



Screening of Semivolatile Organic Compounds (SVOCs) on Aerosol Particles Using the Agilent 7200 Series GC/Q-TOF System

Application Note

Environmental

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Abstract

The composition of organic compounds absorbed in aerosol particles can provide important clues concerning aerosol-based air pollution studies. The full acquisition electron ionization (EI) mode of the Agilent 7200 Series Accurate Mass GC/Q-TOF MS, in combination with Agilent MassHunter Software tools, enabled a nontargeted workflow to screen a large variety of compounds in a complex particle extract. The EI-MS/MS capability was used to study the structure of unknown compounds based on the accurate mass of product ion fragments.



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Introduction

Semivolatile organic compounds (SVOCs) exhibit a wide range of molecular structures, and correlate to the formation and health-related effects of aerosol particles [1,2]. Due to a constantly growing interest in pollution by fine aerosol particles and an increasing diversity of absorbed organic compounds, screening of SVOCs has become a more demanding and complex task that requires enhanced selectivity, sensitivity, and a nontargeted workflow for data analysis.

An accurate-mass approach to the analysis of the organic content of aerosol particles using quadrupole time-of-flight mass spectrometry (Q-TOF) offers more reliable identification, and allows for a virtually unlimited number of SVOCs to be screened simultaneously. It provides an ideal analytical tool that can be used to screen and confirm both target and unknown compounds in complex aerosol particle extracts.

This application note demonstrates a nontargeted screening workflow for SVOCs absorbed in aerosol particles using a high-resolution Agilent 7200 Series GC/Q-TOF system. Compound hits were obtained by using deconvoluted mass spectra that were searched against a NIST nominal mass spectral library. The accurate mass of molecular ion or fragment ions was used in the confirmation of the compound formula. As an added advantage, the GC/Q-TOF system can be operated in MS/MS mode to investigate structures of unknown compounds.

Experimental

Instruments

This study was performed using an Agilent 7890B GC system coupled to an Agilent 7200A Q-TOF system. The instrument configuration is shown in Figure 1, and the instrument conditions are listed in Table 1. The GC operation enabled retention time locking (RTL) with the constant flow midcolumn backflush full screening method included in the Agilent Pesticides and Environmental Pollutants (P&EP) MRM database 3.0 (p/n 9250AA).

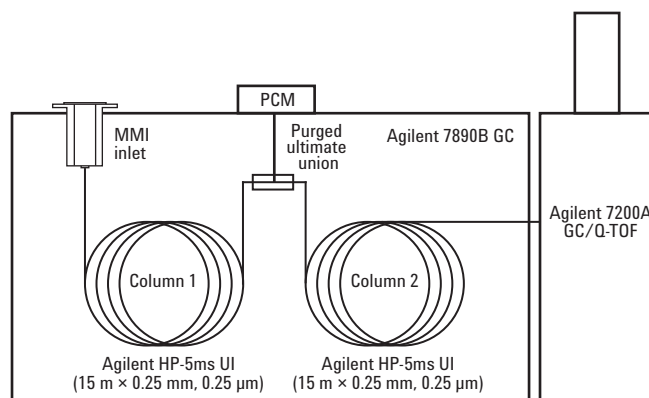


Figure 1. Agilent 7200 GC/Q-TOF System configuration depicting midcolumn backflush. The Agilent 7890B GC was coupled to the Agilent 7200A Q-TOF.

Table 1. Agilent 7890B GC and Agilent 7200A GC/Q-TOF Mass Spectrometer Conditions

GC conditions	
Columns	Agilent HP-5ms UI, 15 m × 0.25 mm, 0.25 μm film (two each)
Carrier gas	Helium
Column 1 flow	1.0 mL/min
Column 2 flow	1.2 mL/min
Inlet temperature	280 °C
Injection mode	Splitless
Injection volume	2 μL
Oven temperature program	60 °C for 1 minute, 40 °C/min to 120 °C, 0 minutes, 5 °C/min to 310 °C, 10 minutes
Run time	50.5 minutes
Backflush	5 minutes (Post run)
Transfer line temperature	310 °C
Q-TOF MS conditions	
Ionization mode	EI
Source temperature	300 °C
Quadrupole temperature	180 °C
Mass range	50 to 500 <i>m/z</i>
Spectral acquisition rate	5 Hz, collecting both in centroid and profile modes

