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A procedure for comprehensive two-dimensional gas chromatography retention time locked dual detection

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ABSTRACT

In this paper, a novel, and easy to perform, retention time locking procedure for locking primary and secondary retention times of detector signals in comprehensive two-dimensional gas chromatography (GCxGC) dual-detection is proposed and its advantages are demonstrated and discussed. The dual detection retention time locking procedure is a 2-step process for a GCxGC system in which the effluent of the primary column is split, by using a pressure regulated splitter, towards the GCxGC modulator using two identical secondary GC columns of which one is installed in the main GC oven and the other is installed in a secondary GC oven. The first step of the locking procedure is to minimize the secondary retention time difference between both detectors of a compound, which has a retention factor (k) close to 0. This is done by stepwise altering the effective secondary column length, simply by sliding the secondary column, which is installed in the main oven, forwards or backwards through the modulator. The second step is to minimize the secondary retention time difference of a compound which has a significant retention in both dimensions. This is done by stepwise altering the secondary oven temperature rate. This locking procedure was successfully demonstrated for the analysis of a diesel sample by GCxGC coupled to a time of flight mass spectrometer (TOFMS) and a nitrogen chemiluminescence detector (NCD) and by GCxGC coupled to a TOFMS and a flame ionization detector (FID). For all compounds the average absolute secondary retention time differences between the NCD or the FID and the TOFMS detectors were 0.03, and 0.07 s, respectively, which are significantly less than the average peak widths at half heights, which was 0.2 s.

1. Introduction

Comprehensive two-dimensional gas chromatography (GCxGC), introduced by Liu and Phillips [1] in 1991, is a powerful analytical technique, especially suitable for the analysis of complex samples. GCxGC is becoming more and more a routine analytical technique for solving all kinds of analytical questions in a wide variety of application fields, e.g. the nitrogen, sulfur and oxygen speciation of complex petrochemical and bio-oil samples [2–6].

For particular GCxGC applications, using two different detectors simultaneously (dual detection) can offer a significant advantage compared to single detection. The main benefits of GCxGC dual-detection are speed and efficiency of the particular analysis, obtaining two signals per analysis while there is no need to alter the chromatographic system [7–16]. For example, when performing a dual-detection GCxGC analysis with a nitrogen chemiluminescence detector (NCD) and a mass spectrometer (MS), in one single analysis the nitrogen containing compounds could be detected with high selectivity and quantified by the NCD and directly be identified and/or verified by the MS detector.

However, practically, GCxGC dual-detection is not that straightforward. The column effluent of the primary or the secondary column(s) needs to be split towards both detectors.

The ***split ratio*** during a temperature programmed GC analysis may vary, which complicates quantitation, especially for detectors operating at different outlet pressures. To overcome this problem, the pressure at the split point needs to be kept constant [17] in order to keep the split ratio constant; this can be performed by using a so-called electronic pressure regulated splitter. Splitting after the primary column and using two secondary columns is highly preferred since it leads to more optimal linear velocity operation in both dimensions [18]. Furthermore, splitting after the secondary

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Table 1
Composition of test mixture 1.

Compounds	Purity %	Conc. ppm
Acetonitrile	99	449
Propanenitrile	99	398
Isobutyronitrile	99	438

column introduces extra-column band broadening which could be critical for the narrow secondary dimension peaks which have a typically peak width at half height in the order of 0.1 s.

Another issue of GCxGC dual-detection is that the secondary retention times of both detectors are in general not equal. ***Retention time differences*** are caused by differences in the column or retention gap dimensions towards both detectors and/or differences in the capillary flow regimes towards both detectors during a temperature programmed GCxGC analysis, again especially for detectors operating at different outlet pressures. When using two detectors which may show non-similar 2D chromatograms, e.g. NCD/FID, NCD/MS, SCD/FID, SCD/MS (FID/MS show similar 2D chromatograms), secondary retention time differences between both detectors may complicate the data processing. e.g. for identifying the nitrogen containing compounds, at low concentration levels, in a complex petrochemical sample matrix, the NCD 2D chromatogram must be compared with the completely different complex MS chromatogram in order to locate the corresponding nitrogen containing compound peaks.

In this paper we proposed a novel, and easy to perform, retention time locking procedure for locking primary and secondary retention times of detector signals in GCxGC dual-detection.

