



TASTE AND ODOUR ANALYSIS IN WATER USING THE ANATUNE ROBOTIC DILLME ANALYSER

APPLICATION NOTE AS249

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Abstract

A Dispersive Liquid-Liquid MicroExtraction (DiLLME) method has been successfully developed and validated to automate the extraction of geosmin, 2-methylisoborneol and other taste and odour compounds in water. Using the sensitivity and selectivity of the Agilent 7010B High efficiency Source, a small sample sizes of 8 mL were used whilst achieving very low limits of detection. This automated solution provides significant advantages, such as reducing the manual preparation steps and the reproducibility that comes with an automated system.

Introduction

Taste and odour analysis is a very important area within the water industry and depending on the area of the country involved, water quality can be affected to a lesser or greater extent regarding the prevalence of geosmin and 2-methylisoborneol (2-MIB); two compounds which can have a big impact on the taste and odour of water. These compounds are responsible for earthy tastes and odours, being most detected in surface waters and are more common during warmer, sunnier weather when combined with rainfall. Climate change also has an impact, increasing the levels of these compounds detected.

These compounds also have low odour thresholds, in very low parts per trillion levels which means that even a small concentration of compounds present in the water can give customers a poor experience when using the water for drinking; this increases the number of water quality complaints which in turn can lead to financial penalties for water companies and increases the water samples sent to the laboratory for testing. Higher sample numbers mean that a laboratory that was once able to cope with the testing is no longer able to keep up with demand and dealing with water complaints takes much longer. All these factors can have a negative impact on the company involved.

The approach that has been taken in this work uses a fully automated dispersive liquid-liquid microextraction¹ method to analyse for geosmin, 2-MIB and other taste and odour compounds for trace level quantitation. By using automation for this analysis, a sample volume of 8 mL accompanied by large volume injection were used reduce the sample volume needing to be collected and reach low limits of detection, less than 1 ng/L.

Experimental

Instrumentation & Materials

- GERSTEL Dual head MultiPurpose Sampler (MPS)
- GERSTEL quickMix
- Anatec CF200 centrifuge.
- GERSTEL Solvent Filling Station (SFS)
- Agilent 7010B High Efficiency Source MSD
- Agilent 8890 GC



Figure 1: DiLLME Analyser setup for taste and odour analysis

Prior to analysis 8 mL of sample is transferred to a high recovery vial and vials placed on the MPS ready for sample preparation and analysis.

An aliquot of internal standard is added, followed by 0.8 mL of isopropyl alcohol. 0.3 mL of extraction solvent (dichloromethane/pentane) is to be added and the vial vigorously shaken using the GERSTEL QuickMix. The sample is then transferred to the centrifuge to separate the sample/solvent mixture. A 40 μ L Large Volume Injection (LVI) was used for this analysis to provide a higher sample concentration factor using a GERSTEL UPC^{Plus} as the method of cooling the inlet down to 10 °C. The overall time taken from start to finish for this analysis, including the automated sample preparation is 24 hours for 50 samples which relies upon the PrepAhead feature of Maestro software which allows for sample preparation to take place in parallel to GC analysis of the previous sample. A summary of the sample preparation sequence is shown in the appendix.

All samples were spiked with internal standard and calibration standards automatically using the instrumentation during the analysis. Table 1 describes all analytes, their retention time, respective multiple reaction monitoring (MRM) transition, associated internal standard compound used for quantitation. A total ion chromatogram (TIC) of an extracted calibration sample at 40 ng/L is shown in figure 2.

To assess method precision, recovery, and limit of detection (LOD), two separate water matrices were spiked at 2 and 10 ng/L with five replicates at each level. A blank sample of each matrix was also analysed. LOD in each matrix

Table 1. List of compounds included in the analysis and their respective retention times and internal standards.

