AMBIENT THERMAL DESORPTION IONIZATION FOR RAPID MASS SPECTROMETRIC ANALYSIS OF CONTAMINANTS

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INTRODUCTION

The application of ambient desorption techniques for sample introduction into mass spectrometers is an emerging technology that has applicability in many areas of contaminants analysis. The atmospheric-pressure solids analysis probe (ASAP) is a unique mass spectrometry technique for direct analysis of volatile, semi-volatile, solid and liquid samples.[1-3] In ASAP, samples are introduced to the mass spectrometer on a sealed glass capillary and vaporized with heated nitrogen desolvation gas. Ionization is achieved using a corona discharge, as shown in Figure 1. While conventional analytical tools, such as LC or LC/MS, require time-consuming sample preparation procedures, ASAP can provide mass spectral information within seconds of sampling.

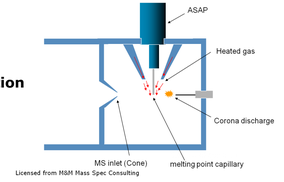

Figure 1. Ionization using ASAP

To ensure the safety of consumers following an oil spill, a rapid screening method is required to analyze food for compounds of concern. Of the many compounds found in oil, a subset of major concern is the polyaromatic hydrocarbons (PAHs). These compounds are known to be carcinogenic and the US Environmental Protection Agency has defined these compounds as priority pollutants.

In order to demonstrate the capabilities of ASAP coupled to a tandem quadrupole mass spectrometer, detection of PAHs in seafood samples was investigated. Spiked samples of fish and shrimp were homogenized and then sampled directly with the glass capillary. PAHs were screened using multiple reaction monitoring (MRM) mode. In addition, PAHs were extracted from the samples using a simple QuEChERS protocol and the extract sampled directly using the capillary. This work provides an interesting example of the potential applications of ASAP for rapid screening of contaminants.

METHODS

Sample Preparation:

Individual samples of a cod fish fillet and the edible parts of whole uncooked shrimp were prepared using a food processor. A homogenized sample of each was then achieved using a blender and adding H_2O:ACN (60:40) in a ratio of 2:1 solid to H_2O:ACN. 5g samples were spiked at 6 levels ranging between 0.32 and 1000 ng/g using a mixture of 16 PAH compounds (AccuStandard M-8310). Specific compounds shown as examples in this work are listed in Table 1, along with the FDA established level of concern[4].

The sample was loaded onto the sealed glass melting point capillary tube of the ASAP probe by direct insertion into the homogenized samples and wiping off excess solid. The acquisition of data was started and the probe inserted into the sealed MS source enclosure of a Xevo TQ-S Mass Spectrometer 30s later, providing consistency in data collection (Figure 2). Data was obtained with a constant desolvation temperature as opposed to using a temperature ramp.

A vial of water was added to the Xevo TQ-S source to favor the formation of the MH^+ adduct, as shown in Figure 3. MS/MS product ion scans (not shown), provided information to obtain the MRM transitions shown in Table 1. The Xevo TQ-S MS was then operated RADAR mode. RADAR mode allows for the simultaneous acquisition of MRM and full scan MS, enabling the monitoring of the background matrix during routine quantitative MRM experiments.

MS Conditions:

- Source Temperature 120 °C
- Cone 15 V
- Desolvation Temperature 600 °C
- Cone Gas 150 L/Hr
- Corona 5 µA
- Source Offset 50 V
- Desolvation Gas 600 L/Hr
- Nebulizer 7 Bar

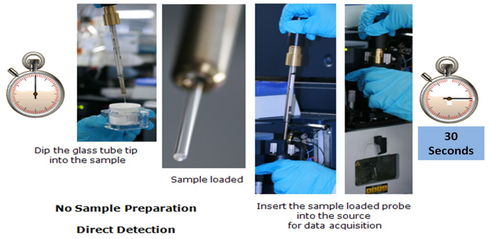

Figure 2. Sample loading protocol for ASAP

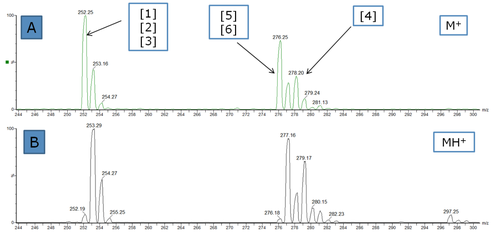

Figure 3. MS Full Scan spectra of PAH standards in Table 1.
(A) Spectrum acquired under source conditions favoring M^+ ion.
(B) Spectrum obtained with a modifier and conditions favoring MH^+ ion.

RESULTS AND DISCUSSION

MRM data for all of the compounds and transitions in Table 1 were obtained. Since there is no chromatographic separation in ASAP, the signal for a particular MRM transition will be the result of all compounds which give rise to that transition. For this poster we focus on the transition 253.15 > 252.15, which comprises of signals from compounds 1, 2 and 3 in Table 1.

