SHIMADZU
Excellence in Science

Application Data Sheet

No.43

LC-MS
Liquid Chromatograph Mass Spectrometer

High Speed Analysis of Haloacetic Acids in Tap Water Using Triple Quadrupole LC-MS/MS

Haloacetic acids (HAAs), by-products of water disinfection, are formed from naturally-occurring organic and inorganic materials in water which react with the disinfectants chlorine and chloramine. Certain haloacetic acids have been shown to cause adverse reproductive or developmental effects in laboratory animals. Three HAAs regulated by numerous government bodies such as the US EPA include chloroacetic acid (CAA), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). A Liquid Chromatography Mass Spectrometry (LC-MS/MS) method for measuring HAAs capable of direct injection of water samples has been developed to replace previously used methods requiring tert-butyl-methyl ether liquid extraction and diazomethane derivitization prior to GC analysis, thus reducing the effort required for sample preparation. Reduced sample preparation times combined with rapid UHPLC chromatography increase the productivity of water control laboratories. This data sheet illustrates results from a high speed method acquired using a LCMS-8050 triple quadrupole mass spectrometer coupled with a Nexera X2 UHPLC.

■ Comparison of Sensitivity and Reproducibility between Standard and High Speed Methods

In the high speed method, CAA, DCAA, and TCAA eluted at 3.1, 3.4, and 5.2 minutes, shortening the run time by 25 minutes relative to the standard method (Figure 1). Figure 2 illustrates each HAA MRM chromatogram and area reproducibility at 0.001 mg/L. Each HAA demonstrates excellent reproducibility and sensitivity at this concentration.

