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Formation of artefacts during air analysis of volatile amines by solid-phase micro extraction

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Solid-phase micro extraction (SPME) is a promising technique for fast and low cost trace analysis. However, some limitations of the technique were encountered when using a PDMS (polydimethylsiloxane)/Carboxen fibre for sampling a mixture of volatile aliphatic amines in air. On the GC chromatogram, two supplementary peaks were noticed in addition to the analyte peaks, thus limiting qualitative and quantitative analysis in this particular case. This paper presents the investigations to identify the artefacts and determine the origin of their formation. First, GC-MS identification, by both electron impact and chemical ionisation modes, demonstrated that the two artefacts were unsaturated amines assumed to be formed by a dehydrogenation reaction of the target amines. This reaction was found to occur during thermal desorption of analytes in the GC injection port and to be catalysed by temperature and by metals consisting of the inox (stainless-steel) needle of the SPME device. It was also demonstrated that artefact formation was not significant when using PDMS or PDMS/divinylbenzene fibres. This difference with PDMS/Carboxen fibre can be explained by the high desorption temperature required for this fibre. Moreover, the microporosity of Carboxen induces a longer desorption time which increases the contact between analytes and inox and thereby enhances artefact formation.

Introduction

Considering air quality, olfactory pollution is of growing interest. Compounds responsible for the olfactory nuisance are mainly volatile amines, sulfur and some oxygenated compounds. Malodorous amines are mainly produced by microbial degradation of amino acids, proteins, urea, *etc.* They are particularly recognisable by their odour of rotting fish. They are frequently identified in the gaseous emissions of wastewater treatment plants, industry involved with transformation of animal by-products, fish conditioning plants, yeast production, *etc.* The human nose is able to detect these compounds at trace levels. As examples, the perception levels range from 1 mg m^{-3} for NH_3 to $20 \text{ } \mu\text{g m}^{-3}$ for propylamine.¹ As analytical techniques are not sensitive enough to ensure their direct detection at the $\mu\text{g m}^{-3}$ level, a preconcentration step is required. Among the methods available for trace enrichment from air samples, solid-phase micro extraction (SPME) can be considered as a promising technique. Indeed, SPME is a fast, inexpensive and solvent free sample preparation technique. The concept is based on sorption of analytes onto a fibre followed by a direct thermal desorption in a GC injection port. Developed by Pawliszyn and co-workers in the 90s mainly for micropollutants in water,^{2,3} the method has since been extended to different fields ranging from blood⁴ to soil analysis.⁵ Performances of the technique are comparable or even better than conventional methods.⁶

For the determination of amines, SPME has been applied in biological fluids,^{4,7} foodstuff^{8,9} and air¹⁰ with PDMS (polydimethylsiloxane), PDMS/Dvb (polydimethylsiloxane/divinylbenzene) or polyacrylate fibres. Among these papers, only one mentioned formation of artefacts. Verhoeven *et al.* on investigation of strawberries with a polyacrylate fibre assumed artefact formation occurred in the injector port originating from a reaction between carbohydrates and amino acids.⁹ Since these experiments, new fibres including a carbon-based adsorbent (Carboxen) have become available such as polydimethylsiloxane/Carboxen and PDMS/Dvb/Car (polydimethylsiloxane/div-

inylbenzene/Carboxen). Studies on volatile organic compounds (VOCs) in air showed that the PDMS/Car fibre was significantly more efficient in terms of sensitivity than commonly used coatings such as PDMS.¹¹

According to these performances, PDMS/Car was first envisaged to sample traces of odorous amines in air. In order to check the potential of the method, experiments were performed by using a standard gaseous mixture of four model compounds. However, in addition to the four standard peaks, two supplementary peaks were observed on the GC chromatogram.

Consequently, this work aims to identify the nature and the origin of these artefacts to define and understand the limits of SPME application in this particular analytical case.

First, GC-MS analyses were carried out to identify the molecular structure of the formed compounds. Then, the influence of the desorption temperature and the presence of metal on the fibre were investigated. Indeed, Haberhauer-Troyer *et al.*¹² observed the formation of artefacts from sulfur compounds and assumed that the reaction of formation was catalysed by the presence of metallic pieces on the fibre surface originating from the septum piercing needle.