Sample preparation

Aerosol particles (PM_{2.5}) were collected on quartz fiber filters (QFF, Whatman, 5 inch × 8 inch), using samplers (Guangzhou, China) at a flow rate of 300 L/min. The QFFs were equilibrated at 20 °C and 40 % relative humidity (RH) in a temperature and humidity-controlled cleanroom chamber for 24 hours before and after sampling. The mass of particles on each QFF was determined by an electronic microbalance (Sartorius, IL, US) with 0.001 mg sensitivity. The filter (half) was extracted by Soxhlet with 50 mL of dichloromethane/hexane (1:1, v/v) at 70 °C for 48 hours. The extract was filtered with a filter device. After concentration by rotary evaporator, the extract was further concentrated to 2 mL under a pure N₂ stream, with solvent exchanged to *n*-hexane.

Data analysis

The data were processed by chromatographic peak deconvolution using the Unknowns Analysis tool in Agilent MassHunter Quantitative Analysis Software (B.07.01), followed by compound identification by comparison with the NIST 14 mass spectral library. The identities of deconvoluted peaks can be further confirmed using accurate mass information and the accurate mass tools in MassHunter Qualitative

Analysis Software (B.07.01). Molecular Structure Correlator (MSC) Software was used to further study the structures of tentatively identified compounds.

Results and Discussion

Chromatographic peak deconvolution and library search

Data were processed using chromatographic peak deconvolution in the Unknowns Analysis Software with a 100 parts per million (ppm) accurate mass Extraction Window setting and variable Retention Time Window Size Factor of 50–200 to find the highest number of components (Figure 2). The comparison with the NIST library with a Match Factor score > 50 identified approximately 2,600 components including alkanes, hopanes, ketones, polycyclic aromatic hydrocarbons (PAHs), oxygenated polycyclic aromatic hydrocarbons (O-PAHs), esters, and heterocyclic compounds. The Molecular Formula Generator and Formula Calculator tools were used to confirm the identity of each compound found by deconvolution. Screening results of PAHs and O-PAHs are shown in the following text as examples (Figures 3 and 4). A similar workflow can be applied to screen for other chemical groups.

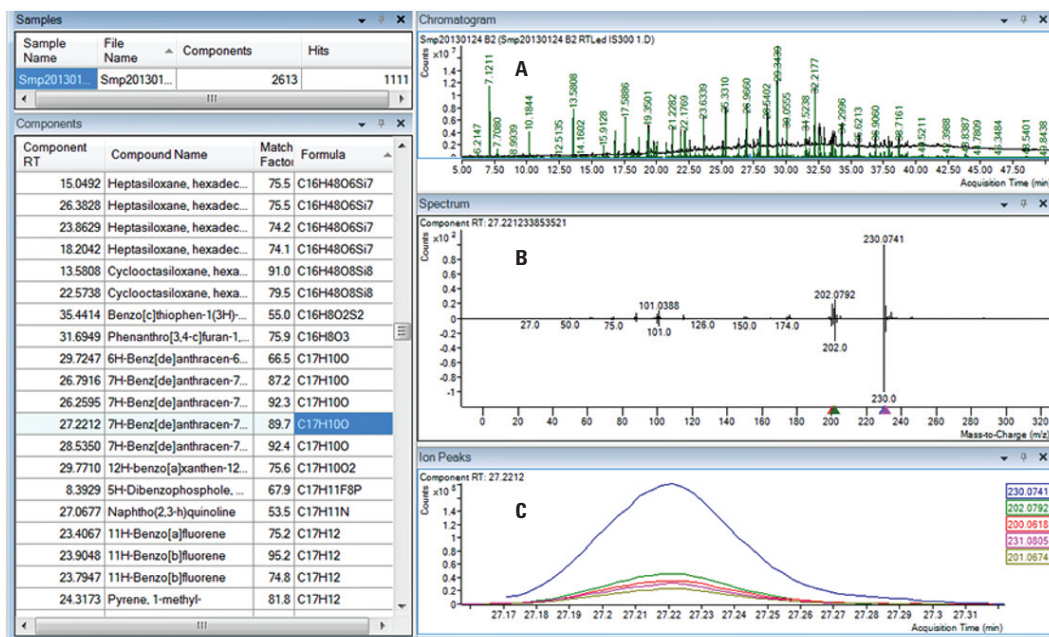


Figure 2. Unknowns Analysis software was used to perform chromatogram deconvolution. The Total Ion Chromatogram (TIC) (A), mirror plot of component and library hit spectra (B), and overlaid Extracted Ion Chromatograms (EICs) of the component (C), are depicted.

