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Quantum Dot-Based Headspace Single-Drop Microextraction Technique for Optical Sensing of Volatile Species

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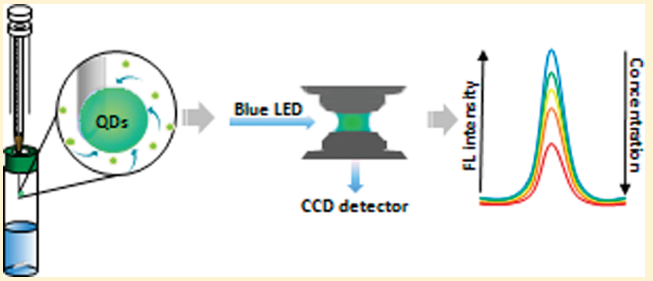
ABSTRACT: Core−shell CdSe/ZnS quantum dots (QDs) dispersed in a droplet of organic solvent have been applied for the first time as luminescent probes for the selective detection of volatile species. Luminescence quenching caused by volatile species was examined after their trapping onto a drop using the headspace single-drop microextraction (HS-SDME) approach along with microvolume fluorospectrometry. The novel method is characterized by low reagent and sample consumption, especially regarding QDs, a reduction about 500-fold for each analysis being attained in comparison with luminescent probing in aqueous phase using conventional luminescence spectrometers with 1 cm quartz cells for measurement. To assess QDs as luminescent probes along with HS-SDME, 14 volatile species were tried. Strong luminescence quenching (i.e., $I_0/I >$ 2.5) was observed for species such as CH_3Hg^+ and Se(IV) after hydridation with $NaBH_4$. Moderate luminescent quenching ($I_0/I \approx$ 2) was observed for species such as Hg(II) after its conversion into Hg(0), H_2S, and methylcyclopentadienyl-manganese tricarbonyl (MMT). Small luminescence quenching effects (i.e., $1< I_0/I <2$) were caused by other hydride forming species such as As(III), Sb(III), Te(IV), and Bi(III), as well as $SnBu_4$, volatile amines, and endosulfan. Detection limits of 6.3×10^{-9} and 1.6×10^{-7} M were obtained for Se(IV) and CH_3Hg^+, respectively. Repeatability expressed as relative standard deviation ($N = 7$) was about 5%. QD-HS-SDME-μvolume-fluorospectrometry allows one to carry out matrix separation, preconcentration, and confinement of QDs, hence achieving a selective, sensitive, fast, environmentally friendly, and miniaturized luminescence assay.



In recent years, the design and development of luminescent probes for the detection of a variety of chemical species have attracted great interest due to their high selectivity and sensitivity. To this end, many fluorescent small molecules (organic dyes) have been used.[1,2] However, conventional organic fluorescent dyes usually have some limitations such as low signal intensities and photobleaching. Furthermore, most of them tend to have narrow excitation spectra and often exhibit broad emission bands with red tailing.[3] Colloidal semiconductor nanoparticles, often referred to as "quantum dots" (QDs), have the potential to overcome these problems. As a result of confinement of the excited electrons and holes, QDs have unique electronic, catalytic, and optical properties unlike the bulk material. Compared with conventional organic fluorescent dyes, QDs generally exhibit important advantages, including a broad absorption spectrum,[4] a narrow, tunable, and symmetric emission spectrum,[4,5] and large luminescence quantum yields,[6] and they are also highly stable against photobleaching.[7]

Due to the unique optical properties of QDs, they have attracted considerable attention as novel luminescence probes with application in chemical analysis as well as in biological and medical fields. Regarding the application of QDs for bioanalysis, some modification of their surface is mandatory in order to provide a reactive functional group for conjugation with biomolecules.[3,5] Usually, this change in the QD surface leads to a decrease of luminescence quantum yield and stability.[8,9] With regard to applications in analytical chemistry, QDs have been employed for the determination of metal ions,[10−12] anions,[13,14] and organic compounds.[15−17] In most analytical applications, functionalization of a QD surface is carried out to solubilize QDs in aqueous media and to increase the selectivity of the method. Nevertheless, modification of the QD surface can cause a decrease in the luminescent quantum yield and stability.[8,9] Dispersion of QDs in nonpolar organic solvents would enhance their performance as luminescent probes.[18]

Owing to the increased use of nanoparticles in many areas of science and technology, a great concern has arisen due to their environmental impact.[19] Usually, the required volume to perform a single fluorescence measurement using cuvettes varies between 0.5 and 2.5 mL. This volume is smaller when fluorescence measurements are carried out with microplate instrumentation, but a further decrease in sample consumption continues to be an objective in the miniaturization of analytical methods.

