SORPTION-CATALYTIC TESTING OF CADMIUM IN WATER SAMPLES

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Abstract

Various test systems are widely used in environmental analysis. Catalytic methods for the determination of metal ions are sensitive, rapid and do not require complicated equipment. In order to improve the selectivity, combinations of catalytic determination with separation methods are used. By the sorption-catalytic method we imply sorption preconcentration of the analyte followed by a catalytic indicator reaction carried out directly on the surface of the sorbent. Cadmium decreases the rate of oxidation of 3,3',5,5'-tetramethylbenzidine **(TMB)** with KIO_4 conducted either with or without Mn(II) as a catalyst. Cadmium is preconcentrated from aqueous solutions on silica plates physically modified with periodate and a reagent for the selective determination of Cd(II), namely 1-[(bromo-2-benzothiazolyl)azo]-2-naphthol **(BBT)**. In order to determine preconcentrated cadmium, the indicator reaction is conducted directly on the sorbent. With this purpose, the silica plate is pressed to a wet piece of filter paper modified with TMB ("sandwich-like test system"), and in 2 min the filter paper color is compared with the scale. The procedure allows semiquantitative determining of $1 \cdot 10^{-4}$ - $5 \cdot 10^{-3}$ ppm cadmium in tap water samples.

Introduction

The determination of trace metals has increasing importance in environmental analysis. Instrumental methods for the determination of cadmium are highly sensitive and selective, but the majority of them are fairly complicated and require the use of specialized and expensive equipment. Test methods are characterized by simple experimental techniques and, as a rule, require little or no instrumentation. In catalytic test methods, the advantages of catalytic assay (high sensitivity) and sorption procedures (selectivity) are used (1). The feasibility of sorption-catalytic approach has been demonstrated in the catalytic determination of copper(II) after its sorption on a hexamethylenediamine sorbent (2) and manganese after its sorption on diethylenetriaminetetraacetate sorbent (3). However, sorbents of this type are not selective. A convenient way for the production of selective sorbents is non-covalent binding of selective organic reagents onto solid supports. We have chosen BBT (Fig. 1) that is known as one of the most selective reagents for the spectrophotometric determination of cadmium (4).

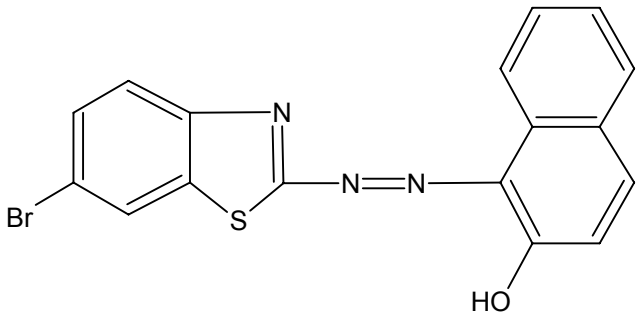

Fig. 1. The structure of bromobenzothiazo (BBT).

Methods

Reagents and Solutions

Distilled water or rectified ethanol were used to prepare solutions. 3,3',5,5'-Tetramethylbenzidine (TMB) "for analysis" from Riedel-de Haën, Germany was stored as an ethanolic solution (0.025 mol/L) and diluted with ethanol when necessary. Stock solution of periodate in water (1 g/L KIO_4) was diluted to an appropriate concentration every 4-5 days. Bromobenzothiazo (BBT, 2 g/L) was dissolved in ethanol; further dilutions were made in ethanol-water (1:1 v.:v.) mixture. The standard cadmium solution contained 10 mg/L Cd(II); the solutions with lower Cd(II) contents were prepared by dilution without additional acidification (the solutions containing 1 mg/L Cd(II) or less were prepared daily). Phosphoric buffer solutions in the pH range 6 – 8 (0.1 mol/L in phosphate) were prepared from Na_2HPO_4 and KH_2PO_4. Buffers of pH 6.5 – 7.5 were prepared by dropwise addition of 0.2 mol/L KOH to a solution of 3.3 g boric acid in 1000 mL of water until the desired pH value was reached. To obtain the BBT-modified sorbent, silica plates for TLC "Sorbfil" (silica particles 5-17 μm, silica sol as the binder, poly(ethylenetherephthalate) as support, from "Sorbpolymer", Krasnodar, Russia) were used.

