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One-Calibrant Kinetic Calibration for On-Site Water Sampling with Solid-Phase Microextraction

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The existing solid-phase microextraction (SPME) kinetic calibration technique, using the desorption of the preloaded standards to calibrate the extraction of the analytes, requires that the physicochemical properties of the standard should be similar to those of the analyte, which limited the application of the technique. In this study, a new method, termed the one-calibrant kinetic calibration technique, which can use the desorption of a single standard to calibrate all extracted analytes, was proposed. The theoretical considerations were validated by passive water sampling in laboratory and rapid water sampling in the field. To mimic the variety of the environment, such as temperature, turbulence, and the concentration of the analytes, the flow-through system for the generation of standard aqueous polycyclic aromatic hydrocarbons (PAHs) solution was modified. The experimental results of the passive samplings in the flow-through system illustrated that the effect of the environmental variables was successfully compensated with the kinetic calibration technique, and all extracted analytes can be calibrated through the desorption of a single calibrant. On-site water sampling with rotated SPME fibers also illustrated the feasibility of the new technique for rapid on-site sampling of hydrophobic organic pollutants in water. This technique will accelerate the application of the kinetic calibration method and also will be useful for other microextraction techniques.

Monitoring of organic and inorganic environmental pollutants represents an ongoing challenge to the environmental chemist.[1−3] Sampling is the most important step of any analytical procedure.[4−6]

Solid-phase microextraction (SPME) was developed to address the need for rapid sampling and sample preparation, both in the laboratory and on-site.[7] On-site sampling devices that are based on SPME integrate sampling with sample preparation and sample introduction.[8,9] Unlike traditional sample preparation methods, SPME typically is a nonexhaustive extraction technique in which only a small portion of the target analyte is removed from the sample matrix. Therefore, calibration of the SPME for quantitative analysis is very important. Several SPME techniques have been developed for on-site sampling based on different calibration methods.[10−12]

The development of SPME calibration methods is based on an understanding of the fundamental principles governing the mass transfer of analytes in multiphase systems. Theory has been developed to understand the principal processes involved in SPME by applying the basic fundamentals of thermodynamics and mass-transfer kinetics.[13] In 1997, Ai proposed a dynamic model of SPME based on a diffusion-controlled mass-transfer process.[14,15] Based on this model, Chen et al. demonstrated the isotropy of absorption and desorption in the SPME liquid coating fiber, and a new concept that is standard in the extraction phase or called the "in-fiber standardization technique" was proposed;[16,17] later, this was termed as the "kinetic calibration method".[18,19] The method uses the desorption of the standards, which are preloaded in the extraction phase, to calibrate the extraction of the analytes. The concentration of the analyte in the sample matrix can be calculated with the amount of the extracted analyte, the preloaded standard, the standard remaining in the SPME fiber coating after sampling time, the volume of the fiber coating, and the distribution coefficient of the analyte between the fiber coating and the sample matrix.

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The concept of a standard in the extraction phase is especially important for the calibration of on-site, in situ, or in vivo analysis, since it is difficult to measure or control the agitation condition in these cases, and direct spiking of standards into the matrix is not possible. This technique has been successfully used for liquid-phase microextraction (LPME),[18,19] fast in vivo drug analysis,[20−23] and other water samplers.[24,25] The concept of a standard in the extraction phase also makes it possible to use a simple polydimethylsiloxane (PDMS) rod or PDMS membrane as a passive sampler.[26,27]

However, the theoretical study and experimental demonstration of the feasibility of this technique for time-weighted average (TWA) water sampling are insufficient, and the existing technique requires that the physicochemical properties of the standard should be similar to those of the analyte, which is normally achieved using isotopical standards. For a group of analytes, the number of isotopical compounds must be preloaded, which limited the application of the technique. To overcome this problem, a dominant desorption method was proposed.[28] In this method, the target analytes in high concentrations serve as the internal standards, which eliminates the use of isotopical standards. The dominant desorption method still requires numbers of standards to be preloaded and a new problem is presented: the sampling of analytes and the desorption of standards must be separately performed with two fibers. If the sampling and the desorption were performed simultaneously at very close positions, the desorbed analytes might pollute the sampling site and results in inaccurate reports, since the concentrations of the analytes in the desorption fiber are very high. If the sampling and the desorption were not performed simultaneously or at different sites, the conditions for the extraction and the desorption might be not the same, and using the desorption to calibrate the extraction will lead to inaccurate results.

