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Promises of a new versatile field-deployable sorbent tube thermodesorber by application to BTEX analysis in CH_4

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ABSTRACT

Characterizing trace compounds in gaseous matrices such as natural gas is challenging owing to the low concentrations and the intricate interactions between compounds and matrices present. In contrast to whole gas sampling methods, direct *in situ* gas sampling with preconcentration of trace compounds on adsorbent tubes followed by thermal desorption and gas chromatography coupled to mass spectrometry (TD-GC–MS) is a powerful method enabling to screen unknown and targeted trace compounds with low detection limits and where moreover sample transfer and associated loss and contamination risks are avoided. Here, a new versatile, field-deployable thermodesorber prototype ('nCx-TD', *nCx Instrumentation*, Garlin, France) fitted with self-assembled purpose-built Tenax TA adsorbent tubes is presented. Its desorption and GC-injection performances are investigated using a 10 ppm_v BTEX in CH_4 synthetic gas and by contrasting the results to those obtained by solid phase microextraction (SPME) and direct injection of the synthetic gas. Unlike most commercial thermodesorbers, the nCx-TD is characterized by a fast "plug" injection without re-focusing trap, leading to high chromatographic peak resolutions. Between the closely eluting ethylbenzene and *m*- and *p*-xylene isomers, the Gaussian resolution obtained at a concentration of 10 ppm_v with the nCx-TD was 2.9 while that obtained by SPME and direct injection was respectively 1.7 and 1.9. The nCx-TD-obtained peak resolutions increased significantly with the concentration (1 to 10 ppm_v) while the SPME- and direct injection resolutions remained at a low constant level across concentrations tested. A real natural gas sample was sampled through the Tenax TA adsorbent tubes and analyzed via TD-GC–MS using the nCx-TD. More than 50 distinct trace compounds were detected, opening exciting perspectives of adsorbent tube multibed configurations and direct *in situ* field sampling on adsorbent tubes with *in situ* analysis through the nCx-TD and field-portable GC's.

1. Introduction

Sampling and analysis methods for the characterization of trace constituents in gaseous matrixes have been developed since the 1970′s notably by the United States Environmental Protection Agency due to the rising environmental and public health concerns with regards to dramatic atmospheric, workplace or urban air pollution events in the 1950–60′s [1–3]. Most studied trace compounds in air are volatile organic compounds (VOC) [4–6], halocarbons [7], volatile Sulphur compounds [8–10] and volatile metals(loids) (As, Sb, Sn, Hg, Pb …) [11–13]. In parallel, analogous methods began to be developed for the analysis of trace compounds in landfill gas and natural gas owing to industrial, safety and occupational health concerns about the damaging effects of some compounds on the integrity of gas production, transport and final-use infrastructures [14,15]. Trace compounds commonly investigated in natural gas are [14] paraffinic and aromatic hydrocarbons, halocarbons, oxygenated organic compounds, inorganic and organic Sulphur compounds [16], inorganic and organic metallic compounds and metalloid species [17–21].

Gas sampling is the first and most critical analytical step to characterize trace compounds. Gas matrices such as air and natural gas are complex systems consisting of gas-, condensate- (or aerosols) and solid phases (e.g. fine particles) [6,22]. Sampling and monitoring trace

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List of abbreviations

BTEX	benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene
CAR	Carboxen
GC	gas chromatography
HS	headspace sampler
MS	mass spectrometry
N_2	dinitrogen gas
nCx-TD	new thermal desorber prototype by *nCx Instrumentation*
PDMS	polydimethylsiloxane
PRS	pressure regulating system
SPME	solid phase microextraction
TA15	self-assembled 15 mg Tenax TA adsorbent tube
TD	thermal desorption / thermal desorber

compounds is therefore challenging since they may partition into these different phases [20], in view of their low concentrations and the fact they lurk in mixtures of (in)organic, metallic and metalloid species having different physicochemical properties and potentially reacting with each other. Collected samples must be representative of the effective gas composition at a given time and under the prevailing gas pressure and temperature. The sampling procedure must ensure the stability of sampled compounds (no loss, no degradation) during the storage phase between sampling and analysis. Two gas sampling categories are distinguished: whole gas sampling versus gas sampling with enrichment ('trapping', 'preconcentration') of targeted trace compounds [6,12,23,24]. In whole gas sampling a bulk gas volume is collected in a specific vessel: sampling bags made of different polymers, aluminum or stainless steel canisters, or stainless steel gas cylinders, the inner surfaces of the two latter usually being passivated with specific coatings. Profuse literature is available on the influence of the bag polymer wall type [12, 25–30] and of the internal passivation coatings of canisters [31–34] or cylinders [35], on the stability of compounds sampled in such vessels. Disadvantageous to whole gas sampling regarding the determination of trace compounds is the need for subsequent preconcentration to bring analyte levels over the detection limits of analytical apparatuses. Preconcentration of whole gas samples is often done in the lab implying vessel transport (special transport for dangerous, explosive, goods in the case of methane gases) with consequent enhanced risks of target compound losses by sorption on or permeation through the vessel walls, losses by conversion or degradation reactions between reactive species in the vessel and contaminations during sample storage periods and sample transfers [12,24,35]. Direct *in situ* gas sampling with preconcentration is therefore preferred since those issues are avoided [35–37]: the gas is passed through a dedicated small-volume support with specific affinity for only given compounds thus being retained. The gas matrix itself passes through but is not retained, hence trace compounds are preconcentrated. For the preconcentration of (halogenated) volatile organic compounds ((H)VOC), adsorbent tubes [4–6,23,38–41] and solid phase microextraction (SPME) fibers [42–45] are particularly efficient solid adsorption supports. Adsorbent tubes are nevertheless more suitable for direct field sampling: on the contrary to fragile SPME fibers rather dedicated to lab analyses, these are robust, small size (commercial tubes are typically ~6.35 mm outer diameter, ~9 cm length), easily handleable glass or stainless steel tubes packed with commercial adsorbents having high sorption affinities and capacities for the targeted compounds.

Shipment of sampled adsorbent tubes to the lab for analysis is easy, fast and secure in view of the absence of the (flammable) gas matrix [4]. Thermal desorption coupled to gas chromatography and mass spectrometry (TD-GC–MS) is the analytical technique the most widely agreed upon for the recovery, segregation, identification and quantification of complex mixtures of low concentrated VOC differing in volatilities and polarities, desorbed from adsorbent tubes [4,46–48]. TD relies on the endothermic desorption of analytes from the adsorbents. Most modern commercial TD units operate a so-called "two-stage desorption". The sampled sorbent tube is heated up to the adsorbent specific desorption temperature while a controlled flow of inert carrier gas continuously blows the gradually desorbed analytes to the outlet of the tube ('primary desorption'). Since quantitative desorption of the analytes may require a long time (5–15 min) and large carrier gas volumes depending on their volatilities and on the tube geometry [23,49], injection of this carrier gas now loaded with analytes directly into the GC column would result in the dilution of analytes in the relatively large carrier gas volume and in unfavorable large chromatographic peaks [49]. Therefore, typically only 100–200 mL of the carrier gas loaded with analytes from the primary desorption are sent to a second, smaller, downstream located re-focusing trap [23,46,49]. This trap is a tiny tube filled with similar but lesser amounts of adsorbents as the sampling adsorbent tubes [4,36,41,49–51], of smaller inner diameter (1–2 mm) and maintained at low temperatures (*e.g.* −30 [51],−10 [49],−5 °C [50]). Analytes are adsorbed ('re-focused') on this trap whereupon it is itself thermally desorbed ('secondary desorption') by rapid heating (up to 100 °C/s [46]) with an ultra-tiny volume of carrier gas (typically 100–200 μL) instantly transferring the analytes into the GC column via a heated transfer line (~200 °C [23,46,49]), as such creating a 'flash' or 'plug' injection resulting in favorable narrow chromatographic peaks. The preconcentration power of this method is determined by the carrier gas volume eventually injected in the GC by the refocusing trap: if analytes from a 100 L gas sample are quantitatively transferred to the GC column into 100 μL final carrier gas, the concentration enhancement factor is 10^6 [46].

To the authors' knowledge, no commercial field-deployable thermodesorber has ever been developed while direct *in situ* analysis of sampled adsorbent tubes with field-deployable TD units coupled to field-portable GC–MS would erase sample transport, storage and associated sample alteration risks. 'Real time' assessment of a gas composition can furthermore be crucial to monitor hazardous compounds and take immediate risk management action when measured values exceed a defined level [21].

Therefore, here, a new versatile, single-stage desorption and field-deployable adsorbent tube TD prototype is presented. As a first prototype development step, the ability of the new TD to generate high chromatographic peak resolutions when coupled to a bench-top GC–MS is demonstrated. The new TD prototype is tested by the thermal desorption of a synthetic BTEX (benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene) gas mixture in CH_4 preconcentrated onto self-assembled purpose-built Tenax TA adsorbent tubes. Tenax TA, a macroporous 2,6-diphenyl-*p*-phenylene oxide polymer, is widely used for the preconcentration of semi-VOC in gases [23,38,39]: its relatively low specific surface area (35 m^2g^{-1} [52]) provides it with a sufficient adsorption strength yet enabling quantitative desorption of semi-VOC such as BTEX (boiling points 80 – 144.4 °C at P_{atm}). TD-results are contrasted to direct GC–MS injection and SPME of the synthetic gas. The application potential of the new TD is then illustrated by preconcentrating a real natural gas sample on Tenax TA tubes. BTEX, stemming from crude oil and natural gas [53,54], were used through this study as they have been extensively studied by means of adsorbent tubes [5,37, 39,55,56] and SPME fibers [42,44,57,58] on account of their hazardous effects on human health and environment.

