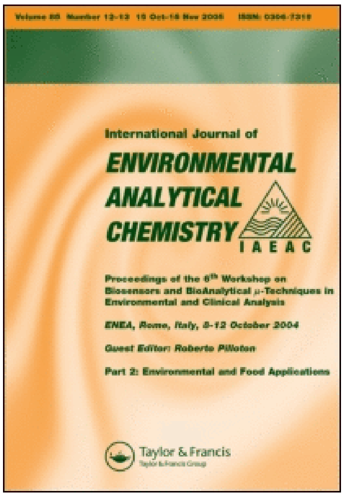

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# Determination of Chromium (VI) in Natural Waters by the Interaction Between Triiodide Ion and Hexadecylpyridinium Chloride Micelles

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# DETERMINATION OF CHROMIUM (VI) IN NATURAL WATERS BY THE INTERACTION BETWEEN TRIIODIDE ION AND HEXADECYLPYRIDINIUM CHLORIDE MICELLES

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The cationic surfactant hexadecylpyridinium chloride (cetylpyridinium chloride, CPC) enhances the sensitivity and selectivity of the spectrophotometric determination of chromium(VI) based on its reaction with iodide ion in an acid medium, which is accelerated by 2,2'-dipyridyl. The triiodide ion produced in the reaction associates with CPC micelles, which results in maximum absorption at 500 nm, with a concomitant substantially increased absorptivity and stability constant of the triiodide complex. The micellar medium allowed the determination of chromium(VI) at concentrations between 15 and 100 ng $ml^{-1}$, with a detection limit of 9 ng $ml^{-1}$ (i.e. about 5 times lower than those of methods implemented in aqueous media). The molar absorptivity for the triiodide-CPC system was found to be $(5.19 \pm 0.08) \times 10^4$ l $mol^{-1}$ $cm^{-1}$. The selectivity towards various ions such as Pb(II), Fe(III), Cd(II), Cu(II) and Ni(II) was also greately enhanced. The proposed method was satisfactorily applied to the determination of chromium(VI) in natural waters after extraction with trioctylamine, with an average recovery of 96%.

**KEY WORDS**: Chromium(VI), hexadecylpyridinium chloride, micelles, waters.

## INTRODUCTION

The chromium content of water is probably increasing steadily as a result of industrial activity in populated areas[1]. Thus, the use of chromates as anti-corrosion agents in cooling waters is a major source of chromium dumped into the environment. Water-soluble hexavalent compounds are extremely irritating, corrosive and toxic to human tissues[2]. Chromate poisoning causes skin disorders and liver damage, and there are some reasons to believe that chromates are carcinogenic. For these reasons, its maximum allowable level in drinking waters has been limited to 0.05 mg $l^{-1}$ hexavalent chromium[3].

In recent years, several sensitive spectrophotometric methods for the determination of chromium(VI) have been developed based on the oxidation of hydriodic acid by chromic acid and quantitation of the triiodide ion produced on the basis of its absorbance at 350 nm [4,5].

Chromium(VI) can be determined at concentrations between 0.05 and 1.8 μg $ml^{-1}$ in a simple, rapid way by a number of these methods; however many of these are confronted with problems arising from the strong absorption of many water samples at 350 nm and serious interferences caused by Cu(II), Ni(II), Co(II) and Fe(III). The sensitivity and selectivity of the determination can be greatly improved through formation of an ion-association compound of triiodide with a basic xanthene dye which is soluble in poly(vinyl alcohol)[6]. This procedure has been applied to the determination of Cr(VI) in waters after extraction with trioctylamine.

In this work, cetylpyridinium chloride (CPC) micelles were used as a simple means of enhancing the sensitivity and selectivity of existing analytical methods for the determination of Cr(VI) based on production of triiodide ion. At CPC concentrations slightly above its critical micelle concentration, triiodide ion undergoes a bathochromic shift from 350 nm to 500 nm with a concomitant substantial increase in its stability constant and absorptivity[7]. These effects can be used to completely overcome or at least minimize the selectivity and sensitivity problems that confront many of the original photometric procedures for monitoring iodine using aqueous media. In this work, such effects were exploited to enhance the spectrophotometric determination of Cr(VI).

