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Technical Report

Importance of Vial Selection in LC and LC/MS Analysis:

Effects on Analysis of Alkaline Metals from Glass

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Abstract:

In recent years, the sensitivity of mass spectrometers and other detectors has improved, enabling trace sample analysis. In LC and LC/MS analyses of trace compounds, vial selection is very important. Certain vial materials can cause unintentional compound adsorption, reducing analytical sensitivity. For instance, polypropylene (PP) vials often adsorb hydrophobic compounds on their surfaces, while glass vials minimize hydrophobic adsorption but may exhibit surface ionic adsorption of silanol bases and basic compounds due to metallic ion interactions. Additionally, the elution of sodium and other alkali metals from glass surfaces can influence analytical outcomes. To address these issues Shimadzu has developed Shim-vial™, a specially treated vial designed to minimize sodium (Na) elution. Comparative studies demonstrated that Shim-vials exhibit significantly lower Na elution levels than conventional vials. Furthermore, results showed a direct correlation between higher Na elution and increased adsorption of basic compounds, suggesting that metallic ions play a key role in this adsorption phenomenon.

Keywords: Low adsorption glass vials, alkaline elution

1. Introduction

The vials used for liquid chromatography are typically manufactured from borosilicate glass. Metallic oxides are included in borosilicate glass for the purpose of increasing their workability[1)]. It is known that many of the metallic components included exist at the surface of the glass vial[2)].

The metallic components on the inner surface of the vial cleave siloxane bonds, resulting in metal silanolate. Metal silanolate ionizes easily[2)-3)], and silanol and basic compounds are believed to be adsorbed through mutual interaction of the ions[3)-4)] (Figure 1).

In this article, we describe the effect of eliminating metals on analytical repeatability using Shim-vial S, in which metal silanolate production is suppressed by removing alkaline metals with a special treatment during formation; and Shim-vial H, in which this special treatment is further strengthened.

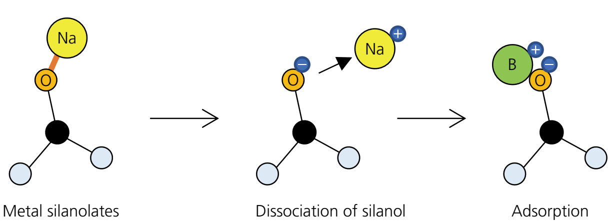

Figure 1: Adsorption image of basic compounds on the vial surface

2. Confirmation of the Amount of Alkaline Metals Eluted

As a representative of the alkaline metals contained in borosilicate glass, we measured the amount of elution of Na from the inner surface of vials using an atomic absorption spectrophotometer (Figure 2).

When Shim-vial and other brands of glass vials were compared, it was evident that the amount of Na dissolving in water was smaller for Shim-vial. In the results, Shim-vial H had the smallest amount of metals, followed by Shim-vial S.

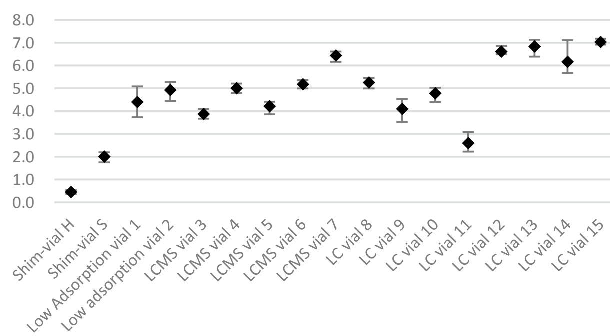

Figure 2: Amount of sodium elution (µg/mL)

3. Adsorption of Basic Compounds

An evaluation of the adsorption for each vial was performed using an aqueous 1 mg/L solution of chlorhexidine, a basic compound. The analytical conditions are shown in Table 1. After adding the sample to each vial, they were left undisturbed at 40 °C, and an LC analysis was performed after 24 hours and 72 hours. Taking the area when chlorhexidine is dispensed into a PP vial as 100 %, the results showed that Shim-vial H had the highest recovery rate, and this value changed very little even with the passage of time (Figure 3).

