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Microcrystalline Anthracene Enrichment-Spectrophotometry Determination of Trace Crystal Violet

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A new method that utilizes microcrystalline anthracene as solid phase extractant was developed for the enrichment of trace crystal violet in water samples. It indicated that the crystal violet in water samples was completely surrounded by microcrystalline anthracene in the presence of NH_4SCN and the microcrystalline anthracene carrier could be recycled after the desorption of crystal violet. Crystal violet could be detected directly by spectrophotometry under the maximum absorption wavelength (λ = 579 nm). The influences of different parameters, such as the amount of NH_4SCN and anthracene, acidity, enrichment time and coexistence of other salts on the enrichment yield of crystal violet have been studied to optimize the experimental conditions. The novel procedure was used to concentrate crystal violet in real water samples and the recovery is 62.4-103.1 %. Analytical results obtained by this novel method are very satisfactory.

Keywords: Crystal violet, Microcrystalline anthracene, Separation and enrichment.

INTRODUCTION

Crystal violet belongs to the triphenylmethane alkaline dye, which is the largest dosage in industry after azo dyes and anthraquinone dyes[1]. It is mainly used in paper, leather, cosmetic, food, textile industries[2]. However, crystal violet may give rise to some side effects, such as high-residual, high-poison and carcinogenesis, teratogenesis, mutagenesis[3]. The industrial wastewater containing crystal violet is not only detrimental to aquatic biological species but threat to human health[4] as well therefore, it is of great importance and significance for environment science and life science to separate and determine trace crystal violet in water samples. Crystal violet could be adsorbed and removed by activated carbon[5] and red mud[6] in water samples, but these couldn't determine the trace of crystal violet in water samples. Although magnetic solid phase extraction[7] could be used to enrich and determine crystal violet in water samples, the preparation of magnetic solid phase extracting agent was a complicated process. Solid phase extraction[8] required to use sophisticated equipments, which included expensive high speed centrifugal equipment working under low temperature (5 °C) and costly solid-phase extraction column (OASIS MCX, 60 mg/^{3} mL, waters company). However, crystal violet was merely enriched under acidic conditions with cloud point extraction[9] and the lowest concentration of crystal violet was only 0.2 μg mL^{-1} in synthetic samples.

This paper proposes a new method for enrichment of crystal violet in water samples *via* microcrystalline anthracene. It indicates that crystal violet can be adsorbed on the microcrystalline anthracene surface and 5 μg of crystal violet can be enriched in the 1 L water sample. Compared to literatures[7-9], this proposed method has many advantages of easy handling, efficient enrichment and low cost. In addition, the adsorbent of microcrystalline anthracene sublimates under higher temperature (150-180 °C), which avoids direct harmfulness to human beings unlike microcrystalline naphthalene sublimating under low temperature (0 °C). The microcrystalline anthracene shields the environment from the secondary pollution of polycyclic aromatic hydrocarbons, which can be recycled after desorption.

EXPERIMENTAL

Preparation of anthracene solution of 25 g/L: Dissolving 2.5 g anthracene and diluting to 100 mL with N,N-dimethylformamide (Tianjin Bodi Chemical Co., Ltd.); crystal violet standard solution (1 g/L): dissolving 0.1 g crystal violet (A.R. Beijing Chemical Works), which was accurately weighed and diluting to 100 mL with distilled water. 1 mol/L of NH_4SCN solution (A.R. Beijing Chemical Works) was prepared. All other reagents in the experiment were of analytical reagent grade.

A model 722 spectrophotometer (Xiamen Analytical Instrument Plant, Xiamen, China) was employed for photometric measurements.

Procedure

1 mL of 50 μg/mL crystal violet, 2 mL of 1 mol/L NH_4SCN and 0.4 mL of 25 g/L anthracene solutions were accurately put into a 25 mL beaker, then the solution was diluted to 10 mL with distilled water, stirring for 5 min and standing for a while. A part of supernatant liquid was taken to a 1 cm thick absorption cell and the absorbance was measured at 579 nm against the reagent blank prepared in the same way. The amount of crystal violet remained in the solution was calculated. Then the enrichment yield of crystal violet (E %) was calculated by difference:

$$E(\%) = [(C_0\text{-}C)/C_0]*100$$

where C_0, C and E represent initial and remained concentrations in the solution and the enrichment yield of crystal violet, respectively.

