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Trace analysis of benzene, toluene, ethylbenzene and xylene isomers in environmental samples by low-pressure gas chromatography–ion trap mass spectrometry

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Abstract

A rapid determination of benzene, toluene, ethylbenzene and the three xylene isomers (BTEX), including a nearly baseline separation of the xylene isomers in environmental samples within 1 min has been carried out using low-pressure gas chromatography–ion trap mass spectrometry (LP-GC–IT-MS). In order to evaluate the different parameters which may influence the performance of LP-GC–IT-MS, different column and mass spectral parameters were varied. Comparing LP-GC–IT-MS with the conventional equivalent, we obtained excellent detection limits as well as a good RSD of 8–13% in addition to a much shorter analysis time. In order to evaluate LP-GC–IT-MS for use in environmental samples, we determined BTEX in air.
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1. Introduction

Shorter analysis times make it possible to analyze more samples per day and, hence, reduce the cost. Shorter columns together with a reduction in column diameter (0.15 mm I.D. or less) have been used with growing popularity [1–5]. The resulting reduction in analysis times and, consequently, in peak widths, makes a fast scanning mass spectrometer, e.g. the time-of-flight analyzer, necessary in order to get enough data points for the signals. However, this analyzer, although increasingly popular, is not abundantly present in conventional laboratories, in contrast with the ion trap or quadrupole analyzer. As

demonstrated by LeClercq and co-workers [6–11], a gain in speed can be obtained by operating a column at vacuum-outlet conditions as compared with atmospheric outlet conditions. This gain in speed becomes considerable for short and/or wide-bore columns. For such columns a gain in speed of a factor of 10 can easily be obtained. De Zeeuw et al. [12] demonstrated the use of 0.53 mm I.D. (i.e. a wide bore capillary) columns in combination with GC–ion trap MS (GC–IT-MS). This method was commercialized by Varian under the name Rapid-MS. Operating the capillary under the reduced pressure of the mass spectrometer permits short wide bore columns (typical length 10 m) to be used with higher gas velocities. On the injector side, a short restriction column (0.6 m×0.25 mm I.D.) is positioned in front of the wide-bore column, connected to the latter with a zero

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death volume connector. The goal of this is to maintain atmospheric injection conditions and to deliver a constant gas flow. The optimum linear velocity in a column depends on the column pressure. In practice, this optimal velocity, using a 0.53 mm column operated at reduced pressure lies a factor of four higher than when using GC columns under normal pressures (i.e. using 0.25 or 0.32 mm columns, having optimal velocities around 25 cm/s), resulting in flow-rates of 90–100 cm/s for helium as the carrier gas. With these velocities and while using a shorter column (10 m instead of 30 m, resulting in a reduction of a factor of 2.5) a reduction of the analysis time by a factor of 10 is theoretically possible. Practically, however, this factor could only be reached for isothermal analyses. For thermal programmed GC analyses, lower reduction factors (i.e. a factor of 3–7) were obtained. Due to the use of wide bore columns with their relatively large internal diameter, Rapid-MS produces broad peaks with typical peak widths at base of 1.6 s (for a component with $k=3$), compared with 0.28 s for a 3 m×0.10 mm column. This makes it possible to use a conventional low-cost ion trap analyzer as the mass spectral detector. In addition, at the high velocities used, a higher peak results and therefore the signal-to-noise ratio (S/N) improves by a factor of around three. Low detection limits (LODs) result from this characteristic. A further advantage is the resulting low elution temperatures (and, hence, low bleed). One disadvantage of this technique is a (relatively) small loss in the number of theoretical plates and, consequently, in separation efficiency. However, using a mass spectrometer, a total chromatographic separation of different compounds is often not necessary, as long as the mass spectral data are different enough. This is not the case when isomers or related compounds have to be analyzed, like in the benzene–toluene–ethylbenzene–xylenes (BTEX)-mixture discussed here. Finally, since we use a wide bore column, the loadability of the column will be enhanced.

De Zeeuw et al. [12] performed analyses using a dimethylpolysiloxane column only. The scope of this work was in the first instance to attain a separation between the different compounds in a BTEX-mixture, including a full separation between the xylene isomers. A separation in a short time, i.e. within 1 min, could be of important economic interest, since the BTEX compounds are regularly encountered in both environmental and petrochemical samples. Until now, the different xylene isomers could only quantitatively be determined using relatively long analysis times. With respect to this goal, we evaluated the Rapid-MS technique, using different columns and different chromatographic parameters. Furthermore, the robustness of the technique was tested. Finally, we analyzed a series of air samples, in order to evaluate the technique for real applications.

