

The MultiFlex GC/Q-TOF as a Tool for the Investigation of Taste and Odour in Drinking Water

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Introduction

Drinking water regulations stipulate national standards for colour, odour and taste and companies are required to investigate the cause of any adverse result. Some water taste and odour issues are well known and routine methods exist for monitoring them. Development and automation of such an approach using solid phase extraction was recently illustrated in Anatune Chromatography Technical Note No AS152^[1].

However, for other, more unusual or less characterized off odours a more investigative approach may be required.

This application note outlines the use of a MultiFlex GC/Q-TOF with an Olfactory Detector (ODP) as a tool for investigation of taste and odour in drinking water and illustrates the need for accurate mass alongside sensory evaluation in some cases.

Samples were provided of a water sample, reported to have an off odour and believed to originate from cross contamination from new flooring. This sample was extracted using an automated ITSP set up and analysed for a suite of known taste and odour compounds by targeted analysis on an Agilent Triple Quadrupole. The same extract was also analysed using the Agilent GC/Q-TOF with a GERSTEL olfactory detection port (ODP) to assess aroma active components. The System set up is shown in Figure 1.

Previous work performed by the customer on a GC-MSD (single quadrupole) had identified a compound suspected to be responsible for an odour described as 'Pencil like'. A standard of the suspect compound was also provided.

Instrumentation

GERSTEL MultiPurpose Sampler (MPS) 2 XL Dual head
GERSTEL Cooled Injection System (CIS) 4
Agilent 7890 GC with a 7200 GC/Q-TOF
GERSTEL Olfactory detection Port (ODP 3)



Figure 1 – (MultiFlex with ODP on the GC/Q-TOF)

Method

Sample extraction:

An aliquot of water (35ml) was taken and extracted using an automated ITSP method, similar to that detailed in application note AS152. Extracts/standards in DCM.

GC/MS conditions:

CIS4 inlet: 10 µl large volume injection
CIS temperature Program 10°C; ramped to 240°C (hold 5 min)
Column: HP-5MS 30 m x 0.25 mm x 0.25 µm
Thermal gradient performed up to 300 °C
MS: EDR (2GHz) acquisition

The system was set up to split to an MSD and Olfactory detector at a ratio of approximately 2:1.

Results

Using single quadrupole EI data alone, found a reasonable hit in the NIST library; this matches the unknown to the structure shown in Figure 2. This structure has an empirical formula of C₁₂H₁₈O; with loss of a radical, this gives an accurate mass of 178.1357. At the top you can see how closely the single quad EI spectrum of the unknown compound (the red trace) matches the library entry for the compound C₁₂H₁₈O (the blue trace). The structure of the matching library entry is shown below.

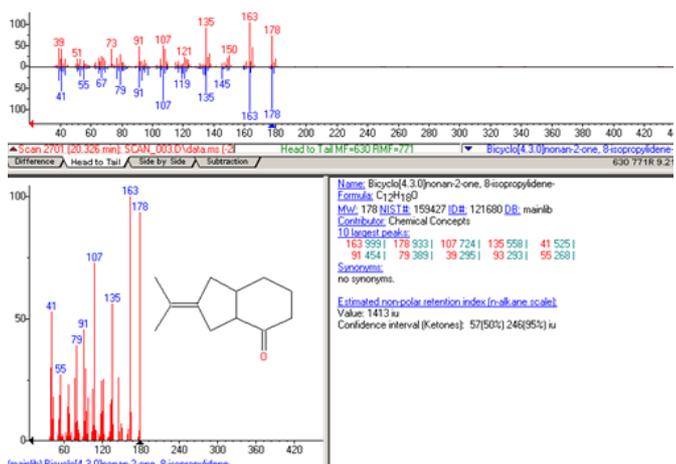


Figure 2 – (NIST Hit and Proposed Structure)

However, the accurate mass data on the GC/Q-TOF suggested an empirical formula of $C_{11}H_{14}O_2$ with an accurate mass of 178.09883. The accurate mass that we measured on the instrument was within 1ppm of this mass at 178.09869.

As part of the investigation, we connected up an olfactory detector to our MultiFlex GC/Q-TOF instrument and assessed the odour of the compound suspected to be responsible. We also assessed an extract of the tainted water.