In the last years, different liquid phase microextraction (LPME) techniques have been developed for sample preparation, due to their advantages over classic extraction approaches, such as relatively low sample consumption as well as the use of negligible volumes of extractant phases, with the consequent

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decrease in waste production. Among LPME techniques,[20,21] single-drop microextraction (SDME) is the most widely used. From the different SDME modes, headspace single-drop microextraction (HS-SDME) allows the preconcentration of volatile and semivolatile compounds into a microdrop of extractant phase exposed to the headspace above the stirred sample solution.[22] HS-SDME integrates sampling, extraction, preconcentration, and sample cleanup in a single stage. Additionally, nonvolatile matrix interferences are reduced or eliminated. The selection of an appropriate extractant phase is of great importance in the HS-SDME process to obtain high extraction efficiency.

Implementation of QDs in the extractant phase used in SDME would involve a further step toward miniaturization of QD-based systems. The required volume of this colloidal dispersion of nanoparticles would vary between 2 and 10 μL, then representing a minimum consumption of QDs and, in turn, minimum generation of toxic wastes. In addition, the phase separation produced in HS-SDME would minimize potential interferences from nonvolatile compounds. To solve the problem of incompatibility between the volume needed to perform the microextraction process and that required for detection, a miniaturized system capable of performing luminescence measurements with a drop of 1 to 2 μL is needed.

The aim of this work is to study the potential applicability of QD-based HS-SDME for the detection of a variety of compounds of environmental interest by microvolume fluorospectrometry.

EXPERIMENTAL SECTION

Reagents and Chemicals. All chemicals were of analytical reagent grade. Deionized water obtained from a Milli-Q water purifier (Millipore, Mol Molsheim, France) was used throughout.

A solution of quantum dots (5000 mg/L) employed was commercialized by Nanoco Technologies Ltd. (Manchester, UK) and distributed by Sigma-Aldrich under trademark of Lumidot. QDs are composed by core−shell CdSe/ZnS, stabilized with hexadecylamine (HDA), and dispersed in toluene. Working QD dispersions were prepared just before use by appropriate dilution in the selected solvent.

To study the applicability of QDs in HS-SDME, stock standard solutions (concentrations ranging from 4.6×10^{-4} to 2.2×10^{-3} M, in all cases corresponding to 1000 mg/L) of CH_3Hg^+ (as Hg), As(III), Hg(II), Se(IV), Te(IV), Sn(IV), methylcyclopentadienyl-manganese tricarbonyl (MMT), endosulfan, tetrabutyltin ($SnBu_4$), trimethylamine (TMA-N), dimethylamine (DMA-N), and monomethylamine (MMA-N) (1000 mg/L as N) and S^{2-} were prepared from CH_3HgCl (Riedel-de Häen, Seelze, Germany), As_2O_3 (Merck, Darmstadt, Germany), $HgCl_2$ (Prolabo, Paris, France), Na_2SeO_3 (Aldrich, St. Louis, MO, USA), Na_2TeO_3 (Aldrich), Sn (Probus, Badalona, Spain), MMT (Aldrich), endosulfan (PolyScience, Niles, IL, USA), $SnBu_4$ (Merck), TMA-N, DMA-N, and MMA-N as hydrochlorides (Merck) and Na_2S, respectively. Stock solutions of As(III), Hg(II), and S^{2-} were prepared in ultrapure water; CH_3Hg^+ was prepared in 0.1 M HCl. Se (IV), Te(IV), and Sn(IV) were prepared in 3 M HCl, MMT, and endosulfan, and $SnBu_4$ was prepared in methanol. TMA-N, DMA-N, and MMA-N were prepared in 0.5 M HCl.

Sodium chloride (Riedel-de Häen) was used to facilitate the mass transfer of volatile analytes and derivatives to the headspace. Sodium acetate (Merck) and tris(hydroxymethyl)aminomethane (Sigma-Aldrich) were used to make acetate and Tris−HCl buffer solutions, respectively. Hydrochloric and acetic acids were purchased from Prolabo. A solution of $NaBH_4$ (Merck) stabilized with NaOH (Prolabo) 0.1 M was prepared daily. All solutions were stored in the dark at 4 °C. Toluene (Prolabo), *n*-octane (Prolabo), dodecane (Sigma-Aldrich), decene (Sigma-Aldrich), aniline (Panreac), bromobencene (Sigma-Aldrich), and chlorobencene (Sigma-Aldrich) containing QDs were tried as extractant phases.

