ISSN 1061-9348, Journal of Analytical Chemistry, 2022, Vol. 77, No. 9, pp. 1119–1130. © Pleiades Publishing, Ltd., 2022.

ARTICLES

A Green Chemosensing Approach for Direct and Liquid-liquid Extractive Spectrophotometric Determination of Platinum

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Received June 27, 2021; revised January 31, 2022; accepted February 1, 2022

Abstract—In this study, a highly selective colorimetric chemosensing behavior of 4-(2'-furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole (FIMMT) was used for the determination of platinum ions. The developed method is simple, cheap, and rapid. It obeys the principle of green chemistry since *n*-butanol used as an extraction solvent for platinum determination in aqueous solutions was further recycled and did not release toxic wastes. Platinum forms a red-colored soluble complex with FIMMT at pH 5.4 on heating. Platinum(II)—FIMMT complex was instantly extracted into *n*-butanol. The complex absorbance in aqueous and *n*-butanol solutions was found at $\lambda_{\max}$ of 510 nm. The complex was stable for more than 24 h in the presence of other ions with the extinction coefficient of 11686 L/mol · cm and Sandell's sensitivity of 0.017 μg/cm^2. The effect of pH, excess of reagent, and foreign ions on the determination of platinum as well as the influence of heating time, stability, and solubility of the complex in various solvents were studied. The system obeyed Beer's law up to 17.5 μg/mL, and the optimum range was evaluated by Ringbom method. The developed method showed excellent linearity and a correlation coefficient of 0.999. The method is precise, and it was applied for platinum determination in synthetic matrices, real samples such as *cis*-platin injection and platinum—rhodium thermocouple wire. The chromogenic reagent FIMMT selectively reacts with nickel, palladium, and platinum, which helps to separate them quantitatively.

Keywords: platinum(IV), chemosensor, group separation, green determination, liquid—liquid extraction, spectrophotometry

DOI: 10.1134/S106193482209012X

Platinum is a precious metal that occurs along with other platinum group metals and base metals in the Earth's crust in trace amounts ranging from ppb to ppm levels [1]. It is a metal of electronic, industrial, and environmental interest. This metal is a good catalyst and is widely used for hydrogenation reactions. Owing to its corrosion resistant nature and alloying ability, platinum and its alloy are used in dental and medicinal devices as well as in manufacture of jewelry. Platinum plays an important role in the pharmaceutical industry, e.g., Oncoplatin AQ, a commonly used cytotoxic anticancer drug, contains *cis*-platin [2]. The development of selective extractants for the separation and concentration of precious metals at trace levels reflects an increasing need for these metals to be recovered and determined. Chelating extractants have been found to be more selective than solvating reagents and anion exchangers, and, in accordance with Pearson's theory [3], better performance is obtained with sulfur containing compounds in the case of platinum(IV). Therefore, a sensitive and selective method for its determination is required to detect the metal in synthetic mixtures, catalysts, and drugs. Various sulfur containing reagents have been recommended for the determination of platinum. Thiosemicarbazones are important organic analytical reagents which act as good chelating agents forming stable complexes with platinum(IV). A number of spectrophotometric reagents have been used for the determination of platinum(IV). The literature survey has revealed that N-(3,5-dimethylphenyl)-N'-(4-aminobenzenesulfonate)-thiourea [4], N-alkylacetamide [5], anisaldehyde-4-phenyl-3-thiosemicarbazone [6], *o*-phenylenediamine [7], mercaptocarboxylic acids [8], dimethyl sulfoxides [9], 5-(4-nitrophenylazo)-8-(*p*-toluenesulfonamido)-quinoline [10], 2-acetylpyridine-4-phenyl-thiosemicarbazone [11], 4-[N,N-(diethyl)amino]benzaldehyde thiosemicarbazone [12], N-(*m*-methylphenyl)-N'-(sodium *p*-aminobenzenesulfonate)-thiourea [13], 3-(2'-thiazolylazo)-2,6-diaminopyridine [14], leuco xylene cyanol FF [15], and 5-chloro-2-hydroxythiobenzhydrazide [16] are the chromogenic reagents used for the extractive spectrometric determination of platinum(IV). Apart from this, platinum(IV) was also determined by using polyurethane foam [17]. Along with these various dyes, such reagents as 1-(2-pyridylazo)-2-naphthol [18], Nile blue [19], Rhodamine 6G [20] were also used for the spectrophotometric determination of platinum(IV). The procedures were highly sensitive but insufficiently selective.

Apart from these spectrophotometric methods, several instrumental techniques and methods have been used for the extraction and determination of platinum(IV). The 191Pt-radiotracer technique was used for the separation and preconcentration of Pt(IV) [21]. Among the recent instrumental techniques, inductively coupled plasma mass spectrometry (ICP-MS) is a more powerful tool and preferred instrument used for the quantification of Pt(IV) at ppb levels in various environmental natural sources [22–26]. Platinum(IV) was also determined in the explosive volcanic eruptions by ICP-MS [27]. Trace amounts of platinum(IV) were determined by atomic emission spectrometry [28], microwave plasma torch atomic emission spectrometry [29], inductively coupled plasma optical emission spectrometry [30], inductively coupled plasma atomic emission spectrometry [31, 32]. In recent years, the reduction method has been applied to determine Pt(IV). Platinum(IV) ions were reduced by sulfur containing nucleophiles such as glutathione, L-cysteine, L-methionine, thiourea, and guanosine-5'-monophosphate, stable coordinated complexes were formed which were investigated by UV-Vis spectrophotometry and stopped-flow spectrophotometry [33–35]. Though most of the above techniques are sophisticated and widely used for platinum(IV) determination, they have some shortcomings such as the need for sample preconcentration, time consuming process, use of adsorbents, expensive instruments, use of reducing nucleophiles, more than two–three complicated steps were involved, etc. Spectrophotometric techniques are also sophisticated and require suitable instruments such as a separating funnel and a spectrophotometer, however, in contrast to the above-mentioned techniques, they possess such advantages as low cost, rapidity, and simplicity.

