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NOTE

Rotating-disk sorptive extraction: effect of the rotation mode of the extraction device on mass transfer efficiency

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Abstract The extraction device used in rotating-disk sorptive extraction consists of a Teflon disk in which a sorptive phase is fixed on one of its surfaces. Depending on the configuration, the rotation axis of the disk device can be either perpendicular or parallel to its radius, giving rise to two different mass transfer patterns when rotating-disk sorptive extraction is applied in liquid samples. In the perpendicular case (configuration 1), which is the typical configuration, the disk contains an embedded miniature stir bar that allows the disk rotation to be driven using a common laboratory magnetic stirrer. In the parallel case (configuration 2), the disk is driven by a rotary rod connected to an electric stirrer. In this study, triclosan and its degradation product methyl triclosan were used as analyte models to demonstrate the significant effect of the rotation configuration of the disk on the efficiency of analyte mass transfer from water to a sorptive phase of polydimethylsiloxane. Under the same experimental conditions and at a rotation velocity of 1,250 rpm, extraction equilibrium was reached at 80 min when the disk was rotated in configuration 1 and at 30 min when the disk was rotated in configuration 2. The extraction equilibration time decreased to 14 min when the rotation velocity was increased to 2,000 rpm in configuration 2. Because the rotation pattern affects the mass transfer efficiency, each rotation configuration was characterized through the Reynolds number; *Re* values of 6,875 and 16,361 were achieved with configurations 1 and 2, respectively, at 1,250 rpm.

Keywords Rotating-disk sorptive extraction · Mass transfer · Convection · Equilibration time · Triclosan · Methyl triclosan

Introduction

Stir-bar sorptive extraction (SBSE) was first described in 1999 [1] as an alternative to solid-phase microextraction (SPME) [2] for the preparation of diverse liquid samples and the determination of organic analytes. The main advantage of SBSE over SPME is the greater sorptive-phase volume contained on the extraction device. Thus, the use of polydimethylsiloxane (PDMS) as a sorptive phase resulted in higher rates of recovery by SBSE for analytes with an octanol–water coefficient partition less than 500 [1], which cannot be extracted by SPME. In 2009, the microextraction technique based on rotating-disk sorptive extraction (RDSE) was introduced [3]; this functions on a basis similar to that of SBSE; i.e., the extraction is performed in the same stirring device, and the rotation velocity of the device promotes the extraction process. The main advantage of RDSE over SBSE is that the sorptive phase is not directly in contact with the extraction vessel; consequently, higher speeds can be achieved without loss or deterioration of the sorptive phase while the device is rotating. Furthermore, the design of the device used in RDSE provides a greater exposed area to volume ratio of the sorbent than does the twister used in SBSE. RDSE has been applied in the extraction of different compounds from aqueous matrices, including nonylphenol, ethoxylates [3], pesticides [4, 5], triclosan and methyl triclosan [6], and colorants [7, 8]. The extraction device consists of a Teflon disk with a diameter of 1.5 cm that contains, on one of its surfaces, a film of PDMS that has been immobilized with silicone. Depending on the configuration, the rotation axis of the disk device can be either perpendicular or parallel to its