Apparatus. A Thermo Scientific NanoDrop 3300 Fluorospectrometer was used for the detection of several volatile species extracted in a drop (3 μL) of organic solvent containing QDs. The fluorospectrometer is equipped with three solid-state light emitting diodes (LEDs) as excitation source, which are oriented 90° in respect to the detector. A 2048-element CCD array detector is connected by an optical fiber to the optical measurement surface. The sample droplet is placed onto the pedestal. The sample arm slightly compresses the droplet, and a liquid column is formed by surface tension. The optical path length is 1 mm. Following excitation with one of the three LEDs, emitted light from the sample passing through the receiving fiber is captured by the detector. Sample pedestals are made of stainless steel and quartz fiber. Moreover, it is powered through a USB connection to a computer without the need for an external power supply, so it is suitable for field analysis. Luminescence measurements were carried out at 510 nm after excitation at a wavelength of 470 nm using the blue LED.

HS-SDME was performed with a commercially available 10 μL high precision microsyringe containing a guided-PTFE plunger (Hamilton model 1701 RN, 10 AL). Microextraction was carried out in a 40 mL amber-vial closed with a silicone rubber septum (Supelco). An ultrasonic cleaner P-Selecta (Spain; 50 W, 50 kHz) was used for homogenization of the colloidal dispersions of QDs.

Procedure for HS-SDME. The general HS-SDME procedure was performed as follows: a volume of 5 or 25 mL, depending on the analyte, of standard solution and a stir bar (20 × 7 mm) were placed in a 40 mL amber vial. The vial was closed and thermostated at 25 °C with a water bath. Subsequently, an appropriate amount of derivatization agent was externally injected when required to generate volatile species. A 3 μL drop of extractant phase containing QDs was exposed to the headspace of the sample stirred at 900 rpm for the optimal microextraction time. Then, the remaining drop was retracted back and deposited onto the pedestal of the fluorospectrometer to obtain the corresponding luminescence measurement. A blank was run before each measurement.

RESULTS AND DISCUSSION

Preliminary Assessment of the QD-HS-SDME Approach for Sensing Different Volatile Compounds. Efficient mass transfer of the analyte present in the sample to the headspace is a prerequisite to employ HS-SDME. Reaction conditions described in the literature were followed for the generation of different volatile compounds (Table 1).

Analytes tried were the following: hydride-forming elements [As(III), Sb(III), Se(IV), Sn(IV), CH_3Hg^+], volatile metals (Hg), methylcyclopentadienyl-manganese tricarbonyl (MMT), tetrabutyl-tin ($SnBu_4$) endosulfan, volatile amines (i.e., TMA-N, DMA-N, MMA-N), and hydrogen sulfide. In some cases,

Table 1. Conditions Employed for the Generation of Volatile Species

analyte	V_{sample} (mL)	reaction medium	derivatizing agent	ref.
CH_3Hg^+	5	0.1 M NaOAc/AcOH (pH 5); 20% (m/v) NaCl; 2.3×10^{-5} M of CH_3Hg^+	1 mL of 1% (m/v) $NaBH_4$	23
Hg(II)	5	0.01 M HCl; 3% (m/v) $K_3[Fe(CN)_6]$; 2.5×10^{-5} M of Hg(II)	1 mL of 1% (m/v) $NaBH_4$	24
As(III)[a]	5	2% (v/v) HCl; 6.7×10^{-5} M of As(III)	1 mL of 0.3% (m/v) $NaBH_4$	25
As(III)[a]	5	30% (m/v) citric acid; 6.7×10^{-5} M of As(III)	1 mL of 1% (m/v) $NaBH_4$	26
Sb(III)	5	0.2 M Tris-HCl; (pH 7,2); 4.1×10^{-5} M of Sb(III)	1 mL of 1.2% (m/v) $NaBH_4$	27
Se(IV)	5	1.5 M HCl; 6.3×10^{-5} M of Se(IV)	0.1 mL of 0.25% (m/v) $NaBH_4$	28
Te(IV)	5	1.5 M HCl; 3.9×10^{-5} M of Te(IV)	0.1 mL of 0.25% (m/v) $NaBH_4$	28
Sn(IV)	5	0.01 M HCl; 3% (m/v) $K_3[Fe(CN)_6]$; 4.2×10^{-5} M of Sn(IV)	1 mL of 1% (m/v) $NaBH_4$	24
$SnBu_4$	25	0.1 M NaOAc/AcOH (pH 5); 1.4×10^{-5} M of $SnBu_4$	without derivatization	29
MMT	25	20% (m/v) NaCl; 2.3×10^{-5} M of MMT	without derivatization	30
MMA	5	15% (m/v) NaCl; 1.5×10^{-4} M of MMA	3 mL of 18.67 M NaOH	31
DMA	5	15% (m/v) NaCl; 1.1×10^{-4} M of DMA	3 mL of 18.67 M NaOH	31
TMA	5	15% (m/v) NaCl; 8.5×10^{-5} M of TMA	3 mL of 18.67 M NaOH	31
endosulfan	25	0.005 M HCl; 1.2×10^{-5} M of endosulfan	Without derivatization	32
H_2S	5	0.025 M NaOH; 1.5×10^{-5} M of H_2S	1 mL of 7.44 M HCl	33

