Simultaneous determination of iron and ruthenium by preconcentration on sulfopropyl sephadex cation exchanger

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Abstract

A new method for the simultaneous determination of iron and ruthenium at ultra-trace levels is proposed. The method is based on the formation of the iron and ruthenium complexes with 2,4,6-tri-(2-pyridil)-1,3,5-triazine (TPTZ) in the presence of hydroxylamine hydrochloride and buffer $CH_2ClCOOH/CH_2ClCOONa$ (pH = 3.0). The formation of the complexes and their retention on a cationic resin SP-Sephadex C25 were integrated in one step at 90 °C, with stirring for 90 min. Under these conditions a high preconcentration level was achieved for both analytes. The complexes retained on the solid phase were evaluated by second derivative spectrophotometry. The selected analytical wavelengths were 539.7 and 553.3 nm for the determination of ruthenium and iron, respectively, by using the zero crossing approach. The detection and quantification limits were 0.54 ng ml^{-1} and 1.79 ng ml^{-1} for ruthenium and 0.41 ng ml^{-1} and 1.38 ng ml^{-1} for iron. The proposed method was applied to the determination of both analytes in synthetic mixtures.

Keywords: Iron and ruthenium determination; Preconcentration in solid phase

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1. Introduction

Different studies have been carried out regarding the preparation of materials containing Fe–Ru. Due to their electrochemical and thermoelectric properties [1–6], such types of materials have shown potential catalytic, analytical and technological applications. For example, Fe–Ru catalysts have been used for NH_3 synthesis [1], pyridine hydrodenitrogenation [2], water gas shift reaction [3], and *n*-butanol conversion [4]. The use of these kinds of catalysts in industrial processes could cause iron and ruthenium contamination in aquatic systems which necessitates the development of analytical methods for the simultaneous determination of these metals in waters at ultra-trace levels.

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A survey of the literature indicates that few methods for the simultaneous determination of iron and ruthenium have been developed. These methods are based on radiochemical neutron activation analysis [7] and X-ray fluorescence (XRF) [8]. Ruthenium has also been determined together with other platinum-group elements by using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) which is rapid and very sensitive [9]. Obviously, all these methods require the use of sophisticated and very expensive instrumentation.

In the field of spectrophotometry, different methods for ruthenium determination have been reported, however, they present low sensitivity, making them unsuitable for the determination ruthenium at trace levels [10–13]. The introduction of a preconcentration step in these kinds of methods, such as liquid–liquid extraction [14–16] or solid phase extraction [17–19], increases the sensitivity. Furthermore, the selectivity of the multielement methods and resolution of the spectra can be increased considerably by means of derivative spectrophotometry.

In the present work, the optimization of different parameters in the implementation of a new method for the simultaneous determination of iron and ruthenium at ultra-trace levels is demonstrated. The method is based on the formation of the iron and ruthenium complexes with 2,4,6-tri-(2-pyridil)-1,3,5-triazine (TPTZ), their retention on a cationic resin SP-Sephadex C25 and determination by solid phase derivative spectrophotometry.

2. Experimental

2.1. Apparatus

A Shimadzu UV–1603 spectrophotometer with 1-mm cells was used for measurements of the absorbance and derivative absorption spectra. The spectral data were processed by the software Shimadzu kit version 3.7. An Orion Research Digital Ion–Analyzer 701 with glass and saturated calomel electrodes was used for pH determinations. A magnetic stirrer BIBBY HB502, with speed and heating control was used for the preconcentration of the complexes.