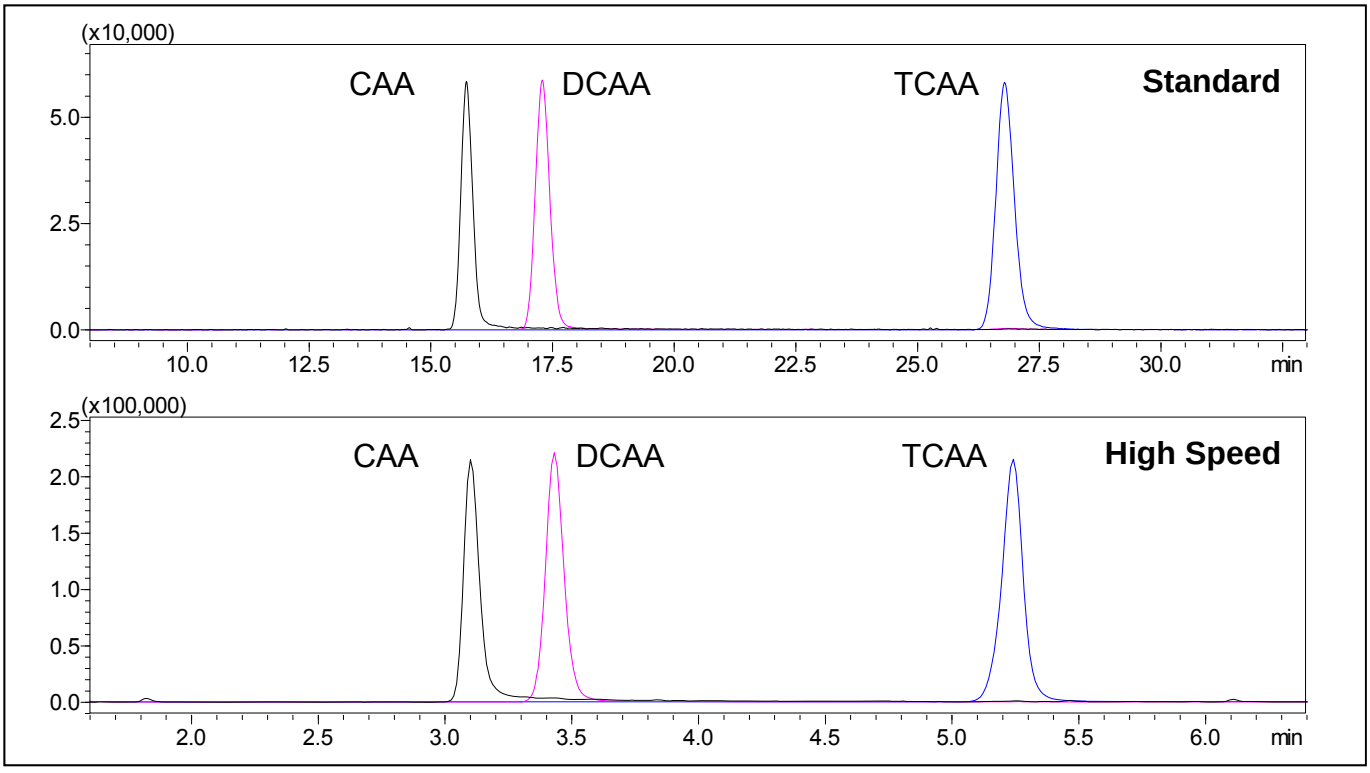

Fig. 1 MRM Chromatograms of Haloacetic Acids
(Top: Standard Analytical Method, Bottom: High Speed Analytical Method)

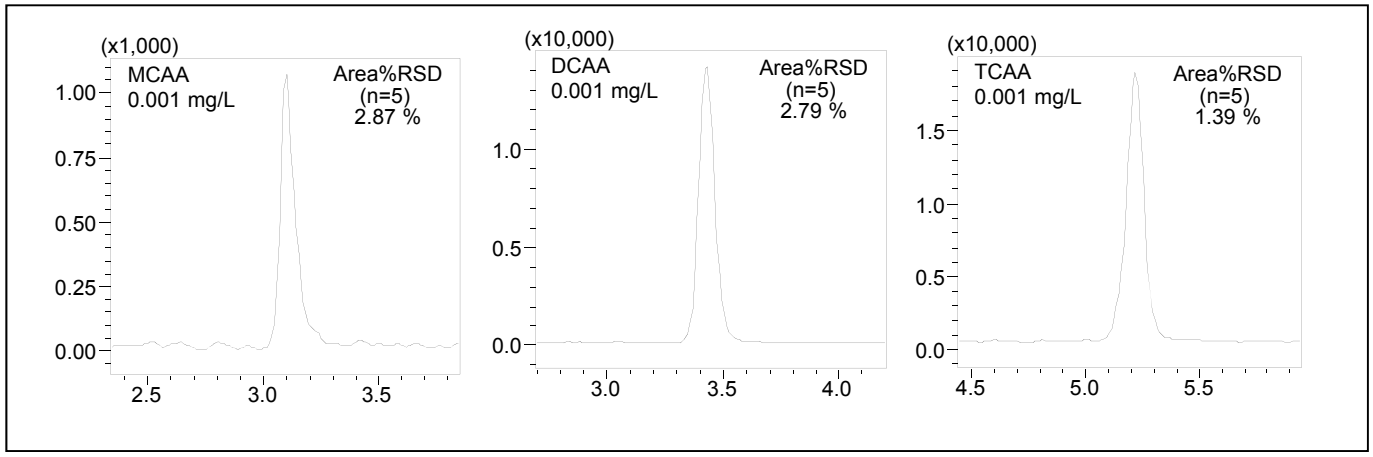

Fig. 2 MRM Chromatograms of CAA, DCAA and TCAA in neat solution at 0.001 mg/L. Reproducibility at 0.001 mg/L, n=5.

