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Qualitative, semi-quantitative and spectrophotometric determination of ruthenium(III) by solid-phase extraction with 3-hydroxy-2-methyl-1,4-naphthoquinone-4-oxime-loaded polyurethane foam columns

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Abstract

A sensitive and selective extraction method was developed for the detection, semi-quantitative and spectrophotometric determination of ruthenium(III) in aqueous media. The method is based on the sorption of the ruthenium(III) complex of 3-hydroxy-2-methyl-1,4-naphthoquinone-4-oxime on a porous polyurethane foam membrane. In batch experiments, it was possible to detect as low as 0.1 and 0.02 ppm of ruthenium(III) with unloaded foam and foam loaded with reagent, respectively. The method was also employed for the detection of 10 ppb of ruthenium in the presence of high concentrations of diverse ions was achieved. Preconcentration of ruthenium(III) from large sample volumes was carried out on a loaded foam column at pH 5–7, eluted with acetone and determined spectrophotometrically at 450 nm. The sorbed complex species on the foam showed an absorption maximum at 460 nm with a molar absorptivity of $2.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. On this basis, a method for the direct spectrophotometric determination of ruthenium(III) based on liquid–solid extraction of the Ru(III)–reagent complex on thin-layer parallelepiped foam was developed. The proposed methods were applied for the determination of ruthenium(III) in water and in its complexes.

1. Introduction

Compared with most other elements, ruthenium has a limited influence on the biosphere [1]. The amount of ruthenium readily introduced into rivers, lake and oceans through industrial wastes, catalyst application and materi-

al sciences [2–4] is minute. Sensitive, reliable and practicable methods are required for the determination of the element at trace levels [5].

The most common reported spectrophotometric procedures include the use of thioridazine hydrochloride [6], 9,10-phenanthrenequinone monoxime [7], sulphochlorophenolazorhodamine [8], *o*-mercaptoacetanilide in the presence of picaline [9], a catalytic method with periodate oxidation [10], ion-pair formation [11] and 3-hydroxy-2-methyl-1,4-naphthoquinone 4-oxime [12]. However, most of these reagents suffer from the lack of selectivity and sensitivity and

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usually require laborious enrichment steps. Several polarographic and voltammetric methods have been developed for the determination of ruthenium [13–16], but neither their sensitivity nor selectivity is very satisfactory.

Recently, several workers have proposed open-cell polyurethane foam as an inexpensive solid extractor for many organic and inorganic species [17–19]. Direct spectrophotometric measurements of the absorbance of a thin layer of solid polyurethane foam, reported as a new trend [20,21], have markedly improved the sensitivity of determination and avoided the tedious preconcentration step that is necessary in trace analysis. This paper reports the application of polyurethane foam loaded with 3-hydroxy-2-methyl-1,4-naphthoquinone-4-oxime reagent for the detection and semi-quantitative and direct spectrophotometric determination of trace levels of ruthenium in aqueous solution.

2. Experimental

2.1. Reagents and materials

Analytical-reagent grade chemicals and doubly distilled water were used throughout. Britton–Robinson (BR) buffer solution (pH 2.5–12) containing sodium hydroxide, glacial acetic acid, orthophosphoric acid and boric acid was prepared with distilled water. A stock standard solution (1 mg ml^{-1}) of ruthenium(III) (atomic absorption standard, BDH) was used and diluted with water for standard addition whenever required. Tributyl phosphate (TBP) (pure grade) was used without further purification. Polyurethane foam (PUF), an open-cell, polyether type (bulk density 30 kg m^{-3}), was supplied by Greiner (Schaumstoff-Werk-Kremsmunster, Austria). The foam materials (cubes of 5-mm edge and a parallelepiped of $10 \times 35 \times 2 \text{ mm}$ dimensions) were washed as reported previously [22]. 3-Hydroxy-2-methyl-1,4-naphthoquinone-4-oxime (HMNQO) was prepared by the method of Sharma [12]. A $1 \cdot 10^{-3} \text{ M}$ solution of HMNQO was prepared by dissolving the required mass of HMNQO in 100 ml of ethanol.

2.2. Reagent foam preparation

About 1 g of the dried white foam cubes and parallelepiped foam were equilibrated with 10 ml of HMNQO in ethanol followed by the addition of 1 ml of TBP with efficient stirring. The foam material was then allowed to remain in contact with the solution for 1 h and dried as reported previously [22].

2.3. Apparatus

A Pye Unicam SP8-400 double-beam UV–Vis spectrometer with a quartz cell of 10-mm path length and a Philips Model 9418 pH meter were used for absorbance and pH measurements, respectively. Glass columns of length 10 and 15 cm and I.D. 20 and 5 mm were used in the dynamic experiments.