[a] Two different reaction media were tried for the generation of arsine.

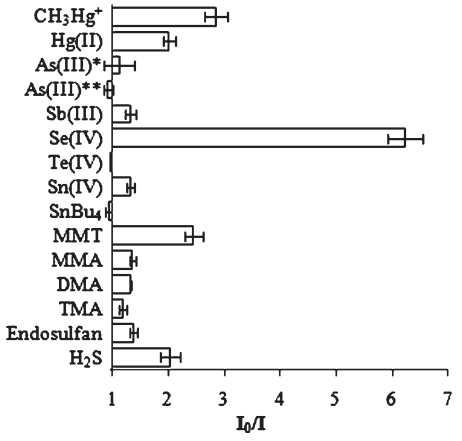

Figure 1. Response of CdSe/ZnS QDs for 14 volatile species.

derivatization was performed, while it was not required for volatile and semivolatile compounds. In all cases, a decrease in the luminescence of QDs was observed in the presence of analyte species. In order to compare the results obtained for different analytes, the Stern−Volmer equation was applied

$$I_0/I = K_{SV}[Q] + C \quad (1)$$

where I_0 is the luminescence intensity before quenching produced by the analyte, I is the luminescence intensity after quenching, K_{SV} is the Stern−Volmer constant, Q is the analyte concentration, and C is a constant.

The results obtained are shown in Figure 1. As can be noted, five of the studied analytes, i.e., Hg(II), H_2S, MMT, Se(IV), and CH_3Hg^+, caused a significant luminescence quenching under the conditions of this study. Two analytes, that provided a ratio of $I_0/I > 2.5$ and, therefore, the highest sensitivity (i.e., Se(IV) and CH_3Hg^+), were selected for full optimization of the QD-HS-SDME approach. In both cases, the corresponding hydride formation was carried out by derivatization with sodium tetrahydroborate. Following this procedure, the mass transfer from the sample solution to the headspace is fast, hence allowing the use of short microextraction time (e.g., 2 min).

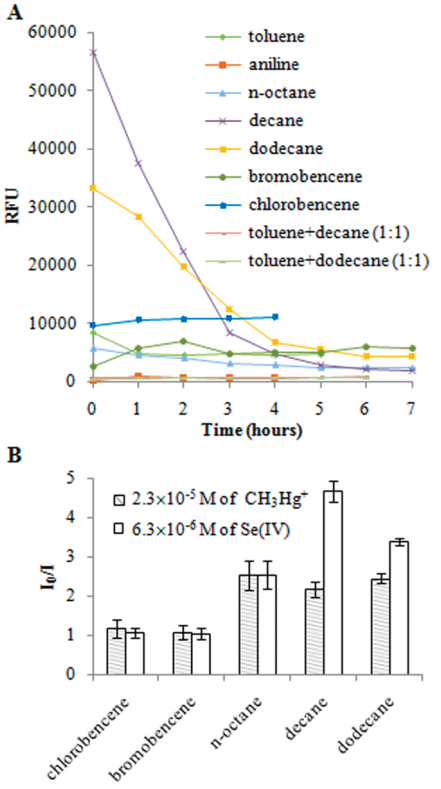

Figure 2. (A) Variation of the luminescence intensity of QDs over time in the absence of analyte. (B) Response of QDs in the presence of analytes using different solvents for dispersion.

In order to achieve an optimal performance with the proposed system for the detection of Se(IV) and CH_3Hg^+, it is necessary to study the variables related to the stability and luminescence properties of QDs confined in a drop as well as those related to the microextraction process.