More recently, a standard-free kinetic calibration method was proposed for rapid on-site sampling by SPME,[29] in which all extracted analytes can be calibrated with two samplings and does not need a standard to be preloaded to determine the desorption rate constant. However, the method requires that the conditions of the two samplings should be kept constant, and it is only suitable for rapid sampling.

In this study, a new method was proposed, which does not require to preload numbers of standards with similar physicochemical properties and all extracted analytes can be calibrated with a single calibrant. The new method was validated by water samplings in laboratory and field, by using commercial SPME PDMS fibers as passive samplers. The feasibility of the kinetic calibration method for TWA water sampling was also demonstrated by theoretical derivation and experimental results.

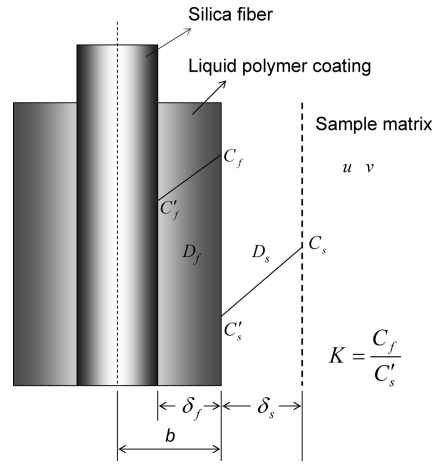

Figure 1. Schematic of the interface for a SPME liquid coating fiber exposed in a sample matrix.

Theoretical Considerations. When a SPME liquid coating fiber is exposed to a sample matrix, mass transfer from the sample matrix to the surface of the SPME fiber coating and from the surface of the fiber coating to its inner layers is the rate-determining step (see Figure 1). This process follows Fick's first law of diffusion:

$$J \equiv \frac{\mathrm{d}n}{\mathrm{d}t} = -D_\mathrm{s}A\frac{\mathrm{d}C_\mathrm{s}}{\mathrm{d}x} = -D_\mathrm{f}A\frac{\mathrm{d}C_\mathrm{f}}{\mathrm{d}x} \quad (1)$$

where J is the mass flux of the analyte from the sample matrix to the SPME fiber, A is the surface area of the fiber, and dn is the amount of the extracted analyte during sampling time dt. D_s and D_f are diffusion coefficients of the analyte in the sample matrix and the fiber coating, respectively; C_s and C_f are the concentrations of the analyte in the sample matrix and the surface of the fiber coating, respectively. A linear concentration gradient in the fiber coating and boundary layer is assumed; then,

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{D_\mathrm{s}A}{\delta_\mathrm{s}}(C_\mathrm{s} - C'_\mathrm{s}) = \frac{D_\mathrm{f}A}{\delta_\mathrm{f}}(C_\mathrm{f} - C'_\mathrm{f}) \quad (2)$$

where δ_f is the thickness of the fiber coating, δ_s the diffusion layer thickness in the sample matrix, C_s' the concentration of the analyte in the sample matrix at the interface of the fiber coating and the sample, and C_f' the concentration of the analyte in the coating at the interface of the fiber coating and the fused silica. Let $R_\mathrm{s} = D_\mathrm{s}A/\delta_\mathrm{s}$ and $R_\mathrm{f} = D_\mathrm{f}A/\delta_\mathrm{f}$; then, eq 3 can be obtained:[14]

$$\frac{\mathrm{d}n}{\mathrm{d}t} = R_\mathrm{f}(C_\mathrm{f} - C'_\mathrm{f}) = R_\mathrm{f}\left[\frac{2KR_\mathrm{s}C_\mathrm{s}}{2KR_\mathrm{f} + R_\mathrm{s}} - \frac{2R_\mathrm{s}n}{V_\mathrm{f}(2KR_\mathrm{f} + R_\mathrm{s})}\right] \quad (3)$$

where K is the distribution coefficient of the analyte between the fiber coating and the sample matrix. Let

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$$a = \frac{2R_f R_s}{V_f(2R_f K + R_s)} \quad (4)$$

and

$$b = \frac{2KR_f R_s}{2KR_f + R_s} \quad (5)$$

Equation 3 then changes to

$$\frac{dn}{dt} = bC_s - an \quad (6)$$

The integrated result for eq 6 (for $t = 0$, $n = 0$) is

$$\int_0^t \frac{dn}{dt} = bC_s - an \Rightarrow n = [1 - \exp(-at)]\left(\frac{b}{a}\right)C_s \quad (7)$$