2.4. Detection and semi-quantitative determination of ruthenium(III)

Batch experiments

To 3–5 ml of the aqueous solution of ruthenium(III) at 60°C and pH 7 in a normal test-tube was added one cube of unloaded, HMNQO-loaded or HMNQO–TBP-treated foam and the mixture was shaken for 3–5 min. The change in the colour of the foam cube from white to red-violet due to the coloured Ru(III)–HMNQO complex collected on the reagent foam is evidence for the detection of ruthenium(III).

Column experiments

A foam column detection test was carried out by percolating 100 ml of the aqueous solution of ruthenium(III) at 60°C and pH 5–7 through the HMNQO–TBP-loaded foam bed in the column ($10 \text{ cm} \times 5 \text{ mm}$ I.D.) at 5 ml min^{-1} . The developed red-violet colour on the foam bed is evidence for the detection of ruthenium(III).

2.5. Direct spectrophotometric determination of ruthenium by liquid–solid extraction on thin-layer parallelepiped polyurethane foam

Standard ruthenium(III) solutions (1–10 ml) containing 1–50 μg of ruthenium(III) were

pipetted into a 100-ml erlenmeyer flask, followed by 10 ml of buffer (pH 7) and 10 ml of 0.001 M HMNQO solution and the solution was heated at 60°C for 0.5 h. The volume of each solution was made up to 50 ml with distilled water, a piece of thin-layer parallelepiped foam was added and the solution was shaken for 10 min. The parallelepiped foam was then removed from the solution by decantation, washed thoroughly by squeezing twice with water, placed in a 10-mm quartz cell containing ethanol and set in the light path of the spectrometer. The absorbance of the coloured complex sorbed into the foam was measured at 460 nm against the HMNQO–thin-layer parallelepiped foam in ethanol. The net absorbance of the Ru–HMNQO chelate in the foam, A_F^* , was calculated from the equation

$$A_F^* = A_{F(Ru)} - A_{F(B)}$$

where $A_{F(Ru)}$ and $A_{F(B)}$ are the absorbances of the ruthenium complex on foam and blank, respectively.

2.6. Determination of Ru(III) in its complexes

The ruthenium(III) complexes were prepared as described previously [4] and digested employing the oxygen flask method as reported [11]. The resultant solution was reduced with 10 ml of 5% sodium sulphite solution followed by adding 5 ml of concentrated HCl. After boiling to remove the excess of SO_2 and transfer into a 50-ml volumetric flask, the solution was diluted to volume with water and the procedure in Section 2.5 was followed. The concentration was determined by reference to a calibration graph prepared under the same experimental conditions.

3. Results and discussion

The reaction of ruthenium(III) with HMNQO represents one of the most recent sensitive and selective approaches to the spectrophotometric determination of ruthenium after solid-phase extraction into microcrystalline *p*-dichlorobenzene [12]. The coloured product is formed rapid-

ly and the equilibrium between the two phases is attained in a few seconds.

3.1. Qualitative and semi-quantitative determination of ruthenium(III)

The solution of ruthenium(III) was coloured (red-violet) by the addition of HMNQO at pH 5–7 [12]. This colour reaction was tested for the detection of ruthenium(III) with unloaded, HMNQO-loaded and HMNQO–TBP-treated foams. The surface area of the foam cube acts as an efficient collector for Ru(III)–HMNQO from aqueous solution at low concentration. The characteristic colour of the reaction product on the thin membranes of the foam material also allowed the detection of ruthenium(III) in extremely dilute aqueous solution.

On shaking one cube of the unloaded foam with 3–5 ml of hot Ru(III)–HMNQO at pH 7, it was possible to detect as little as 0.1 ppm of ruthenium(III). On shaking one cube of each HMNQO-loaded and HMNQO–TBP-treated foam with 3–5 ml of a hot aqueous solution of ruthenium, it was possible to detect as little as 0.05 and 0.02 ppm of ruthenium, respectively. The colour density on the foam cubes was found to depend on the concentration of Ru(III) in the aqueous solution. Hence it was possible to determine Ru(III) semi-quantitatively by comparison of the colour of the foam cubes with a standard colour scale (0.1–10 ppm) of ruthenium(III) employing HMNQO–TBP-treated foams under the same experimental conditions. The results obtained with HMNQO–TBP-treated foams are far better than those obtained with unloaded foams and HMNQO-loaded foams. The added TBP acts as a plasticizer of the foam material and enhances the diffusion of the species through the solid membrane and allows the collection of ruthenium(III) on the foam matrix [17,18,22].

