Talanta 106 (2013) 305–308

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Short communication

Determination of crystal violet in water by direct solid phase spectrophotometry after rotating disk sorptive extraction

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ARTICLE INFO

Article history:
Received 24 July 2012
Received in revised form
5 November 2012
Accepted 6 November 2012
Available online 15 November 2012

Keywords:
Rotating disk sorptive extraction
Polydimethylsiloxane
Water samples
Crystal violet

ABSTRACT

The microextraction of crystal violet (CV) from water samples into polydimethylsiloxane (PDMS) using the rotating disk sorptive extraction (RDSE) technique was performed. The extracting device was a small Teflon disk that had an embedded miniature magnetic stirring bar and a PDMS (560 μL) film attached to one side of the disk using double-sided tape. The extraction involves a preconcentration of CV into the PDMS, where the analyte is then directly quantified using solid phase spectrophotometry at 600 nm. Different chemical and extraction device-related variables were studied to achieve the best sensitivity for the determination. The optimum extraction was performed at pH 14 because under this condition, CV is transformed to the neutral and colorless species carbinol, which can be quantitatively transferred to the PDMS phase. Although the colorless species is the chemical form extracted in the PDMS, an intense violet coloration appeared in the phase because the –OH bond in the carbinol molecule is weakened through the formation of hydrogen bonds with the oxygen atoms of the PDMS, allowing the resonance between the three benzene rings to compensate for the charge deficit on the central carbon atom of the molecule.

The accuracy and precision of the method were evaluated in river water samples spiked with 10 and 30 μgL^{-1} of CV, yielding a relative standard deviation of 6.2% and 8.4% and a recovery of 98.4% and 99.4%, respectively. The method detection limit was 1.8 μgL^{-1} and the limit of quantification was 5.4 μgL^{-1}, which can be decreased if the sample volume is increased.

1. Introduction

Crystal violet (CV) is an aromatic organic dye that is soluble in water, and it is used in the textile industry, medicine and aquaculture. This compound is highly toxic to organisms and the aquatic environment, and it can result in death or mutations in organisms that are exposed to it [1]. The use of CV is currently banned in Europe, USA and Japan. Although the use of CV as a fungicide has been banned in Chilean aquaculture, it is still used as an industrial dye and it could also be illegally used in aquaculture. Therefore, this compound is likely discharged into the sewer system, where it then reaches surface waters such as rivers or seas, thereby affecting aquatic life [2].

The extraction of organic compounds is generally performed using methods that use solvents, which introduce additional contamination into the environment. Although progress has been made to reduce the use of solvents during organic extractions, the development of new techniques that use the least amount of chemical solvents is desirable. Solid phase microextraction (SPME) [3] is a solvent-free technique that is based on the use of a fused silica fiber coated with an adsorbent phase that is polymeric in nature. This technique has allowed the development of new extraction techniques that improve the extraction efficiency by increasing the volume of the polymeric phase and its surface area to volume ratio. In this regard, new sorption techniques have been described including stir bar sorptive extraction (SBSE) [4], silicone rod extraction (PDMS-rod extraction) [5], micro-extraction with a thin sheet of PDMS (thin film PDMS) [6,7] and rotating disk sorptive extraction (RDSE) [8,9]. The advantage of these techniques is that they reduce solvent usage and are rapid and efficient.

All of these microextraction techniques have primarily been used with gas or liquid chromatography. However in RDSE the analyte can also be directly evaluated using solid phase spectrophotometry in the PDMS phase because of its geometry. In this context, a RDSE method has been described for malachite green [10].

In the case of the crystal violet dye, different analytical methods have been described for its determination in water

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http://dx.doi.org/10.1016/j.talanta.2012.11.004

samples, such as dispersive microextraction using ionic liquids and HPLC [11], cloud point extraction coupled with spectrophotometry [12] and magnetic solid phase extraction that is also coupled with spectrophotometry [13]. All of these methods require more than one sample preparation step.