Equation 7 means that the relationship between C_s and n is an integrative result, and it can be used for the determination of TWA concentration of the analytes in the sample. Based on eqs 4 and 5, we have

$$\frac{b}{a} = KV_f \quad (8)$$

Equation 7 then becomes

$$C_s = \frac{n}{KV_f[1 - \exp(-at)]} \quad (9)$$

For field sampling, the dynamic process for the desorption of a preloaded calibrant from a SPME fiber can be described by[17]

$$\frac{Q}{q_0} = \exp(-a't) \quad (10)$$

where a' is the desorption rate constant of the preloaded calibrant, q_0 the amount of preloaded calibrant in the fiber coating, and Q the amount of the calibrant remaining in the fiber after exposure of the fiber to the sample matrix for sampling time t.

When the rate constants a and a' have the same value (which requires that the physicochemical properties of the analytes and the calibrants should be quite similar, since the rate constants a and a' are dependent on the diffusion coefficients of the compounds in the sample matrix and the extraction phase, the distribution coefficients between the sample matrix and the extraction phase, etc.), then eqs 9 and 10 can be combined:

$$C_s = \frac{n}{KV_f[1 - (Q/q_0)]} \quad (11)$$

Equation 11 means that we can directly deploy the samplers, which preloaded a certain amount of calibrant, into the sample matrix and retrieve them after different sampling times; then the concentration or TWA concentration of the target analyte during the sampling time can be calculated, since n and Q can be determined, and K, V_f, and q_0 are already known.

The feasibility of eq 11 requires that the physicochemical properties of the target analyte and preloaded calibrant should be quite similar, which typically achieves by using an isotopically labeled compound as the calibrant. When several analytes are determined simultaneously, many calibrants are required. It is inconvenient for real applications, since the process of preloading numbers of calibrants will be complex and sometimes isotopically labeled compounds are difficult to find. Therefore, using a single calibrant to calibrate all analytes is very important.

Let us assume that 10% deviation of C_s is reasonable for on-site and in vivo analysis; then, an ~10% difference in the value of $\exp(-at)$ is acceptable, based on eq 9. Typically, the sampling will be interrupted after ~40%–60% of the preloaded calibrant was lost, and the value of $\exp(-a't)$ is ~0.4–0.6, according to eq 10. Let us assume that $\exp(-a't) = 0.5$ and $\exp(-a't)/\exp(-at) = 0.9$–$1.1$ (which means the deviation of C_s is ~10%); then, we can get $\exp(-at) = 0.455$–0.556, and $a'/a = 0.88$–1.18, which means if the difference between a and a' was <12%, the deviation of the calculated C_s value is <10%.

Based on eq 4, the definition of rate constant a, if the value of R_s is <12% of $2KR_f$, $2KR_f + R_s$ can be replaced by $2KR_f$. The difference in the value of a caused by this approximation will be <12%.

We know that the value of D_f, which is the diffusion coefficient of analyte in the PDMS fiber coating, is ~10 times lower than the value of D_s, which is the diffusion coefficient of analyte in water.[30–32] Using 100-μm PDMS fiber, the thickness of the fiber coating (δ_f) is 100 μm. Let us assume $K > 1000$ (for water sampling of hydrophobic compounds, the log K values of the analytes are typically >3), and based on the definition of R_f and R_s ($R_s = D_s A/\delta_s$, $R_f = D_f A/\delta_f$), we can prove that the thickness of the diffusion layer in the sample matrix (δ_s) should be >4.17 μm, if $R_s/(2KR_f)$ should be <0.12.

The diffusion layer thickness in the sample matrix (δ_s) can be calculated using the relation[33]

$$\delta_s = 9.52\left(\frac{b}{Re^{0.62}Sc^{0.38}}\right) \quad (12)$$

where b is the outside radius of the fiber coating (see Figure 1), Re the Reynolds number ($Re = 2ub/v$), u the linear velocity of water (cm/s), v the kinetic viscosity for water (cm^2/s), and Sc the Schmidt number ($Sc = v/D_s$). For water sampling with 100-μm PDMS fiber, $b = 1.6 \times 10^{-2}$ cm and $v = 1.0 \times 10^{-2}$ cm^2/s for water at 20 °C, and we can obtain the following relationship between δ_s and u, the linear velocity of water (for simplify, the diffusion coefficient in water was approximated to 1×10^{-5} cm^2/s):

$$\delta_s(\mu m) = \frac{53.7}{u^{0.62}} \quad (13)$$

Based on eq 13, we know if $\delta_s > 4.17$ μm, then u should be <62 cm/s. Table 1 lists the estimated limitations of the water flow velocities for different K values and different desorption