2. Experimental

2.1. Equipment and materials

All GCxGC analyses were performed using a Leco Pegasus 4D (St. Joseph, MI, USA) GCxGC system, equipped with a secondary GC oven, an Agilent Technologies (Santa Clara, CA, USA) capillary flow technology splitter, a hot split/splitless injector, a Leco Pegasus time-of-flight mass spectrometer (TOFMS), an Agilent Technologies Nitrogen Chemiluminescent Detector (NCD 255) and an Agilent flame ionization detector (FID). Instrument control and data processing were performed by Leco ChromaTOF software version 3.25 and NIST MS-Search 2.0. A VF1ms column (50 m × 0.25 mm; 0.4 μm film thickness) and a VF17ms column (10 m × 0.10 mm; 0.2 μm film thickness) were purchased from Agilent Technologies (Santa Clara, CA, USA).

2.2. Test mixtures and samples

Two different test mixtures containing nitrogen containing compounds were prepared in toluene. All compounds were purchased from Sigma-Aldrich. For test mixtures 1 and 2, the compounds, compound purities and compound concentrations, are summarized in Tables 1 and 2, respectively. Furthermore, a real-life diesel sample was purchased from a local gas station.

2.3. Chromatographic conditions

For all analyses the non-polar VF1ms column was used for the first dimension separation and two, in parallel coupled, 2 m medium-polar VF17ms columns were used for the second dimension separations. The end of the primary column and both the beginnings of the secondary columns were attached to the Agilent electronic pressure regulated (EPC) splitter. Both secondary columns were directed through the cryogenic modulator. The end

Table 2
Composition of test mixture 2.

Compounds	Purity %	Conc. ppm
Hydantoine	99	439
Acridine	97	344
Penanthridine	98	362
2,5-Dimethyl-pyrrole	98	438
Quinaldine	99	413
Isobutyronitrile	99	459
4-Picoline	98	452
Propionitrile	99	442
N,*N*-Dimethyl-cyclohexylamine	98	583
3-Ethyl-4-methyl-pyridin	>95	451
1-Ethyl-2-pyrrolidon	99	558
4-Pentennitrile	98	444
Pyrrolidine	99	518

of one secondary column was connected to the TOFMS retention gap (0.5 m × 0.10 mm i.d.), by means of a Siltite® coupling (SGE Analytical Science, Ringwood Victoria, Australia), and the end of the other secondary column was connected directly into the NCD (NCD/TOFMS) detector or directly into the FID (FID/TOFMS) detector. The secondary column leading to the NCD or FID was installed in the main GC oven and the secondary column leading to the TOFMS was installed in the secondary GC oven. A schematic overview of the GCxGC-NCD/TOFMS or GCxGC-FID/TOFMS dual detection set-up is given in Fig. 1.

The GCxGC instrument was operated under temperature programmed conditions from 40 °C, held for 1 min, to 330 °C, held for 5 min, for the primary GC oven and from 45 °C, held for 1 min, to 335 °C, held for 5 min, for the secondary GC oven. The temperature rate for the main oven was 2 °C/min. For retention time locking, the temperature rate for the secondary oven was 2 + ΔT °C/min. The modulation time was 10 s. A hot pulse of 2 s, having a temperature of 20 °C higher than the actual primary GC oven, was used. Helium was used as the carrier gas. All separations were carried out using a constant head pressure of 35 PSI. A constant split pressure of 18 PSI and 23 PSI was used for the NCD/TOFMS and the FID/TOFMS setup, respectively. The injector temperature was 300 °C. An injection volume of 1 μl and a split ratio of 1:50 was applied for all analyses. The NCD was operated at a burner temperature of 925 °C, with an oxidizer flow of 10 sccm, a hydrogen flow of 5 sccm and using a data-acquisition rate of 100 Hz. The FID temperature was 280 °C, using an air flow of 450 ml/min and a hydrogen flow of 40 ml/min. The TOFMS was operated in electron impact mode using 70 eV, a source temperature of 250 °C and a mass range of 15–550 amu.

2.4. Dual detection retention time locking procedure

The dual detection retention time locking procedure is an easy to perform 2-step process. The first step in the locking procedure is to minimize the secondary retention time difference of a compound, which has a retention factor (k) preferably close to 0, between both the NCD or FID and TOFMS detector signals. For this, the compound acetonitrile, present in the test mixture 1, was used. In order to minimize this retention time difference, the effective secondary column length of the NCD or FID was stepwise (using equal steps) increased or decreased, by sliding the secondary column through the modulator. The effective secondary column length is the length of the column after the modulator, from the cryogenic modulator to the detector, so the part of the secondary column which is effectively used for the second dimension separation. Adjusting the secondary retention time, by stepwise altering the effective secondary column length, was already described by Mommers et al., for comprehensive two-dimensional gas chromatography retention time locking [19].