

GC-O AND SNIFF&TRAP (S&T): AN ALTERNATIVE 2D APPROACH IN SENSORIAL AROMA INVESTIGATION

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ABSTRACT

GC-O is a powerful technique able to combine analytical results arising from GC/MS and sensorial perception. Recently introduced Olfactory Detection Port 4 (ODP4), By Gerstel GmbH, consists of a dual-detection system, pushing such combination of analytical and sensorial results to a new level of reliability.

A sample injected in a standard GC system is diverted at the end of the column by means of splitting device: part of the effluent reaches the MS detector, while a second aliquote is directed to an olfactometric port where a trained operator sniffs in a proper way. The two traces (i.e. **chromatogram** and **olfactogram**) are then overlayed to combine sensorial and analytical results.

It often happens that coeluting compounds are not clearly detectable either by detector or operator; such situation can be elegantly fixed using the S&T option provided by Gerstel GmbH ODP4. Briefly, instead of a funnel suitable for sniffing, at the ODP exit is installed a desorption tube able to trap the analytes. Such tube is then desorbed in a GC/MS system where a different column is used: this allows to separate the previously eluting compounds in order to identify them.

A further improvement is related to the new Gerstel ODI2, which provides a streamlined GC-O data processing workflow, featuring deconvolution followed by RI-MS library search and compatibility with commercial and user-generated databases.

INTRODUCTION

GC/MS-O is a powerful technique able to combine analytical results arising from GC/MS and sensorial perception [1]. The recently introduced olfactory detection port GERSTEL ODP4 offers an integrated software workflow to evaluate these combined data sets as well as a novel hardware extension to allow trapping on the sniffing port (Sniff&Trap).

In GC/MS-O, a sample injected in a standard GC system is diverted at the end of the column by means of splitting device: part of the effluent reaches the MS detector, while a second aliquote is directed to an olfactometric port where a trained operator sniffs in a proper way (Fig.1). The two traces (i.e. **chromatogram** and **olfactogram**) are then overlayed to combine sensorial and analytical results. Sensory perception data from the trained test person is recorded via 4 or 6 button intensity device and a voice recognition SW and stored as a combined data set together with GC/MS data. The figure 2 shows an example of a single combined GC/MS-O data file. The GC/MS peaks within the yellow odour ranges were identified using the automated ODI2 workflow consisting of deconvolution, MS library search and RI library confirmation with a single mouse click.