2. Materials and methods

2.1. Instrumentation

For all the experiments, a Varian Saturn 2000 ion trap MS system was used in combination with a Varian 3800 gas chromatograph (Walnut Creek, CA, USA). The GC had a universal injector (Varian 1079), used in the split mode. Samples were introduced using an 8200 Varian autosampler. The different gas chromatographic and mass spectral parameters were varied as described in Table 1.

Six different columns were tested: a non-polar CP-Sil 8 (10 m×0.53 mm I.D.; $d_f=1$ μm, Varian-Chrompack, Middelburg, The Netherlands), a polyethylene glycol CP Wax 52 (10 m×0.53 mm I.D.; $d_f=1$ μm, Varian-Chrompack), a polyethylene glycol CP Wax 52 (10 m×0.53 mm I.D.; $d_f=2$ μm, Varian-Chrompack), a polyethylene glycol CP Wax 57 (10 m×0.53 mm I.D.; $d_f=1$ μm, Varian-Chrompack), a polyethylene glycol CP Wax 57 (15 m×0.53 mm I.D.; $d_f=1$ μm, Varian-Chrompack), and a polar ChiraSil Dex (10 m×0.53 mm I.D.; $d_f=1$ μm, Varian-Chrompack). All of them were coupled to a non-coated restriction column of 60 cm×100 μm I.D. (Varian-Chrompack) by a single ferrule column connector and a vespel ferrule 0.53–0.25 mm I.D. Helium (Air Liquide, Liège, Belgium) was used as the choice of reagent gas in all cases.

2.2. Solvents and standards

All reagents used were of analytical reagent grade. Benzene, toluene, 2-fluoro-toluene, [^{2}H$_8$]toluene (toluene-d$_8$; I.S.), p-xylene, m-xylene, and o-xylene

Table 1
Chromatographic and mass spectrometric parameters studied for optimisation of BTEX analysis using the Rapid-MS technique (LP-GC–IT-MS). Optimised values were recorded on a ChiralSil Dex CB column (further details: see Section 2)

Parameter	Studied range	Optimised value
Rate ($^{\circ}$C min^{-1})	5–90	80 [40 $^{\circ}$C (0.25 min)$\rightarrow$100 $^{\circ}$C]
Split ratio	4–400	100
Injector temperature ($^{\circ}$C)	170–270	200
Flow pressure (p.s.i.)[a]	8–16	15
Injection rate (μl s^{-1})	0.5–10	10
Transfer line temperature ($^{\circ}$C)	80–220	220
Column length (m)	10 and 15	10
Film thickness (μm)	1 and 2	1
Scan time (s scan^{-1})	0.22–0.8	0.25
Multiplier offset (V)	-20 to $+50$	0
Emission current (μA)	20–60	50
Target total ion current (TIC; counts)	10,000–30,000	10,000
Max. ionization time (μs)	10,000–50,000	40,000

[a] 1 p.s.i. = 6894.76 Pa.

were purchased from Aldrich (Steinheim, Germany). Dichloromethane was purchased from Merck (Darmstadt, Germany), pentane from Fluka (Steinheim, Germany) and CS_2 was purchased from Riedel-de Haën (Seelze, Germany).

2.3. Sampling and extraction of the air samples

Air samples were collected using Radiello diffusive samplers (Fondazione Salvatore Maugeri, Padova, Italy), filled with activated charcoal. The samples were taken at different places in the Antwerp region (A12, beside the A12 highway Antwerp–Brussels; P1 and UIA are different locations at the university campus; PH (Pothoekstraat) is a residential area; PB (Prins Boudewijnlaan) is a heavy traffic crossing point). Sampling time was 7 days. After sampling, the samplers were desorbed using 2.5 g of dichloromethane. This extract was then analysed using the conditions mentioned in Table 2.

3. Results and discussion

3.1. Influence of the solvent

For the separation of the compounds, the type of solvent in which the BTEX compounds were dissolved appeared to be of great importance. With respect to the chemical desorption of these compounds from activated charcoal tubes, only carbon disulfide and dichloromethane were powerful enough to extract the compounds from the adsorbents. Hence, with respect to our goal of determining BTEX in air samples we were restricted to these solvents (alkanes, e.g., are incapable of desorbing BTEX from the charcoal tubes, as was verified experimentally using calibrated charcoal tubes). From these solvents, we observed that dichloromethane gave the best results, although on most stationary phases co-elution of benzene and the solvent peak could not be avoided. CS_2 gave extensive

Table 2
Repeatability experiments (repeated injections ($n=20$) under the conditions, mentioned in Table 1)

