Smart MID Mode: increased instrument robustness for complex samples using the DFS Magnetic Sector GC-HRMS

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Abstract

The Smart MID feature of the Thermo Scientific™ DFS SmartTune™ Operating Software enables to reduce the potential negative effects of complex matrices in the analysis of Dioxins and POPs.

The measurement conditions were according to EPA 1613 method.

By determining all MID mass calibration parameters before the injection of the sample extract (when no sample matrix is present in the instrument), a very narrow lock mass scan width can be applied in the following sample analysis run, excluding potential matrix interference signals.

Introduction

DFS magnetic sector GC-HRMS

The analysis of Dioxins and Furans can be challenging due to the matrix remaining in the extract, also after sample clean-up. This can affect the robustness of the analytical process. The critical step in the MID process is the first locking and the following calibration using two masses of the reference gas such as Perfluorokerosene (PFK). During this step, the instrument scans a certain range over the exact theoretical value of the lock mass of the reference, which is the basis for the following calibration. In the Default MID Mode, the locking is done during the analysis of the sample at the start of each MID time section. At that point, the sample with its matrix is already present and the temperature in the GC is high so that matrix contaminants are eluting from the GC column into the ion source. With the presence of high matrix during the locking process, there is a risk that a mass signal from a matrix compound is close to the lock mass peak of the reference gas. An intensive matrix peak within the mass scanning range of the lock window can be misinterpreted as lock mass, which would result in a wrong locking**.**

To solve this issue, an optional MID analysis mode was specifically developed for difficult samples. In this Smart MID Mode, a calibration table is created prior to the injection of the sample extract when no matrix is present and the GC temperature is still low. During the analysis, this calibration table is applied. That allows minimizing the scanning width of the lock scan range, as the mass position of the lock mass is already very close to its theoretical value by using the pre-calibration parameters. Matrix peaks cannot affect the lock process anymore as they will mostly be outside of the narrow scanning mass range of the locking window.

Materials and methods

Equipment

All experiments were carried out on a Thermo Scientific™ DFS™ Magnetic Sector HR-GCMS, a Trace™ 1310 GC and a TriPlus™ RSH Autosampler.

Test Method

The measurement conditions were according to EPA 1613 method.

Data Analysis

For the data evaluation Thermo Scientific™ Xcalibur™ 4.2 and Target Quan 4.0 software was used.

Results

Background

Generally, the analysis of Dioxins and Furans and related persistent organic pollutants (POPs) is a targeted quantitative analysis of known contaminants with typically very low levels. For this challenging analysis the mass spectrometric approach of so-called multiple ion detection (MID), sometimes also called selected ion monitoring (SIM), is employed. In this analysis mode the data acquisition covers specifically the mass traces of the analytes only, rather than full scan data. The benefit using this approach is that the instrument can concentrate analysis time to detect a higher number of target ions by using higher dwell times. The dwell time is the assigned measuring time for every single target ion according to the MID setup. Due to longer dwell times (measuring times) for the critical target analyte masses better ion statistics are achieved which is beneficial in terms of sensitivity.

For Dioxin and Furan analysis based on the isotope dilution technique, typically the two most abundant isotope masses for each native analyte and 13C labeled internal standard are simultaneously monitored. Isomers of the same chlorination degree and therefore with same masses, however, are chromatographically separated in time on the GC.

Multi Ion Detection (MID)

The analysis is divided into multiple time sections each containing different specific target masses. In the section dialog all specific target masses for each MID time section are defined plus two reference gas masses, the Lock- and Cali-mass used for the constant automatic mass recalibration of the mass spectrometer. This approach ensures maximum mass accuracy and stability for the high-resolution analysis of low-level contaminants.

Figure 1. Example of a typical 5 section Dioxin analysis.

Segment Settings

Times

Start [min]: 29.00 End [min]: 37.50 Measure [min]: 8.50 Cycle [sec]: 1.20

Section 2	L/C	Mass	Gr.	Int.	Time[ms]	Compound	Comment
1	Lock	313.98336	1	20	11	FC43	
2		339.85915	1	1	223	pcdf	QM native pcdf
3		341.85620	1	1	223	pcdf	RM native pcdf
4		351.89941	1	5	44	PCDF	QM[13]C-PCDF
5		353.85702	1	1	223	pcdd	QM native pcdd
6		353.89646	1	5	44	PCDF	RM[13]C-PCDF
7		355.85407	1	1	223	pcdd	RM native pcdd
8	Cali	363.98017	1	20	11	FC43	
9		367.89433	1	5	44	PCDD	QM[13]C-PCDD
10		369.89138	1	5	44	PCDD	RM[13]C-PCDD

Figure 2. Example of the penta-chlorinated dibenzo dioxin/furans mass table.