2. Materials and methods

2.1. Thermodesorber prototype

The new adsorbent tube thermodesorber prototype was developed and patented by *nCx Instrumentation*, Garlin, France and will be further referred to as 'nCx-TD'. It works in 'single-stage' desorption mode,

meaning no re-focusing nor cryofocusing trap nor heated transfer line are present. Its small size and compatibility to most GC injection ports including miniaturized field-portable GC contribute to its versatility and field-deployability. Fig. 1 presents the nCx-TD, dimensioned to only accommodate custom-built glass tubes (Fig. 2). The nCx-TD is screwed on the GC inlet port via an adaptable nut and is connected to its monitor casing where to a carrier gas line (mostly Helium) and a pneumatic line (compressed air) are connected. A sampled adsorbent tube is placed manually into the nCx-TD heating core in the reverse direction as compared to the gas sampling flow direction. A computer software defines the few operational parameters of the nCx-TD (Table S1 in the Supplemental Information). The thermal desorption cycle starts at a defined safe temperature and the heating core is then heated up to the adsorbent material-specific desorption setpoint temperature. The heating rate is not linear but rather follows this pattern at 25 °C ambient temperature: from 100 to 200 °C: 140 °C·min^{-1}, from 200 to 400 °C: 100 °C·min^{-1}. During this heating phase, analytes are desorbed from the adsorbent material while the carrier gas valve is still closed, meaning volatilized analytes remain trapped in the tube. Once the temperature setpoint is reached, it is maintained during a user-defined time lapse, still without carrier gas flow. When this temperature stabilization phase is over, injection is instantly launched: two injection needles are pneumatically actuated: one piercing the upper septum of the adsorbent tube through which the carrier gas then flows, and one piercing the bottom septum of the tube which is then immediately connected to the GC-column inlet. As such, the carrier gas blows the desorbed analytes from the extremity of the tube directly into the GC column during a user-defined time lapse of as short at 5 s. This very fast, 'flash' or 'plug' injection of all analytes in a short time interval leads to narrow chromatographic peaks, justifying the non-necessity of a re-focusing trap.

2.2. Tenax TA adsorbent tube self-assembly

Empty amber glass tubes (ID 4.8 mm, L 44 cm, ActionEurope, Sausheim, France) are packed with 15 mg Tenax TA (60–80 mesh, surface area 35 m^{2}g^{-1}, Supelco, Bellefonte, PA, USA) retained between two untreated quartz wool plugs (Helios Italquartz™) (Fig. 2): a first quartz wool plug is manually inserted into the tube where after 15 ± 0.2 mg Tenax TA are sucked up inside the tube by means of a flexible vinyl tubing pushed in the tube extremity and connected to a small volumetric pump (Xylem Flojet, RS Components, Beauvais, France). A second quartz wool plug is then manually inserted on top of the Tenax TA bed to secure it. Thereupon, these 15 mg Tenax TA tubes (here after referred to as "TA15") are conditioned at 320 °C under a continuous pure nitrogen flow (99.999% purity) during 8.5 h in a purpose-built 20-positions conditioning support (aluminum 2017A, colorless anodic oxidation) installed in a disused GC oven (Fig. S1 in the Supplemental Information). Each of the 20 positions of the support's bottom plate is provided with an 11 mm o-ring (Dupont™ Kalrez® Spectrum™ metric o-ring 7075) ensuring the N_2 flow effectively enters every single tube. The oven is gently heated from 25 to 320 at 10 °C·min^{-1}. The N_2 flowrate through each individual tube varies between 140 and 510 mL·min^{-1} with an

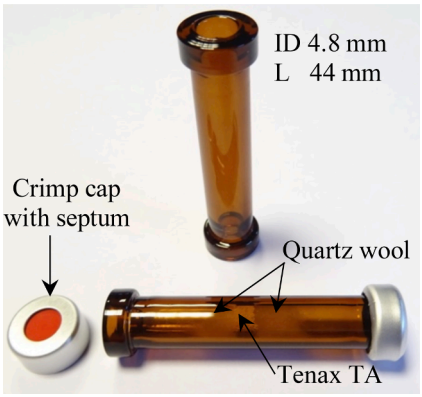


Fig. 2. Custom-built glass tube intended for packing with adsorbents and thermal desorption in the nCx-TD. ID = internal diameter, *L* = length.

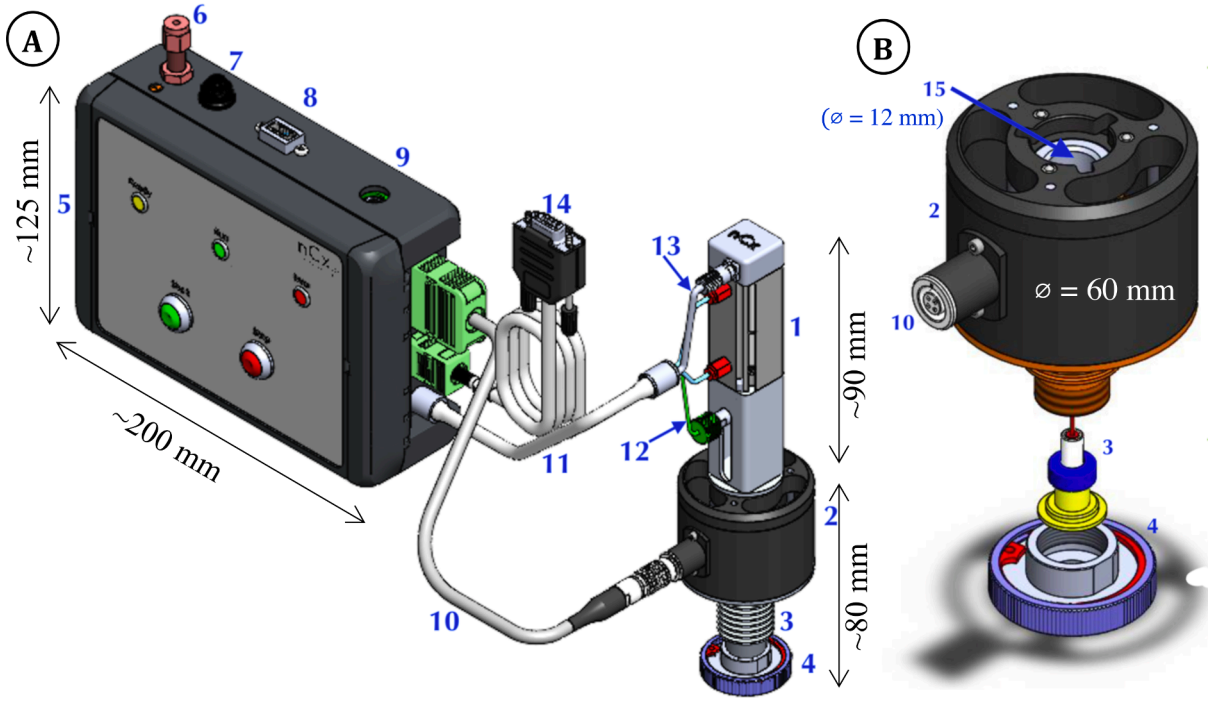


Fig. 1. Schematic of the nCx-TD. (A) 1 = injection head, 2 = heating core, 3 = injection needle, 4 = adaptable GC-fixation nut, 5 = monitor casing, 6 = carrier gas inlet, 7 = compressed air inlet (pneumatic line), 8 = USB connection to computer, 9 = electrical alimentation, 10 = monitor connection to the heating core, 11 = monitor connection to the injection head with distribution of the compressed air (12) and carrier gas 13, 14 = monitor connection to the GC for synchronization. (B) Detail of the heating core with dismantlement of the injection needle. Same numbering as in (A). 15 = adsorbent tube location.

average of 375 mL·min^{-1}. As soon as the conditioning sequence is completed and tubes cooled down to a temperature allowing manual grip, tubes are sealed with aluminum crimp caps with PTFE/silicone/PTFE septa (11 mm, high temperature ultra-low-bleed silicone, ActionEurope) and stored until utilization in individual hermetic polyethylene zip bags in a larger zip bag in a desiccator at 4 °C.