Analyte	Retention time (mins)	MRM transition	Internal standard
2-EDD	6.7	115→69	Naphthalene d8
Isopropyl methoxy pyrazine (IPMP)	9.7	137→109	Naphthalene d8
2-Methylisoborneol (2-MIB)	11.2	108→93.1	Geosmin d5
Naphthalene d8	12.2	136→83	-
2,4,6-trichloroanisole d5	15.1	214.2→196.4	-
2,4,6-trichloroanisole (2,4,6-TCA)	15.2	210→195	2,4,6-trichloroanisole d5
Geosmin d5	16.7	116→100	-
Geosmin	16.8	112.1→97.1	Geosmin d5
2,4,6-tribromoanisole (2,4,6-TBA)	21.5	346→303	2,4,6-trichloroanisole d5

was calculated as three times the standard deviation from the 2ng/L spike. This style of assessment provides a good evaluation of the method under real circumstances, however for a more rigid testing, a full method validation following NS30 guidelines which requires that eleven batches be analysed in duplicate.

A video of the automated preparation can be seen [here](#).

RESULTS AND DISCUSSION

A five-point calibration set at 2, 5, 10, 20 and 40 ng/L was used for quantitation with a minimum calibration coefficient (R^2) of 0.995 or greater required. This was met for all analytes. Figure 3

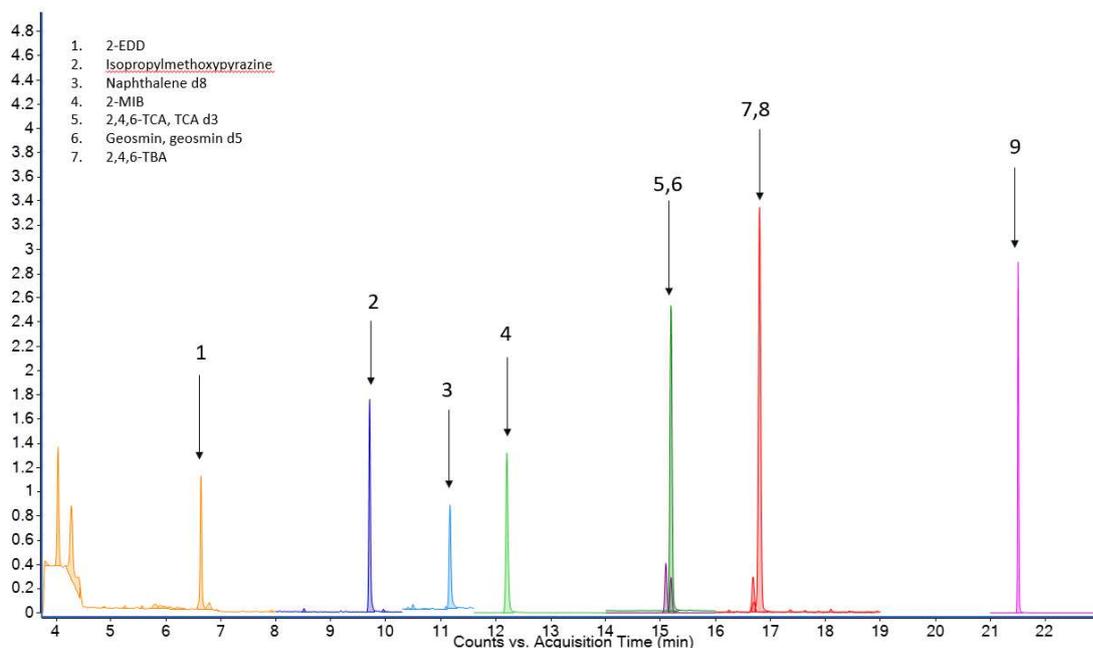


Figure 2. Extracted ion chromatogram obtained from a 40ng/L extract.

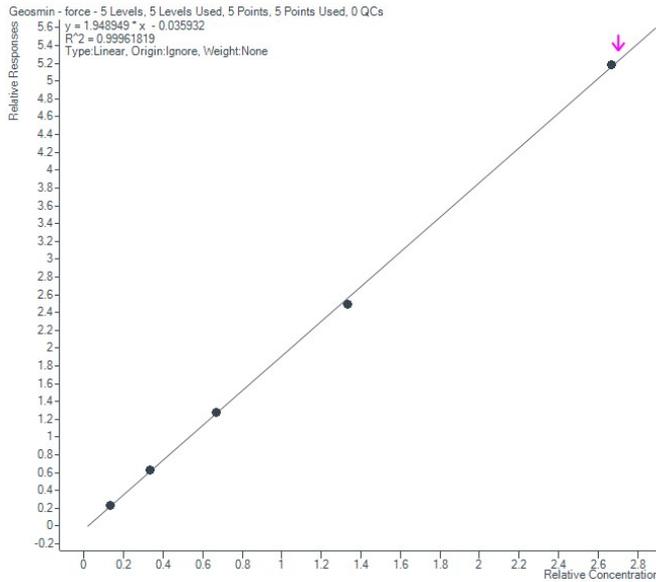


Figure 3. Geosmin calibration, $R^2 = 0.9996$.

shows the calibration for geosmin, with an R^2 of 0.9996. Calibration curves for all analytes are shown in the appendix.

