ASMS 2017
Poster number:
TP - 167

Analysis of Persistent Organic Pollutants in Atmospheric Aerosol Using a Novel Ultrasound Assisted Extraction Micro-scale Cell and a Triple Quadrupole GC/MS/MS System

Eleazar Rojas[1]; Gelasio Pérez[1], Eliana Arias-Loaiza[2], Erik Beristain-Montiel[2], Omar Amador-Muñoz[2]
[1]Agilent Technologies Inc, MEXICO, DF; [2]Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México

Introduction

Persistent Organic Pollutants (POPs) are synthesized organic compounds globally distributed in the environment. POPs include organochlorine pesticides (OCIs), polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs) and polyhalogenated dibenzo dioxins and furans (PCDDs/Fs). Atmospheric aerosol is one of the major constituents of air pollution, and was classified as carcinogenic to humans (Group 1) [1]. Selective and sensitive techniques are required to detect POPs in aerosol. This work shows POPs in atmospheric aerosol collected at several sites around the country of Mexico. Using the 7010A Triple Quadrupole GC/MS System with the new High Efficiency Source (HES) has increased the ion flux over traditional tandem GC/MS instruments by a factor of 10 to 20-fold, with a multi-fold improvement in EI detection limits.

Experimental

Sampling

Atmospheric aerosol samples were collected in Hermosillo (northern part of the country, elevation 210 masl), Mexico City (middle of the country, 2250 masl) and Altzomoni (middle of the country, 3985 masl), during 2013 and 2015. An outdoor passive air sampler housing (TE-200-PAS, Tish Environmental Inc.) was used for a duration of 80 to 110 days in each case.

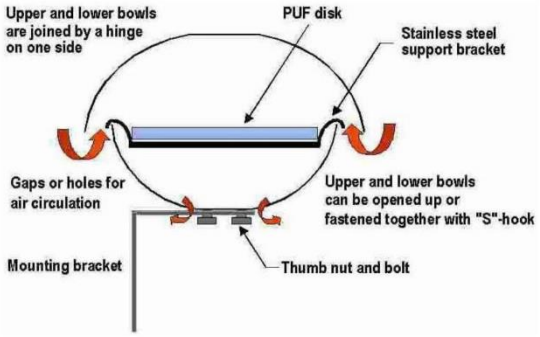

Figure 1. Passive sampler

Experimental

Sample Preparation

A novel ultrasound assisted extraction micro-scale cell (UAE-MSC), recently patented [2], was used to extract POPs from atmospheric aerosol [3].

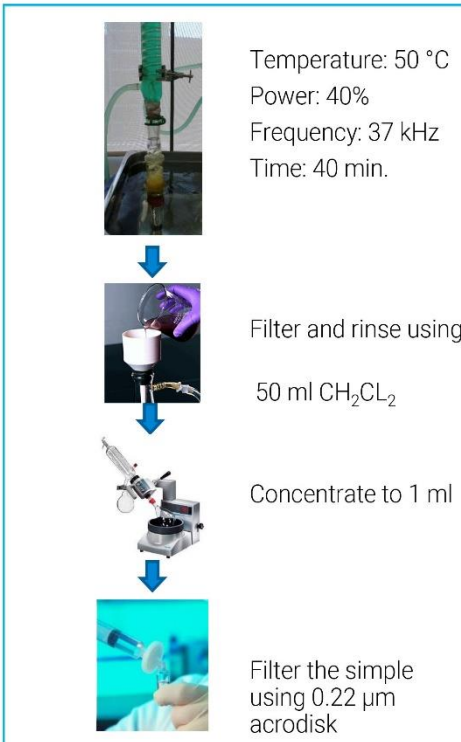

Figure 2. Sample preparation

Sample Analysis

Analysis was performed using the Agilent 7890A/7010A GC/MS system equipped with the High Efficiency Source(HES) operated in MRM mode. The 7890A GC was equipped with a MultiMode Inlet (MMI) and an HP-5ms UI column, 30m x 250µm x 0.25µm. Backflushing at the column midpoint was accomplished using a Purged Ultimate Union (PUU) controlled by an Aux EPC module. All of the method parameters were obtained from the Agilent G9250AA Pesticides and Environmental Pollutants database (P&EP); no further optimization was required. Three transitions were used for each compound, the most intense as the quantifier transition and the other two as qualifier transitions.

