Enhanced performance of a triple stage quadrupole mass spectrometer with a novel axial field collision cell and fast switching high voltage power supplies

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Abstract

Purpose: A novel PCB based collision cell and fast switching high voltage power supplies have been developed for a triple stage quadrupole mass spectrometer (TSQ MS). The enhanced design is expected to benefit a range of Thermo Fisher mass spectrometry products.

Methods: In order to evaluate the performance of the new collision cell and new power supplies we carried out quantitation of Haloacetic acids (HAAs), Bromate and Dalapon in drinking water with IC-MS/MS using Thermo Scientific™ ICS 6000 and TSQ Fortis™MS based prototype system.

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. Reduction of polarity switching bellow 5ms was confirmed as well.

Introduction

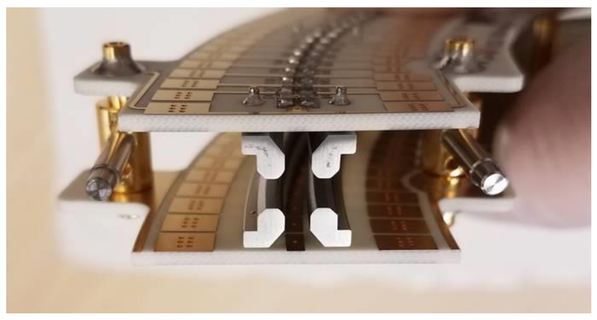
We present a newly developed PCB collision cell with improved electrode dimensions and profiles and overall mechanical design which enhances sensitivity and robustness.

Practical benefits of the new ion optical system and speed improvements due to newly introduced fast switching high voltage power supplies have been verified using a 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%.

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

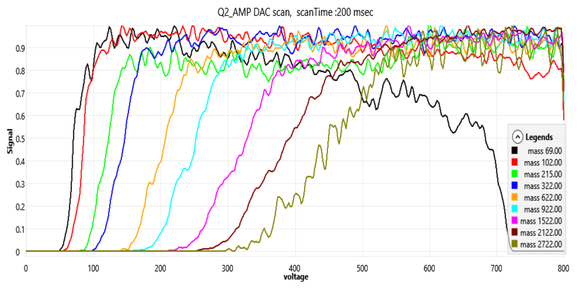


Front and back lens stacks comprised of three lenses each are attached to each end of the 90 degrees quadrupole. The RF-carrying rods are mounted on two parallel PCBs and the drag vanes are realized as metallization regions on the boards. Variable field penetration from DC pads allows for axial acceleration 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.

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.

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



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 a Dionex ICS-6000 system. The mobile phases used for separation were IPA and water. 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.

Materials and methods continued

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 15ºC.

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.

Table 1. 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]
MCAA	6.27	6	92.9	35.1	10
MCAA_IS	6.27	6	93.9	35.1	10
MBAA	6.95	6	136.9	79.0	10
MBAA_IS	6.95	6	137.9	79.0	10
Bromate	7.4	5	126.9	110.0	22
Dalapon	11.35	6	140.9	96.9	7.7
DCAA	12.2	6	126.9	83.0	10
DCAA_IS	12.2	6	128.0	83.9	10
BCAA	13.15	6	172.8	128.9	11
DBAA	14.45	6	216.8	172.8	12
DBCAA	22	14	206.8	78.9	14
TCAA_IS	20	8	161.9	117.9	7
TCAA	20	8	162.8	118.9	5
TBAA	24	10	250.7	78.9	19
BDCAA	24.2	8	162.8	80.9	7

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 3. The response improvement for the new collision cell varies between 1.2 and 2.2 and is summarized in table 2.

Figure 3. 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.

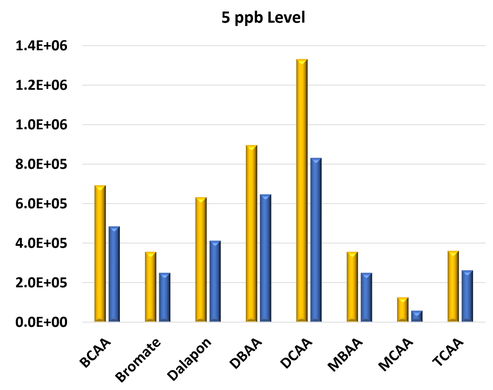


Table 2. Response comparison for each compound analyzed in this experiment.

