Spectrophotometric determination of micro amount of palladium(II) platinum (II)By using pyrazolone azo resorcinol

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Abstract:

A sensitive and selective method have been developed for the determination of palladium (II)and platinum (II) . A new reagent and two complexes have been prepared in ethanolic solutions .The method is based on the chelation of metal ions with 4-(4′- pyrazolon azo) resorcinol (APAR) to form intense color soluble products, that are stable and have a maximum absorption at 595 nm and at 463 nm and ε_{max} of 1.11×10^{4} and.1.35×10^{4} $Lmole^{-1}cm^{-1}$ for Pd(II) Pt(II) respectively. A linear correlation of (1.4 – 0.2) and (3.2 -0.4) ppm for pd(II) pt(II) respectively .The stability constants , relative errors , a relative standard deviations for Pd(II) and Pt(II) were 0.40×10^{5} , 0.4×10^{4} L mol^{-1} ,0.34 - 0.21% and 2.4 – 0.91% respectively. The conductivity measurements for complexes are consistent with those expected for an electrolyte. The proposed method was successfully applied to the analysis of dust and synthetic mixtures without any preliminary concentration or sparation.

Key words: 4-(4′- pyrazolon azo) resorcinol (APAR), palladium(II), Platinum (II), determination, *spectrophotometry*

Introduction:

Platinum group elements (PGE′s) are very valuable elements due to wide use not only in automotive catalytic converters but as a drug and in food production –has led to more uncontrolled release of those metals in the environment.These PGE particles will then ,be adsorbed on to environment surface such as road dust ,soils and vegetations or accunmulated into water beds or being distributed by natural transportation agents i.e winds , water and rain[1].Mechaniz and thermal erosion are the main causes of PGE release where PGE and promoters impregnated on the catalyst active surface are easily loosened and emitted in to the environment ,along with vehicle emissions [2] Azo-dyes are widely used in analytical chemistry according to their ability to form coloured complex with many metal ions in water .In recent years they have been employed in sorption spectroscopic test method more extensively than in conventional spectrophotometry[3].Azo compounds are of a great biological activity [4,5] . Pyrazolone moiety(a five- membered lactam ring containing two nitrogens and ketone in the same molecule alternatively a derivative of pyrazole possessing an additional carbon/hydroxyl group) has been medicinal chemists for over last 100 years because of the outstanding pharmacological properties several of its derivatives [6]. Azo pyrazole derivaties and its metal complexes can be used as ink jet due to fast uess properties for dying papers , possess

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high dying power on fibers and having many application´s [7].

Materials and Methods:

Equipments

Spectrophotometric measurements were made with ShimadzuUV-Visible -1700 double beam Spectrophotometer using 1.00-cm glass cells ,Electric molar conductivity measurements were carried out at room temperature using an Alpha digital conductivity model-800. The pH measurements were performed with a WTW pH- meter 720. The FT-IR measurements were made with Shimadz 8000 Seriers Japan. and phoemix-986 spectrophotometer flam atomic absorption Spectrophotometric measurements were made Japan

A)Preparation of reagent (APAR)

The reagent was prepared by coupling resorcinol with diazotate 4-amino antipyrian in alkaline alcoholic solution. A diazonium solution was prepared by taking 1g 4- amino antipyrian in 15 ml of ethanol and concentreated hydrochloric acid with 5 ml of distilled water ,and adding sodium nitrite solution dropwise at 0-5°C. Resorcinol 1.2 g was dissolved in 50 ml of ethanol and 30 ml of 0.1M were added at (-5°C) .The mixture was left to stand over night .The precipitate was filtered off and recrystallized from ethanol [8] [figure (1)]

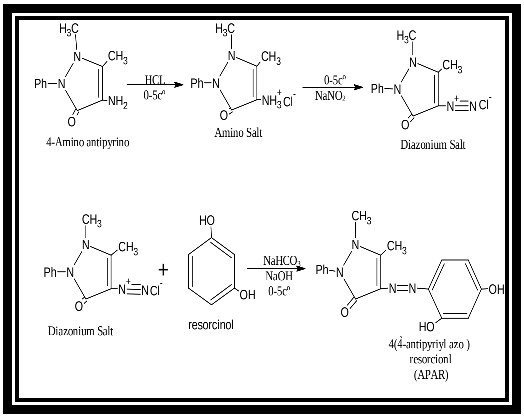


Fig.(1): Preparation of (APAR)

B) Preparation of complexes

The complexes were prepared by stoichiometric from ligand in 50 ml of ethanol then added dropwise with stirring to a stoichiometric amount 1:1 for Pd(II) and 1:1 for Pt(II) chloride salt in 25 ml hot distilled water . The solid products thus formed was filtered off , washed with ethanol and dried .

