Chromatography Technical Note No AS109

Analysis of Formaldehyde and Acetaldehyde using automated DNPH derivatisation

Dan Carrier, Anatune Ltd. Girton, Cambridgeshire, UK.

Introduction

Airborne aldehydes and ketones are collected by passing air through a cartridge containing 2,4-dinitrophenylhydrazine (DNPH). Carbonyl compounds react with the DNPH to form hydrazones which are immobilized on the cartridge. These compounds can be easily eluted from the cartridge with acetonitrile and analysed by HPLC with UV detection.

Manual Process

A required amount of air to be tested is passed through the DNPH cartridge. Each cartridge is then placed into a vacuum manifold and acetonitrile is used to elute the derivatised aldehyde or ketone from the cartridge. The extract is collected into a 5 ml volumetric flask and the flow of acetonitrile is stopped when 5ml has been collected. This is performed by eye, checking that the top of the meniscus has reached the 5 ml mark. The volume of extract collected is critical as the concentration of the derivatised product will be dependent on the volume collected. The extract is then shaken to ensure that the solution is adequately mixed and subsequently filtered using a 0.2 micron Nylon filter, and a portion of this solution is then pipetted into a vial for HPLC analysis by UV detection.

Automation of the process

To automate this method, a good seal is required between the DNPH cartridge and the injection needle from the syringe which is attached to Multi Purpose Sampler head (MPS). This will allow delivery of the solvent through the cartridge. Figure 1 shows a photograph of DNPH cartridge with sealing unit (transport adaptor) and 0.2 micron filter.

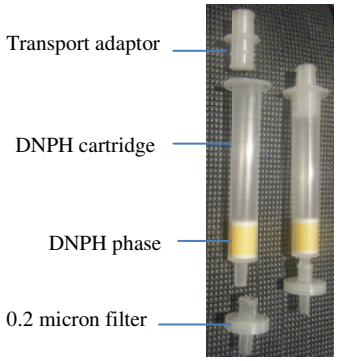

Figure 1 Photograph of DNPH cartridge.

In a previous application note titled “Automating DNPH derivatisation for aldehyde and ketone analysis”, acetonitrile was collected from 20 different automated extractions and the precision of the volume extracted was calculated to be 1.5% relative standard deviation on a 5 ml extract. From these promising results, analysis on real samples was progressed. Airborne formaldehyde and acetaldehyde was collected onto various DNPH cartridges and analysed using the automated system. Levels of Formaldehyde and Acetaldehyde were quantified using an external standard.

Instrumentation

Gerstel Multi Purpose Sampler MPS 2 XL (dual head)
Maestro Version 1.4.8.14/3.5
CTC Analytics Cooled tray
Agilent 1260 Quaternary Pump
Agilent 1260 Diode Array detector
Agilent 1260 Column Oven
Anatune 300 Automated DNPH unit

Figure 2 shows a photograph of the automated DNPH instrumentation. For each extraction, the MPS head on the right hand side pulls the top drawer forward so that the cartridge is in line with an empty 10 ml vial which is situated on the bottom shelf. The second MPS head is used to close the drawer so that a 1 ml aliquot can be taken from the 10 ml vial into an empty HPLC vial which is situated in a cooled tray.

Figure 2 Automated DNPH instrumentation in our new site at Girton.

Figure 3 shows a close up of the automated DNPH unit (Anatune 300).

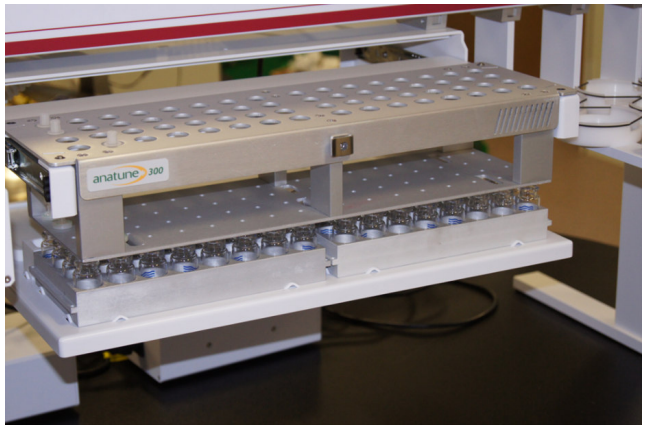

Figure 3 Anatune 300.

Anatune Ltd, Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223 279210 Fax: +44 (0) 1223 279253 Email: info@anatune.co.uk Internet: www.anatune.co.uk

Method

From previous experimental work, it has been found that the addition of 5.6 ml of acetonitrile to the cartridge will produce a 5 ml extract. A 5 ml extract is obtained as residual acetonitrile is left on the cartridge. Figure 2 shows the instrumentation used to automate the DNPH process.