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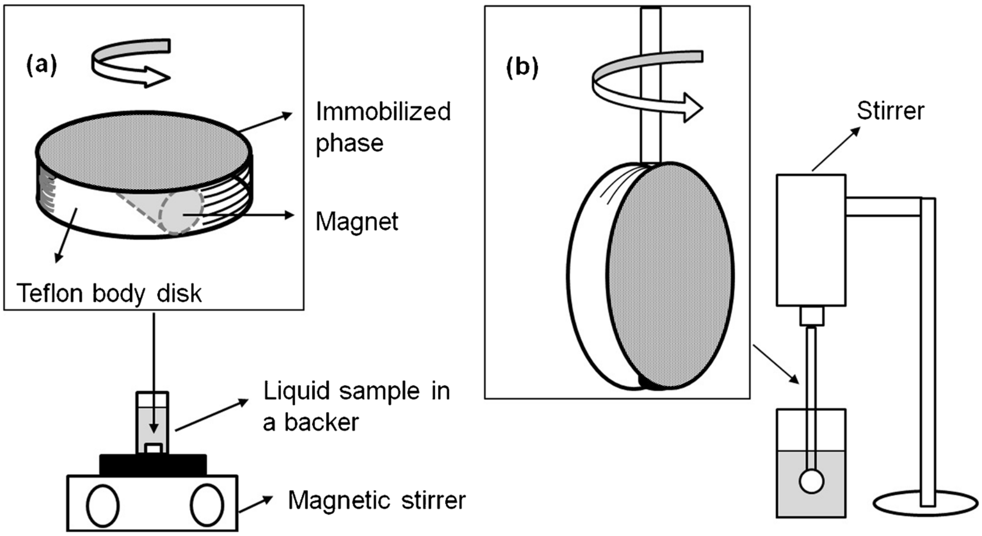

Fig. 1 Rotating-disk device in configurations 1 (**a**) and 2 (**b**)

radius, giving rise to two different mass transfer patterns when RDSE is applied in liquid samples (Fig. 1). In the former case, the disk contains an embedded miniature stir bar that allows the disk rotation to be driven by a common laboratory magnetic stirrer (configuration 1). In the latter case, the disk is driven by a rotary rod connected to an electric stirrer (configuration 2).

Until now, the RDSE technique has been used only in configuration 1; this report represents the first time that the applicability of configuration 2 has been shown.

In general, two types of flows occur in a stirring system: turbulent flow and laminar flow. The predominance of one of these flow types depends on the stirring speed [9]. In microextraction techniques, when the extraction device is rotated at high speed, a boundary layer of water (interface) is formed adjacent to the PDMS surface, where convection is not significant; the analyte to be extracted must traverse this boundary layer by diffusion [10, 11]. The boundary layer is an integral part of the hydrodynamic system, and it exists irrespective of the speed at which the solution is stirred. However, increased convection is the key to efficient mass transport because the thickness of boundary layer is minimized [12–14] and the analyte diffusion distance is shortened with more energetic stirring.

In extraction techniques such as RDSE and SBSE, the boundary layer thickness (δ) can be estimated by the following empirical expression [15]:

$$\delta = 9.52\frac{d}{Sc^{0.38}Re^{0.62}}, \tag{1}$$

where d corresponds to the phase diameter in RDSE, Re is the Reynolds number, and Sc is the Schmidt number, which is equal to υ/D, where D is the diffusion coefficient of the analyte in the liquid. With an increase in Re, viscous forces become less important in relation to the inertial forces; therefore, δ decreases [16].

Normally, the equilibration time and the extraction rate in mass transfer between water and PDMS are controlled by diffusion of the analyte through the boundary layer to the extraction phase. The influence of the boundary layer decreases, and its relation to the equilibration time (T_{eq}) of the analyte between the aqueous sample and the PDMS phase can be theoretically understood through the following equation, which was previously described for SPME [17, 18]:

$$T_{\mathrm{eq}} = 3\delta K_{\mathrm{d}} P_{\mathrm{t}}/D, \tag{2}$$

where δ is the boundary layer thickness, D is the sample solution diffusion coefficient, K_{d} is the analyte distribution coefficient for the PDMS phase and the solution, and P_{t} is the thickness of the PDMS phase. Accordingly, the reduction in the boundary layer thickness that results from an increase in the rotating velocity clearly facilitates extraction because the equilibration time is decreased.

On the basis of the previous arguments, the aim of this study was to assess the effect of the configuration of the rotating disk on the analyte mass transfer in the extraction process. In this context, the time to reach the analyte extraction equilibrium was determined when the disk was rotated in both configurations, and the mass transfer patterns were described by the Reynolds numbers. Triclosan and its metabolite methyl triclosan were used as model analytes; both compounds have been classified as emerging pollutants, and they have recently been determined by RDSE–gas chromatography–mass spectrometry (GC–MS) in water samples [6]. This effect has been investigated by other researchers [19], who compared the extraction rates for thin-film microextraction and SBSE. Therefore, the novelty in this comparison lies in the use of a single extraction device (rotating disk), which maintains a constant surface area and surface area to volume ratio in the sorptive phase.