Reagents

palladium (II)stock solution (1000 µg ml^{-1})

Dissolve0.3330 g of $PdCl_2$ (99%, Riedel-Dehaeng Seelz- Hannover) in 10 ml of 1M HCl and dilution the volume to 200 ml with distilled water Working standard Pd (II) solutions were prepared by dilution of the appropriate volume of standard Pd (II) solution (1000µg.ml^{-1})with distilled water .

platinum(II)stock solution (1000 µg ml^{-1})

preparation K_2PtCl_4 from $H_2PtCl_6.6H_2O$ (99%,Fluke)[9]. dissolve 0.2128g of K_2PtCl_4 in 10 ml of distilled water and dilution the volume to 100 ml distilled water. Working standard Pt(II) solutions were prepared by dilution of the appropriate volume of standard Pt (II) solutions (1000 µg ml^{-1})with distilled water .

4(4–pyrazolon azo) resorcinol (1×10^{-3}M).

A 0.081g of reagent (APAR) was dissolved in 250 ml of ethanol . Working (APAR) solution (5×10^{-4} M) was prepared by simple dilution of appropriate volume of the reagent solution (1×10^{-3} M) with ethanol .

Foreign ion solutions (100 µg ml^{-1})

These solutions were prepared by dissolving an amount of the compound in distilled water completing the volume in a volumetric flask.

Recommended procedure for determination of Pd (II) and Pt(II)

In to a series of 10 ml calibrated flask, transfer increasing volume of Pd (II) and Pt(II) working solutions (1000 µg ml^{-1}) to the range of the calibration curve, add 1.2 ml and 3.0 ml of $5x10^{-4}$M of APAR, respectively .The pH (5, 5.5) for pd (II) and Pt (II) respectively , was adjusted by 0.05 M HCl and NaOH. The complexes formed were solubilized in water and diluted up to 10 ml with distilled water. The concentration range 0.5-3 µg/ml of Pd(II) and Pt(II), respectively . Measure the absorbance at 595 nm for Pd(II) and at 463 nm for Pt(II) complexes against a reagent blank .

Determination of Pd(II) and Pt(II) by recommended method

The samples were collected from AL –Muthana and AL- Najaf governorates in Iraq. 0.5 g of dust road sample was weighed 5 ml of aqua regia were added .The mixture was heated almost to dryness .After addition of 5 ml aqua regia and 1 ml of 40 % HF, the mixture was heated to dryness again for 2 hrs. Then 2 ml of 65% HNO_3 were added, and the mixture was heated to dryness. The residue was diluted to 50 ml with distilled water. The digest was filterated in order to separate the solid residue.

Results and Discussion :

Properties of APAR and its metal chelates APAR is a tridentate with coordination of azo group nitrogen, hydroxide and carbonyl groups; it has following structure:

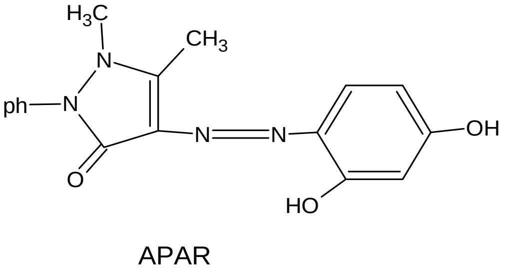


Fig. (2): structure of (APAR)

Owing to the large conjugated, the compound showed excellent chelation ability to form metal chelates. APAR and its metal chelates can be easily solubilited in an aqueous solutions .

