Advion


# TOLUENE-ASSISTED APCI AND ELEMENTAL COMPOSITION PREDICTION USING A COMPACT MASS SPECTROMETER

## APPLICATION NOTE

**MS Method:** expression CMS
**Sampling:** FIA

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In this application note, we review how combining both Toluene-assisted APCI (TAPCI) and Tal Aviv Molecule Identifier (TAMI) with the Advion expression Compact Mass Spectrometer (CMS) provides a cost-effective analysis platform for analyte identification of an increased compound space.

## INTRODUCTION

Many compounds in organic synthetic chemistry either have no functional group, a C=O carbonyl group, or protected functional groups and are difficult to ionize by electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) for detection by mass spectrometry. TAPCI has been shown to ionize compounds to $(M)^{+\bullet}$ and $(M+H)^{+}$ protonated molecules[1] not accessible by ESI– or APCI–MS analysis. The ionization is believed to include a charge transfer reaction in the APCI plasma region of the source[2]. Elemental formula prediction using TAMI allows analyte identification on a single quadrupole mass spectrometer with mass accuracy in the 250 ppm range, isotope pattern analysis, and auto comparison to NIST databases[3]. Here, we investigate the use of both techniques on the Advion expression CMS as an attractive and cost-effective solution for analyte identification covering an increased compound space.

## METHODS

Analytical standards were prepared in the solvent tested for TAPCI ionization (e.g. 2 µg/µL Anthracene in 50/50 Toluene/Hexane) and delivered to the source by FIA with a syringe driven flow of 30 µL/min. The CMS was tuned normally and standard source settings were applied with a capillary voltage of 120 V and a constant APCI discharge current of 7.5 µA (Figure 1).

## RESULTS

Testing various solvent compositions (data not shown) suggest that a mixture of 50/50 Toluene/Hexane is the optimal balance of ion spray stability (best in 100% Toluene), ionization efficiency/signal intensity (best at 90% Hexane), and chemical background noise (worst at 100% Toluene).

Methanol and Acetonitrile can be used with Toluene as well; however, Acetonitrile reduces ion signal factor of 3-10 compared to Methanol and Hexane (data not shown).


**Figure 1:** The CMS with standard APCI source at 4 L/min Nitrogen gas flow, additional source exhaust to house vacuum and FIA sample introduction using a syringe pump at 30 µL/min, a 10 µL loop and all PEEKSil tubing to the source.

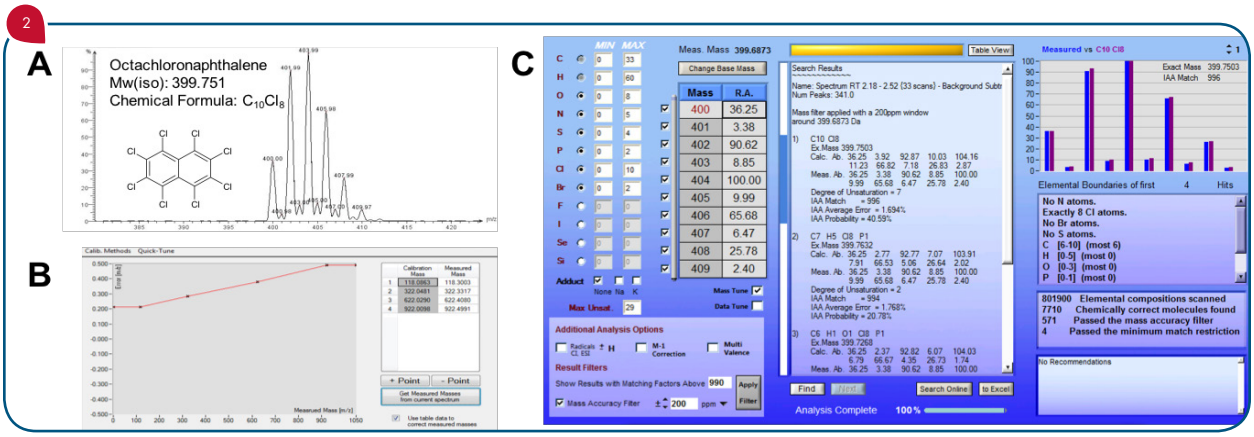


**Figure 2:** Applying TAMI software processing to the TAPCI analysis of Octachloronaphthalene. (A) Background subtracted TAPCI mass spectrum; (B) post acquisition mass calibration adjustment made by TAMI based on calibrant injected prior to sample and (C) TAMI showing predicted isotope distribution, chemical composition suggestion of $C_{10}C_{l8}$ as Nr. 1 hit within a mass accuracy of 200 ppm and an isotope distribution score of >990.