2.3. Gas samples

To assess the chromatographic peak resolution of the nCx-TD injections, a synthetic 10 ppm$_v$ BTEX in CH_4 gas mixture (700 L, 140 bar$_a$, mélange crystal, AirLiquide France Industrie) was sampled on self-assembled TA15 tubes (10 replicates), on a commercial SPME fiber with 75 µm thick Carboxen/polydimethylsiloxane (CAR/PDMS) coating (Supelco) (3 replicates) and in 20 mL crimp-cap glass vials (Chromoptic, Courtaboeuf, France) (14 replicates) as follows. The synthetic gas bottle is connected to a pressure regulating system (PRS) lowering the gas pressure to ~1.4 bar$_a$ and equipped with a final needle "n" allowing gas flow (Fig. S2). Each TA15 tube is sampled by pricking one of its septa on this needle "n" and the other septum on a needle with tubing connected to a mass flowmeter (Bronkhorst Mass-View® MV-302) (Fig. S2 A). 300 mL$_n$ synthetic gas are passed through each TA15 tube at 50 mL$_n$·min^{-1} and the gas sampling direction through the tube is recorded. Sampled tubes are stored in individual hermetic polyethylene zip bags in a larger zip bag in a desiccator at 4 °C until TD-GC–MS analysis. For the other two sampling means, 20 mL glass vials crimp-capped with PharmaFix Butyl/PTFE septa (Chromoptic) are vacuumed to 0.003 bar$_a$ (Fig. S2 point 8) and subsequently immediately filled at 1.20 bar$_a$ with the 10 ppm$_v$ BTEX-CH_4 synthetic gas by pricking the vial septum to the needle "*n*" of the PRS (Fig. S2 B). As such filled vials are stored at room temperature until analysis by either direct gas injection in the GC or by SPME. The 10 ppm$_v$ BTEX synthetic gas is sampled on a CAR/PDMS SPME fiber (handled with a SPME fiber holder for use with manual sampling, Supelco) by introducing the fiber in a vial filled as explained and exposing the fiber to the gas during 5.00 min where after it is retrieved from the vial and promptly inserted in the heated GC-inlet for analysis.

For calibration purposes, 6 BTEX concentrations C_i with i={1→6} (0,1,2.5,5,7.5,10 ppm$_v$) were generated by volumetric dilution of the 10 ppm$_v$ BTEX in CH_4 synthetic gas in pure synthetic CH_4 (≥99.9995% purity, Linde, France). Each concentration C_i was prepared in a 5 L Tedlar bag (Supelco) by transferring adequate volumes of pure CH_4 and of 10 ppm$_v$ BTEX in CH_4 synthetic gas into the bag. To keep the prepared dilutions as fresh and stable as possible in the bags, all analyzes on one concentration C_i were performed before preparing the next concentration C_{i+1}. Sampling of each concentration C_i from its Tedlar bag onto TA15 tubes, SPME and into vials (3 replicates for each sampling means) occurred as follows. 300 mL$_n$ gas is passed through the TA15 tubes at 50 mL$_n$·min^{-1} by connecting the Tedlar bag to the TA15 tube via a vinyl tubing with needle and connecting the end of the TA15 tube to a needle with vinyl tubing itself connected to the mass flowmeter (Fig. S3 A). A constant force is applied on the bag to trigger the gas flow through the TA15 tube. For the two other sampling means, 20 mL crimp-capped glass vials are first vacuumed to 0.003 bar$_a$ and then connected to the Tedlar bag mouth via a needle (Fig. S3 B). The pressure gradient between vacuumed vial and Tedlar bag (~1 bar$_a$) results in the vacuumed vial getting instantly filled with ~1 bar$_a$ gas C_i. As such filled vials are stored and analyzed by direct gas injection or SPME as described above.

Lastly, real natural gas from the lab building distribution grid ('NG-A', P ~ 1.05 bar$_a$) was sampled with the three methods on the same day. Ten TA15 tubes were individually loaded at ~80 mL$_n$·min^{-1} with 500 mL$_n$ NG-A by pricking the tubes to the grid wall valve. NG-A was also sampled in vacuumed glass vials for direct gas injections and SPME analyses (10 vials each) as described above. NG-A samples were stored as explained above until analysis.

All samples were taken at room temperature.

2.4. Analysis

All gas samples were analyzed with their respective injection technique (TD of TA15 tubes; SPME; direct gas injection) via gas chromatography (Agilent 6890A GC) coupled to mass spectrometry detection with quadrupole mass filter (Agilent 5973*Network* Mass Selective Detector) (GC–MS) programmed as in Table 1 using the MSD ChemStation E.02.02.1431 (Agilent) software and the NIST Mass Spectral Search Program version 2.0 d, 2005. Note the 200 °C temperature programmed in the nCx-TD corresponds to an effective desorption temperature of 300 °C inside the TA15 tube. Glass vials intended for direct gas injection in the GC–MS were placed in an Agilent G1888A Network Headspace Sampler (HS) with a 3 mL sampling loop programmed as in Table 1. Glass vials intended for SPME preconcentration are sampled in turn on the CAR/PDMS SPME fiber during 5:00 min as explained above whereupon the fiber is promptly inserted in the heated GC inlet (230 °C) for thermal desorption of the analytes from the fiber during the first

Table 1
Operational parameters for the GC–MS, nCx-TD and Network Headspace Sampler.

Instrument	Parameter	Value / reference
GC	Inlet temperature	230 °C
Agilent 6890A	Inlet septum for nCx-TD and direct gas injections	Premium Inlet Septa, Bleed/Temp optimized, non-stick (Agilent)
	Inlet septum for SPME injection	Molded Thermogreen® LB-2 septa with injection hole (Supelco)
	Inlet liner for nCx-TD and direct gas injections	Ultra Inert Liner, Splitless, Single taper, no wool, 4 mm ID (Agilent)
	Inlet liner for SPME injection	Inlet Liner, Direct (SPME) Type, Straight Design, 0.75 mm ID (Supelco)
	Split ratio	5 :1
	Split flow	7.5 mL·min^{-1}
	Carrier gas	Helium (quality detector 5.0, Linde, France)
	Gas saver	Off
	Column	HP-5MS, 30 *m* × 250 µm ID × 0.25 µm film thickness (Agilent)
	Constant column flow mode	1.5 mL·min^{-1}
	Carrier gas linear velocity in column	44 cm·s^{-1}
	Oven	30 °C (4 min) - 7 °C·min^{-1} - 180 °C (2 min)
MS	GC–MS interface temperature	280 °C
Agilent 5973Network Mass Selective Detector	Electron Impact Mode	70 eV
	Electron Multiplier Voltage	Relative (100)
	Selected Ion Mode (SIM)	Ions: 51, 65, 77, 78, 91, 92, 105, 106
	Dwell time	Peak resolution study: 20 ms (5.37 cycles/s) Calibration curve study: 100 ms (1.21 cycles/s)
	Resolution	'Low'
nCx-TD	Safe temperature	35 °C
	Temperature	200 °C
	Stabilization time	15 s
	Pressure	1170 mbar
	Injection time	10 s
HS	Oven	70 °C
Agilent G1888A Network Headspace Sampler	Loop	90 °C
	Transfer line	110 °C
	Vial equilibration time	10 min
	Pressurization time	0.15 min
	Loop fill time	0.5 min
	Loop equilibration time	0.1 min
	Injection time	0.5 min

5.00 min of the GC cycle where after the fiber is removed from the GC inlet. The fiber is reconditioned in the GC inlet at 280 °C during ≥30 min under He flow between each vial. NG-A natural gas sampled on TA15 tubes and NG-A vials for direct injection and SPME were analyzed as in Table 1 but with a GC-oven program of 30 (4 min) – 10/min – 250 °C (5 min), in split 1:1 and in MS-scan mode (10–450 a.m.u.) with a scan rate of 3.28 scan·s^{-1}.

2.5. Calculations

2.5.1. Chromatographic peak resolution

Three chromatographic peak resolution indicators were calculated following the IUPAC recommendations [59] between subsequently eluting BTEX peaks:

- Peak resolution $R = 2\frac{(t_2 - t_1)}{(\omega_1 + \omega_2)}$ with t_1 and ω_1 respectively the chromatographic retention time and baseline peak width of the first eluting compound and t_2 and ω_2 those of the second eluting compound between which the resolution is calculated;
- Gaussian peak resolution $R_G = 1.18\frac{(t_2 - t_1)}{(\omega_{0.5h,1} + \omega_{0.5h,2})}$ with t_i as above $\omega_{0.5\ h,i}$ the half-height peak width;
- Peak separation factor $\alpha = \frac{t_2 - t_0}{t_1 - t_0}$ with t_i as above and t_0 the retention time of a non-retained compound (here the CH_4 matrix of the 10 ppm_v BTEX synthetic gas)

2.5.2. Instrument detection limit

The instrument detection limit (IDL) for each BTEX compound was determined as 3 times the standard deviation of its corresponding peak height in the background noise of 10 blanks for each injection technique using the analytical parameters of Table 1. For TA15 tubes, 10 new conditioned tubes were used. For SPME, a single new 75 μm CAR/PDMS fiber was used that was initially pre-conditioned at 300 °C in the GC inlet under He flow. The 10 SPME fiber blanks were acquired by reconditioning the fiber between BTEX sorption experiments. For the vials, 10 vials were filled via the PRS with pure CH_4. Further, IDL for TA15 tubes and SPME were also calculated for some compounds determined in NG-A (Table 2). 10 new blank TA15 tubes and 10 SPME fiber blanks were acquired as in Table 1 but with a GC-oven program of 30 (4 min) – 10/min – 250 °C (5 min), in split 1:1 and in MS-scan mode (10–450 a.m.u.) with a scan rate of 3.28 scan·s^{-1}. Then, the target ion of each compound (Table 2) was extracted from each scan (Extracted Ion Chromatogram, EIC), each EIC was integrated on the time intervals where its compounds would elute (based on the NG-A sample data) and the corresponding blank background peak heights were recorded for IDL calculation: 3 times the standard deviation on peak heights ($n = 10$).

Table 2
Target ions for the IDL determination of compounds determined in NG-A.

