Anatune Ltd
Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223279210 Fax: +44 (0) 1223279253
Email: info@anatune.co.uk Internet: www.anatune.co.uk

Initial work on Automating Dispersive Liquid Liquid Micro Extraction for EPA 8270

John Quick, ALS Environmental., Coventry, West Midlands, UK.
Dan Carrier, Jon Dunscombe, and Jeff Stubbs, Anatune Ltd., Girton, Cambridgeshire, UK

Introduction

The United States Environment Protection Agency (USEPA) Method 8270 methodology is widely used for solid, liquid and gaseous analysis of environmental samples using Gas Chromatography/Mass Spectrometry (GC-MS). This method contains over 70 analytes ranging from Polycyclic Aromatic Hydrocarbons (PAHs), Pesticides, and Polychlorinated biphenyls (PCBs).

This analytical method for solids and liquids is a routine, high volume and high throughput task for many environmental laboratories. Being able to streamline and enhance this process, and overcome many of the challenges associated with method 8270 is possible with new instrumentation and extraction techniques that are constantly being developed.

Automated Dispersive Liquid Liquid Micro Extraction (DLLME) is one such advancement which has been applied. Automation of the EPA 8270 method has been carried out by John Quick at ALS Environmental using a GERSTEL MultiPurpose Sampler (MPS) with automated mixing and centrifugation. Extracts from the sample preparation were analysed on an Agilent 5977B GC/MSD with High Efficiency Source, coupled to the Agilent 7890B Gas Chromatograph. DLLME is a technique used to extract analytes from an aqueous solution into a small volume of solvent. Enrichment factors can be in the range of 20-40 times depending on the amount of solvents selected.

A dispersive agent (Propan-2-ol) is added to the water sample in addition to dichloromethane.

The dispersive agent allows dichloromethane to form an emulsion thus creating a huge surface area for the dichloromethane to extract the analytes of interest. After the solution is mixed for a period of time, the sample is centrifuged and forms 2 layers within the vial. The bottom layer contains the extracted compounds and can be injected onto the GC.

Figure 1 shows an illustration of how DLLME is performed.

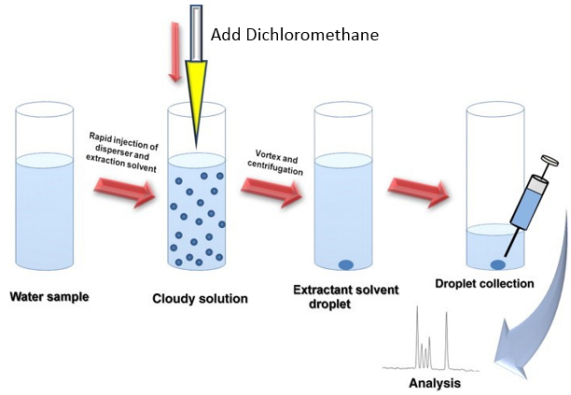

Figure 1. Illustration of Dispersive Liquid Liquid Extraction (DLLME)

Figure 2. Automated Vortex (mVorx) and Centrifugation (CF-200) using a GERSTEL Dual Head xt MultiPurpose Sampler on an Agilent Technologies 5977B High Efficiency Source, GC/MSD and 7890B GC

A video is enclosed below which shows the addition (in slow motion) of dichloromethane to a solution containing Propan-2-ol and water. It can be seen how quickly the dichloromethane is broken up into an emulsion.

Enclosed Video

Figure 3 shows the solution after it has been centrifuged at 4500 rpm. The vial is a high recovery vial enabling withdrawal of a low volume (typically less than 50 µL) of the dichloromethane from the bottom of the vial.

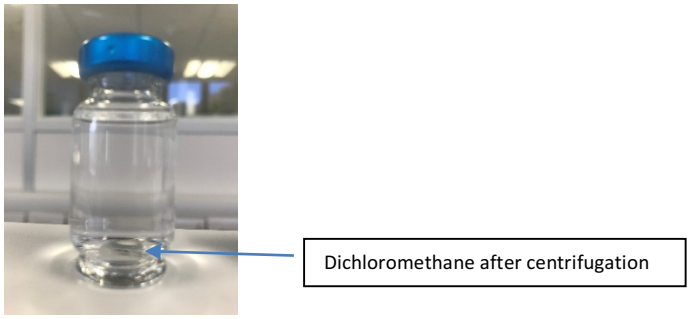

Figure 3 – High recovery vial with low volume of the dichloromethane present at the bottom of the vial