Results and Discussion

Figure 3. High Efficiency Source (HES)

UAE-MSC optimized extraction conditions reduced by 30X the solvent consumption and decreased the extraction time from several hours to ten minutes, with respect to Soxhlet extraction[4]. Atmospheric samples are extremely complex and advanced technology is required to differentiate OCIs, PCBs, polycyclic aromatic hydrocarbons, PBDEs, organophosphates and other targets from organic interferences at low ppb concentrations.

The GC/MS/MS conditions (chromatographic parameters, precursor ion, collision energy, and product ions of the MRMs) were adequate to perform the quantitative analysis without further optimization.

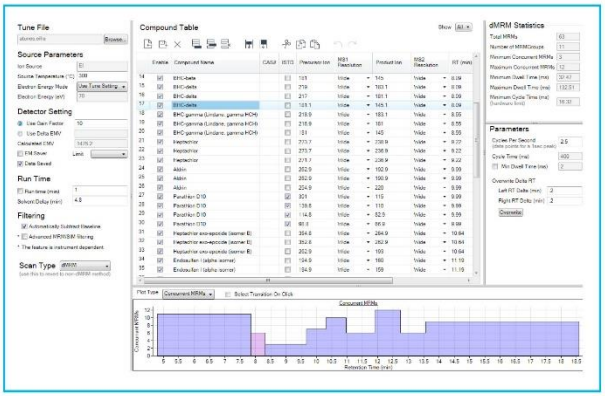

Figure 4. The G9250AA P&EP database has up to 8 transitions for each compound. This allows the user to choose alternative transitions to minimize matrix interferences and improve quantitation results.

Due to the presence of a large number of background compounds, backflushing was deemed necessary. Backflushing the GC column ensures that high-boiling compounds in the matrix are not passed through the column, thereby reducing column bleed, eliminating ghost peaks, and minimizing contamination of the mass spectrometer. Run time is also reduced because the traditional long post-run bakeout is avoided.

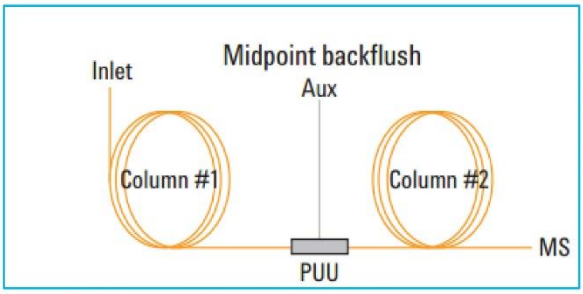

Figure 5. Diagram Midpoint Backflushing

The 7010A triple quadrupole MS was extremely sensitive to OCIs (around 0.125 pg/µL) and less sensitive to some PBDEs and PCBs. High selectivity was achieved; 50 different compounds were quantitated in a single run of 20 min.

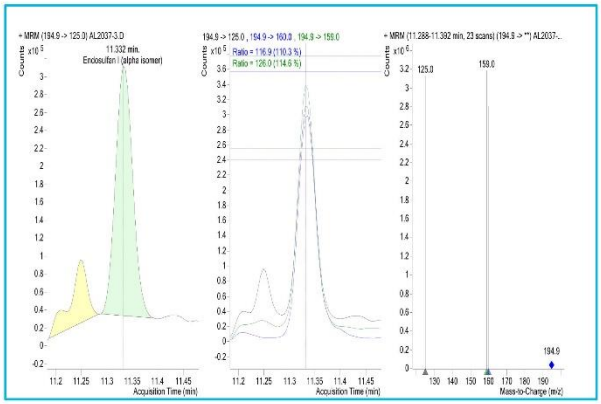

Figure 6a. Quantification and Qualifier signals for Endosulfan I for a calibration point of 5 ppb