Compound	Target ion
Benzene	78
Toluene	91
Ethylbenzene	91
m-,*p*-Xylene	91
o-Xylene	91
Cyclohexane	56
Heptane	43
3-Ethylhexane	43
Octane	43
Thiophene	84
Tetrahydrothiophene	60

2.5.3. Statistical tests

Linear regression analyses (least squares method) and *analysis of variance* statistical F-tests were performed at a significance level $\alpha = 0.05$ using Microsoft® Excel 16.50 to question the relationship between (1) the concentration (0,1,2.5,5,7.5, 10 ppm_v) and the average chromatographic peak area of 3 replicates for each BTEX compound for each injection technique (calibration curves) and (2) the concentration (1,2.5,5,7.5,10 ppm_v) and the average chromatographic Gaussian peak resolution between ethylbenzene and *m*-,*p*-xylene isomers for 3 replicates for each injection technique.

3. Results and discussion

3.1. Chromatographic peak resolutions

The chromatographic peak resolution performance of the nCx-TD injections is compared in Figs. 3 and 4 and in Table S2, to the resolution obtained with SPME and HS injections of the 10 ppm_v BTEX-CH_4 synthetic gas. The peak resolution R and the Gaussian peak resolution R_G both measure how well subsequently eluting peaks are distinctly separated in time on the chromatogram. The larger the difference between elution times and the narrower the peaks, the better the resolution. As the SPME-acquired peaks right-tail and do not go back to the original-baseline immediately (Fig. 3), the peak resolution R relying on the baseline-peak width was not calculated between the three closely eluting ethylbenzene and xylene-isomers since peak-end extrapolations should have been made. For those compounds, the half-height peak width-based Gaussian peak resolution was considered. From Figs. 3 and 4 it is clear nCx-TD injections yield the highest peak resolutions between all BTEX compounds even between ethylbenzene and the co-eluting *p*- and *m*-xylene isomers being close in boiling point (respectively 136, 138.4 and 139 °C at P_{atm}). Despite the absence of preconcentration in the HS-injected vials as visible on Fig. 3 (small, broad peaks), a slightly better resolution is obtained with HS- than with SPME-injections due to the systematic and non-negligible SPME-peak tailing to the right. On the contrary to BTEX on TA15 tubes thermally desorbed and injected via the nCx-TD into the GC-column, thermal desorption and injection of BTEX from the SPME fiber in the heated GC-inlet does not occur in a "flash" mode but in a rather continuous mode during the 5 min the fiber is left in the inlet. BTEX compounds from the fiber get only gradually simultaneously desorbed and injected in the GC-column, with desorption from the inner bulk of the SPME fiber film coating being slower than the almost immediate desorption from the surface of the film coating, leading to long desorption times and associated right-tailing peaks [60,61]. These results point out the preconcentration power of TA15 tubes combined to the flash-injection working mode of the nCx-TD yield highly efficient thermal desorption runs with narrow peaks and corresponding high peak-resolutions.

The peak separation factor α was recorded as well. An α equal to 1.00 indicates the two considered peaks are not separated. The more α>1, the better the peaks are separated in time. As B,T,E,X-retention times do not shift across the three injection techniques tested, α keeps the same value in nCx-TD, SPME and HS injections (Fig. 4), with α between the closely eluting ethylbenzene and *m*-,*p*-xylene being the closest to one.

3.2. Preconcentration of natural gas trace compounds

The application potential of the nCx-TD is illustrated by the TD-GC–MS analysis of a real natural gas (NG-A) sampled onto TA15 tubes for preconcentration of its trace compounds. NG-A samples were analyzed in MS-scan mode to screen their global trace compounds' composition and not only BTEX, since Tenax TA has a great adsorption potential for many other semi-volatile chemical compounds from different families [16,39,40,62,63]. Inasmuch as this is only a proof of concept, so far no (semi-) quantification was performed on the natural

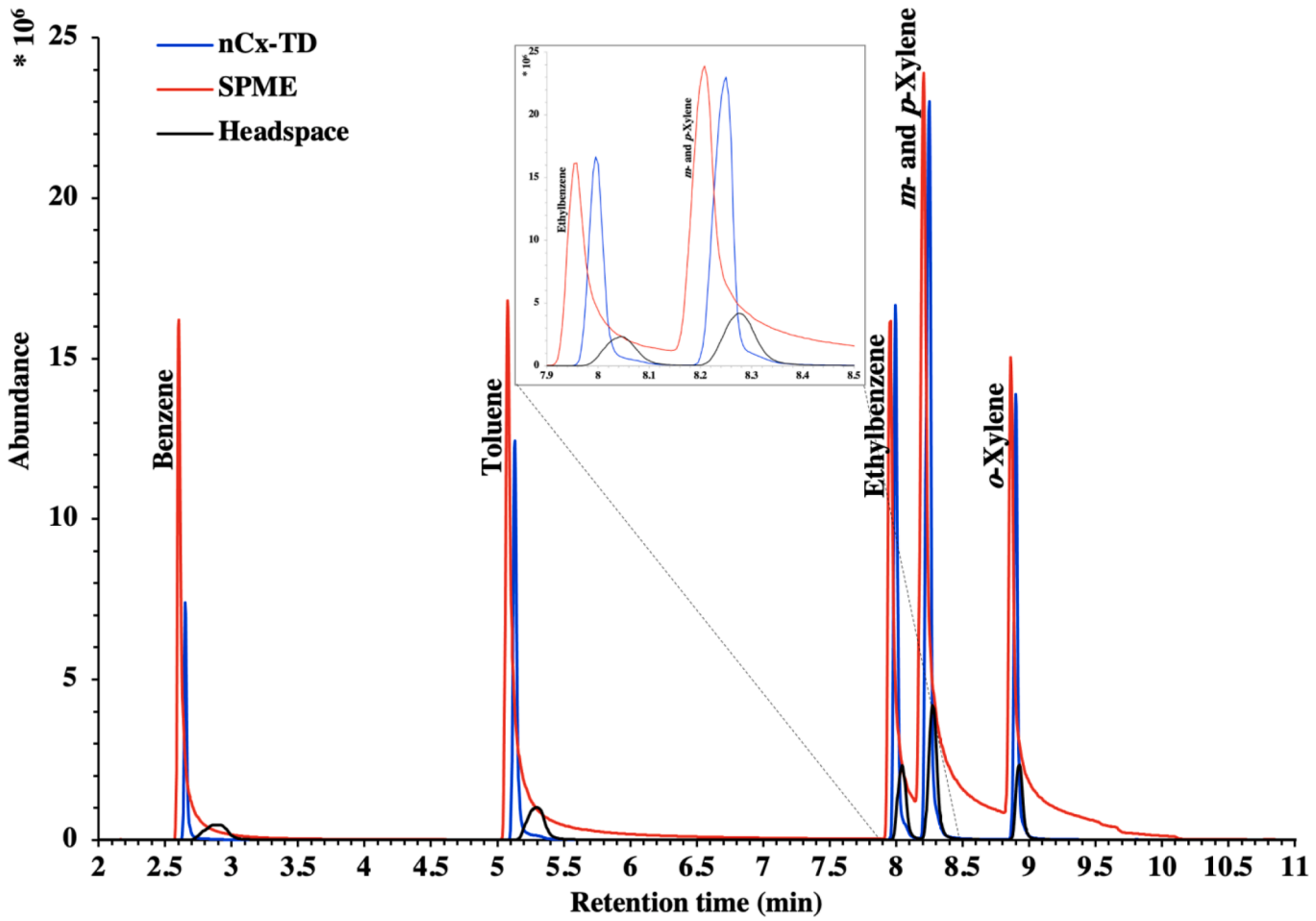


Fig. 3. Total ion current chromatograms for the determination of the peak resolution between B,T,E,X chromatographic signals obtained from the different injection techniques tested for the 10 ppm_v BTEX-CH_4 synthetic gas.

gas samples data.

Fig. 5 compares the chromatograms of NG-A samples obtained via the three sampling and injection techniques. As no preconcentration occurs in vials with direct gas injection (headspace), the bulk CH_4 matrix of natural gas is injected and generates a broad peak from ~1.30 to 2.60 min hiding at least the main other light hydrocarbons of natural gas (ethane, propane, butane). With the exception of 4 bulky peaks (cyclohexane at 3.10 min; methylcyclohexane at 4.25 min; toluene at 5.38 min; tetrahydrothiophene at 6.31 min), no other compounds are detected and the chromatographic resolution is extremely poor. On the other hand, sampling on the SPME fiber and on TA15 tubes clearly operates a strong preconcentration of natural gas constituents (Fig. 5). With TA15 tubes, 50 compounds were detected in NG-A against 46 when SPME is used (Table 3). The building grid natural gas is globally characterized by aliphatic and cyclic alkanes up to C9, BTEX and organic Sulphur-compounds related to the natural and artificial odorization of natural gas (thiophene, 2,3-dihydrothiophene, tetrahydrothiophene), corresponding to the literature-mentioned natural gas composition [14,53,64,65]. Across the 10 replicates, the CAR/PDMS 75 μm SPME fiber did not enable to detect thiophene, 2,3-dihydrothiophene, methyloctane isomers, nonane and 1-ethyl-3-methylbenzene while the TA15 tubes did. Also, the SPME chromatographic baseline is higher and noisier than the one of TA15 tubes (Fig. 5). The diversity of compounds successfully detected from the thermal desorption of NG-A loaded TA15 tubes henceforth demonstrates the efficiency and relevance of the preconcentration and analysis method developed as well as the valuable capacity of the nCx-TD in giving high chromatographic peak resolutions and pure baselines. Furthermore, notwithstanding some analogous qualitative preconcentration performances between TA15 tubes and CAR/PDMS SPME fibers, adsorbent tubes are more solid than fragile SPME fibers and are more convenient for field manipulations with an eye on direct *in situ* preconcentration of trace compounds from gas samples.