Then, other SPME fibres were tested in order to determine the role of the coating in the artefact formation.

Experimental

Reagents

Propylamine, diethylamine, triethylamine and dipropylamine were obtained from Acros Organics (Geel, Belgium). All these reagents were at least 99% grade. A liquid equimolar mixture of these four compounds was prepared to produce a $9 \text{ } \mu\text{mol m}^{-3}$ standard gas. The gas generation was performed as described by Tuduri *et al.*¹¹ The four model compounds were chosen because they are encountered in malodorous gaseous emissions and also because they could be detected with a flame ionization detector

(FID) according to their carbon structure and to the level of concentration used.

Solid-phase micro extraction

A manual SPME device and three different types of fibres were used. Polydimethylsiloxane 100 μm (PDMS), PDMS/Carboxen 85 μm (PDMS/Car) and PDMS/divinylbenzene 65 μm (PDMS/Dvb) were all from Supelco (Bellefonte, PA, USA). SPME fibres were conditioned in the GC injection port according to the manufacturer's recommendations. Sampling time was set at 15 min to allow significant extraction of analytes (between 60 and 100% of maximum extraction, defined at sorption equilibrium). Desorption was held for 2 min at 250 $^{\circ}\text{C}$ for PDMS and PDMS/Dvb fibres and 300 $^{\circ}\text{C}$ for PDMS/Car fibre since no carry over was observed at these settings. Maximum desorption temperature is 270 $^{\circ}\text{C}$ for PDMS and PDMS/Dvb fibres and 320 $^{\circ}\text{C}$ for PDMS/Car.

GC analysis

GC-FID. A Hewlett Packard HP 5890 gas chromatograph (Bios Analytique, France), equipped with a split/splitless injection port operating in the splitless mode with a dedicated SPME liner (0.75 mm id), and with a flame ionisation detector (FID) (air flow-rate: 450 mL min^{-1} , hydrogen: 50 mL min^{-1} , helium (make-up gas): 30 mL min^{-1}), was used. The column was an SPB1-sulfur 30 $\text{m} \times 0.25 \text{ mm} \times 5 \mu\text{m}$ from Supelco. Helium was the carrier gas at 1.6 mL min^{-1} flow-rate. The initial oven temperature was set at 40 $^{\circ}\text{C}$ then ramped at 15 $^{\circ}\text{C min}^{-1}$ to the final temperature of 200 $^{\circ}\text{C}$ and held for 1 min. Signals were collected and recorded with HPCHEM software (Bios Analytique, France).

GC-MS. Identification of the artefacts was performed with a Varian 3400 chromatograph equipped with a septum programmable injector Varian SPI 1093 with a 0.75 mm id liner and coupled to a Saturn II ion trap mass spectrometer. Carrier gas, column and oven settings were identical as for GC-FID analysis. The mass spectrometer was used in electron impact (EI) and chemical ionisation (CI) modes. EI mass spectra were obtained with an ionisation energy of 70 eV and an ionisation time of 25 000 μs and recorded in full scan ionisation mode. The acquisition was performed from 30 to 349 u at 1 scan per second. For CI mode, methane was employed as the chemical reactant. The same settings as EI mode were used except that ionisation time was set at 2000 μs .

ATD-GC-MS. This analytical technique was used to determine the eventual influence of inox (stainless-steel) in the catalysis of artefact formation. Analyses were carried out with

a Perkin Elmer device configured as follows: an automatic thermal desorber Model ATD 400 on-line with an Autosystem gas chromatograph coupled to a Q-mass quadrupole mass spectrometer. The thermal desorption of sorbent tubes was carried out in two steps by heating at 300 $^{\circ}\text{C}$ for 5 min and then flushing the sampling tube with helium at a gas flow-rate of 20 mL min^{-1} . Desorbed analytes, after 1/10 split, were cryofocused on a cold trap packed with Tenax-TA and Carboxen 564 (20 mg each) and maintained at -30°C by the Peltier effect. The cold-trap was then heated quickly to 250 $^{\circ}\text{C}$ at 40 $^{\circ}\text{C s}^{-1}$. Compounds were then injected in the chromatographic system via a transfer line at 200 $^{\circ}\text{C}$ without splitting. Carrier gas, column and oven settings were identical as for GC-FID analysis.

