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Journal of Chromatography A, 1090 (2005) 126–132
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Possibilities and limitations of quadrupole mass spectrometric detector in fast gas chromatography

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Received 4 January 2005; received in revised form 16 June 2005; accepted 22 June 2005
Available online 19 July 2005

Abstract

In this work the application and limitations of a common bench top quadrupole mass spectrometer was evaluated for the qualitative and quantitative measurement of *n*-alkanes and pesticides of a wide range of volatilities and polarities with fast GC separations using 0.15 mm I.D. narrow-bore capillary columns. It was found that the spectra acquisition rate has a great impact on sensitivity (peak areas, peak shapes and S/N ratios). The quality of the obtained spectra is not significantly influenced in the full scan monitoring mode for the fastest scan rates. For quantitative analysis a selected ion monitoring mode is able to acquire the sufficient number of data-points for the proper peak shape reconstruction and good repeatability of peak areas measurements expressed by RSD (<5%) for all tested dwell times shorter than 75 ms. However, for shorter dwell times, S/N ratio is lower, while peak areas are not influenced.

Keywords: Fast GC–MS; Fast gas chromatography; Mass spectrometry; *n*-Alkanes; Pesticides

1. Introduction

Utilisation of fast gas chromatography (fast GC) on narrow-bore capillary columns is advantageous for the use in routine laboratories due to the higher sample throughput, the same and even higher separation efficiency than conventional capillary GC (CGC), higher sensitivity and/or precision and simultaneous reduction of operating costs of a GC analysis [1,2].

For proper operation of any "fast" column with MS, the peak broadening caused by extra-column effects must be small enough to preserve the column efficiency. The sampling frequency of a detector must be high enough to provide the sufficient number of data points across the peak for the accurate representation of a peak. Trends in GC are the ever increasing need for the positive identification and the need for more flexible systems that allow the analysis of a wide variety of samples in one system. These trends clearly results in the need of mass spectrometric detection [3]. In fast GC mostly time of flight (TOF) mass spectrometers are preferred due to their fast data acquisition rates reaching up to 500 Hz and the subsequent possibilities of chromatographic and spectral peak deconvolution [4,5]. Quadrupole instruments have been most widely used in conventional CGC. Proving their abilities for adequate detection of narrow peaks without the loss of sensitivity would therefore help to extend the use of the fast GC to routine laboratories.

Only few papers are dealing with questions arising, such as the influence of fast MS operation on sensitivity, repeatability of measurements and quality of mass spectra, when slower scanning quadrupole MS instruments are utilized for detection of narrow peaks in fast GC on narrow-bore capillary columns. Hada et al. [6] and Korenková et al. [7] have used quadrupole MS as detectors in fast GC on narrow-bore columns for determination of pesticide residues. In both papers satisfactory results were obtained with regards to analytes quantitation in full scan and selective ion monitoring

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doi:10.1016/j.chroma.2005.06.090

modes, but there is neither specification and/or discussion on settings of MS parameters and its impact on satisfactory chromatogram reconstruction when narrow peaks are detected, nor data on the measured peaks width. Dallüge et al. [8] utilized quadrupole MS as a detector in the resistively heated GC and published the results of quantitative analysis. Also the relationship between the peak area measurements repeatability (expressed as the relative standard deviation (RSD)) and the question of data points across the peak is discussed. The number of scan data points—six obtained across the peak was considered as satisfactory [8].

In literature there are general discussions concerning how many data points are actually needed to define the chromatographic peak; the values in the ranges of 15–20 was found to be the minimum for the accurate representation of a peak [9], but in other papers [4,10,11] also three to four data points are published that work well enough for quantitative analysis.

In this work possibilities of commercial quadrupole MS detector Agilent 5973N coupled to fast GC on a 0.15 mm I.D. narrow-bore column are studied for analytes of the wide range of physico-chemical properties. The 0.15 mm I.D. columns will allow more flexibility in loadability, sample introduction (flow rate) and operate at lower inlet pressures when compared to 0.1 mm I.D. columns [12]. Important searched parameters are the relationship between scan rate and sensitivity and repeatability of measurements (peak area, signal to noise ratio (S/N)) and the quality of the obtained spectra in full scan mode. In selective ion monitoring (SIM) the relation between dwell time and peak shape, response and S/N ratio were searched.