What emerges from the results is that on tiny adsorbent tubes packed with as little as 15 mg Tenax TA (whereas the commercial and scientific literature on adsorbent tubes rather refers to adsorbent masses of at least ~100–200 mg [39,41,47]) and where through only 0.5 L_n gas was sampled, more than 50 distinct compounds were detected in the natural gas (Table 3). This is a promising fact with an eye on adsorbent tube optimization to sample more complex gases such as biogases and biomethane being composed of a much larger variety trace compounds from diverse chemical families [24,36,37,48] (alkanes, alkenes, terpenes, alcohols, aldehydes, ketones, ethers, esters, aromatics, halogenated-, Nitrogen-, Sulphur-, Silicon-compounds…). In particular, multibed adsorbent tube configurations where an adsorbent with a low sorption strength (lower surface area) is placed first in the tube ("front bed") with respect to the gas sampling direction, and is followed by one or two "mid" and "back" beds made of adsorbents of increasing sorption strengths (increasing surface areas), are extremely useful to preconcentrate a large number of trace compounds in a wide volatility range and of different families since, upon sampling, heavier compounds get first trapped on the weaker front adsorbents and lighter ones on the stronger downwards located adsorbents [5,23,38,39].

Another advantage of the developed sampling and preconcentration method on tiny adsorbent tubes is the extremely small gas volumes that need to be sampled to trap sufficient amounts of targeted compounds.

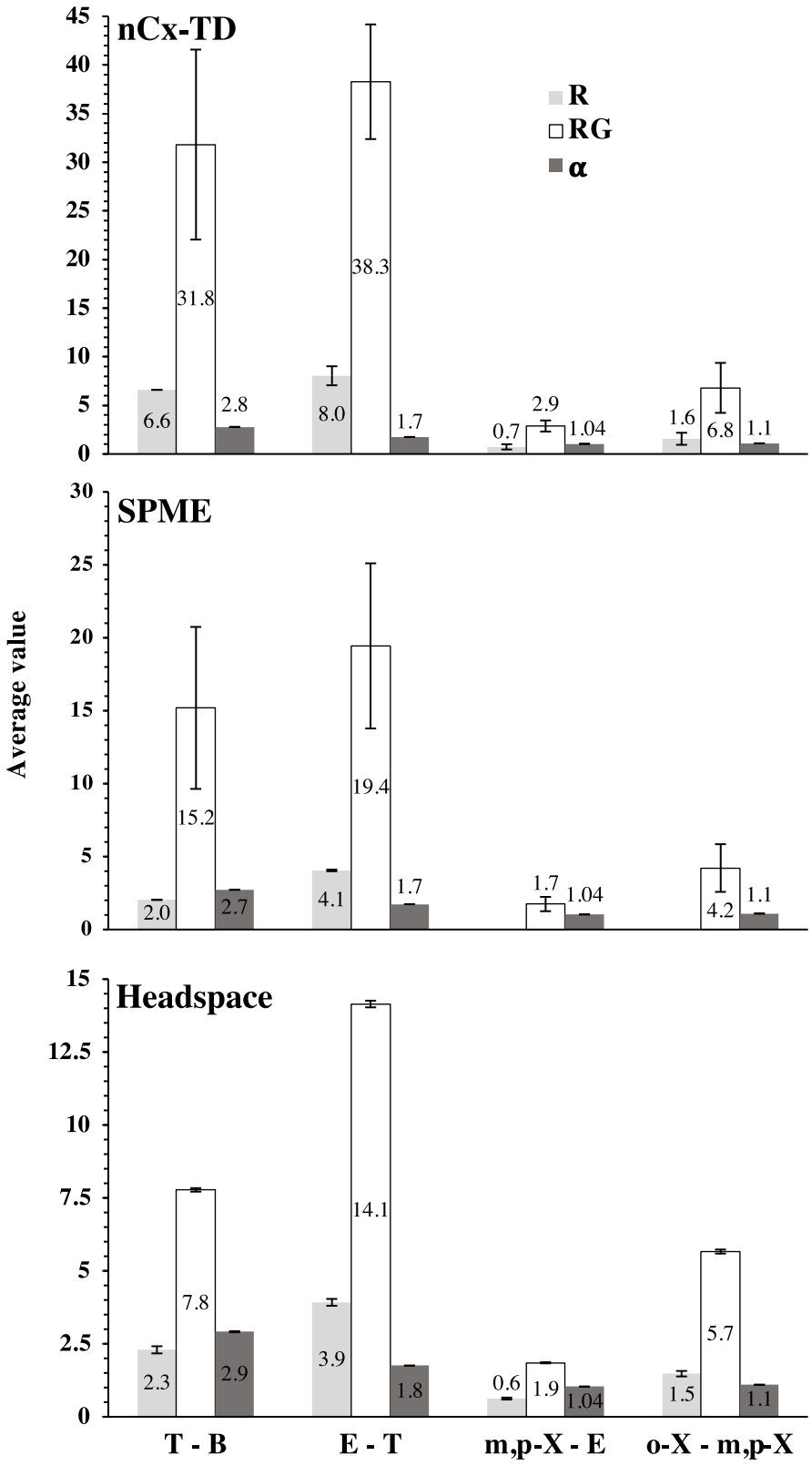


Fig. 4. Peak resolution R, Gaussian peak resolution R_G and peak separation factor α of the 10 ppm_v BTEX-CH_4 synthetic gas injected via the nCx-TD (n = 7 successful injections on 10 performed), SPME (n = 3) and Headspace (n = 14). T – B: resolution between benzene and toluene. E – T: resolution between toluene and ethylbenzene. *m,p*-X – E: resolution between ethylbenzene and *m*- and *p*-xylene. *o*-X – *m*,p-X: resolution between *m*- and *p*-xylene and *o*-xylene. Error bars indicate the standard deviation.

Here, only 0.5 L_n gas needed to be sampled to acquire a deep characterization of the natural gas sample. Yet the sampling volume has to be optimized for each gas to sample with an eye on breakthrough avoidance, it seems reasonable to declare sampling volumes with the presented adsorbent tubes will be in the range of 0.5 – 2 L_n gas. Smaller gas volumes to sample *in situ* is synonym of less vent CH_4 emissions to the atmosphere during sampling campaigns of e.g. natural gas, biogas or biomethane inasmuch as the CH_4 matrix passes through the adsorbent tubes without being trapped. This contributes to lessen the relative atmospheric pollution generated during such sampling operations.

