EVALUATION OF PDMS-COATED STIR BARS FOR THE USE AS PASSIVE SAMPLERS IN THE ANALYSIS OF ORGANOCHLORINE PESTICIDES AND POLYCYCLIC HYDROCARBONS IN AIR

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Abstract

There is an increasing interest of passive sampling methods, which produce reliable data about air contamination with persistent organic pollutants (POPs). These should be easy to handle and the analyses should be capable of being automated. In this context, first validation experiments were performed, which focused on uptake studies and the quantitative analysis of organochlorine pesticides (OCPs) and polyaromatic hydrocarbons (PAHs) adsorbed on PDMS-coated stir bars. The results present that the quantitative detection of adsorbed compounds is possible in the observed concentration range (10 to 4000 pg) by using the isotope dilution technique. The sampling properties of the stir bars reflect well different atmospheric concentrations they were exposed to. The method does not need any time-consuming sample pretreatment and the detection can be highly automated.

Introduction

Through the Stockholm Convention national und international controls on the production and use of persistent organic pollutants (POPs) have been introduced. This includes the examination of the atmosphere as a pathway from primary or secondary sources of POPs to terrestrial or aquatic foodwebs.

The classical method for air monitoring is the “active” sampling by use of high volume samplers. Because of being expensive and the requirement of electricity and trained operators only limited sampling sites can be established. In the recent years there has been increasing interest in developing new analytical tools for atmospheric monitoring of these contaminants which allow routinely and cost-effective sampling at a larger numbers of sites[1]. This led to the introduction of passive samplers like semipermeable membrane devices (SPMDs), polyurethane foams (PUFs) or other materials, which proved their utility for monitoring gaseous pollutants[2]. But these materials still have the need for sample preparation before analysis, which is labour-intensive and time-consuming. The development of sensitive, easy to handle methods, which allow an automation of the analytical process is still of interest.

To establish a new sampling and assay technique, tests with PDMS-coated stir bars were carried out. These bars were established for the analysis of organic compounds from aqueous matrices and were used only as aqueous media passive samplers so far[3,4]. But it is also supposed that they are capable of atmospheric sampling. The accumulated substances can be directly analyzed after thermodesorption, a sample pretreatment is not necessary and a high degree of automation is possible.

In this paper results of first validation experiments will be published, which focused on uptake studies and the quantitative detection of organochlorine pesticides (OCPs) and polyaromatic hydrocarbons (PAHs) on the stir bars.

Materials and Methods

Standards and Materials. All used solvents were of trace analysis grade and supplied by LGC Promochem (Wesel, Germany). The PDMS-coated stir bars (Twister^{TM}, length: 20 mm, film thickness: 1.0 mm) were purchased from Gerstel (Mülheim, Germany). The ^{13}C-labeled OCPs were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The deuterated PAH standards were acquired from Dr. Ehrenstorfer (Augsburg, Germany), as well as the unlabeled OCPs and PAHs. The standards were available as individual solution or as mixtures. Diluted mixtures were prepared in cyclohexane separated according to the group of analytes.

Directly Spiking of the Stir Bars. For this experiments the standards were directly spiked onto the coating of the stir bars at volumes of 0.1 to 4 µl applied with zero dead volume microsyringes: Hamilton model no. 7001 or

7002 (Hamilton Company, Reno, NV, USA) and ILS Series T 10 µl (ILS GmbH, Stuetzerbach, Germany).

Indirectly Loading of the Stir Bars. To load the stir bars via the gaseous phase the unlabeled standard mixtures were spiked at the glass wall of 10 ml amber screw cap vials. In each vial one stir bar was placed, ensuring that it has no direct contact to the spiked spot. The vials were closed and kept for at least 3 days at room temperature. Right before analysis the stir bars were directly spiked with the labeled standard mixture as above mentioned.

