

Enhanced Performance of a Triple Stage Quadrupole Mass Spectrometer with a Novel Axial Field Collision Cell

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ABSTRACT

Purpose: A novel PCB-based collision cell has been developed for a prototype triple stage quadrupole mass spectrometer (TSQ MS). The enhanced design is expected to provide improved performance in mass spectrometers utilizing collision-induced dissociation.

Methods: The newly developed collision cell has new electrode profiles which have been optimized using ion simulations in order to achieve a wider m/z transmission. In order to evaluate the performance of the new collision cell we carried out quantitation of haloacetic acids (HAAs), bromate and dalapon in drinking water with IC-MS/MS using a Thermo Scientific™ Dionex™ ICS-6000 RFIC system coupled to a modified Thermo Scientific™ TSQ Fortis™ mass spectrometer.

Results: The performed tests confirmed improvements in the ion transmission at the low end of the m/z mass range. This can particularly benefit transitions where there is a large difference between parent and product masses.

INTRODUCTION

Performance of a collision cell is a significant determinant of product ion production by collision-induced dissociation (CID) for MS² analysis. Both parent and product ions need to maintain stable trajectories inside the cell to ensure maximum transmission.

We present a newly developed PCB-based collision cell with improved electrode dimensions and profiles and overall mechanical design which enhances sensitivity and robustness.

Practical benefits of the new ion optical system have been verified using regulated method for the analysis of haloacetic acids (HAA). HAAs are among the disinfection byproducts produced (DBP) during chlorination of water containing natural organic matter and bromide.

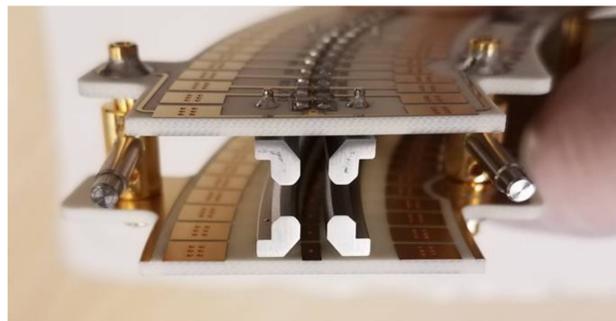
MATERIALS AND METHODS

New electrode profiles have been developed and optimized using ion simulations in order to achieve the most effective wide m/z ion transmission. Balancing RF field responsible for containing ions along the 90 degree turn as well as DC field penetration from drag vanes has been used to achieve the best performance in SRM mode. Figure 1 shows the final shape of electrodes along with the DC drag vanes. In addition to shape optimization, the rod separation was increased by about 20%.

Front and back lens stacks comprised of three lenses each are attached to each end of the 90-degree quadrupole. The RF-carrying rods are mounted on two parallel PCBs and the drag vanes are realized as metallization regions on the boards. Variable field penetration from DC pads allows for axial acceleration of ions along the beam path. Mounting of all elements on opposing PCBs allows for much easier distance and alignment control critical for reducing performance variability.

Several prototypes of the new collision cell have been built and evaluated in prototype TSQ MS systems using a wide variety of compounds.

Figure 1. Electrode profile designed for best RF-field distribution, DC-field penetration

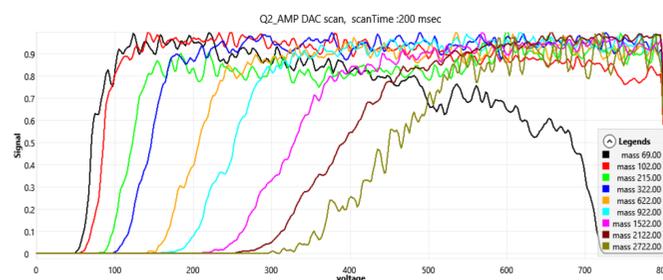


Additional emphasis was placed on finding optimum RF amplitude settings that balance precursor and product transmission for large mass differences.

Figure 2 shows the RF amplitude dependent transmission for a mass range from m/z 69 to 2722 which demonstrates a significant RF amplitude overlap even for ions at the highest and lowest extremes of mass range. This provides more uniform performance with less need for optics tuning.

MATERIALS AND METHODS continued

Figure 2. RF amplitude depended transmission profile for masses between m/z 69 and 2722



In order to evaluate performance, a TSQ Fortis MS system has been modified with the newly developed collision cell and HAAs, bromate and dalapon have been analyzed with IC-MS/MS.

