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Short communication

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

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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 $\mu g L^{-1}$ 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 $\mu g L^{-1}$ and the limit of quantification was 5.4 $\mu g L^{-1}$, 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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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

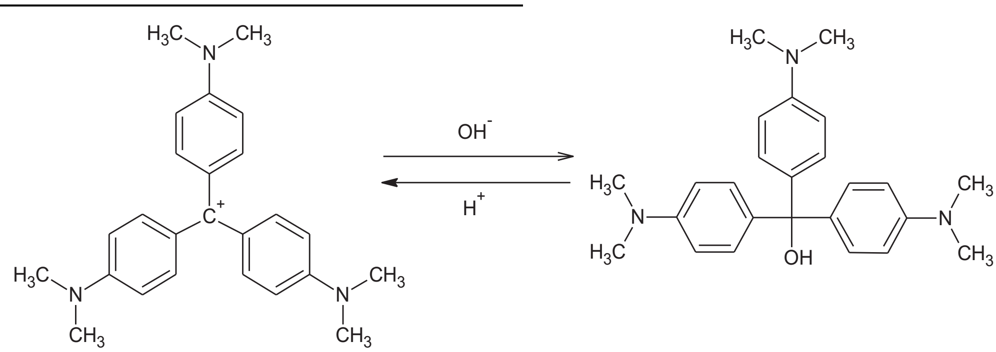
To assess the applicability of the method, water samples were analyzed from the Maipo River using the general procedure. The sample was enriched with different concentrations of CV.

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