A PROTOTYPE DIRECT SAMPLING INLET FOR THE RAPID ANALYSIS OF TARGET ANALYTES IN THE CHEMICAL INDUSTRY

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INTRODUCTION

Mass spectrometry can be a powerful tool for routine analyses such as residue monitoring[1] or targeted screening,[2] but the need for expert users or extended chromatographic separations can limit its deployment by non-scientific personnel outside of a laboratory setting.

In many screening methods, several targeted species are monitored either to check that they are above a certain level or that they do not exceed a certain level. In these cases, a simple monitoring test with a pass/fail or yes/no output would be ideal.

In this work, we demonstrate how a simple, direct sampling technique can be implemented with a small, easy to use quadrupole mass spectrometer for rapid, routine monitoring and reporting of typical industrial samples, such as polymers or formulated lubricant oils.

We also highlight how this system can be used to separate constituent components of a sample with different boiling points.

Figure 1. ASAP-QDa prototype.

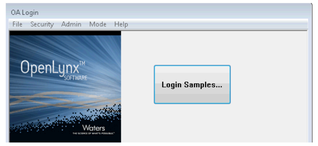

Figure 2. OpenAccess Login.

METHODS

Sample preparation:

A solution of a model polymer formulation was prepared comprising a PEG600 standard combined with a polymer additives standard mix diluted in methanol. Commercial, off the shelf, car engine lubricant oils were diluted in toluene.

Instrument conditions:

An Atmospheric Solids Analysis Probe (ASAP) (Waters Corporation) was installed on a quadrupole mass spectrometer (ACQUITY QDa) (Waters Corporation) (*Figure 1*).

MS conditions were as follows:

- Ionization mode : ASAP+
- Cone voltage: 20 V
- Source temperature: 120 °C
- Corona voltage: 3 kV
- Probe temperature: Three different methods were used. See method details below.

Method 1: Temperature Ramp

The probe capillary was dipped in the sample for 30 seconds before insertion into the system. The temperature was step ramped by 100 °C over 5 minutes (*Table 1*) producing a step type chromatogram (*Figure 3A*).

Time (min)	Temp (°C)	Action
0.0	100	Sampling
0.5	100	Insert probe
1.0	200	
2.0	300	
3.0	400	
4.0	500	
5.0	600	
6.0	600	

Table 1. Temperature gradient for temperature ramp.

Method 2: Ballistic Ramp

The probe capillary was dipped in the sample for 30 seconds before insertion into the system. The temperature was immediately ramped to 600 °C (*Table 2*) producing a broad peak chromatogram (*Figure 3B*).

Time (min)	Temp (°C)	Action
0.0	100	Sampling
0.5	100	Insert probe
0.5	600	
3.0	600	

Table 2. Temperature gradient for ballistic ramp.

Method 3: Load on Probe

The sample was pipetted directly onto the probe tip and the probe was immediately inserted. This was repeated over 5 minutes (*Table 3*) producing a chromatogram with well defined peaks (*Figure 3C*).

Time (min)	Temp (°C)	Action
0.0	500	Probe inserted
0.3	500	Remove probe
0.4	500	Pipette sample on probe
0.5	500	Reinsert probe
1.3	500	Repeat steps above
5.0	500	Finish analysis

Table 3. Temperature gradient for load on probe.

Data Acquisition and Processing:

Datasets were acquired and processed using MassLynx v.4.2 and TargetLynx. OpenLynx was also examined with OpenAccess login.

RESULTS & DISCUSSION

LUBRICANT OIL APPLICATION

Depending on the user's purpose, different chromatograms can be acquired from the different methods and temperature profiles described in the method section (*Figure 3*). For a lubricant oil sample, the temperature ramp method was used; and from the spectra, constituent components were separated out at different temperature points (*Figure 4*). At the lower temperatures, a selection of lubricant oil additives desorbed (*Figure 4* and *Figure 5*). From 200 °C, the lubricant oil started to desorb (*Figure 4*). Other components, presumed to be additives, appear at high temperatures but are, as yet, uncharacterized.

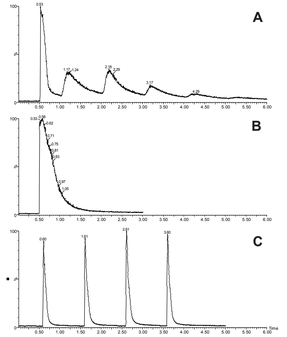

*Figure 3. Example chromatograms from a lubricant oil sample. **A**: Temperature Ramp **B**: Ballistic Ramp **C**: Load on Probe*

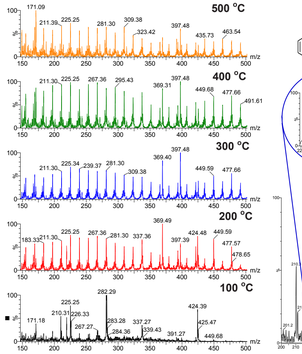

Figure 4. The spectra generated from chromatogram A in Figure 1 at temperatures 100 to 500 °C.