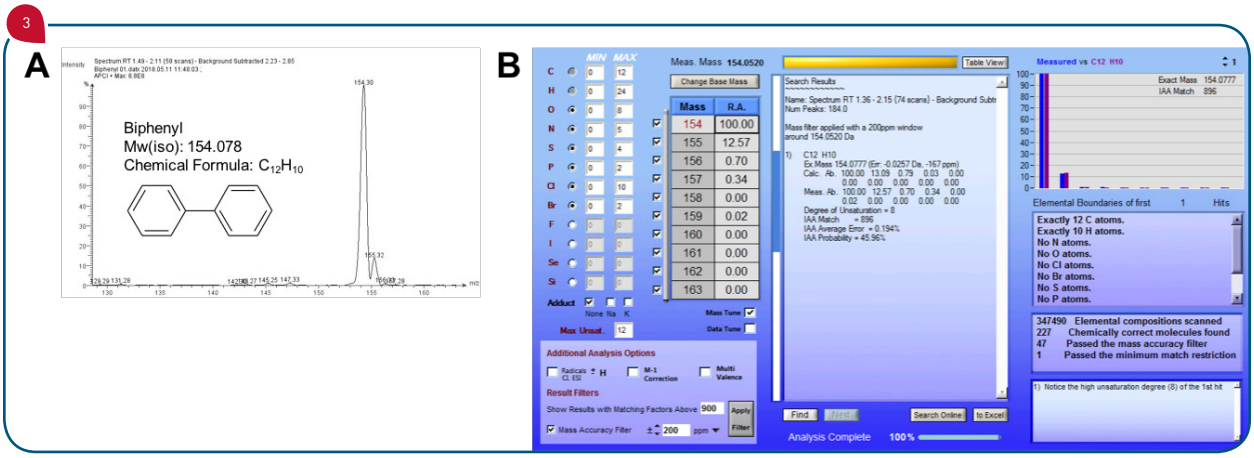


**Figure 3:** Applying TAMI software processing to the TAPCI analysis of Biphenyl. (A) Raw TAPCI MS data; (B) TAMI showing predicted isotope distribution, chemical composition suggestion of $C_{12}H_{10}$ as the only hit within a mass accuracy of 200 ppm and a score of >900.

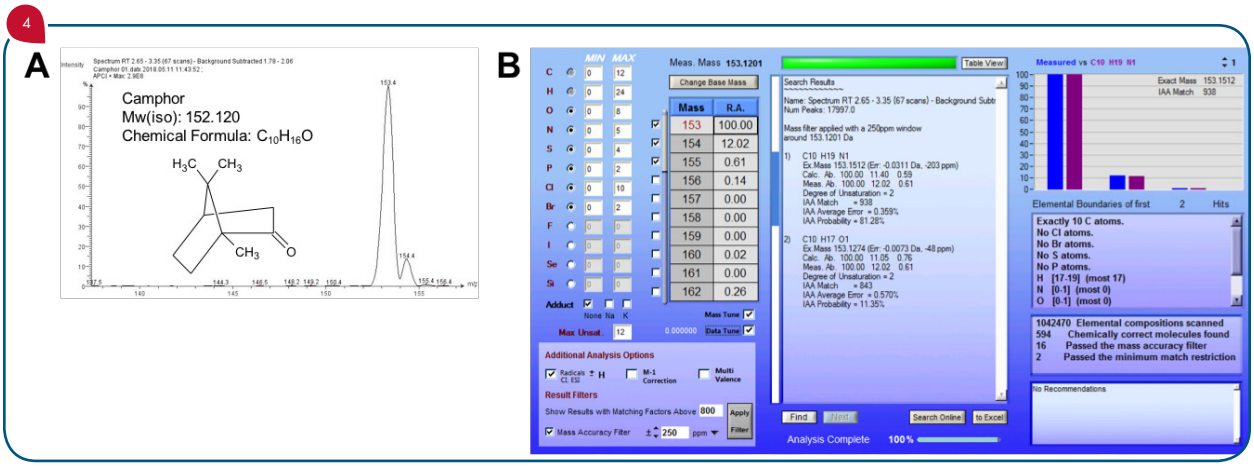


**Figure 4:** Applying TAMI software processing to the TAPCI analysis of Biphenyl. (A) Raw TAPCI MS data; (B) TAMI showing predicted isotope distribution, chemical composition suggestion of $C_{12}H_{10}$ as the only hit within a mass accuracy of 200 ppm and a score of >900.