Compound	Retention Time [min]	RT Window [min]	Precursor [m/z]
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 that 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.

Results continued

Figure 4. Calibration curve for MCAA

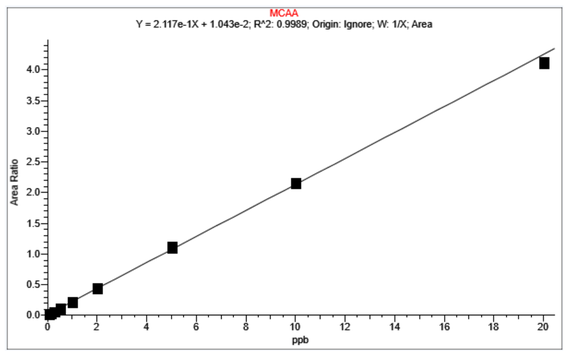
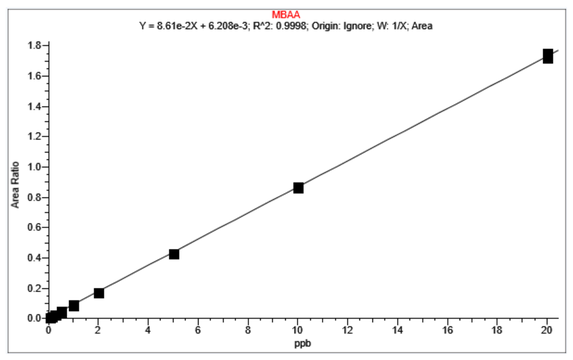


Figure 5. Calibration curve for MBAA



Comparison regular High Voltage Power Supplies with new fast Power Supplies

Faster than then 5 ms polarity switching time was achieved by implementing newly developed series of power supplies from Spellman High Voltage Electronics Corporation.

Comparison between regular power supplies and new fast power supplies have been executed while performing quantitative analysis of steroids in plasma.

In a first set of experiments the switching time of the conversion dynode with the regular power supplies and the new fast switching power supplies were compared. When a switching time of 5ms is applied the measurements show that the old power supply can not reach the required constant potential levels within 5ms before the first acquisition step starts as shown in figure 6 while with the new implemented power supplies the levels can be reached within 5ms as presented in figure 7.

Figure 6. 5ms switching time with regular power supply

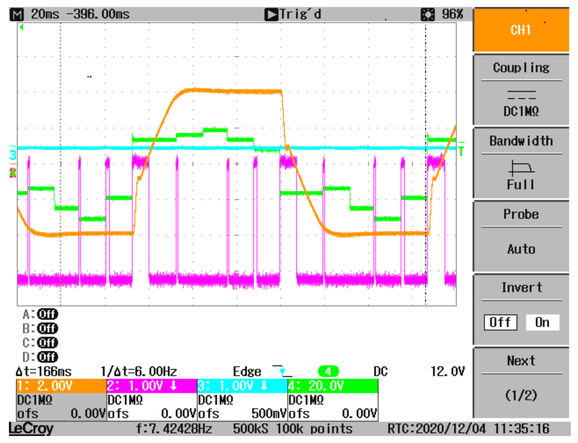
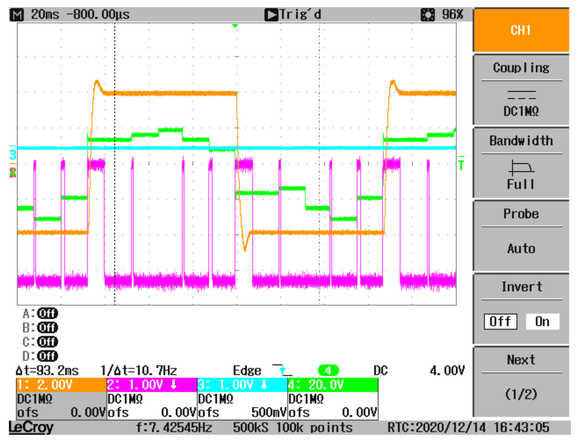


Figure 7. 5ms switching time with newly implemented power supplies



To test the polarity switching performance of the source power supply low flow experiments were performed by measuring the time that is required to establish a stable ion current after a polarity switch.

