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Sorption of iron(II) and ruthenium(III)-triazine complexes on silica gel and its analytical applicability

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Abstract 2,4,6-Tri(2′-pyridyl)-s-triazine (TPTZ) complexes with iron(II) and ruthenium(III) were prepared. Their sorption and desorption features on silica gel have been investigated. Both complexes were strongly adsorbed. This has been utilized for separating and preconcentrating iron(II) and ruthenium(III) using TPTZ-impregnated silica gel. The chromatographic behavior of TPTZ on silica gel column was examined and found to be effective modifier for silica gel surface. The sorption capacity of silica gel for those metal-triazine complexes has been determined under static conditions and was found to be 5.28×10^{-3} mM ($Fe(TPTZ)_2^{2+}$) and 2.9×10^{-3} mM ($Ru(TPTZ)_2^{3+}$). Saturated methanolic solutions of KI or 25% $NaClO_4$ solutions desorbed both complexes quantitatively from the silica gel surface.

1. Introduction

Iron and ruthenium are used in the preparation of materials that are required for their electrochemical and thermoelectric properties (Seddon, 1985). Other applications include their use as process catalyst in certain chemical industry operations (Keiste, 1987). Ruthenium complexes were found to be chemotherapy agents for the treatment of cancer as they were found to be less toxic and to mimic the binding of iron to biological molecules (Clarke, 2003; Clarke, 2002). Normal and derivative spectrophotometry were applied in the analysis of iron(II) and ruthenium(III) (Toral et al., 1999). Other analytical methods included fluorimetry, potentiometry voltammetry, and atomic absorption spectrometry (Neubauer et al., 1999; Pal et al., 1999; Akl et al., 2004). TPTZ forms ferroin-like complexes with many metal ions, the cationic complex ion is deeply colored and applied for the spectrophotometric determination of many metal ions including ruthenium(III) (Embry and Ayres, 1968) and iron(II) (Collins et al., 1959).

The use of solid adsorbents in trace metal ion analysis led to a clean and reliable way for the separation of these ions from their complex matrices and their preconcentration so that ordinary analytical methods could be used without the

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need for highly sophisticated and costly ones (Appendix Chapter 1, 2000; Madrakain et al., 2008). Silica gel has long been known for its ion exchange capability (Unger, 1979). Chemical modification of its surface with many chelating agents has further widened its usefulness (Terada and Kawamura, 1980). The followings are some of the examples; silica gel modified with 1-(2-aminoethyl)-3-phenylurea was used for the selective solid-phase extraction and preconcentration of scandium(III) from environmental samples (Tu et al., 2010). Copper(II) was preconcentrated with high selectivity using amidoamidoxime silica (Ngeontae et al., 2009). Nine trace heavy metals were preconcentrated from natural aqueous systems using 5-formyl-3-(1′-carboxyphenylazo) salicylic acid-bonded silica gel and are subjected to flame atomic absorption spectroscopy (Akl et al., 2004). Sulfopropyl sephadex was used for the simultaneous determination of iron and ruthenium as their complexes with TPTZ in chloroacetic\chloroacetate buffer (pH = 3.0) and in the presence of hydroxylamine hydrochloride (Toral et al., 2002). The formation of the complexes and their retention on the cationic resin were integrated in one step at 90 °C. While stirring for 90 min, a high preconcentration level was achieved for both analytes. The retained complexes on the solid phase were evaluated by second derivative spectrophotometry.

A selective and sensitive sorption of trace amounts of cobalt in the presence of iron was described (Vydra and Talanta, 1964) based on the fact that sorption of cobalt 1,10-phenanthroline complex on silica gel is not affected by EDTA or citric acid at appropriate pH.

Sorption–desorption of cationic species on silica gel have contributed to analytical chemistry (Clark et al., 1982). Enhanced sensitivity due to preconcentration meant that colorimetric finish was possible. This could be done by exploitation of strong sorption capacity of metal complexes on silica gel in a chromatographic procedure either under static conditions or under column operation. Selectivity was achieved by competitive complexation, using anionic complexing agents such as EDTA or citric acid which give unadsorbed anion complexes on silica gel. The sorbed cationic complexes could be easily desorbed on the form of their neutral ion-association complexes with some counter ions, such as iodide, acetate or formate anions.