Our research group has reported various spectrophotometric chemosensing extractive methods for the determination of platinum group metals and transition metals. Recently, we have synthesized 1-(2',4'-dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol as a chelating spectrophotometric extractant for the determination of gold(III) [36], silver(I) [37], nickel(II) [38]. Along with this, we have synthesized 4-(4'-chlorobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole for the spectrophotometric determination of copper(II) [39], bismuth(III) [40], and selenium(III) [41].

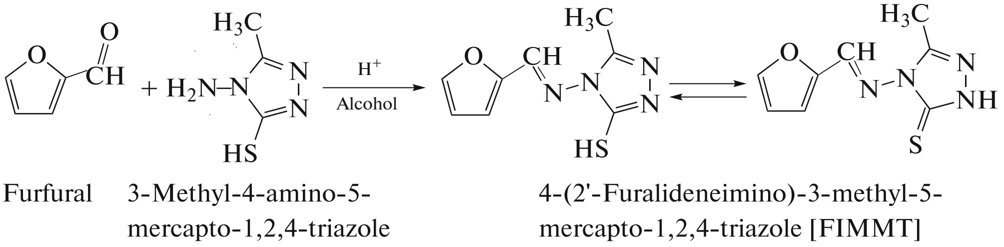
In view of the above, in the present work we have reported a highly selective, simple, green, and rapid chemosensing colorimetric procedure for the determination of platinum(IV) by using 4-(2'-furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole (FIMMT). Platinum(IV) formed a red-colored soluble complex with FIMMT at pH 5.4 on heating in a water bath (approx. temperature was 60–70°C) for 25 min, then it was extracted with *n*-butanol, and determined at 510 nm by spectrometry. The main advantages of the proposed method are that the equilibrium distribution between two phases is attended instantly; therefore, there is no need to shake the separating funnel, which decreases sample preparation time.

EXPERIMENTAL

Apparatus. An Elico digital spectrophotometer model CL-27 with 1-cm quartz cells was used for absorbance measurements. pH measurements were carried out using an Elico digital pH meter (Model LI-120). Standard glassware was used for volumetric measurements. All glass vessels were cleaned with $K_2Cr_2O_7$ solution, followed by washing with soap water and rinsing with distilled water before use.

Preparation of reagents and standard platinum(IV) solution. Pure platinum wire (0.100 g) was dissolved in *aqua regia*. The solution was repeatedly evaporated by the addition of concentrated hydrochloric acid until all nitric acid was removed. The residue was dissolved in 2 mL of concentrated hydrochloric acid, and the obtained solution was hydroplatinic chloride ($H_2Pt_{IV}Cl_6$) [42]. This solution was diluted to 100 mL with distilled water. It was then diluted to obtain 100 μg/mL platinum(IV) standard solution.

FIMMT reagent was prepared by refluxing a mixture of 3-methyl-4-amino-5-mercapto-1,2,4-triazole (2.6 g) and 2-furfural (1.36 mL) in 50 mL of alcohol containing 3 drops of glacial acetic acid for 3–4 h (Scheme 1). The product, i.e., yellow-colored needles, was obtained and recrystallized from hot alcohol (M.P. 165°C). The purity was checked by thin layer chromatography, and the product was characterized by CHNS analyzer, infrared and nuclear magnetic resonance spectroscopy [43]. Alcoholic solution of FIMMT (0.015 and 0.03 M) was used for the determination procedure. Buffer solution (pH 5.4) was prepared by mixing 88 mL of 0.2 M acetic acid and 412 mL of 0.2 M sodium acetate and diluting to 1000 mL with water. Double distilled water was used throughout the experiments. All the solvents and reagents were of analytical reagent grade.



Scheme 1. Synthesis of 4-(2'-furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole.

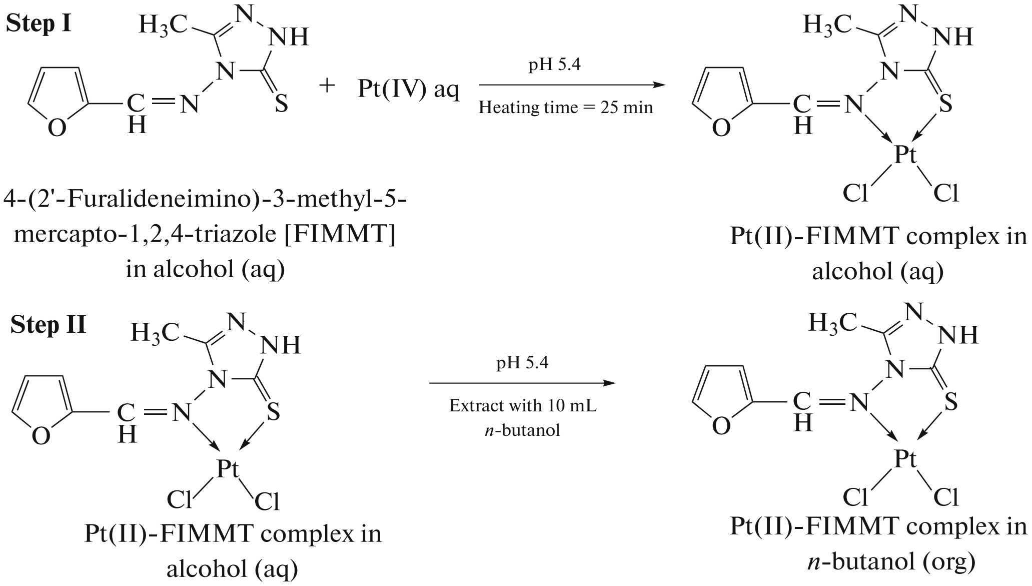
Recommended procedure. *Determination of platinum in aqueous medium.* Platinum in aqueous medium was determined by adding 100 μg of Pt(IV) in a 10-mL calibrated flask. Then, the buffer (pH 5.4) and 1.5 mL of 0.05 M FIMMT in ethanol were added to the flask. The solution was made up to the mark with the buffer, and the flask was heated in a hot water bath for 25 min. A red-colored water-soluble complex of platinum with FIMMT was formed. The volumetric flask was taken out and allowed to attain room temperature. Finally, the solution in the flask was made up to the mark if necessary. Absorbance of the aqueous phase (Scheme 2, Step I) containing Pt(II)–FIMMT complex was measured at 510 nm against the reagent blank prepared similarly without Pt(IV) addition.