The method was shown to have good sensitivity and reproducibility, table 2 displays the calculated LODs (three times standard deviation of five replicates) obtained from both matrices. Values much below 1 ng/L were obtained which is very desirable for the environmental industry as some of the compounds involved in this testing have very low thresholds and so having low limits of detection would assist in investigating any customer complaints.

Table 2. Calculated LOD for all analytes in both matrices.

	2-EDD	IPMP	2-MIB	2,4,6-TCA	Geosmin	2,4,6-TBA
Matrix 1, ng/L	0.73	0.40	0.47	0.16	0.10	0.23
Matrix 2, ng/L	0.61	0.25	0.24	0.09	0.10	0.33

Figures 4 and 5 show chromatograms for 2-MIB and geosmin in calibration blank, matrix blank and 2 ng/L spike. A small amount of each compound is evident in the matrix blanks. Given the calculated LOD of the method for each compound is far below 1 ng/L, the matrix blanks confirm that this is the case.

As an addition, blank spring water, which was used for calibration samples, was spiked to a level of 1 ng/L. Figure 6 shows the chromatogram and signal-to-noise for geosmin and 2-MIB with values of 28 and 5, respectively. It was later found that one of the internal standards being used was the source of an interferent affecting geosmin.

Further method precision and recovery calculated from replicates at 10 ng/L in matrix 1 is shown in table 3 and data for matrix 2 in table 4. As this method would be tested under ISO:17025 conditions, a limit of $\pm 12.5\%$ for precision and $\pm 25\%$ for recovery was applied with all compounds achieving this. All recovery values were blank corrected using the value obtained from the matrix blank.

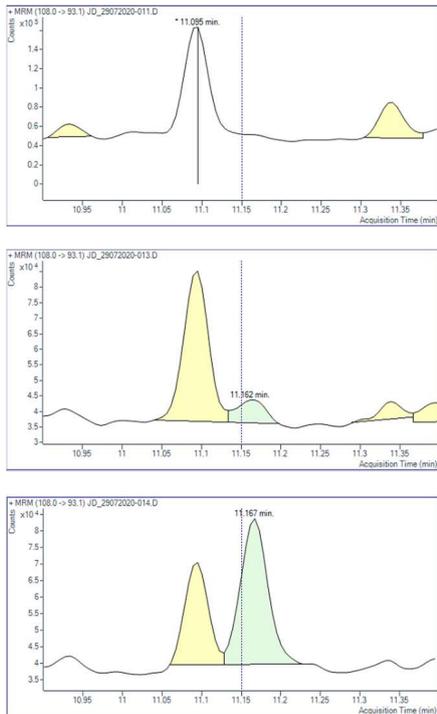


Figure 4. 2-MIB (11.15 minutes) chromatogram in calibration blank (top), matrix blank (middle), 2 ng/L matrix spike (bottom).

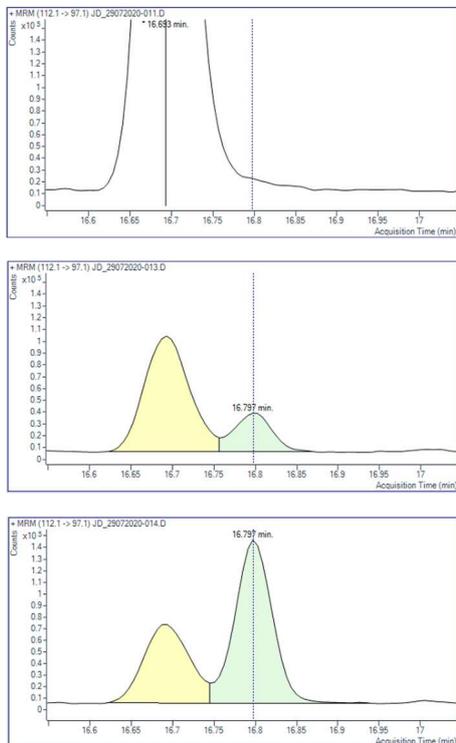


Figure 5. Geosmin (16.8 minutes) chromatogram in calibration blank (top), matrix blank (middle), 2 ng/L spike (bottom).

