

Improve the sensitivity of haloacetic acids and phenols by increasing ion transmittance of an ion guide at higher pressure vacuum

Manabu Ueda¹, Takanari Hattori¹, Wataru Fukui¹, Tsubasa Ibushi², Kazuo Mukaibatake¹

1 Shimadzu Corporation, Kyoto, Japan., 1, Nishinokyo-Kuwabaracho Nakagyo-ku, Kyoto 604-8511, Japan. 2 Shimadzu Techno-Research, Inc., Kyoto, Japan. 2, Nishinokyo-Shimoaicho, Nakagyo-ku, Kyoto, 604-8436 Japan

1. Overview

Improve the sensitivity of low-mass compounds such as haloacetic acids and phenols by increasing ion transmission efficiency of an ion guide at higher pressure vacuum region. Ion trajectory simulations considering gas dynamics was conducted to achieve the improvement.

2. Introduction

A LC-MS has several vacuum stages between an atmospheric pressure ion source and a mass filter located at a low pressure region (~10E-3 Pa) (Fig. 1). There is an ion guide in each stage and its electric field is optimized to transport ions. However, the ion trajectories are affected by not only electric field but gas dynamics at higher pressure vacuum region (~100 Pa). Therefore, we conducted ion trajectory simulations considering both effects of electric field and gas dynamics to maximize ion transmittance of the ion guide at higher pressure vacuum region. Based on that result, we also analyzed some compounds such as haloacetic acids and phenols to confirm the improvement of the sensitivity.

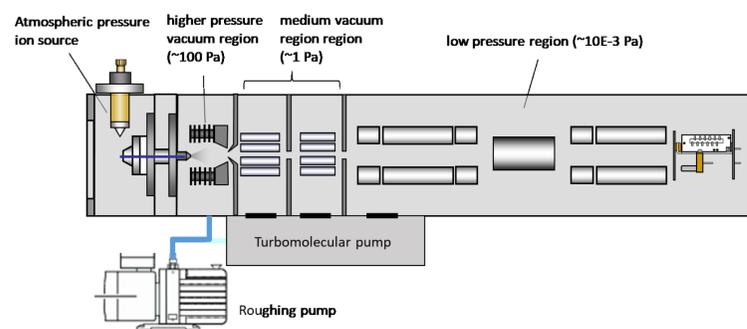


Fig.1 An example of configuration of LC-MS

3. Materials and Methods

3-1. Ion Trajectory Simulation

We modeled the ion guide in the higher pressure vacuum region and the MS inlet that connects the atmospheric pressure ion source and the chamber of the LCMS-8060NX, triple quadrupole mass spectrometer (Shimadzu Corporation, Japan). Then we executed simulations of gas dynamics by using the ANSYS Fluent (ANSYS Inc., U.S.). After that, we imported the result into the SIMION (Scientific Instrument Services, Inc., U.S.) and executed ion trajectory simulations considering both effects of electric field and gas dynamics.

3-2. Analyses of Haloacetic Acids and Phenols

We also conducted the analyses of 3 haloacetic acids (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid) and 4 phenols (phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol) by using the Nexera™ X2 UHPLC system (Shimadzu Corporation, Japan) coupled with the LCMS-8060NX to confirm the improvement of the sensitivity by applying the higher RF voltage to the ion guide at higher pressure vacuum region. The multiple reaction monitoring (MRM) transition of each compound was shown in Table 1.



Fig.2 The Nexera and the LCMS-8060NX LC-MS/MS system

Table 1 MRM transitions of the target compounds

Compound Type	Compound Name	MRM Transition
haloacetic acids	monochloroacetic acid (MCAA)	93.0 > 35.0
	dichloroacetic acid (DCAA)	127.0 > 82.9
	trichloroacetic acid (TCAA)	161.0 > 116.9
phenols	phenol	93.0 > 65.0
	2-chlorophenol	127.0 > 35.1
	2,4-dichlorophenol	161.0 > 35.1
	2,4,6-trichlorophenol	194.9 > 35.1

3-3. Analytical Conditions

■ Analysis of Haloacetic Acids

UHPLC (Nexera X2™ system)

Column: CAPCELL PAK C18 MGIII (3 mm I.D. x 150 mm, 3 μm, OSAKA SODA CO., LTD., Japan)
 Mobile phase A: 0.2% Formic acid/water B: 0.2% Formic acid/methanol
 Flow rate: 0.5 mL/min
 Injection vol.: 25 μL
 Column temp.: 50°C

MS (LCMS-8060NX)

Ionization: IonFocus (ESI, Negative)
 DL temp.: 150°C HB temp.: 100°C
 Interface temp.: 130°C Nebulizing gas: 3 L/min
 Drying gas: 5 L/min Interface voltage: -2 kV
 Heating gas: 15 L/min Focus voltage: -4 kV

■ Analysis of Phenols

UHPLC (Nexera X2™ system)

Column: Shim-pack GIST-HP C18 (2.1 mm I.D. x 100 mm, 3 μm, Shimadzu Corporation, Japan)
 Mobile phase A: water, B: methanol
 Flow rate: 0.5 mL/min
 Injection vol.: 20 μL
 Column temp.: 40°C

