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Gas chromatography–mass spectroscopy optimization by computer simulation, application to the analysis of 93 volatile organic compounds in workplace ambient air

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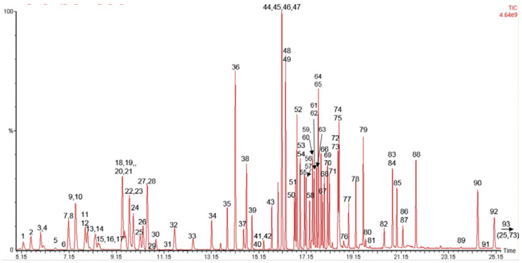
HIGHLIGHTS

- Determination of GC thermodynamic retention parameters from only few preliminary experiments.
- Simulation of GC separation for any kind of temperature program.
- Identification of coelutions and automatic ion selection for MS quantification.
- Example of application to two sets of VOC with 16 and 93 compounds.
- Such methodology can be easily transposed to any set of volatile compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

GC–MS optimization method including both advantages from chromatographic separation and mass spectrometric detection was designed for a set of 93 volatile organic compounds. Only a few experiments were necessary to determine the thermodynamic retention parameters for all compounds on a RTX-VMS column. From these data, computer simulation was used in order to predict the retention times of the compounds in temperature programmed gas chromatography. Then, an automatic selection of ions from the NIST database was performed and compared to the optimum conditions (full separation of VOC). This simulation-selection procedure was used to screen a numerous set of GC and MS conditions in order to quickly design a GC–MS method whatever the set of compounds considered.

Volatile organic compounds (VOC) includesa variety of chemical which may have adverse health effects. For numerous VOC, the National Institute for Health and Safety (INRS) in France has set the regulatory values for professional exposition and it should regularly check that these values are respected by measuring the concentration of atmospheric pollutants in ambient air. Ambient air quality has been already evaluated for several workplaces such as photocopy center [1–3], LCD manufactures [4] or semi conductor foundries [5], but the number of VOC studied was limited, even if there is a clear increase of the tendency to characterize the exposure to every single VOC in workplace environments. For gas chromatography–mass spectrometer (GC–MS) studies with larger number of VOC [6,7], analysis were performed by selecting only one specific ion per compound assuming no

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interference during quantification. Such method is questionable when numerous compounds can coelute in the detector leading to potential isobaric interferences. For the University Claude Bernard Lyon1, due to a wide field of researches conducted, 93 compounds have been defined as critical and an analytical procedure based on automated thermal desorption-gas chromatograph-mass spectrometer (ATD–GC–MS) was needed. With such large set of compounds, a "trial and error" approach cannot be considered and a more systematic strategy based on the fundamental thermodynamic of chromatography and mass spectral library appeared to be the most valuable alternative to design GC–MS analysis.

Even if the basics of gas chromatography have been designed in the 60s [8,9], predictive models for GC separation have been intensively discussed only in the late 80s and early 90s, when computer facilities became available in chemistry labs. In 1987, E.V. Dose [10,11] achieved the simulation of gas chromatographic retention and peak width, including the effect of carrier gas. This author proposed to use the thermodynamic quantities ΔS and ΔH as a new set of retention indexes, and used them as initial thermodynamic data for simulation. Later, the same author [11] also designed an optimization of the chromatographic temperature program based on these indexes and demonstrated the convergence of the optimization program to the experimental optimum temperature program. During the same year, Sanz et al. [12] implemented a mathematical approach for the prediction of the separation of 31 volatile components of wine flavors. Le Vent and Taylor [13–17] started a series of paper dedicated to the calculation of programmed temperature gas chromatography characteristics from isothermal data. In 1990, Snyder's group [18] demonstrated that the initial thermodynamic data required for simulation can be obtained from two experimental runs using programmed-temperature GC rather than a large number of time consuming isothermal runs. In the following years, several authors [19–24] confirmed that computer simulation can be a reliable approach in method development for gas chromatography. The simulation of linear head pressure program was introduced by Gonzalez and Nardillo [25–27] to study the effect of several systems of flow control. More recently, developments were dedicated to the numerical resolution of the different models equations of gas chromatography [28,29] and only few applications related to GC temperature programmed optimization have been reported [30,31].

The global strategy for GC temperature programmed optimization was, up to now, always performed assuming a universal detector (non specific) which required a full separation of all solutes. However, nowadays MS detectors are fully available and are widely used, even in control analysis laboratories. Because the signal can be recorded for each m/z values, when two compounds reach the detector at the same time, an appropriate set of ions can be defined to selectively record independently the signal of each compound. With such detector, the full chromatographic separation of all solutes in a mixture will not be required anymore. However, the selected set of ions used for quantification and confirmation of a compound has to be defined in order to avoid any isobaric interference but also has to lead to significant signal in the detector. So, ions with the highest contribution in the fragmentation pattern have to be selected in order to lower the limit of quantification of the analytical method, but still avoiding isobaric interferences.