Within each MID analysis time section, the traces of target masses and reference masses are acquired. During the acquisition, a permanent automatic mass re-calibration is carried out. This automatic mass calibration process includes the following steps: first step is the first so called locking of the reference mass signal specified as lock mass, secondly, an electric calibration using a second reference mass peak, the so-called cali mass, is carried out, and in the third and final step the successive monitoring of the target masses takes place. While step 2 and 3 describe a so-called MID mass scanning cycle which is constantly repeated, the locking process is executed only once at the start of each of the MID analysis time sections.

During the lock process at the start of each MID time section the system identifies the reference mass, labeled as lock mass using a small mass scan over a defined narrow mass range, called lock window. It corrects its position to the exact theoretical value which is the basis for the following calibration.

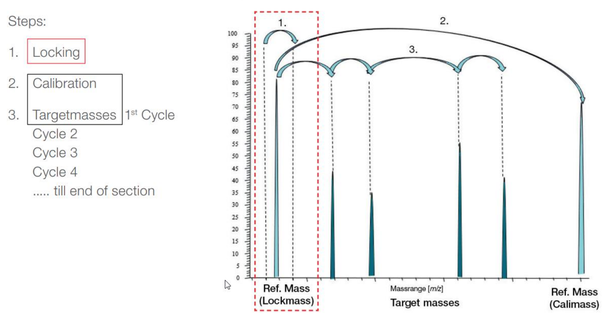

Figure 3. Steps carried out in each MID analysis section.

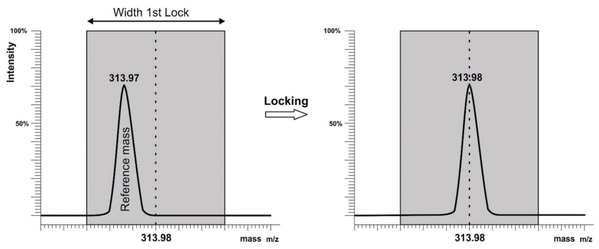

Figure 4. Lock process in Default MID Mode.

In the Default MID Mode the locking is done during the analysis of the sample at the start of each MID time section. At that point, the sample with its matrix is already present and the temperature in the GC is high so that matrix contaminants are eluting from the GC column into the ion source of the mass spectrometer together with the target analytes of interest.

Problem statement

With the presence of high matrix during this locking process, there is a risk in the Default MID Mode that a mass signal from a matrix compound is close to the lock mass peak, which can disturb the locking process. An intensive matrix peak within the mass scanning range of the lock window can be misinterpreted as lock mass, which would result in a wrong locking (Figure 6). As a consequence, the complete mass calibration for the specific MID time section would be false and the MID section would fail, which means chromatograhic peaks of the target compounds are not or not correctly detected.

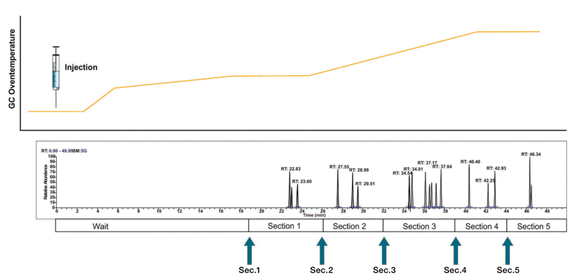

Figure 5. Default MID Mode: The locking for each section is done during the analysis when sample matrix is present, and the GC is hot

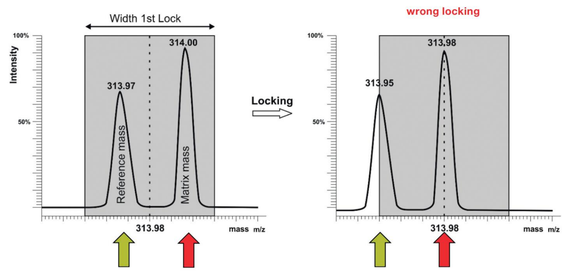

Figure 6. Matrix interference can disturb the lock process which leads to a wrong locking.

