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Investigation of Matrix Effect in the Determination of Bisphenols in Aquatic Products by Liquid Chromatography-Mass Spectrometry

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Abstract: In this study, techniques such as liquid chromatography-ultraviolet photometric detector and evaporative light scattering detector were used to search for substances in the matrix that produced matrix effects when LC-MS was used to determine bisphenol compounds in aquatic products. This study provides new insights for researchers dealing with matrix effect problems. Bisphenols are introduced, with a focus on BPA and BPS. LC-MS is a commonly used method for the determination of bisphenols, but it is often affected by matrix effects, primarily due to phospholipids present in aquatic products. To confirm this, a chromatographic method was established to identify substances in the matrix that may co-elute with BPs. Phospholipids were confirmed as significant contrib- utors to matrix effects. Finally, commonly used methods to eliminate matrix effects are summarized.

Keywords: bisphenol compounds, matrix effect, LC-MS, aquatic products.

1. Introduction

Bisphenols (BPs), such as Bisphenol A (BPA) and Bisphenol S (BPS), are extensively used in industrial products, posing significant environmental and health risks. BPA, due to its higher solubility, is the most frequently detected bisphenol in aquatic environments, while other bisphenols are less soluble. The widespread usage of bisphenols has resulted in their occurrence in both surface water and drinking water, raising concerns about potential health risks. BPA and BPS, in particular, are known for their bioaccumulation potential and endocrine-disrupting properties, which necessitate accurate detection and monitoring [1-3].

One of the major challenges in detecting bisphenols in aquatic products is the matrix effect, which refers to interference caused by other substances present in the sample matrix, potentially affecting the detection accuracy of LC-MS. In aquatic products, matrix effects are primarily attributed to the high content of phospholipids, which may co-elute with bisphenols during chromatographic separation, resulting in signal suppression or enhancement during ionization. Addressing matrix effects is essential to improve the reliability and accuracy of bisphenol detection, especially in complex matrices like aquatic products.

This study aims to investigate the sources of matrix effects and identify effective mitigation strategies. The findings will contribute to enhancing the detection accuracy of bisphenols, providing valuable insights for environmental monitoring and public health protection. The paper is organized as follows: Section 2 describes the materials and methods used, including chromatographic conditions and reagents. Section 3 presents the results and discusses the matrix effects observed, as well as the impact of phospholipids. Finally, Section 4 concludes the study by summarizing key findings and future directions.

2. Materials and Methods

2.1. Chemicals and Reagents

Bisphenol A (BPA) and Bisphenol S (BPS) standards were obtained from Sigma-Aldrich (USA). Methanol and acetonitrile were of HPLC grade, and ultrapure water was obtained from a purification system (Exceed-AD-16, China).

2.2. Chromatographic Conditions

An UltiMate 3000 HPLC system (ThermoFisher, USA) was used with a Symmetry C18 column (4.6 mm ×250 mm, 5 µm, Waters, USA). The mobile phase consisted of methanol (70%) and water (30%), with a flow rate of 1.0 mL/min. The injection volume was 20 µL, and detection was performed at 224 nm.

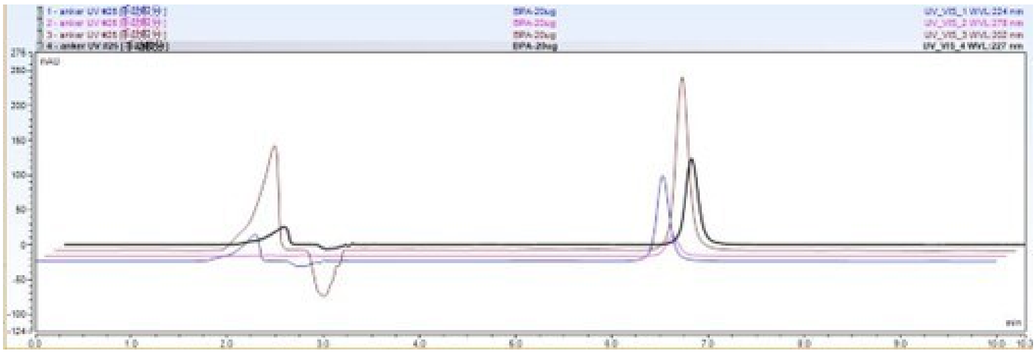

Figure 1: Chromatogram of BPA and BPS standard solutions under optimized chromatographic conditions.