MS (LCMS-8060NX)

Ionization: APCI (Negative)
 DL temp.: 200°C HB temp.: 200°C
 Interface temp.: 350°C Nebulizing gas: 3 L/min
 Drying gas: 5 L/min Needle voltage: -3 kV

4. Result

4-1. Ion Trajectory Simulation

The examples of result of gas dynamics simulation and ion trajectory simulation considering gas dynamics are shown in Fig.3 and Fig.4 respectively. According to the results, it was found that in case of the analysis of the low-mass molecular ions (at m/z of 150 or smaller), the amplitude of the radio frequency (RF) voltage of the ion guide to converge ions sufficiently was higher than the theoretical value. This is because the low-mass molecular ions easily collide with gas molecules and diffuse at a higher pressure vacuum region, we think.

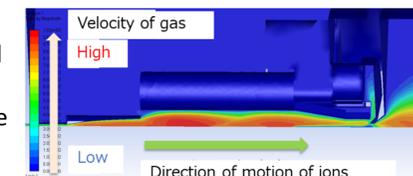


Fig.3 An example of result of gas dynamics simulation at a higher vacuum region

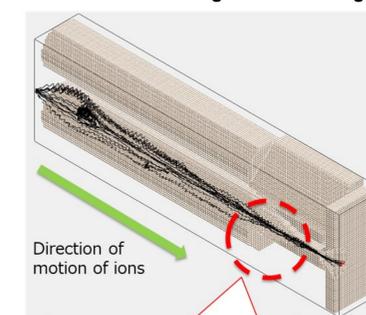


Fig.4 An example of result of ion trajectory simulation at a higher vacuum region

4-2. Analyses of Haloacetic Acids and Phenols

The relationship between RF voltage of the ion guide at higher pressure vacuum region and ion intensity is shown in Fig.5. As a result, there was a difference between the theoretical and the actual optimum RF voltage for low-mass compounds (at m/z of 150 or smaller). This corresponded to the result of the simulation. On the other hand, the actual optimum RF voltage was same as the theoretical one for higher-mass compounds (at m/z of 150 or larger). By applying the actual optimum RF voltage, the sensitivity of low-mass compound was improved by about two times (Fig.6).

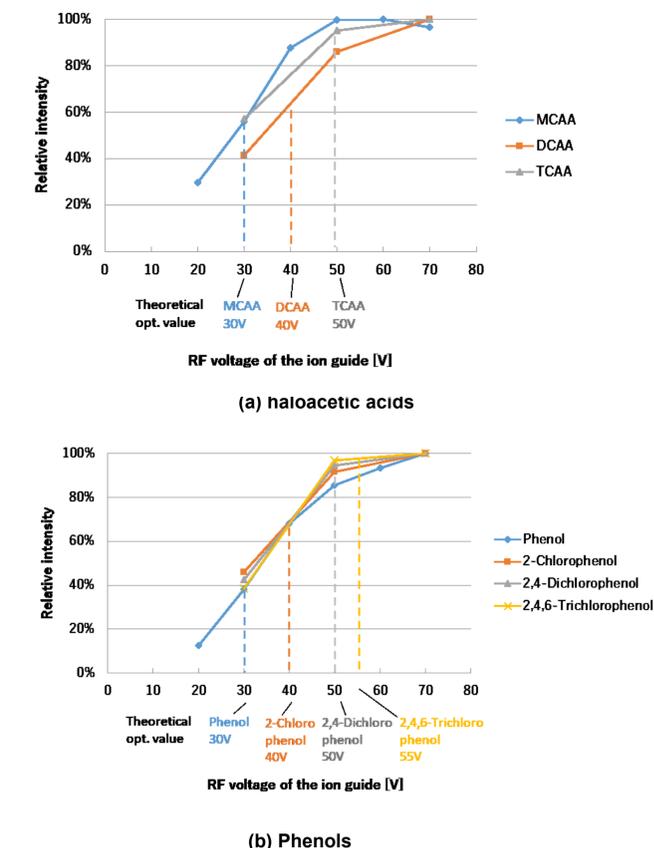


Fig.5 The relationship between RF voltage of the ion guide at higher pressure vacuum region and ion intensity

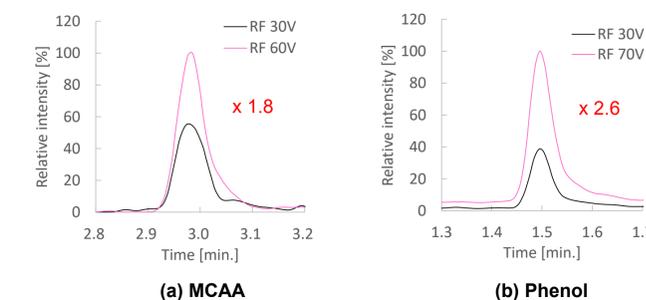


Fig.6 The examples of MRM chromatogram

5. Conclusions

Improve the sensitivity of low-mass compounds (at m/z of 150 or smaller) by increasing ion transmission efficiency based on the ion trajectory simulation considering gas dynamics at the higher pressure vacuum region.