2.2. Reagents

All reagents were of analytical grade and the solutions were prepared with high purity water from a Millipore Milli-Q Water Purification System device. A Sigma ruthenium atomic absorption standard solution (concentration 1005 μg ml^{-1} Ru in 5% HCl) and a Titrisol Merck standard solution of Fe (1000 μg ml^{-1}) were used as standards. Other concentration ranges were prepared by appropriate dilution. A solution of 0.025 M TPTZ was prepared by dissolving 3.9043 g of the salt (Aldrich), 1 ml of 12 mol/l HCl was added and diluted in 500 ml of water. Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) solution was prepared by dissolving 100 g of the salt in 1000 ml of water. Sodium chloroacetate–chloroacetic acid buffer (pH 3.0) was prepared by dissolving 15.7248 g of sodium chloroacetate (Merck) and 9.4509 g of chloroacetic acid (Merck) in 1000 ml of water. Solutions of foreign ions for the interference studies were prepared by dissolving the calculated amount of each compound to give solutions of 10 μg ml^{-1} of each species. All these solutions were stored in polyethylene containers.

For validation, high purity standards were used: (a) the Quality-Control Standard 19 (QCS-19), contained 100 μg ml^{-1} of each of the following elements: Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Tl, Ti, V and Zn in a 5% solution of HNO_3 containing trace amounts of HF; (b) ICP Working Calibration Standard 3 (ICP-WS-3), had the following composition (μg·ml^{-1} ±0.5%): Au, 10; Ir, 10; Os, 10; Pd, 10; Pt, 50; Rh, 10; Ru, 10; Te, 50 into a matrix of HCl 5%; and (c) River Certified Sediment (CRM-RS-A), had the following content in μg·ml^{-1} ±0.5% in 5% HNO_3: Fe, 1200.0; Al, 250.0; K, 150.0; Cu, 10.0; Ni, 0.50; V, 0.25; Ca, 300.0; Na, 50.0; Co, 0.10; Tl, 0.01; As, 0.60; Se, 0.50; Cr, 300.0; Pb, 7.0; Th, 0.02; Sr, 0.02; Ba, 0.50; Mg, 70.0; Cd, 0.10; Mn, 80.0; U, 0.01; Zn, 15.0.

A sulfopropyl Sephadex cation exchanger (SP-Sephadex C25) with a capacity of 2.0–2.6 mEq g^{-1} was used as the resin.

Table 1
Study of preconcentration variables and selection of working values[a]

Variable	Range studied	Optimum range		Working value
		Fe	Ru	
Mass of resin (mg)	60–300	60	60	60
Stirring at 90 °C (min)	30–105	30–105	75–105	90
Temperature at 90 min (°C)	20–95	90	90	90

[a] Fe(II)-TPTZ; Fe, 40 ng ml^{-1} ; Ru(III)-TPTZ; Ru, 40 ng ml^{-1}.

2.3. Procedure

An aliquot of iron and/or ruthenium standard solution that contained less than 40 μg and 60 μg, respectively, was added to 100 ml of de-ionized water in a glass beaker. Then 2 ml of 10% (w/v) hydroxylamine hydrochloride solution, 10 ml of buffer $CH_2ClCOOH/CH_2ClCOONa$ (pH = 3.0) and 15 ml of 0.025 M TPTZ solution were added and the total volume was adjusted to 200 ml. After, the solution was stirred for 2 min, 60 mg of SP-Sephadex C25 resin was added. Finally, the mixture in the beaker was heated at 90 °C with stirring for 90 min. After cooling, the solution was discarded and the solid phase was washed twice with high purity water. The resin was packed using a pipette into 1-mm spectrophotometric cell. The zero-order spectra of the solid phase was recorded over the range 700–400 nm against a reagent blank resin prepared under the same experimental conditions. Digital derivative spectra were obtained with a smoothing factor of 16 and a scale factor of 10^4.

3. Results and discussion

Iron in the presence of hydroxylamine hydrochloride, TPTZ and buffer pH = 3.0, rapidly forms a binary complex, $Fe(TPTZ)_2^{2+}$. Under the same conditions, ruthenium also forms the complex $Ru(TPTZ)_2^{3+}$, which shows a kinetic dependence on its formation, therefore it was required to use heating in order to improve the complex formation.

Taking into account that both complexes are positively charged, they can be preconcentrated on a cation exchanger resin prior to their evaluation by derivative spectrophotometry.