3. Results and Discussion

3.1. Matrix Effect in LC-MS Analysis

The matrix effect is a significant factor influencing the accuracy of LC-MS analysis, particularly for polar compounds such as BPA and BPS. In this study, it was observed that BPA could be reliably detected without interference, whereas BPS co-eluted with substances in the matrix, likely phospholipids, leading to signal suppression. The chromatogram of BPA and BPS standard solutions under optimized chromatographic conditions is shown in Figure 1, illustrating the separation of these compounds and the retention times observed under the established method.

Phospholipids are amphipathic molecules that are prone to cause matrix effects during electrospray ionization (ESI), leading to ion suppression or enhancement of co-eluting analytes [4, 5]. The presence of matrix effects indicates that careful method development is essential to obtain reliable results for bisphenols in aquatic products.

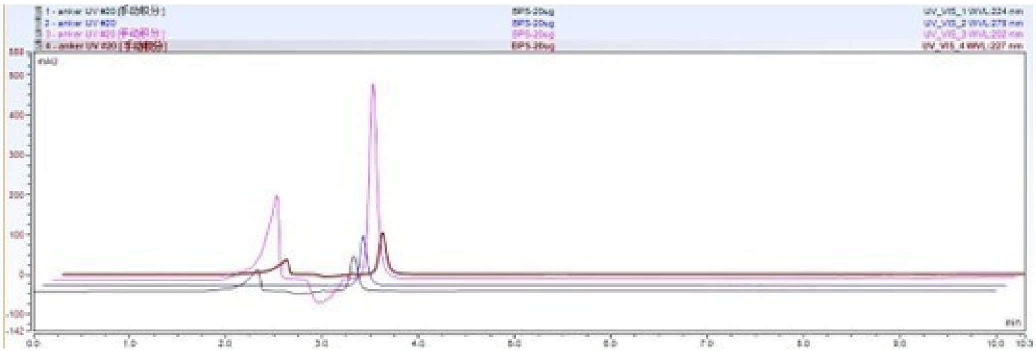

Figure 2: Comparison of BPA chromatograms under different wavelengths: 224 nm, 278 nm, 202 nm, 227 nm.

Figure 2 shows the chromatograms of BPA at different detection wavelengths. The results indicate that the choice of detection wavelength can have a significant impact on sensitivity and accuracy.

3.2. Phospholipids as a Source of Matrix Effect

To confirm the presence of phospholipids and their contribution to the matrix effect, samples of fish, crabs, and shellfish were analyzed. Phospholipids were detected in all three types of matrices, with fish samples having the highest phospholipid content. The use of evaporative light scattering detection confirmed the presence of phospholipids, and their co-elution with BPS demonstrated their role in causing matrix effects during LC-MS analysis [6, 7]. This observation is consistent with previous studies that indicate phospholipids are a major contributor to ion suppression in ESI-MS, primarily due to their amphipathic nature, which allows them to compete with analytes for ionization [8, 9].

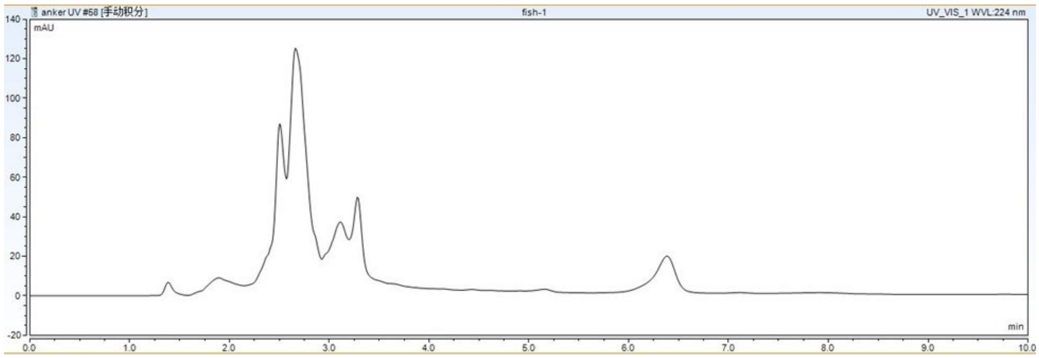

Figure 3: Phospholipid content in different aquatic matrices analyzed by evaporative light scattering detection.