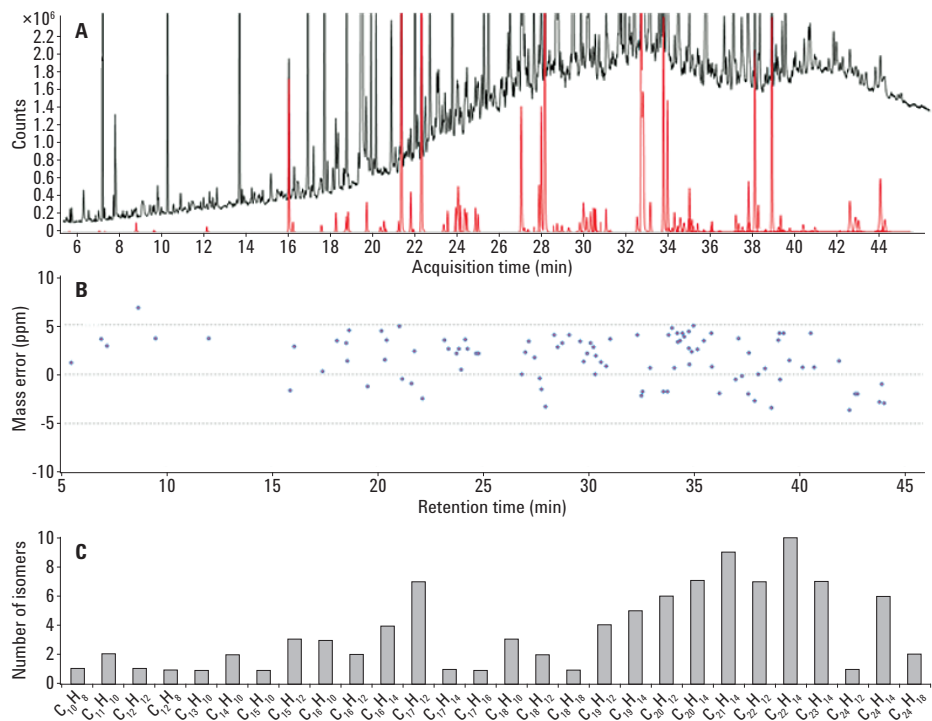


Figure 3. Screening results of PAHs. The chromatogram (A) overlays the TICs (black) and the component profiles of identified PAHs (red), while the mass errors of molecular ions of the identified PAHs calculated by the Formula Calculator are shown in B, and formula distribution is shown in C.

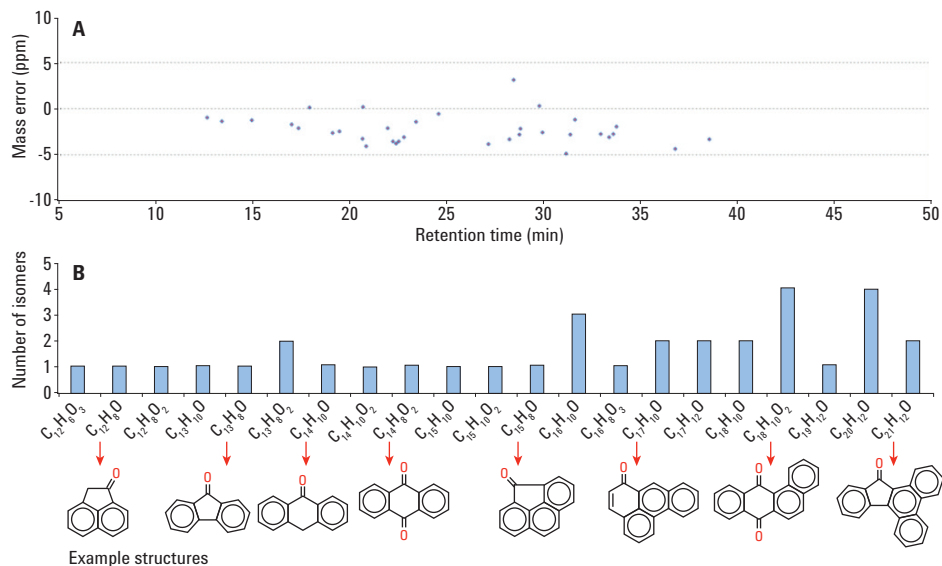


Figure 4. Confirmation of O-PAHs using accurate mass information. The mass errors of molecular ions of the identified O-PAHs calculated using the Formula Calculator are shown in A, while formula distribution and example structures are shown in B.