3.1. Study of the preconcentration variables

All the variables were optimized separately by the univariate method. Table 1 shows the range studied, the optimum ranges and the working values selected for the preconcentration variables. The selection of the working values was based on sensitivity and resolution of the derivative signals.

3.2. Spectral features

The zero-order spectrum of the Fe(II)–TPTZ retained on SP-Sephadex C25 vs. a reagent blank resin, exhibits one band centered at 625 nm, corresponding to the absorption of the complex (Fig. 1a). Under similar conditions Ru(III) shows one band centered at 532 nm, which has been attributed to the absorption of the Ru(III)–TPTZ complex (Fig. 1b).

Because of the solid phase preconcentration, the sensitivity of the proposed method increases 50 times for iron and 41 times for ruthenium when compared with their measurement in the aqueous phase without preconcentration.

3.3. Spectral parameters selection

The spectral signals were evaluated directly in the solid phase. In order to minimize both the dispersion phenomena and the background noise, the digital derivative spectrophotometry with smoothing was adopted. Traditionally, the differentiation mode of the classic spectra is considered to modulate the $\Delta\lambda$ value; a low value of this variable giving a high resolution of the spectra, but usually the background noise increases also. Savitzky and Golay [20] have proposed a least squares procedure in digital derivative spectropho-

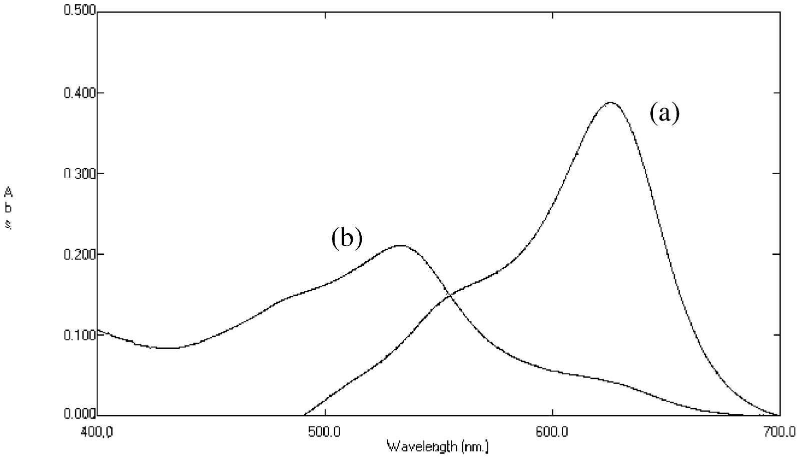

Fig. 1. Absorption spectra of Fe(II)-TPTZ and Ru(III)-TPTZ complexes retained on SP-Sephadex C25 resin measured against reagent blank resin. (a) Fe(II)-TPTZ; Fe, 40 ng ml^{-1}; (b) Ru(III)-TPTZ; Ru, 40 ng ml^{-1}.

tometry in order to smooth and differentiate the spectra numerical data. In this procedure, $\Delta\lambda$ is constant and the noise is minimized. In this work, the latter option was used.

3.4. Derivative order selection

Starting from the zero-order spectra the first to the fourth derivative spectra were for Fe(II)–TPTZ and Ru(III)–TPTZ complexes retained on the resin.

According to Fig. 2a,b, the second derivative is more useful for the simultaneous determination of both analytes. The third and fourth derivative spectra were discarded because the signal/noise ratio is clearly unfavorable.

3.5. Smoothing and scale factors selection

Using the second derivative spectra, the smoothing factor was varied between 2 and 16. These values have a direct relation with the wavelength range scanning; the best signal/noise ratio was obtained when a smoothing factor of 16 was selected.

