The analysis of volatile fatty acids by Headspace GC-FID

Dr Claire Rossouw[1], Mr Jonathan Angove[2]
1 Omex Environmental, Estuary Road, King's Lynn, UK.
2 Ellutia Ltd, 200 Lancaster Way Business Park, Ely, UK.

Volatile fatty acids (VFAs) are analysed to aid in the optimisation of the anaerobic digestion process. The role of anaerobic digestion is the decomposition of organic matter and thus the production of gasses, such as methane and carbon dioxide.

The typical methods to analyse VFAs include titration, distillation, steam distillation and chromatographic.

Titration: Titration provides approximate results and is a quick analysis method. This is widely used in the treatment of wastewater to track the status of the microorganisms available.

Distillation: Distillation provides approximate results, though a significant percentage of the VFAs may be lost during the analysis due to volatility of the various VFAs. As with titration, this is often used in wastewater treatment plants.

Steam distillation: This tends to exhibit greater recoveries of the VFAs and is more precise than the titration and distillation methods but is more time consuming.

Chromatographic techniques: These tend to give the most precise and accurate results, while having the capability of qualitatively and quantitively analysing each VFA.

Ellutia Ltd was approached by Omex Environmental to increase throughput and to reduce the consumable cost of their current, validated method. This method involved a pH adjustment of the samples, followed by a large volume liquid:liquid extraction prior to their GC-FID analysis. As Omex Environmental is analysing VFAs between C2 and C6, it was proposed that a headspace analysis method could achieve similar results to the liquid:liquid extraction, but with the desired increase in productivity and also the elimination of the use of a solvent, hence the generation of hazardous solvent waste.

The equipment proposed was the Ellutia 500 series GC-FID with a CTC PAL-RSI mounted to perform the headspace sampling.

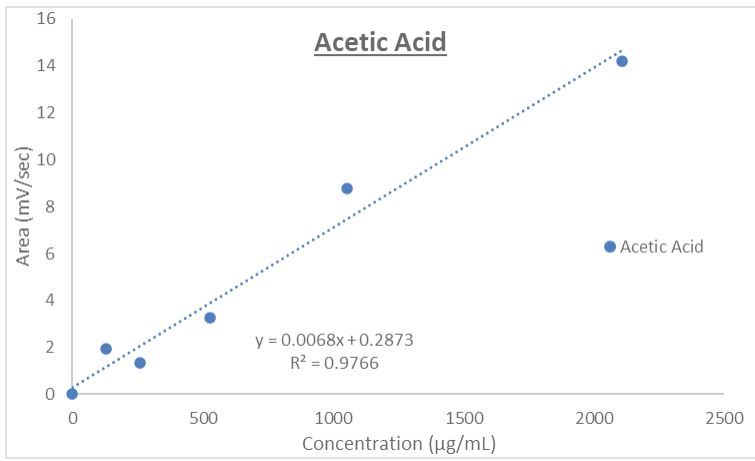
Method Summary

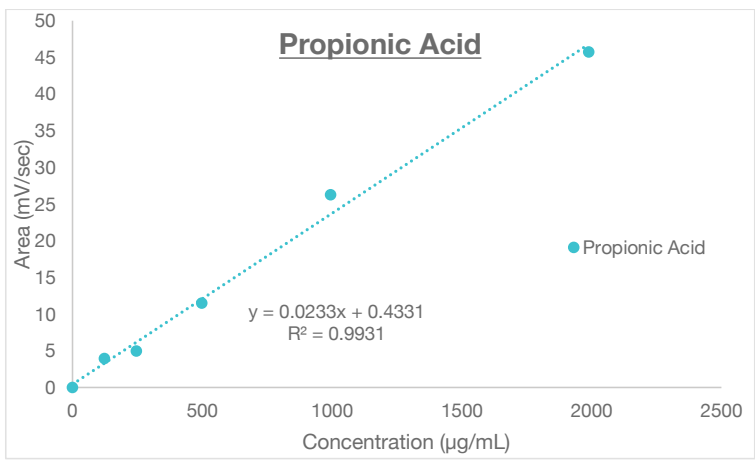
The liquid:liquid extraction involved a series of repeated steps involving sample acidification, centrifugation and agitation, addition of an internal standard together with addition of a drying salt.

