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IMPORTANCE OF THERMAL PARAMETERS IN SOLID-PHASE MICRO-EXTRACTION (SPME) ANALYSIS

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Abstract

SPME is a powerful trace analysis technique which involves several thermal processes: fiber cleaning, conditioning, surface analyte adsorption, and desorption in the analytical device. Fiber conditioning is a main operation, since it results in a severe modification of the fiber surface, enhancing its adsorptive properties. The influence and orders of magnitude of the thermal parameters required for desorption are evaluated and discussed. The cooling down due to adsorbate desorption is completely negligible in comparison with the heat transfer capabilities of the system. Thus, the limiting factor is not heat transfer, but desorption activation energy.

Keywords: SPME, surface, trace analysis

Introduction

Although solid-phase micro-extraction (SPME) is not directly a thermoanalytical technique, it requires several highly heat-dependent processes. Special care therefore has to be taken as regards all thermal steps involved in order to achieve accurate and reproducible SPME analytical determinations. In its first developments, SPME was essentially devoted to determinations of volatile, light molecules.

In a natural environment, and especially in lacustrine waters, many species are present at ultratrace levels. However, their molecular masses are often higher than those for which the SPME technique was initially developed. Since SPME is an excellent preconcentration technique, it seemed natural to try to adapt it for such determinations. We recently demonstrated [1] that trace amounts of molecules with molecular mass up to about 500 g mol^{-1} could also be determined by this technique.

However, a large number of the determined species are merely slightly soluble in water, and some of them are virtually completely insoluble. Nevertheless, they can be present in water as metastable solutions, their high dilution level hindering (by kinetic factors) their nucleation and precipitation. A thermodynamic and kinetic study of such properties shows [2] that conventional sampling, even in large vessels, will result in rapid alterations in the composition, due to interactions with the vessel walls.

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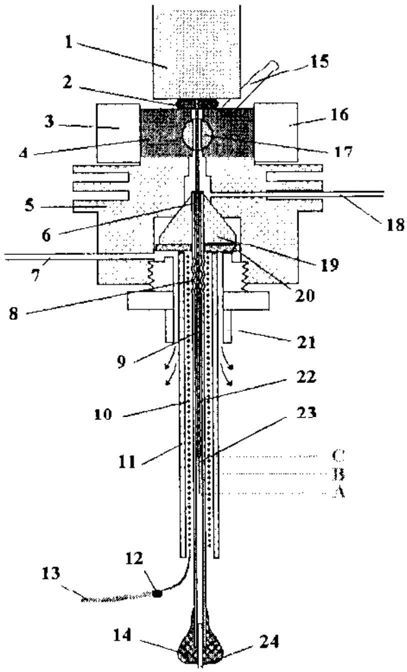

Fig. 1 SPME modified manual injector: 1 – adjustable needle guide, 2 – o-ring seal, 3 – valve bed, 4 – valve seal, 5 – primary cooling, 6 – silica tubing, 7 – secondary cooling, 8 – fiber holder centering windings, 9 – septum piercing needle, 10 – heating resistor (Ni–Cr), 11 – external quartz glass protective coating, 12 – welding, 13 – nickel–chromium wire, 14 – sodium metasilicate seal, 15 – valve lever, 16 – valve bed, 17 – stainless steel rotating valve, 18 – carrier, 19 – graphite cone, 20 – lead seal, 21 – cooling sleeve, 22 – fiber holder, 23 – SPME fiber, 24 – capillary column; A, B and C: SPME fiber reference points of Fig. 2

A specially designed on-site sampling system [3] based on SPME preconcentration allows the problems of sample handling, transfer and storage to be overcome. However, since the sampling has to be done in a natural environment, thermal control of the sample is no longer possible. It was therefore of primary importance to examine all the thermal aspects correlating the preconcentration phenomena and the composition of the analyte.