Although the sorption–desorption technique was mainly used for metal analysis, it should be also applicable to indirect determination of anions and certain organic species. It is noticeable that the sorption capacity of silica gel for metal complexes has not yet been fully utilized in analysis. However, the technique has found practicability for certain organic classes (Clark et al., 1982) and should be feasible for other organic species and also to anions. This practicability has been reflected by devising a new, simple, rapid and accurate procedure for saccharin determination. In this paper, the iron(II)-triazine and ruthenium(III)-triazine complexes adsorption on silica gel is investigated. The fact that silica gel will function as a weakly acid ion-exchanger and adsorb the metal complexes of cationic nature has been utilized. The sorption capacity of metal triazine complexes on silica gel was determined. The adsorbability behaviour of triazine on silica gel column has been described. The triazine-impregnated silica gel served as a collector for iron(II) or ruthenium(III) ions on the column. The products; iron(II)-triazine-impregnated silica gel and ruthenium(III)-trazine-impregnated silica gel which are intensive violet and red-purple in colour, respectively, were provided as dried matrices for future analytical purposes.

2. Experimental

2.1. Apparatus

Absorbance measurements were carried out using 1 cm silica cell and Varian 2300 spectrophotometer. A digital corning pH-meter Model 109 fitted with a combined glass and calomel electrode was used for pH-measurements at 23 °C.

2.2. Reagents

Analytical reagent grade chemicals were used through out this work.

Ruthenium(III) solution. 1.0×10^{-3} M dissolve 0.02615 g of the solid; $RuCl_3 \cdot 3H_2O$ in 1:20 hydrochloric acid, diluted to 100 ml with same solvent.

TPTZ solution. 2,4,6-Tri(2′-pyridyl)-1,3,5-triazine; 1.0×10^{-3} M dissolve 0.1562 g of TPTZ in 50% ethanol, add drops of concentrated hydrochloric acid, dilute to 500 ml with same solvent.

Ammonium iron(II) sulphate. 1.7907×10^{-3} M dissolve 0.7022 g of the hexahydrate salt in 300 ml of water containing 2 ml of concentrated sulphuric acid, dilute to 1 l.

Iron(II)-triazine complex solution. $Fe(TPTZ)_2{}^{2+}$, 1.7907×10^{-3} M a stable intense colour is formed when TPTZ solution is added to Fe(II) ions solution with 1:2 metal/ligand ratio.

Ruthenium(III)-trazine complex solution. $Ru(TPTZ)_2{}^{2+}$, 1.0×10^{-3} M. Mix 40 ml of Ru(III) solution (1.0×10^{-3} M) with 80 ml of TPTZ solution (1.0×10^{-3} M), the ethanol content is adjusted to 25% by volume. The solution was heated in a water bath at 87 °C for 1 h.

Silica gel. Chromatographic grade silica gel, 60–120 mesh, was used in this work after being washed by sodium hydroxide followed by distilled water.

2.3. Analytical procedures

2.3.1. Conditioning of silica gel

Weigh out 315 g of silica gel into a beaker, wash several times with 450 ml of 0.1 M NaOH, follow with successive amounts of distilled water to a total volume of about 450 ml. Remove any fine particles of silica gel or any turbidity by decantation. The resulting pH should be about 5.5. Activation of the silica gel surface is achieved by heating in an oven at 120 °C for 12 h.

2.3.2. Determination of sorption capacity of iron(II)-triazine and ruthenium(III)-triazine complexes on silica gel

The sorption capacity is defined as the maximum amount of metal complex adsorbed for each gram of silica gel. The batch technique was used in these determinations.

One gram-quantity of washed and conditioned silica gel was placed in 25 ml bottles. Varying amounts of $Fe(TPTZ)_2{}^{2+}$ (1.7907×10^{-3} M ranging from 0.2 to 10 ml), or $Ru(TPTZ)_2{}^{3+}$ complex (1.0×10^{-3} M ranging from 0.2 to 10 ml) complex were added. The volume of solution in each bottle was made up to 10 ml with distilled water and the contents were shaken for 20 min using an electric shaker. The supernatant liquid was filtered through a No. 41 Whatman filter paper and the absorbances of $Fe(TPTZ)_2^{2+}$ or $Ru(TPTZ)_2^{3+}$ remaining in the solution (unadsorbed) were measured at 592 nm and 510 nm, respectively, using 1 cm silica cells.