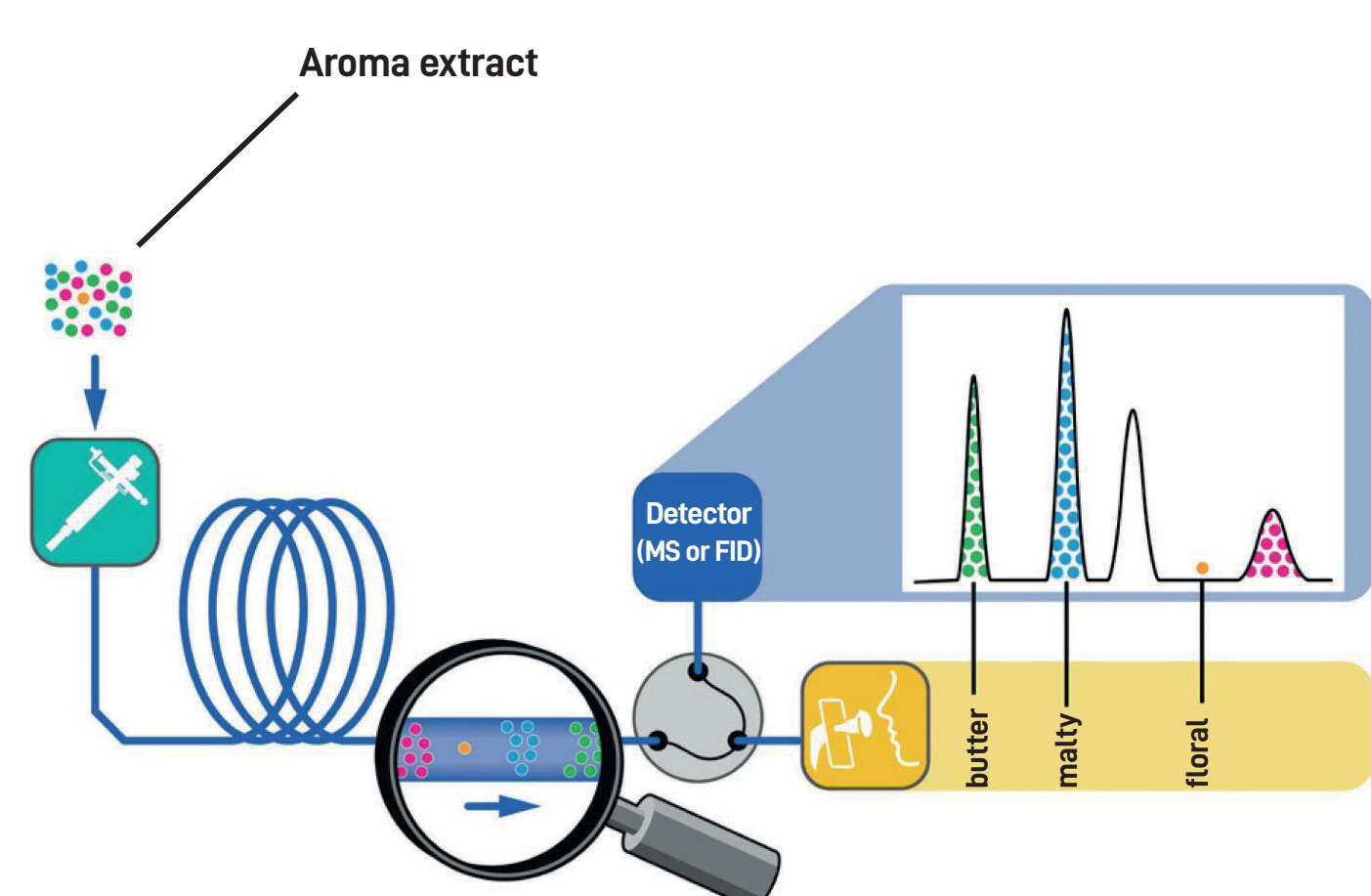


Fig. 1: Parallel MS-O Detection scheme

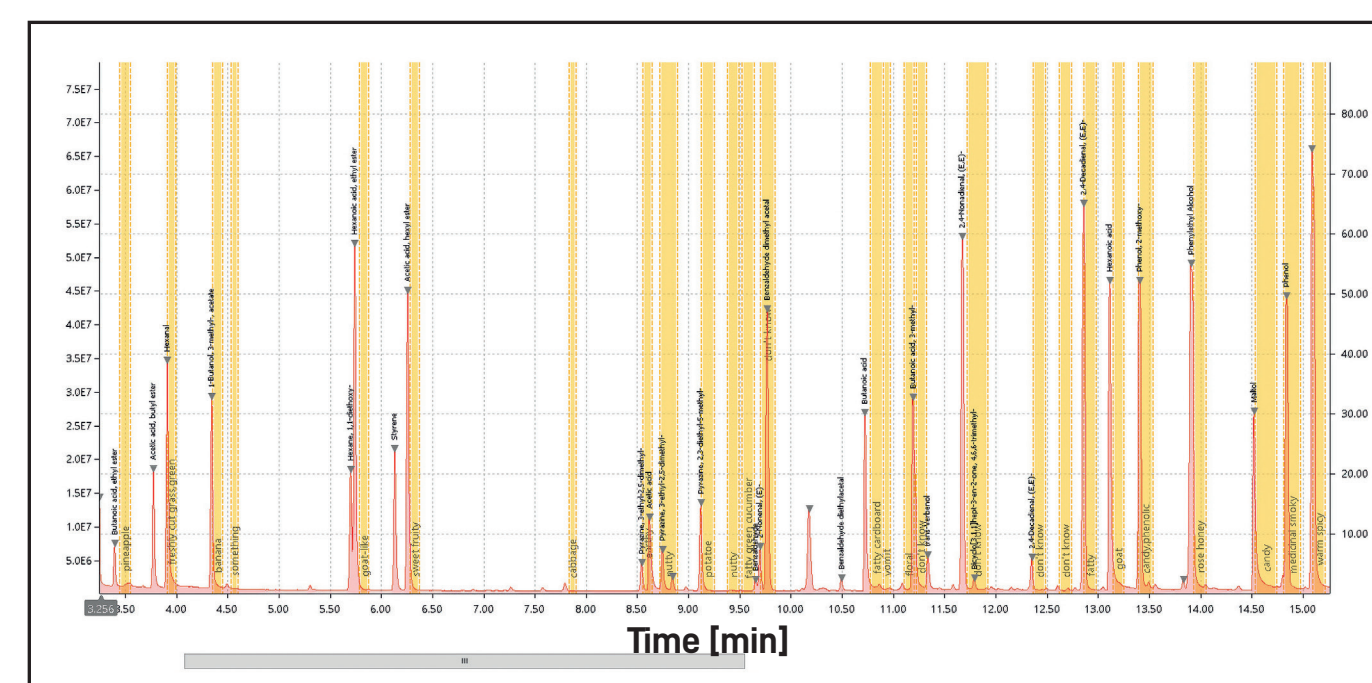


Fig. 2: Example visualization of combined GC/MS-O results. The red trace represents the TIC, the yellow ranges indicate odour-active retention times ranges. Voice recognition results of odour descriptors are automatically annotated, as well as compound names after identification using MS/RI libraries

EXPERIMENTAL

Instrumentation. Experiments were performed using an Agilent 7890 B GC with MSD 5977B, a GERSTEL CIS4 PTV, thermal desorption system TDU2 and MPS Autosampler with 10µl syringe. System was configured for mode liquid injection to inject the standard solution and with thermal desorption system TDU2 to reinject the trapped compounds. The software used to analyze the GC/MS-O was GERSTEL Olfactory Data Interpreter2 using NIST20 mass spectral library and a dedicated RI library. GC column was a DB-5MS for the first separation and a WAX for the thermal desorption run.

METHOD AND RESULTS

The typical situation of two coeluting odour compounds was investigated by injecting one microliter of a diluted standard solution (Fig.3). Amongst others, two substances of identical RI on a DB-5 type column were selected to achieve this.