Instrumental Analysis. The quantitation and qualitative control of the compounds loaded on the stir bars was performed by thermodesorption-GC/MS. An Agilent (Palo Alto, CA, USA) GC 5890 Series II was equipped with an autosampler Gerstel MPS 2, a tray for 98 desorption tubes Gerstel VT98t, and a desorption unit Gerstel TDU which was coupled to a cold injection system Gerstel CIS 3. The Gerstel MASter software was used to control and set the parameters for the autosampler, desorption unit and the injection system.

For thermal desorption the spiked stir bar was placed in a cleaned desorption tube of the autosampler tray and afterwards automatically handled by the control program. The applied conditions are listed in Table 1.

The GC system was connected to a high resolution mass spectrometer Thermo Scientific MAT 95 (Bremen, Germany) and a Restek (Bellefone, PA, USA) Rtx-CLPesticides2 capillary column (length: 30 m, 0.25 µm i.d., 0.20 µm film thickness) was used for the chromatographic separation. Helium served as carrier gas at a head pressure of 16 psi.

The MS was operated in SIM mode at a resolution of >8000. For chlorinated compounds the two most intense ions of the molecular ion cluster or a high abundant fragment ion cluster were monitored. For the PAHs only the single mass of the molecular ion was recorded.

Results and Discussion

Optimizing of the thermodesorption. The parameters desorption temperature, desorption time and cryofocusing temperature had to be optimized to achieve an almost quantitative transfer of the adsorbed compounds from the stir bar to the GC column and hence an optimum response at the detector.

A second desorption of the same stir bar was performed to detect the amount of compounds which were remaining after the first step. These quantities were minimized by varying the desorption time (4, 6, 8 min) and temperature (260, 280, 300°C).

The desorbed chemicals were cryofocused in the cold injection system by cooling the device with liquid nitrogen before they were transferred to the GC column. The cryofocusing temperature should be low enough to sufficiently trap the highest volatile compound to be analyzed, but too cold temperatures could also have a negative effect on the compound's response as described by León et al.[3]. The ratio of high to low volatile components at different cryofocusing temperature (-100, -65, -30, 0°C) were monitored, as well as the absolute response of the chemicals. The optimum parameters found for the thermodesorption separated by the group of compounds are listed in Table 1.

Table 1: Optimum parameters for the thermodesorption

	OCP	PAH
Desorption temperature	280°C	280°C
Desorption time	8 min	6 min
Cryofocusing temperature	-30°C	-65°C
Desorption flow (helium)	70 ml/min	70 ml/min

Validation experiments. To exactly determine the concentration of a compound adsorbed on a stir bar a linear relation between the standard and the analyte has to exist. To proof that a set of stir bars were spiked with a constant amount of labeled standards (1000 pg) and varying amounts of unlabeled standards (10, 100, 500, 1000, 2000, 4000 pg). The mass ratio ($m_{i,12C}/m_{i,13C}$) was plotted versus the ratio of the resulting signal areas ($A_{i,12C}/A_{i,13C}$) and a linear regression was applied. The results for the slope of the graph and the coefficient of determination (R^2) for selected compounds are listed in Table 2. The R^2 values indicate a good linearity in the observed concentration range for the correct quantitation of all compounds, except Benzo(g,h,i)perylene. Due to its low volatility this compound desorbs from the stir bar to a minor extend and thereby shows a low response resulting in a larger uncertainty. The slope of the regression curve is close to 1 for all substances, showing that no discrimination in either direction, towards the labeled or unlabeled compound, occurs.

A similar experiment was performed where the linearity of the quantification was examined not only by directly spiking the stir bars, but by exposing them to different simulated atmospheric concentrations. For that the stir bars were placed in screw cap vials, where the standards (100, 500, 1000, 2000, 4000 pg) were spiked at the glass wall (see experimental section). The results of this experiment are shown in the two right columns of Table 2. As the coefficients of determination indicate a linear relationship between the analyses of the different simulated gaseous concentrations is confirmed. The quality of the results is similar to the previous experiments with the directly spiked standards, which shows that the coated stir bars perform well as passive samplers for the gas phase and reflect the variable concentrations of chemicals they were exposed to.