## EXPERIMENTAL

### *Reagents*

All reagents used were of analytical grade and were used as supplied. Distilled water was used throughout. A chromium(VI) stock solution (1 $gl^{-1}$) was prepared by dissolving potassium dichromate in water; more dilute solutions (5 μg $ml^{-1}$) were prepared daily by direct dilution of appropriate aliquots of the stock solution. A 0.6 M solution of potassium iodide was prepared and stored in the dark as usual to avoid any photochemical reactions. Aqueous solutions of 2,2′-dipyridyl ($1\times10^{-2}$M), hydrochloric acid (0.1 M), CPC (Serva, $1.4\times10^{-3}$ M), sulphuric acid (1 M) and sodium hydroxide (0.3 M) were also made. Trioctylamine (TOA) solutions (5%) were prepared by dissolving the reagent in chloroform.

### *Apparatus*

Spectrophotometric measurements were made on a Hitachi U-2000 spectrophotometer fitted with cells of 1-cm pathlength. The spectrophotometer cell compartment was thermostated by circulating water from a Neslab RTE bath through it with a temperature stability of ±0.1 °C.

### *Procedure*

To a 10-ml volumetric flask were added, in sequence, appropriate volumes of Cr(VI) standard solution (5 μg $ml^{-1}$) to give a final concentration between 15 and 100 ng $ml^{-1}$, 0.5 ml of

2,2′-dipyridyl ($1\times10^{-2}$ M), 1 ml of hydrochloric acid (0.1 M, final pH 2.2), 0.25 ml of potassium iodide (0.6 M) and 0.2 ml of CPC ($1.4\times10^{-3}$ M). The stopwatch was then started and the solution was diluted to the mark with water. An aliquot of the reaction mixture was transferred to a thermostated cell at 20±0.1 °C after 45 s, and the absorbance at 500 nm was exactly measured at 6 min. The blank signal obtained from a solution containing all the reactants except chromium(VI), was subtracted from each absorbance value provided by the standards.

### *Determination of chromium(VI) in natural waters*

Concentrate 500 ml of water sample to 25 ml by heating. Pipet a 5-ml aliquot of this solution into a test tube, add 2 ml of 1 M sulphuric acid and dilute to about 10 ml with water. Shake with 1 ml of TOA solution in chloroform for 2 min, centrifuge and discard the aqueous layer. Wash twice with 3 ml of water. Back-extract the Cr(VI) in the organic phase twice with 1 ml of 0.3 M sodium hydroxide, shake the mixture for 2 min each time, centrifuge and transfer the aqueous layer to a 10-ml standard flask. Wash the organic layer twice with 1 ml of water and add the washings to the 10-ml volumetric flask. Make to the mark with water. Then analyse aliquots of less than 1 ml as described under **Procedure**.

## RESULTS AND DISCUSSION

2,2′-Dipyridyl catalyses the reaction between chromic acid and hydriodic acid[5]. In the presence of CPC micelles, the following reactions are involved.

$$Cr_2O_7^{2-} + 9\,I^- + 14\,H^+ \overset{2,2'\text{-dipyridyl}}{\Longleftrightarrow} 2\,Cr^{3+} + 3\,I_3^- + 7\,H_2O$$

$$3\,I_3^- + CPC_{\text{micelles}} \Longleftrightarrow 3\,I_3^-\text{–}CPC_{\text{micelles}}$$

where the absorbance of the $I_3^-$–$CPC_{\text{micelles}}$ associate at 500 nm is used to determine chromium(VI).

Figure 1 shows the absorbance-time kinetic curves obtained for the Cr(VI)-$I^-$ system in CPC micelles (curve 1) and water (curve 2). As can be seen by comparing these curves, the micellar system provides a net sensitivity gain in the determination of Cr(VI). Absorbance measurements at 500 nm were carried out 6 min after the reaction was started, by which time the maximum sensitivity had been reached.