Extractive spectrophotometric determination of platinum. A solution containing 100 μg of platinum(IV) was taken in a 25-mL calibrated flask, and the pH was adjusted to 5.4 by the addition of dilute sodium acetate–acetic acid buffer solution. 2.5 mL of 0.03 M FIMMT solution in ethanol was added. The solution was mixed well and heated at a constant temperature in a hot water bath for about 25 min to obtain a red color (Scheme 2, Step I). The volumetric flask was taken out and allowed to attain room temperature. In this step, the half mass of FIMMT was consumed for the reduction of Pt(IV) into Pt(II) due to the presence of thiol group [33, 44, 45]. The remaining half of FIMMT reacted with Pt(II), and a stable red-colored complex was formed. The red-colored platinum(II)–FIMMT complex was instantly (rapidly) extracted into the organic phase by using of 10 mL *n*-butanol (Scheme 2, Step II) in a single extraction without shaking. The two phases were allowed to separate, and the organic layer was dried over anhydrous sodium sulfate. The absorbance of the colored organic phase was measured in a 1-cm quartz cell at 510 nm against a reagent blank prepared similarly but without platinum addition. The concentration of platinum was calculated from a calibration curve obtained in the same way. Percentage extraction (*E*, %) and metal distribution ratio (*D*) were calculated according to Eqs. (1) and (2), respectively:

$$E,\ \% = [\mathrm{Pt}^{2+}]_{\mathrm{org}}/[\mathrm{Pt}^{2+}]_{\mathrm{aq\ init}} \times 100, \qquad (1)$$

$$D = [\mathrm{Pt}^{2+}]_{\mathrm{org}}/[\mathrm{Pt}^{2+}]_{\mathrm{aq}}, \qquad (2)$$

where $[\mathrm{Pt}^{2+}]_{\mathrm{aq\ init}}$ represents the initial concentration of the metal ion in the aqueous phase. $[\mathrm{Pt}^{2+}]_{\mathrm{aq}}$ and $[\mathrm{Pt}^{2+}]_{\mathrm{org}}$ reflect the total concentrations of the metal ion in the aqueous and organic phases after equilibrium, respectively. The analysis of blank solutions did not show any traces of platinum(IV).



Scheme 2. Extraction of platinum(IV) with 4-(2'-furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole (FIMMT) and formation of red-colored Pt(II)-FIMMT complex.

RESULTS AND DISCUSSION

Absorption spectra and spectral characteristics. Preliminary studies for the determination of platinum(IV) with 4-(2'-furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole have indicated the formation of a red-colored complex on heating in a water bath. The red-colored Pt(II)–FIMMT complex was found to be quantitatively extracted in *n*-butanol. The absorption spectra of the reagent and its platinum(II) complex obtained in the wavelength range of 300–600 nm are shown in Fig. 1.

The maximum absorbance of the colored complex was observed at 510 nm in *n*-butanol, and it was stable for more than 48 h. The optimum conditions for the effective extraction of platinum were established by studying the effect of pH, ligand concentration, choice of solvent, heating time, and interferences from diverse ions. The optimized conditions and spectral characteristic properties are shown in Table 1.

Effect of pH. To study the effect of pH on the absorbance of the red-colored platinum complex, dilute solutions of sodium hydroxide and acetic acid were used. The complexation was found to be maximum in the pH range of 4.8–5.6; it becomes convenient that one can prepare a series of buffer solutions (sodium acetate–acetic acid) each differing by 0.2 pH units, and the color is developed at different pH in the presence of these buffers by heating for 25 min in a hot water bath. The absorbance values of each solution were measured in the aqueous and extracted organic phase as well. It is evident from the results that the absorbance values are maximum and remain steady in the pH range of 5.0–5.6 (Fig. 2). Therefore, for all subsequent studies, the pH was maintained at an optimum level of 5.4 by using acetate buffer solution. However, the complexation was found to be incomplete in other buffer solutions such as citric acid–sodium hydrogen phosphate and boric acid–borax.

Effect of solvent. In the extraction of red-colored Pt(II)–FIMMT complex, solvent plays an important role in the solvation of Pt(II)–FIMMT. For this purpose, the influence of various organic solvents was examined for the effective extraction of the complex. The results are reported in Table 2. It was observed that the percentage extraction (*E*, %) values increased in the order of carbon tetrachloride < kerosene < amyl acetate < iso-amyl alcohol < xylene < butyl acetate < methyl isobutyl ketone < toluene < ethyl acetate < 1,2-dichloroethane < chloroform < *n*-butanol. Therefore, *n*-butanol was chosen for the further extraction studies.

Effect of heating time. It is often necessary to investigate trace amounts of metal ions with high efficiency at a minimum temperature and time. Pt(IV) reacts with FIMMT and initially gets reduced to platinum(II) by thiol form of FIMMT and then forms a red-colored complex on heating in a water bath by thione form of the ligand. The heating temperature of a hot water bath was maintained above 80°C. The results indicated in Fig. 3 demonstrate the effect of heating time on the color development of the complex by varying the time from 0 to 40 min. The color formation was found to gradually increase and then remain constant after 20 min. Prolonged heating time did not affect the absorbance. Hence, the heating time of 25 min was selected for further studies.

Effect of chromogenic ligand concentration. The effect of ligand concentration on the complex formation was studied at pH 5.4 (Fig. 4). For maximum color intensity, the minimum amount of the reagent required is about 100-fold excess. To ensure complete complexation, 150 molar ratios, i.e., 2.5 mL of 0.03 M FIMMT, are recommended in the procedure. No adverse effect was noticed on the absorbance of the solution when higher molar ratios of the reagent were used. To study the effect of reagent concentration, it was dissolved in ethanol, 1,4-dioxan, and dimethylformamide separately. The absorbance values were found to be maximum and remained constant in the range of 2–20% ethanol solution in total volume of the aqueous phase.