Sample preparation

Reagent water samples were spiked with the target analyte mixtures at known amounts. Ammonium chloride (NH₄Cl) was added as a preservative at 100 mg/L to all samples. No further sample preparation was performed prior to injection.

IC Method/Application Set Up

The primary class of compounds associated with drinking water contamination is disinfection by-products (DBPs). A subgroup of DBPs is haloacetic acids (HAAs), which together are specifically linked to cancer and other issues.

IC analysis was performed on an ICS-6000 RFIC system. The mobile phases used for separation were IPA and water, and IC gradient conditions are shown in Table 1. A 100 µL sample was injected onto a 2 x 250 mm Thermo Scientific™ Dionex™ IonPac™ AS31 RFIC analytical column, which is specifically designed to separate method analytes from the following common anions (matrix components) in drinking water: chloride, carbonate, sulfate, and nitrate. A Dionex IonPac AG31, 2 x 50 mm guard column and Thermo Scientific™ Dionex™ ADRS 600 2 mm conductivity suppressor were used. Mobile phases were IPA at 300 µL/min and water at 300 µL/min. AXP pump water for suppressor regeneration was maintained at 600 µL/min. The column temperature was maintained at 15 °C.

Table 1. IC gradient information used in the application note

Time (min)	Concentration (mM)
0	17
5	17
7	85
18	85
40	85
40	17

Mass spectrometry

All compounds for this study were analyzed in negative, heated electrospray mode (HESI). The experimental conditions were identical to the previously published method and briefly described here. The cycle time was 1.3 s. Q1 resolution was set at 0.7 Da FWHM and Q3 resolution at 1.2 Da FWHM. The SRM table and other critical MS features for all target analytes are listed in Table 1.

MATERIALS AND METHODS continued

Table 2. Optimized MS transitions for each compound analyzed in this experiment.

Compound	Retention Time (min)	RT Window (min)	Precursor (m/z)	Product (m/z)	Collision energy (eV)	Tube Lens (V)	Source Fragmentation (eV)
MCAA	6.27	6	92.9	35.1	10	79	14.6
MCAA_IS	6.27	6	93.9	35.1	10	82	13.1
MBAA	6.95	6	136.9	79.0	10	86	9.8
MBAA_IS	6.95	6	137.9	79.0	10	84	14.7
Bromate	7.4	5	126.9	110.0	22	85	24.5
Dalapon	11.35	6	140.9	96.9	7.7	84	13
DCAA	12.2	6	126.9	83.0	10	86	24.5
DCAA_IS	12.2	6	128.0	83.9	10	84	13.1
BCAA	13.15	6	172.8	128.9	11	89	22.8
DBAA	14.45	6	216.8	172.8	12	87	14.7
DBCAA	22	14	206.8	78.9	14	91	22.9
TCAA_IS	20	8	161.9	117.9	7	78	18
TCAA	20	8	162.8	118.9	5	79	22.9
TBAA	24	10	250.7	78.9	19	87	26.1
BDCAA	24.2	8	162.8	80.9	7	79	22.9

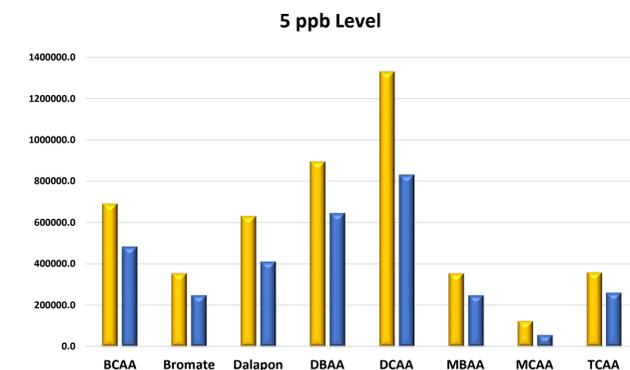
RESULTS

Comparison regular TSQ Fortis and TSQ Fortis upgraded with new collision cell

In a set of experiments, we compared the response for 5ppb samples of a TSQ Fortis equipped with a regular collision cell with a TSQ Fortis upgraded with the newly designed collision cell. For both experiments we used the same samples, solvent composition, and IC method as described earlier.

The results of this comparison are presented in figure 3a and 3b. The response improvement for the new collision cell varies between 1.2 and 2.2 and is summarized in table 3.

