THE ON-LINE COMBINATION OF LIQUID CHROMATOGRAPHY-LARGE VOLUME INJECTION-COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY TRIPLE QUAD MASS SPECTROMETRY: A POWERFUL FOUR-DIMENSIONAL SEPARATION-SCIENCE TOOL

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Introduction

The present research is focused on the on-line combination of high performance liquid chromatography (HPLC), comprehensive two-dimensional gas chromatography (GC×GC), and triple quadrupole mass spectrometry (QqQ MS), generating a very powerful 4D separation science tool. The selectivity of the HPLC dimension enables the separation of chemical classes, or sub-classes of compounds. Then, the whole fraction of interest can be transferred, through a syringe-type transfer device, to a programmed temperature vaporizer (PTV) injector. Each transferred fraction can then be subjected to cryogenically-modulated GC×GC. The latter is an excellent way to increase selectivity, peak capacity and sensitivity for a GC-based analysis. The analytes eluting form the GC×GC system were directed to a highly flexible and rapid QqQ MS instrument. The potential of the novel LC-GC×GC-QqQ MS combination was evaluated in the analysis of a highly challenging sample, namely coal tar. The normal-phase LC step was successful in the separation of the following groups of compounds: I) hydrocarbons, II) aromatic compounds (with and without S), III) oxygenated constituents. Each LC fraction was subjected to a specific untargeted or targeted GC×GC-QqQ MS approach. For example, the coal tar S-containing compounds were pinpointed through MRM analysis, while full-scan MS information was sufficient for the hydrocarbons.
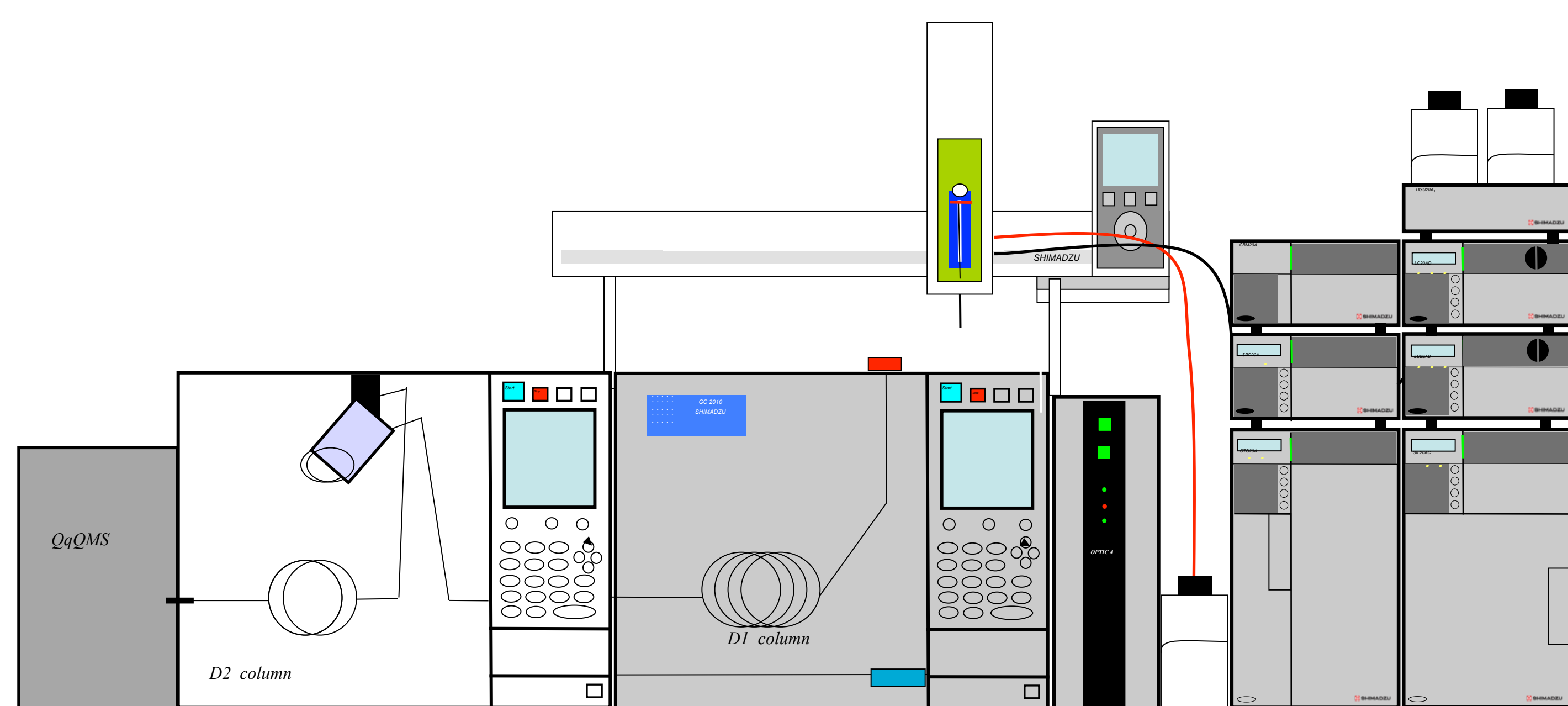

Figure 1. Scheme of the LC-GC×GC-QqQ MS.