The proposed HMNQO-loaded foam cubes can be easily packed in columns, producing a foam bed suitable for the detection and semi-quantitative determination of ruthenium in extremely dilute aqueous solutions. This was achieved by percolating 100 ml of the test ruthenium(III) solution through the foam col-

umn at a reasonable flow-rate (5 ml min^{-1}). The detection limit was found to be 10 ppb. The length of the coloured zone is proportional to the concentration of ruthenium. Semi-quantitative determination was possible using a colour scale covering concentrations from 5 to 50 ppb ruthenium(III).

Effect of diverse ions

The selectivity of the proposed HMNQO-loaded foam method was examined by detecting $1 \mu\text{g}$ of Ru(III) in the presence of a relatively high excess (10 mg) of each of Ba^{2+} , Cd^{2+} , La^{3+} , Zn(II) , Al(III) , Cr(III) , Hg(II) , Pt(IV) , Ca^{2+} , Sr^{2+} , HPO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, NO_3^- , VO_3^- , SeO_3^{2-} , SeO_4^{2-} , acetate and formate ions. No interferences were observed using the straightforward procedures; V^{4+} , Pd^{2+} , Pt^{2+} and Os^{3+} interfered seriously. In the presence of some other ions, e.g., permanganate, copper(II), nickel(II), cobalt(II) and iron(III), simple modifications to the aqueous solution were introduced to eliminate their interferences in the proposed method. The results obtained are summarized in Table 1.

3.2. Quantitative determination of ruthenium(III)

Colourless polyurethane foam showed that the absorbance of the foam matrix is consistently lower than the absorbance of the corresponding thin layer of ion-exchange resin and has no absorption peaks in the range 400–800 nm [20].

The electronic spectrum of the parallelepiped thin-layer HMNQO-loaded foams showed no bands and the absorbance was negligible in the visible region, whereas the spectrum of Ru(III)–HMNQO sorbed on a thin layer of foam showed a well defined absorption peak at 460 nm (Fig. 1). This peak was tentatively assigned to ligand (π) \rightarrow metal (d) charge transfer [23]. The electronic spectrum of the reagent HMNQO showed no absorption in the visible region (Fig. 1). Preliminary experiments showed that Ru(III) is quantitatively extracted by the HMNQO-loaded foam and a 3–5-min shaking time is sufficient to reach equilibrium for 100 ml of aqueous Ru(III) solution at pH 7 and 60°C . Lower or higher acidity gives incomplete extraction, as indicated by the decrease in the absorbance at 460 nm.

Validity of Beer's law

The absorbance of the HMNQO-loaded foam was measured against the concentration of Ru(III). A good linear relationship between the absorbance of the Ru(III) complex species in the foam and ruthenium(III) concentration was obtained under the experimental conditions used. Beer's law was obeyed up to 20 ppm of ruthenium. The molar absorptivity obtained from Beer's law and the Sandell sensitivity [23] for Ru(III)–HMNQO sorbed on the foam at 460 nm were found to be $2.8 \cdot 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.0022 \mu\text{g cm}^{-2}$, respectively. A detection limit of 0.02 ppm of ruthenium was found. Reproducibility tests with five measurements of 10 ppm of ruthenium in the thin-layer foam showed a standard deviation of $0.2 \mu\text{g cm}^{-3}$.

Table 1
Effect of foreign ions on the detection of $1 \mu\text{g}$ of ruthenium(III)

| Foreign ion | Added as | Amount added (mg) | Masking agent |
|---------------------|---------------------------|-------------------|--|
| Fe^{3+} | FeCl_3 | 0.05 | Add one crystal of KF |
| Ni^{2+} | NiCl_2 | 0.05 | Add a few drops of 1% KCN solution |
| V^{5+} | NH_4VO_3 | 0.05 | Add one crystal of NaF |
| MnO_4^- | KMnO_4 | 0.01 | Add a few drops of 1% NaN_3 solution |
| MoO_4^{2-} | Na_2MoO_4 | 0.01 | Shake the solution with diethyl ether–carbon tetrachloride (1:1, v/v) followed by addition of Ag_2SO_4 |