### *Study of the optimum reaction conditions*

The effect of different variables affecting the reaction between iodide and chromium(VI) in a CPC cationic micellar medium was studied in order to optimize the working conditions

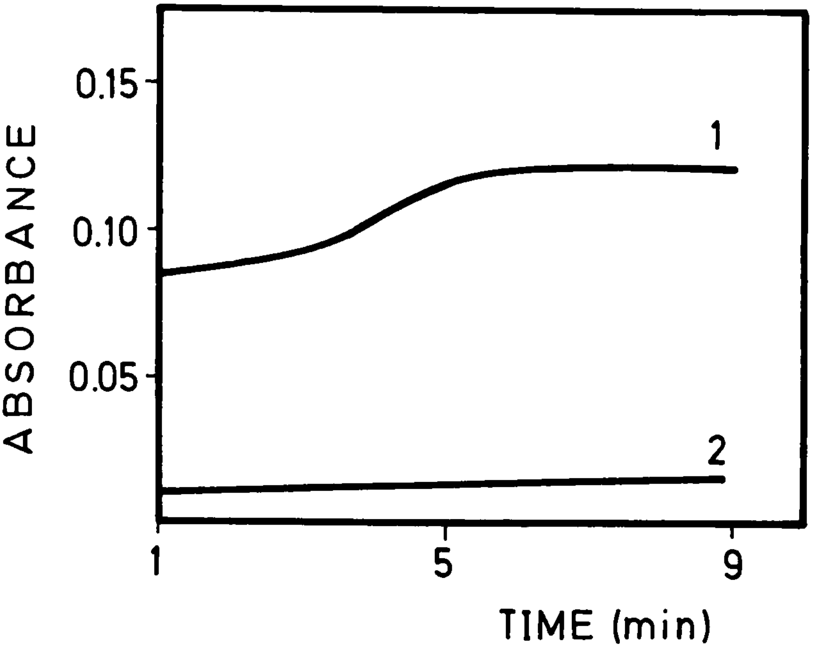

**Figure 1** Absorbance-time kinetic curves for the 2,2′-dipyridyl-accelerated chromium(VI)-iodide system in CPC ($\lambda$=500 nm) (1) and water ($\lambda$=350 nm) (2). [Cr(VI)]=75 ng ml$^{-1}$. Conditions as described under *Experimental.*

for the determination of chromium(VI). Conditions were optimized for maximum absorbance at 6 min, measured at 500 nm, and minimum variations in this parameter with the assayed concentration. Blank reactions involving no chromium(VI) were also studied.

The effect of the CPC concentration on the absorbance at 6 min, measured at 500 nm, for four chromium(VI) concentrations is shown in Figure 2. The absorbance yielded by the blanks was subtracted prior to plotting. The surfactant concentration at which maximum absorbance was obtained depended on the chromium(VI) concentration: the number of micelles required for optimum reaction development increased proportionally to the analyte concentration. Beyond the line breaks ( | | ) in the curves there is turbidity in the reaction medium covered by the low solubility of cetylpyridinium iodide salt ($P_s \approx 5.2 \times 10^{-7}$). Discontinuous lines denote that turbidity influences the absorbance measurements. Concentrations of CPC above ca. $2\times10^{-4}$ M resulted in nil absorbance at the lower chromium(VI) concentrations (curve 1) owing to the effect of dilution of triiodide over the increased concentration of micelles in the solution. A $2.8\times10^{-5}$M CPC concentration was chosen to permit the determination of chromium(VI) over the range 15–100 ng ml$^{-1}$ with maximum sensitivity.

Figure 3A shows the variation of the absorbance at 500 nm as a function of pH. This parameter did not influence the measured absorbance over the range 1.9–2.6. Higher acidity caused the triiodide-CPC associate to degrade. Above pH 4, the iodide was hardly oxidized