Scanning electron microscopy (SEM). Scanning electron microscopy (JEOL, JSM 35 CF) was used to examine the surface of the studied SPME fibres. Samples were covered with a 25 nm carbon layer before analysis. Qualitative analysis was performed with a micro-analysis X-Ray dispersive energy instrument (KEVEX Quantum).

Results and discussion

Identification of artefacts by GC-MS

In the chromatogram obtained after SPME sampling (PDMS/Car fibre) of the standard gaseous mixture of the four amines, two supplementary peaks, called artefact 1 and 2, were detected at respective retention times of 5.60 min and 7.19 min [Fig. 1(a)]. They represented the 5% and 18% of the total areas obtained by GC-FID analysis. To identify these two unknown compounds, a GC-MS analysis was carried out. To ensure structural identification, two modes were used: electron impact (EI) leading to characterisation of ions and chemical ionisation (CI) which allows the determination of molecular mass with a better reliability due to the lower energetic fragmentation.

GC-MS electron impact mode. Among the different structures proposed by the mass spectra library, a wide majority corresponds to amines. However, the similarities between reference and experimental spectra were not high enough to postulate a molecular structure at this stage of the study.

For both artefacts, EI mode also highlighted the decomposition fragments m/z 56 and m/z 70, which are characteristic of compounds containing nitrogen (*cf.* following structures). As noticed in this case, α -cleavage of a methyl group [$M - 15$] was present but the base peaks were always found at [$M - 29$] corresponding to an α -cleavage at the secondary carbon. These series are indicative of a general type of unsaturated structure.¹³

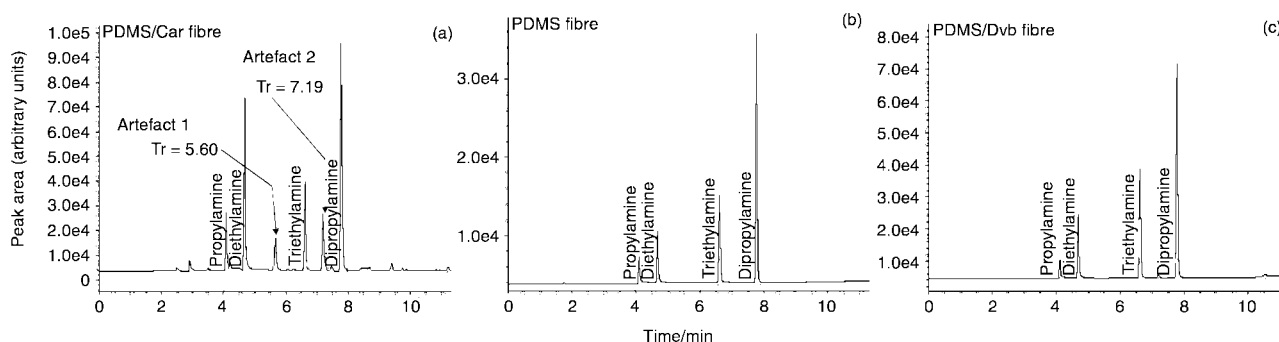
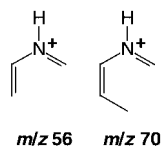


Fig. 1 Comparison of GC-FID chromatograms for four amines sampled with different SPME fibres [1(a): PDMS/Car; 1(b): PDMS; 1(c): PDMS/Dvb] (concentration generated: 9 $\mu\text{mol m}^{-3}$, sampling time: 15 min, desorption temperature: 250 $^{\circ}\text{C}$ for PDMS and PDMS/Dvb fibres, 300 $^{\circ}\text{C}$ for PDMS/Car fibre).