Experimental

Reagents

Nanopure water from a Barnstead (Dubuque, IA, USA) water system was used throughout the work. The analytes triclosan and methyl triclosan (both 99.5 % purity) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). A standard stock solution of the analytes was prepared in methanol (GC–MS/pesticide grade analysis; Fisher Scientific, Fair Lawn, NJ, USA). Hexachlorobenzene (99.5 % purity), which was used as an internal standard, was purchased from Dr. Ehrenstorfer. Nitrogen 5.0 and helium 6.0 were purchased from Linde (Santiago, Chile) and were used for final extract evaporation and as a chromatographic carrier gas, respectively. Ethyl acetate, acetone (both high-performance liquid chromatography grade, 99.8 % purity), and sodium chloride (99.5 % purity) were purchased from Merck (Darmstadt, Germany). The PDMS phase was prepared from a Sylgard 184 silicone elastomer kit (Dow Corning, Midland, MI, USA) in accordance with the manufacturer's recommendations. Citrate buffer (0.1 mol L^{-1} disodium citrate; Merck) was adjusted to pH 4.0 with hydrochloric acid (Merck). *N*-Methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide, which was acquired from Sigma-Aldrich (Milwaukee, WI, USA), was used as a derivatizing agent.

Instruments and software

A Thermo Scientific (Milan, Italy) Focus gas chromatograph coupled to a Thermo Fisher Scientific (Austin, TX, USA) ISQ mass-selective detector was used for final determinations. A Restek (Bellefonte, PA, USA) RTX-5MS fused-silica capillary column (30 m×0.25-mm inner diameter, 0.25-μm film thickness) coated with 5 % phenyl–95 % methylpolysiloxane was used. Two microliters of sample extract was injected into the gas chromatograph using the splitless mode. The injector temperature was 250 °C. The initial column temperature was 100 °C (1 min) and was increased to 300 °C at 10 °C min^{-1}. Helium at a constant flow rate of 1.0 mL min^{-1} was used as the carrier gas. The solvent delay was 7 min. A dwell time of 0.1 s was used for each *m*/*z* value. The transfer line of the mass spectrometer was maintained at 250 °C, and quantification was based on calibration with the standard analyte using the mass spectrometer in selective ion monitoring mode. Two significant ions from each analyte were chosen for quantification and identification: 345 and 347 *m*/*z* for triclosan, 302 and 304 *m*/*z* for methyl triclosan, and 284 and 286 *m*/*z* for hexachlorobenzene as an internal standard.

Two stirrers were used for the extraction: a Heidolph model RZR 2050 stirrer and a Heidolph model MR 3002 S magnetic stirrer.

Data treatment was performed using OriginPro 8.

Procedure

A standard that contained both analytes at 8 μg L^{-1} in water (25 mL) was poured into a beaker containing 5 g of NaCl, and the pH was adjusted to 4.0 with 0.1 mol L^{-1} citrate buffer. The rotating disk in both configurations coated with the PDMS phase was placed inside the beaker, and the disk was rotated at 1,250 rpm in both cases at room temperature. The extraction profiles were obtained over periods that ranged from 15 to 180 min. In both cases, after extraction, the disk was placed in a 10-mL beaker containing 5 mL of methanol as a desorbing solvent, and the solvent was stirred for 30 min at 1,250 rpm. The methanol extract containing the concentrated analyte was then evaporated to dryness under a stream of N_2 at room temperature, and the residue was redissolved in 1 mL of ethyl acetate. A 50-μL aliquot of *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide was added to 500 μL of this extract (the other 500 μL was kept for an eventual replicate), and derivatization was performed for 45 min at 80 °C. Before injection, 10 μL of 5 mg L^{-1} hexachlorobenzene was added as an internal standard, and the analytes were determined by GC–MS.