Using the second derivative spectra and a smoothing factor of 16, the scale factor was varied from 10 to 10^4. The maximum value of 10^4 was

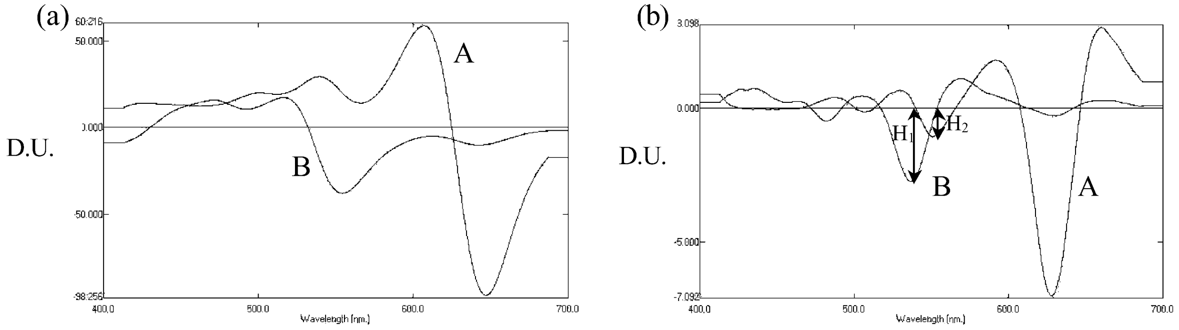

Fig. 2. Different order derivative spectra for Fe(II)-TPTZ and Ru(III)-TPTZ. (A) Fe, 40 ng ml^{-1} and (B) Ru, 40 ng ml^{-1}. (a) First derivative, (b) second derivative. All conditions as in the text.

selected, in order to minimize the distortion of the spectra.

3.6. Analytical wavelengths selection

The derivative units at H_1 (539.8 nm) (Fig. 2b) permits an effective determination of the ruthenium concentration, because at this point the iron signal is zero. Similarly, at 553.6 nm where the ruthenium signal is zero, the length of the distance H_2 is useful for the determination of iron (Fig. 2b).

3.7. Optimization of the chemical variables

3.7.1. Effect of TPTZ concentration

An unusual dependence of TPTZ concentration on the formation and retention of Ru(III)–TPTZ complex was found. It is known that reaction between TPTZ and ruthenium gives rise to different cationic complexes as products depending on the concentration of the TPTZ. When a Ru(III)/TPTZ molar ratio of 1.98×10^{-3} is used, the $Ru(TPTZ)^{3+}$ complex is formed giving rise a low sensitive signal. When the Ru(III)/TPTZ molar ratio is 9.89×10^{-4}, a change in the shape and intensity of the spectra was observed, suggesting that at this concentration of TPTZ the complexes $Ru(TPTZ)^{3+}$ and $Ru(TPTZ)_2^{3+}$ are obtained simultaneously.

Between a range of 6.60×10^{-4} and 3.30×10^{-4} of the Ru(III)/TPTZ molar ratio, a well-defined band is obtained. This band can be attributed to $Ru(TPTZ)_2^{3+}$ complex. The intensity of this band increased with the TPTZ concentration between this range, which indicates that the quantitative formation of the complex has not been reached.

When the Ru(III)/TPTZ molar ratio is lower than 2.83×10^{-4}, the intensity of the band is constant. Under these conditions the band is attributed to the exclusive formation of the complex $Ru(TPTZ)_2^{3+}$, which is quantitative.

The study of the effect of the TPTZ concentration on the formation and retention of the complex Fe(II)–TPTZ, using a Fe(II)/TPTZ molar ratio between 0.43 and 2.69×10^{-4} was carried out. These conditions gave a well-defined band for this complex, whose shape is independent of TPTZ concentration although its intensity increases with the TPTZ concentration. Starting from a Fe(II)/TPTZ molar ratio of 3.6×10^{-4}, a maximum and constant absorbance is obtained. In this condition the formation and retention of this complex is quantitative.

According to these results, in order to assure a quantitative formation and retention of both complexes, 15 ml of 0.025 M TPTZ were used for all subsequent determinations.

3.7.2. Effect of the pH

The effect of pH was seen from 2.0 to 5.0. At pH values lower than 2.5, the complexes are not formed. The optimum range for the formation and retention of both complexes was between 2.5 and 3.6. At pH values higher than 4.0 the TPTZ precipitates. A value of pH = 3.0 was selected which was achieved with a buffer of chloroacetic acid (0.1 M)/sodium chloroacetate (0.13 M).