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Table 1. Limitations of the Flow Velocity for Different *K* Values and Different Desorption Rates of the Preloaded Standard[a]

desorption rate (%)	limitation of diffusion layer (μm)	limitation of flow velocity (cm/s)
	$K = 1000$	
40	>5.00	<46
50	>4.17	<62
60	>3.13	<98
	$K = 5000$	
40	>1.00	<617
50	>0.83	<828
60	>0.63	<1317
	$K = 10000$	
40	>0.50	<1887
50	>0.42	<2532
60	>0.31	<4028

[a] The estimated results are based on water sampling with 100-μm PDMS fiber and the deviation of the calculated C_s is <10%.

proportions of the preloaded standard. The data indicated that the water flow velocity can be much faster if the K value is larger.

If $2KR_f + R_s$ can be replaced by $2KR_f$, then eq 4 changes to

$$a = \frac{R_s}{V_f K} = \frac{D_s A}{V_f K \delta_s} \tag{14}$$

For the desorption of the calibrant,

$$a' = \frac{D'_s A}{V_f K' \delta'_s} \tag{15}$$

where D_s' is the diffusion coefficient of the calibrant in water and K' is the distribution coefficient of the calibrant between the PDMS fiber coating and water. Since the thickness of the diffusion layer in the sample is the same for both the extraction of the target analytes (δ_s) and the desorption of the calibrant (δ_s'), then relationship between the rate constants a and a' can be expressed by

$$\frac{a}{a'} = \frac{D_s K'}{D'_s K} \tag{16}$$

The distribution coefficients of the analytes and calibrant between the fiber coating and water can be found in the literature or determined by experiment. The diffusion coefficients of the analytes and calibrant in water can be found in the literature or calculated with the following empirical equation:[32]

$$D_w = \frac{1.326 \times 10^{-4}}{\eta_w^{1.14} \bar{V}^{0.589}} \tag{17}$$

where η_w is the kinematic viscosity of water and $\bar{V}$ is the molar volume of the analyte. Equation 16 built a relationship between the rate constants of different compounds, which means that all extracted analytes can be calibrated with a single preloaded calibrant; this is called the one-calibrant technique.

EXPERIMENTAL SECTION

Chemicals and Supplies. High-performance liquid chromatography (HPLC)-grade methanol was purchased from BDH (Toronto, Canada). Acenaphthylene, acenaphthene, d_{10}-acenaphthene, anthracene, d_{10}-anthrane, fluoranthene, d_{10}-fluoranthene, fluorene, pyrene, and d_{10}-pyrene and benz[a]anthracene were purchased from Supelco (Oakville, Canada). The SPME fiber holder and the 100-μm PDMS fibers were also obtained from Supelco. The fibers were conditioned at 250 °C for 1 h prior to their use. Ultrahigh-purity helium was purchased from Praxair (Kitchener, ON, Canada).

Instrument. A Varian 3800 GC/Saturn 2000 ITMS system fitted with a SPB-1 column (30 m, 0.25 mm i.d., 0.25 μm film thickness) (Supelco, Mississauga, ON, Canada) was used for the analysis. Helium was used as the carrier gas and was set at 1 mL/min. For the SPME injection, the 1079 injector was set to 270 °C, and the desorption time was set at 10 min. For liquid injection, the injector was set at 40 °C and then increased to 250 °C at a rate of 100 °C/min, which ensure that the sample transfer efficiency was identical for both the SPME injection and the liquid injection.[34] The column temperature was maintained at 40 °C for 2 min and then programmed to increase by 30 °C/min to 250 °C; then it was held for 6 min. The total run time was 15 min. The MS system was operated in the electron ionization (EI) mode and tuned with perfluorotributylamine (PFTBA). A mass scan from 40 to 300 was obtained, and the base peak of each compound was selected and integrated. The instrument was calibrated with a five-point calibration plot. Peak shape quality, resolution, and retention times were also carefully monitored to ensure that the chromatography was within the required specifications.