RESULTS AND DISCUSSION

Effect of anthracene: To investigate the effect of the amount of crystal violet on the enrichment yield of crystal violet, 50 μg of crystal violet and 2 mL of 1 mol/L NH_4SCN were applied to the proposed procedure with total volume of 10 mL (concentration of crystal violet ion (CV^+) can be calculated as 1.22×10^{-5} mol/L). The effect of the amount of anthracene on the enrichment yield of crystal violet was shown in Fig. 1. The enrichment yield of crystal violet was 0 in the absence of anthracene in the solution. The solubility product of ion-association precipitation [(CV^+)(SCN^-)] was measured by the experiment (Ksp = 2.1×10^{-6}). According to the above conditions of experiment ([CV^+] = 1.22×10^{-5} mol/L, [SCN^-] = 0.20 mol/L), it was found that the product of the concentrations of [CV^+] and [SCN^-] is 2.44×10^{-6}, which was higher than the solubility product of ion-association precipitation [(CV^+)(SCN^-)].

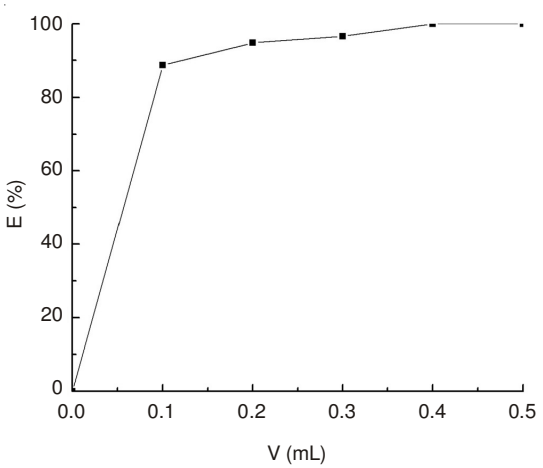

Fig. 1. Effect of anthracene on the enrichment yield. Crystal violet: 50 μg, NH_4SCN (1.00 mol/L): 2 mL, anthracene: 0.14 mol/L, reaction time: 5 min, total volume: 10 mL

However, the precipitation of ion-association complex still couldn't be formed without anthracene, the resulting the concentration of [CV^+] had not been reduced. It was likely that the supper solution of [CV^+] and [SCN^-] was formed. The enrichment yield of crystal violet suddenly increased from 0 to 88.7 % corresponding to an increase in anthracene from 0 to 0.10 mL (2.5 mg). It indicated that a small amount of microcrystalline anthracene could induce the formation of ion-association complex of [SCN^-] and trace [CV^+], thus crystal violet was enriched. The reason was probably that the molecular structure of the crystal violet matrix (organic groups) has stronger hydrophobicity and microcrystalline anthracene molecule has a large conjugated system and the superficial area.

Then due to interaction between the hydrophobic groups (aromatic conjugation system) of CV^+ matrix and the conjugated system of microcrystalline anthracene, [CV^+] and [SCN^-] could form ion-association complex [(CV^+)(SCN^-)] easily and the ion-association complex could be adsorbed on the surface of microcrystalline anthracene. And the concentration of CV^+ from 5 μg mL^{-1} reduced to 0.565 μg mL^{-1} in the solution. The enrichment rate of crystal violet had reached more than 99.7 % when the amount of anthracene increased to 0.30 mL. It lead to a decrease in the concentration of crystal violet from 5 to 0.015 μg mL^{-1}. It indicated that crystal violet could be quantitatively retained on the surface of microcrystalline anthracene. When the amount of anthracene increased to 0.40 mL, the enrichment rate of crystal violet was 100 % and the solution had become completely colorless. In order to assure crystal violet could be completely enriched, 0.40 mL anthracene (10 mg) was selected in the subsequent experiments.

Effect of NH_4SCN: In order to investigate the effect of the amount of NH_4SCN on the enrichment yield of crystal violet, 10 mg of anthracene and 50 μg of crystal violet were applied to the proposed procedure with total volume of 10 mL (the concentration of crystal violet could be calculated as 1.22×10^{-5} mol/L), the effect of the amount of NH_4SCN on the enrichment yield of crystal violet was shown in Fig. 2. The enrichment yield of crystal violet was 0 in the absence of NH_4SCN in the solution, which showed that the crystal violet in the solution couldn't be enriched. The enrichment yield of crystal violet increased from 79.2 to 95.7 % corresponding to an increase in NH_4SCN from 0.10 mL (0.010 mol/L) to 1.50