In this study, RDSE technique was used for the extraction of CV from water samples using a rotating Teflon disk coated on one surface with a layer of polydimethylsiloxane (PDMS). After extraction of the CV using RDSE, the analyte can be measured directly on the solid phase using UV–Visible spectrophotometry. The extraction mechanism of CV in PDMS involves that although the colorless species (carbinol) is the extracted chemical form at pH 14, an intense violet coloration appeared in the phase because interaction between analyte and PDMS allows a change in the charge density of the molecule.

2. Experimental

2.1. Reagents

All reagents were analytical grade, and the solutions were prepared with high-purity water from a Milli-Q PLUS ultrapure water system. A stock solution of 1000 mgL^{-1} crystal violet (Sigma Aldrich, Milwaukee, WI, USA) was prepared by dissolving 0.1 g of the reagent into water and diluting to 100 mL in a volumetric flask. Other concentrations were prepared by appropriate dilutions of this stock solution. All solutions were stored in amber bottles at 4 °C.

A 0.1 M phosphate buffer (Merck, Darmstadt, Germany) was prepared for the pH studies. The pH was adjusted using HCl or NaOH (Merck). Sodium sulfate (technical grade, Merck) was used to study the salting out effect.

The PDMS phase was prepared from a Sylgard 184 silicone elastomer kit (Dow Corning Co. MI, USA) according to the recommendations of the manufacturer.

2.2. Instrumental

All absorbance measurements were performed using a Unicam UV2 UV/Vis spectrophotometer. An AWTW Model pMX 3000 pH meter with a combined glass electrode was used for pH determinations. A Heildolph MR 3002 magnetic stirrer with speed and heating control was used for the CV pre-concentration.

2.3. Preparation of the rotating disk devices

The extraction device used in this study (Fig. 1) was a Teflon disk that had an embedded miniature magnetic stirring bar (Teflon-coated Micro Stir bar from VWR International, Inc.).

The PDMS films were prepared as follows: the ratio of base to catalyst mixture was 10:1 (w/w), and the curing time at room temperature was 48 h. Before curing, the gel solution was poured into a square tile for PDMS gelation, in which the area is delimited by a rubber band with a width of 2 mm. The thickness of the formed PDMS film may be modified by the rubber band width. One circular part of the phase, equivalent to the desired area (1.5 cm), was cut using a hollow punch and fixed onto the Teflon disk using double-sided tape.

2.4. General procedure

A 50 mL volume of the water sample (or standard) containing CV with concentrations from 5 to 200 μgL^{-1} was poured into a beaker, and sodium hydroxide was used to adjust the pH value to 14. The rotating disk containing the PDMS phase was placed inside the beaker, and the disk was rotated at 1250 rpm for 100 min at 70 °C.

After extraction, the PDMS film was detached from the disk and placed into a specially designed framed holder. The holder was then inserted into the light path of the UV–Vis spectrometer. Absorbance measurements were performed at 600 nm against a PDMS blank phase located in a second PDMS film framed holder.

2.5. Real sample analysis

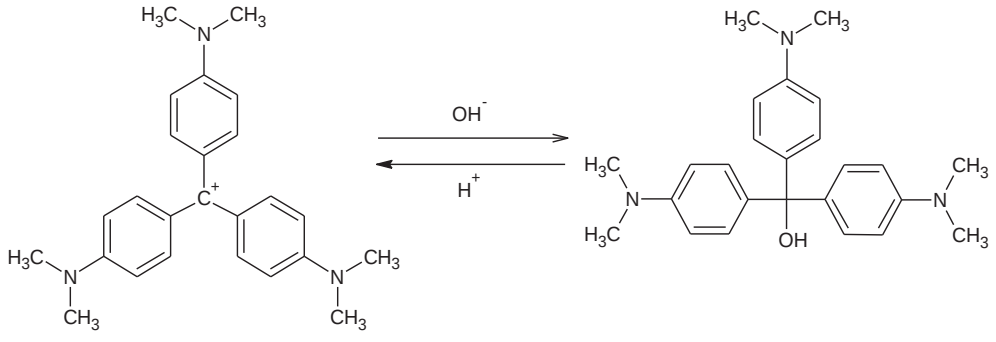
To assess the applicability of the method, water samples were analyzed from the Maipo River using the general procedure. The sample was enriched with different concentrations of CV.