Results and Discussion

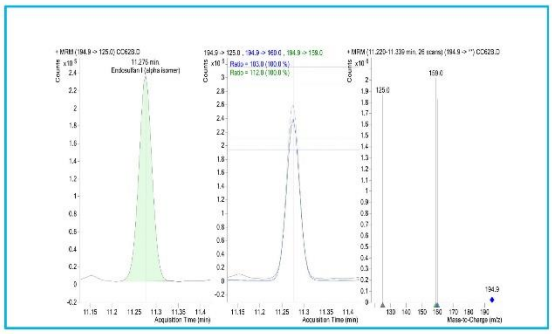

Figure 6b. Quantifier and qualifier signals for Endosulfan I for a sample with a concentration of 6.5 ppb

The linearity for most of the compounds was found to be between an r^2 of 0.902 and 0.999 in the range 0.125 to 250 pg/µL.

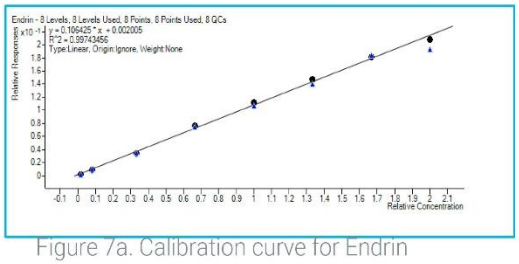

Figure 7a. Calibration curve for Endrin

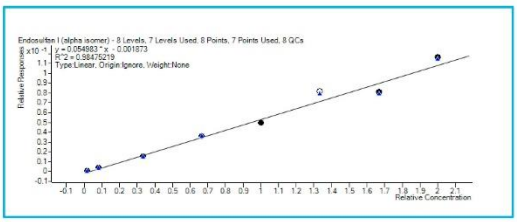

Figure 7b. Calibration curve for Endosulfan I

POPs analysis showed heptachlor, delta-HCH and p,p'-DDE in Hermosillo, Mexico City and Altzomoni. Some PCBs and PBDEs were also found in Mexico City. The highest POPs concentrations were observed in Hermosillo and Altzomoni. Since Altzomoni is located between the volcanoes Popocatepetl and Iztaccihuatl, the predominant wind trajectory suggests POPs are transported from the north to the south of the country.

Conclusions

- UAE-MSC effectively extracts pesticides from the passive sampler, using less time and solvent than Soxhlet technique.
- The 7010A GC/MS/MS system detects POPs at very low concentrations (0.125 pg/µL) in highly complex atmospheric aerosol samples.
- Use of the Agilent P&EP database parameters without additional modification allows one to detect and quantify more than 50 different POP´s in aerosol samples with an excellent linearity.
- Use of the backflushing technique helps to keep both the GC and the MS clean.
- The highest concentrations of POPs were observed in Hermosillo.
- POPs are transported from the northern part of the country to the southern part.

References

[1] IARC (2013). Outdoor air pollution a leading environmental cause of cancer deaths, WHO Press Release N° 221. 2–5.

[2] Amador-Muñoz et al. (2014). Celda de extracción a microescala, asistida por ultrasonido, con y sin reflujo, acoplada a un sistema de filtración., Mexican patent 325624.

[3] Beristain-Montiel et al. (2016). An Innovative Ultrasound Assisted Extraction Micro-Scale Cell combined with Gas Chromatography / Mass Spectrometry in Negative Chemical Ionization to Determine Persistent Organic Pollutants in Air Particulate Matter. J. Chromatogr. A, 1477, 100-107.

[4] Chen et al. (2011). Handbook on Applications of Ultrasound: Sonochemistry for Sustainability, 1st ed., CRC Press.