The 'pencil' compound (2-tert-butyl-5-methyl-1,4 benzoquinone) standard was observed to give a strong pencil/graphite odour as expected. The water sample was assessed and a number of aroma active compounds were perceived, including a region described as 'pencils'. In this instance, the main odour seemed to be from Phenol itself, and also a number of substituted phenols, adding a medicinal/perfume note. Later in the chromatogram several 'burnt' or plastic odours were perceived, which seem to correlate to adipates and potential antioxidant breakdown products. The Chromatogram and olfactogram are given in Figure 3.

On closer inspection of the peak corresponding to a pencil odour, although very similar mass spectra were obtained, the identity of the compound was not the same as the standard provided. The accurate mass data indicated a different formula as illustrated in Figure 4. In order to confirm this, the water extract was then spiked with the standard and re-evaluated. This confirmed 2 regions in the chromatogram giving an odour described as 'pencils' (one at 13.8 minutes corresponding to the standard provide and one at 21.7 minutes as observed in the unspiked sample).

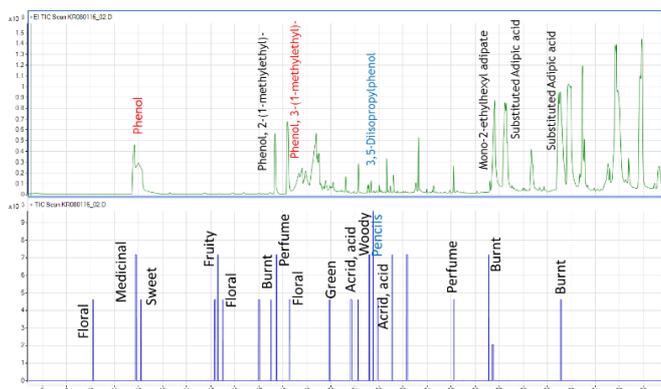


Figure 3 – (TIC Chromatogram and Olfactogram from Analysis of Tainted Water Extract)

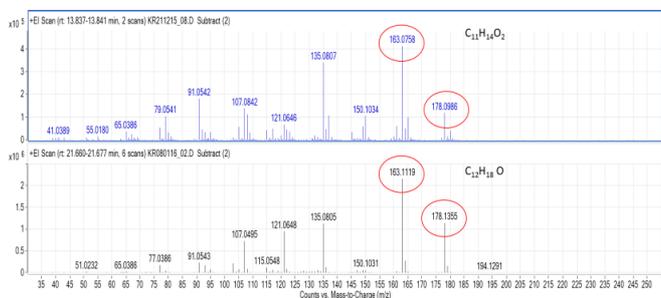


Figure 4 – (Compounds have some Nominal Mass Ions, but Different Accurate Mass for M+ and 163 Fragment)

Further confirmation of identity can be achieved by performing MS/MS experiments as shown in Figure 5. Fragments following MS/MS agree with those obtained by MS spectra.

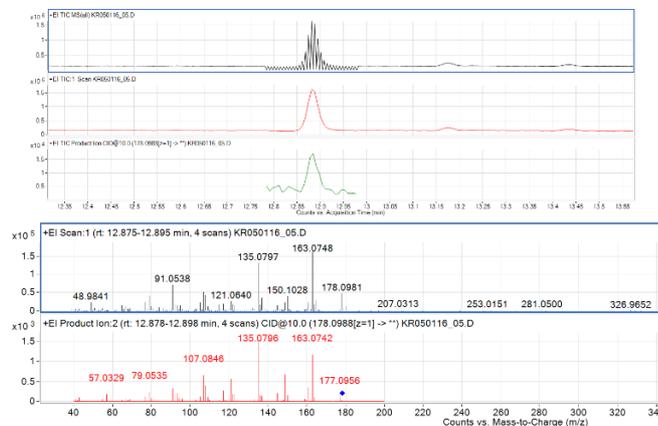


Figure 5 – (MS/MS Experiment on Pencil Compound with Formula $C_{11}H_{14}O_2$ and an accurate mass of 178.0988)

Discussion

This application note illustrates the need for accurate mass for structural elucidation and identification of unknowns. The ability to do CI and/or MS/MS further enhances the capability for unequivocal identification.

The MultiFlex GC/Q-TOF system with an Olfactory Detection Port (ODP) is an invaluable tool in investigation of taste and odour issues in water.

If you would like to discuss this further, please do not hesitate to contact us, either by emailing enquiries@anatune.co.uk, or call us now on +44 (0)1223 279210.

References

[1] AS152: Optimisation and validation of an ITSP method for the determination of Taste and Odour compounds in water.

Acknowledgement

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