Overloading of the second-dimension column in comprehensive two-dimensional gas chromatography

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Abstract

Comprehensive two-dimensional gas chromatography (GC × GC) is based on a coupling of two GC columns of different characteristics by means of a device that allows portions of the effluent from the primary column to be injected onto the second dimension column for an additional separation. The time available for the separation in the second-dimension column is very short. Thus, this separation should be very efficient. The vast majority of GC × GC practitioners use very narrow bore columns for the second dimension. While this approach is justified in principle, if peaks in the second dimension overload this column, its peak capacity is severely reduced. A series of second-dimension columns of varying internal diameters, but similar phase ratios, were used to study these effects. The results indicate that 250 μm columns often provide comparable second dimension peak widths to 100 μm columns, while at the same time being less prone to overloading, indicating that they may often be a better choice than smaller diameter columns in the second dimension of GC × GC systems.
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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is receiving more and more attention recently owing to its vastly improved separation power over conventional GC. The improvement is accomplished through coupling of two GC columns coated with different stationary phases by a special GC × GC modulator, which helps preserve the separation achieved in the first column while enabling additional separation in the second column. The technique has been reviewed recently in a number of contributions (see e.g. [1,2]).

In order to maintain the "comprehensive" nature of a GC × GC separation, the second dimension must operate fast enough for the separation accomplished in the first-dimension to be preserved. To achieve the most faithful representation of this primary separation, each peak eluting from the first dimension column should be sampled as often as possible.

However, in practice, the sampling rate in the first dimension is limited by the duration of a single separation cycle in the second dimension. Thus, it would be advantageous to use as short a time for second-dimension separation as possible in order to achieve high sampling frequency. On the other hand, for the separation in the second dimension to be efficient, it is advantageous to use longer time. Consequently, a compromise usually has to be struck between the first dimension sampling frequency and the second dimension separation time. Theoretical studies indicated that the optimum primary dimension sampling frequency is achieved when each primary dimension peak is sampled three to four times [3].

With typical peak widths for 1-D GC being about 6 s at the base, either a modulation period of at most 2 s must be used, or the analysis must be carried out under conditions that broaden the primary peaks to 12–18 s (or more) so that modulation periods of 4–6 s may be used. To accomplish this, thick-film primary columns, slow oven temperature programming rates, slow carrier gas linear velocities in the primary column, or a combination of these are used. The net result is an analysis time that is usually increased substantially over

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that for a 1-D GC analysis. If one wishes to shorten analysis times, the second-dimension separation must be made faster. This means shortening the secondary column, which decreases its separation power, or using narrower secondary columns, which allow for higher linear flow rates, greater speed, and lower loss of efficiency with the increased speed. This allows for very rapid separations to be performed in the second dimension, with the losses in separation efficiency from choosing a short secondary column and a very fast linear flow rate being compensated for by the gains in efficiency from the narrow column diameter. The most extreme example of the narrow second-dimension column found in the literature is that presented by Adahchour et al., who used a 50 μm diameter second-dimension column [4].

The idea that a narrower column should be used in the second dimension has become the conventional wisdom when choosing column sets for GC × GC separations, as evidenced by the experimental sections of the vast majority of papers published in the literature. However, relatively little work has been done to prove that it is in fact the best choice under any and all circumstances. While the line of reasoning presented above is generally correct, problems may arise when the second dimension column becomes overloaded, which happens frequently in GC × GC with thermal modulation. Modulators of this type are currently the most widely used. They collect and focus portions of the effluent from the primary column into very narrow, concentrated bands. It has been shown that under such circumstances, second dimension column can easily become overloaded, even when the primary dimension column is not overloaded [5]. This results in reduced peak capacity in the second dimension. Since the amount of second dimension separation space is highly limited, any losses here, including those due to overloading, could seriously impair the performance of the system.

The goal of this study was to compare the performance of second-dimension columns of different internal diameters under the conditions of different mass loadings in order to assess how easily they become overloaded, and to evaluate whether this phenomenon is of any significant importance in GC × GC separations. To the best of our knowledge, this is a first comprehensive study of this kind. Presented in this paper are preliminary results obtained for four different second dimension column diameters and the same primary column.

2. Experimental

The separations were performed using an Agilent 6890 GC (Agilent Technologies, Mississauga, ON) fitted with a liquid nitrogen-based single cryojet modulator described elsewhere [6].

The samples analyzed included a linear *n*-alkane test mix consisting of *n*-pentane through *n*-tridecane, and unleaded gasoline. Pentane was obtained from Sigma–Aldrich (Oakville, ON). Hexane was obtained from Fisher Scientific (Toronto, ON), and the remaining linear alkanes

were obtained from PolyScience Corporation (Niles, IL). Regular unleaded gasoline was obtained from a local gas station. The linear alkane test mix was prepared as a neat mixture with the following concentrations: pentane (65.9 μg/μl), hexane (72.4 μg/μl), heptane (76.0 μg/μl), octane (78.5 μg/μl), nonane (79.8 μg/μl), decane (81.6 μg/μl), undecane (82.8 μg/μl), dodecane (83.2 μg/μl), and tridecane (84.6 μg/μl). This mixture was then diluted from 10 to 100,000 times in CS_2 (Fisher Scientific).

The primary dimension column was a 30 m × 0.25 mm × 0.25 μm VF-5MS, an arylene stabilized equivalent of 5% phenyl/95% methyl polydimethylsiloxane (Varian Inc., Middelburg, The Netherlands). The second-dimension columns that were tested had diameters (and stationary phase film thicknesses) of 0.32 mm (0.25 μm), 0.25 mm (0.15 μm), 0.15 mm (0.1 μm) and 0.10 mm (0.1 μm). All these columns were one metre in length and were coated with VF-23MS stationary phase, which is a stabilized >70% cyanopropyl polysiloxane (Varian Inc.). This combination of columns can be used up to 290 °C. Connections between the columns were made with press-fit connectors (Chromatographic Specialties, Brockville, ON). The trapping capillaries were made of 0.10 mm i.d. deactivated fused silica tubing (Polymicro Technologies, Phoenix, AZ), and the delay loop between the two trapping stages was a segment of 0.25 mm i.d. deactivated fused silica tubing (Chromatographic Specialties, Brockville, ON).

The separations were conducted with hydrogen carrier gas under conditions of constant flow of 2.0 ml/min measured with a flow meter at 45 °C. The oven was programmed from 45 to 180 °C at 3 °C/min. The detection was performed by FID at 100 Hz, and the samples were injected in split mode with a split ratio of 1:100 to 1:200 for gasoline.

3. Results and discussion

The study was carried out by comparing the widths and the symmetry of peaks eluting from the second dimension columns of different diameters for progressively lower amounts of the analytes injected on column. The columns used in the study were custom-made for the project to have as similar phase ratios as possible. For the 0.1 mm column, a minimum film thickness of 0.1 μm had to be used, as thinner films result in surface interactions changing the polarity of the column. All other parameters, including the carrier gas volume flow rate and the second dimension column length, were kept constant in all experiments. While certain important parameters (e.g. elution temperatures of the analytes) differed somewhat from one column to another under these conditions, this approach was chosen because in our opinion it reflected everyday practice in the best way. The experiments allowed the evaluation of the useful range of mass loadings for each column, resulting in little or no overloading. Normal alkanes were chosen as model compounds for the study. The results were verified by analyzing gasoline in the GC × GC