3. Results and discussion

3.1. Sorption capacity of $Fe(TPTZ)_2^{2+}$ and $Ru(TPTZ)_2^{3+}$ on silica gel

Fig. 1 represents the sorption capacity curve showing the resulting absorbance of the unadsorbed $Fe(TPTZ)_2^{2+}$ in solution plotted as a function of the total amount of the complex originally added to silica gel. For this graph, the amount of $Fe(TPTZ)_2^{2+}$ sorbed per 1 g of silica gel was determined by extrapolation to zero absorbance. It was found that 5.28×10^{-3} mM of $Fe(TPTZ)_2^{2+}$ is adsorbed per 1 g of silica gel.

It must be indicated here that the value of sorption capacity is taken as a guide for the amount added to the gel to provide a matrix capable of giving reproducible results in quantitative desorption step (future work). It is also useful value for estimating the amount of metal, concentrated on silica gel column.

Fig. 2 shows the sorption capacity graph demonstrating the resulting absorbance of $Ru(TPTZ)_2^{3+}$ remained in solution plotted against the total amount of ruthenium-triazine complex which was added to the silica gel. The sorption capacity of $Ru(TPTZ)_2^{3+}$ was found to be 2.9×10^{-3} mM of the ruthenium complex per gram of silica gel.

The sorption process of $Fe(TPTZ)_2^{2+}$ and $Ru(TPTZ)_2^{3+}$ complexes on silica gel can be written schematically as follows:

$$2(-SiOH) + Fe(TPTZ)_2^{2+} \leftrightharpoons [Fe(TPTZ)_2][SiO]_2 + 2H^+$$
$$3(-SiOH) + Ru(TPTZ)_2^{3+} \leftrightharpoons [Ru(TPTZ)_2][SiO]_3 + 3H^+$$

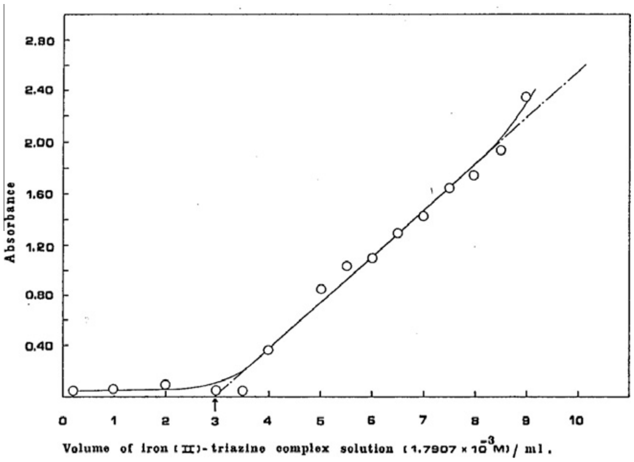

Figure 1 Determination of sorption capacity of iron(II)-triazine on silica gel. 1 g amount of conditioned silica gel; 0.2–10 ml of 1.7907×10^{-3} M $Fe(TPTZ)_2^{2+}$ solution were added and the volume was made up to 10 ml with distilled water. Shaking time, 20 min. Unadsorbed $Fe(TPTZ)_2^{2+}$ was measured at 592 nm using 1 cm cell.

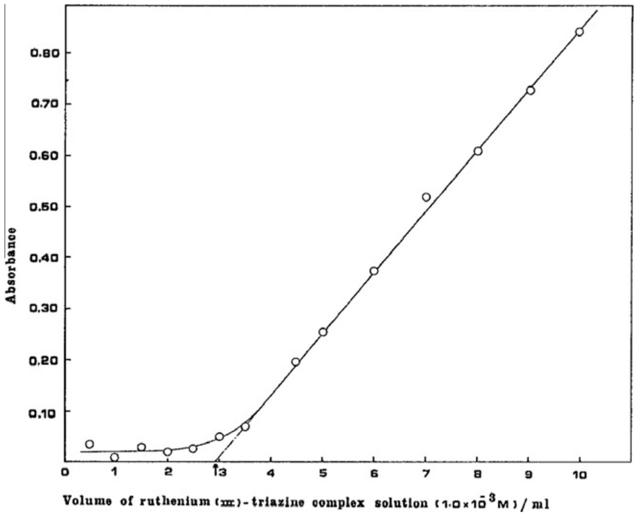

Figure 2 Determination of sorption capacity of ruthenium(III)-triazine on silica gel. 1 g amount of conditioned silica gel; 0.2–10 ml of 1.0×10^{-3} M $Ru(TPTZ)_2^{3+}$ solution were added and the volume was made up to 10 ml with distilled water. Shaking time, 20 min. Unadsorbed $Ru(TPTZ)_2^{3+}$ was measured at 510 nm using 1 cm cell.