GC-MS chemical ionisation mode. Using CI mode, major fragments were found at m/z 86 and m/z 100 for artefacts 1 and 2 respectively. Fragments m/z 114 and m/z 130, corresponding to mass $[M + 28]$ due to the association of analyte and C_2H_4 (from methane), were also noticed. Molecular masses were respectively assessed to be of 85 and 99 since amines have a strong tendency to undergo protonation and then to exhibit an $[M + 1]$ molecular mass when ion trap technology is used.¹³

Among the various possibilities of structures, the presence of oxygen in these formed compounds was investigated. Haberhauer-Troyer *et al.*¹² noticed an oxidation of sulfur compounds in the injection port catalysed by oxygen in air which was the sample matrix. When they replaced air by nitrogen, no extra peaks were observed, confirming that the artefacts formed from sulfur compounds were oxidation by-products. In our case, tests with helium instead of air in the gas generating system were performed. The same artefacts as those obtained previously with air were identified. Therefore, reaction with oxygen was supposed not to occur.

To conclude, compounds formed were assumed to be unsaturated amines with respective molecular masses of 85 and 99. From CI results, molecular formulae were found to be $C_5H_{11}N$ and $C_6H_{13}N$.

Origin of the artefacts

Impurities in reagents. A first hypothesis consisted of assuming that the two artefacts observed were initially present in reagents as synthesis by-products. In order to verify this assumption, 0.1 μ L samples of pure liquid standards of the four model amines were individually injected under the same conditions as those applied to SPME analysis (300 °C). The same artefacts were effectively found but at a very low level (0.5% of total areas) compared to SPME. However, when the injection temperature was lowered to 150 °C, proportions of artefacts were decreased two-fold. It was then assumed that the artefacts were not impurities in the commercial solutions but that they were formed from standards under a significant influence of temperature.

Decomposition of standards. To determine compounds responsible for artefact formation among the standards used, individual sampling of each model compound in the gaseous phase was carried out with a PDMS/Car fibre. For each aliphatic amine tested, additional peaks appeared in the chromatogram. Relative percentages of additional peaks compared to standard areas were calculated. Propylamine led to the formation of two artefacts representing 11% of the propylamine area each. Diethylamine produced one main artefact representing around 50% of the diethylamine area. Triethylamine was assumed to decompose into diethylamine and two other artefacts. Decomposition of dipropylamine was the most important since it gave exclusively artefact 2 to represent 120% of dipropylamine area. Although artefact 1 was detected, relative proportions were not comparable to those found in the mixture. It appeared then that this compound did not originate from the decomposition of a single compound but may have come from a reaction involving several precursors.

Therefore, sampling of two compound mixtures was achieved to find out if associated compounds were able to form new products not detected in single compound experiments. Generally, these mixtures led to the same artefacts as those

found in single compound experiments but usually at higher levels. It is supposed that the simultaneous presence of several amines enhances production of artefacts. Artefact 1 was detected in the presence of diethylamine or triethylamine (C_2 lateral chain compounds) and propylamine (C_3 lateral chain compound) and assumed to be produced by the reaction between two amines in relation with molecular formulae determined previously ($C_5H_{11}N$). Dipropylamine did not react with any other standard to produce extra compounds. It was concluded that artefact 2 originated from dipropylamine decomposition only.

Influence of injection port temperature on artefact formation. Variation of the temperature of injection was investigated on the PDMS/Car fibre. Desorption temperature was set at 200, 250 and 300 °C. It was observed that artefact formation increased significantly with temperature (Fig. 2). This could however be explained by incomplete desorption at the lower temperature tested, as the optimal desorption conditions for Carboxen ranged from 300 to 320 °C. Therefore, carry over was verified by performing a second desorption at 300 °C of the PDMS/Car fibre after the initial one. Carry over in the presence of dipropylamine and artefact 2 was noticed after the first desorption at 200 °C. An additional product either has been formed on the fibre but not desorbed at 200 °C or originated from decomposition of remaining standard trapped on the fibre. As dipropylamine was the only standard detected in the carry-over run, the second hypothesis is assumed to occur considering, as demonstrated before, that artefact 2 is produced exclusively from dipropylamine. Consequently, the increase of artefacts with temperature cannot be related to a partial desorption of the compounds.