Instrumentation

For reflectance measurements, portable reflectometer "Malysh" (Yu.L.Shishkin, Kurnakov Institute of General and Inorganic Chemistry, Russia) was used; pH values of solutions were measured by pH-millivolmeter ("Econix", Moscow, Russia). All experiments and measurements were carried out in an air-conditioned laboratory at room temperature (23±1 °C).

Preparation of the Sorbent Modified with BBT and KIO_4

To obtain BBT/KIO_4/silica sorbent, 33 μL of 0.04 mg/L ethanolic solution of BBT were pipetted over the whole surface of silica plate (1.5×1.5 cm^2). The obtained faintly purple-colored sorbent was then dried with a stream of pressured air for 1 min; the surface concentration of BBT on silica plate was about $2 \cdot 10^{-12}$ mol/cm^2. Then 33 μL $4.3 \cdot 10^{-2}$ mol/L aqueous solution of KIO_4 were pipetted and the sorbent was dried on the air.

Preparation of the Sorbent Modified with TMB

To obtain TMB/filter paper sorbent, a filter paper plate (1.5×1.5 cm^2) was sprinkled twice by 33 μL of $8 \cdot 10^{-3}$ mol/L ethanolic solution of TMB. The sorbent was then dried on the air.

Preconcentration of Cadmium(II) on Silica Plates Modified with BBT and KIO_4
A silica plate specimen (1.5×1.5 cm^2) modified with BBT and KIO_4 was placed into a glass cylinder containing 2 mL of buffered Cd(II) solution (phosphate buffer, pH 6.8). The sorption was carried out using shaking procedure during 5 min.

Indicator Reaction on the Silica Plates (Pipetting)
In order to study the sorption of cadmium and optimize the conditions of the indicator reaction, the reaction is carried out directly on the sorbent using the following procedure. For this purpose, a 7 μL aliquot of borate buffer (pH 6.8) is pipetted, then the plate is dried and 7 μL of a $8 \cdot 10^{-3}$ mol/L TMB is pipetted, and the reflectance coefficient of the plate at 650 nm is measured and taken as the initial value R_{ini}. The plate is then dried and 7 μL of a $2.2 \cdot 10^{-3}$ mol/L KIO_4 is pipetted to the spot, which is taken to be the beginning of the reaction. Reflectance of the wet plate at 2 min (R_2) is measured. The difference $R_{Cd} = R_{ini} - R_2$ is taken as the analytical signal. For the reaction TMB-KIO_4 when run without cadmium, $R_{ini} - R_2$ is designated as R_0. The inhibiting effect of cadmium is calculated as $R_0 - R_{Cd}$.

Indicator Reaction (Test Procedure)
In order to determine preconcentrated cadmium, the TMB modified filter paper is wetted by 30 μL of the borate buffer (pH 6.8) and pressed to the BBT/KIO_4/silica plate containing preconcentrated cadmium. Mutual diffusion of the components makes the indicator reaction start in that paper-silica “sandwich”. In 2 min the silica plate is removed and the reflectance of the wet paper is measured, or the paper plate color is compared with the color scale (visual detection).

Results and Discussion
Choice of the indicator reaction
For the purpose of the determination of cadmium we have chosen the oxidation of TMB (Fig. 2) by periodate because of low toxicity of TMB and high molar absorptivity of products. An appreciable inhibiting effect of cadmium had been shown while studying its catalytic action in this reaction (3). The inhibiting effect of cadmium is observed both in solutions and on supports for which we used silica TLC plates.

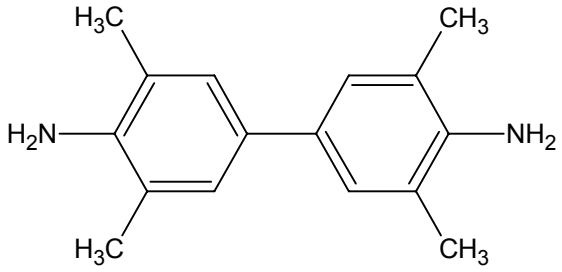

Fig. 2. The structure of 3,3',5,5'-tetramethylbenzidine (TMB).