Instrumentation

GERSTEL Dual Head MultiPurpose Sampler (MPS) xt version
GERSTEL mVORX vortexer option
Agilent Technologies 5977B (High Efficiency Source) GC/MSD and 7890B GC
Anatune CF-200 Centrifuge
Anatune High recovery 9.5 mL vial

Method

Propan-2-ol (8 mL) was added to 32 mL of deionised water. 6 mL of this solution was added to an 8 mL high recovery vial using an autopipette. The vial was placed on a tray on the GERSTEL MPS. From this point, the method was fully automated using the GERSTEL MPS and associated sample preparation objects. 300 µL of Dichloromethane containing a small amount of pentane was added to each sample. An emulsion is formed, this being the way the technique extracts the analytes of interest. Each sample was then transported to the mVorx and vortexed at 2000 rpm for 2 minutes. To break up the emulsion, the sample was then transported automatically to the CF-200 and was centrifuged at 4500 rpm for 1 minute. Up to 6 samples can be centrifuged at one time. After centrifugation, the sample can be directly injected onto the GC. On this occasion, the extractions were performed at ALS by John Quick and analysed on Agilent Technologies 5977B (High Efficiency Source) GC/MSD and 7890B GC instrumentation in Cambridge.

Spiked samples in deionised water were prepared at 0.05 µg/L, 0.25 µg/L, 0.5 µg/L, and 1.00 µg/L. The test mixture includes approximately 70 analytes ranging from Polycyclic Aromatic Hydrocarbons, Pesticides, and Polychlorinated biphenyls (PCBs). 1 µL splitless injection was performed with a thermal gradient from 40 °C to 350 °C on a DB 5MS 30 M 0.25 mm id column.

Results

Figure 4 shows the linearity plot for Naphthalene from water spiked with 0.05 µg/L, 0.25 µg/L, 0.5 µg/L, and 1.00 µg/L

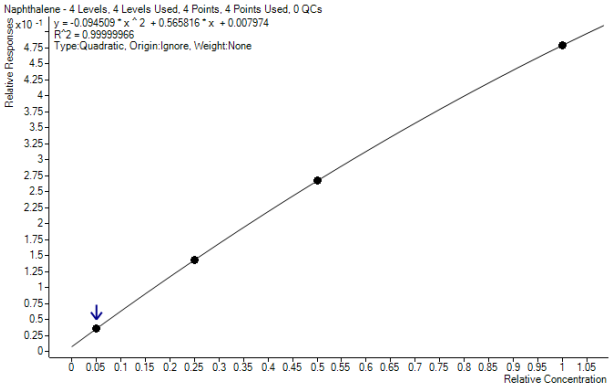

Figure 4 – Linearity for Naphthalene

Figure 5 shows linearity plot for Trifluralin from water spiked with 0.05 µg/L, 0.25 µg/L, 0.5 µg/L, and 1.00 µg/L

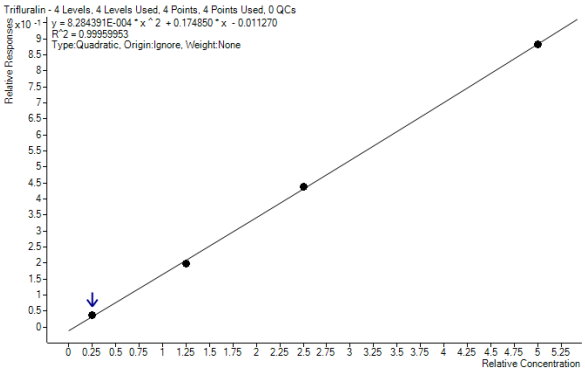

Figure 5 – Linearity for Trifluralin

Figure 6 shows extracted ion chromatogram for Heptachlorobenzene (Retention time 6.0 minutes) at the lowest calibration level (0.05 µg/L)

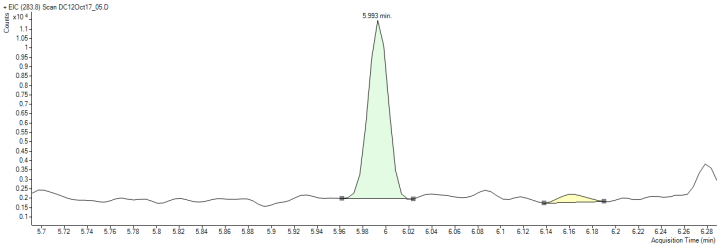

Figure 6 – Extracted Ion Chromatogram Heptachlorobenzene (spiked into water at 0.05 µg/L).