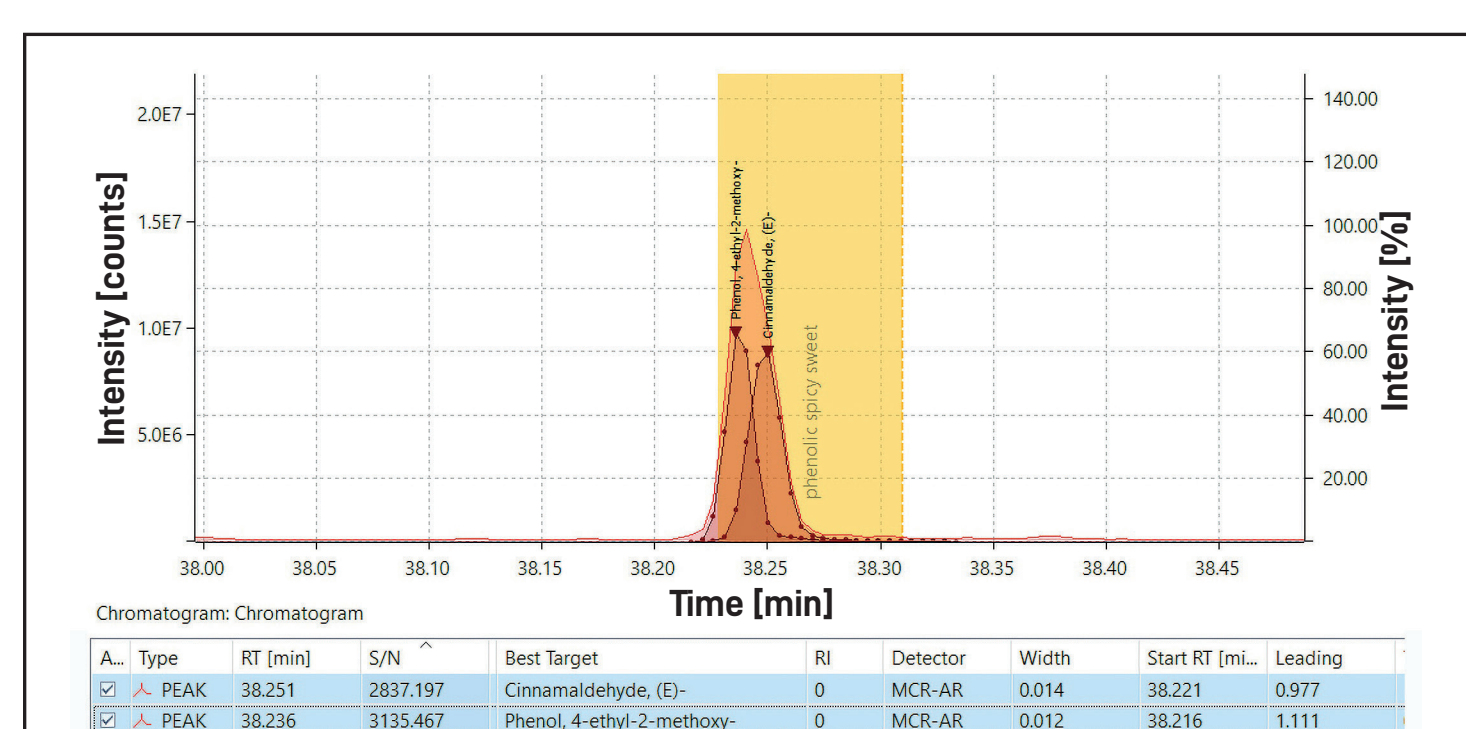


Fig.3: Coelution on DB5: automated identification after deconvolution with MCR-AR, NIST search and RI confirmation

Accordingly, the correlated GC-O signal showed of a peak at 38.24 a rather complex mix of descriptors. Automated deconvolution confirmed the presence of two overlaid GC/MS peaks and extracted the related spectra.

To perform the deconvolution, a recent and faster alternative to the common AMDIS [2] approach has been implemented into a prerelease version of the GERSTEL ODI2 Software. Multivariate curve resolution - alternating regression (MCR-AR) [3] is a matrix-based method to deconvolute signals. In general, it can be applied on multi-dimensional data originating from various sources like spectroscopy and spectrometry. In contrast to other algorithms, it allows to allow an automated as well as an interactive deconvolution of GC/MS data.

After deconvolution, the peaks were identified using the NIST20 mass spectral library. To increase the confidence in RI search, the ODI workflow allows the optional use of an additional RI database. All potential CAS numbers proposed by NIST search can be confirmed using by a n-Alkane RI calibration file and a RI database. Commercial libraries in NIST (.db) format as well as user contributed libraries in Excel spreadsheet format can be imported via a template. This database might also contain olfactory data that can be searched interactively as a database query.

In order to clearly assign olfactory properties to each of the overlapping compounds, it is useful to physically separate the coeluting peaks. So the sample was injected again to selectively trap the affected RT range on the GC-O port using a Tenax tube. While this Sniff&Trap technique has been used before using custom-made connectors [4], the ODP4 features an out-of-the-box quick-release sealing mechanism for common thermal desorption tubes.

The Tenax a trap was inserted using the ODP4 trap interface (Fig. 4) about 10 seconds before the coelutions RT. The trap was removed again about 10 seconds after the coelution. Then a thermal desorber on top of the PTV and a column of orthogonal polarity (WAX) was installed to desorb the trap (Fig. 5). The figure 6 shows the baseline separated peaks, so that sensory attributes can be clearly assigned to the related GC/MS peaks.

In order to demonstrate the suitability of this approach, a Linalool solution was repeatedly (n=3) injected, trapped and reinjected using this technique and revealed an area repeatability of <3% (Fig. 7).