It was then assumed that temperature has a significant influence by enhancing artefact formation. Reactions were determined requiring a high amount of energy to be produced so it was assumed decomposition took place in the GC injection port only.

Investigation of inox influence. Amines do not however decompose at the usual temperature of injection (250 °C). Reactions also involve a catalyst which is usually metallic. Therefore, an hypothesis would be that the materials used as the sorbent phase (here Carboxen) contain traces of metal. The Environmental Protection Agency (EPA) in a compendium for the determination of volatile organic compounds in ambient air warns against 'varieties of charcoal which contain metals which will catalyse the degradation of some organic analytes during thermal desorption at elevated temperatures, thus producing artefacts'.¹⁴ During injection, metals for catalysis could also have been provided by the needle. Liquid injection and SPME desorption, both involving the inox needle, highlighted the formation of the same artefacts. Moreover, Haberhauer-Troyer

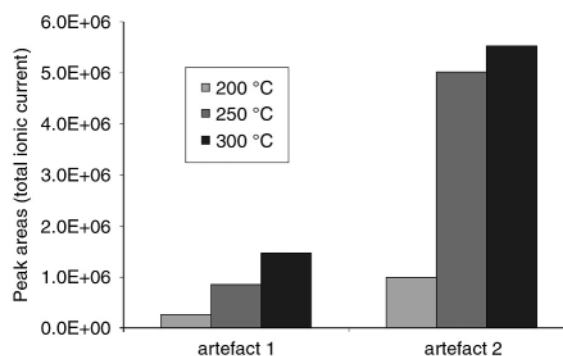


Fig. 2 Influence of desorption temperature on artefact formation after sampling amines with PDMS/Car fibre and analysis by GC-MS (concentration generated: 9 μ mol m^{-3} , sampling time: 15 min).

*et al.*¹² observed, by optical microscopy, a high number of metallic particles on PDMS fibres. They assumed that they originated from the syringe needle and suggested that the artefacts were formed by oxidation of the standard catalysed by metal particles.¹⁵

The PDMS, PDMS/Dvb and PDMS/Car fibres were studied using SEM. Analysis of Carboxen1006 (type of Carboxen used in SPME fibre) did not display any trace of metal within the material. For comparison, Carboxen 564, involved in sorbent tubes classically used for air sampling, was also investigated but no trace of metal was found either. On both PDMS and PDMS/Dvb fibres, no metal particles or manufacturing default could be detected while on the PDMS/Car fibre, several particles were found on the surface (Fig. 3). The analysis of the particles showed only a fragment composed mainly of iron then nickel and chromium corresponding to the composition of inox. It was therefore assumed that the metal did not originate from Carboxen but from an external source which could be the SPME needle.

To ensure the validity of this hypothesis, experiments involving inox were carried out. As the SPME fibre cannot be discarded from its inox support, tests involving the sorbent tube followed by analysis by ATD-GC-MS were performed. As Carboxen 1006 was not easily commercially available, the similar Carboxen 564 was used. To reproduce as well as possible the SPME system, an inox tube was filled with Carboxen 564 and its effect was assessed by using the same experiment performed with a glass tube. Tests were done only with dipropylamine since it gave the most significant artefact formation (artefact 2) when using SPME. The same artefact was identified when using the inox tube while no extra product was detected with the glass tube. Inox was then assumed to have a significant influence on artefact formation.