Figure 3 presents the phospholipid content in different aquatic matrices. The highest content was found in fish, which correlated with the highest matrix effect observed during analysis.

3.3. Ionization Mechanisms: IEM and CEM

Two ionization models, the ion evaporation model (IEM) and the chain ejection model (CEM), were introduced to explain the matrix effect in the ionization process. In the IEM, the strong polarity of BPS hinders its migration to the droplet surface, which reduces ionization efficiency. Phospholipids, on the other hand, are readily ionized due to their ability to access the droplet surface efficiently, as explained by the CEM. This disparity in ionization efficiency between BPS and phospholipids accounts for the observed signal suppression during mass spectrometric detection [9, 10].

3.4. Mitigation Strategies

To mitigate the effects of the matrix, several strategies were evaluated. Modifying chromato- graphic conditions, such as adjusting the mobile phase composition and pH, proved effective in reducing the matrix effect. The use of solid-phase extraction (SPE) was also investigated as a sample cleanup step to remove phospholipids before LC-MS analysis. SPE significantly reduced the phospholipid content in the sample, which in turn reduced the matrix effect. Additionally, the use of isotopic internal standards was found to be an effective strategy for compensating for matrix-induced signal suppression or enhancement [3, 11].

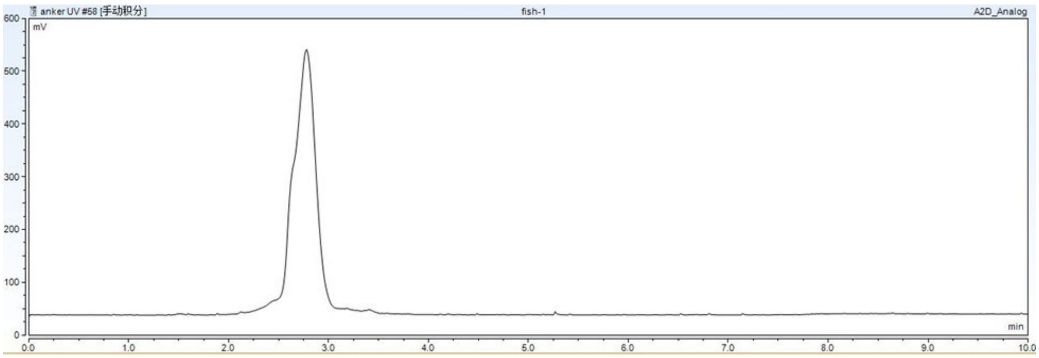

Figure 4: Chromatogram showing the effect of solid-phase extraction (SPE) on reducing matrix interference for BPS.

Figure 4 shows the effect of solid-phase extraction on reducing matrix interference for BPS. The results clearly demonstrate that SPE can effectively remove interfering substances, thereby improving the accuracy of LC-MS analysis.

Isotopic internal standards can help correct for variability in the ionization process by co- eluting with the target analyte and undergoing the same ionization conditions. This approach has been widely applied in LC-MS/MS analysis to improve the accuracy and precision of quan- titative results, especially for challenging matrices such as aquatic products [8, 12].

4. Conclusion

A rapid chromatographic method was established for the detection of bisphenol compounds in aquatic products. The study confirmed that phospholipids are a significant contributor to the matrix effect, particularly in the detection of BPS. Mitigation strategies such as modify- ing chromatographic conditions, using solid-phase extraction, and employing isotopic internal standards were found to be effective in reducing matrix effects. These findings highlight the importance of addressing matrix effects in the analysis of bisphenols to ensure accurate and reliable results.

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