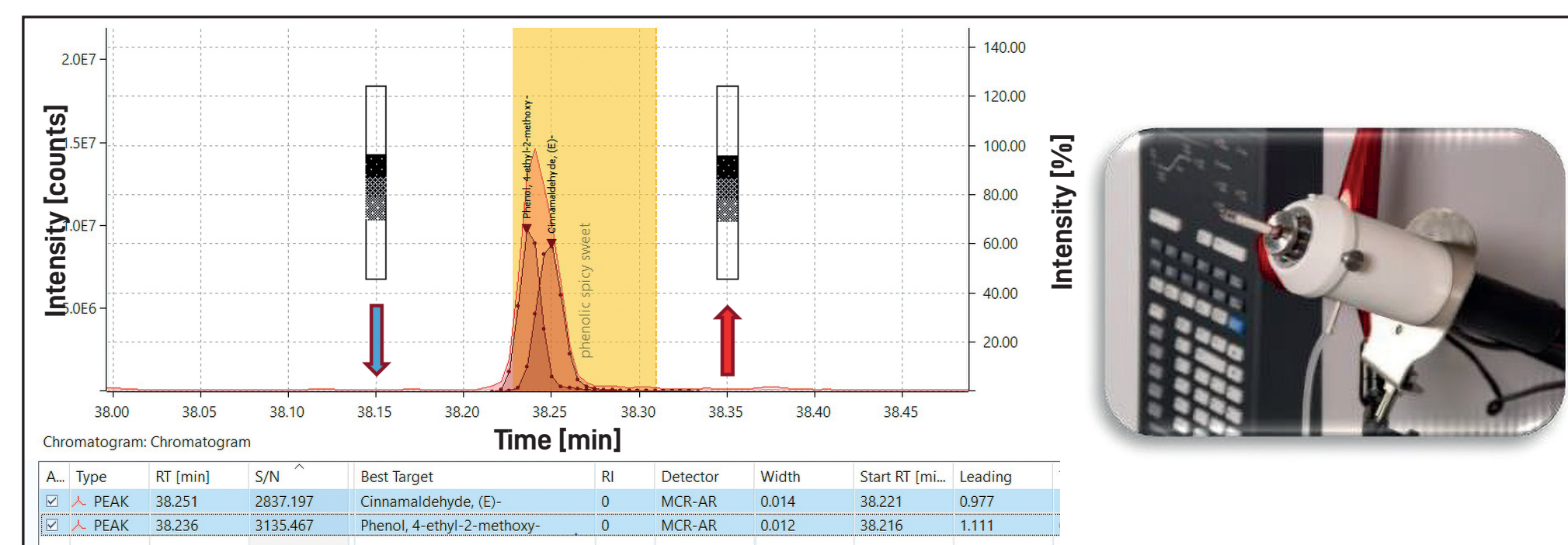


Fig.4: During a second run, the trap is attached the coelution takes place

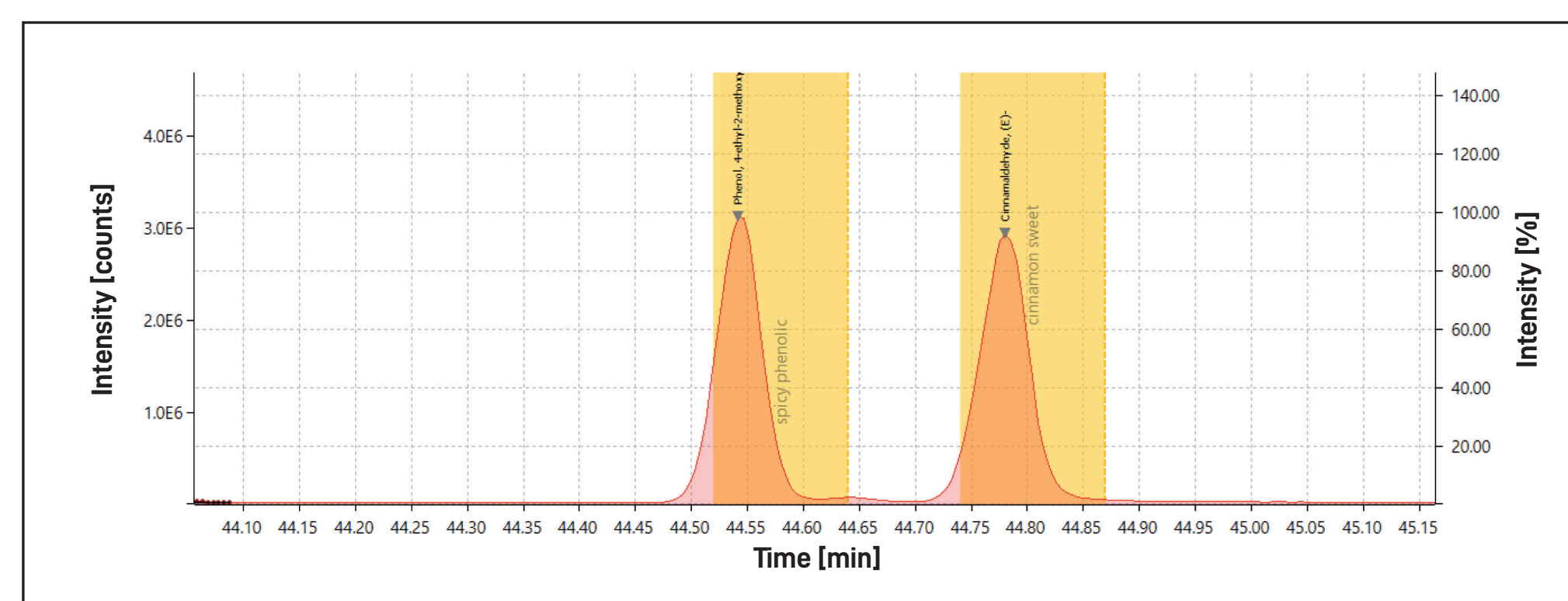


Fig.6: Baseline resolved GC/MS-O peaks after TD reinjection of the coelution fraction on a WAX column