After the DNPH cartridge has been aligned with an empty 10 ml vial, 5.6 ml of acetonitrile is added to the cartridge using a 5 ml syringe on an MPS head. An additional air push through the cartridge performed. This is to maximize the amount of extract produced. The extract is then mixed and a 1 ml aliquot of the extract (using a 1 ml syringe) is then added to a sealed 2 ml HPLC vial which is seated within the cooled tray. The extract is subsequently injected onto the HPLC. Up to 64 extractions can be automated. The cooled tray which is set to 4 ^{0}C allows re-injection of the samples and standards if required.

For this study, levels of Formaldehyde and Acetaldehyde were quantified from cartridges

The LC method uses a C18 50 x 4.6 mm id column with a gradient starting at 30/70 acetonitrile/water (v/v) up to 95/05 acetonitrile/water (v/v) with UV detection at 365 nm.

Results

Figure 4 shows an example chromatogram of 0.075 ppm Formaldehyde and Acetaldehyde standard. Formaldehyde elutes at 3.7 minutes and acetaldehyde at 5.3 minutes.

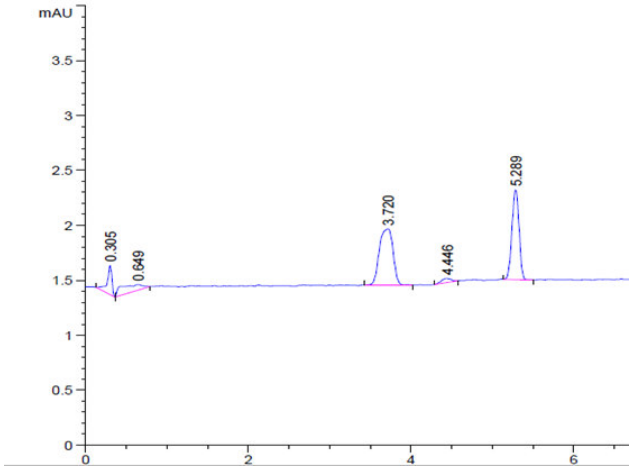

Figure 4 0.075ppm Formaldehyde and Acetaldehyde standard.

Six replicate injections of the 5ppm standard were performed giving a percent relative standard deviation of 1.2 % for Formaldehyde and 1.3 % for Acetaldehyde.

Levels of Formaldehyde and Acetaldehyde in the sample were consistent with the manual method.

Figure 5 shows an example chromatogram of a sample containing Formaldehyde and Acetaldehyde. Formaldehyde and Acetaldehyde were extracted from the DNPH cartridge using the automated method described.

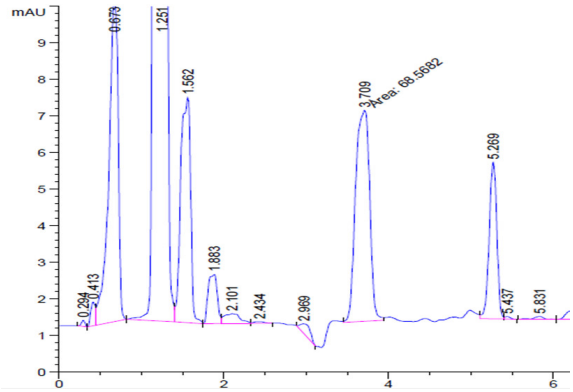

Figure 5 Example chromatogram of a sample containing Formaldehyde and Acetaldehyde.

Table 1 shows the results obtained from 5 different sampled DNPH cartridges for Formaldehyde and Acetaldehyde using the automated process. Levels calculated from injecting an external 0.075ppm standard of Formaldehyde and Acetaldehyde.

Sample Description	Formaldehyde (ppm)	Acetaldehyde (ppm)
Sample A-1	0.95	0.45
Sample A-2	0.91	0.49
Sample B-1	0.85	0.44
Sample B-2	0.85	0.44
Sample C-1	0.61	0.38
Sample C-2	0.61	0.37
Sample D-1	0.76	0.46
Sample D-2	0.75	0.45
Sample E-1	0.80	0.43
Sample E-2	0.79	0.43

Table 1 Formaldehyde and Acetaldehyde results for samples using the automated process as described above.

Discussion

Automating this extraction will drastically free up manual labour of this technique and this will hopefully improve any potential experimental errors associated with the method. No manual sample preparation is now required on this method leading to high throughput for determining airborne Formaldehyde and Acetaldehyde. With the Prep-Ahead function, in the Maestro software, the automated sample preparation can be incorporated within the HPLC Run time which is 12.5 minutes long.

A video of the automated process can be found on Anatune's website. Anatune are currently looking into modifying the Anatune 300 for automated SPE.

Anatune Ltd, Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223 279210 Fax: +44 (0) 1223 279253 Email: info@anatune.co.uk Internet: www.anatune.co.uk