Standards Loading. An 100 μg/mL stock solution of four d_{10}-PAHs was prepared in methanol. The standard aqueous solutions for the loading of standards (d_{10}-PAHs, 50 ng/mL) were prepared daily by spiking the stock solution in pure water with a CTC CombiPAL autosampler. The CTC autosampler was also used for the loading of the standards. The 100-μm PDMS fiber was directly immersed into 10 mL of a 50 ng/mL d_{10}-PAHs standard solution to extract 20 min. The agitation speed was 500 rpm, and the temperature of the agitator was kept at 30 °C. The relative standard deviation (RSD) of this standards loading method for four d_{10}-PAHs was <5% for six replication.

Flow-Through System. In this study, the flow-through system for the generation of standard aqueous PAHs solution[35] was modified to imitate the variety of environment. Figure 2 is the schematic diagram of the modified flow-through system. In this new flow-through system, two minipumps were added. Minipump 1 was used for feeding pure water into the sampling chamber to create the shift of the PAHs concentration and flow velocity of water in the sampling chamber and cylinder. Hot or cold water was transferred by minipump 2 and flows through the copper tubing inside the sampling chamber, which can create a temperature shift of the sampling system. The modified flow-through system can create waves of temperature, flow velocity, and concentration of analyte. It is more similar to the real environment. The effect of environmental variables to the sampling results, including temperature, turbulence, and

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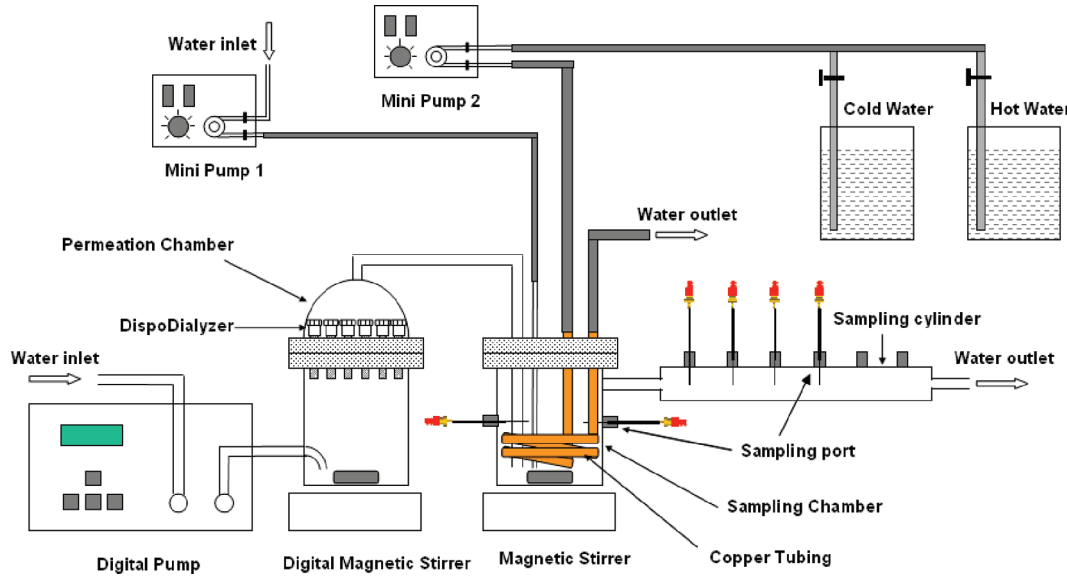

Figure 2. Modified flow-through system for the generation of standard PAHs in aqueous solution.

Table 2. Distribution Coefficients of PAHs between PDMS and Water and the Diffusion Coefficients of PAHs in Water at 25 °C

polyaromatic hydrocarbon, PAH	K	D_w ($\times 10^5$ cm^2/s)[a]
acenaphthene	4266[b]	0.766
anthracene	9549[b]	0.684
fluoranthene	28626[c]	0.659
pyrene	31097[c]	0.659

[a] Calculated using eq 17. [b] Data taken from ref 36. [c] Data taken from ref 37.