Absorption spectra

The results of this investigation indicated that the reactions of Pd(II) and Pt(II) with 4(4–pyrazolon azo) resorcinol yields highly soluble coloured complexes which can be utilized as a suitable assay procedure for determination of Pd(II) and Pt(II). These coloured complexes have a maximun a absorption at 595 nm for Pd(II) and at 463 nm for Pt(II),the blank at these wavelengths shows zero absorbonce (Fig 3 and 4). The effect of various parameters on the absorption intensity of the formed products was studied and the reactions condition were optimized. The bands appearing in the range of 290-445 nm are attributed to $\pi\rightarrow\pi^*$ transition. The other bands observed in the region of 569 nm for Pd(II) and 463 nm for Pt(II) are attributed to $n \rightarrow\pi^*$ electronic transition [10,11]

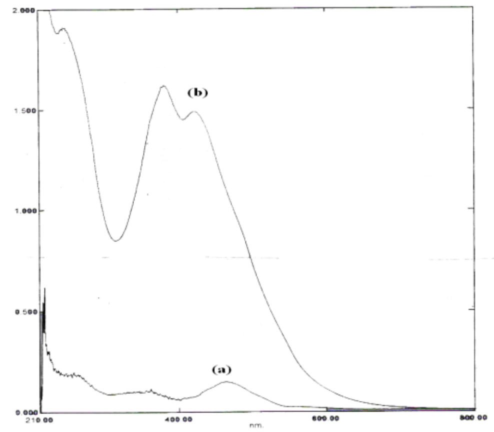


Fig.3 Absorption spectrum of (a) APAR- Pt(II) complex and (b) reagent blank .

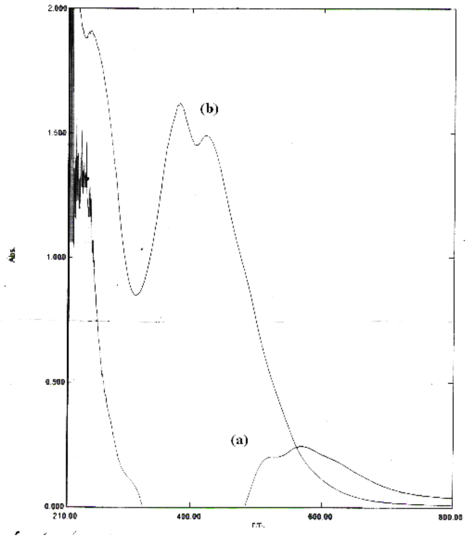


Fig.4:-Absorption spectrum of (a) APAR-Pd(II) complex and (b) reagent blanc.

Effect of reagent concentration

various concentrations of APAR solution were added to a fixed amount of Pd(II) and Pt(II) 2 ml and 2 ml of 5×10^{4-} M where found enough to develop the colour to its full intensity and give a minimum blank value and were considered to be optimum for the concentration range 0.5-3 µg/ml of Pd(II) and Pt(II) respectively (Fig 5) .

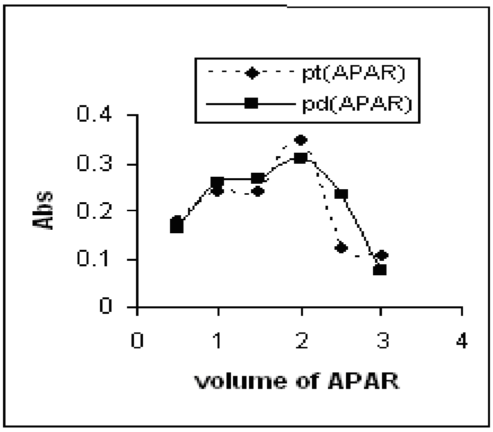


Fig .5.Effect of APAR concentration

Effect of pH

The pH of metal complexes solution was adjusted using dilute solutions of 0.05 M HCl and 0.05 M NaOH. The effect on absorbance was studied. The absorbance of the complex was maximum and constant in the pH range (5, 5.5) for pd (II) and Pt (II) respectively (Fig 6).

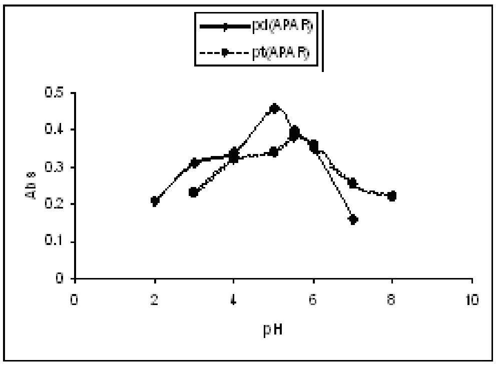


Fig .6:Effect of pH

Effect of reaction time

The colour intensity reached a maximum after the Pd(II) and Pt(II) has been reacted immediately with APAR, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for a least 24 hr (Fig 7).

