ANALYSIS OF SELECTED HALOGENATED CONTAMINANTS USING SBSE-TD-PTV-GCxGC-IDTOFMS

Jef Focant, Andreas Sjödin, Larry L. Needham and Donald G. Patterson Jr.

Organic Analytical Toxicology Branch, Division of Laboratory Sciences, National Centers for Environmental Health, Centers for Disease Control and Prevention, 4770 Buford Hwy, Atlanta, GA 30341, USA.

Many compound classes are grouped together and referred to as 'halogenated environmental contaminants'. Among them are the chlorinated compounds such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and persistent pesticides (PPs), as well as the more recently recognized polybrominated diphenyl ethers (PBDEs), which are used as flame retarding chemicals. These compounds are also classified as persistent organic pollutants (POPs) because they have been shown to accumulate and persist in human fat at significant levels. There is therefore a need to develop high throughput specific and sensitive methods to ensure fast and reliable environmental and human monitoring. Currently, methods are available for the measurement of these compounds but those generally require fractionation in analyte sub-groups containing a reasonable number of compounds to allow efficient GC-MS analysis (limited number of compounds per unit of time). Generation of global data for these human toxicants therefore requires the use of

several protocols and analytical tools that require independent sample preparation, injections and data processing steps before final recombination of results.

There are two sample preparation approaches each with their desirable and undesirable characteristics. First, a single method to collect the extract containing all or as many of the compounds of interest as possible. The advantages of simplicity and speed are obvious. This approach does limit the variety of compounds types that will be extracted. The second approach is to combine extracts from a number of different cleanup methods into a single extract for MS analysis. This approach has the advantage of allowing analysis of many different compound classes but is more complex and time consuming. Alternatively, we are also working on a semi-automated comprehensive extraction and multiple fractionation method (SACEMF), which would allows the extraction of polar and non-polar analytes from the same sample matrix. This approach will be the focus of future work in our lab.

In the context of the first approach, we decided to investigate a new approach based on the combination of different state-of-the-art methodologies for 'multi-group analysis'. Stir bar sorptive extraction (SBSE) is based on the use of greater volumes of poly(dimethylsiloxane) (PDMS) than used for the sensitivity-limited solid-phase microextraction (SPME). This technology was selected because of its potentially lower detection limits for a broad range of compounds exhibiting different octanol-water partitioning coefficients ($K_{o/w}$). Subsequent use of two programmable temperature vaporization (PTV) units placed in series allows thermal desorption (TD) and sharp

injection of trapped analytes onto the first GC column. Comprehensive multi-dimensionnal gas chromatographic (GCxGC) separation powered by non-scanning time-of-flight mass spectrometry (TOFMS) were then selected as chromatographic and analytical resolution enhancers. In this technique, we use isotope-dilution mass spectrometry (IDMS) to achieve the maximum accuracy and precision.

Some of the preliminary results obtained using the SBSE-TD-PTV-GCxGC-IDTOFMS method will be presented as well as future directions including additional analyte groups (e.g. metabolites of PCBs and PAHs, PCNs, toxaphenes, halogenated alkanes, …) to the screening procedure. The screening procedure could be used to monitor the fat of a national human population for new analytes that might be finding their way into humans. This approach could be a proactive way of quickly finding new environmental contaminants in human rather than many years after the start of the exposure.