Table 1: HPLC analytical condition

Column	: Shim-pack™ XR-ODS (100 mm L., 3.0 mm I.D., 2.2 µm)
Mobile Phase	: 100 mmol/L Sodium perchlorate containing 10 mmol/L phosphoric acid solution (pH 2.6) / Acetonitrile (55 / 45, v/v)
Flow rate	: 0.5 mL/min
Injection volume	: 5 µL
Sample solution	: Water
Column temperature	: 40 °C
Detection	: UV 254 nm

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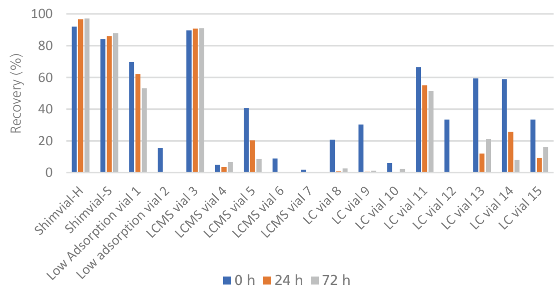

Figure 3: Recovery rate of Chlorhexidine

To check the impact on adsorption by the Na eluted from the vials, Figure 4 shows a plot of the relationship between the amount of Na eluted in the vial and the recovery rate for chlorhexidine after 24 hours. The results showed a correlation of -0.77, indicating a strong tendency for adsorption of chlorhexidine to increase (the chlorhexidine recovery rate to decrease) as the amount of Na elution in vials increases.

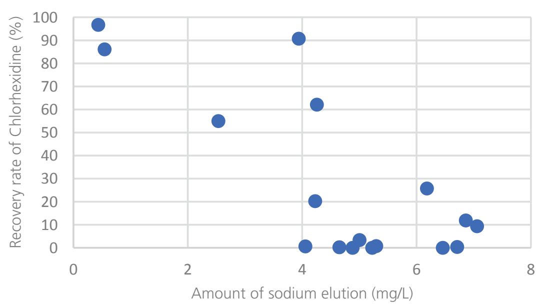

Figure 4: Correlation of Adsorption and Sodium Elution

4. Production of Na Adducts in LC/MS

It is evident that in LC/MS analysis, the Na dissociated from the inner surface of the vial reacts with the ionized target compounds, and is sometimes detected as Na adducts (Figure 5).

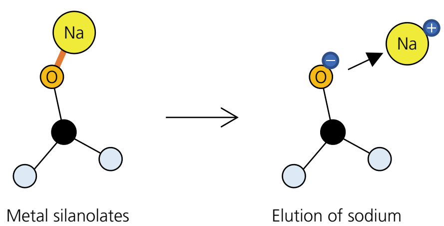

Figure 5: Elution image of sodium on the vial surface

In order to check the impact on LC/MS analysis results due to vial differences, an aqueous solution of 5 mg/L meloxicam was dispensed into various glass vials. Measurements were performed by LC/MS after leaving the vials for 48 hours. The analytical conditions are shown in Table 2.

The adduct ratios were calculated and the results are shown in Figure 6. The value adopted for the ratio of each adduct was found by dividing the peak area for the adduct in question by the total peak area value for m/z 352 (+H), 359 (+NH_4), 374 (+Na), 391 (+K), 407 (+Fe), and 414 (+Cu).

From the results, it was evident that the H adduct ratio is highest for Shim-vial H, and that it is less susceptible to metal ions from the vial. In contrast, some of the vials were confirmed to have an Na adduct ratio of 50 % or higher.

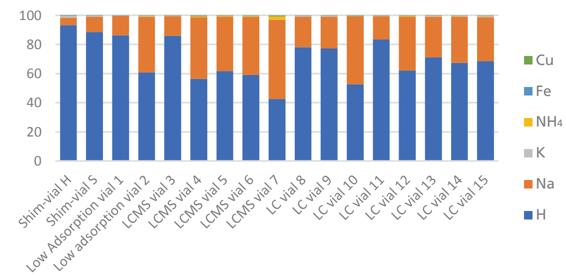

Figure 6: Proportion of adduct ions

Table 1: HPLC analytical condition

Mobile Phase	: Water / Acetonitrile = 90 / 10 (v / v)
Flow rate	: 0.2 mL/min
Injection volume	: 1 µL
Sample	: 5 mg/L Meloxicam in Water
Sample Temperature	: 15 ˚C
Ionization	: ESI, Positive
Mode	: SIM (*m/z* 352, 359, 374, 391, 407, 414)

5. Summary

It is evident that reducing Na in glass vials limits adsorption of basic compounds. Further, in LC/MS analysis, analytes become Na adducts due to the presence of Na ions, which has an impact on the sensitivity at the original m/z as well. Because adsorption and the production of Na adducts are so noticeable in the analysis of low concentration compounds, there are likely cases where the results obtained differ from the actual results, without anyone noticing. To prevent such issues, the use of high quality, low adsorption vials is recommended. The Shim-vial H/S series feature very low Na elution amounts due to a special treatment, enabling their use as vials that provide stable analysis results for both basic and acidic compounds.

References

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