Stability and Luminescent Properties of QDs in a Solvent Drop. Working conditions with different extractant phases containing QDs (type of organic solvent for microextraction,

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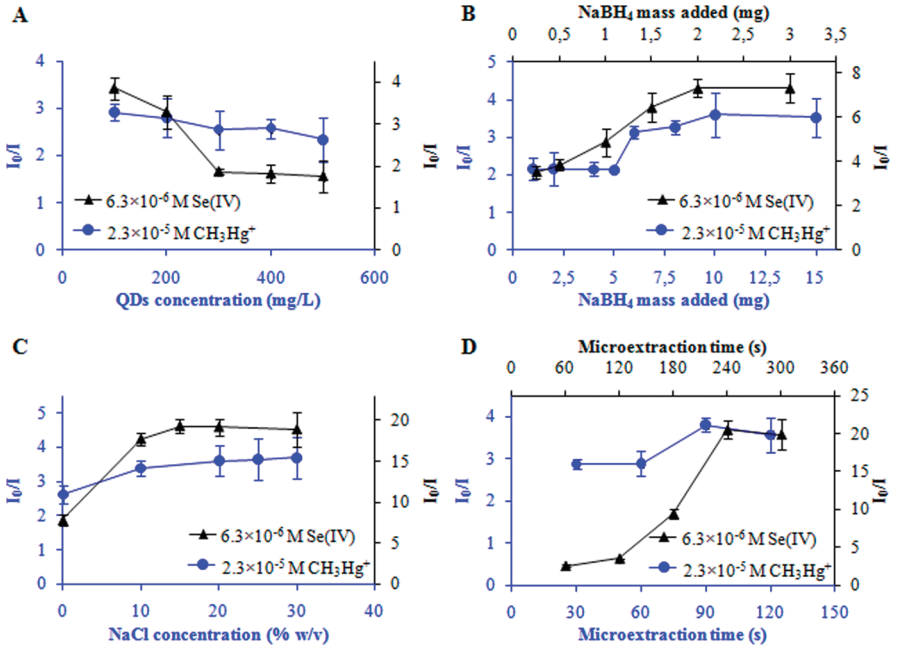

Figure 3. Optimization of (A) QD concentration, (B) $NaBH_4$ mass added, (C) NaCl concentration, and (D) microextraction time. The bottom and left axis correspond to CH_3Hg^+, and the top and right axis correspond to Se(IV).

methods for the preparation of dispersions, presence of light, presence of air, and storage time) were investigated.

The commercial solution of QDs employed in this work consists of CdSe/ZnS nanoparticles stabilized with hexadecylamine (HDA) and dispersed in toluene. When HS-SDME is applied, the extractant phase should have low vapor pressure and a high boiling point in order to minimize evaporation losses during microextraction. Bearing in mind the relatively high volatility of toluene in which QDs are originally dispersed, the change of solvent to another one with reduced volatility and similar polarity to that of the analytes would be desirable to improve the performance of HS-SDME.

The evolution with time of luminescence intensity of QDs dispersed in *n*-octane, decane, dodecane, bromobencene, chlorobencene, aniline, and mixtures of toluene with decane and dodecane after dilution in these solvents was monitored (Figure 2A).

For those solvents where QDs showed a high luminescence intensity such as dodecane or decane, considerable variations of luminescence occurred over time. Dodecane, decane, *n*-octane, chlorobencene, and bromobencene were tested for microextracton of Se(IV) and CH_3Hg^+.

According to Figure 2B, the best results for the extraction of CH_3HgH were obtained employing *n*-octane as extractant phase. For H_2Se, the best results were obtained using decane as extractant phase.

Moreover, the effect of light over QDs has been studied in recent works, showing in some cases an enhancement of luminescence intensity.[34,35] However, this effect depends on the polarity of the dispersion solvent of QDs.[36] When QDs are dispersed in solvents with low dipolar moment, light causes a decrease in luminescence intensity whereas if the solvent has high dipolar moment the presence of light causes an enhancement of luminescence intensity. In this work, the effect of light was studied over solvents with small dipole moment including toluene, *n*-octane, decane, and dodecane. As expected, the luminescence intensity decreased and subsequently was lost.

To study the effect of air, the extractant phase was prepared in the presence of air and nitrogen and the luminescence intensity was monitored every hour. It was found that the luminescence intensity of QDs varied with time in the presence of both air and nitrogen, but this variation is lower for air.