Further, not only the composition and the temperature of the analyte are essential for accurate determinations. The sampling device itself, generally a modified silica fiber, preconcentrates the determined species by adsorption phenomena. Thus, its specific surface is of basic importance. Moreover, under certain thermal conditions, especially in contact with water, silica may result in the formation of nanoporous species. Since the SPME fiber is thermally desorbed in order to introduce the adsorbed species into the analytical device, such conditions are attained during the desorption process. This work shows how such phenomena occur, and how important they can be for a description of the evolution of the adsorption properties of the fiber during its use.

To this end, the adsorbed species require the desorption of thermal energy from the fiber. Therefore, this work examines the heat transfer onto the fiber surface during the desorption step and compares the available energy with the work required for good desorption without degradation of the adsorbates.

Experimental

The SPME measurements were carried out on aqueous test samples. Capillary gas chromatography with a Fisons Instrument GC 8000 chromatograph fitted with an apolar DB 5 capillary column coupled to a flame ionization detector was used for detection and determination. The carrier gas was hydrogen, fed at 50 kPa. The SPME injection head was a manual injector [4] specially modified for the described purpose (Fig. 1). The SPME fiber was a Supelco Carboxen-PDMS (polydimethylsiloxane) 75 μm type, ref. 5–7318, recommended by its manufacturer for 'light' species determinations.

Temperature measurements were made by means of an inconel-coated chromel–alumel (K-type) thermocouple, insulated from the coating, with external diameter 0.25 mm and length 0.5 m, provided with a 2 m extension (ref. Thermocoax 2 AB I 025/500 mm/TI/FI K/2 AB 25 NN/2M). The inner insulating filling was magnesia powder.

A typical SPME determination was carried out within three steps as follows.

Fiber cleaning

The fiber was introduced into the chromatograph, followed by heating up for 5 min to 200–300°C. Any adsorbed species were desorbed and fed to the inlet of the capillary column. A thermal program developed for the good separation of species in the molecular mass range from about 50 to 450 g mol^{-1} consisted in a thermal ramp of 6 K min^{-1} from 50 to 310°C, followed by a constant temperature plateau at 310°C for 42 min.

Normally, this first run resulted in a blank. When unidentified signals appeared during the run, the same procedure was repeated until the blank signal became reproducible. Some signals resulting from the polymer used to fix the SPME fiber on its metallic fiber holder were unavoidable, however.

Adsorption

The fiber was immersed in the aqueous sample under constant stirring and temperature control. During this step, adsorption occurred. The adsorption of ultratrace species was controlled by the transportation kinetics (convection, diffusion, migration, etc.). At equilibrium, the amounts of adsorbed species depended on thermodynamic factors. More particularly, the sharing coefficient of the determined species between the sample and the fiber surface defined the evolution of the corresponding equilibria following the Van't Hoff law. This work showed that the fiber only became efficient for heavy molecule determinations after numerous adsorption-desorption cycles. During the early cycles, the fiber was completely unable to adsorb the heaviest molecules. Its adsorbing capabilities increased as a function of the number of adsorption-desorption cycles; this first period of the lifetime of a fiber is called the conditioning period.

Desorption and determination

The fiber was returned to the chromatograph injector and treated in exactly the same way as described for fiber cleaning. The corresponding signal was then compared with that of the previously obtained blank.

Results and discussion

Although the detection is chromatographic, SPME is essentially a thermal technique, even if most commonly performed at room temperature.Therefore, it appears to be of main importance to define clearly all thermal parameters which determine the behaviour of the fiber.

Thermal longitudinal profile

In the injector, the fiber is leached by the hydrogen carrier flow. The thermal energy produced by the heater along the external side of the injector tubing surrounding the fiber has to cross over the flowing hydrogen layer (Fig. 1). Depending on the relative velocities of heat transfer and hydrogen flow, the upper part of the SPME fiber could be expected to be cooled down by insufficiently heated hydrogen.