Table 3. Values of the Determined Desorption Rate Constants (a_d) for d_{10}-PAHs and the Comparison Results of a_d and a_c, the Desorption Rate Constants Calculated Using d_{10}-Pyrene as the Calibrant

polyaromatic hydrocarbon, PAH	a_d ($\times 10^4$ s^{-1})	a_c/a_d
Sampling Cylinder (Flow Velocity = 0.012 cm/s, n = 3)		
d_{10}-acenaphthene	0.440 (±0.011)	0.71
d_{10}-anthracene	0.128 (±0.005)	1.11
d_{10}-fluoranthene	0.040 (±0.002)	0.92
d_{10}-pyrene	0.034 (±0.001)	1
Sampling Chamber (Flow Velocity = 78.5 cm/s, n = 3)		
d_{10}-acenaphthene	5.14 (±0.38)	0.78
d_{10}-anthracene	1.26 (±0.10)	1.01
d_{10}-fluoranthene	0.511 (±0.032)	1.09
d_{10}-pyrene	0.513 (±0.033)	1

the concentration of the analytes, was tested in this modified flow-through system.

The feed rate of water for the flow-through system was set at 5 mL/min. The concentrations of four PAHs in the system were determined through direct-immersing SPME with external calibration method using a CTC CombiPAL autosampler. The change of the PAH concentrations in the flow-through system was <10% during the experiments.

RESULTS AND DISCUSSION

Validation of Equation 16. SPME (100 μm PDMS) fibers were used as passive samplers to validate the feasibility of eq 16. Six preloaded calibrants (d_{10}-PAHs) PDMS fibers were exposed in the sampling cylinder and sampling chamber for 24 and 2 h, respectively, and then injected into GC for analysis. Table 2 presents the distribution coefficients of four PAHs between PDMS fiber coating and water, and the diffusion coefficients of four PAHs in water.

The water flow velocity in the sampling cylinder is much different from that in the sampling chamber. In the sampling chamber, the agitation speed is 300 rpm, and the flow velocity in the sampling position is ~78.5 cm/s. In the sampling cylinder, the flux of the sample solution is 5 mL/min, and the flow velocity is ~0.012 cm/s, which means the flow velocity of the sampling chamber is more than 5000 times higher than that of the sampling cylinder.

The determined rate constants (a_d) of four d_{10}-PAHs and the comparison results of a_d and a_c, the calculated rate constants, are listed in Table 3. Rate constants a_d were determined by the desorption of the respective d_{10}-PAHs, and calculated with eq 10. Rate constants a_c were calculated with eq 16, and d_{10}-pyrene was used as the only calibrant.

The a_c/a_d ratios listed in Table 3 were very close to 1, although the turbulence of two sampling sites greatly differed, which demonstrated the validity of eq 16. From Table 3, we can also find that the determined rate constants (a_d) of the four d_{10}-PAHs in the sampling cylinder were much lower than those in the sampling chamber, since the rate constant will be affected by the flow velocity of the water.

Passive Water Sampling with SPME Fiber. Experiments to validate the feasibility of the kinetic calibration and one-calibrant kinetic calibration techniques for passive water sampling were performed in the modified flow-through system. The effect of environmental variables, such as turbulence, temperature, and the concentration of the analytes, was tested.

1. Turbulence. To test the effect of turbulence for the calibration results, six 100-μm SPME PDMS fibers, which were

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Table 4. Quantitative Results of the Experiments in the Flow-through System via the Kinetic Calibration Method ($n = 3$)

	Concentration (ng/mL)			
	acenaphthene	anthracene	fluoranthene	pyrene
sampling cylinder (24 h, 0.012 cm/s, 25 °C)				
calculated using the desorption of respective deuterated compounds	6.08 (±0.25)	1.14 (±0.08)	1.66 (±0.16)	1.60 (±0.13)
calculated with the one-calibrant approach[a]	6.53 (±0.27)	1.08 (±0.08)	1.78 (±0.17)	1.60 (±0.13)
sampling chamber (2 h, 78.5 cm/s, 25 °C)				
calculated using the desorption of respective deuterated compounds	5.56 (±0.12)	1.05 (±0.03)	1.16 (±0.05)	1.09 (±0.03)
calculated with the one-calibrant approach[a]	5.72 (±0.13)	1.04 (±0.03)	1.09 (±0.05)	1.09 (±0.03)
sampling chamber (2 h, 78.5 cm/s, 15−30 °C)				
calculated using the desorption of respective deuterated compounds	7.13 (±0.46)	1.25 (±0.14)	1.38 (±0.14)	1.25 (±0.16)
calculated with the one-calibrant approach[a]	7.46 (±0.48)	1.25 (±0.14)	1.47 (±0.14)	1.25 (±0.16)
determined concentration	6.38 (±0.13)	1.02 (±0.02)	1.38 (±0.06)	1.29 (±0.05)

[a] Here, d_{10}-pyrene was used as the calibrant.

