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“A Step Towards Sustainability: Application of Potentiometric Titration for the Analysis of Anionic Surfactants”

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1. Introduction

The hair and bath care market is experiencing continuous growth, driven by the increasing demand for health and beauty. This sector encompasses a wide range of products, including shampoos, conditioners, soaps, and shower gels. Surfactants are a key raw material in this sector, acting as cleaning agents, emulsifiers, and thickeners due to their chemical properties [1]. In 2022, the global surfactant market was estimated at US\$43.5 billion [2].

Their ionic nature allows for classification into different groups: anionic, cationic, amphoteric, and non-ionic. Anionic surfactants are so named due to the presence of a negative charge in their polar group and dissociate into negative ions in aqueous solution. They are the most commonly used surfactants due to their good compatibility with skin pH, stability, and low toxicity [1].

Sodium Laureth Sulfate (SLES) stands out as one of the most common anionic surfactants used in these formulations due to its good cleaning power and low cost [5].

Generally, these substances can be used pure or in solution in product formulations. The precise quantification of these substances, whether in the raw material or the finished product, is intimately linked to the quality and efficacy of the final product for the consumer.

In the cosmetics industry, quality control of these formulations requires precise analytical methods to analyze the content of these substances.

Traditionally, the quantification of anionic surfactants in cosmetic matrices is performed by two-phase titration, such as the Epton method (ISO 2271) [3]. The methodology is based on the reaction between an anionic surfactant and a cationic surfactant, benzalkonium bromide (Hyamine 1622), and uses methylene blue as an indicator [4].

Despite being a relatively simple and low-cost method, two-phase titration has drawbacks such as subjectivity in determining the endpoint (EP), the toxicity of chloroform, and the generation of organic waste, making it a less sustainable option [4].

Alternatively, automated potentiometric titration emerges as a technique for detecting these substances. This technique uses selective and reference electrodes to detect the potential

difference during the analysis. The potential change is measured as a function of the volume of titrant added, whose concentration is known, and the analyte concentration can be determined based on the titrant volume at the endpoint and the known stoichiometry of the chemical reaction between the analyte and the titrant [2].

Potentiometric methods are more advantageous due to their specificity, reduced organic waste, and increased speed of analysis. In an industrial context, automated titration proves capable of offering greater economic efficiency in the medium and long term, optimizing reagent use and reducing variability between repeated analyses.

Therefore, this work analyzes and discusses the application of automated potentiometric titration in the determination of anionic surfactants in raw materials and finished cosmetic products, compared to manual two-phase titration, observing aspects of technological efficiency, sustainability, and operational costs. The research contributes to informing the choice of the most appropriate analytical method for the diverse needs of the cosmetics industry, reinforcing the role of analytical technology in improving quality control processes and aligning with green chemistry guidelines.

2. Materials and Methods

This study evaluated the applicability of automated potentiometric titration for the quantitative determination of anionic surfactants in cosmetic matrices. Six samples were analyzed: two Sodium Laureth Sulfate (SLES) samples with theoretical SLES concentrations of 70% and 27%, one Sodium Lauryl Sulfate (SDS) sample at 99%, two cleaning gel samples with theoretical SLES concentrations of 4% and 4.8%, respectively, and one shampoo sample with a theoretical SLES concentration of 8.4%. Product samples were obtained directly from industrial production and stored under appropriate conditions to maintain their physicochemical characteristics. Potentiometric titration was performed using a Metrohm Titrando 888 automatic titrator with Tiamo 2.5 software. The titrant used was a 0.004 M commercial solution of benzalkonium bromide (Hyamine 1622) (SpecSol). The equivalence point was determined from the maximum of the first derivative of the potentiometric curve obtained using a Metrohm 6.0507.120 indicator electrode, specific for anionic surfactants, and an Ag/AgCl reference electrode (Metrohm 6.0733.100). For sample preparation, 250 mL volumetric flasks and volumetric pipettes were used. The mass (m) of each sample was calculated individually, considering the molecular weight of the active substance (MW) multiplied by a constant (0.15) and divided by the concentration of the active substance in the sample (%MA). The calculated masses of each sample were transferred to 250 mL volumetric flasks and diluted with Type I distilled water (Resistivity > 18 [MΩ.cm](#)) to the final volume. Then, a 10 mL aliquot of each solution was transferred to a new container and diluted again with distilled water to approximately 50 mL. Afterwards, they were titrated in the automated system under constant stirring. Six independent replicates were performed for each sample to ensure the accuracy and reproducibility of the results. The standard deviation and relative error were calculated to assess the method's accuracy.