Solution

In the Smart MID Mode, an MID calibration table is created prior to the injection of the sample extract when no matrix is present, and the GC temperature is still low. During the analysis, this calibration table is applied. That allows minimizing the scanning width of the lock window, as the mass position of the lock mass is already very close to its theoretical value by using the pre-calibration parameters. (Figure 7). Matrix peaks cannot affect the lock process anymore as they will mostly be outside of the narrow scanning mass range of the locking window. In the unlikely case where interference matrix peaks still fall within the narrow Smart MID lock window, they practically overlap with the lock mass peak and thus show the same mass assignment.

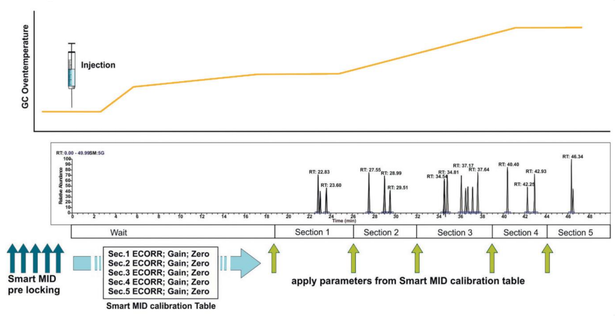

Figure 7. Principle of the Smart MID locking and calibration. pre-calibration parameters

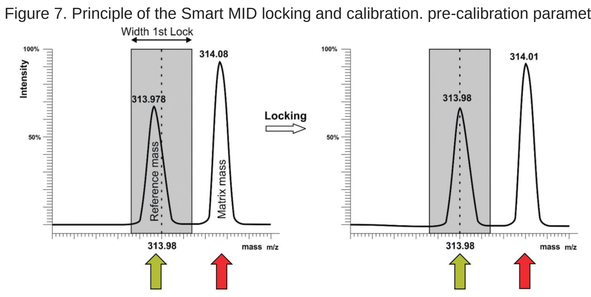

Figure 8. In the Smart MID Mode, the Lock window is much narrower so that no matrix peak can interfere.

Experimental proof of concept

A Matrix Simulation Experiment based on column bleed can demonstrate the advantages of the Smart MID Mode by setting up an MID analysis experiment with a reference (lock) mass close to one of the GC column bleed peaks, which is used to simulate the matrix peak. At a sufficiently high GC temperature, the column bleed peak will be more intensive than the reference peak and will accordingly interfere with a correct locking when using a standard locking window as in the Default MID Analysis Mode (Figure 9). The column bleed peak (right) in the lock window is more intensive than the reference peak (left). The system misinterprets the column bleed peak as lock mass. Therefore, the whole following MID analysis section fails due to a failed mass calibration (Figure 10). The system locks on the more intensive column bleed peak and not on the reference peak.

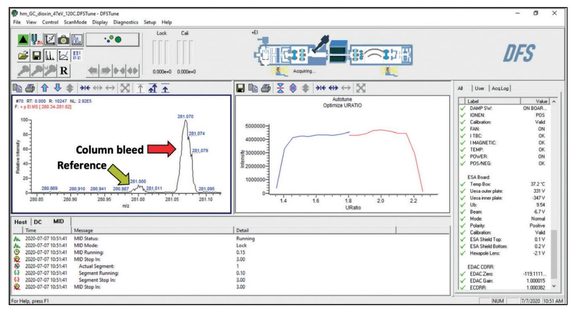

Figure 9. The column bleed peak (right) in the lock window is more intensive than the reference peak (left).

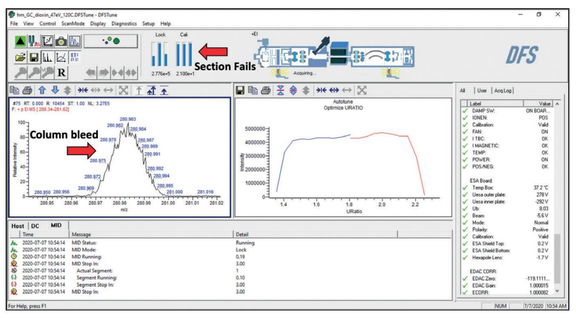

Figure 10. The system locks on the more intensive column bleed peak and not on the reference peak.