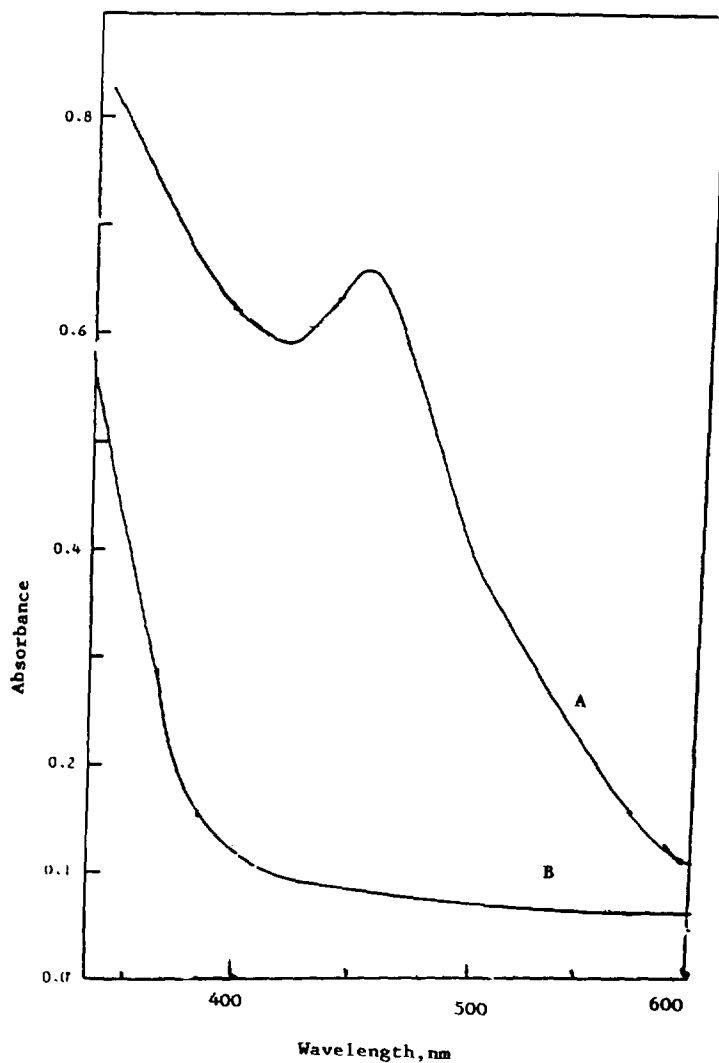


Fig. 1. Absorption spectra of ruthenium-HMNQO complex on thin-layer foam (A) against reagent blank HMNQO-loaded foam and (B) in aqueous solution at pH 7.

These results are better than those reported by Sharma [12].

The sensitivity of the method is better than or comparable to those of well known methods for ruthenium determination [12,13,24].

3.3. Analytical applications of the method

Determination of ruthenium(III) in water

The proposed extraction procedure was been applied for the determination of ruthenium in

tap and sea waters employing the procedure in Section 2.5. Negative results were obtained, indicating the absence of ruthenium. Tap water (0.5 dm^3) samples containing various amounts of Ru(III) were added to the natural water and analysed by the proposed method; a 98–99% recovery of the added Ru(III) was obtained. The applicability of the method to the determination of lower than nanomolar levels of Ru(III) in water is also possible by filtration of the sample solution through a $0.45\text{-}\mu\text{m}$ membrane followed

Table 2

Results for the foam extractive spectrophotometric determination of Ru in its complexes

| Complex ^a | Ru calculated (%) | Ru found (%) ^b | Standard deviation (%) |
|---|-------------------|---------------------------|------------------------|
| RuCl ₂ (PPh ₃) ₂ (koj) | 24.52 | 24.8 | 0.26 |
| RuCl ₂ (PPh ₃) ₂ (malt) | 24.46 | 24.60 | 0.20 |
| RuCl ₂ (PPh ₃) ₂ (trop) | 24.7 | 24.4 | 0.20 |
| RuCl ₂ (PPh ₃) ₂ (acac) | 25.32 | 24.7 | 0.20 |

^a Abbreviations: kojic acid (koj), maltol (malt), tropolone (trop) and acetylacetone (acac).^b Average of three determinations.

by extraction of the element with the HMNQO-loaded foam column (15 cm × 2 cm I.D.) at 5 ml min⁻¹. The sorbed complex is then eluted with acetone as reported [25] and analysed either by the procedure in Section 2.5 at 460 nm or by measuring the absorbance of the effluent solution of acetone containing the Ru(III)–HMNQO complex at 350 nm.

Determination of ruthenium(III) in its complexes

The microdetermination of ruthenium(III) in its complexes employing the proposed spectrophotometric procedures after digestion of the complexes was carried out. The results of these determinations are given in Table 2. The results obtained are in good agreement with the calculated values.

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