Finally, the luminescence quenching caused by the analytes was employed to evaluate the effect of storage time of working dispersions of QDs. Thus, working dispersions of QDs with variable I_0 (prepared at the time of performing the microextraction) and constant I_0 (prepared 24 h before performing the microextraction) were employed for comparison purposes. The best results were obtained when working solutions of QDs were prepared at the time of performing the microextraction.

Study of Variables That Affect the Microextraction Process. *Effect of Temperature.* Temperature can influence the mass transfer of volatile analytes to the headspace. The effect of temperature on microextraction of the volatiles was assessed by exposing a QDs containing organic solvent microdrop to the headspace of a sample solution thermostated at 20, 25, 30, and 35 °C. The response increased with increasing temperature, but at temperatures above 30 °C, the drop partially evaporated. Consequently, a 25 °C temperature was chosen for further experiments.

Effect of the QDs Concentration. The CdSe/ZnS QD concentration in the droplet can affect the response of CH_3Hg^+ and Se(IV). The influence of the QD concentration on the luminescence quenching caused by CH_3Hg^+ and Se(IV) hydrides was studied in the range of 100−500 mg/L. As shown in Figure 3A, the ratio of luminescence intensities (I_0/I) increased with decreasing concentration of QDs. Lower concentrations were not studied since I_0 was too low. In view of these results, the concentration of QDs in the extractant phase was fixed at a 100 mg/L level for further studies. It is remarkable to observe the low concentration of QDs required for each measurement, apart from the small volume of QD dispersion employed (3 μL versus ~2 mL typically used in all papers so far). Therefore, the use of

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the QD-HS-SDME approach allows a reduction of approximately 500-fold in QD consumption as compared to other procedures concerning QD-based systems.

Effect of the $NaBH_4$ Mass Added. The mass of $NaBH_4$ added to carry out hydride generation was optimized in the ranges of 1−15 mg and 0.25−3 mg for CH_3Hg^+ and Se(IV) detection, respectively. As shown in Figure 3B, an increase in the quenching effect caused by both CH_3Hg^+ and Se(IV) with increasing $NaBH_4$ mass added was observed. In the case of CH_3Hg^+, the use of larger masses of $NaBH_4$ gave rise to the partial evaporation of the drop due to the significant amounts of hydrogen generated inside the vial. For this reason, 6 mg and 2.5 mg of $NaBH_4$ were used for CH_3Hg^+ and Se(IV), respectively.

Effect of the NaCl Concentration. Addition of salt to aqueous samples can improve the mass transfer of hydrophobic analytes to the headspace and, in turn, the extraction efficiency. Concentrations of NaCl in the range of 0−30% (m/v) were examined. As can be observed in Figure 3C, an increase in the response of QDs for CH_3Hg^+ and Se(IV) occurs with increasing NaCl concentration up to 15% (m/v), this effect being more significant in the case of Se(IV). A 15% (m/v) NaCl concentration was selected for both analytes in further experiments.

Effect of Extraction Time. The sampling time is one of the most important parameters to be studied in the application of HS-SDME. The effect of extraction time was studied in the ranges of 30−120 s and of 60−300 s for CH_3Hg^+ and Se(IV), respectively. Figure 3D shows that a maximum response is obtained with a microextraction time of 90 s in the case of CH_3Hg^+. Using longer microextraction times, evaporation of the drop may occur. In the case of Se(IV), a microextraction time of 4 min provided the best results. Optimal microextraction times used for detection of CH_3Hg^+ and Se(IV) were 90 and 240 s, respectively.

Analytical Characteristics. When the target analytes interact with CdSe/ZnS QDs, a significant luminescence quenching was produced and no optical shift of the luminescence emission bands was observed, which indicates that there is no change in surface states (e.g., due to oxidation of QDs)[13] or in the size of QDs (e.g., by replacement of one of their constituents by the analyte).[37] It was found that volatile species quenched the luminescence intensity of QDs following the Stern−Volmer equation.

