comparative Analysis of Zeta Potential in Expired About-to–Expire, and Long-Shelf-Life Sunscreen Spray

- **Expired Sample (13 months expired):** Referred to as "Generic Expired Sample" has a zeta potential of approximately -2 mV. Which is the lowest among the three samples.
- **About-to-Expire Sample (3 months left):** Referred to as "Generic Sunscreen 3 months exp" showing a zeta potential of about -4.7 mV, which is higher than that of the expired sample.

- **Sample with 24 months until expiration:** Named as "Generic Sunscreen Spray" has a zeta potential of approximately -9.6 mV, which is the highest among the three samples.

Thanks to STABINO ZETA, the zeta potential is measured without any dilution, in less than a minute with excellent reproducibility (measurement done in triplicate). These results indicate a small change in the surface charge during aging. For further exploration of these changes, the STABINO ZETA offers a fully automatic and one-click titration for a complete understanding of the surface charge and charge density.

Effect of Charge density of the three Sunscreen Spray

Polyelectrolyte titration was conducted on three sunscreen samples, each with varying expiration dates, using a 0.0025 N p-DADMAC solution. The titration was done fully automatically via embedded pumps at the desired flow rate. Mixing is ensured by the piston motion. The full titration is obtained in less than **20 minutes** and **fully automatically**. The results are illustrated in Figure 4.

Sample Name	Titrant Conc.	Titrant	Consumption [mL]	Charge Conc.[C]
Generic Expired Sample	0.0025 N	P-DADMAC	2.824	0.681
Generic Sunscreen 3 Months	0.0025 N	P-DADMAC	5.473	1.320
Generic Sunscreen Spray	0.0025 N	P-DADMAC	8.209	1.980

Sample Name	Titrant P-DADMAC Conc.	Initial Zeta potential P (0mL)	Highest Zeta potential P min [mV]	Volume needed for zero Zeta potential [mL]
Generic Expired Sample	0.0025 N	-1.6	2.824	2.824
Generic Sunscreen 3 Months	0.0025 N	-4.6	5.473	5.473
Generic Sunscreen Spray	0.0025 N	-9.5	8.209	8.209

Figure 4: Polyelectrolyte titration graph

From the polyelectrolyte titration graph (Figure 4) we can get the following results.

- **Expired Sample (13 months expired):** This sample required the least p-DADMAC (2.824 mL) to reach the zero point of charge, resulting in the lowest charge concentration (0.681 Coulombs). This indicates the fewest active ingredients and the lowest total surface charge of its particles.
- **About-to-Expire Sample (3 months left):** This sample required a moderate amount of p-DADMAC (5.473 mL) to reach the zero point of charge, resulting in a charge concentration of approximately 1.32 Coulombs
- **Sample with 24 months until expiration:** This sample required the most p-DADMAC (8.209 mL) to reach the zero point of charge, resulting in the highest charge concentration (1.980 Coulombs). This indicates the highest number of active ingredients and the greatest total surface charge of its particles.

The charge concentration values and the titrant volume to reach 0mV zeta potential indicate important different charge concentrations between the three samples. Combining both high precision - non-dilution zeta potential measurements with titration measurement gives a complete understanding of the surface charge environment and a better understanding of stability variation.

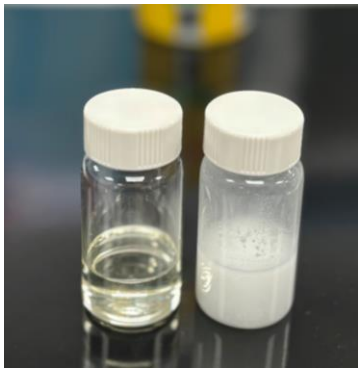

Figure 5: Sunscreen samples before (left) and after (right) polyelectrolyte titration

Conclusion:

From the polyelectrolyte titration, it can be concluded that charge concentration decreases as sunscreen samples approach or surpass their expiration dates. The expired sample had the lowest values, indicating reduced stability, while the sample with 24 months remaining showed the highest values, suggesting higher stability and better performance. These findings imply that the electrostatic properties of sunscreen degrade over time, affecting stability and effectiveness.