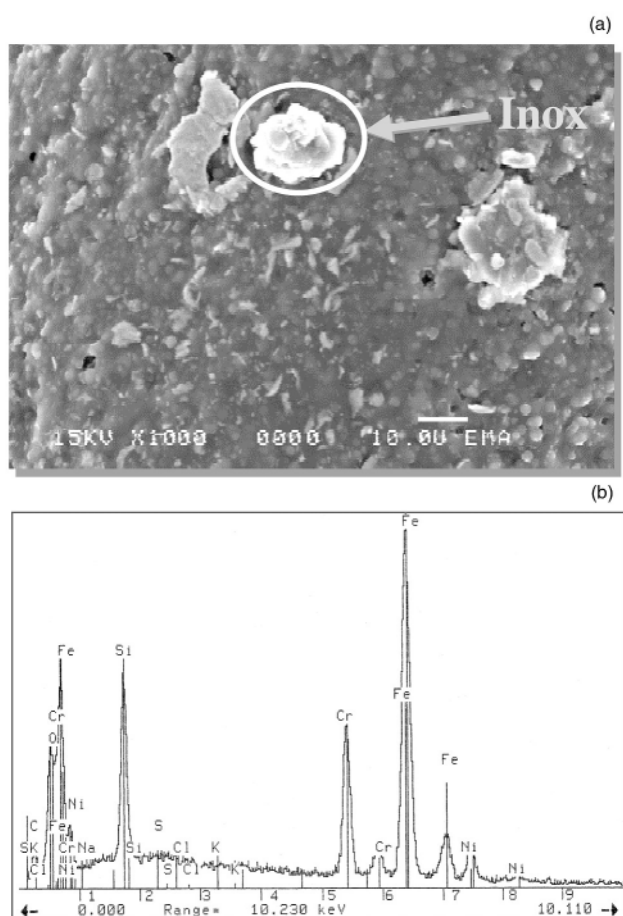
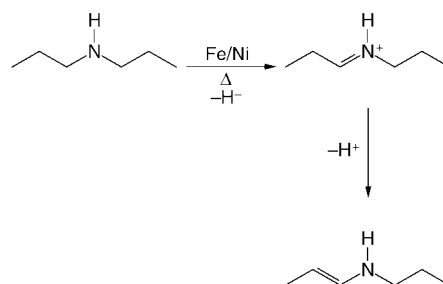
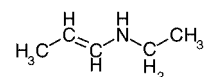


Fig. 3 Inox particles on PDMS/Car fibre by scanning electron microscope [3(a)] and elemental analysis by X-ray dispersive energy [3(b)].

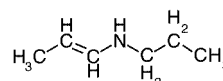
Mechanism of artefact formation. From structural identification by mass spectrometry, it was assumed that artefact 1 originated from an association of a primary C₃ aliphatic chain amine and a secondary C₂ aliphatic chain amine with a molecular formula of C₅H₁₁N, and artefact 2 (C₆H₁₃N) was exclusively formed from dipropylamine. From results of experiments and by comparing with NIST mass spectra library, examples of artefact structures are proposed in Fig. 4. Compounds formed are thought to be unsaturated and provided by a dehydrogenation reaction. Dehydrogenation is not usually a feasible process especially for aliphatic compounds. However, in special cases, this reaction can occur when the new double bond formed is in conjugation with another double bond or with an unshared pair of electrons such as a nitrogen atom.¹⁶ Under an elevated temperature and metal presence, the nitrogen atom loses its proton which is followed by a second proton loss to achieve the formation of the double bond. Delocalisation of the charge occurs between the double bond and the unshared electrons allowing a more stable compound as shown.



Comparison of characteristics of SPME fibres. For sampling amines, fibres did not behave in the same way. Important artefact formation was detected with a PDMS/Car fibre while PDMS fibre did not lead to any extra-product and only a trace could be detected with PDMS/Dvb fibre (Fig. 1). Similar results were found when experiments were repeated with two different fibres for each coating. The difference in behaviour could be related to the nature of the coating. PDMS is a very viscous liquid which involves an extraction process governed by absorption. On the other hand, divinylbenzene and Carboxen are both porous solids which implies analyte extraction proceeds *via* adsorption.¹⁷ However, pore size distribution is quite different. While divinylbenzene is a meso-macro-porous structure, Carboxen exhibits a higher proportion of micropores (Table 1). This microporosity is particularly efficient for the extraction of small molecules such as VOCs since capillary condensation occurs usually when pore size is less than 100 Å.¹⁷ Thus for amine sampling, extraction with a PDMS/Car fibre increased the efficiency 3-fold compared to PDMS fibre. The difference in amount extracted is not however sufficient to explain the enhanced formation of artefacts, since PDMS/Dvb and PDMS/Car fibres absorbed roughly the same quantity of amines. Moreover, when the concentration of standard amines increased and, consequently, the amount