Table 5. Results of the TWA Water Sampling Experiments in the Flow-Through System ($n = 3$)

	TWA Concentration (ng/mL)			
	acenaphthene	anthracene	fluoranthene	pyrene
calculated	3.28	0.52	0.71	0.66
kinetic calibration with the desorption of respective deuterated compounds		0.67 (±0.06)	0.85 (±0.14)	0.79 (±0.08)
one-calibrant technique		0.65 (±0.06)	0.85 (±0.14)	0.79 (±0.08)

preloaded calibrants, were exposed in the sampling ports of the flow-through system (three in the sampling chamber and three in the sampling cylinder). The samplers were retrieved after 2 h, for the fibers set in the sampling chamber, and after 24 h, for the fibers set in the sampling cylinder. The passive samplings were quantified with the kinetic calibration method. The concentrations of the PAHs in the flow-through system were also determined by direct-immersing SPME method. The quantitative results are presented in Table 4. Compared with the determined concentrations, the recoveries of the four PAHs were in the range of 84.1%−120.3% and 79.0%−129.0% for quantitation with respective deuterated compounds and the one-calibrant technique, respectively. The results illustrated that the effect of turbulence can be successfully compensated through the desorption of a single calibrant.

2. Temperature. The environmental temperature always changes day and night, which will affect the sampling rate of the passive sampler. To test the effect of temperature, three SPME fibers were deployed in the sampling chamber, and the temperature of the sampling chamber was changed from 15 °C to 30 °C by pumping hot/cold water with minipump 2 (Figure 2). The temperature was monitored with a digital thermometer. The calculated results of the sampling with the temperature shift are also listed in Table 4. The results illustrated that the effect of the environmental temperature can be compensated with the kinetic calibration method, since the change of the temperature will affect the rates of absorption and desorption simultaneously, and the one-calibrant technique is suitable for on-site water sampling with temperature shift.

3. TWA Sampling. Although the kinetic calibration technique has been used for field TWA water sampling, validation was not performed in the laboratory. To validate the correctness of eq 7 and the feasibility of the kinetic calibration method for TWA sampling, three SPME PDMS fibers were used as passive samplers and set in the sampling cylinder, and a concentration wave was created in the flow-through system. The flux of the flow-through system was 5 mL/min. In this experiment, pure water was intermittently fed into the sampling chamber at a flow rate of 45 mL/min by minipump 1 (Figure 2). The concentrations of the analytes in the sampling cylinder were intermittently changed (0.64−6.4, 0.1−1.0, 0.14−1.4, and 0.13−1.3 ng/L for acenaphthene, anthracene, fluoranthene, and pyrene, respectively). The flow velocity of the sample solution in the sampling cylinder was also intermittently changed over a range of 0.012−0.12 cm/s, because of the change in the water flux. In the 24-h sampling time, a total of 7000 mL of pure water was fed into the sampling chamber, and the average concentration of the analytes in the sampling cylinder ($\bar{C}_s$) was calculated by

$$\bar{C}_s = \frac{C_0 rt}{rt + 7000} \tag{18}$$

where C_0 (ng/mL) is the original concentration of the analytes of the flow-through system, r (mL/min) the original concentration of the flux of the flow-through system, and t the sampling time. The calculated $\bar{C}_s$ value of the sampling cylinder and the quantitative results of the passive samplings by the kinetic calibration method are listed in Table 5. Satisfied results were obtained using the desorption of respective deuterated compounds or the one-calibrant technique, which demonstrated the feasibility of kinetic calibration and the one-calibrant technique for TWA sampling.

The TWA concentration of acenaphthene is not presented in Table 5, since the extraction of acenaphthene already reached equilibrium after 24 h sampling under the experimental conditions.

Rapid On-Site Water Sampling with Rotated SPME Fiber. In fact, the flow velocities listed in Table 1 exhibit very wild turbulence. For example, direct-immersing SPME fiber into a vial for sampling in an aqueous solution, when the agitation