The observed heat profiles (Fig. 2) are determined by means of a thermocouple chosen so as to exhibit approximately the same thermal behaviour as that of the

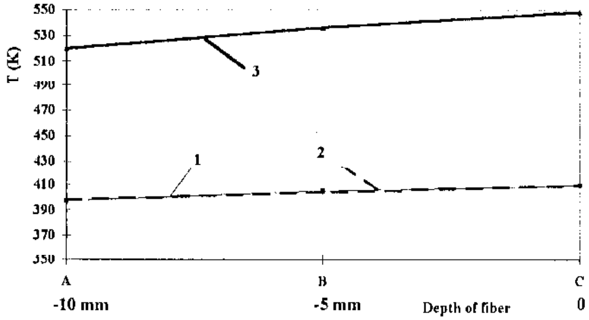

Fig. 2 Longitudinal thermal profile of SPME fiber: A, B and C: reference points of the fiber as shown in Fig. 1; 1 – (full line) heating power: 3 W, hydrogen carrier flow on; 2 – (dotted line) heating power: 3 W, hydrogen carrier off; 3 – (full line) heating power: 8 W, hydrogen carrier on

SPME fiber (0.25 mm diameter for the thermocouple, 0.30 mm for the SPME fiber, thermocouple filling: powdered magnesia in an inconel housing; fiber material: monolithic silica).

It appears that all along the fiber the temperature is very constant, within less than ±1.2% at 130°C, corresponding to a heating power of 3 W, and less than ±3%, at 265°C, corresponding to a heating power of 8 W. The indicated heating powers correspond to the total required power, including losses towards the instrument and heat transport towards the GC column by the hydrogen flow.

Heat flow towards the fiber surface

In order to estimate the effective heat flow towards the SPME fiber, measurement of the time constant of the temperature risetime was carried out. The time constant τ was found to be 5.8 s and the temperature rise rate $\mathrm{d}T/\mathrm{d}t$ as 0.2 K s^{-1} per degree temperature difference between the carrier gas and the thermocouple. For an approximate evaluation of the heat flow towards the fiber in the injection head, we assume the mean specific heat to be the same for the SPME fiber (bulk: silica) and the thermocouple (two metallic wires, powdered magnesia filling, inconel coating) used for thermal behaviour determination, since the shape of the thermocouple was chosen to be as similar as possible to that of the SPME fiber.

The specific surface of the thermocouple is

$$\mathrm{d}S=\pi d\mathrm{d}L$$

for a corresponding volume

$$\mathrm{d}V=\frac{\pi d^2}{4}\mathrm{d}L$$

so that the heat exchange coefficient between the SPME fiber and the hydrogen carrier gas can be evaluated as follows

$$k=\frac{\mathrm{d}Q/\mathrm{d}t}{\mathrm{d}S\Delta T}$$

where $\mathrm{d}Q=\mathrm{d}mc_\mathrm{p}\mathrm{d}T=\rho\mathrm{d}Vc_\mathrm{p}\mathrm{d}T$, so that finally

$$k=\frac{\rho\pi d^2/4\mathrm{d}Lc_\mathrm{p}\mathrm{d}T/\mathrm{d}t}{\pi d\mathrm{d}L\Delta T}=\frac{\rho dc_\mathrm{p}}{4\Delta T}\frac{\mathrm{d}T}{\mathrm{d}t}$$

where k heat transfer coefficient (J s^{-1} cm^{-2} K^{-1}), d fiber diameter (cm), S fiber surface (cm^2), V fiber volume (cm^3), Q heat (J), t time (s), T temperature (K), ρ specific mass (g cm^{-3}), c_p specific heat (J g^{-1} cm^{-3}), ΔT temperature difference between fiber and carrier gas (K), m mass of the fiber (length L), $\mathrm{d}m$ differential mass of the fiber (length $\mathrm{d}L$). For the thermocouple, we assume the following numerical values:

d=0.025 cm ρ=2.6 g cm^{-3} [5]
L=1.0 cm c_p=0.91 J g^{-1} cm^{-3} [5]
$dT/(dt\Delta T)$=0.2 s^{-1},
so that k=0.12 J s^{-1} cm^{-2} K^{-1},
and for the whole fiber kS=9.3·10^{-3} J s^{-1} K^{-1} ≅10^{-2} J s^{-1} K^{-1}