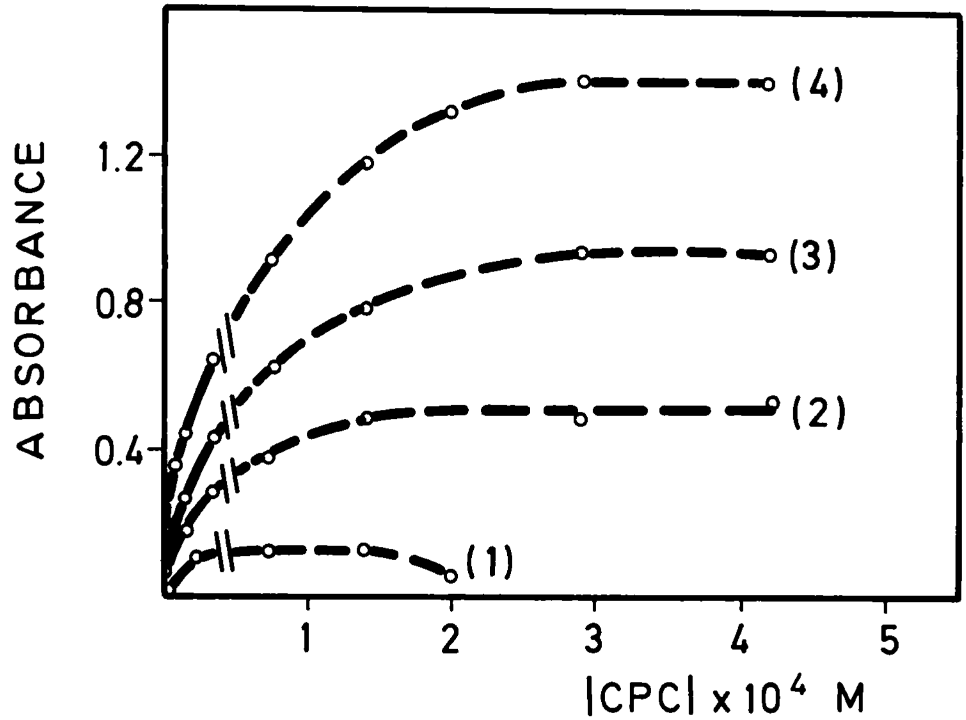

Figure 2 Influence of the CPC concentration on the 2,2′-dipyridyl-chromium(VI)-iodide system at different chromium(VI) concentrations ($\lambda$=500 nm). [Cr(VI)]: (1) 0.05 μg $ml^{-1}$; (2) 0.25 μg $ml^{-1}$; (3) 0.5 μg $ml^{-1}$ and (4) 1μg $ml^{-1}$. Line breaks ( | | ) denote the start of the precipitation of the cetylpyridinium iodide salt.

by chromium(VI). A pH value of 2.2, adjusted with hydrochloric acid, was chosen as optimal. The dependence of the absorbance at 500 nm of triiodide-CPC on the iodide concentration at a reaction time of 6 min is shown in Figure 3B. The maximum signal was obtained at ca. $1.5\times10^{-2}$ M, above which the absorbance gradually decreased due to the insolubility of the cetylpyridinium iodide salt. The effect of 2,2′-dipyridyl concentrations in the range $0–1\times10^{-3}$ M on the reaction was also studied. No significant acceleration of the reaction rate was observed up to about $2.5\times10^{-4}$ M (Figure 3C). The maximum absorbance was obtained at 2,2′-dipyridyl concentrations between ca. $3.5\times10^{-4}$ M and $8.0\times10^{-4}$ M. A $5\times10^{-4}$ M 2,2′-dipyridyl concentration was selected to ensure maximum sensitivity.

Increased temperatures had an adverse effect on the absorbance of triiodide-CPC[7] which remained virtually constant between 10 and 20 °C. On the other hand, since the iodide-chromium(VI) system has a relatively small temperature coefficient and the blank signal increased as the temperature was raised, 20°C was selected as optimal. In order to obtain maximum precision, the reactants were kept in a water bath at 20±0.1 °C when used.

The ionic strength, adjusted with sodium chloride, had only a slight influence on the absorbance of the iodide-chromium(VI)-CPC system, at least up to about 0.3 M.