Results and discussion

Extraction through RDSE of triclosan and methyl triclosan has previously been systematically studied by our research group [6]. The extraction time profiles were obtained for both analyte models under the same optimized conditions using both rotating-disk configurations (Fig. 1). In both cases, the rotation velocity was 1,250 rpm. The best adjustments for the time profiles were achieved with the equation $y=A_1\exp(-x/t_1)+y_0$ from OriginPro 8, and equilibration times were defined from this function.

With configuration 1, the extraction equilibrium was reached at approximately 80 min for both analytes (Fig. 2, left), whereas with configuration 2, the equilibration time was reduced to approximately 30 min (Fig. 2, right).

In configuration 1, the rotation axis is perpendicular to the disk radius; in configuration 2, the rotation axis is in the same direction as the disk radius and forms part of an impeller that exerts a mechanical force for agitation. Thus, in configuration 1, the aqueous solution imposes less resistance to rotation of the disk; consequently, the analyte takes longer to reach equilibrium. In contrast, the aqueous

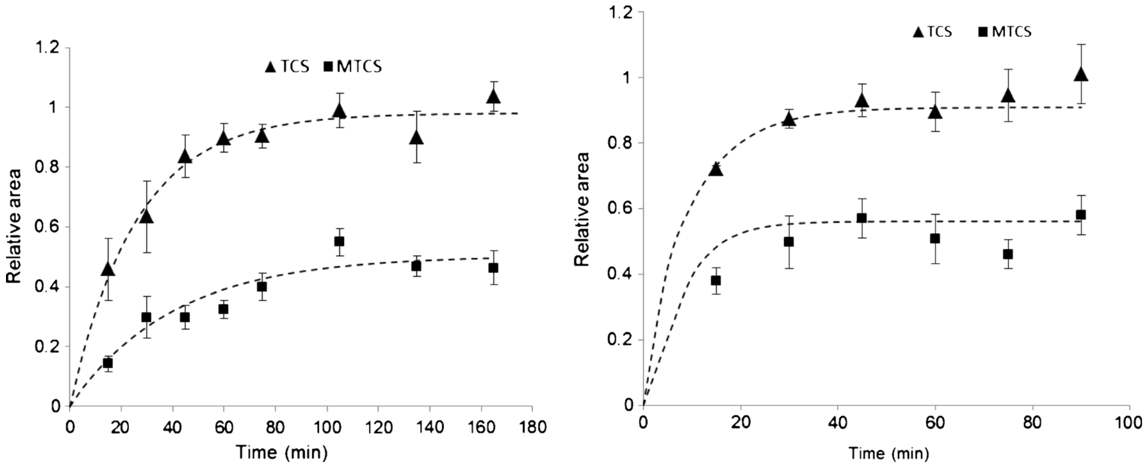

Fig. 2 Extraction time profiles for the extraction of triclosan (*TCS*) and methyl triclosan (*MTCS*) in configuration 1 (*left*) and configuration 2 (*right*); the rotation velocity was 1,250 rpm in both cases. The relative area is the ratio of the analyte peak area to the internal standard peak area

solution in configuration 2 opposes the rotation of the disk. This configuration, therefore, results in an enhanced and evident convection (Fig. 3) and much stronger contact, and causes the analyte to rapidly reach the extraction phase because of the greater reduction in the boundary layer thickness of water. Given that the extraction disk in configuration 2 rotates along its diameter via the stirring rod, the mass transfer mechanisms in each half of the disk should differ owing to the movement of the rotating disk relative to the sample solution. For the "pushing" half of the disk, the mass transfer is due to forced convection, whereas for the "pulling" half of the disk, the mass transfer should be much less efficient. Consequently, a higher concentration of the analyte is expected to sorb into the PDMS in one of the disk halves. In contrast, a more homogeneous distribution of the analyte is expected to sorb into the PDMS when the disk rotates in configuration 1. This hypothesis was visually confirmed by extracting the dye crystal violet from water into the PDMS [7] using both disk configurations. As indicated in Fig. 4, the distribution of the dye varies with the different configurations. The forced convection that clearly occurs in one half of the disk in configuration 2 favors extraction of the analyte into this PDMS fraction. In contrast, the distribution of the extracted analyte in configuration 1 is much more homogeneous.