In this paper, a chromatographic optimization method taking into account the advantages of mass spectrometric detection was defined. A preliminary set of experiments was necessary to determine the thermodynamic retention parameters of the compounds, the optimization procedure was fully described for a set of 16 compounds, and finally the optimization procedure was used for the separation of 93 VOC.

1. Material and methods

A total of 93 VOC (isopentane, pentane, diethyl ether, ethanol, iodomethane, 2-propanol, dichloromethane, acetone, hexane, methyl tert-butyl ether, acetonitrile, di-isopropyl ether, 1,1-dichloroethane, acrylonitrile, allyl alcohol, 1-propanol, vinyl acetate, cyclohexane, chloroform, ethyl acetate, methyl acrylate, ethyl acrylate, carbon tetrachloride, tetrahydrofuran, methyl ethyl ketone, 2,2,4-trimethylpentane, heptane, pentafluorobenzene, benzene, tert amyl methyl ether, isobutanol, isopropyl acetate, methylcyclohexane, 1-methoxypropan-2-ol, propyl acetate, octane, toluene, pyridine, methyl isobutyl ketone, ethyl methacrylate, ethylene glycol, n-butyl acetate, 2-hexanone, 2-picoline, nonane, ethylbenzene, chlorobenzene, 1-methylbutyl acetate, L-ethyl lactate, m+p-xylene, isopentyl acetate, propylene glycol monomethyl ether acetate, o-xylene, 5-methylhexan-2-one, n-butyl acrylate, cumene, 2-heptanone, pentyl acetate, 3-heptanone, 2-butoxy ethanol, decane, propylbenzene, bromobenzene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-chlorotoluene, cyclohexanone, 5-methylheptan-3-one, 2-phenylpropene, 1,2,4-trimethylbenzene, 2-(2-methoxyethoxy) ethanol, limonene, 1,2,3-trimethylbenzene, benzaldehyde, undecane, octanal, 2-methoxymethylethoxy-propanol, 1,2-dichlorobenzene, 2-butoxyethyle acetate, benzylalcool, dodecane, nonanal, nitrobenzene, 2-(2-butoxyethoxy)ethanol, decanal, naphtalene, 2-nitrotoluene, geraniol, tetradecane, nicotine, hexamethylbenzene, resorcinol, hexadecane, coumarine) have been obtained from Sigma Aldrich with purity higher above 99%. Stock solution was prepared by weight in methanol (50 mg of each compounds in a total volume of 50 mL) so the final concentration in the standard mixture solution was close to $1.0\,\mathrm{g\,L^{-1}}$ for each compound. The stock solution was stored in the fridge at 4° and diluted (v/v) with methanol just prior to use. 1 μL to 5 μL of the standard mixture solution was transfer to an adsorption tube by the mean of vaporization of the solution in a GC injector (150 °C) using N_2 as carrier gas ($100\,\mathrm{mL\,min^{-1}}$, 2 min). The tube was maintained at 35 °C in the GC oven for solute adsorption and two tubes in series were used (see fig. 1S in supplementary data). The analysis of the second tube has been performed in order to check the absence of compounds on the second tube (i.e. all compounds have been entirely adsorbed on the first tube). The tubes were filled with Tenax sorbent (250 mg) purchased from Tera Environnement, France. Tube preparation was previously conducted at 300 °C, 60 min with a nitrogen flow of $70\,\mathrm{mL\,min^{-1}}$. For considerations on such standard preparation, readers can refer to Kim et al. studies [32,33].

The analysis was performed by an automatic thermal desorption unit coupled to a GC/MS (ATD 650, GC Clarus 580, MS Clarus 600T PerkinElmer, France). Helium (purity 6.0, from Linde Gaz, France) was used as carrier gas, as well as for desorption gas. Tube desorption was performed at 280 °C during 15 min with a He flow of $40\,\mathrm{mL\,min^{-1}}$. The trap used in ATD 650 was an air monitoring trap maintained at −30 °C during the primary desorption and flash-heated at 300 °C for the secondary desorption. The analytical column used was a Rtx-VMS (Restek, France) capillary column of 60 m, 0.25 mm I.D. and 1.4 μm film thickness. The transfer line connecting ATD to GC–MS was at 220 °C. Mass acquisition was performed with an electron ionisation mode (Ion Energy 70 eV, Full Scan mode from $m/z = 19$ to 169, scan time 0.1 s). The fragmentation pattern data from 2012 NIST/EPA/NIH Mass Spectral Library (EI) were used for the selection of fragments.