Reaction rate and color stability. No reaction occurs between Pt(IV) and FIMMT at room temperature, but reaction is initiated when the solution is heated in a water bath (above 80°C). The time required for maximum color development is 20 min. To ensure maximum color development, in all subsequent studies the solution was heated for 25 min. There was no adverse effect of further heating on complexation. Further, the intensity of the developed color remained stable for more than 24 h without any substantial change in absorbance values.

Adherence of Beer's law and sensitivity. The validity of Beer's law for the system was studied by measuring absorbance values of a series of aqueous solutions and extracts with different platinum contents. The results showed that Beer's law was obeyed up to 17.5 ppm. The optimum concentration range for maximum precision was determined by Ringbom's plot method [46]. The percentage transmittance of the solution was plotted against $\log c_{[\mathrm{Pt(IV)}]}$ (Fig. 5). The linear portion of the curve indicates that platinum can be precisely determined in the range of 3–15 ppm. The sensitivity estimated according to Sandell's criterion is 0.017 μg/cm^2 of platinum for $\log(I_0/I_t) = 0.001$, and the molar absorptivity of the red-colored complex is 1.1686×10^4 L/mol cm at 510 nm.

Precision and accuracy. To assess the precision and accuracy of the method, the determinations were carried out at different Pt(IV) concentrations under optimum conditions. The average of 10 determinations of 10 ppm platinum was 10.00 ppm with the standard deviation of 0.03, coefficient of variance of 0.26, and the variation from mean at a 95% confidence limit was 10.00 ± 0.02.

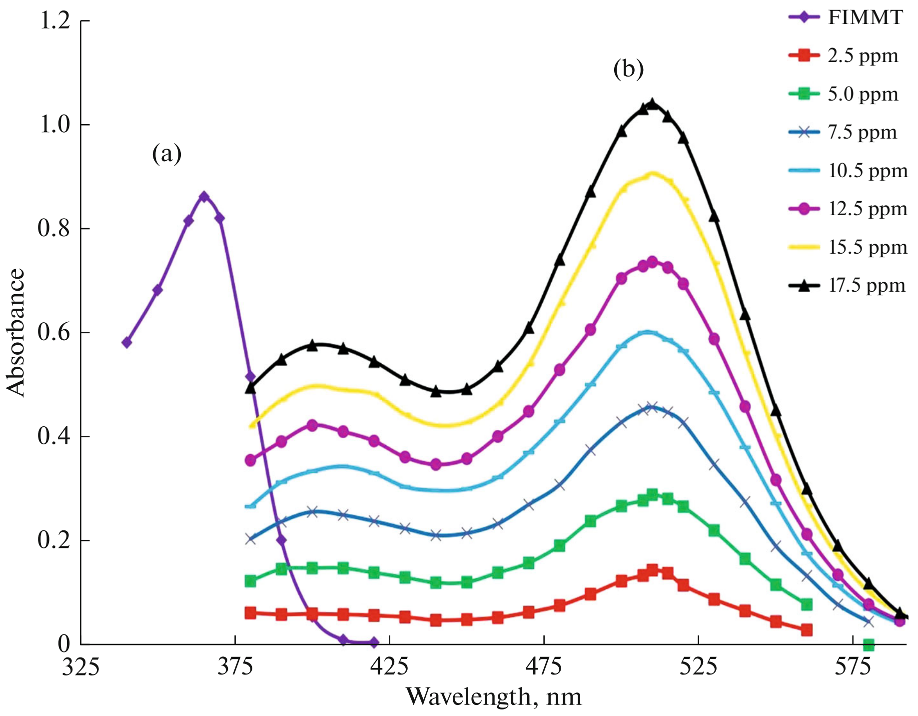


Fig. 1. Absorption spectra of (a) FIMMT and (b) platinum(II)–FIMMT complex in ethanol. 10 μg/mL Pt(IV); 1.5 mL of 0.05 M FIMMT for aqueous medium; 2.5 mL of 0.03 M FIMMT in ethanol; pH 5.4; 25-min heating time; 10 mL of *n*-butanol; λ_{max} of 510 nm.

Composition of the complex. To apply the extraction system for Pt(IV) separation in real samples, the extraction properties of platinum were evaluated at pH 5.2. The composition of the platinum(IV) complex with FIMMT was studied by the method of log–log plot (Fig. 6). The plots of $\log D_{[\mathrm{Pt(IV)}]}$ –

Table 1. Spectral characteristics and precision data of platinum(II)-4-(2'-furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole complex

Optical characteristic and precision	Parameter
Solvent	*n*-Butanol
λ_{max}, nm	510
pH range	4.8–5.6
FIMMT concentration	1.5 mL (0.05 M) for direct determination in aqueous solution; 2.5 mL (0.03 M) for extractive determination
Heating time, min	25
Stability, h	>24
Beer's law range, μg/mL	2.5–17.5
Ringbom optimum concentration range, μg/mL	3–15
Molar absorptivity, L/mol cm	1.1686×10^4
Sandell's sensitivity, μg/cm^2	0.017
Relative standard deviation[a], %	0.13
Range of error	±0.2
Mean recovery, %	99.80 ± 0.06
Stoichiometry of the extracted complex	1 : 1

[a] Average of five determinations.

