Identification of an unknown biocide by volatile atmospheric pressure chemical ionization (vAPCI) and compact mass spectrometry (CMS)

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Advion

Overview:

A rapid unknown sample analysis is performed using a novel volatile APCI source with CMS detection and on-line database search.

Introduction:

Volatile sampling and APCI generation of ions (vAPCI) is characterized by a spatial separation between the APCI sample ionization in the MS source region and the analyte sampling through a flexible and heated transfer line (Figure 1). vAPCI allows headspace sampling over targets in various aggregate states such as gaseous samples, solids or liquids. vAPCI has been predominantly used for highly volatile analytes such as flavor components of food stuffs (spoiled meats or cheeses) and breath analysis[1]; however, vAPCI can also be used for other applications in a rapid sample screening fashion for detection of unknowns in 'white powders'.

Methods and Materials:

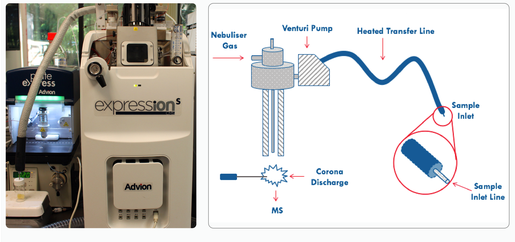

Figure 1: A vAPCI system set up with corresponding schematic. The system is coupled with the APCI source of the expression^S CMS. This includes the 120° C heated transfer line in which the headspace is moved through the system via the venturi effect.

50 mg unknown lawn treatment pellets (Figure 2) were collected, crushed and heated to ca. 50°C. The headspace was transported by venturi effect through a 120°C heated transfer line towards the APCI source of the expression^S compact mass spectrometer (Advion Inc.). Two different ion source settings were utilized to collect data for positive and negative ion mode as well as in-source fragmentation for both. The data was analyzed for mass-to-charge ratio, isotopic pattern and fragmentation information and searched against the free online mzcloud database (Highchem LLC - https://www.mzcloud.org/)[2].

Figure 2: Advion HQ in Ithaca, NY and collected lawn treatment pellets

Results:

- Crushing and heating the sample to ca. 50°C significantly increased signal intensity, however temperatures above 60°C resulted in carry over that could be avoided at 50°C.
- MS analysis showed a strong signal at *m/z* 351.15 in positive ion mode and *m/z* 349.15 in negative ion mode, both signals showed an isotope distribution indicating a singly charged molecule and not indicating any halogen atoms present. The unknown substance mono-isotopic mass could therefore be assumed to be Mw(iso) 350.15.
- Further in-source fragmentation showed an informative spectrum only in positive ion mode with strong signals at *m/z* 333.25, 309.15; 291.10, 275.05, 267.05 and 247.05 (Figure 3).

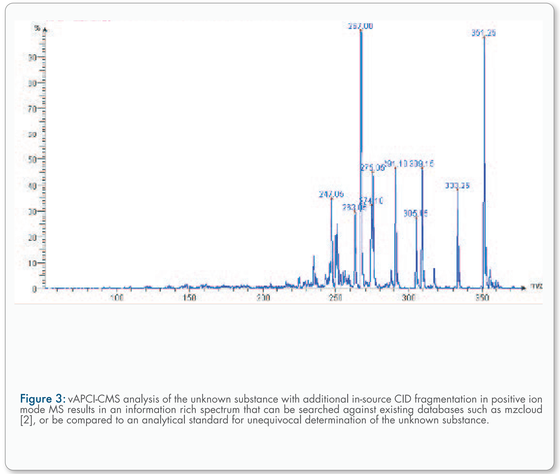

Figure 3: vAPCI-CMS analysis of the unknown substance with additional in-source CID fragmentation in positive ion mode MS results in an information rich spectrum that can be searched against existing databases such as mzcloud [2], or be compared to an analytical standard for unequivocal determination of the unknown substance.

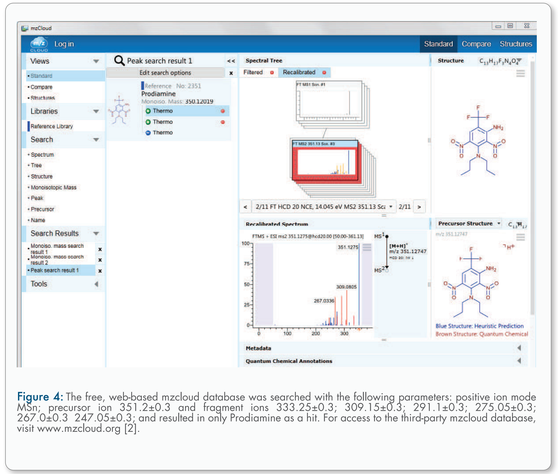

Figure 4: The free, web-based mzcloud database was searched with the following parameters: positive ion mode MSn; precursor ion 351.2±0.3 and fragment ions 333.25±0.3; 309.15±0.3; 291.1±0.3; 275.05±0.3; 267.0±0.3 247.05±0.3; and resulted in only Prodiamine as a hit. For access to the third-party mzcloud database, visit www.mzcloud.org [2].

- Two databases were queried with this information; the off-line excel based herbicide specific database[3] resulted in two potential herbicides; Prodiamine and Cafenstrole as likely candidates for the unknown sample (data not shown). The only hit returned from the mzcloud database[2] was Prodiamine with an excellent correlation and additional overlap of fragment ions (Figure 4).
- In combination with additional background information (Prodiamine being a NY state approved pre-emergent lawn herbicide) and comparison to an analytical standard (data not shown); Prodiamine can unequivocally be determined as the active ingredient of the previously unknown sample.

Conclusions:

- vAPCI allows measurement from the headspace of unknown samples in gas, liquid or solid state (eg white powder) with little to no sample preparation or carry over.
- CMS detection combined with polarity switching, in-source fragmentation and database searches is a versatile analytical tool to identify unknown compounds

Literature and Acknowledgements:

[1] Heaney LM, Ruszkiewicz DM, Arthur KL, Hadjithekli A, Aldcroft C, Lindley MR, Thomas CLP, Turner MA and Reynolds JC: Real-time monitoring of exhaled volatiles using atmospheric pressure chemical ionization on a compact mass spectrometer. Bioanalysis 2016 doi/full/10.4155/bio-2016-0045

[2] ESI-MS/MS spectrum of Prodiamine from m/z cloud database for comparison: https://www.mzcloud.org/DataViewer#Creference2351#T3285#c#318704

[3] Gandy M, Corral M, Mylne J and Stubbs K: An interactive database to explore herbicide physicochemical properties. Organic and Biomolecular Chemistry 2015 13(20) 5586-5590; http://www.mylne.org/herbicides.html

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