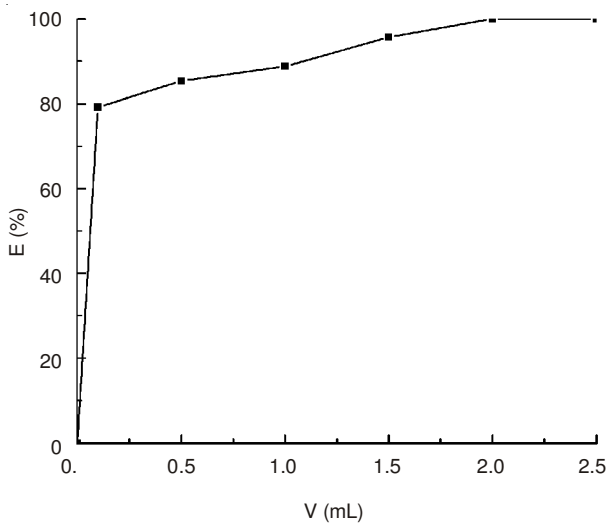

Fig. 2.. Effect of NH_4SCN on the enrichment yield. Crystal violet: 50 μg, NH_4SCN: 1.00 mol/L, anthracene (0.14 mol/L): 0.4 mL, reaction time: 5 min, total volume: 10 mL

mL (0.15 mol/L). As can be seen from the experiment, the solubility product constants of precipitated [CV^+] [SCN^-] can be calculated as $K_{sp} = 2.1 \times 10^{-6}$.

Although the product of the concentrations of [CV^+] and [SCN^-] was [CV^+] [SCN^-] = 1.22×10^{-7} when the addition of NH_4SCN was 0.1 mL, that was still less than K_{sp} of ion-association complex [(CV^+)(SCN^-)], the enrichment yield of crystal violet was close to 80 %. It suggested that microcrystalline anthracene had good induced precipitation and enrichment effect on crystal violet and the reason was accordant with the "effect of anthracene". Enrichment of crystal violet could be reached 100 % when the amount of NH_4SCN was 2 mL. Hence, the rest study was carried out with 2 mL of 1 mol/L of NH_4SCN.

Effect of various salts: In order to investigate the effect of the various salts [$(NH_4)_2SO_4$, KNO_3, KBr, KCl] on the enrichment yield of crystal violet, 10 mg of anthracene, 50 μg of crystal violet and 2 mL of 1 mol/LNH_4SCN were applied to the proposed procedure with total volume of 10 mL under the optimum conditions. The results were shown in Fig. 3. The enrichment yield of crystal violet decreased from 100 to 98 % corresponding to an increase in the concentration of $(NH_4)_2SO_4$ from 0.05 to 0.20 mol/L. However, in the range from 0.05 to 0.10 mol/L, the enrichment of crystal violet decreased in greater degree in the presence of $(NH_4)_2SO_4$ in comparison with the same concentration of $NaNO_3$, KBr or KCl. Fixing a certain concentration of $NaNO_3$, KBr, KCl and $(NH_4)_2SO_4$ and changing the concentration of crystal violet, the anions (NO_3^-, Br^-, Cl^-) in different salts can, respectively, react with CV^+ to form ion-association complex [(CV^+)(NO_3^-)], [(CV^+)(Br^-)] and [(CV^+)(Cl^-)], but there was no precipitation of ion-association complex [$(CV^+)_2(SO_4^{2-})$] even under the higher concentration of CV^+ and SO_4^{2-}. It indicated that the reason for the decrease of enrichment yield may be the salt effect made by $(NH_4)_2SO_4$. As can be seen from the experiment, the solubility product constant of precipitated [(CV^+)(NO_3^-)], [(CV^+)(Br^-)] and [(CV^+)(Cl^-)] can be calculated as $K_{sp} = 1 \times 10^{-5}$, 8.6×10^{-6} and 1.6×10^{-5}. There was no influence on the enrichment of CV^+, the reason was that the precipitation of ion-association complex [(CV^+)(Cl^-)] can also be formed with the concentration of KCl ranged from 0.05 to 0.10 mol/L. But the enrichment yield of crystal violet was apparently declined corresponding to an increase in the concentration of KCl, which may be result of salt effect made by higher concentration of KCl.

Due to the ionic radius of NO_3^- is much bigger than that of Cl^-, the solubility product constant of precipitated [(CV^+)(NO_3^-)] is much less than that of precipitated [(CV^+)(Cl^-)] and the enrichment yield of crystal violet was apparently declined when the concentration of KNO_3 was greater than 0.15 mol/L. The change of the concentration of KBr had no significant effect on the enrichment yield of crystal violet, it may be likely that the solubility product constant of precipitated [(CV^+)(Br^-)] was smaller and the precipitation of ion-association complex [(CV^+)(Br^-)] was beneficial to the enrichment of crystal violet. However, the slightly soluble ion-association complex of [$(CV^+)_2(SO_4^{2-})$] was hard to formed, the possible reason was that the reaction of CV^+ and SO_4^{2-} with the reaction stoichiometric ratio 2:1, then the effect of steric hindered made the precipitation of ion-association complex [$(CV^+)_2(SO_4^{2-})$] couldn't be formed. So the decrease of enrichment yield of crystal violet was mainly influenced by the salt effect of different concentrations of $(NH_4)_2SO_4$. Fig. 3 shows that various salts, respectively, influence the enrichment yield of crystal violet in different degree, but the enrichment yield of crystal violet remains above 90 %. It indicates that the enrichment yield of crystal violet is still higher so as to meet the demand for the analysis of trace crystal violet in the presence of the certain amount of salts.