3.2. Adsorbability of TPTZ on silica gel column

In a preliminary work, the chromatographic adsorption behaviour of the organic reagent on silica gel was examined using a mobile measurement. A small glass column of 20 cm in length and 1 cm in diameter, containing 2 g of preconditioned silica gel was used for this purpose. The flow rate was regulated at ml/min. The triazine solution (1.0×10^{-4} M in 2.5% ethanol) was passed through the column and the concentration of triazine in the effluent was followed the spectrophotometrically (Embry and Ayres, 1968). Three milliliters of the effluent was collected and scanned (210–340 nm). Its absorbance at

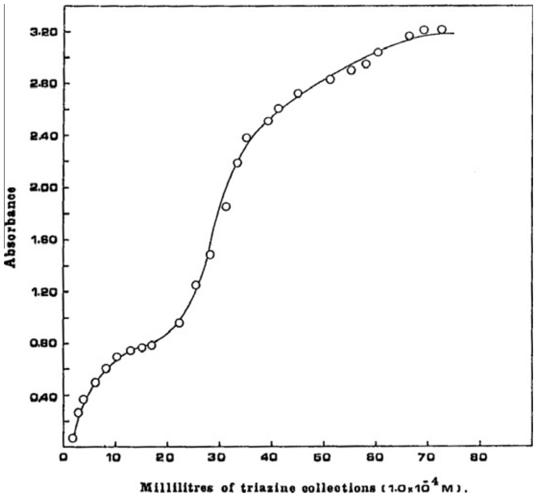

Figure 3 Adsorbability of triazine on silica gel in a small column; TPTZ solution (1.0×10^{-4} M in 2.5% ethanol) was passed through at flow rate of 1 ml/min. Absorbance at 285 nm for each 3 ml of the effluent was measured.

285 nm has been measured. Fig. 3 shows the absorbance readings change in 3 ml increments up to 80 ml.

As can be seen, Fig. 3 resembles a spectrophotometric titration curve. It has been known that the solutes are adsorbed on silica gel via hydrogen bonding with surface hydroxyls usually serving as hydrogen donors (Unger, 1979). Amines and other bases are preferentially retained owing to the mild acidity of the silica surface (Aboul-ghait and Al-Hajjaji, 1987). The triazine is a weak base due to the presence of the pyridyl nitrogen.

The strong adsorption of iron(II) or ruthenium(III) on silica gel may be possible by the impregnation of silica gel with TPTZ which introduce an adsorbent with high selectivity based on the formation of $Fe(TPTZ)_2^{2+}$ or $Ru(TPTZ)_2^{3+}$. These complexes are strongly adsorbed on silica gel according to specific conditions. It is recommended to pass 3.5×10^{-3} mmol of TPTZ through a column per each gram of conditioned silica gel at a flow rate of 1 ml/min. This is prior to concentrating iron(II) and ruthenium(III) on the column.

The desorption of triazine-metal complex is performable using methanolic saturated potassium iodide or perchlorate ion (25% $NaClO_4$). The desorption process is based on the formation of ion-association complex, $\{Fe\ (TPTZ)_2^{2+}, 2ClO_4^-\}$ or $\{Ru(TPTZ)_2^{3+}, 3ClO_4^-\}$ when using ClO_4^- and $\{Fe(TPTZ)_2^{2+}, 2I^-\}$ or $\{Ru(TPTZ)_2^{3+}, 3I^-\}$ when using iodide ion.

3.3. The analytical usability of modified-surface silica matrix

The results obtained from the present work led to the development of a new chemically modified-surface silica matrix. The matrices are; $[Fe(TPTZ)_2][SiO]_2$ and $[Ru(TPTZ)_2][SiO]_3$. The two gel systems have been prepared and conditioned in dried form under specific technique. The recommended method for this preparation was described elsewhere (Vydra and Talanta, 1964). These matrices may serve as a greener alternative to the extraction procedures that apply toxic solvents such as nitrobenzene. Although this solvent have numerous attributes such as high distribution coefficient for such system and a high dielectric constant which is suitable for extracting ion pair complexes (Aboul-ghait and Al-Hajjaji, 1987).

4. Conclusion

Several desirable aspects are offered by the approach of 'sorption–desorption' of metal complexes on silica gel that makes it a practically suited technique for trace metal analysis. The technique may be also adaptable for indirect determinations of anions and certain organic species. It is noticed that the sorption capacity of silica gel for metal complexes has not yet been fully utilized in analysis.

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