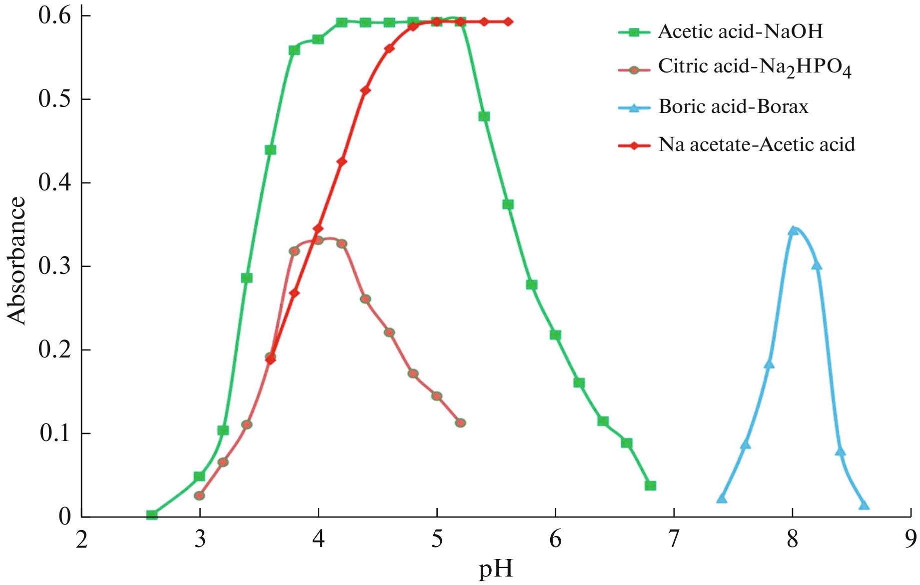


Fig. 2. Effect of pH on complexation reaction of platinum with FIMMT. 10 µg/mL Pt(IV); 1.5 mL of 0.05 M FIMMT for aqueous medium; 2.5 mL of 0.03 M FIMMT in ethanol; 25-min heating time; *n*-butanol extraction solvent; $\lambda_{\max}$ of 510 nm.

log$c_{[\mathrm{FIMMT}]}$ showed the slopes of 1.20, 1.06, and 1.17 at pH 4.0, 4.4, and 4.8, respectively, indicating that the metal to ligand stoichiometry is 1 : 1.

The literature data suggest that sulfur containing ligands first reduce platinum(IV) to platinum(II) and then form a complex [47] with it. However, the Job's method of continuous variation and mole ratio method failed to determine the complex composition, because in equimolar metal to ligand ratio a red-colored compound was formed which could not be extracted into the organic solvent. Therefore, platinum(IV) reacts with FIMMT to form platinum(II) first and then giving an uncharged chelate according to the Eq. (3) [33] and (4) [45]. The uncharged chelate Pt(II)–FIMMT was then quantitatively extracted in 10 mL of *n*-butanol.

$$[\mathrm{PtCl_6}]^{2-}_{\mathrm{aq}} + 2\mathrm{R{-}C{-}SH_{aq}} \rightleftarrows [\mathrm{PtCl_4}]^{2-}_{\mathrm{aq}} + 2\mathrm{R{-}C{-}SCl_{aq}} + 2\mathrm{H}^+, \tag{3}$$

$$[\mathrm{PtCl_4}]^{2-}_{\mathrm{aq}} + \mathrm{R{-}C{=}S_{aq}} \rightleftarrows [\mathrm{PtCl_2}(\mathrm{R{-}C{=}S})]_{\mathrm{aq}} + 2\mathrm{Cl}^-, \tag{4}$$

where R–C–SH and R–C=S are tautomeric forms of FIMMT as mentioned in Scheme 1.

On the basis of the above reactions, the extracted red-colored compound most likely corresponds to platinum(IV). Based on this investigation, the proba-

Table 2. Effect of solvent on platinum(II)–FIMMT complex extraction

Solvent	Dielectric constant	Absorbance at 510 nm, $\lambda_{\max}$	Extraction, %
Carbon tetrachloride	4.40	0.016	2.7
Kerosene	1.80	0.044	7.4
Amyl acetate	17.10	0.061	10.3
Amyl alcohol	2.30	0.108	18.2
Xylene	5.00	0.158	26.7
Butyl acetate	5.00	0.287	48.5
Methyl isobutyl ketone	13.11	0.325	54.9
Toluene	2.38	0.365	61.7
Ethyl acetate	6.01	0.418	70.6
1,2-Dichloroethane	2.24	0.449	75.8
Chloroform	10.50	0.450	76.0
n-Butanol	11.20	0.592	100.0

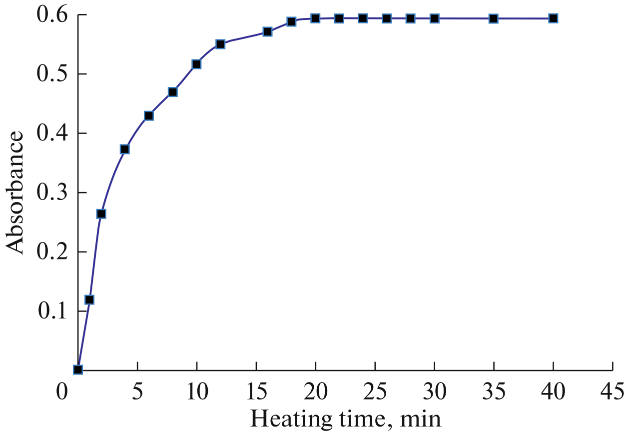


Fig. 3. Effect of heating time in the range of 0–40 min on reaction of platinum(IV) with FIMMT in ethanol. 10 μg/mL Pt(IV); 1.5 mL of 0.05 M FIMMT for aqueous medium; 2.5 mL of 0.03 M FIMMT in ethanol; pH 5.4; *n*-butanol extraction solvent; λ_{max} of 510 nm.

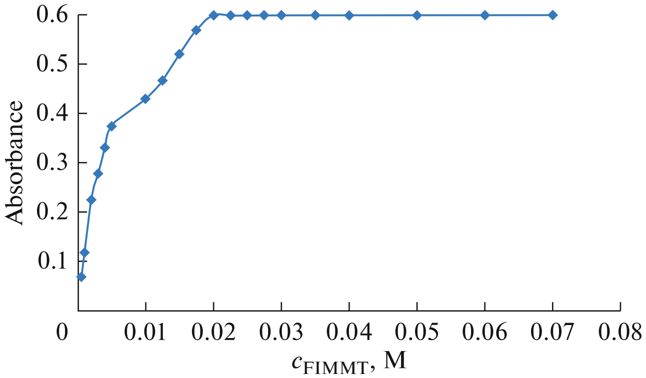


Fig. 4. Effect of FIMMT concentration in the range of 0.001–0.08 M on extraction of platinum(IV). 10 μg/mL Pt(IV); 2.5 mL of FIMMT in ethanol; pH 5.4; 25-min heating time; *n*-butanol extraction solvent; λ_{max} of 510 nm.

ble structure of platinum(II)–FIMMT chelate is shown in Scheme 2. As a result, we can report that the solution of platinum(IV) taken initially for the study was then reduced to platinum(II) by ethanolic solution of FIMMT at pH 5.4 after heating.