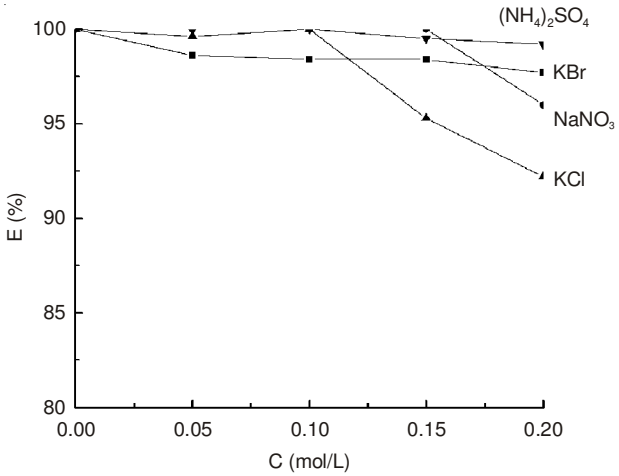

Fig. 3. Effect of various salts on the enrichment yield. Crystal violet: 50 μg, NH_4SCN (1.00 mol/L): 2 mL, anthracene (0.14 mol/L): 0.4 mL, reaction time: 5 min, total volume: 10 mL

Effect of pH: Under the optimum conditions, the influences of acidity (pH = 1-6) on the enrichment yield of crystal violet were investigated. It indicated that the enrichment rates of crystal violet were 100 % at the range of pH from 1 to 6. The reason was that the species of crystal violet cation (CV^+) wasn't influenced by acidity, that is to say, crystal violet only exists in solutions with a single cationic species. Consequently, the acidity had no influence on enrichment yield of crystal violet.

Effect of stirring time: The enrichment yield of crystal violet was strongly correlated with the stirring time. The enrichment yield of crystal violet was increased gradually by increasing the stirring time. Adsorption reached equilibrium after stirring 5 min and crystal violet was completely retained on the surface of microcrystalline anthracene. Therefore, it was required that the stirring time was at least 5 min in condition experiments.

Concentration of crystal violet in samples: 10 g of NH_4SCN, 15 mL of 25 g/L anthracene and different amount of crystal violet were put into 500 mL water samples, 20 g NH_4SCN, 20 mL of 25 g/L anthracene and different amount of crystal violet were put into 1000 mL water samples respectively, stirring for 40 min under 200 rpm and standing for 5 min at least. Then, the mixture was filtered with G4 crucible. The microcrystalline anthracene, which had adsorbed crystal violet, was fully soaked with little ethanol in G4 crucible and filtered. The final volume of filtrate was diluted to 5 mL with distilled water. The amount of crystal violet in the filter liquor was determined according to the proposed procedure, then, the recovery rate of crystal violet was calculated. The results were shown in Table-1.

TABLE-1
DETERMINATION RESULTS OF CRYSTAL VIOLET IN WATER SAMPLES

Water samples (mL)	Added (μg)	Concentration (μg/mL)	Found (μg)	Determination (μg/mL)	Recovery (%)
500	0.00	0.00	-	-	-
500	5.00	0.01	4.27	0.00854	85.4
500	10.00	0.02	9.34	0.01868	93.4
500	20.00	0.04	20.63	0.04126	103.1
1000	5.00	0.005	3.12	0.00312	62.4
1000	10.00	0.01	9.16	0.00916	91.6
1000	20.00	0.02	19.24	0.01924	96.2

Conclusion

In this work, an alternative method has been proposed to determine the trace crystal violet after separation and enrichment using microcrystalline anthracene as a sorbent. The effects of different parameters, such as the amounts of anthracene and NH_4SCN, stirring time and acidity on the enrichment yield of crystal violet have been studied to optimize the experimental conditions. It indicates that the microcrystalline anthracene has a good effect on enrichment of crystal violet and the recovery is in the range of 62.4-103.1 %. The proposed method has advantages of good repeatability and reproducibility, a high recovery rate and shorter separation time and it was successfully applied to determine the trace crystal violet in water samples.

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