Identification of PAHs and O-PAHs

Unknowns Analysis was able to identify a large number of PAHs that coeluted in the unresolved complex mixture, as shown in Figure 3. The accurate mass information was used to confirm approximately 100 PAHs, with mass errors of less than 5 ppm. The P&EP MRM database contains retention times (RTs) for several of the PAHs, and was used to further confirm hits. The RT differences between database and sample were all within a window of 0.03 minutes. The good RT match further verifies the use of accurate-mass information as a confirmation tool. The formula distribution shows a wide range of PAHs in the extract of aerosol particles, with carbon numbers from 10 to 28.

Similarly, O-PAHs were also identified in the extract of aerosol particles, with 34 components confirmed by the accurate mass information. Figure 4 indicates the mass errors and the formula distribution of all identified O-PAHs. The structures for some typical O-PAHs are also displayed in Figure 4.

Structure of an unknown compound proposed by MS/MS

The chromatographic peak deconvolution was able to discover unknown compounds, as shown in Figure 5. The closest match for this spectrum in the NIST library was anthra[1,9-*cd*]pyrazol-6(2*H*)-one, with a formula of $C_{14}H_8N_2O$. However, this tentative match could be readily rejected based on mass accuracy alone, since the error on the molecular ion is 48.62 ppm. This highlights the advantage of accurate mass data obtained from a Q-TOF versus a unit mass instrument.

Using accurate mass information, the proposed formula for this unknown compound was $C_{15}H_8O_2$, with a mass error of 2.83 ppm. However, no compound with this formula was found in the NIST MS library. One of the other advantages of the 7200 GC/Q-TOF is the ability to perform accurate mass MS/MS experiments, which are very valuable for structural elucidation of unknowns.

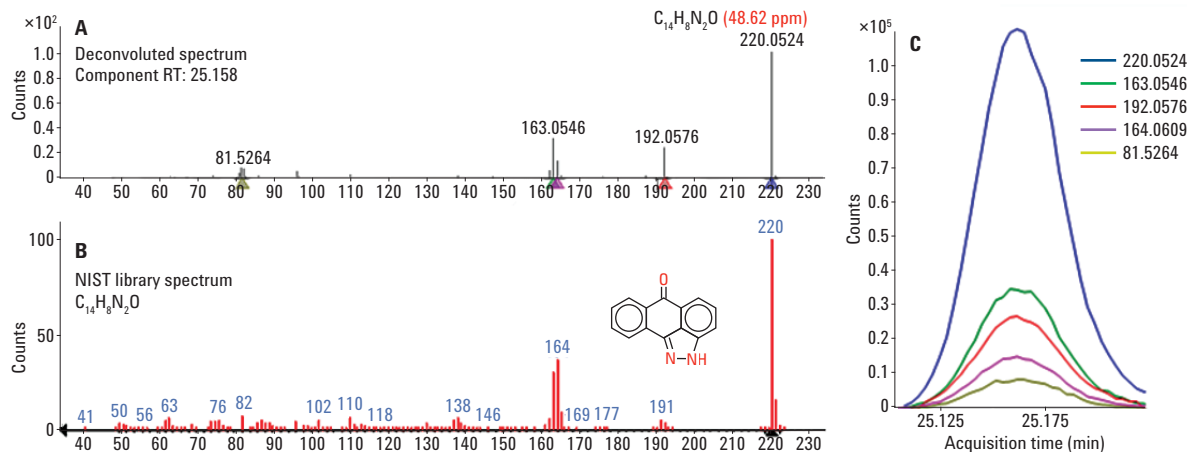


Figure 5. Comparison of mass spectrum between an unknown compound and a tentative NIST library match (A,B). The coelution profiles of deconvoluted ions (C) confirm that they all belong to the same component. However, this compound can be readily rejected based on mass accuracy alone, since the error on the molecular ion is 48.62 ppm.