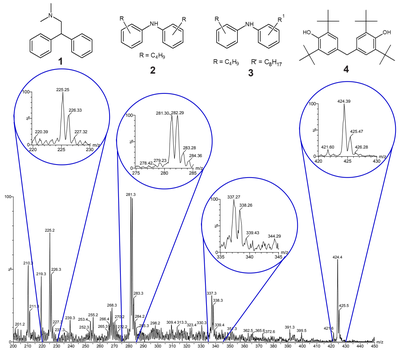

*Figure 5. At 100 °C we see these additives **1**: N,N-dimethyl-2,2-diphenylethylamine (m/z 225), **2**: Irganox 5057 (m/z 281), **3**: Antioxidant L57[3] (m/z 338), **4**: 4,4'-methylene-bis-(2,6-di-tert-butylphenol) (m/z 424).*

POLYMER APPLICATION

The temperature ramp method was applied to a polymer solution to separate out the polymer and its additives. *Figure 8* highlights three different temperature points along the chromatogram with resulting spectra. The first evolution of polymer ions occurred at 200 °C but the main polymer distribution, centred on *m/z* 636, occurred at 400 °C. Furthermore, the lower molecular weight polymer additives were observed immediately at 100 °C, whereas the heavier polymer additives were not observed until 400 °C.

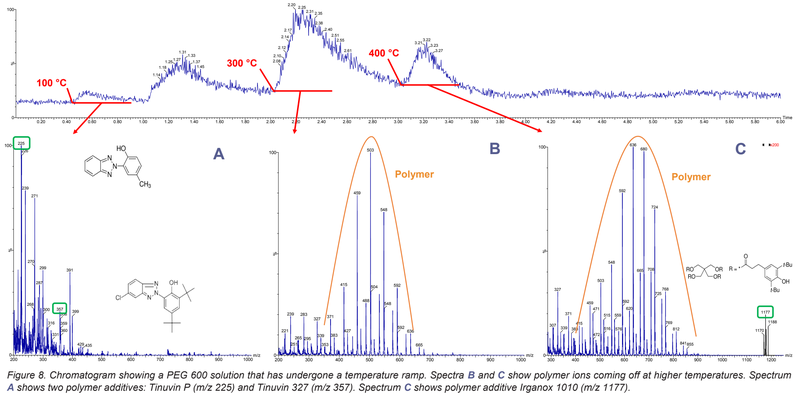

*Figure 8. Chromatogram showing a PEG 600 solution that has undergone a temperature ramp. Spectra **B** and **C** show polymer ions coming off at higher temperatures. Spectrum **A** shows two polymer additives: Tinuvin P (m/z 225) and Tinuvin 327 (m/z 357). Spectrum C shows polymer additive Irganox 1010 (m/z 1177).*

Figure 6 illustrates the OpenLynx results from an analysis using the ballistic ramp method. Ions of interest were quickly evolved upon insertion of the probe and a Total Ion Chromatogram (TIC) was generated. From this TIC, Extracted Ion Chromatograms for ions of interest were generated and integrated. The targeted ions were monitored and shown simply to pass or fail set criteria depending on their response.

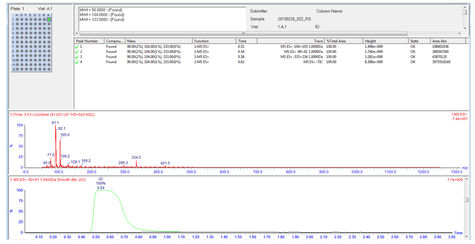

Figure 6. OpenLynx results view showing three targeted screening masses. The results show the masses have been found and pass the criteria specified.

Sample Summary:

Sample	ID	Date	Time	Target	Found	
1		26-Feb-2019	5:40	90.00		YES
				104.00		YES
				333.00		YES

Figure 7. Example summary report.

OpenAccess Login (*Figure 2*) can make it easy to run samples in a controlled setting and reports can be generated to create a yes/no output depending on whether ions are above or below a prescribed level (*Figure 7*).

CONCLUSION

- **Atmospheric Solid Analysis Probe (ASAP) coupled with a simple quadrupole mass spectrometer (QDa) has been demonstrated to be applicable to the analysis of target analytes in the chemical industry.**
- **This approach offers potential for a simple to use sample inlet and software solution to provide an accessible tool for any user.**
- **The proposed methodology was successfully used for rapid targeted screening and for the separation of components for typical industrial samples.**
- **The pipetting load on probe method was more reproducible than the direct dipping methods but required some level of dexterity when using the pipette. It also meant that components from the pipette could potentially contaminate the system. A fixed temperature allowed for a very short acquisition time and all the ions of interest evolved simultaneously upon insertion of the probe.**
- **Both ballistic ramp and the temperature ramp methods were easier to undertake and could be run with pre-set automated methods. The ballistic ramp was the quickest method and, with the profile of the chromatograms generated, target analysis of specific ions could be undertaken.**
- **The stepwise temperature ramp required a longer acquisition time but conferred a degree of sample deconvolution due to the different boiling points of the constituent components of the sample. This could be a preliminary 'method development' step before using the ballistic ramp method for quality control analysis.**
- **The simple automated software enabled the user to receive reports about the levels of ions of interest in their sample and provided a quick alert to indicate whether targeted ions were above or below a prescribed level.**

Acknowledgements
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References

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2. G. John Langley, et al.; *Energy & Fuels*, 32 (**2018**), 10580—10585 .
3. Jinchuan Yang and Alice J. Di Gioia, Waters Corporation, Application note 720003221en, https://www.waters.com/waters/library.htm?cid=511436&lid=10132961 (accessed 20 May 2019).

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