Figure 3a. Response comparison for standard TSQ Fortis and TSQ Fortis equipped with new collision cell. The blue bars represent the response for regular TSQ Fortis while the yellow bars depict the results of the upgraded TSQ Plus.



RESULTS continued

Figure 3b. Response comparison for standard TSQ Fortis and TSQ Fortis equipped with new collision cell. The blue bars represent the response for regular TSQ Fortis while the yellow bars depict the results of the upgraded TSQ Plus.

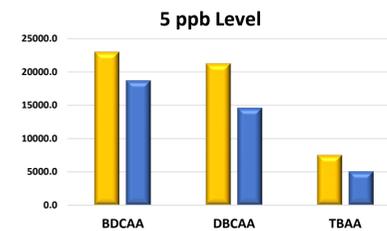


Table 3. Response comparison for each compound analyzed in this experiment.

Compound	Response TSQ Fortis New Collision Cell	Response TSQ Fortis Regular Collision Cell	Ratio
BCAA	693334.3	484466.7	1.4
BDCAA	23015.3	18715.3	1.2
Bromate	356154.0	249224	1.4
Dalapon	632960.3	411601	1.5
DBAA	896414.3	645889.7	1.4
DBCAA	21276.0	14607.7	1.5
DCAA	1330530.0	830561.3	1.6
MBAA	356153.7	249197.3	1.4
MCAA	125387.7	57730	2.2
TBAA	7558.0	5086	1.5
TCAA	360869.3	261704.7	1.4

The results from the nine-point calibration curve covering a spiked range of 0.0625 to 20 µg/L showed outstanding linearity was achieved. Regression values greater than 0.995 were measured for all analytes over the calibration range. Figures 4 and 5 show two example calibration curves while Table 4 lists the average peak response of seven replicate injections per calibration level for the eleven compounds.

Table 4. Average peak response of seven replicate

Conc. range (µg/L)	MCAA	MBAA	DCAA	DBAA	TCAA	TBAA	BCAA	DBCAA	BDCAA	Bromate	Dalapon
0.0625	2301	15498	27835	17432	NQ	NQ	12248	NQ	1136	4362	11213
0.125	3753	22467	44504	33443	11863	NQ	22689	NQ	1919	8931	20916
0.25	6482	35520	75867	63903	18953	819	43096	2912	3409	17861	40394
0.5	12879	65665	142186	130122	35034	1767	84821	5575	6840	36996	80311
1	24330	123967	268652	260030	68435	3707	167688	11564	13206	75387	157858
2	47187	231783	538981	524611	132908	7289	336849	23376	25880	152266	322875
5	118422	577387	1328144	1306167	321226	18292	848378	57565	63337	379347	786428
10	237138	1191108	2676337	2709708	667078	37618	1702624	117625	131184	783722	1604926
20	459971	2424168	5431702	5429038	1328064	75219	3468464	238087	269930	1690160	3252401

RESULTS continued

Figure 4. Calibration curve for MCAA

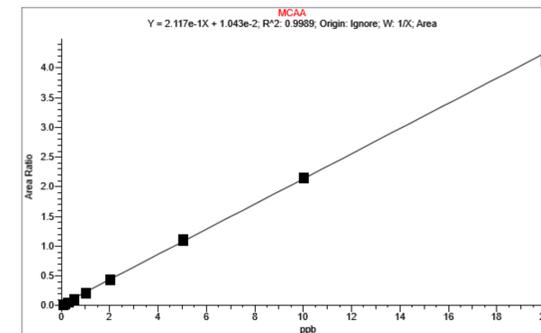
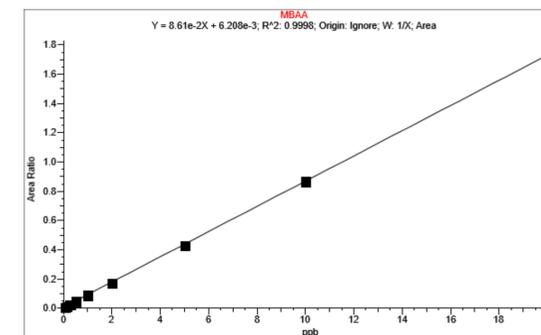


Figure 5. Calibration curve for MBAA



CONCLUSIONS

- A newly developed collision cell was installed and tested in a TSQ Fortis instrument.
- The TSQ Fortis equipped with the new collision cell showed an increase of response for HAAs between 1.2 and 2.2 when compared with a TSQ Fortis equipped with a conventional collision cell.

TRADEMARKS/LICENSING

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