The results presented in figures 8 and 9 confirm that a switching time of not more than 5ms have been measured for positive to negative and negative to positive polarity switching. As shown in both cases a stable ion signal is established within 5ms.

Results continued

Figure 8. Positive to negative polarity switch for m/z=69

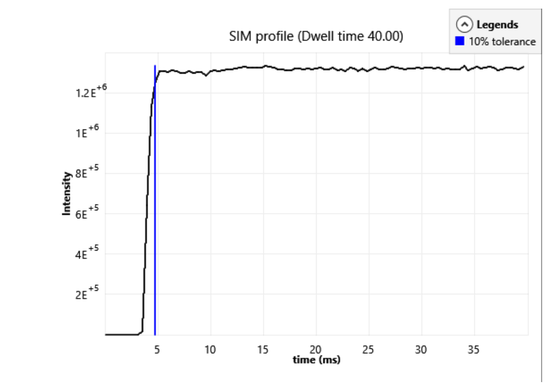
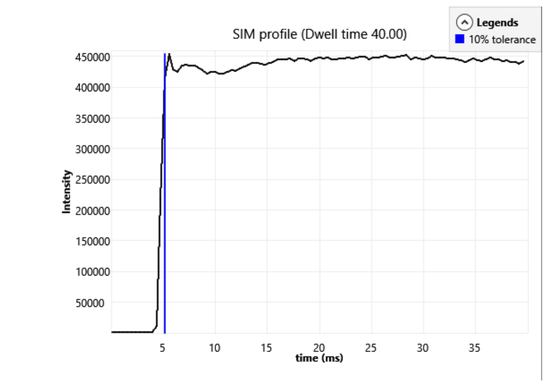


Figure 9. Negative to positive polarity switch for m/z=922



The overall switching performance of the instrument was evaluated via a high flow LC based approach. Comparing switching times of 25ms and 5ms confirm that the system performance produces the same results in real world high flow applications. The results in figures 10 and 11 show the results for a mix of Atrazine, Tolbutamide and Warfarin for 25ms and 5ms switching times.

Figure 10. High Flow LC results for 25ms switching time.

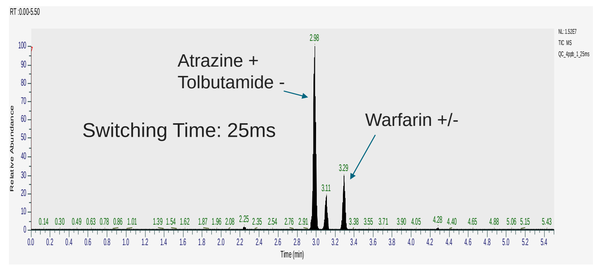
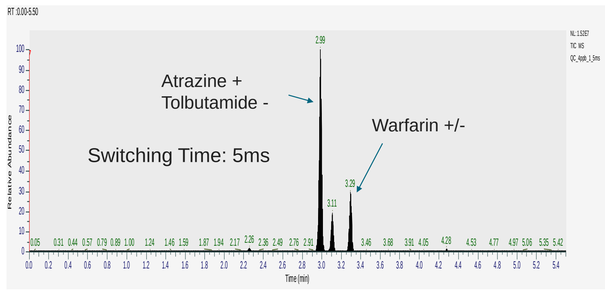


Figure 11. High Flow LC results for 25ms switching time.



Conclusions

- A newly developed collision call 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 regular collision cell.
- New Power Supplies establishing real ion signal after polarity switching in under 5 milliseconds.
- The PCB based Collison cell and the new fast switching power supplies have been implemented in the Thermo Fisher Scientific TSQ Altis/Quantis/Fortis Plus product line.

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