Figure 6 shows the workflow using the MS/MS mode with accurate mass fragments to propose the structure of this unknown compound. The Formula Generator tool was used to assign an accurate empirical formula to the molecular and major fragment ions. To propose the structure of this unknown compound, the spectrum was imported into Molecular Structure Correlator (MSC) software as a CEF file,

and MSC searched the ChemSpider database to find all possible structural isomers. Although this type of confirmation is not completely unambiguous, it provides additional validation for this tentatively identified O-PAH. Figure 7 illustrates a proposed fragmentation pathway based on fragments listed in MSC software.

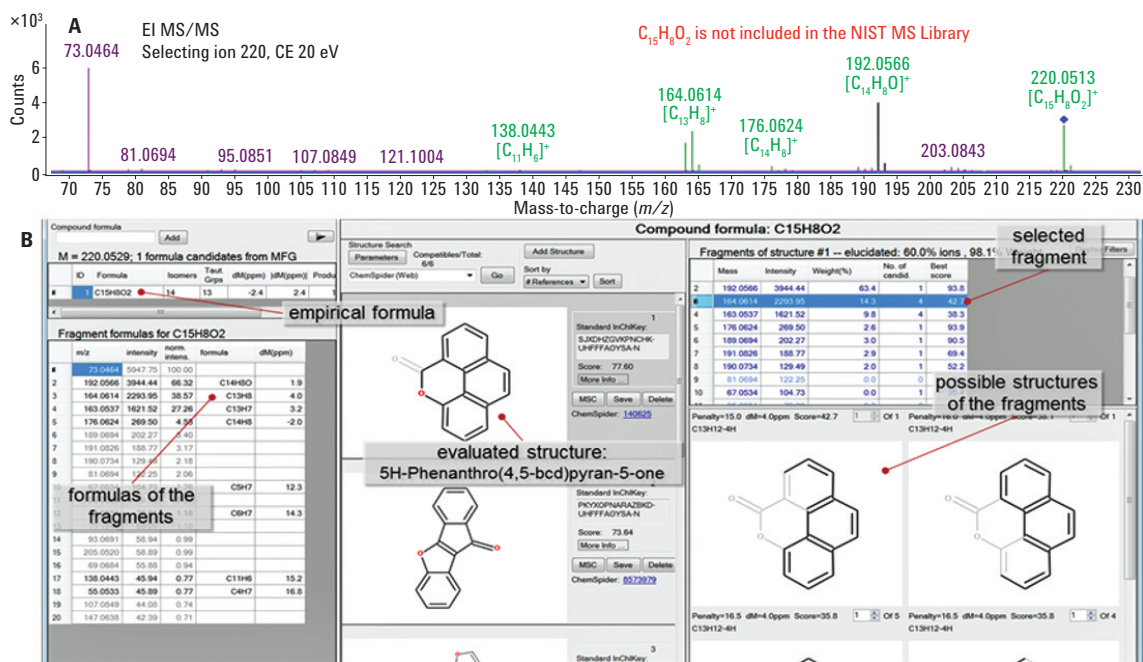


Figure 6. Empirical formulas generated from a MS/MS spectrum using the Formula Generator tool (A), and structure elucidation results of the compound with an empirical formula of $C_{15}H_8O_2$ using MSC software (B). Each individual fragment ion is ranked based on mass error corresponding to the proposed formula, along with a penalty based on how many bonds needed to be broken to generate that proposed formula.

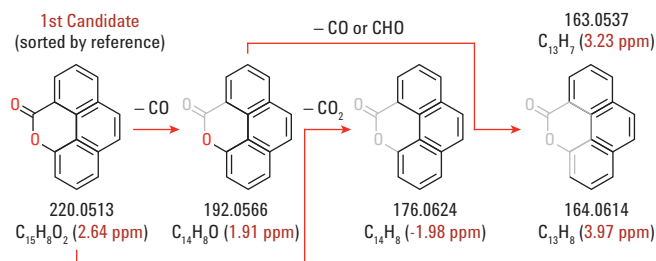


Figure 7. Fragmentation pathway of $C_{15}H_8O_2$ candidate based on fragments listed in MSC software.

Conclusion

Studies of SVOC compounds absorbed in aerosol particles can be greatly enhanced by using the multiple features of the Agilent 7200 GC/Q-TOF such as accurate mass information, high sensitivity in full spectrum mode, and MS/MS capabilities. The use of Agilent MassHunter Software capabilities such as deconvolution, automatic fragment formula annotation, and structure elucidation enabled the nontargeted approach in SVOC screening. Compound confirmation from library searches and structure suggestions for unknown compounds are also important investigative tools.

References

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