	Compound	Primary Transition (CE)	Secondary Transition (CE)	FDA Established Levels of concern ng/g
1	Benzo(a)pyrene	253.15 > 252.15 (35)	253.15 > 250.12 (50)	132
2	Benzo(b)fluoranthene	253.15 > 252.15 (35)	253.15 > 250.12 (50)	1,320
3	Benzo(k)fluoranthene	253.15 > 252.15 (35)	253.15 > 250.12 (50)	13,200
4	Dibenzo(a,h)anthracene	279.16 > 278.12 (30)	279.16 > 276.11 (50)	132
5	Benzo(g,h,i)perylene	277.30 > 276.13 (25)	277.30 > 274.12 (55)	Not Applicable
6	Indeno(1,2,3-cd)pyrene	277.30 > 276.13 (25)	277.30 > 274.12 (55)	1,320

Table 1. PAH transitions and established levels of concern.

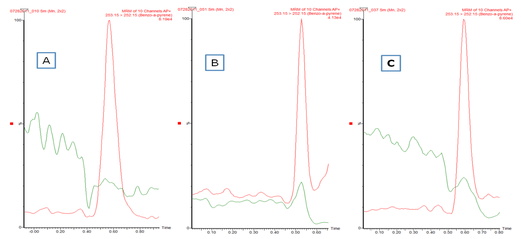

Figure 4. MRM *m/z* 253.15>252.15 in (A) 0.64 ng/g in H_2O:ACN (60:40), (B)Spiked Fish at 8 ng/g , (C) Spiked Shrimp at 1.6 ng/g. Red trace shows spiked sample. Green trace shows equivalent matrix blank.

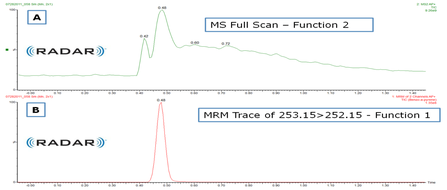

Figure 5. Full scan TIC (A) and MRM (B) data of PAHs standards at 400 ng/g in H_2O:ACN (60:40), acquired simultaneously using RADAR.

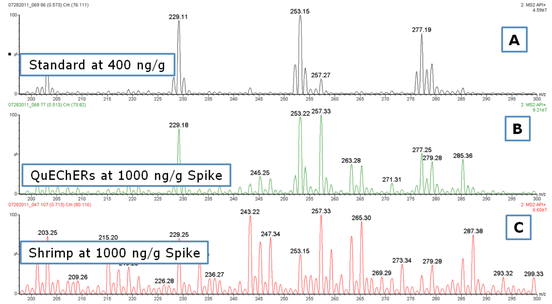

Figure 6. Summed full scan spectra from RADAR acquisition of (A) PAH standards at 400 ng/g in H_2O:ACN, (B) A QuEChERS extract from shrimp spiked at 1000 ng/g and (C) Homogenized shrimp spiked at 1000 ng/g.

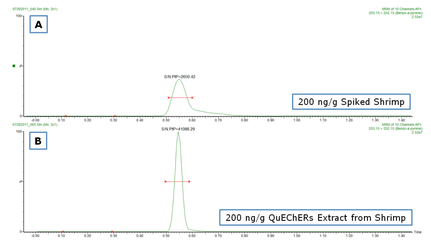

Figure 7. MRM *m/z* 253.15>252.15 from

(A) PAHs spiked at 200 ng/g in homogenized shrimp and sampled directly.

(B) Quechers extract of PAHs spiked at 200 ng/g in homogenized shrimp.

Direct sampling of the spiked homogenized seafood samples and acquisition of MRMs enabled the detection of low ng/g (ppb) levels of the PAHs with the transition 253.15 > 252.15, as shown in Figure 4. The lowest level that was detected in homogenized shrimp was 1.6 ng/g of each PAH (Figure 4C). This translates to a total concentration of 4.8 ng/g for the summed PAHs in that transition. For fish the lowest level was 8 ng/g of each PAH (Figure 4B). Both these values are well below the lowest level of concern of 132 ng/g, which is for benzo(a)pyrene.

The use of RADAR for background monitoring of matrix interference during an MRM experiment is of particular interest when using ASAP as, with no extraction or chromatography, the background may be very complex. Data from RADAR are shown in Figures 5 and 6. The trace for both MRM and full scan data are shown in Figure 5.

By summing the full scan spectra over the region defined by the MRM peak, the spectra in Figure 6 were obtained. These spectra show the full scan data from m/z 200 - 300 for a standard (A), a QuEChERS extract from shrimp (B), and a non-extracted shrimp sample (C). As can be seen, the QuEChERS extract has removed many ions that could interfere with the analysis. This observation is also supported by the improvement in signal-to-noise ratio in the MRM data seen in Figure 7 for the extracted (Figure 7B) versus non-extracted (Figure 7A) sample with 200 ng/g of each PAH.

For the purposes of screening PAHs at low ppb levels in seafood, however, the QuEChERS extraction was not required. For lower detection levels, different matrices or less sensitive instrumentation, some sample preparation (such as QuEChERS extraction) may be required.

CONCLUSIONS

- ASAP can be used to rapidly detect volatile and semi-volatile compounds without sample extraction or chromatographic separation.
- The combination of ASAP with the Xevo TQ-S enabled the rapid screening of PAHs below 10 ng/g in homogenized shrimp and fish.
- RADAR allows for the simultaneous acquisition of full scan MS and MRM data to enable monitoring of the background matrix during routine analyses.
- The data illustrate the potential of using ASAP for the rapid screening of environmental samples with minimal sample preparation.
- The ASAP solution can increase lab productivity through analytical time savings and reducing operating costs.
- In addition, the ASAP approach lessens the impact on the environment by reducing solvent consumption.

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