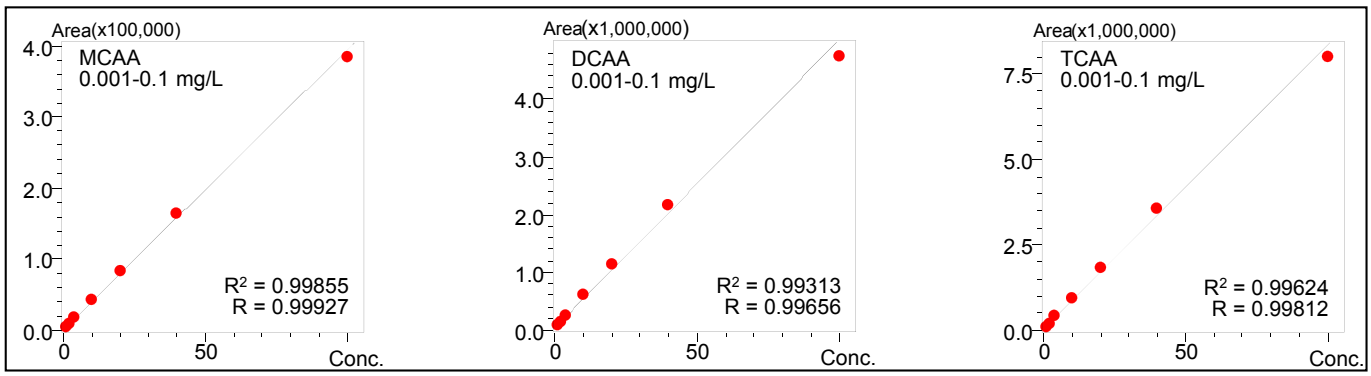

Fig. 3 Linearity of Peak Area of CAA, DCAA and TCAA

Table 1 Analytical Conditions

Column	: CAPCELL PAK MGIII (150 mm X 3 mm, 3 µm)
Mobile Phases	: A 0.2 % Formic acid-water
	: B 0.2 % Formic acid-methanol
Flow Rate	: 0.5 mL/min
Column Temperature	: 50 ℃
Injection Volume	: 25 µL
Probe Voltage	: -3.5 kV (ESI-negative mode)
DL Temperature	: 150 ℃
Block Heater Temperature	: 100 ℃
Interface Temperature	: 100 ℃
Nebulizing Gas Flow	: 3 L/min
Drying Gas Flow	: 5 L/min
Heating Gas Flow	: 15 L/min
MRM Transition	: CAA; *m/z* 93.00>35.00, DCAA; *m/z* 126.90>82.90, TCAA; *m/z* 161.10>116.90

■ Recovery Test on Tap Water

A recovery test on tap water from four locations was conducted using this high speed method. Figure 4 demonstrates the quality of chromatograms produced when these three HAAs were spiked at 0.001 mg/L into each of the four tap water samples with no further sample preparation. Regardless of tap water location (Figure 5), excellent recoveries ranging from 90 to 110% were obtained for each sample. (Table 2)

Table 2 Quantitative Results and Recovery Tests of Tap Water

	Sample 1		Sample 2		Sample 3		Sample 4	
	Tap water conc. (mg/L)	Recovery (%)	Tap water conc. (mg/L)	Recovery (%)	Tap water conc. (mg/L)	Recovery (%)	Tap water conc. (mg/L)	Recovery (%)
CAA	Tr.	102.6	0.00076	103.6	0.00069	94.9	0.00034	100.4
DCAA	Tr.	108.3	0.01151	101.7	0.00742	102.9	0.00635	92.3
TCAA	Tr.	107.1	0.00861	107.2	0.00622	104.5	0.00452	102.9

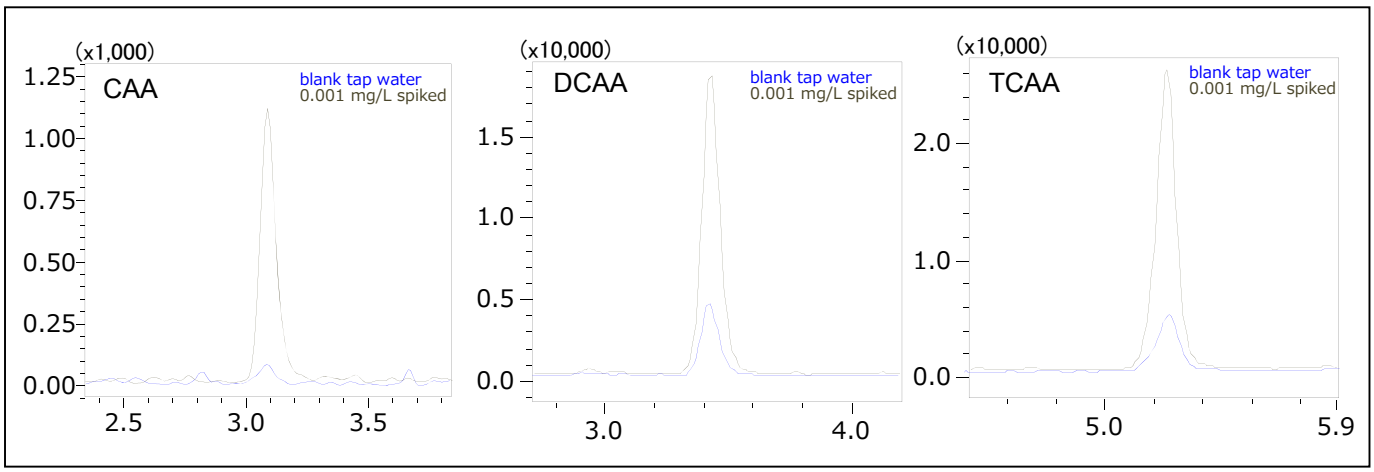

Fig. 4 MRM Chromatograms of Blank Tap Water (Blue) and CAA, DCAA and TCAA Spiked on Blank Tap Water (Sample 1: 0.001 mg/L each)

