

Targeting the Unknowns?

Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry (LC-QToF-MS)

Eurofins have adopted high resolution accurate mass LC-QToF-MS for not only the identification of Per- and Polyfluoroalkyl substances (PFAS) and their precursors and subsequent “fingerprinting” but this technique is also very useful for determining “unknown unknowns” in the area of emerging contaminants.



There are KNOWN KNOWNS, KNOWN UNKNOWNs and UNKNOWN UNKNOWNs!

*Reports that say that something hasn't happened are always interesting to me, because as we know, there are **known knowns**; there are things we know we know. We also know there are **known unknowns**; that is to say we know there are some things we do not know. But there are also **unknown unknowns** – the ones we don't know we don't know. And if one looks throughout the history of our country and other free countries, it is the latter category that tend to be the difficult ones....United States Secretary of Defense Donald Rumsfeld.*

There has been an almost exponential growth in the number of organic contaminants of concern listed in the past few years with the OECD¹ releasing a study listing 4730 PFAS compounds, the increasing awareness surrounding microplastics and their ability to adsorb persistent organic pollutants (POPs) as they migrate around the world's waterways and biomagnify through the food chain plus the omnipresent pharmaceutical and personal care products (PPCPs) found in municipal wastewater treatment plants. The detection of the myriad of different classes of compounds in

environmental compartments has led to a complex array of different analytical methods being employed where sample extraction and clean-up techniques are targeted along with the different instrumental methods leading to quite expensive analytical costs and lengthy analysis times.

Case Study

Recently, near some sensitive mangroves some discarded plastic drums were found that contained unknown “smelly” chemicals of unknown origin with no labels or any identifying symbols. An aliquot of the liquid was prepared and then analysed using LC-QToF-MS.



Within a few hours of receiving the samples in the laboratory the resulting mass spectrum indicated a dissociated anion with a unique isotope abundance pattern containing sulfur atoms in the major peak. Further deconvolution of the mass spectrum indicated a thiocarbamate pesticide most probably the sodium salt of methyl dithiocarbamate – metham sodium. This analytical evidence was sufficient for action to be taken to ensure that the area was made safe and the potentially toxic chemical contained in a safe manner and further investigations undertaken by the regulator in uncovering the source.

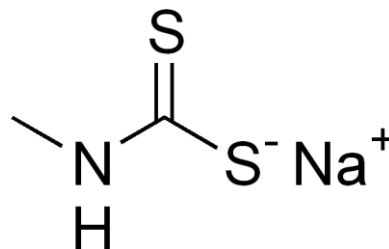


Figure 1: Metham sodium

¹ ENV/JM/MONO(2018)7 Summary Report on Updating the OECD 2007 List of Per- and Polyfluoroalkyl Substances (PFASs) 4 May 2018

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EnviroNote No. 1078 - August 2018

ABN 50 005 085 521

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Emerging Contaminants

While non-targeted analysis has always existed it has only been in recent years that improved technologies such as accurate mass or high-resolution mass spectrometers (HRMS) have become available whereby the full mass spectra are collected with associated sensitivities such that their routine use now matches that of targeted analyses. These instruments combined with either gas chromatography or liquid chromatography offers the ability to screen environmental samples for unknown unknowns or non-targeted compounds by using the exact mass to four decimal places, retention time plus the individual isotopic ratios along with expert systems from available databases such as ChemSpider, MassBank or NORMAN as well as user compiled Personal Compound Database and Library (PCDL) both using artificial intelligence and expert analytical knowledge of the analysts. Retrospective analysis of past collected data allows for an electronic databank without the need to re-extract and reanalyse the samples by choosing a generic extraction with clean-up and associated addition of isotopically labelled compounds that cover the different classes of compounds to ensure that the workflow is quantitative or semi-quantitative at best. Unmistakably, the screening non-targeted workflows are best combined with targeted methodologies but the major issues with the latter are lack of available traceable standards especially for the myriad of PFAS and PPCP metabolites.

For polar compounds like PFAS, PPCPs including anti-depressants (fluoxetine, citalopram, sertraline, paroxetine, escitalopram) modern pesticides including neonicotinoids (acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid, thiamethoxam) azole fungicides (climbazole, clotrimazole, ketoconazole, miconazole, fluconazole, itraconazole, thiabendazole, and carbendazim), insect repellents (N,N-diethyl-3-methylbenzamide (DEET), and icaridin (also known as picaridin)), isothiazolinone antifouling agents (1,2-benzisothiazolinone (BIT), 2-n-octyl-4-isothiazolinone (OIT), and 4,5-dichloro-2-n-octyl-isothiazolinone (DCOIT)), paraben preservatives (methylparaben, ethylparaben, propylparaben, and butylparaben), and disinfectants (triclosan and triclocarban) in surface water, wastewater, sediment, sludge, and soil, and brominated flame retardants (BFRs) hexabromocyclododecane (alpha, beta and gamma HBCD diastereoisomers) and tetrabromobisphenol A (TBBPA).

Notably, all these different compounds can be determined in the one LC-QToF-MS experiment and if a new contaminant of concern is identified in the future, retrospectively, this can also be determined. Moreover, metabolites and conjugated compounds can also be determined using the accurate mass high resolution isotopic pattern recognition procedure.

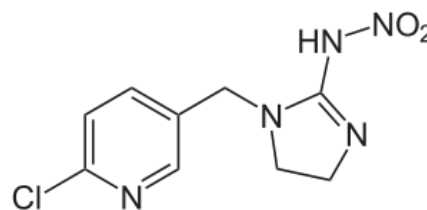


Figure 2: Imidacloprid

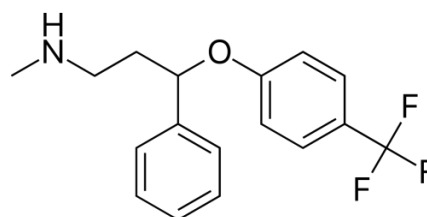


Figure 3: Fluoxetine

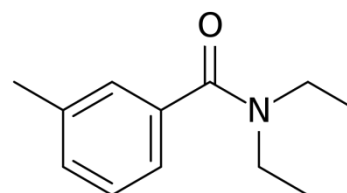


Figure 4: DEET

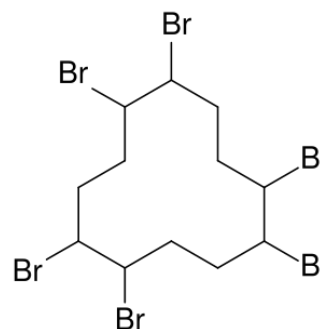


Figure 5: HBCD (1,2,5,6,9,10-Hexabromocyclododecane)

Eurofins | mgt Expertise

If you would like to discuss logistical details for your upcoming projects then please contact your local Analytical Service Manager or one of our Business Development team listed below.

Technical support can be provided by contacting Dr Jack Thompson or Dr. Bob Symons.

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