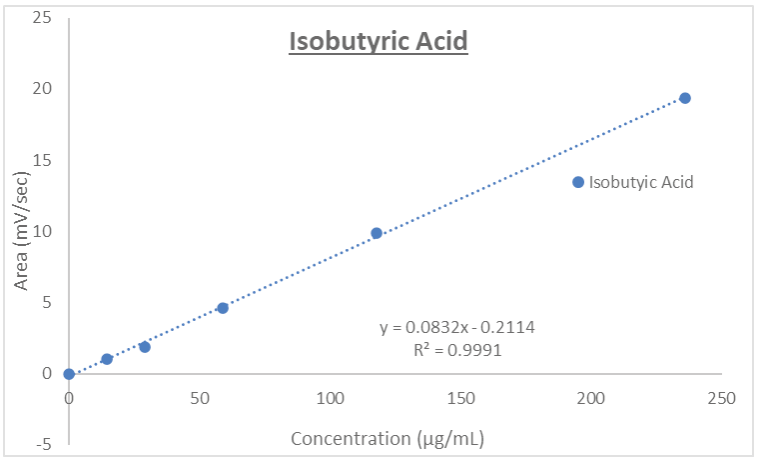
The headspace technique involved much fewer steps, with only sample acidification, centrifugation, addition of an internal standard together with addition of a drying salt.

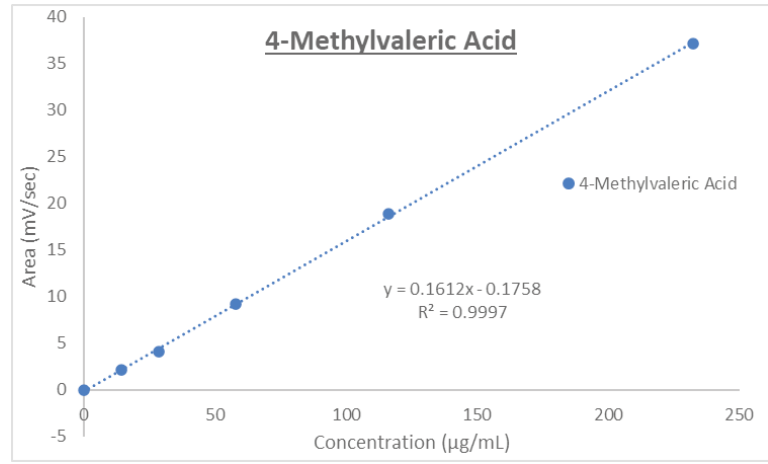
Results

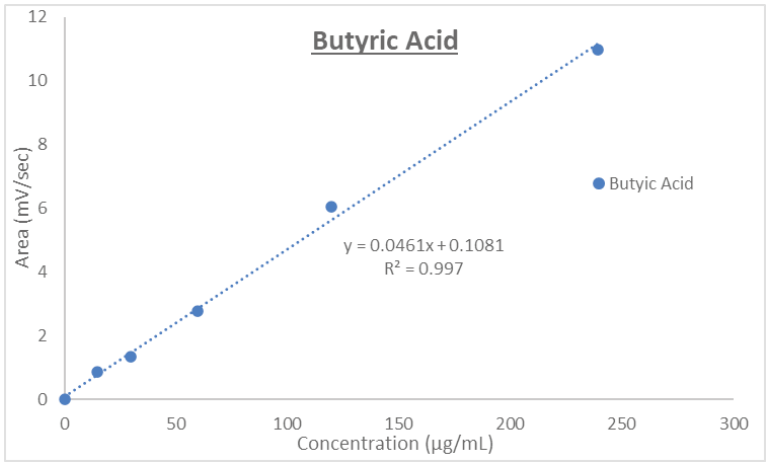
Calibration curves were prepared for the analytes, correcting the area responses using the internal standard response.