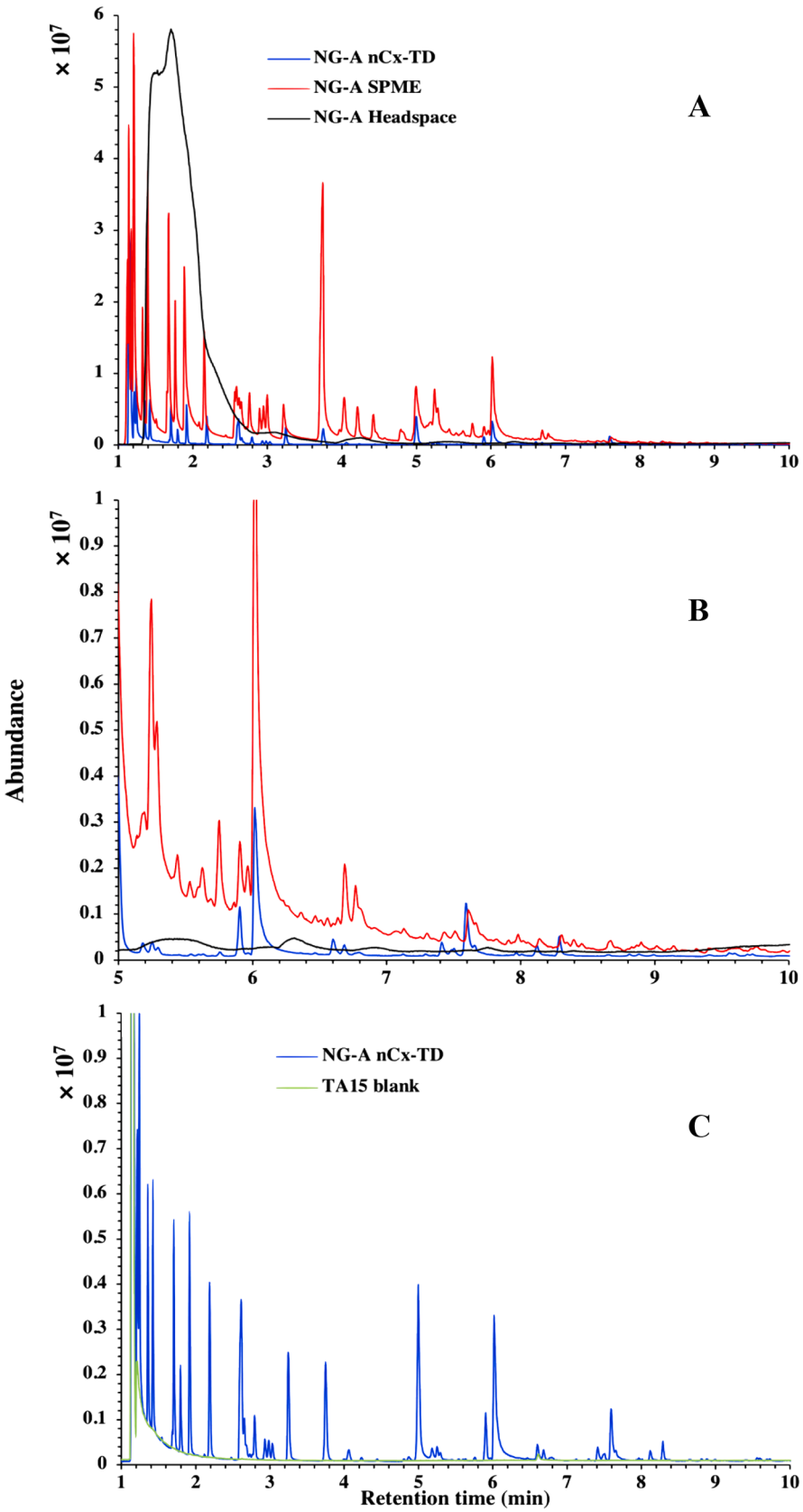


Fig. 5. A and B: Total ion current chromatograms of the building grid natural gas (NG-A) sampled on TA15 tubes (nCx-TD injection), on the CAR/PDMS 75 μm SPME fiber and in vials (Headspace injection) on the same day. C: the nCx-TD-GC–MS output of a new blank TA15 tube is contrasted to a NG-A sampled TA15 tube, analyzed with the same parameters. Note a tiny benzene (2.62 min) contamination inherent to new blank TA15 tubes (see §3.3) and hexamethylcyclotrisiloxane (6.61 min) released from the silicone layer of the TA15 tube capping-septum.

Table 3
Main trace compounds identified via the NIST-library from the building grid natural gas (NG-A) chromatograms (Fig. 5) obtained by sampling on TA15 tubes, CAR/PDMS 75 μm SPME fiber and in headspace vials.

Compound	Retention time (min)		
	TA15 tube	CAR/ PDMSSPME	Headspace
Ethane	1.12	1.12	1.62 – 1.71
Propane	1.15	1.14	1.62 – 1.71
Isobutane	1.19	1.17	
Butane	1.22	1.20	1.71
2-methylbutane	1.34	1.33	
Pentane	1.41	1.39	
2,2-dimethylbutane	1.53	1.51	
2,3-dimethylbutane	1.67	1.65	
2-methylpentane	1.69	1.67	
3-methylpentane	1.78	1.76	
Hexane	1.90	1.88	
2,2-dimethylpentane	2.11	2.08	
Methylcyclopentane	2.18	2.15	
Cyclohexane	2.59	2.56	3.10
Benzene	2.61	2.58	
2-methylhexane	2.65	2.62	
2,3-dimethylpentane	2.68	2.65	
Thiophene	2.72		
3-methylhexane	2.79	2.76	
1,2-dimethylcyclopentane (*cis*/ trans)	2.93	2.89	
1,2-dimethylcyclopentane (*cis*/ trans)	2.98	2.95	
1,3-dimethylcyclopentane (*cis*/ trans)	3.03	3.00	
Heptane	3.25	3.22	
Methylcyclohexane	3.75	3.74	4.25
2,5-dimethylhexane	3.99	3.97	
Ethylcyclopentane	4.06	4.03	
1,2,4-trimethylcyclopentane	4.23	4.21	
1,2,3-trimethylcyclopentane	4.45	4.42	
2,3-dimethylhexane	4.80	4.79	
2,3-dihydrothiophene	4.87		
Toluene	5.00	4.99	5.38
3-ethylhexane	5.18	5.19	
1,3-dimethylcyclohexane (*cis*/ trans)	5.25	5.24	
1,4-dimethylcyclohexane (*cis*/ trans)	5.29	5.29	
1,2-dimethylcyclohexane (*cis*/ trans)	5.75	5.75	
Octane	5.90	5.90	
1,4-dimethylcyclohexane (*cis*/ trans)		5.97	
Tetrahydrothiophene	6.02	6.02	6.31
Ethylcyclohexane	6.68	6.69	
1,1,3-trimethycyclohexane		6.77	
1,2,3-trimethylcyclohexane	7.12	7.13	
Ethylbenzene	7.41	7.43	
4-methyloctane	7.49		
2-methyloctane	7.50		
m- and *p*-Xylene	7.59	7.61	
1-ethyl-2-methylcyclohexane	7.97	7.98	
1-ethyl-4-methylcyclohexane	8.01	8.02	
o-Xylene	8.12	8.14	
Nonane	8.29		
1-ethyl-3-methylbenzene	9.56		
1,2,3-trimethylbenzene	9.60	9.60	
1,2,4-trimethylbenzene	9.69	9.72	

3.3. Instrument detection limits

Table 4 lists the instrument detection limits (IDL) obtained for each BTEX with the three injection techniques (analysis parameters Table 1) for each of which a chromatogram of a blank is displayed in Fig. 6. SPME fiber blanks are free from any BTEX and the low peak-height standard deviations, relatively constant in order of magnitude across all BTEX, indicate a similar background noise on the 10 blanks, so low IDL are obtained (Table 4). The slight linear increase in IDL from benzene to *o*-xylene probably comes from the slightly rising blank baseline (Fig. 6) due to increasing temperatures along the GC cycle. In contrast, new blank TA15 tubes systematically contain inherent benzene, toluene, ethylbenzene, *m*-,*p*-xylene and styrene (co-eluting with *o*-xylene) traces. Now precisely those BTEX compounds with benzene being the most abundant contamination followed by toluene and styrene are well-known typical thermal degradation products of the 2,6-diphenyl-*p*-phenylene oxide Tenax TA matrix [5,66,67] certainly generated during the thermal conditioning of the new TA15 tubes although the Supelco-recommended conditioning specifications for Tenax TA were observed (320 °C for at least 8 h under clean nitrogen flow [52]). These inherent contaminations are to bear in mind and the TA15 tube conditioning procedure should be optimized to minimize them. As each single new TA15 tube probably undergoes unique thermal degradation intensities related to its very own location and effective nitrogen flowrate on the 20-positions conditioning support, the BTEX background peak-height standard deviation across the 10 blanks and associated IDL are high especially for the most abundant thermal degradation products benzene, toluene and *o*-xylene (because of its co-elution with styrene). Ethylbenzene and *m*-,*p*-xylene have an IDL of the same order of magnitude as with SPME. Finally, in the pure CH_4 vials for HS injections, relatively high BTEX levels are found due to the vial filling procedure through the PRS where dead volumes in the tubing, despite thorough cleaning procedures, are likely contaminated with minute amounts BTEX from numerous previous gas transfers. Across the 10 'blank' vials, the intensities of ethylbenzene and *m*-,*p*-xylene contaminations look the highest and the least stable, yielding the highest IDL for those species while IDL for benzene, toluene and *o*-xylene are in the same order of magnitude as for SPME.

However, when gases are sampled to preconcentrate and screen all their unknown trace compounds without following particular species, GC–MS data is most often acquired in scan mode rather than in SIM mode. New blank TA15 tubes analyzed in scan mode (Fig. 5C) only display a small benzene peak surpassing the scan baseline, hence the inherent Tenax-BTEX contaminations reaching high levels in SIM mode, are almost offset. Moreover, the IDL of TA15 tubes for other compounds than BTEX reach satisfying low levels comparable in order of magnitude to or lower than those obtained by SPME, as demonstrated by Fig. 7 where the IDL of TA15 tubes and of the CAR/PDMS 75 μm SPME fiber were calculated for several compounds identified in NG-A (Tables 2,3) based on the extracted ion chromatograms of the scans of the blank tubes and fiber blanks. Cyclohexane, thiophene and tetrahydrothiophene have lower IDL in TA15 tubes than in SPME while heptane, 3-ethylhexane and octane have an IDL slightly higher yet still of the same order of magnitude compared to SPME. This demonstrates TA15 tubes are highly suitable for the preconcentration of (ultra-) trace amounts of non-BTEX compounds. When targeting (ultra-) trace amounts of BTEX, other adsorbents free of inherent BTEX-contamination should therefore be preferred.

3.4. A first step towards semi-quantification

The calibration curves built for each BTEX compound and for each injection technique upon the average chromatographic peak area data of 3 replicates at the 6 concentrations (0,1,2.5,5,7.5,10 ppm_v) were fitted with a linear regression model (intercept= 0) and an F-statistical test at a significance level $\alpha = 0.05$ (Table 5, Fig. S4). The expected positive linear relationship between peak area and concentration for each BTEX compound is verified to be significant for each injection technique by the close-to-one linear determination coefficients R^2, by the p- (not shown) and significance F-values being $< \alpha = 0.05$ and by the observed F-test values exceeding the critical F-test value ($F_{1,5}$ at $\alpha = 0.05$ is 6.6079) (Table 5). The model fit is nevertheless stronger for SPME and HS injections than for nCx-TD injections. Overall, the significance F-values giving the probability that the analysis of variance model is wrong, are definitely higher for nCx-TD than for other injections (yet

Table 4
Standard deviation (Std dev), relative standard deviation (RSD% = 100 Std dev/average) and instrument detection limit (IDL = 3 Std dev) (signal abundance) of the BTEX background noise (peak height) in 10 blanks of the CAR/PDMS 75 μm SPME fiber, in the blanks of 10 new Tenax TA15 tubes and in 10 vials of pure CH_4 for HS injections.