Table 2: Results of the spiking experiments after performing a linear regression without intercept (y=bx), R^2=coefficient of determination, Recovery=percentage of spiked standard detected on the stir bar

	direct		exposed	
	Slope (b)	R^2	R^2	Recovery %
α-HCH	0.9454	0.9925	0.9973	103
γ-HCH	0.9148	0.9937	0.9985	92
Hexachlorobenzene	0.8727	0.9935	0.9942	94
4,4'-DDT	0.8659	0.9979	0.9977	101
4,4'-DDD	0.9401	0.9948	0.9896	97
4,4'-DDE	0.9861	0.9943	0.9975	110
trans-Chlordane	0.9234	0.9978	0.9969	104
Heptachlor	0.9519	0.9992	0.9976	97
Aldrin	0.9990	0.9958	0.9975	110
Endosulfan-I	0.9472	0.9973	0.9961	107
Naphthalene	1.1374	0.9875	0.9796	129
Fluorene	1.0587	0.9955	0.9895	99
Pyrene	0.9010	0.9951	0.9833	84
Chrysene	0.9272	0.9973	0.9923	59
Benzo(a)pyrene	0.8237	0.9977	0.9697	29
Benzo(g,h,i)perylene	0.7008	0.9727	0.8343	3

The detected percentages of the total amounts spiked into the vial are listed in the recovery column of Table 2. Interestingly, for a certain compound the recoveries were constant over all concentration levels, only small variations were observed; thus, the mean values are displayed. For the OCPs it can be stated that the total amount spiked finally was adsorbed by the stir bars, whereas within the group of the PAHs the recovery is decreasing with declining volatility.

The constant recoveries let conclude that a state of equilibrium was reached over the time of exposure (at least 3 days). To get an impression about the kinetcs of the adsorption in a simulated environment and the achievement of the equilibrium a set of screw cap vials were spiked at a certain starting point with equal amounts of standards and one stir bar was placed inside, respectively. The stir bars were exposed over different time periods (5, 24, 48, 168 h) and afterwards directly spiked with labeled standards and analyzed. The results for selected compounds are listed in Table 3.

Table 3: Recoveries in % of spiked standards after different exposure times

	Exposure time			
	5 h	24 h	48 h	168 h
γ-HCH	76	95	96	103
Hexachlorobenzene	89	95	94	103
4,4'-DDT	5.8	35	40	79
trans-Chlordane	35	79	61	95
Aldrin	71	84	86	97
Endosulfan-I	17	74	55	78
Acenaphthene	77	99	62	88
Pyrene	69	83	60	103
Chrysene	27	52	38	101
Benzo(b)fluoranthene	1.4	8.8	0.8	47
Benzo(a)pyrene	0.4	1.9	0.4	29
Benzo(g,h,i)perylene	n.d.	n.d.	n.d.	1.1

High volatile compounds were transferred to the stir bar to the greatest amount already after 5 h exposure, whereas the semi-volatiles need at least a period of 7 days to equilibrium. The amounts adsorbed for the low volatile substances were increasing over the whole observed period; it is likely that they will arise further if exposed over a longer time and that they are still in the phase of linear uptake. Because of the design of the experiment it can not be concluded that the adsorption of high volatile compounds on the stir bars is preferred. It has to be considered that the substances first have to desorb from the glass wall before they can be adsorbed to the coated bar. This process takes a longer time for the low volatile chemicals and has an impact on the results presented.

In summary, the obtained experimental data present that the PDMS-coated stir bars are suitable passive samplers for the analysis of OCPs and PAHs in gaseous environments. It could be shown that the quantitative detection of adsorbed compounds is possible in the observed concentration range by using the isotope dilution technique. They reflect well different atmospheric concentrations they were exposed to. Compared to other established samplers they do not need labour-intensive and time-consuming sample preparation and no solvents have to be used. With the help of modern instrumental equipment a large number of samples can be analyzed automatically. A disadvantage is that a sample can only be analyzed one time; therefore the employment of replicate stir bars is advisable.

Comparisons of PDMS-coated stir bars with other passive samplers, such as SPMDs or pine needles, are ongoing.

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