When GC measurements are carried out on the fiber, the maximum total amount of all adsorbed species on the fiber is near 20 μg at fiber surface saturation. A similar amount of water simultaneously wets the fiber surface. The total volume of the SPME fiber is about 0.7 mm^3 and its surface area is 9.5 mm^2. Since the heat of vaporization of water H_{vap} (about 2.25 kJ g^{-1} [5]) is 5–10 times higher than those of volatile organic compounds, the most important part of the heat required for desorption is consumed by water evaporation.

Thus, it becomes possible to evaluate the energy W_{des} required for desorption of the adsorbate on the fiber:

$$W_{des} = mH_{vap} = 20\cdot10^{-6}\cdot2250 = 4.5\cdot10^{-2}\ \mathrm{J}$$

As compared with the value of kS determined above to be near 10^{-2} J s^{-1} K^{-1}, it appears that the cooling down due to adsorbate desorption is completely negligible in comparison with the heat transfer capabilities of the system. Thus, the limiting factor of desorption is not related to the heat transfer, but rather to the kinetic limitation of the rate of desorption of the adsorbed species, and essentially the activation energy required to overcome the adsorption energies of the analytes.

Thus, the desorption temperature has to be as high as possible without degradation of the adsorbates, not in order to enhance heat transfer, but rather in order to increase the desorption velocity following the Arrhenius law.

Fiber cleaning

The first prerequisite for SPME determinations is a clean, well-defined adsorption surface of the fiber. Figure 3 depicts the evolution of the fiber adsorbates. During the first run of the fiber (line 1), numerous ghost peaks appear in the chromatogram (peaks 'A'). Therefore, a thermal cleaning of the fiber is carried out at 250°C over a period of 2 h, in a continuous flow of hydrogen. After three such runs (Fig. 3, line 2), the ghost peaks have completely disappeared. Merely one huge peak remains. Its presence is due to the polymer fixing the fiber on its holder (peak 'B'). Once this state has been reached, the fiber conditioning can be started.

Fiber conditioning

Just after cleaning as described above, a new fiber generally has very poor adsorptive properties. The development of its properties is generally attained by a conditioning step, consisting in repeated heating under a convenient gas flow after a complete adsorption procedure in an aqueous test sample, until the fiber leads to ghostless, reproducible signals. A complete conditioning cycle consists in an analyte adsorption step (duration: a few minutes up to several tenths of an hour) followed by the desorption step in the gas-chromatograph injector. In order to verify the quantitative character of the first desorption, two identical desorption steps are carried out under the same heating conditions, but without the previous adsorption step.

The desorption temperature is limited by the fiber stability, essentially in relation with the polymer sealing the fiber on its holder. Heating temperatures up to 300°C are generally the maximum allowed by the fiber manufacturer. Figure 3 shows the evolution of the fiber behaviour with increasing numbers of preconditioning: after the first cycle, no analyte peak is observable (Fig. 3, line 3, peaks 'C' are absent) and even after 6 preconditioning cycles, no observable adsorption of peaks 'C' occurs (Fig. 3, line 4). After about 10 preconditioning cycles, however, the fiber is ready for use: analytical peaks 'C' appear (Fig. 3 line 5), and allow qualitative determinations. Quantitative determinations require the use of internal standards.