3.8. Features of the method

In the selected conditions, calibration graphs were obtained by plotting the second derivative value H_1 for ruthenium and H_2 for iron vs. the concentration of the respective analytes. The linear regression equations and the correlation coefficients calculated for mixtures of both analytes were:

$$H_1 = 0.0413\ C\ (\mathrm{ng\ ml^{-1}}) + 0.0116 \quad r = 0.9981$$

$$H_2 = 0.0213\ C\ (\mathrm{ng\ ml^{-1}}) + 0.3340 \quad r = 0.9979$$

The determination ranges were 1.58–200 ng ml^{-1} for iron and 1.12–300 ng ml^{-1} for ruthenium. The detection limits (3σ criterion) were 0.47 ng ml^{-1} for iron and 0.33 ng ml^{-1} for ruthenium. The relative standard deviations for 10 standard samples containing 25 ng ml^{-1} of each element were 2.3% and 1.3% for iron and ruthenium, respectively.

3.9. Effect of foreign ions

The effect of various foreign ions on the simultaneous determination of iron and ruthenium was studied by adding known quantities of a selected

Table 2
Effect of foreign ions on solutions containing 40 ng ml^{-1} of each analyte

Foreign species Cations[a]	Tolerance limit ($\mu g\ ml^{-1}$)		Foreign species Anions[b]	Tolerance limit ($\mu g\ ml^{-1}$)	
	Ruthenium	Iron		Ruthenium	Iron
K(I)	10	5	Nitrate	300	300
Na(I)	10	10	Nitrite	0.5	0.5
Ca(II)	10	10	Sulfate	200	100
Mg(II)	5	1	Thiosulfate	10	10
Sr(II)	10	10	Phosphate	10	20
Ba(II)	4	2	Oxalate	40	40
Al(III)	0.7	0.7	Tartrate	20	10
Ir(II)	0.5	0.5	Citrate	40	50
Pd(IV)	0.6	0.6	Thiocyanate	20	20
Pt(IV)	0.6	0.6	Fluoride	50	50
Cd(II)	1	1	Chloride	300	300
Zn(II)	1	1	Bromide	300	300
Cr(III)	0.6	0.6	Iodide	60	60
Ni(II)	0.4	0.4	EDTA	It interferes in the whole range	
Hg(II)	5	5			
Cu(II)	0.4	1			
Pb(II)	1	0.6			
Co(II)	0.5	0.5			
Mn(II)	0.9	1			
Au(III)	0.1	0.8			

[a] Maximum tested 10 $\mu g\ ml^{-1}$.
[b] Maximum tested 300 $\mu g\ ml^{-1}$.

foreign ion to solutions of 40 ng ml^{-1} of each element. The tolerance limit was taken as being the amount causing an error not exceeding ±4% in the analytical signal of these analytes. The tolerance values obtained are shown in Table 2. The interference could be attributed to that cations use the coordination centers of the resin. However, in the study of the foreign anions, sodium salts were used. In this case, the maximum concentration tested was 300 $\mu g\ ml^{-1}$ of Na^+ which exceeds the retention capacity of the resin used (13.8–17.9 $\mu g\ ml^{-1}$ Na^+). In this context, it is possible to establish that the interaction between the resin and the cationic complexes is not only electrostatic but also an interaction at organic level prevails. In the study of foreign anions, it was found that the most common anions are tolerated even when they are present in large amounts. The system did not tolerate EDTA in all the range studied. However, the organic compounds as well as nitrite can be eliminated by previous acid digestion of the sample. It is important to indicate that during the study of foreign ions, the spectral bands were not altered.

3.10. Accuracy of the proposed method

The proposed method was applied to the determination of both analytes in synthetic mixtures. In this context, the recoveries of samples containing standard solutions of ruthenium and iron in different ratios were carried out. It can be seen in the Table 3, good recoveries were obtained.