Using the Smart MID mode in contrast resolves the problem. Applying the MID pre-calibration the reference (lock) mass peak is already almost in the center of the lock window. Therefore, in the following MID analysis run when the GC is heated up the mass range scanning width of the lock window can be set almost as narrow as the peak base of the reference (lock) mass. The column bleed peak is still present, but far outside of this window and can not interfere with the locking process.

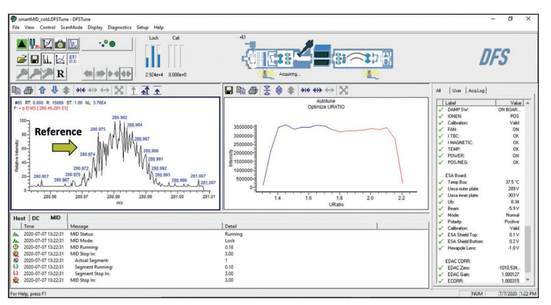

Figure 12. By using the Smart MID Mode, the MID section works correctly, and it is not affected by the column bleed peak.

Smart MID applied to Samples with heavy matrix

Example of a sample with very high Matrix background, which could not be measured with standard MID. The locking was not successful which resulted in no target Peaks.

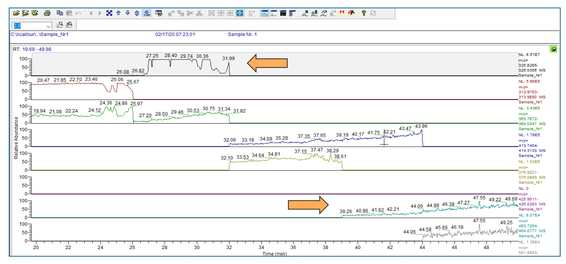

Figure 12. Lock- and Cali-mass traces of a heavy matrix sample with standard MID.

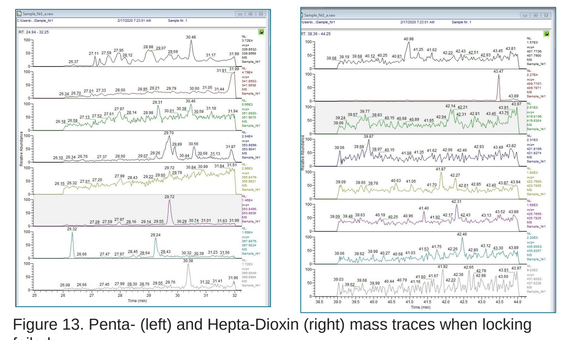

Figure 13. Penta- (left) and Hepta-Dioxin (right) mass traces when locking failed.

Applying the Smart MID mode to the same sample enables the instrument to lock correctly and acquire the target masses correctly.

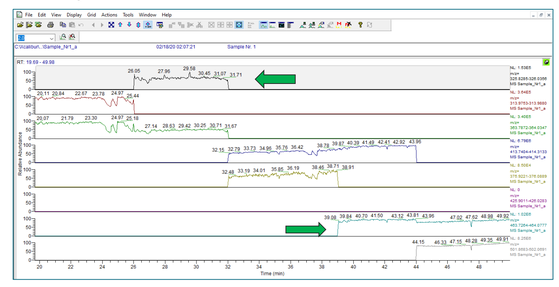

Figure 12. Lock- and Cali-mass traces of a heavy matrix sample with Smart MID.

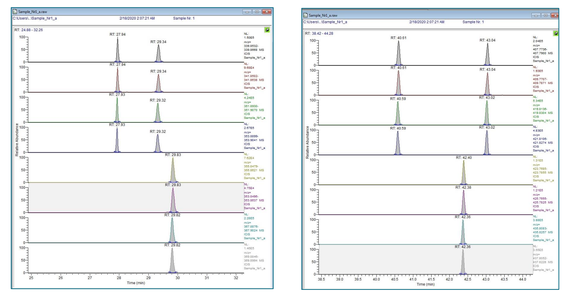

Figure 13. Penta- (left) and Hepta-Dioxin (right) mass traces when locking correctly

Conclusions

The Smart MID Mode is offered as an option for difficult samples alongside the Default MID Analysis Mode, which continues to be the default mode, due to it's ease-of-use operation.

The highlights of the Smart MID Mode :

- Robustness of the system towards challenging samples.
- Cost and time savings. (no repeated sample analysis).

References

US EPA Method 1613 revision B

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Science at a scan

Scan the QR code on the right with your mobile device to find out more about the DFS Magnetic Sector GC-HRMS System.