Effect of foreign ions. The effect of the presence of various cations and anions on platinum(II)–FIMMT complex absorbance was studied by carrying out the determinations of 10 ppm platinum(IV) according to the recommended procedure. An error of ±2% in the absorbance value was considered as a tolerable limit. The cations such as Bi(III), Re(VII), Ru(III), Os(VIII), Rh(III) form either turbidity or precipitate in the aqueous solution. However, the interference of these cations can be removed by the recommended extraction procedure (Scheme 2, Step II). Hence, as mentioned in the recommended procedure, extraction was needed from the aqueous phase to the organic phase, which was achieved by using 10 mL of *n*-butanol to avoid the formation of precipitate or turbidity associated with interference ions in the aqueous phase. The selectivity of the method was increased by using suitable masking agents such as ethylenediaminetetraacetic acid (EDTA), tartrate (Table 3). Thiosulfate, thiourea, and malonate cause negative error in the determination of platinum(IV).

The interference study showed that the tolerance limit was lower in the aqueous system as compared to the organic phase. Hence, in the studies of analytical applications, the extractive method was used.

Applications. *Separation of platinum, palladium, and nickel as VIIIB (10th) group elements.* As nickel, palladium, and platinum are the VIIIB (10th) group elements, the separation of these elements is one of the great challenges. We have overcome this major challenge by taking the advantage of physicochemical approach of FIMMT as per the recommended method of platinum determination by the extraction procedure.

In the aqueous solution containing 100 μg of platinum(IV), 150 μg of palladium(II), 2500 μg of nickel(II), and 50 mg of EDTA were added. In the above mixture, EDTA was used to mask nickel(II). In the proposed mixture of metal ions, initially we preferentially separated palladium(II) ion as it instantly reacted at room temperature by the addition of 10 mL of 0.015 M FIMMT in *n*-butanol and gave a yellow-colored complex. The absorbance of yellow palladium(II) complex was measured at 410 nm (λ_{max}) against the reagent blank [43]. Under this condition, platinum(IV) and nickel(II) remained in the aqueous phase quantitatively. Further process was carried out

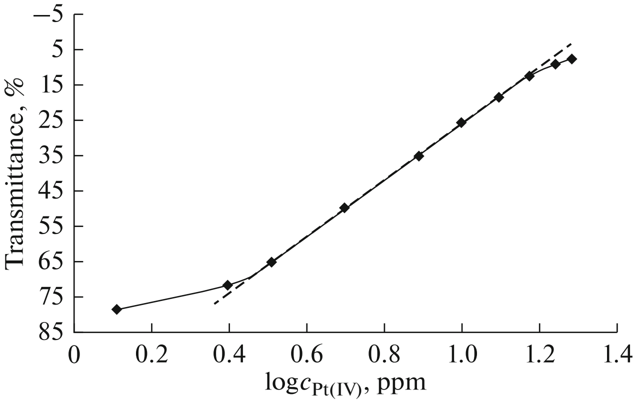
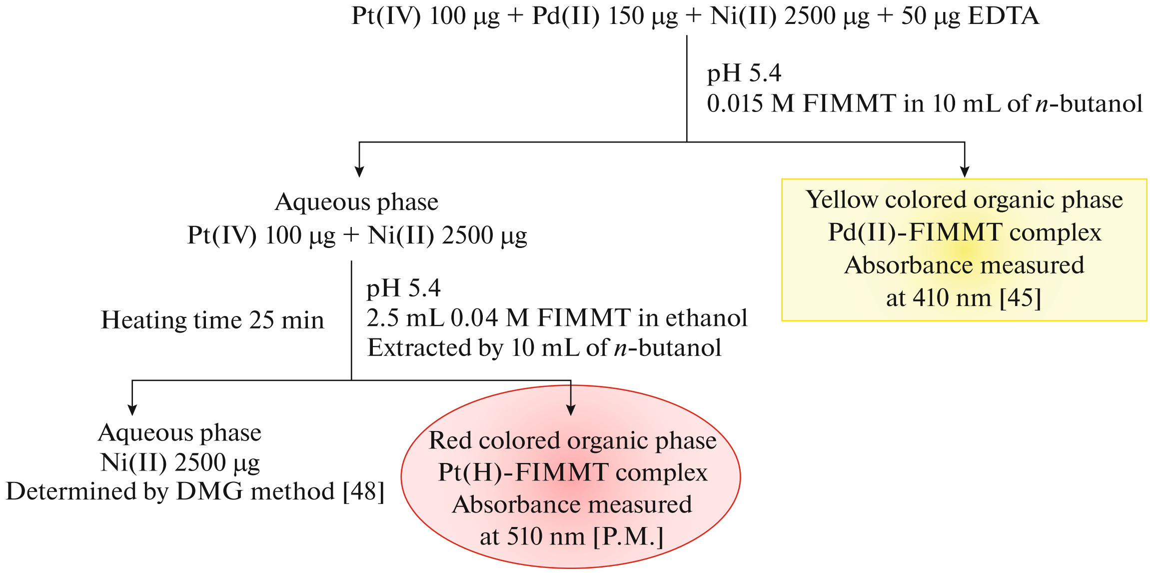


Fig. 5. Ringbom's plot for platinum(II)–FIMMT complex. 2.5–25 μg/mL Pt(IV) concentration; 2.5 mL of 0.03 M FIMMT in ethanol; pH 5.4; 25-min heating time; *n*-butanol extraction solvent; λ_{max} of 510 nm.

as per the recommend procedure for platinum(IV): 2.5 mL of 0.03 M FIMMT was added into the aqueous phase, and pH was maintained at 5.4 by acetate buffer in the presence of EDTA as a masking agent for nickel(II); then, the solution was heated for 25 min in a hot water bath. The red-colored platinum(II)—FIMMT complex was formed and extracted by 10 mL of *n*-butanol. The absorbance of platinum(II)—FIMMT complex was measured at λ_{max} of 510 nm. After that, the aqueous phase containing nickel(II) was evaporated to moist dryness, and nickel—EDTA complex was decomposed by treatment with perchloric acid. The residue was extracted into dilute hydrochloric acid, and aqueous nickel(II) was estimated by dimethyl glyoxime (DMG) [48]. The separation procedure of these metal ions is elaborated in Scheme 3, and the results are given in Table 4.