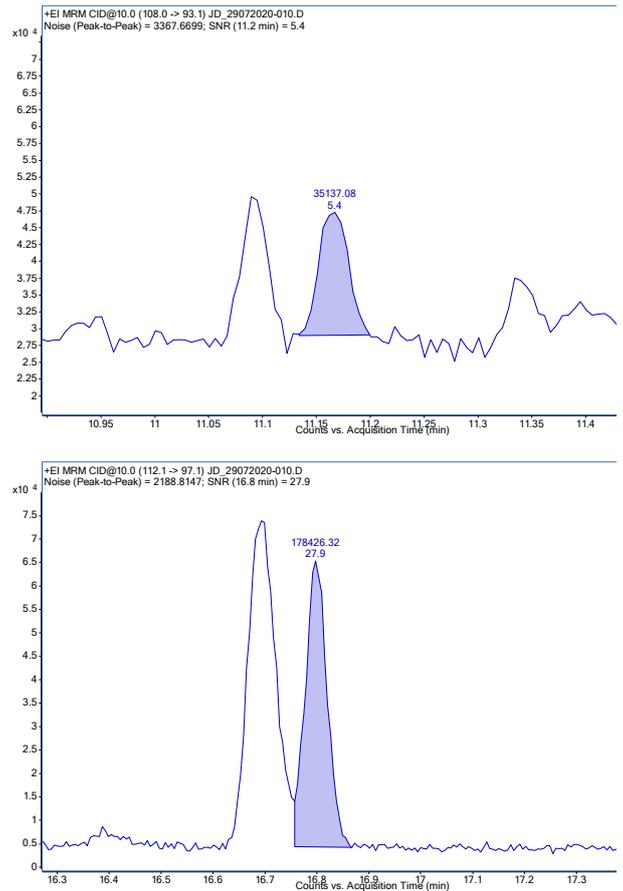


Figure 6. 1 ng/L spike in bottled spring water. 2-MIB (top), S/N 5. Geosmin (bottom), S/N 28

Table 3. Precision and recovery data for Matrix 1 at 10 ng/L (n=5).

	2-EDD	IPMP	2-MIB	2,4,6-TCA	Geosmin	2,4,6-TBA
Spike Avg. (ng/L)	10.69	9.81	10.54	10.18	10.41	10.01
% RSD	4.73	5.14	8.03	1.94	0.35	5.79
% Recovery	106	98.1	101	97.9	96.5	99.7

Table 4. precision and recovery data for Matrix 2 at 10 ng/L (n=5).

	2-EDD	IPMP	2-MIB	2,4,6-TCA	Geosmin	2,4,6-TBA
Spike Avg. (ng/L)	11.53	10.56	10.66	10.18	10.14	9.80
% RSD	11.67	6.11	4.56	1.51	0.73	5.09
% Recovery	113	106	101	97.1	99.7	97.6

CONCLUSIONS

A fully automated dispersive liquid-liquid microextraction for analysis of geosmin, 2-MIB and other taste and odour compounds in water was developed.

Good recovery, precision and sensitivity was achieved ensuring that LODs that are currently obtained using manual methods are met.

Automation of the method reduces overall cost per test by reducing solvent usage and disposal costs, sample transport costs and improved method time efficiency savings. Use of automation in this manner also means that valuable labour time can be spent on sample preparation on methods previously subcontracted, increasing sample throughput on other methods or method development and validation for those methods that need modernising. To further increase throughput, the GC chromatography could be optimised further still to reduce cycle times as far as possible.

This method also has the potential to be adapted for real-time on-line monitoring² so that decisions on water treatment can be taken before water quality is affected and customer complaints start to increase.