3. Results and discussion

The chemical variables and those related with the stirring extraction/preconcentration device were assessed to obtain the highest sensitivity for the determination of CV.

3.1. Effect of pH and salt addition (salting out)

The effect of pH on the extraction of CV was examined between pH values of 3 and 14. The signal had a significant dependence on the pH. In acidic, neutral and slightly alkaline media, the CV remains colored in aqueous solution due to the presence of the cationic form of CV. Above pH 10, the solution becomes colorless due to the formation of carbinol base (Eq. (1)) [14].



(1)

However, the coloration in the PDMS phase as a function of pH is completely different than the coloration observed in the water phase (Fig. 2). In acidic media, the coloration of the phase was

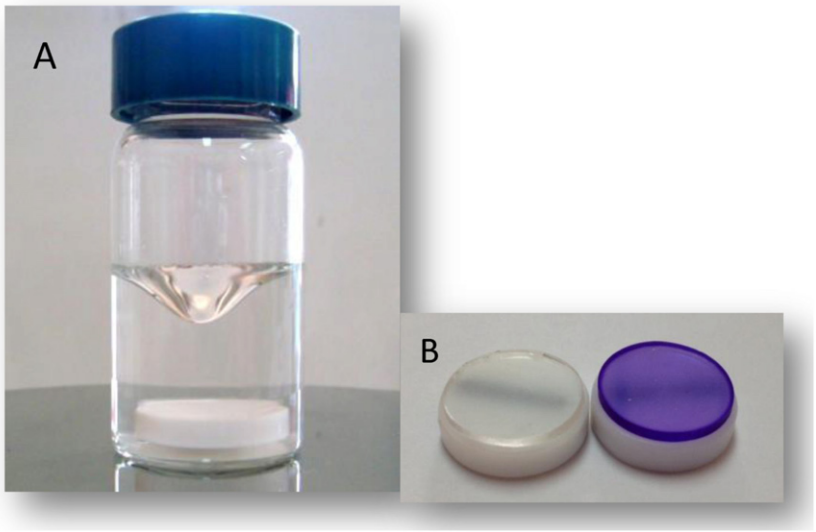


Fig. 1. Photograph of the RDSE system: (A) sample under extraction with the rotating disk, and (B) teflon rotating disk containing the PDMS phase; before and after extraction of a water sample containing CV.

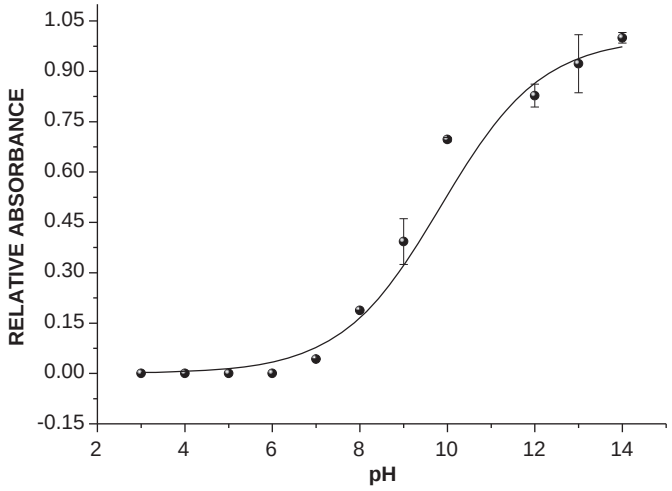


Fig. 2. Effect of pH on the absorbance in PDMS phase. CV was concentrated for 100 min at 1250 rpm from 50 mL of an aqueous solution containing 20 μgL^{-1} of CV at 70 °C.