Optimization of Sorption of Cadmium(II)
Retention of BBT on the supports and its effect on the indicator reaction rate were studied in the previous paper (5). It was shown that modified sorbent would be stable at pH ≥ 6. BBT did not affect the indicator reaction rate and did not decrease the precision of the determination of Cd(II) within the concentrations less than $1 \cdot 10^{-7}$ mol/cm^2.

Sorption of cadmium on the sorbent has been studied and the optimal conditions were selected by use of the pipetting procedure. It was found that quantitative sorption is observed on the silica plates modified by 0.03 mg/cm^2 of BBT from the solution with pH 6.8. Sorption should be carried out during 5 min.

Construction of "sandwich-like test system"

One of the potential advantages of sorption-catalytic techniques is the feasibility of rapid determinations of analytes directly on the sorbents with no use of instrumental detection. We use the separation of oxidizing and reducing agents on two different sorbents to avoid the premature start of the indicator reaction (before the sorption of cadmium has been carried out). Before applying TMB, KIO_4, and BBT onto the sorbents, it was necessary to investigate the stability of these compounds on the sorbents and their compatibility with each other in the adsorbed state. It was found that TMB cannot be used on the sorbent together with BBT because of the decrease in the indicator reaction rate. KIO_4 cannot be carried on filter paper from which it readily washes out. BBT is compatible with KIO_4, while the both are strongly retained on silica. Thus, the "sandwich" consists of two 1.5×1.5 cm^2 sorbents: silica plates modified with BBT and KIO_4 and filter paper modified with TMB. We have shown that this combination of the sorbents and reagents is convenient for the development of the test system.

Determination of cadmium with instrumental detection

Optimizations were performed so that the difference in the rate of the inhibited and uninhibited reactions was maximum (in choosing the conditions, we used the pipetting technique described above). The maximum inhibiting effect of Cd(II) was observed at pH 6.8 (borate buffer). The selected optimum amounts of the components in the indicator reaction are as follows: $2.5\cdot10^{-7}$ mol/cm^2 TMB, $6.3\cdot10^{-7}$ mol/cm^2 KIO_4. The characteristics of the "sandwich" procedure for the determination of cadmium after its sorption preconcentration on the modified sorbents are presented in Table 1.

Table 1. Equation for the calibration graph (Y = a + bX) and the linear range for the determination of Cd(II) by oxidation of TMB with KIO_4 in "sandwich-like test system" after sorption of cadmium on silica plates modified with BBT.

Y = $\Delta R_2 = R_0 - R_{Cd}$, which is the difference in reflectance coefficients with and without cadmium, X = C_{Cd}, mg/L

Linear range, mg/L	a	s_a	b	s_b	r	RSD (for $1\cdot10^{-4}$ mg/L Cd(II))	C_{min}, mg/L
$1\cdot10^{-4} - 3\cdot10^{-3}$	5.67	0.03	0.24	0.01	0.998	0.08	$5\cdot10^{-5}$

Determination of cadmium with visual detection

Instead of measuring the reflectance of the sandwich, the color was observed visually. Various concentrations in the range $1\cdot10^{-4} - 5\cdot10^{-3}$ mg/L of cadmium were studied. It was found that confident discrimination of the color intensities could be

done for cadmium concentrations that differ by not less than half an order of magnitude. The determination allows a color scale to be constructed for the semiquantitative determination of cadmium in the range $1 \cdot 10^{-4}$ – $5 \cdot 10^{-3}$ mg/L. The whole procedure requires 7-10 min starting with the sorption of cadmium on the BBT/KIO_4/silica plate.

The developed technique was successfully applied for determining cadmium in tap water samples.

Table 2. Analysis of tap water samples

Sample No	Found cadmium (mg/L) by	
	Sorption-catalytic method	Reference method
1	$(6.4 \pm 0.6) \times 10^{-4}$	$(7 \pm 3) \times 10^{-4}$ *
2	$(2.0 \pm 0.6) \times 10^{-3}$	$(2.4 \pm 0.3) \times 10^{-3}$ **

* Stripping voltammetry

** Preconcentration on diethylenetriaminetetraacetate chelating sorbent with the subsequent flame AAS

Conclusions

Selective preconcentration of cadmium on a support with a physically immobilized reagent was successfully combined with a catalytic determination procedure directly on the sorbent. We developed simple and rapid on-site test for cadmium with visual detection or determination with portable reflectometer.

Acknowledgments

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