Figure 7 shows extracted ion chromatogram for Triallate (Retention time 6.5 minutes) at the lowest calibration level (0.05 µg/L)

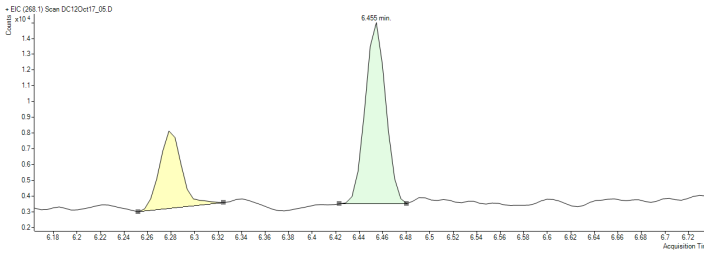

Figure 7 – Extracted Ion Chromatogram Triallate (spiked into water at 0.05 µg/L).

Figure 8 shows extracted ion chromatogram for Trifluralin (Retention time 5.6 minutes) at the lowest calibration level (0.05 µg/L)

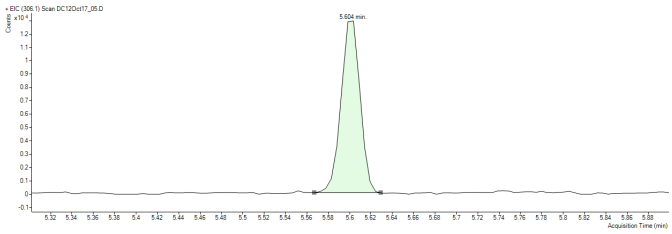

Figure 8 – Extracted Ion Chromatogram Triallate (spiked into water at 0.05 µg/L).

Table 1 shows the linearity achieved for a number of analytes within the test mixture from a 4 point calibration from 0.05 µg/L to 1.00 µg/L.

Analyte	Retention time (min)	r^2
1,3,5 Trichlorobenzene	3.3	0.99907
1,2,4 Trichlorobenzene	3.5	0.99797
Naphthalene	3.4	0.99999
Hexachlorobutadiene	3.5	0.99986
Dichlorobenil	4.1	0.99957
Acenaphthylene	4.6	0.99994
Acenaphthene	4.8	0.99997
Pentachlorobenzene	5.0	0.99780
Fluorene	5.3	1.00000
Tecnazene	5.4	0.99994
Trifluralin	5.6	0.99960
Alpha-HCH	5.9	0.99745
Simazine	6.0	0.99992
Hexachlorobenzene	6.0	0.99879
Atrazine	6.0	0.99999
Propazine	6.1	0.99999
Propetamphos	6.1	0.99748
Trietazine	6.2	0.99998
Diazinon	6.3	0.99991
Phenanthrene	6.4	0.99996
Anthracene	6.4	0.99995
Triallate	6.5	0.99999
Pirimicarb	6.5	0.99983
PCB 28	6.7	0.99943
Alachlor	6.8	0.99897
Heptachlor	6.9	0.99817
Fenpropidin	6.9	0.99999
Terbutryn	7.0	0.99981
ppTDE	8.5	0.99999
Coumaphos	10.3	0.99985

Table 1. r^2 values for the linearity experiments

Discussion

It is now possible to fully automate Dispersive Liquid Liquid Micro Extraction using the high recovery vials with automated mixing and centrifugation.

By using the Automated Dispersive Liquid Liquid Micro Extraction technique, it opens up new possibilities to the routine Environmental Laboratory to gain a number of advantages and overcome current challenges that the method 8270 poses.

Miniaturisation of the procedure allows for smaller sample sizes to be sampled, allowing for smaller sample bottles, and also less weight and space when transporting samples to the laboratory and storing them.

Scaling down the sample size also means a much smaller amount of solvent(s) is used. As only 300 µL of Dichloromethane is used, this gives the capability of reducing solvent usage, exposure and disposal. This importantly saves money and increases health and safety.

Automation of this procedure reduces the need for sample preparation to be conducted manually, thus saving on analyst effort. This time can be spent on other more profitable activities within the laboratory like results processing

and method development.

Significant sample throughput gains will be achieved over manual DLLME experiments. Reducing the turnaround time of these samples is possible as the extraction can be performed just in time, before the sample is injected into the GC. Sample preparation and analysis can commence as soon as the sample is received into the laboratory, rather than having to undergo a laborious, time-consuming and error-prone manual preparation.

Excellent detection limits and good linearity was achieved on a number of analytes in the test mixture.

Further work is planned looking at different water matrix in early 2018 with ALS environmental.