Analytical figures of merit were established under optimal conditions for the detection of CH_3Hg^+ and Se(IV) using the Stern−Volmer equation. The calibration curve was linear in the ranges of 4.6×10^{-6}−3.5×10^{-5} M and of 6.3×10^{-7}−9.5×10^{-6} M for CH_3Hg^+ and Se(IV), respectively. The slopes of calibration curves (i.e., K_{SV} values) were 1.3×10^5 and 3×10^6 M^{-1} for CH_3Hg^+ and Se(IV), respectively. The limits of detection (LOD), calculated as $3\,s/m$, where s is the standard deviation of 10 blank measurements and m is the slope of calibration curve, were 6.3×10^{-9} and 1.6×10^{-7} M for Se(IV) and CH_3Hg^+, respectively. For MMT, Hg(II), and H_2S, LODs were estimated to be 1.8×10^{-6}, 1.6×10^{-6}, and 9.4×10^{-6} M, respectively. The repeatability, expressed as relative standard deviation, was around 5.0% ($N = 7$) for the above-mentioned species. An interference study was carried out for sensing Se(IV) following hydridation. The presence of concomitants such as $CaCO_3$, $Fe(NO_3)_3$, KNO_3, and Hg(II) at a concentration of 1.9×10^{-2}, 4.1×10^{-5}, 9.9×10^{-3}, and 1.3×10^{-5} M, respectively, did not cause any interference on the quenching effect due to 1.3×10^{-7} M Se(IV), thus showing the high selectivity of the QD-HS-SDME approach.

The figures of merit for this method compare favorably with those of other methods for the determination of Se using more expensive and complex instrumentation. Thus, the LOD corresponding to the QD-HS-SDME approach is better than that of graphite furnace-atomic absorption spectrometry (LOD: 1.3×10^{-8} M Se),[38] although somewhat worse than those of hydride generation-inductively coupled plasma-mass spectrometry (LOD: 3.8×10^{-10} M Se)[39] or hydride generation-atomic absorption spectrometry (LOD: 6.3×10^{-10} M Se).[40] Repeatability values are also comparable to those obtained by the above techniques (in the range of 2−5%).

In order to study the applicability of the proposed method for the determination of Se(IV) in real samples, a recovery study of Se(IV) was carried out in a spiked tap water. Results were found to be satisfactory for tap water samples providing a recovery of 97% for a spike of 6.3×10^{-7} M Se(IV).

CONCLUSIONS

The potential of QD-HS-SDME for sensing some volatile metal species such as CH_3Hg^+ and Se(IV) after hydridation has been clearly demonstrated. As no water-soluble QDs are required, no replacement of the hydrophobic surface ligand incorporated during the synthesis is needed. Furthermore, the proposed system provides an adequate selectivity to determine Se(IV) and CH_3Hg^+ without changing the QD surface coating. Under optimal conditions, volatile species quenched the luminescence intensity of QDs in a concentration dependence that is best described by the Stern−Volmer equation. Advantages of the QD-HS-SDME approach in comparison with earlier strategies regarding the use of QDs as luminescent probes in aqueous solution are (i) increased selectivity due to the separation of the target species by volatilization; (ii) preconcentration onto an organic droplet where volatile species can be easily solubilized; (iii) use of QDs directly in organic phase where they display superior luminescent properties as compared to their water-based counterparts; (iv) minimum consumption of QDs with the subsequent decrease in waste production, which is very important due to their environmental impact as they contain toxic elements. Further efforts are needed for a better understanding of the quenching mechanism involved in order to extend the applicability of this approach to other volatile species, something that is currently under investigation.

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REFERENCES

(1) Saleh, N. *Luminescence* **2009**, *24*, 30–34.

(2) Zheng, A.; Chen, J.; Wu, G.; Wei, H.; He, C.; Kai, X.; Wu, G.; Chen, Y. *Microchim. Acta* **2009**, *164*, 17–27.

(3) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013–2016.