P.M.= Proposed Method

Scheme 3. Separation of platinum(IV), palladium(II), and nickel(II) ions from their mixture.

Analysis of synthetic mixture corresponding to composition of catalyst containing platinum(IV). Standard samples of catalysts containing platinum were not available for testing; hence, synthetic samples corresponding to platinum catalyst on alumina (Pt, 0.3—0.8), Pt—Pd catalyst on alumina (Pt, 0.03—0.15; Pd, 0.02—0.12), Pt—Rh monolith on cordierite (Pt, 0.03—0.25; Rh, 0.005—0.03), and Pt—Pd—Rh catalyst on alumina (Pt, 0.03—0.2; Pd, 0.03—0.15; Rh, 0.005—0.05) were prepared, and their platinum contents were determined by the procedures described above after bringing them into solutions with *aqua regia*. The results are shown in Table 5. As can be seen, the recoveries are satisfactory, indicating that the proposed method can be used for the determination of platinum in the real samples.

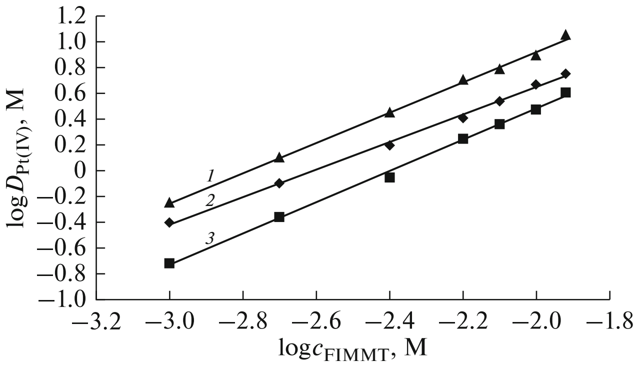


Fig. 6. Log—Log plot of distribution ratio for log$D_{Pt(IV)}$ vs. logc_{FIMMT}. 10 μg/mL Pt(IV); 2.5 mL of 0.0001—0.025 M FIMMT in ethanol; 25-min heating time; *n*-butanol extraction solvent; λ_{max} of 510 nm. (*1*) pH 4.0, slope 1.20; (*2*) pH 4.4, slope 1.06; (*3*) pH 4.8, slope 1.17.

Analysis of platinum—rhodium thermocouple wire. A known weight (0.100 g) of Pt—Rh thermocouple wire [49] was preliminarily fused with zinc powder, and the melt was cooled and dissolved in hydrochloric acid. The remaining black powder was treated with 5 mL of *aqua regia*. When the reaction was over, the solution was heated with two 5-mL portions of concentrated hydrochloric acid for complete removal of nitrogen oxides and diluted to 10 mL in a standard volumetric flask. The sample solution aliquot was taken, and platinum(IV) was determined using the procedure described earlier. The results of analysis are given in

Table 3. Study of diverse ions influence on the determination of 100 µg of platinum(IV) with FIMMT at 510 nm (relative error ±2%) (1.5 mL of 0.05 M FIMMT for aqueous medium and 2.5 mL of 0.03 M FIMMT in ethanol; pH 5.4; *n*-butanol extraction solvent; λ_{max} of 510 nm)

Ion added	Absorbance of Pt(II)-FIMMT at 510 nm without extraction			Absorbance of Pt(II)-FIMMT at 510 nm after extraction in *n*-butanol		
	amount tolerated, mg	without masking	with masking	amount tolerated, mg	without masking	with masking
Be(II)	20.0	0.597		20.0	0.593	
Ca(II)	20.0	0.597		20.0	0.597	
Mg(II)	20.0	0.597		20.0	0.595	
Sr(II)	20.0	0.598		20.0	0.597	
Ba(II)	20.0	0.597		20.0	0.598	
Th(IV)	10.0	0.597		10.0	0.597	
U(VI)	10.0	0.597		10.0	0.597	
Se(IV)	3.0	0.598		3.0	0.598	
Te(IV)	5.0	0.597		5.0	0.596	
Sn(II)	10.0	0.597		10.0	0.597	
Cr(III)	7.0	0.596		7.0	0.597	
Mo(VI)	4.0	0.597		4.0	0.596	
Zr(IV)	1.5	0.597		1.5	0.595	
Bi(III)	10.0	Precipitate	–	10.0	0.597	
	5.0	Precipitate	–	5.0	0.598	
	1.0	Precipitate	–	1.0	0.597	
V(V)[a]	7.0	Interference	0.599	7.0	Interference	0.597
	5.0	Interference	0.597	5.0	Interference	0.598
	1.0	Interference	0.597	1.0	Interference	0.598
Fe(III)[a]	5.0	Precipitate	0.597	5.0	Interference	0.597
	2.5	Precipitate	0.598	2.5	0.259	0.597
	1.0	Precipitate	0.598	1.0	0.343	0.596
Co(II)[a]	3.0	Precipitate	0.597	3.0	0.164	0.598
	1.0	Precipitate	0.597	1.0	0.124	0.599
Cu(II)[a]	3.0	Precipitate	0.597	3.0	0.189	0.596
	1.0	Precipitate	0.597	1.0	0.243	0.596
Ni(II)[a]	7.0	Turbid	0.598	7.0	Interference	0.597
	5.0	Turbid	0.597	5.0	Interference	0.597
	1.0	Turbid	0.598	1.0	Interference	0.597
Zn(II)[a]	10.0	Precipitate	0.597	10.0	Interference	0.598
	5.0	Precipitate	0.597	5.0	Interference	0.598
	1.0	Precipitate	0.597	1.0	0.153	0.597
Cd(II)[a]	7.0	Interference	0.598	7.0	Interference	0.595
	5.0	Interference	0.595	5.0	Interference	0.597
	1.0	Interference	0.597	1.0	0.139	0.596
Al(III)[a]	10.0	Interference	0.597	10.0	Interference	0.597
	5.0	Interference	0.597	5.0	Interference	0.597
	1.0	Interference	0.598	1.0	Interference	0.597
Ga(III)[b]	2.5	Interference	0.597	2.5	Interference	0.595

Table 3. (Contd.)