According to Eq. 2, the ratio T_{eq}/δ should be constant and, therefore, the same in both configurations. Consequently, the boundary layer in configuration 1 is thicker, approximately 2.66 times the thickness of the boundary layer formed on the disk in configuration 2.

In addition, when the rotation velocity of the disk was increased to 2,000 rpm in configuration 2, the equilibration time was significantly reduced to 14 min (Fig. 5). Under this condition, the thickness of the boundary layer is reduced 2.1-fold compared with that formed in configuration 1 at 1,250 rpm. The following equation shows that, theoretically, δ is inversely proportional to the square root of the rotation

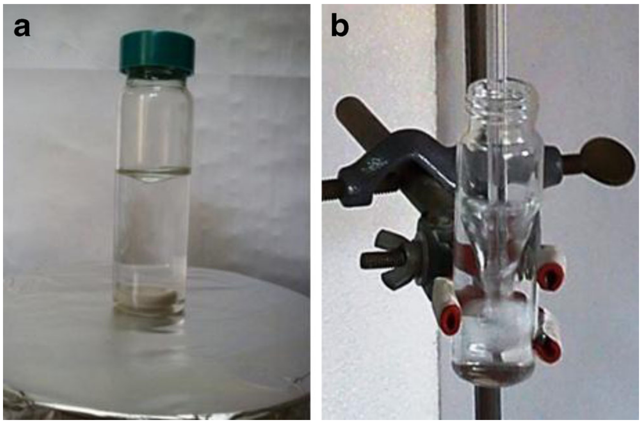

Fig. 3 Photographs of the rotating disk in **a** configuration 1 and **b** configuration 2 under stirring at 1,250 rpm

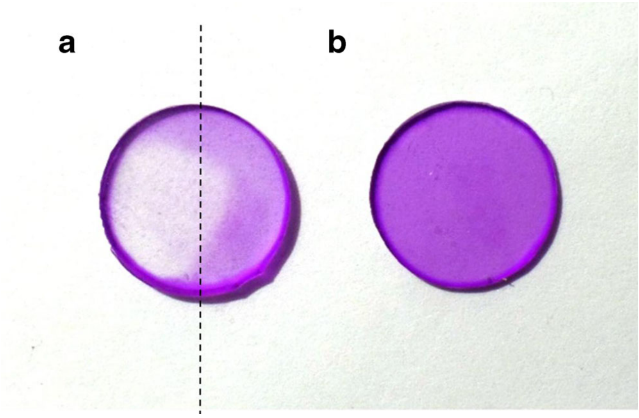

Fig. 4 Rotating-disk sorptive extraction (RDSE) of 15 mg L^{-1} crystal violet from water at 2,000 rpm. RDSE in **a** configuration 2 (the *line* indicates the rotation axis) and **b** configuration 1. Other experimental conditions were as in [7]

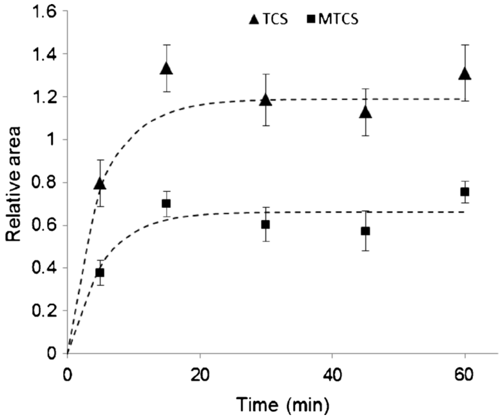

Fig. 5 Extraction time profiles for the extraction of triclosan (*TCS*) and methyl triclosan (*MTCS*) under rotation of the disk at 2,000 rpm in configuration 2

velocity [20, 21] of the device:

$$\delta = 1.61D^{1/3}\upsilon^{1/6}\omega^{-1/2}, \quad (3)$$

where ω is the rotation velocity in radians per second.