	Std dev ($n = 10$)			RSD%			IDL		
	CAR/PDMS 75	TA15	Vial	CAR/PDMS 75	TA15	Vial	CAR/PDMS 75	TA15	Vial
Benzene	106.1	18,920.8	133.2	17.7	119.0	12.7	318.2	56,762.3	399.5
Toluene	125.2	1335.3	106.6	19.7	84.9	5.4	375.6	4005.9	319.7
Ethylbenzene	183.7	306.0	531.6	26.7	38.4	20.2	551.2	917.9	1594.9
***m*- and *p*-Xylene**	201.9	220.0	772.3	28.5	28.1	21.4	605.8	660.0	2316.8
***o*-Xylene**	219.5	43,095.0	216.0	30.7	132.7	19.8	658.6	129,285.0	648.0

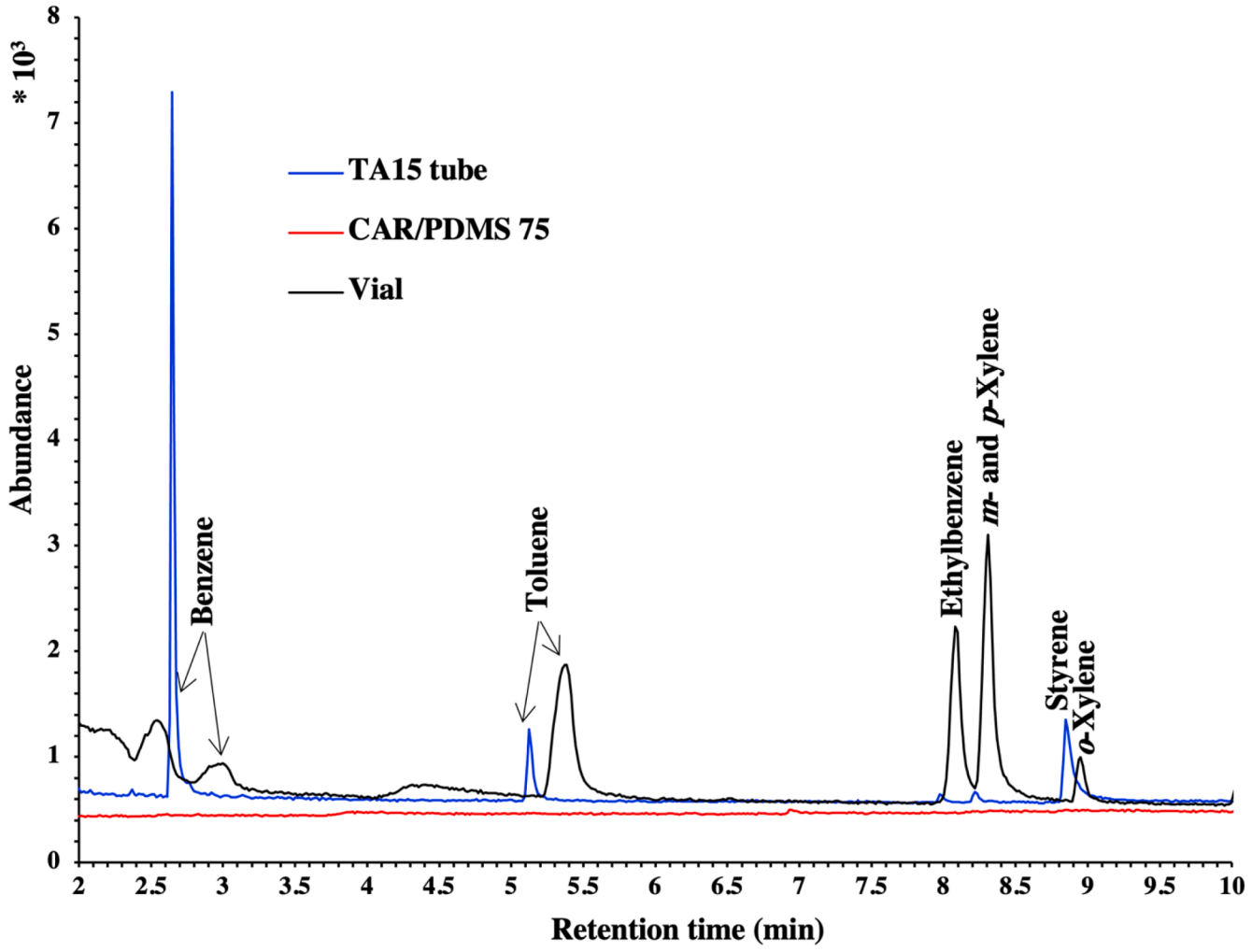


Fig. 6. Total ion current chromatograms of a blank TA15 tube, a blank of the CAR/PDMS 75 μm SPME fiber and a pure CH_4-filled vial.

still lower than $\alpha = 0.05$ thus enabling to reject the hypothesis that no relationship would exist between nCx-TD obtained peak areas and concentrations). Also, the linear determination coefficients R^2 of each BTEX-calibration curve obtained with the nCx-TD, although relatively high (ranging 0.866 – 0.968), are systematically lower than the R^2 achieved by SPME or HS injections. Further, the F-test values observed for ethylbenzene and xylene isomers with the nCx-TD are only slightly higher than the critical F-value (Table 5), indicating a relatively weaker relationship between peak areas and concentrations for nCx-TD injections compared to SPME and HS injections.

What negatively affects the quantitative nCx-TD performance and associated statistics is its low quantitative repeatability as demonstrated by the high relative standard deviations (RSD) obtained (Table S2 and S4).

Firstly, peak resolution experiments on the 10 ppm_v BTEX-CH_4 mixture revealed only 7 on 10 injections occurred successfully and the RSD on the peak areas of the individual BTEX compounds on these $n = 7$ were high: ranging 35% (*m,-p*-xylene) to 50% (benzene) (Table S2). Although each TA15 tube has an individual inherent BTEX background contamination level (see §3.3), the contribution of the variability in individual blank BTEX levels to the RSD of BTEX peak areas in the 7 replicates of the 10 ppm_v sampled TA15 tubes is likely negligible: the average peak areas of benzene, toluene, ethylbenzene, *m-,p*-xylene and *o*-xylene in the 10 blank TA15 tubes represent respectively only 0.185,0.007,0.001,0.001 and 0.097% of the average peak areas of these compounds in the 7 replicates 10 ppm_v sampled TA15 tubes. Also, in blank TA15 tubes, *o*-xylene has the highest signal and RSD for both peak height (Table 4) and peak area (not shown) due to its co-elution with