2. Experimental

GC–MS measurements were performed on an Agilent 6890N GC equipped with a programmed temperature vaporizer (PTV) connected to 5973N MSD (Agilent Technologies, Avondale, PA, USA) providing maximal scan range 1.6–800 amu with maximal scan rate 5650 amu/s. For tuning autotune procedure available through ChemStation software was used, perfluorotributylamine (PFTBA) was default calibration standard. Chromatographic column CP-Sil 8 low bleed/MS 15 m long, 0.15 mm I.D., film thickness 0.15 μm, Varian (Middleburg, The Netherlands) was connected to 1 m long 0.32 mm I.D. retention gap (Supelco, Bellefonte, USA) with press-fit connector (Agilent Technologies, Switzerland) and polyimide resin (Supelco, Bellefonte, USA).

Helium with purity 5.0 (Linde Technoplyn, Bratislava, Slovak Republic) was used as a carrier gas in the constant flow mode 1.2 ml min^{-1}. PTV inlet was operated in a cold splitless mode with the following temperature programme: initial temperature 150 °C, ramp 400 °C min^{-1} to 350 °C and splitless time 1.13 min. The injection volume was 1 μl. The following oven temperature programme was used: initial temperature 100 °C hold 1.13 min, ramp 24 °C min^{-1} to 300 °C hold 1.29 min. In this study, six *n*-alkanes and 21 pesticides belonging to different chemical classes were used. Their list with chemical class, retention time and target ions for full scan and target ions and qualifiers for SIM is given in Table 1. Standards of the used *n*-alkanes (C_{12}, C_{14}, C_{16}, C_{18}, C_{22} and C_{26}) were obtained from Fluka (Buchs, Switzerland), standards of pesticides were obtained from different sources and were of purity >95%. Stock solutions of *n*-alkanes and pesticides was prepared at approximate concentration 0.5 mg ml^{-1} and were stored in a refrigerator (−18 °C). Working solutions were prepared by dilution of stock solutions in toluene.

3. Results and discussion

3.1. Full scan experiments

In Agilent 5973N mass selective detector, the data acquisition rate—scan rate in full scan mode is given by the number of samples (abundance measurements of each mass before going on to the next mass during the measurement of one cycle) that are taken and afterwards saved as one data point. The number of measurements of each mass is given by 2^N, where N is the number set by operator in the ranges of 0–7 only for integers. The other parameter controlling scan rate is the range of scanned masses. The gain in speed of a data acquisition rate by narrowing the scanned mass range is advantageous only up to the highest mass of an expected molecular ion to prevent the loss of information for the proper compound identification. However, the gain in scan rate controlled by narrowing the range of masses to be scanned is less powerful than by setting the number of samples.

In our experiments scans were performed over the range of masses 50–510 *m/z* (molecular ion of deltamethrine is at *m/z* 503 with ion cluster up to *m/z* 509). A solution of *n*-alkanes and pesticides in toluene with approximate concentration 3 ng μl^{-1} was used. For the data acquisition the following sampling rates were used: 0–4 resulting in scan rates 10.68, 5.98, 3.18, 1.64 and 0.84 scan s^{-1}, respectively, indicated by the ChemStation software. However, from the obtained data, slightly lower scan rates were calculated; 10.60, 5.93, 3.17, 1.63 and 0.83 scan/s for samples 0–4, respectively.

Peak widths at half heights were dependent on a compound and elution time and were in the range of 0.5 s for *n*-C_{12} with retention time 2.67 min to 1.07 s for deltamethrin with elution time 9.94 min; elution times and peak widths at half height are presented in Table 1. Measured peak widths are below the range 1–3 s used for defining the fast GC according to van Deursen et al. [3]. Chromatogram with all measured compounds obtained in full scan mode is presented in Fig. 1. Chromatographic conditions were optimized (column carrier gas flow according to Blumberg [13] and oven temperature gradient was set to 10 °C per void time [14]). In Fig. 2, the average peak areas (eight replicates), its RSDs and (S/N) ratios of *n*-alkane C_{22} and selected pesticides are