Other authors have reported that PDMS can be deformed while the extraction device rotates, such as during thin-film microextraction [19, 22, 23] in a configuration similar to configuration 2 used in the current study. In the present case, configuration 2 can reach high rotation velocities without causing deformation of the extraction phase because the PDMS phase is fixed to the disk face. The advantage of this support disk is reflected in the extraction efficiency because the effective area of PDMS is kept constant during the extraction process.

RDSE, particularly with configuration 2, resulted in a considerable increase in the extraction speed compared with that of extractions performed with other devices [24–27]. However, from an analytical perspective, the precision and accuracy of the RDSE technique involving both rotation modes should also be considered. Both analytical features were determined at 1,250 rpm, by calculating the relative standard deviation of the signal and the recovery after processing four aliquots of a single water sample spiked with the analyte at 800 ng L^{-1} (Table 1). As indicated in Table 1, the recovery and precision were similar for both configurations at 1,250 rpm; however, when the rotation velocity of the disk in configuration 2 increased to 2,000 rpm, the measurement precision decreased significantly, resulting in relative standard deviations of 14.5 % for triclosan and 18.2 % for methyl triclosan. The high turbulence achieved in configuration 2 at this rotation velocity affected the measurement precision.

Table 1 Precision and recovery of the method with different rotation modes at 1,250 rpm

Analytical feature	Configuration 1		Configuration 2	
	Triclosan	Methyl triclosan	Triclosan	Methyl triclosan
Recovery (%)	96.8	80.9	90.0	91.7
Precision (RSD, %)	6.1	8.7	8.8	7.7

RSD relative standard deviation

To characterize the turbulence generated in both systems, the Reynolds number (*Re*) was determined according to the following expression [28, 29]:

$$Re = \mu d/\upsilon, \quad (4)$$

where μ is the fluid's linear speed, d is the disk diameter, and υ is the kinematic viscosity (0.009 cm^2 s^{-1} for water at 25 °C). The tangential velocity of the rotating disk in configuration 1 was calculated from the equation proposed in the case of a stir bar stirring a solution in a cylindrical container [30].

The *Re* values obtained were 6,875 and 16,361 for configurations 1 and 2, respectively, at a rotation velocity of 1,250 rpm. When the rotation velocity was increased to 2,000 rpm for configuration 2, *Re* increased to 26,179.

Considering the *Re* values obtained at 1,250 rpm, the ratio of the thicknesses of the boundary layer for both configurations, calculated from Eq. 1, is 1.71. The difference between this value and the value of 2.66 obtained from Eq. 2 is probably due to experimental uncertainly associated with accurate determination of equilibration times.

In general, a turbulent flow occurs when *Re* is greater than 10,000 [31, 32]. Consequently, configuration 2 works in a turbulent flow profile, which provides swirling that drives the analyte by convection rapidly toward the PDMS phase. While the disk rotates under this condition, a thinner diffusion layer (Eq. 3) is formed because the thickness of this boundary layer decreases with increasing *Re* [33].

Conclusions

This study demonstrated that the rotation mode of a disk in RDSE affects the mass transfer of the analyte from the aqueous phase to the extraction sorbent, thus modifying the extraction equilibration time. The more highly efficient analyte transport achieved in configuration 2 decreases the boundary layer thickness, thus reducing the equilibration time for the same disk rotation velocity. At a rotation velocity of 1,250 rpm, equilibria are reached at approximately 80 min and 30 min for configurations 1 and 2, respectively, with similar precision and accuracy for both configurations. However, increasing the rotation velocity to 2,000 rpm in configuration 2 decreases the precision because of the high turbulence generated within the system. The Reynolds number was determined to characterize the turbulence generated in both systems.

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