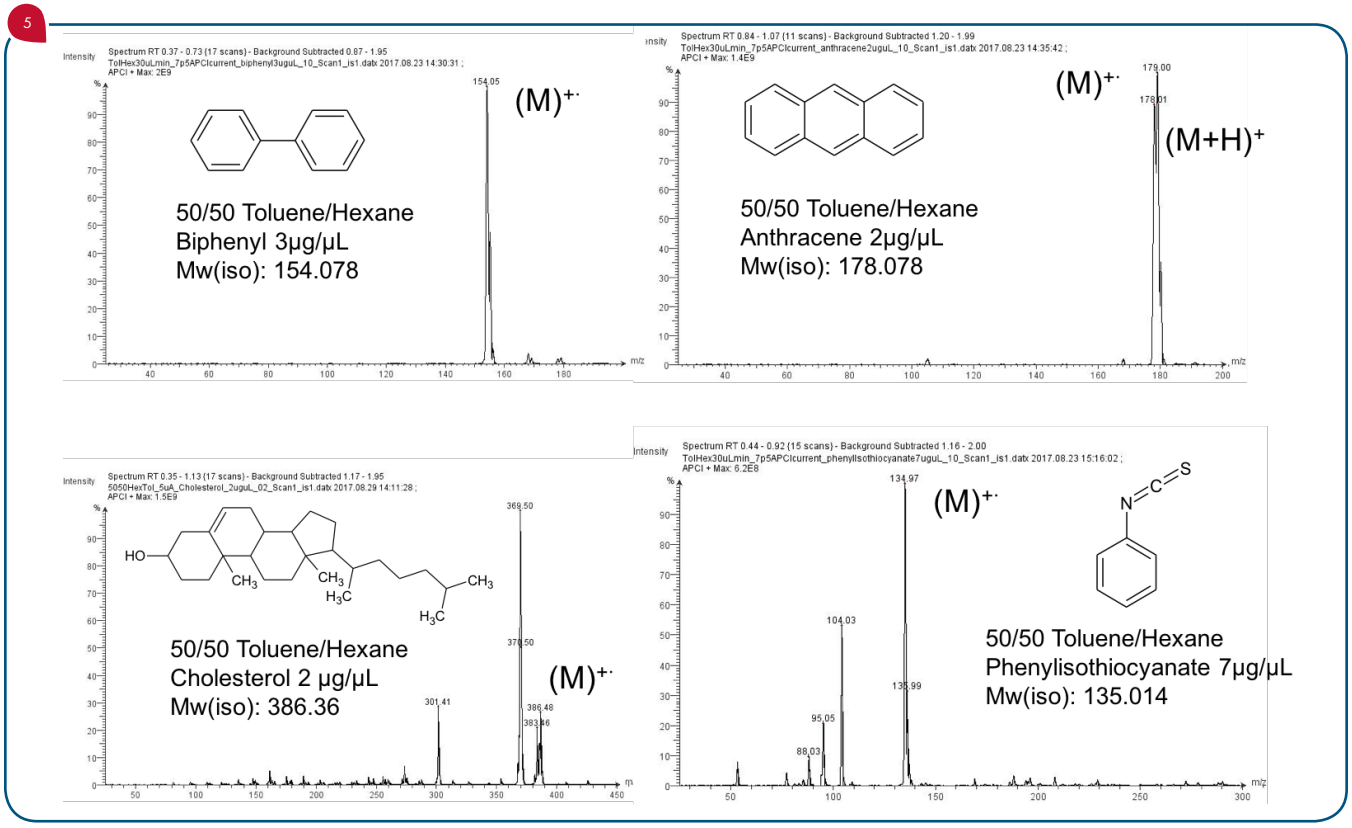


**Figure 5:** TAPCI - example mass spectra of analytes ionizing to $(M)^{+\bullet}$ or $(M+H)^{+}$

## CONCLUSION

- Toluene is a simple solvent modifier for APCI allowing ionization of molecules to their $(M)^{+\bullet}$ and /or $(M+H)^{+}$
- It can be used in combination with Methanol, Hexane, and Acetonitrile; however, the latter causes significantly lower signal intensities
- TAPCI widens the compound space to analyze for MS including compounds not carrying heteroatoms.
- TAMI provides accurate chemical composition prediction within 250 ppm mass accuarcy and isotopic match analysis based on CMS data
- The Advion expression CMS in combination with TAPCI and TAMI is a cost-effective analysis platform for a wide range of chemical compounds.

REFERENCES AND ACKNOWLEGEMENTS

[1]Williams TD, Seib L, Drake R and Mays JR: My ZAB is dying! Exact mass determinations of ESI invisible molecules on Qtofs with TAPCI, Toluene Atmospheric Pressure Chemical Ionization. Poster contribution ASMS 2014

[2]Alon T and Amirav A: Isotope Abundance Analysis Method and Software for Improved Sample Identification with the Supersonic GC-MS. Rapid Commun. Mass Spectrom. 2006 (20) 2579-2588.

[3]Kim YH and Kim S: Improved Abundance Sensitivity of Molecular Ions in Positive-Ion APCI MS Analysis of Petroleum in Toluene. JASMS 2010 (21) 386-392

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