Component	Calibration curve equation	R^2	LOD (pg on column)	LOD (μg m^{-3})	RSD (%)
Benzene	$y = 0.0263 + 0.1456x$	0.9992	8.32	0.010	12.7
Toluene	$y = 1.606 + 0.6793x$	0.9995	6.12	0.008	9.6
p-Xylene	$y = 0.0189 + 0.4467x$	0.9989	9.32	0.014	8.4
m-Xylene	$y = 0.0396 + 0.4350x$	0.9996	4.86	0.007	12.4
o-Xylene	$y = 0.0185 + 0.3409x$	0.9988	9.44	0.014	9.6
Ethylbenzene	$y = 0.0246 + 0.4913x$	0.9994	7.13	0.010	13.3

tailing of the solvent peak on most polar columns (but not on the CP Sil 8 column). This resulted in a high background signal and, hence in poor signal-to-noise ratios and detection limits. This tailing was due to the column, since changing the injector or the liner did not give any improvement. Changing the film thickness from 1 μm into 2 μm only gave longer retention times and an even longer tailing of the solvent peak. Hence, in the following experiments, we only worked with a film thickness of 1 μm.

3.2. Influence of the stationary phase and column length

In addition to the commercially available CP Sil 8 CB Rapid-MS column, we coupled existing wide bore columns to a restrictor column. The different stationary phases used were a dimethylpolysiloxane phase (CP Sil 8 CB), two polyethylene glycol phases (CP Wax 52 CB and CP Wax 57 CB) and finally a cyclodextrin modified phase (CP-ChiraSil Dex CB). A nearly full separation in less than 1 min of the different xylene isomers could only be achieved using the latter column (Fig. 1a), while for the other columns only the CP Wax 52 gave any separation between the ethylbenzene, *para*- and *ortho*-xylene isomers (Fig. 1b; conditions: initial temperature, 35 °C (holding, 0.6 min) going to 90 °C (40 °C/min); split 1/50 and injection volume, 0.5 μl). When comparing these results with a conventional column (e.g. for the CP Wax 52 CB: Fig. 2a), one can derive two conclusions.

1. The total analysis time has been reduced by a factor of eight.
2. The resolution was reduced enormously in the case of the CP Wax 52 column, making quantitative determination of ethylbenzene, *para*- and *meta*-xylene, impossible, while nearly baseline separation was obtained for the modified cyclodextrin column.

Another possibility implied a slightly longer column, i.e. 15 m instead of 10 m. This resulted, however, only in a longer analysis time, without any improvement of the resolution. This did not surprise us, since in the case of a 15-m column, there is apparently no longer an appreciable pressure drop in the beginning of the column. Consequently, a col-
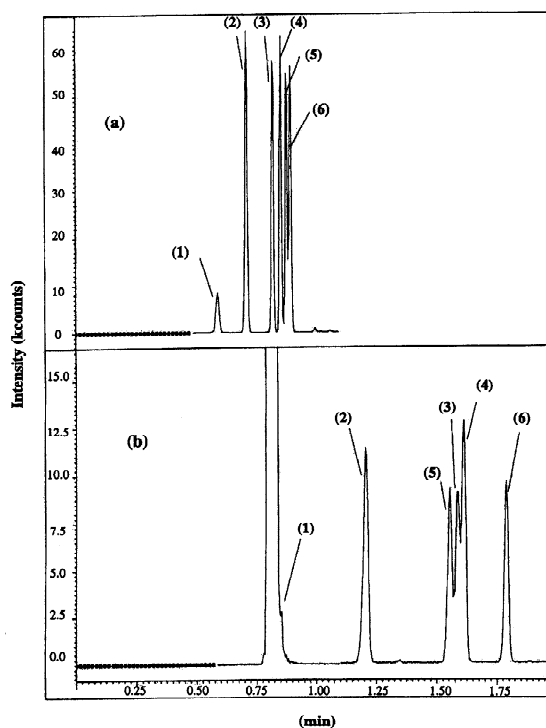

Fig. 1. Comparison of the analysis of a standard BTEX mixture using (a) a ChiraSil Dex CB column (for conditions, see Table 1) and (b) a CP Wax 52 column (both 10 m×0.53 mm I.D.; $d_f = 1$ μm). Identification of compounds: (1) benzene; (2) toluene; (3) *para*-xylene; (4) *meta*-xylene; (5) ethylbenzene; (6) *ortho*-xylene.

umn length of 10 m appears to be the optimum length.