3. Results

Table 1 summarizes the results of the analysis of six replicates of the following samples: Sodium Laureth Sulfate (SLES) at 70% and 27%, Sodium Lauryl Sulfate (SDS) at 99%, two cleaning gels with theoretical SLES concentrations of 4% and 4.8%, and one shampoo with a theoretical SLES concentration of 8.1%. Six replicates were performed for each sample. The table presents the theoretical value, the average experimental value, the standard deviation, the relative standard deviation (RSD), and the relative error.

Table 1: Experimental Values, Precision, and Accuracy of the Analyses

Sample	Theoretical value (%)	Experimental value (%)	RSD (%)	Relative Error (%)
SLES 70%	70.0	70.8	0.18	1.14
SLES 27%	27.0	26.7	0.12	1.12
SDS 99%	99.0	97.9	0.72	1,09
Cleansing gel 4%	4.0	3.9	0.04	3.5
Cleansing gel 4,8%	4.8	4.9	0.05	2.08
Shampoo 8,1%	8.1	8.2	0.03	1.85

Potentiometric titration demonstrated high precision, evidenced by the low RSD values (all below 0.72%), indicating excellent method reproducibility. Accuracy, assessed by the relative error, was also satisfactory for most samples, with values below 2%, showing good agreement between measured and theoretical values. Notably, even in complex matrices such as cleaning gels and shampoo, the matrix effect was low, with relative errors within an acceptable range for quantitative analysis in cosmetic products. The largest discrepancy, observed for the 4% cleaning gel (3.5% relative error), can be attributed to factors specific to that formulation, and not to an inherent limitation of the method. The inclusion of SLES samples with different concentrations (70% and 27%) and SDS (99%) demonstrates the robustness of the method across different concentration ranges and types of anionic surfactants.

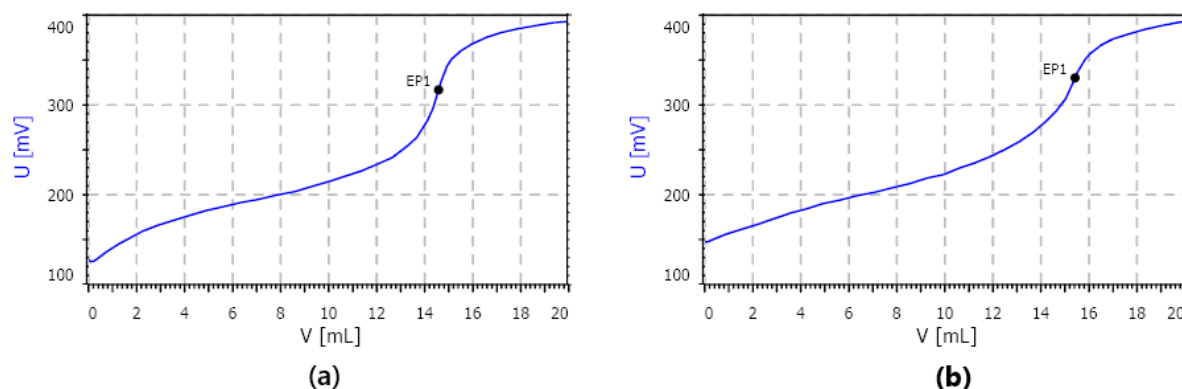


Figure 1: Potentiometric Titration Curves, showing potential versus titrant volume for: (a) SLES 70%; (b) shampoo 8.1%