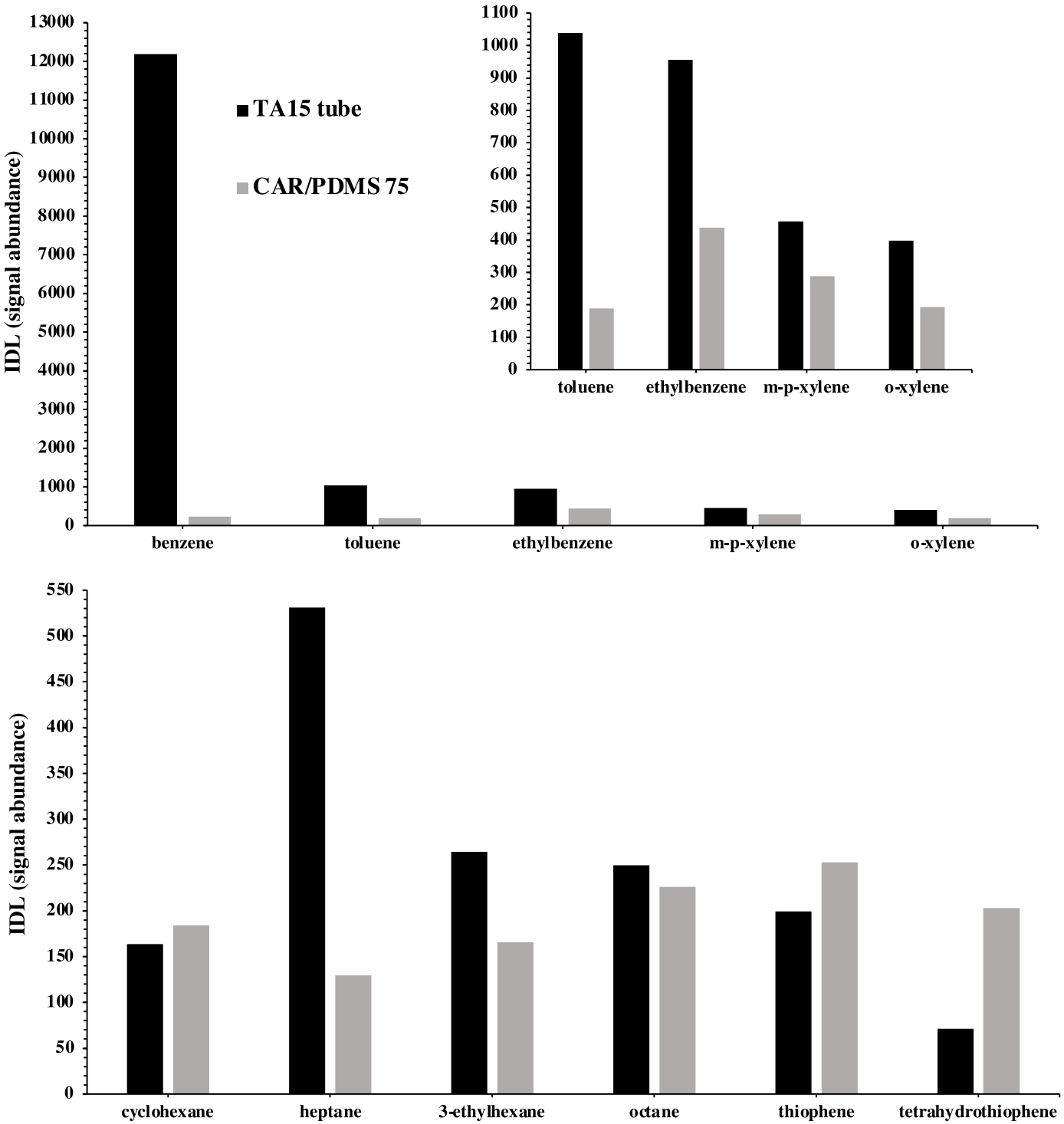


Fig. 7. Instrument detection limits (peak height signal abundance) of trace compounds determined in the NG-A building grid natural gas sample on TA15 tubes and on the CAR/PDMS 75 μm SPME fiber. Numerical values are available in Table S3.

styrene (Tenax TA thermal degradation product), followed by benzene, whereas the highest signals (peak height and area) in 10 ppm_v sampled tubes are recorded for the co-eluting *m*- and *p*-xylenes. Benzene has the lowest signals in those sampled tubes but the highest RSD (Fig. 3, Table S2). This supports the statement that blank background contamination levels are not a key contributor to the high RSD's observed for sampled TA15 tubes.

Secondly, RSD ($n = 3$) on the nCx-TD BTEX calibration curves range the largest across the 6 concentrations tested: 1 – 62% against ~ 4 – 35% for SPME and HS (Table S4). The nCx-TD has also the highest RSD's for benzene on all 6 concentrations and the highest RSD's at 5 and 10 ppm_v for all compounds. The reason of this behavior is unclear and can not originate from the Tedlar bag dilution preparations since nCx-TD, SPME and HS samples were taken from the very same bag and RSD's for SPME and HS do not present particular trends at 5 and 10 ppm_v.

Actually, the discussed repeatability issues of the current nCx-TD prototype originate from a too short injection needle (Fig. 1 point 3) insufficiently penetrating the GC inlet liner, causing the carrier gas to

Table 5
Linear regression output (Peak Area = slope a · Concentration) and analysis of variance (F-statistical test) between average peak area of BTEX compounds and concentration, at a significance level $\alpha = 0.05$. The critical F-value $F_{(1,5)}$ at $\alpha = 0.05$ is 6.6079.

	Benzene	Toluene	Ethylbenzene	*m,p*-Xylene	*o*-Xylene
			nCx-TD		
Slope *a*	1.3E+07	2.4E+07	1.7E+07	2.4E+07	0.9E+07
R^2	0.95	0.97	0.92	0.88	0.87
Observed F-value	103.1	152.0	59.1	35.9	32.2
Significance F-value	529.5E-06	248.7E-06	1542.0E-06	3901.7E-06	4756.1E-06
			SPME		
Slope *a*	5.8E+07	9.2E+07	4.6E+07	10.5E+07	6.4E+07
R^2	0.99	1.00	0.99	0.98	0.97
Observed F-value	828.4	10,207.6	415.9	276.0	163.0
Significance F-value	8.7E-06	0.06E-06	34.1E-06	76.9E-06	216.8E-06
			Headspace		
Slope *a*	0.6E+07	0.8E+07	0.6E+07	1.0E+07	0.4E+07
R^2	1.00	1.00	0.98	0.96	0.94
Observed F-value	2287.1	4406.3	227.6	121.8	74.2
Significance F-value	1.1E-06	0.3E-06	112.5E-06	383.3E-06	997.3E-06

not enter the liner and the column on a repeatable way upon injection. Also, the exact position of the two holes made in each of the upper and bottom adsorbent tube capping septa upon manual sampling and upon thermal desorption was found to influence the injection repeatability of the nCx-TD prototype. Indeed, when upon injection the injection needle pierces the septum at a location closely adjacent to or overlapping to some extent the hole created during manual sampling, variable proportions carrier gas leaks were observed as a result of septum tearing. When both holes were distinctly away from each other, no carrier gas leak was observed. In spite of these faults, the excellent nCx-TD desorption performance and chromatographic peak resolutions justify the prototype is worth being improved by a lengthened injection needle and by a needle guide to achieve satisfying quantitative repeatabilities.

Notwithstanding the above and the relatively high inherent BTEX contamination levels in new blank TA15 tubes, a simple semi-quantification rule of three based on the BTEX peak areas in the blanks and in the 10 ppm_v BTEX-CH_4 samples (SIM acquisition) indicates blank levels and associated detection thresholds in TA15 tubes can be as low as 0.07 ppb_v for *m-,p*-xylene (Table 6). As discussed, the thresholds are the highest for benzene (18.52 ppb_v) and *o*-xylene (9.68 ppb_v) owing to the high contamination of those compounds in the blank TA15 tubes Table 4. Table 6 also shows the absence of preconcentration in headspace vials, giving detrimental higher detection thresholds.

Lastly, the existence of a relationship between concentration and the chromatographic Gaussian peak resolution R_G between the closely eluting ethylbenzene and *m*- and *p*-xylene isomers was statistically tested (linear regression with intercept and F-test) at a significance level $\alpha = 0.05$ for 5 concentrations (1,2.5,5,7.5,10 ppm_v) and the three injection techniques handled, taking the average of 3 replicates at each concentration. For SPME and headspace injections, results reveal no significant linear relationship between those variables: the linear determination coefficients R^2 are low (SPME-$R^2 = 0.018$; HS-$R^2 = 0.662$), the observed F-test values are lower than the critical F-test value $F_{(1,3)} = 10.13$ and the significance F-values are higher than the significance level $\alpha = 0.05$ indicating the model is unable to predict the measurements (Table S5 and Fig. S5). In contrast, the statistical analysis performed indicates a significant ($R^2 = 0.852$; observed F-value > critical F-value; significance F-value < $\alpha = 0.05$) yet weak positive linear relationship between concentration and Gaussian peak resolution of nCx-TD-injected ethylbenzene and *m-, p*-xylene peaks. Gaussian peak resolutions obtained from the nCx-TD not only are higher than those obtained by SPME and headspace but also improve with the concentrations, once again pointing out the high resolutive power (narrow peaks) of the nCx-TD prototype.

Table 6
Semi-quantification (ppb_v) of the BTEX contamination background in new TA15 blank tubes, a blank SPME fiber and 'blank' (pure CH_4) vials based on the BTEX peak areas in 10 ppm_v BTEX-CH_4 samples.

	TA15	CAR/PDMS 75	Vial
Benzene	18.52	0.18	2.62
Toluene	0.67	0.11	7.93
Ethylbenzene	0.10	0.04	6.81
m-p-Xylene	0.07	0.05	5.62
o-Xylene	9.68	0.32	1.40

4. Conclusions and perspectives

Thermal desorption of purpose-built self-assembled Tenax TA tubes loaded with a synthetic BTEX-CH_4 gas using the new versatile thermodesorber prototype (nCx-TD) has proved to yield much higher chromatographic peak resolutions than thermal desorption of a BTEX-loaded CAR/PDMS 75 μm SPME fiber and than direct BTEX-CH_4 gas injection via a headspace autosampler. Additionally, nCx-TD peak resolutions tend to significantly improve at higher BTEX concentrations (from 1 to 10 ppm_v). The resolutive power of the nCx-TD stems from its fast "plug" injection working mode where furthermore no re-focusing trap is called for. Also, the low adsorbent mass (15 mg) and low sampling volumes (0.5 L_n) required make the whole adsorbent tube sampling operations attractive with regards to economical, practical and environmental considerations. Moreover, the nCx-TD is mountable on the inlet ports of any commercial GC-units and it can be deployed *in situ* on field-portable GC's. To the authors' knowledge, this is the sole thermal desorber device combining all of these qualities and properties. The current nCx-TD prototype version needs however physico-mechanical re-sizing improvements to ensure quantitatively repeatable injections.

Besides, the analysis of a real natural gas sample revealed the future application potential of the self-assembled adsorbent tubes. The Tenax TA tubes allowed to detect thiophene, 2,3-dihydrothiophene, methyloctane isomers, nonane and 1-ethyl-3-methylbenzene while the CAR/PDSM 75 μm SPME fiber did not. Tenax TA is a highly polyvalent adsorbent able to trap a broad range of semi-volatile compounds, and its functionalities could be even further valorized in multibed adsorbent tube configurations for the preconcentration of complex mixtures of trace compounds in gases like biogas and biomethane.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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