Experimental

The LC-GC×GC-QqQMS system employed is reported in Figure 1, and consists of an HPLC (Shimadzu, Kyoto, Japan), a large volume injector (OPTIC 4, GL Science, The Netherlands), an AOC-5000 autosampler (Shimadzu), two independent Shimadzu GC2010 gas chromatographs (GC1 and GC2), and a TQ-8030 triple quadrupole mass spectrometer (Shimadzu). Data were acquired using the GCMSsolution software (Shimadzu). Bidimensional chromatograms, in all applications, were generated by using the ChromSquare software v. 2.0 (Shimadzu Europe). The entire system is totally automated and controlled by the LC×GC-MS software (Shimadzu).

Sample: coal tar (dilution 1:200)

LC conditions: a 100 × 3 mm ID × 5 µm d_p silica column (SUPELCOSIL LC-Si, Supelco) was operated under the following gradient conditions (flow: 0.35 mL/min): 0-6.5 min (100% hexane); from 6.5 to 7.5 min 100% CH_2Cl_2 (until the end of the analysis). Injection volume: 2 µL.

LC fractions: 1°: hydrocarbons, from 1.35 to 1.85 min (vol. 350 µL, time 30 s); 2°: aromatic compounds (with and without S), from 1.85 to 7.00 min (vol. 1802 µL, time 309 s), 3°: oxygenated constituents, from 8.95 to 14.10 min (vol. 1802 µL, time 309 s). A Shimadzu AOC-5000 autosampler, equipped with a dedicated dual side-port syringe, was employed as transfer device.

Figure 2. TIC LC-GC×GC-QqQ MS chromatogram of the 2° fraction

PTV conditions: 35°C (100 sec) to 300°C at 5°C/sec.

Injection mode: the split mode was used for all fractions, with different split ratios used according to the volume of the fraction.

GC×GC-QqQ MS conditions: D1: SLB-5ms 30 m × 0.25 mm ID × 0.25 µm d_f column (Supelco), loop: 1.5 m × 0.18 mm ID, D2: Supelcowax-10 1.0 m × 0.10 mm ID × 0.10 µm d_f column (Supelco), union: SGE SilTite mini-union (SGE). Carrier gas: He, initial pressure of 175.8 kPa (constant linear velocity).

GC oven temp. prog.: 50°C to 280°C at 3°C/min, with different off-set values in the second oven according to the fraction.

Modulation time: 5 s, by using a loop-type modulator (Zoex Corporation); hot pulse (350°C) was 400 ms.

Figure 3. LC-GC×GC-QqQ MS MRM results for some 2° fraction constituents.

Results and discussion

As can be observed, the pre-separation step was very useful in generating simplified sub-samples of coal tar, which is an extremely complex sample. The purification step made quali/quantitative analysis easier. All the fractions were analyzed in the full-scan mode; moreover, the second fraction was analyzed also in the MRM mode, for the determination of the sulphur compounds.

1° fraction - hydrocarbons -: a series of linear, branched and cyclic hydrocarbons, from C_{12} up to C_{28}, were detected.

2° fraction - aromatic compounds (with and without S): a TIC LC-GC×GC-QqQ MS chromatogram is reported in Figure 2; as can be observed, the generation of a highly organized chromatogram, made chemical-class identification easy. A positive off-set of 10°C was used, which enabled a full exploitation of the entire 2D space, with only residual wrap-around of the perylene group.

Figure 4. TIC LC-GC×GC-QqQ MS chromatogram of the 3° fraction

The MRM results, for three families of sulphur compounds, namely C4-thiophene (7 compunds), C2-benzothiophene (13 compounds) and naphthothiophene/dibenzothiophene (3 and 1 compounds), are shown in Figure 3. In total, 129 organic sulphur compounds were detected.

3° fraction - oxygenated constituents -: Figure 4 shows the TIC chromatogram of the third fraction; a positive off-set of 60°C was applied to reduce the extensive band broadening of the O-containing compounds in the second dimension. A well-organized chromatogram was generated with the phenol and naphthol groups of simple identification.

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