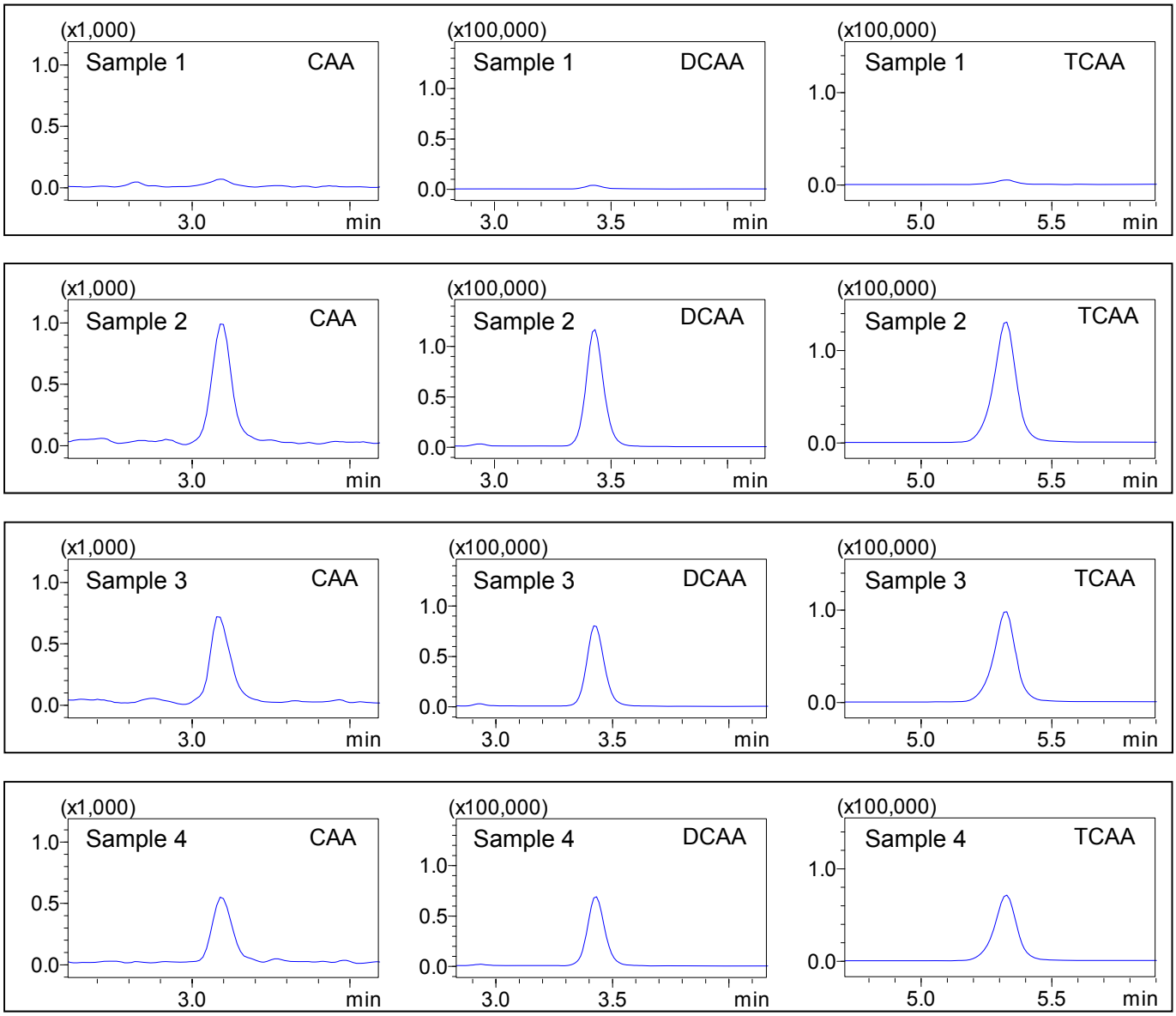

Fig. 5 MRM Chromatograms of Tap Water (Sample 1 to 4)

■ Intuitive Data Processing with LabSolutions Quant Browser

In a busy water control laboratory, it is important to not only increase the speed of measurement but also the throughput of data processing. Quant Browser provides an intuitive, quantitative data processing environment allowing multi-chromatogram visualization of different data files synchronized to analyze a compound of interest.