(4) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463–9475.
(5) Alivisatos, P. *Nat. Biotechnol.* **2004**, *22*, 47–51.
(6) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, 307.
(7) Jaiswal, J. K.; Simon, S. M. *Trends Cell Biol.* **2004**, *14*, 497–504.
(8) Yu, W. W.; Chang, E.; Drezek, R.; Colvin, V. L. *Biochem. Biophys. Res. Commun.* **2006**, *348*, 781–786.
(9) Gao, X.; Chan, W. C. W. *J. Biomed. Opt.* **2002**, *7*, 532–537.
(10) Koneswaran, M.; Narayanaswamy, R. *Sens. Actuators, B* **2009**, *139*, 91–96.
(11) Liang, G.; Liu, H.; Zhang, J.; Zhu, J. *Talanta* **2010**, *80*, 2172–2176.
(12) Wang, X.; Guo, X. *Analyst* **2009**, *134*, 1348–1354.
(13) Chun-Ran, T.; Zhong-hua, S.; Bao-Gang, L.; Hao-Wen, H.; Yun-Long, Z.; Shuang, L.; He, H.; Ya-Jing, W.; Chun-Xiang, L.; Guo-Li, S.; Ru-Qin, Y. *Anal. Chim. Acta* **2010**, *678*, 203–207.
(14) Jin, W. J.; Costa-Fernández, J. M.; Pereiro, R.; Sanz-Medel, A. *Anal. Chim. Acta* **2004**, *522*, 1–8.
(15) Qu, F.; Li, H. *Sens. Actuators, B* **2009**, *135*, 499–505.
(16) Shi, G. H.; Shang, Z. B.; Wang, Y.; Jin, W. J.; Zhang, T. C. *Spectrochim. Acta, Part A* **2008**, *70*, 247–252.
(17) Vassiltsova, O. V.; Zhao, Z.; Petrukhina, M. A.; Carpenter, M. A. *Sens. Actuators, B* **2007**, *123*, 522–529.
(18) Carrillo-Carrión, C.; Cárdenas, S.; Simonet, B. M.; Valcárcel, M. *Anal. Chem.* **2009**, *81*, 4730–4733.
(19) Nowack, B.; Bucheli, T. D. *Environ. Pollut.* **2007**, *150*, 5–22.
(20) Pena-Pereira, F.; Lavilla, I.; Bendicho, C. *TrAC, Trends Anal. Chem.* **2010**, *29*, 617–627.
(21) Pena-Pereira, F.; Lavilla, I.; Bendicho, C. *Spectrochim. Acta, Part B* **2009**, *64*, 1–15.
(22) Theis, A. L.; Waldack, A. J.; Hansen, S. M.; Jeannot, M. A. *Anal. Chem.* **2001**, *73*, 5651–5654.
(23) Gil, S.; Fragueiro, S.; Lavilla, I.; Bendicho, C. *Spectrochim. Acta, Part B* **2005**, *60*, 145–150.
(24) Gil, S.; Loos-Vollebregt, M. T. C.; Bendicho, C. *Spectrochim. Acta, Part B* **2009**, *64*, 208–214.
(25) González, J. C.; Lavilla, I.; Bendicho, C. *Talanta* **2003**, *59*, 525–534.
(26) Fragueiro, S.; Lavilla, I.; Bendicho, C. *Spectrochim. Acta, Part B* **2004**, *59*, 851–855.
(27) Cabon, J. Y.; Madec, C. L. *Anal. Chim. Acta* **2004**, *504*, 209–215.
(28) Fragueiro, S.; Lavilla, I.; Bendicho, C. *Talanta* **2006**, *68*, 1096–1101.
(29) Xiao, Q.; Hu, B.; He, M. *J. Chromatogr., A* **2008**, *1211*, 135–141.
(30) Pereira, F. J. P.; Bendicho, C.; Kalogerakis, N.; Psillakis, E. *Talanta* **2007**, *74*, 47–51.
(31) Pena-Pereira, F.; Lavilla, I.; Bendicho, C. *Food Chem.* **2010**, *119*, 402–407.
(32) Ruey-An, D.; Pei-Lin, L. *J. Chromatogr., A* **2001**, *918*, 177–188.
(33) Pena-Pereira, F.; Lavilla, I.; Gil, S.; Costas, M.; Bendicho, C. *Anal. Chim. Acta* **2009**, *647*, 112–116.
(34) Jones, M.; Nedeljkovic, J.; Ellingson, R. J.; Nozik, A. J.; Rumbles, G. *J. Phys. Chem. B* **2003**, *107*, 11346–11352.
(35) Manna, L.; Scher, E. C.; Li, L. S.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2002**, *124*, 7136–7145.
(36) Biju, V.; Kanemoto, R.; Matsumoto, Y.; Ishii, S.; Nakanishi, S.; Itoh, T.; Baba, Y.; Ishikawa, M. *J. Phys. Chem. C* **2007**, *111*, 7924–7932.
(37) Lai, V.; Chang, X.; Fu, C. *Microchim. Acta* **2009**, *165*, 39–44.
(38) Alexiu, S.; Vladescu, L. *Anal. Sci.* **2005**, *21*, 137–141.
(39) Menegário, A. A.; Giné, M. F. *Spectrochim. Acta, Part B* **2000**, *55*, 355–362.
(40) Stripeikis, J.; Costa, P.; Tudino, M.; Troccoli, O. *Anal. Chim. Acta* **2000**, *408*, 191–197.