3.3. Influence of the temperature programming and mass spectral parameters

De Zeeuw et al. [12] have stated that theoretically isothermal conditions would give a maximum gain in analysis time reduction. However, an isothermal analysis of the sample did not give any further improvement using the ChiraSil Dex column, since there was an incompatibility between a short analysis time and the higher analysis temperature, which caused a reduction in peak resolution. This was especially the case for benzene, which could not be resolved from the solvent peak. Very fast temperature program rates (80 °C/min) gave, however, a better result; when starting at a temperature of 40 °C, this
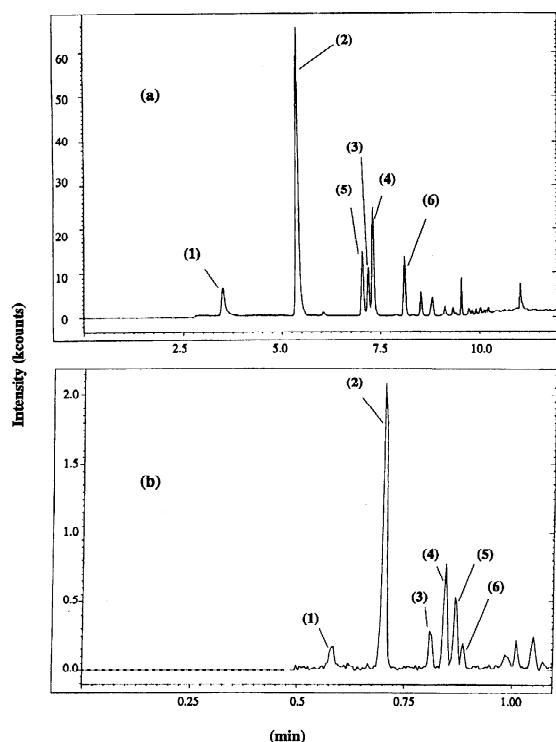
Fig. 2. Comparison of the determination of BTEX in an air sample using (a) a CP Wax 52 column (25 m×0.32 mm I.D.; $d_f = 1$ μm; conditions: 40 °C (holding 3 min) to 100 °C (10 °C/ min); split 1/4; injection temperature, 175 °C) and (b) a ChiraSil Dex CB column (for conditions, see Table 1). Identification of compounds: (1) benzene; (2) toluene; (3) *para*-xylene; (4) *meta*-xylene; (5) ethylbenzene; (6) *ortho*-xylene.

led to a very fast analysis, yielding nearly baseline separation of the different isomers.

Also, the mass spectral parameters were varied, but this did not give an appreciable effect, except for the scan time, which had to be adjusted to four scans per second, in order to have a better peak profile.

The different conditions, both gas chromatographic and mass spectral, are summarized in Table 2 and the analysis of a standard BTEX mixture, as carried out using these conditions, is depicted in Fig. 1a.

3.4. Analytical figures of merit

In order to further evaluate the method, we calculated analytical parameters like detection limits of the different BTEX compounds, linearity and precision. The detection limits of the different compounds, as obtained from the calibration curve, were around 10 pg on-column for all compounds, which is better than in the conventional analysis. For environmental analysis, using diffusive samplers with a sampling time, we calculated detection limits of around 0.01 μg/m^3 of the different compounds in air.

Using a series of repeated injections, a precision of 5–17% was obtained for the different components. Calibration curves and correlation coefficients are also given in Table 3.

3.5. Analysis of a series of environmental air samples

In order to evaluate the performance of the Rapid-MS technique in environmental samples, we sampled air using diffusive sampling tubes, filled with activated charcoal. After desorption with dichloromethane, which appeared to be the best solvent for analysis, we obtained similar results as with conventional columns. A comparison is given in Fig. 2a (conventional column; CP Wax 52) and 2b (low-pressure GC–IT-MS; CP Chirasil Dex CB). The results of this campaign are given in Table 3.

Table 3
Results of the air samples, taken at various places in the Antwerp agglomeration

Sample[a]	Concentration (μg m^{-3})					
	Benzene	Toluene	Ethylbenzene	*p*-Xylene	*m*-Xylene	*o*-Xylene
A12	6.06	4.00	5.43	2.53	7.22	1.6
P1	<0.010	<0.008	1.31	2.05	2.02	<0.014
PB	3.41	1.50	3.30	1.63	4.06	0.8
PH	<0.010	<0.008	1.38	<0.014	2.78	<0.014
UIA	<0.010	<0.008	1.41	<0.014	2.21	<0.014

[a] For abbreviations, see Section 2.

4. Conclusions

In this work we demonstrated the successful application of low-pressure GC–IT-MS as an affordable and readily introducible alternative for other fast gas chromatographic methods. Using standard samples, we found that a column length of 10 m and fast temperature programs give the best results.

We further applied this technique to environmental samples and found it to be useful as well for air samples. In the future we wish to further elaborate the method, both for the series of compounds analyzed and for the number of applications (especially petrochemical samples).

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