Artefact 1 : N-ethyl 1-propenylamine

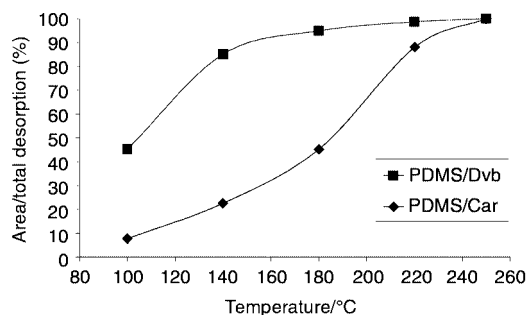


Artefact 2 : N-propyl 1-propenylamine

Fig. 4 Supposed structure for artefacts noticed in the chromatogram of amines mixture.

Table 1 Characteristics of SPME coatings

	Nature of coating	Density/g mL ⁻¹	BET surface area/m ² g ⁻¹	Porosity/mL g ⁻¹		
				Micro 2–20 Å	Meso 20–500 Å	Macro >500 Å
Carboxen 1006	Solid	0.47	720	0.29	0.26	0.23
Dvb	Solid	0.36	750	0.11	0.85	0.58
PDMS	Liquid	0.97	—	—	—	—

**Fig. 5** Desorption rate of dipropylamine vs. injection port temperature for PDMS/Dvb and PDMS/Car fibers (concentration generated: 9 $\mu\text{mol m}^{-3}$ of dipropylamine, sampling time: 15 min).

trapped onto the fibre, the relative percentages of artefacts formed decreased. Artefact formation was then assumed to be favoured by low concentrations (< 10 $\mu\text{g m}^{-3}$). This could be due to the small amount of inox trapped on the fibre which limited the catalysis of artefact formation.

Even if we had not observed metal particles on the PDMS and PDMS/Dvb fibres tested, as they have already been found on PDMS,¹⁵ it was considered that metal particles can be present on all coatings and, thereby, no differences should be considered on that point between fibres.

Therefore, to explain the differences between fibres in artefact formation, the residence time of analytes on fibres during desorption was considered.

Influence of residence time. A long residence time can favour contact with the inox catalyst and lead to enhanced by-products synthesis. To check this hypothesis, the desorption rate of dipropylamine from porous fibres was evaluated by changing the temperature of the injection port from 100 °C to 250 °C (Fig. 5). For the amines tested, the total desorption was achieved at 140 °C with PDMS/Dvb fibre, while with PDMS/Car fibre, maximal desorption only occurred at 250 °C. This slower desorption rate is probably due to the microporosity of Carboxen which induces stronger interactions between analytes and adsorbent. Therefore, contact between inox particles on the fibre and amines is long enough to favour a reaction, compared to the divinylbenzene fibre.

Conclusion

When using the PDMS/Carboxen fibre for air sampling of odorous amines, artefacts were observed in the GC chromatogram. Identification by GC-MS suggested that these com-

pounds were unsaturated amines which were further demonstrated to be formed from the studied amines. Reactions were found to occur in the GC injection port, enhanced by temperature and catalysed by metal particles provided by the inox needle of the SPME device. It was also assumed that the long desorption time occurring with the PDMS/Car fibre favoured the production of artefacts in contrast to the other SPME fibres studied (PDMS and PDMS/Dvb). Consequently, even if Carboxen is a very interesting coating for the sampling of small molecules such as VOCs, its application to aliphatic amines is not recommended. Indeed, this can lead to uncertainty in the identification of the amines initially present in the sample, and to unreliable quantitative results. However, these problems were not significant when using PDMS or PDMS/Dvb fibres. So, a compromise should be found between the performances of SPME fibres and their ability to stay inert towards the sample.

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