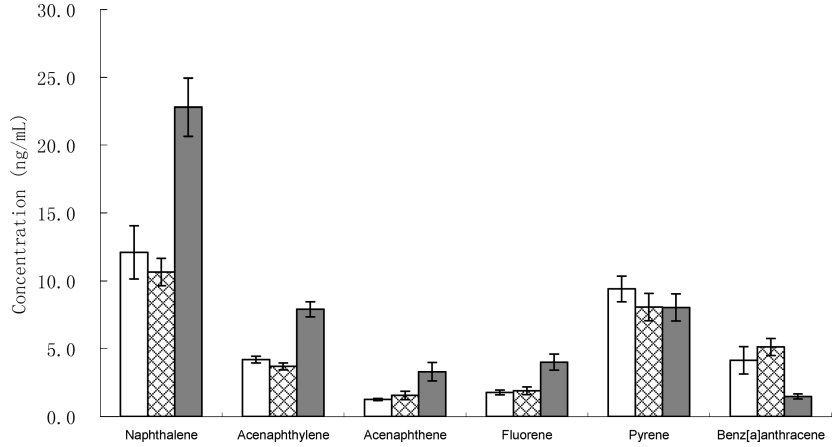

Figure 3. Analysis results of PAHs in Laurel Creek. The white column represents data from the SPME direct-immersing method by standard addition quantitation; the crosshatched column represents data from rotated SPME fiber obtained via one-calibrant kinetic calibration; and the gray shaded column represents data obtained directly, using the desorption rate constant of d_{10}-pyrene for the quantitation of all compounds.

speed was set at 1200 rpm and the fiber was placed at the position ~0.5 cm from the center of the vial, the flow velocity of the water that crossed the fiber was ~62.8 cm/s, which is still acceptable for the compounds with $K = 1000$ and far from the limitation of flow velocity for the compounds with larger K values. This fact indicated that eq 16 can be used for rapid water sampling.

The feasibility of the one-calibrant technique for rapid water sampling was validated with rotated SPME fibers. The experiments were performed in Laurel Creek (Waterloo, ON). Three 100-μm SPME PDMS fibers, which preloaded d_{10}-pyrene as the calibrant, were fixed on a metal rod with an outer diameter (OD) of 1 cm, and a portable drill was used for rotating the fibers at a constant rate of 1200 rpm. The sampling time was 10 min. After sampling, the SPME fibers and ~1 L of water (grab sampling with a clean bottle) were transported to the laboratory for analysis. The SPME fibers were analyzed directly and quantitated using the one-calibrant kinetic calibration method. The water was analyzed with the direct-immersing SPME technique and quantified using the standard addition method.

The analysis results of six PAHs in Laurel Creek are presented in Figure 3. Using the desorption rate of d_{10}-pyrene and eq 16, the quantitated results of the samplings were very similar to those determined by SPME direct-immersing method, which demonstrated the validity of the one-calibrant technique for rapid on-site water sampling.

If we directly use the desorption rate constant of d_{10}-pyrene for quantitation, without using eq 16 for calibration, the quantitative results are overestimated for lower hydrophobic compounds and underestimated for more hydrophobic compounds, as shown in Figure 3, which illustrates the importance of eq 16.

Application of the SPME kinetic calibration method requires one to know the distribution coefficients (K) of the analytes between the fiber coating and water. The reported K values include those of PAHs,[36−40] polychlorinated biphenyls (PCBs),[41−46] polybrominated biphenyl ethers (PBDEs),[47] polybrominated biphenyls (PBBs),[48] pesticides,[49] and phthalates,[50] etc.[51] These data are very useful for the application of SPME equilibrium and the pre-equilibrium extraction approach.

It was reported that the mass transfer of PAHs in water can be enhanced by the dissolved humic acid, etc., especially for benzo[a]pyrene and benz[a]anthracene.[52] In our field trial, the effect was negligible. More experiments will be conducted in the future to observe the effect of dissolved organic matter or inorganic salt concentration on the quantification method.

CONCLUSION

The concept of a standard in the extraction phase is particularly useful for on-site and in vivo investigations, where the addition of standards to the sample matrix, or control of the velocity of the sample matrix, is very difficult. In this work, a new direction of the concept was proposed: using the desorption of a single calibrant to calibrate all extracted analytes. The one-calibrant technique eliminates the requirement of several isotopical compounds or high-concentration standards, and it simplifies the standard loading and quantitation procedures, which is extremely important for future applications of the kinetic calibration technique. The one-calibrant kinetic calibration technique can be also applied to other microextraction approaches, such as liquid-phase microextraction (LPME) and microdialysis.

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In typical internal standard method, one standard is used to compensate the matrix effect and the loss of analytes during the sample preparation of several analytes. In this study, it was proven that a big error might be introduced if we directly used the rate constant of single calibrant for the quantitation of all analytes. The quantitation should be based on the relationship between the rate constants of the analyte and the calibrant.

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