3.11. Validation and application of the proposed method

Certified samples containing simultaneously trace amounts of iron and ruthenium in presence of other ionic metals were not available for the validation of the method. Therefore, validation samples mixing high purity standards (a) and (b) were prepared in order to assess this method in a complicate matrix containing a considerable number of elements, between the elements of the platinum group (Table 4). As can be seen in Table 4, in all cases good recoveries were obtained in spite of the simultaneous presence of foreign ions as Cr, Co, Cu, Ni, Ir, Pd and Pt which could increase the signal of both analytes.

The method was also validated in Certified River Sediment (c) in order to study the possibility of applying this method to real samples. In this

Table 3
Simultaneous determination of iron and ruthenium in synthetic mixtures

Concentration added (ng ml^{-1})		Concentration found, (ng ml^{-1}); recovery (%)	
Iron	Ruthenium	Iron	Ruthenium
50	50	51.7 (103.4)	49.8 (99.5)
40	80	38.9 (97.2)	78.1 (97.6)
40	120	39.1 (97.7)	118.8 (99.0)
40	160	39.1 (97.6)	164.2 (102.6)
40	200	39.0 (97.4)	205.8 (102.9)
80	40	77.5 (96.9)	38.7 (96.8)
120	40	119.4 (99.5)	38.9 (97.1)

Table 4
Simultaneous determination of iron and ruthenium in synthetic mixtures made with high purity standards

Fe	Ru	Synthetic mixtures (ng ml^{-1})			Recovery (%)	
		Sb, As, Be, Cd, Ca, Cr, Co, Cu, Pb, Mg, Mn, Mo, Ni, Se, Tl, Ti, V, Zn	Au, Ir, Os, Pd, Rh	Pt, Te	Ru(III)	Fe(II)
40	40	40	–	–	98.6	98.9
80	40	40	–	–	99.0	96.5
80	80	40	–	–	99.8	100.2
40	80	40	–	–	101.1	100.9
40	40	–	40	200	99.6	98.6
80	40	–	40	200	101.4	97.4
80	80	–	40	200	100.9	103.2
40	80	–	40	200	102.2	100.4
40	40	40	40	200	101.9	101.5
40	80	40	80	400	104.2	103.2
80	40	80	40	200	102.7	101.6

context, 0.83 ml of the certified sample was diluted in 1000 ml of water. An aliquot of 8 ml of this solution was added to 200 ml of de-ionized water (iron concentration = 40 ng·ml^{-1}). A sample of 800 μl of ruthenium of 1000 mg l^{-1} was added to the solution in order to spike the ruthenium content (ruthenium = 40 ng·ml^{-1}). The recovery for iron and ruthenium were 101.4 and 99.5%, respectively. In all cases the relative standard deviation was $<3.0\%$.

Real industrial liquid waste samples of catalysts from industrial processes were not available in our country for the application of this method. However, taking into account the results of the validation of the proposed method, it is possible to establish that the method can be used for the simultaneous determination of iron and ruthenium in this type of matrix and other environment samples. In cases in which the sample has a high iron content, the sample must be enriched with ruthenium prior to the application of the proposed method.

4. Conclusions

A systematic optimization of the different variables allowed the development of a new method for the simultaneous determination of iron and ruthenium at ultra-trace levels. This method is easy to implement in any control laboratory because it uses inexpensive instrumentation and yields accurate and reproducible results. Furthermore, the analysis of 10–20 samples can be made in 2 h.

In the optimal conditions, the sensitivity of the method increases 50 times for iron and 41 times for ruthenium when compared with the counterpart method in aqueous phase.

The proposed method was applied for the determination of both analytes on synthetic mixtures; in spite of the fact they simultaneously contained a great number of foreign ions, which could interfere in the analytical determination, optimum recoveries were obtained. This method can be used for the simultaneous determination of iron and ruthenium in real industrial liquid waste samples, because no matrix effect was noted despite the fact that the method was validated with different and varied components.

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