Analysis of the titration curves allows for the assessment of method sensitivity and the influence of matrix complexity. Sensitivity, reflected by the slope of the curve in the EP region, demonstrates the method's ability to detect small variations in analyte concentration. Curves with steeper slopes, as observed, for example, in the SLES 70% sample, indicate higher sensitivity. Samples with lower anionic surfactant concentrations, such as the cleaning gels, exhibit curves with less pronounced slopes, although the EP is still clearly defined. This behavior is expected, since at lower concentrations, the potential variation around the EP is less pronounced.

Curve analysis allows for a visual assessment of method sensitivity. Curves with a steep slope in the EP region indicate higher sensitivity; that is, small additions of titrant generate significant potential changes, facilitating precise EP determination. Comparing the slopes of the curves for the different samples can provide insights into the influence of matrix

complexity on titration sensitivity. Sample (b) shows a lower slope in the potential curve, indicating lower sensitivity. The same is observed for the other two finished product samples, suggesting that the formulations exhibit some type of matrix effect that may impair electrode selectivity in the analysis medium.

4. Discussion

The results obtained by automated potentiometric titration demonstrate the technique's effectiveness for quantifying anionic surfactants in different cosmetic matrices. Low RSD values ($<0.72\%$) indicate high precision and reproducibility of the method, corroborating previous studies demonstrating the superiority of potentiometric titration over traditional titrimetric methods with visual indicators. Relative errors, mostly below 2%, demonstrate good method accuracy, with agreement between experimental and theoretical values. The largest discrepancy, observed in the 4% cleaning gel (3.5% relative error), can be attributed to matrix interferences, such as the presence of other ionic components and salts in the formulation, which may compete with the surfactant of interest in the interaction with the indicator electrode. In this case, performing a recovery study or using a prior separation method, such as chromatography, could help obtain more accurate results.

Analysis of the titration curves (Figure 1) allows for assessment of the method's sensitivity. The steep slope of the curve in the EP region indicates high sensitivity, allowing for precise detection of the titration endpoint. The lower slope observed for the finished product samples (cleaning gel and shampoo) suggests a possible matrix effect, which can decrease the method's sensitivity. This can be attributed to the interaction of other matrix components with the electrode, hindering the detection of the potential variation at the EP. Comparison of the results obtained by potentiometric titration with the theoretical values (Table 1) demonstrates good agreement, validating the method's applicability for quantifying anionic surfactants in complex cosmetic matrices.

Automated potentiometric titration offers significant advantages over the traditional two-phase method, such as the elimination of chloroform, a toxic and environmentally harmful solvent. This characteristic aligns the technique with the principles of green chemistry, which seeks to minimize the environmental impact of chemical processes (Anastas & Warner, 1998). Furthermore, process automation reduces analysis time, minimizes operational errors, and increases productivity, making potentiometric titration an advantageous alternative for quality control of anionic surfactants in cosmetic formulations.

A potential limitation of the method is its linearity range in different matrices, which must be determined experimentally for each type of anionic surfactant. The presence of other surfactants or anionic substances in the sample may interfere with the titration, requiring additional separation or purification steps.

5. Conclusion

This study demonstrated that automated potentiometric titration is an effective, precise, and reproducible technique for the determination of anionic surfactants in various cosmetic matrices, including raw materials (SLES, SDS) and finished products (cleaning gel, shampoo). The elimination of chloroform use makes the method more sustainable and aligned with the principles of green chemistry. Automated potentiometric titration offers significant advantages over the traditional two-phase method, providing greater precision, shorter analysis time, and reduced operational errors, making it a promising alternative for

anionic surfactant quality control in the cosmetics industry. Future studies could investigate the method's application in other cosmetic matrices and evaluate the influence of different types of indicator electrodes on the technique's sensitivity and selectivity.

6. References

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