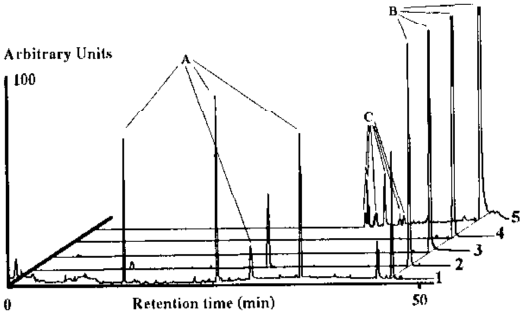

Fig. 3 SPME fiber thermal conditioning: fiber chromatograms as a function of thermal treatment; 1 – first run of the fiber; 2 – after 3 dry cleaning steps for 2 h at 250°C; 3 – first conditioning run with adsorption cycle in water; 4 – after 6 conditioning cycles; 5 – after 10 conditioning cycles; A – initial ghost peaks; B – ghost peak remaining from fiber attachment; C – analyte peaks

To explain the observed behaviour, the following assumptions are made:

At 300°C, a study of water desorption by vacuum monitoring on glass vessels revealed that the desorption occurs with a time constant of several hours. Such behaviour demonstrates that the water is very strongly bound to the fiber surface and requires very high activities for it to become able to leave the adsorption layer. During the water desorption step, the activity of the water in the adsorption layer is in equilibrium with that of the gaseous water present in the gas diffusion layer close to the SPME fiber surface. Since the hydrogen gas flow along the fiber is maintained throughout the whole desorption step, the partial pressure of water in the hydrogen flow is far below the hydrogen inlet pressure.

The activity a of a component in an ideal gas phase is given by the ratio of its prevailing pressure P to its pressure P_0 under the standard conditions defining the unit value of activity. Hence:

$$a=\frac{P}{P_0}$$

The activity of water in the gaseous carrier phase is kept at very low values by means of the continuous regeneration of the gaseous interface layer at the fiber surface, and at all event below the saturation value, i.e. at a value lower than unity.

On the other hand, the vapour pressure of water is 3.13 kPa at 25°C, 1500 kPa at 200°C, 3900 kPa at 250°C and 8500 kPa at 300°C [5], leading to activities of water (with reference to the standard conditions of water at 25°C) up to 490 at 200°C, 1250 at 250°C and 2700 at 300°C.

Since the SPME fiber is maintained at such high temperatures for at least 5 min, the silica substrate will not be able to release all its adsorbed water content.

Silica is the anhydride of silicic acids, the equilibria of formation which from silica and water can be schematically represented by the following equations:

$$n\mathrm{SiO_2} + m\mathrm{H_2O} \leftrightarrow \mathrm{Si_nO_{(2n-m)}(OH)_{2m}}$$

For m/n=2, this equilibrium corresponds to the theoretical formation of orthosilicic acid, $\mathrm{Si(OH)_4}$.

In fact, the actual equilibria are extremely complex and lead to a particularly wide series of products, most of which possess microporous structures. The mechanisms, thermodynamics and kinetics of such reactions have been thoroughly examined [7, 8], as a consequence of the mobility of the silicon atoms in fiber strongly hydrated environment due to silicon–oxygen–silicon bridges opening on silanol function formation during hydrothermal treatment.

In fact, the extremely high activities of water under the described experimental conditions are equivalent to high pressures of steam interacting with the silica substrate of the fiber. They lead to the stabilization of the hydrated forms of silica generally obtained in hydrothermal syntheses by working under high steam pressures in an autoclave heated at the corresponding temperatures.

Only after the fiber has been repeatedly conditioned by wetting and subsequent water desorption at temperatures from 200 to 300°C does the commercially available fiber become able to adsorb larger molecules than those for which it was initially designed by the manufacturer.

Analytical determinations by fiber desorption

Figure 4 shows part of a chromatogram obtained by SPME as described above. Identification of the observed products, the molecular masses of which are in the range 300–400 g $\mathrm{mol^{-1}}$, is not the aim of this work and will therefore not be discussed here. It is important to observe that the amounts of different products adsorbed on the fiber depend on the time of contact between fiber and analyte. For some products, the variations in their adsorbed amounts as a function of time may be quite opposite, depending on the contact time, some of them increasing with time (Fig. 4, lines B), while others decrease (Fig. 4, lines A). This is due to competition