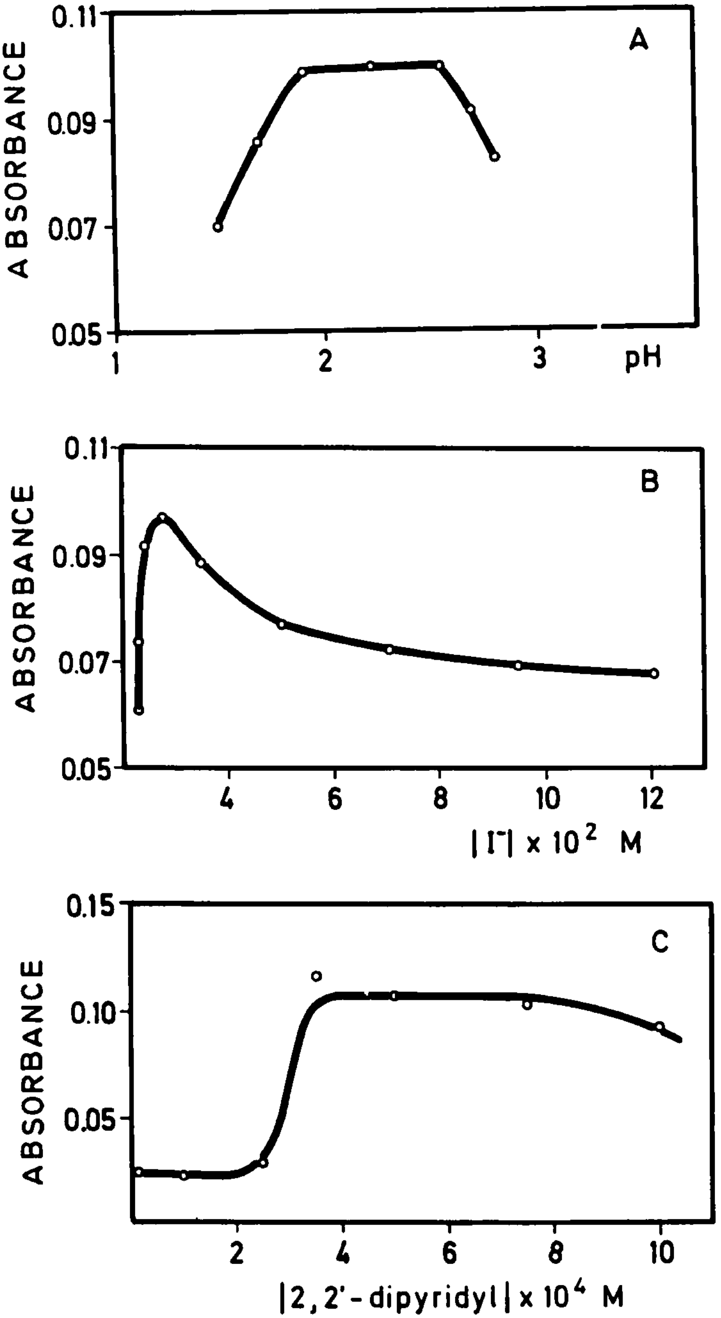

**Figure 3** Influence of (A) pH and (B) concentration of iodide and (C) concentration of 2,2′-dipyridyl on the absorbance of the 2,2′-dipyridyl-accelerated reaction between chromium(VI) and iodide (6 min, 500 nm).

### *Analytical features*

A calibration graph was constructed under the above-described optimal conditions. The determination of chromium(VI) was feasible over the range 15–100 ng $ml^{-1}$. The equation for the calibration graph was:

$$\text{absorbance (6 min, 500 nm)} = (-0.8\pm6.0)\times10^{-3} + (1.5\pm0.1)\times10^{-3}\,[\mathrm{Cr(VI)}]\ (\mathrm{ng\ ml^{-1}})$$

with a Pearson's correlation coefficient, r=0.990 (n=6) and a standard error of the estimate $9\times10^{-3}$. The detection limit ($3\sigma$) was 9 ng $ml^{-1}$. The relative standard deviation for 40 ng $ml^{-1}$ Cr(VI) was 3.1% (n=11).

Earlier comprehensive interference studies on the determination of Cr(VI) based on the Pb oxidation of iodide showed[5,6] the main interfering ions to be Hg(II), pB(II), Sb(III,V), Fe(III), Ag(I), Cu(II), Ni(II), Se(IV) and Co(II) in addition to strong oxidants and reductants. Since micelles enhance the selectivity of many spectrophotometric methods[8], the selectivity-enhancing effect of the $I_3^-$-CPC system was investigated by determining 50 ng $ml^{-1}$ of Cr(VI) in the presence of various other ions including those most likely to interfere. Table 1 summarizes the results obtained. The maximum tested ion concentration was 100 μg $ml^{-1}$, i.e. 2000 times the concentration of chromium(VI). CPC micelles provided substantially enhanced selectivity towards such ions as Pb(II), Fe(III), Cd(II), Cu(II) and Ni(II). Strong oxidants and reductants caused serious interferences. Actually, nitrite ion could be determined under the same experimental conditions as Cr(VI).