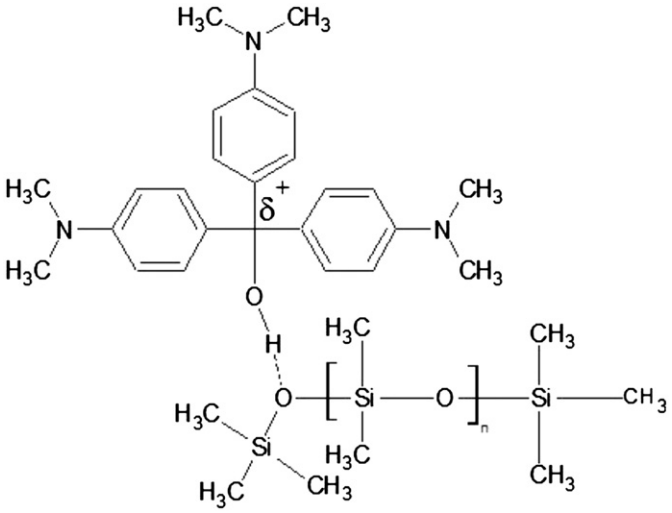


Fig. 3. Interaction by hydrogen bond between carbinol-CV and PDMS.

practically negligible because in this condition, the cationic form of the analyte was not extracted because the PDMS favorably sorbs anions at such pH values [15]. From pH 7, the extraction of the compound began, and it reached a maximum absorbance value at pH 14 (Fig. 2). As stated above, in basic media, the colorless and neutral form of CV, carbinol, is present in the aqueous phase, which transferred into the PDMS phase during the extraction. Once carbinol was extracted, the coloration appeared in the PDMS phase due to the weakening of the carbinol C–OH bond resulting from the formation of hydrogen bonds between its hydrogen atom and the oxygen atom of the PDMS. The formation of this hydrogen bond resulted in a strong resonance between the three benzene rings to compensate for the charge deficit on the central carbon atom of the molecule (Fig. 3).

The extraction process and coloration of the phase can be clearly seen in Video 1, in which a aqueous solution of 20 mgL^{-1} CV was used.

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.talanta.2012.11.004.

According to Fig. 2, the absorbance of CV starts to increase from pH 8, and considering that maximum extraction for malachite green is from pH 6.5 [10], would be feasible to perform a simultaneous determination of both dyes by varying the pH of the sample. This possibility will be checked elsewhere.

Because crystal violet is relatively soluble in water, the effect of adding sodium sulfate to the aqueous phase was studied to improve PDMS extraction by "salting out". While salt addition had a positive effect on the extraction of similar compounds in PDMS [10], in this case, its presence was not favorable and even produced a slight decrease in the signal when this salt was present at concentrations greater than 5%.

3.2. Effect of factors related to the rotating disk

The rotation velocity of the disk is the key factor for achieving efficiency in the analyte mass transport to rapidly obtain the partition equilibrium. It has been previously determined in different microextraction techniques that increasing the stirring speed of the solution [3,4,8,10] (rotation of the disk in this case) decreases the boundary layer of water adjacent to the surface of PDMS, thereby resulting in a faster extraction of the analyte. This property is one of the technical advantages of RDSE compared to

SBSE because the disk can be rotated at high speed without damaging the phase because it is only in contact with the solution [8,10]. In the case of the device used in SBSE, the friction of the phase with the bottom of the vessel containing the sample decreases its durability; therefore, the authors tend to stir at lower velocities [16].

The extraction response of CV was coincident with the previously established behavior; i.e., increasing the rotation velocity of the disk also significantly increased the amount of extracted CV. Finally, extractions were performed at the maximum power provided by the magnetic stirrer of 1250 rpm.