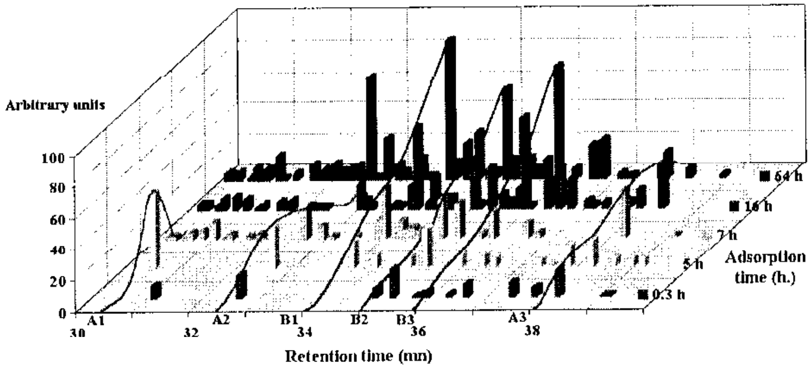

Fig. 4 SPME chromatogram evolution as a function of adsorption time: A1, A2 and A3 – kinetic species disappearing with long adsorption times; B1, B2 and B3 – thermodynamic species increasing with long adsorption times

phenomena between some first, but weakly adsorbed species, and other slowly, but strongly adsorbed ones.

It can be assumed as a first approximation that for a given species *i*, the adsorption rate dn_i/dt is proportional to its concentration C_i, and to the still free surface area S_f of the fiber (not yet occupied by the adsorbing species, nor by other previously adsorbed ones), and depends on a kinetic velocity coefficient (diffusion, stirring, etc.) *D*, and a thermodynamic stability factor *k* related to the strength of the adsorptive interactions between the adsorbate and the fiber surface. This factor *k*, defined as the ratio between S_c and S_t, i.e. the covered and the total fiber surfaces at a given reference concentration C_{i0} of the species *i*, can be correlated with the sharing coefficient (taking into account the corresponding units). Thus:

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = C_i S_f D, \text{ where } S_f = S_t - S_c \text{ and } \frac{S_c}{S_t} = r$$

Both *D* and *r* are functions of the temperature. Zhang *et al.* [9] mentioned the possibility of overcoming the kinetic limitation by heating the sample. However, heating not only increases the kinetics (*D*), but also has severe effects on the thermodynamic parameters (*r*, the solubility and hence the activity of the dissolved species, etc.). Thus, in complex analytes, one cannot simply heat the sample in order to accelerate the studied phenomena without completely altering the relative behaviour of the different components.

As long as merely one kind of species is present in the analyte, no problem arises in quantitative determinations. However, as soon as several species are present (which is obviously the most common and most interesting case), the magnitude S_{fi} for a given species *i* no longer remains independent of the presence of species *j*, covering a surface S_{cj}, so that

$$S_{fi} = S_t - \sum(S_{cj})$$

Although all parameters required for the numerical solution of these equations have not yet been determined, we could observe both kinetic species (Fig. 4, lines A), and thermodynamic ones (Fig. 4, lines B), in a natural water determined in this way. Some kinetic species, noticeably adsorbed on the fiber after a short adsorption time (Fig. 4, line A-1), are rapidly desorbed on longer contact times by very stable species such as those corresponding to lines B. Since both stability (Van't Hoff law, etc.) and rate (Arrhenius law, etc.) depend on temperature, the control of temperature and contact time allows selection of the adsorbed species in a complex analyte.

Conclusions

This work demonstrates how important all thermal parameters are when SPME determinations are to be carried out. As concerns the fiber behaviour, it was revealed that thermal treatment is extremely important for the development of the adsorptive properties of the fiber. The fiber surface undergos strong modifications during water desorption above 100°C, presumably because of the formation of a nanoporous superficial structure on the silica fibers. To achieve such fiber surface state, more than 20 adsorption-desorption cycles are required. As concerns the sample behaviour, thermal control in relation with time control allows control of the selectivity of the fiber. Neglect of these aspects may lead to major errors when quantitative measurements are carried out, since the interferences between different species are highly temperature-dependent.

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