The determination of this ion was possible in the range 15–200 ng $ml^{-1}$. The equation for the calibration graph in the range 15–60 ng $ml^{-1}$ was

$$\text{absorbance (6 min, 500 nm)} = (2.1\pm3.5)\times10^{-3} + (1.41\pm0.09)\times10^{-3}\,[\mathrm{NO_2^-}]\ (\mathrm{ng\ ml^{-1}})$$

with a Pearson's correlation coefficient r=0.990 (n=6) and a standard error of the estimate of $5.2\times10^{-3}$. The detection limit was 10 ng $ml^{-1}$. The equation for the calibration graph in the range 60–200 ng $ml^{-1}$ was

$$\text{absorbance (6 min, 500 nm)} = (-1.8\pm0.3)\times10^{-2} + (1.79\pm0.02)\times10^{-3}\,[\mathrm{NO_2^-}]\ (\mathrm{ng\ ml^{-1}}),$$

with a Pearson's correlation coefficient r=0.9999 and a standard error of the estimate of $2.6\times10^{-3}$.

### *Determination of chromium (VI) in water samples*

Interferences by strong oxidants and reductants and a number of metal ions in the determination of chromium(VI) are usually overcome by extraction with inert solvents of the association complexes formed between chromium(VI) and high-molecular-weight amines in acid media[9]. One of the amines most commoly used for this purpose is trioctylamine[10]. The procedure involves extraction of chromium(VI) from 0.1–0.2 M sulphuric acid into a

**Table 1** Effect of interfering ions on the determination of 50 ng $ml^{-1}$ of Cr(VI)

| *Ion* | *Tolerated ion concentration (ng $ml^{-1}$)* | *Ion* | *Tolerated ion concentration (ng $ml^{-1}$)* |
|---|---|---|---|
| $B_4O_7^{2-}$ | 15 000 | V(V) | 500 |
| $AsO_4^{3-}$ | 3 000 | Ti(IV) | 100 |
| $SO_3^{2-}$ | 8 | Se(IV) | 800 |
| $S_2O_3^{2-}$ | 50 | Ag(I) | 20 |
| $NO_3^-$ | 50 000 | Mg(II) | 100 000 |
| $NO_2^-$ | 12 | Se(IV) | 70 |
| $Ac^-$ | 25 000 | Cr(III) | 700 |
| $HCO_3^-$ | 100 000 | Sb(III) | 5 |
| $ClO_4^-$ | 2 500 | Ca(II) | 5 000 |
| $F^-$ | 70 000 | Co(II) | 100 |
| $Br^-$ | 30 000 | Pb(II) | 500 |
| U(VI) | 10 000 | Cu(II) | 2 000 |
| Mo(VI) | 750 | Al(III) | 400 |
| Sb(V) | 8 | Hg(II) | 200 |
| Cd(II) | 200 | Fe(III) | 400 |
| Zn(II) | 400 | Mn(II) | 900 |
| Ni(II) | 5 000 | | |

chloroform solution of trioctylamine, followed by stripping of the chromium with 0.3 M sodium hydroxide.

The triiodide-CPC method was applied to the determination of chromium(VI) in various natural waters after extraction with trioctylamine. Table 2 lists the analytical recoveries obtained for 75 ng $ml^{-1}$ of chromium(VI) added to the water samples. The mean recovery was 96%. There were no significant differences in the recoveries for the different types of water. The results show that the proposed method is suitable for the determination of low concentrations of chromium(VI) in waters.

## *Acknowledgement*

The authors gratefully acknowledge financial support from the Spanish CICyT (Project No. PB91-0840)

**Table 2** Recovery of chromium(VI) from water samples

| *Sample type* | *Added (ng $ml^{-1}$)* | *Found* (ng $ml^{-1}$)* | *Recovery (%)* |
|---|---|---|---|
| Spring water | 75.0 | 74.2 | 98.9 |
| Tap water | 75.0 | 73.5 | 98.0 |
| Swamp water | 75.0 | 68.8 | 91.7 |
| Mineral water | 75.0 | 74.2 | 98.9 |
| Distilled water | 75.0 | 70.4 | 93.8 |

*Average of three determinations.

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