The extraction temperature was assessed from 30 to 90 °C at an extraction time of 100 min. The absorbance was increased with increasing temperature to 70 °C due to an increase of the diffusion coefficient of the CV molecule, which facilitates the extraction into the PDMS. At temperatures greater than 90 °C, the signal sharply decreased because bubbles were produced on the surface of the sorbent, which prevents the interaction between the analyte and the PDMS.

Under the selected conditions of each variable, the time at which the partition equilibrium of the extraction is reached was studied between 5 and 300 min. Equilibrium was achieved at approximately 100 min for sample volumes of 50 mL. For larger volumes of sample, the equilibrium time was similar when the amount of analyte was constant. Conversely, when the analyte concentration remains constant, the equilibrium time increased concomitantly with the increment in sample volume.

This effect was studied using three volumes of sample, 50, 100 and 1000 mL. For larger sample volumes, the sensitivity was significantly increased; however, in the time scale implicit in the experiment, the equilibrium was not achieved at a sample volume of 1000 mL. If more sensitivity is required, it would be feasible to process sample volumes of 1000 mL in non-equilibrium conditions, which would involve careful control of the extraction time.

3.3. Analytical features

The calibration curve was constructed in duplicate at a concentration range between 5 and 225 μgL^{-1} of crystal violet in 50 mL of sample.

The calibration equation is

$$A = 0.00164[CV]\ \mu gL^{-1} + 5.1 \times 10^{-4}; \quad r = 0.9998$$

where A is the absorbance in the solid phase and [CV] is the concentration of analyte in microgram per liter (μgL^{-1}) in the aqueous phase. The accuracy and precision of the method were determined by analyzing six 50 mL samples of river water enriched with 10 and 30 μgL^{-1} CV. The analyte was extracted in all samples using the method in the selected conditions. The relative standard deviations were 6.2% and 8.4% and the recoveries were 98.4% and 99.4%, respectively. This good level of analytical properties indicates that the sample matrix does not affect the determination of CV. River water samples were also analyzed without being spiked, and the analyte was not detected.

The limit of detection (LOD) and the limit of quantitation (LOQ) (for a 50 mL sample volume) were determined according to the IUPAC criterion (3σ- and 10σ- criterion, respectively), yielding 1.8 μgL^{-1} and 5.4 μgL^{-1} CV, respectively. The LOD could be decreased by increasing the sample volume that was subjected to extraction, as stated above.

4. Conclusions

The applicability of sample preparation using RDSE coupled with direct solid phase spectrophotometric measurement for the determination of CV in water samples has been demonstrated in this study. Optimization of the CV extraction was achieved with favorable conditions for each factor. The selected conditions for the extraction were as follows: rotation velocity of the disk, 1250 rpm; pH, 14; temperature, 70 °C; and extraction time, 100 min.

In the study of extraction variables, the pH was determined to be the most significant variable for optimizing the extraction because of the presence of the non-charged species carbinol, which allowed its extraction into the apolar phase of PDMS. Therefore, it is possible to use solid phase UV/Visible spectrophotometry to detect carbinol following its extraction. Once carbinol was extracted, coloration appeared in the PDMS phase due to the weakening of the carbinol C–OH bond that resulted from the formation of hydrogen bonds between its hydrogen atom and the oxygen atom of the PDMS. The formation of this hydrogen bond resulted in a strong resonance between the three benzene rings to compensate for the charge deficit on the central carbon atom of the molecule.

In addition to being simple, this method has the advantage of being more economical because the PDMS is readily synthesizable and the phase can be easily changed after each experiment from the disk surface.

The good level of the obtained analytical features allowed the determinations of the analyte in real samples. The obtained detection and quantification limits are low, and they can be further reduced by increasing the sample volume.

Acknowledgments

The authors would like to thank FONDECYT (Project 1100085) for financial support. Two of the authors (VM and KS) would like to thank CONICYT for their doctoral fellowship.

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