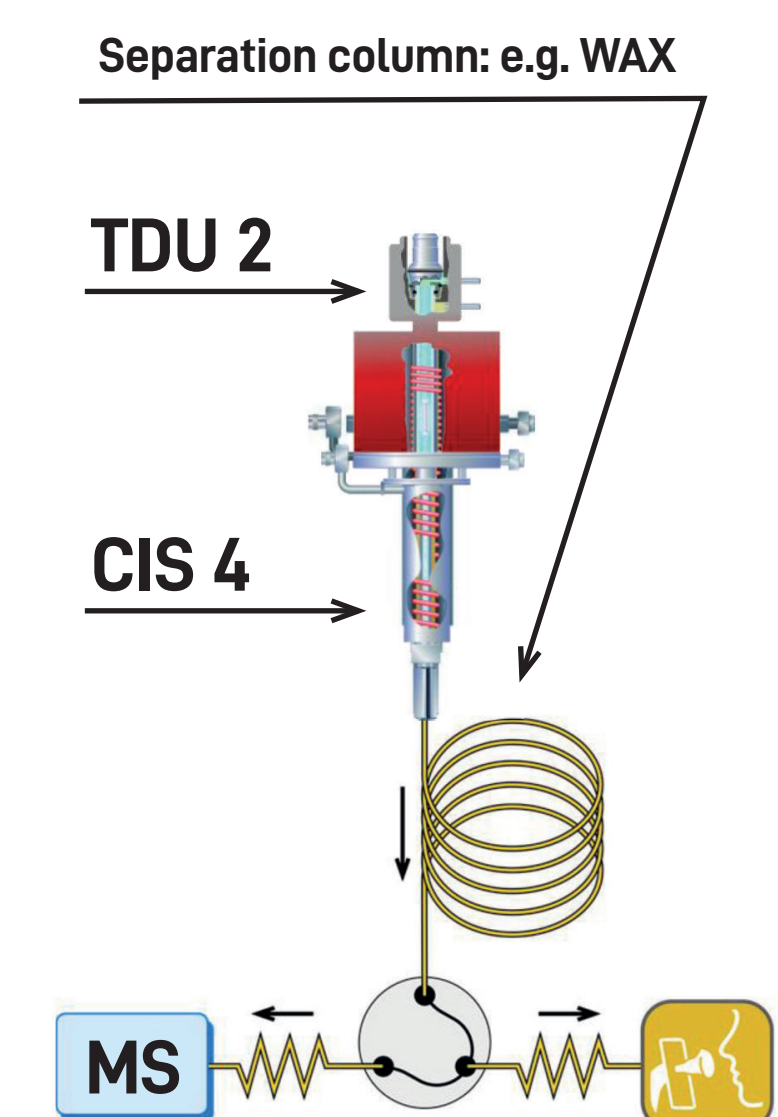


Fig.5: Installation of a TDU and change of column to orthogonal phase. The trapped fraction is being reinjected using the TD Injector onto different polarity column