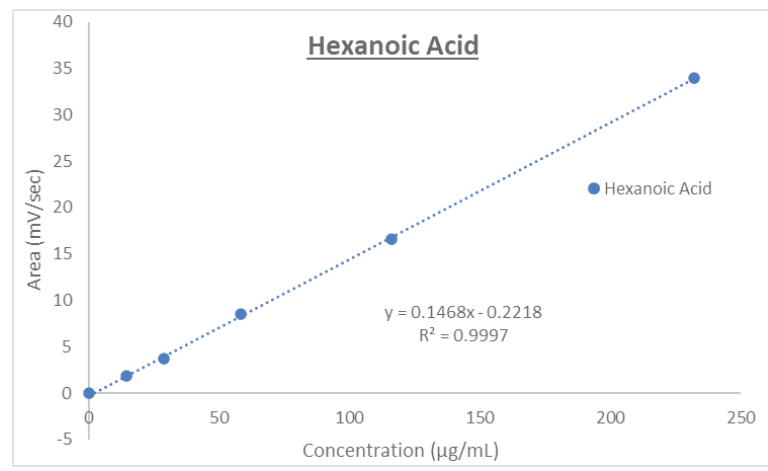


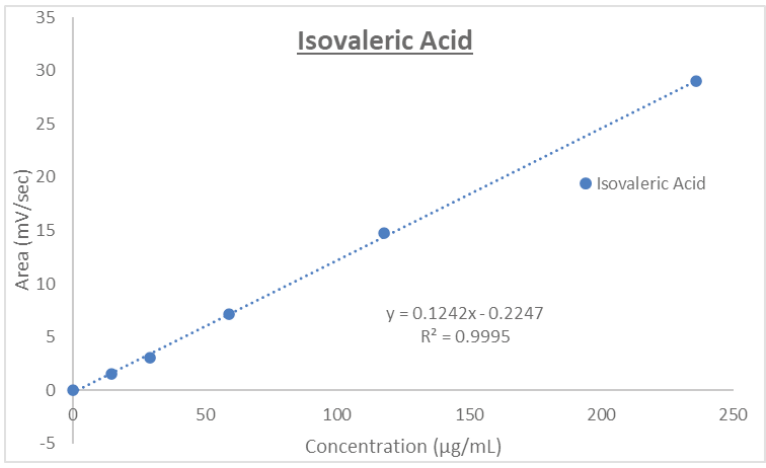


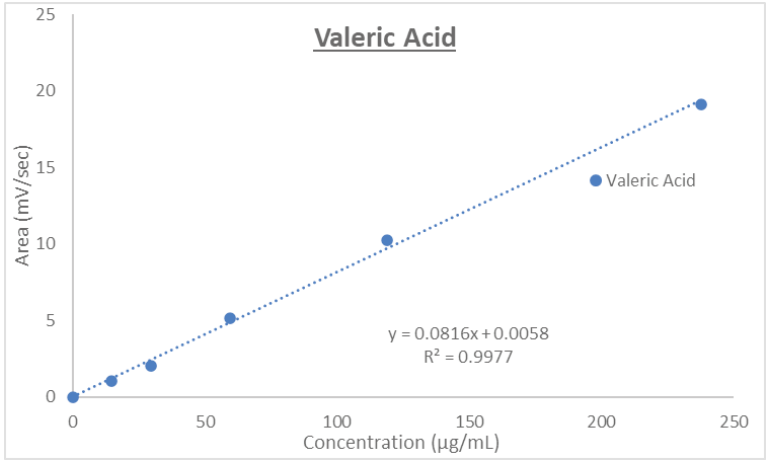












Further fine-tuning of the headspace analysis can be achieved by, for example, changing the headspace sample volume, changing agitation parameters or adjusting the mass of salt added.

To demonstrate the reproducibility of the headspace method, the standard concentration also used for the quality control samples was prepared and analysed five times, the results are summarised below:

Corrected Area Data						Std 4/QC Reproducibility		
Name	Std 4	QC Std 4_1	QC Std 4_2	QC Std 4_3	QC Std 4_4	MEAN	SD	% RSD
Acetic Acid	3.2762	3.3464	3.3264	4.6567	3.6037	3.642	0.581	15.96
Propionic Acid	11.5019	11.3950	11.1731	13.9362	11.5934	11.920	1.138	9.55
Isobutyric Acid	4.6103	4.6849	4.6300	5.2004	4.7454	4.774	0.244	5.11
Butyric Acid	2.7673	2.7943	2.7106	3.3278	2.7288	2.866	0.260	9.08
Isovaleric Acid	7.1013	7.0029	6.9085	7.0601	6.8517	6.985	0.104	1.49
Valeric Acid	5.1773	4.7791	4.8054	5.2401	4.7094	4.942	0.247	4.99
4-Methylvaleric Acid	9.2444	9.2259	8.9294	8.5411	8.7371	8.936	0.306	3.43
Hexanoic Acid	8.5192	8.2416	8.1437	8.0153	7.7782	8.140	0.274	3.37

Conclusions and Discussion

By moving to a headspace method from a liquid:liquid extraction method, the sample preparation has been greatly simplified; significantly reducing the sample preparation time. The use of hazardous solvents has been eliminated and the number of consumables and pieces of equipment has been greatly reduced. Additionally, there is no solvent waste generated; further reducing the analysis cost per sample to Omex Environmental.

Acknowledgements

We would like to thank Dr. Claire Rossouw, Emma Hastie and Jonathan Eracleous from Omex Environmental for providing the calibration standard, internal standard, GC column and samples.