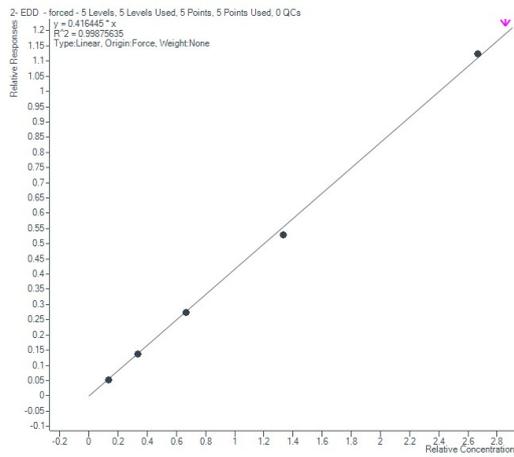
REFERENCES

1. Method Validation of the Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls Using DiLLME and GC-MS/MS, AS230. Anatune 2019
2. On-line Monitor for Metaldehyde in Surface and Ground Water, AS166. Anatune 2019

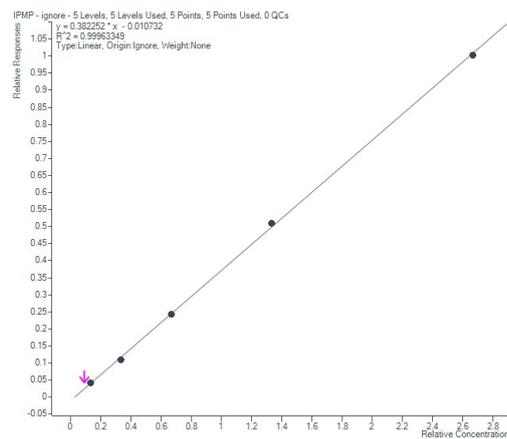
To discuss implementing this application solution for your E&L workflows, contact us and we will be delighted to work with you from conception to method transfer into your laboratory.

We also offer fully validated methods, according to your validation protocol, where required.

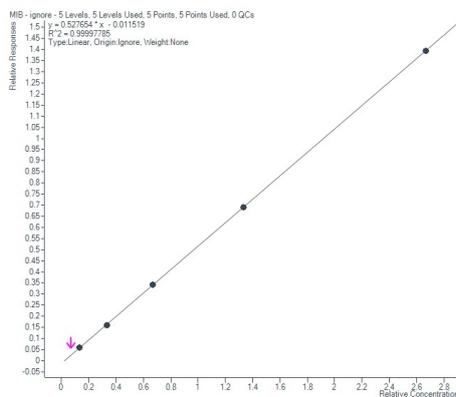
APPENDIX



2-EDD – R² 0.9988

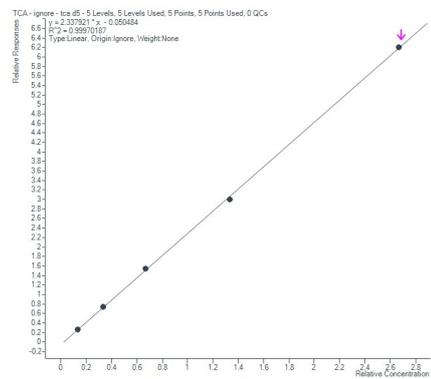


isopropyl methoxy pyrazine – R² 0.9996

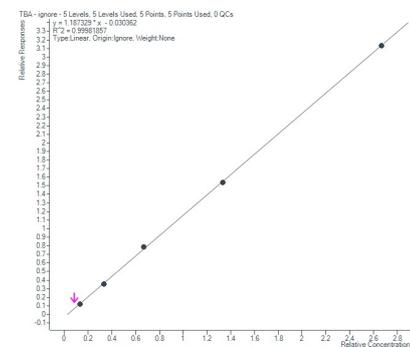


2-MIB – 1.0000

Figure 7. Calibration curves for 2-EDD (R² 0.9988, Top), IPMP (R² 0.9996, middle) and 2-mib (R² 1.0000, bottom).



2,4,6-TCA – R² 0.9997



2,4,6-TBA – R² 0.9998

Figure 8. Calibration curves for 2,4,6-TCA (R² 0.9997, Top) and 2,4,6-TBA (R² 0.9998, bottom).