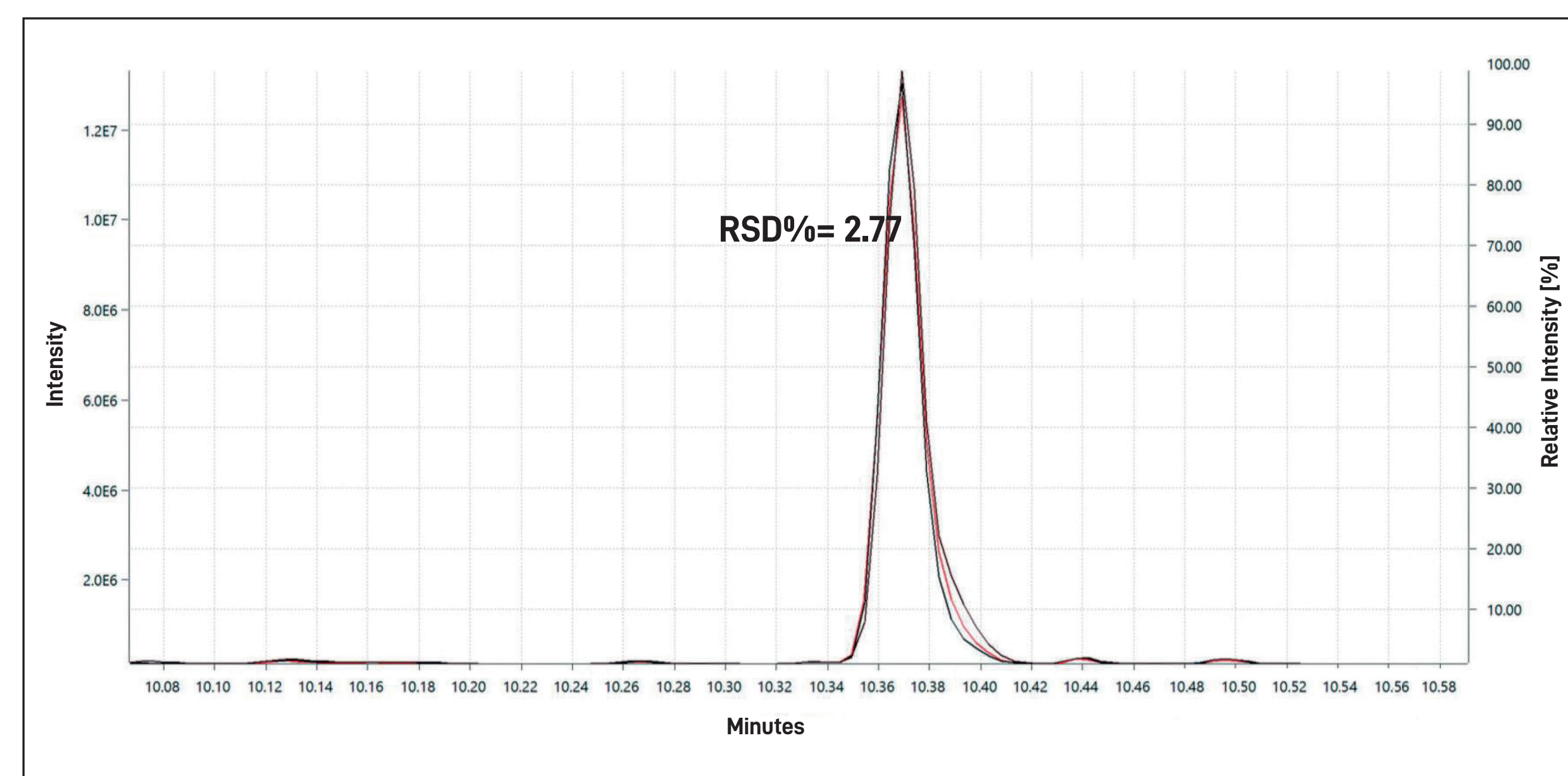


Fig.7: Repeated trapping and reinjection experiment of a Linalool Standard solution (n=3)

CONCLUSION AND OUTLOOK

Sniff&Trap technique within a commercial available instrument setup offers additional separation power similar to conventional GC-heartcutting systems. The required manual intervention makes it suitable for occasional use when fully automated multidimensional GC systems are not at hand. The full power of combining the enrichment with a Deans switch for repeated trapping needs to be evaluated.

The integrated SW approach to combine sensory, mass spectral and RI data in one Software package represents a significant relieve in the work of flavour chemists.

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