Ion added	Absorbance of Pt(II)-FIMMT at 510 nm without extraction			Absorbance of Pt(II)-FIMMT at 510 nm after extraction in *n*-butanol		
	amount tolerated, mg	without masking	with masking	amount tolerated, mg	without masking	with masking
	1.0	Interference	0.595	1.0	Interference	0.599
In(III)[b]	3.0	Interference	0.597	3.0	Interference	0.597
	1.0	Interference	0.596	1.0	Interference	0.598
Tl(III)[b]	3.0	Interference	0.597	3.0	Interference	0.597
	1.0	Interference	0.598	1.0	Interference	0.597
Re(VII)	1.0	Turbid	0.598	1.0	0.597	
Au(III)	0.7	Gel	0.597	0.7	0.597	
Pd(II)[c]	1.0	0.597	–	1.0	0.597	
Os(VIII)	0.2	Brown ppt	–	0.2	0.597	
Ru(III)	0.2	Brown ppt	–	0.2	0.597	
Rh(III)	0.7	Brown ppt	–	0.7	0.597	
Ir(III)	0.5	0.597		0.5	0.597	
Fluoride	50	0.597		50	0.597	
Bromide	100	0.597		100	0.597	
Iodide	100	0.597		100	0.597	
Oxalate	50	0.597		50	0.597	
Tartrate	50	0.597		50	0.597	
Acetate	100	0.597		100	0.597	
EDTA	100	0.597		100	0.597	
Thiocyanate	100	0.597		100	0.597	
Citrate	100	0.597		100	0.597	

[a]Masked with 100 mg of EDTA solution, [b]masked with 50 mg of tartrate solution, [c]prior extraction with the same reagent at room temperature.

Table 4. Separation of platinum(IV), palladium(II), and nickel(II) in the ratio of 1 : 1.5 : 25 as a group separation

Metal ion	Amount taken, μg	Recovery[a], %	RSD, %	Determination method	Reference
Pt(IV)	100	99.98	0.10	FIMMT	Present study
Pd(II)	150	99.90	0.10	FIMMT	[45]
Ni(II)[b]	2500	99.92	0.08	DMG	[48]

[a]Average of five determinations, [b]masked with EDTA.

Table 6. The obtained results were compared with atomic absorption spectroscopy (AAS).

Procedure for platinum determination in pharmaceutical sample. The proposed method was used for the determination of platinum(IV) in a pharmaceutical sample, namely, Oncoplatin AQ (*cis*-platin injection). A known volume (2 mL) of *cis*-platin injection solution (0.5 mg/mL) was digested in concentrated perchloric—nitric acid (10 : 1) and evaporated to dryness until organic matter, if present, was removed. The obtained residue was dissolved in concentrated hydrochloric acid and diluted with double distilled water to 10 mL in a standard volumetric flask. A 1.5-mL aliquot of the sample solution was taken, and platinum(IV) was determined using the recommended procedure (Table 6). Similar results were obtained by direct absorbance measurements in aqueous medium. The results obtained by the proposed method were in good agreement with the AAS.

Table 5. Determination of platinum(IV) in synthetic mixtures corresponding to catalysts

Alloy	Pt(IV) taken, μg	Pt(IV) found[a], μg		Average recovery, %	RSD, %	Confidence limit (α = 0.95)
		proposed method	AAS			
Pt-catalyst on alumina	100	99.9	99.9	99.9	0.1	0.03
Pt—Pd catalyst on alumina	100	99.9	99.9	99.9	0.1	0.02
Pt—Rh monolith on cordierite	100	99.8	99.8	99.8	0.2	0.02
Pt—Pd—Rh catalyst on alumina	100	99.9	99.9	99.9	0.08	0.01

[a] Average of five determinations.

Table 6. Determination of platinum(IV) in real samples

Sample	Manufacturer	Certified value	Pt(IV) found[a]		RSD, %	Confidence limit (α = 0.95)
			proposed method	AAS		
Platinum-rhodium thermocouple wire (Pt, 87%; Rh, 13%)	Ruia Resistance Wire Mumbai, India	87%	86.9%	86.9%	0.11	0.021
Oncoplatin AQ *cis*-platin anticancer (*cis*-platin, IP, 0.5 mg/mL; water for injection)	Unimed Technologies Basku-Ujeti Road, Ujeti, Halol—389350, Gujrat, India	65 μg/mL	64.99 μg/mL	64.99 μg/mL	0.18	0.025

[a] Average of five determinations.

CONCLUSIONS

4-(2'-Furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole has been used as a colorimetric chemosensing reagent for platinum(IV) determination in aqueous samples as well as after extraction in *n*-butanol. The developed method is simple, reproducible, and rapid; it requires less time for the separation and determination of platinum(IV). Low reagent concentration is required for quantitative recovery of platinum(IV). The extraction occurs in a single stage, and it is free from interference of a large number of foreign ions which are associated with platinum(IV) in its natural occurrence. The selectivity was enhanced by the use of suitable masking agents. The probable stoichiometry of the extracted species was calculated to be 1 : 1 (metal : ligand). The developed method was successfully applied to the determination of platinum(IV) in the real samples. The extractive procedure permits separation of nickel(II), palladium(II), and platinum(IV) from the mixture. The proposed method obeys the principle of green chemistry as non-hazardous *n*-butanol was applied as an extraction solvent.

ACKNOWLEDGMENTS

Authors wish to thank Dr. B.Y. Yadav, Mr. N.N. Jagdale, Mr. P.T. Patil, Mr. A.B. Debadwar of Shri Shivaji Shikshan Prasarak Mandal, Barshi and Principal Mrs. B.D. Revadkar for providing necessary facilities.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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