When measuring analytes from any matrix, there is a possibility of interferences, therefore, the results can be easily reviewed and confirmed by comparing the sample and standard data within a single chromatogram panel.

Figure 6 provides a Quant Browser screen capture displaying a CAA chromatogram from tap water (upper) and from standard solution (lower). With only a glance, it is clear there is no interference in the tap water chromatogram.

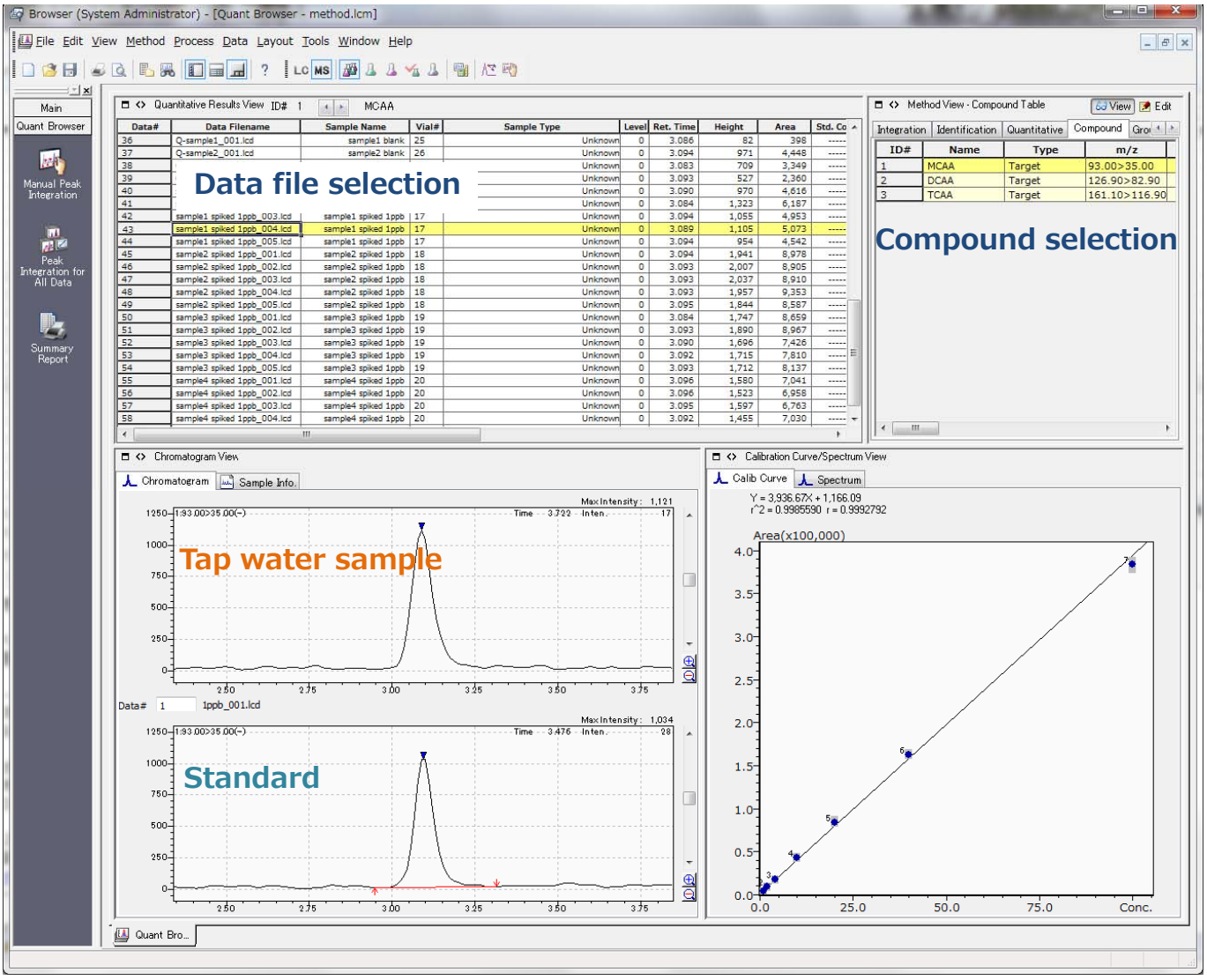

Fig. 6 Multiple Quantitative Data Processing with Quant Browser in LabSolutions

First Edition: June, 2014

Shimadzu Corporation
www.shimadzu.com/an/