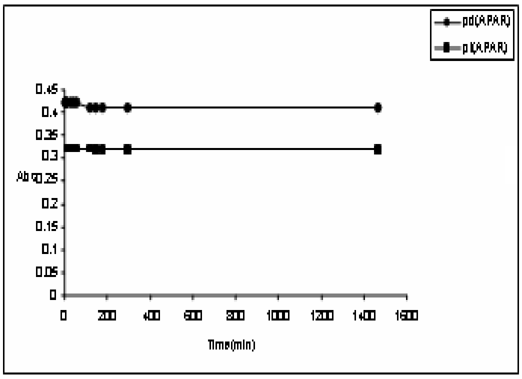


Fig .7:Effect of time

Effect of order of addition

To obtain optimum results, the order of addition of reagents should be followed as given under the procedure, otherwise a loss in colour intensity and stability were observed .

Effect of temperature

The effect of temperature on the colour intensity of the product was studied .In practice, the same absorbance was obtained when the colour was developed at room temperature (25-30°C), but when the volumetric flask were placed in an ice-bath at (0°C) or in a water-bath at (40°C) a loss in colour intensity and stability were observed ,therefore it is recommended that the colour reaction should be carried out at a room temperature for both complexes(Fig 8).

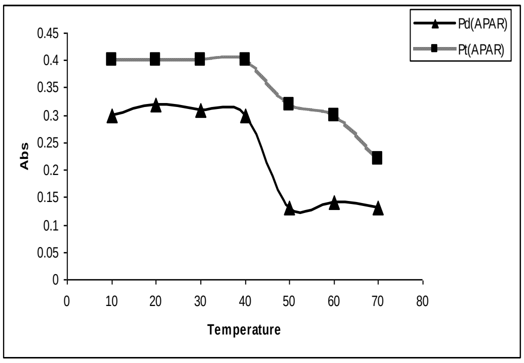


Fig .8:Effect of temperature

Calibration Graph

At optimum conations ,a linear calibration graphs for Pd (II) and pt(II) were obtained ,that Beers low is obeyed over the concentration range of (0.2-1.4 ppm) and (0.4-3.2 ppm) with a correlation coefficient (0.9996) and (0.9861) respectively. The results of analytical performance are summarized in Table (1).

Table.1:Analytical characteristics of metal-APAR Complexes

Characteristic	Pd(II)	Pt(II)
Absorption maxima (λ_{max})	569	463
Bee's law range(µg/ml)	(0.2-1.4)	(0.4-3.2)
Molar absorptivity ($Lmol^{-1}cm^{-1}$)	(1.11×10^4)	(1.35×10^4)
Sandell's sensitivity (μgcm^2)	0.0025	0.0125
pH range	(4.5-5.5)	(4.5-6)
Stability constant(L^2mole^{-2})	0.5×10^5	0.4×10^5
K_f	0.693×10^3	0.576×10^3
ΔG (KJmole)	-16170	-52.3

Accuracy and precision :

To determine the accuracy and precision of the method, Pd(II) and pt(II) were determined at two different concentrations. The results shown in Table 2 a satisfactory precision and accuracy with the proposed method.

Table.2:-Accuracy and precision of the proposed method.

Amount Taken (µg/ml)		Amount found (µg/ml)		*E % n =6		R.S.D% n =6	
Pd (II)	Pt(II)	Pd (II)	Pt(II)	Pd(II)	Pt(II)	Pd(II)	Pt(II)
0.5	1	0.259	0.049	0.2	0.2	0.34	2.3
1	2	0.419	0.120	0.1	0.1	0.21	0.91

*for six determinations

Conductivity measurements

The solubility of the complexes in dimethy sulfoxide and ethanol permitted of the molar conductivity of 10^{-3} M solution at 25C° and , by comparison, the electrolytic nature for complexes .The low values of the molar conductance data listed in Table 3 indicate that the complexes are non electrolytes.

Table.3:Conductivity values of complexes

Complex	Molar conductivity S mole^{-1} cm^{2} DMSO	Ethanol
Pd(APAR)	7.6	15
Pt(APAR)	9.8	20

Interferences

The effect of diverse ions in the determination of these metal ions were studied. To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions. In the experiment, a certain amount of standard palladium (II) or platinum (II)

Solution, coexisting ion solution and masking agent (or absence of masking agent) were added. The results are listed in Table 4. They found that large amount of NO_3^{1-} , Cl^{-1}, CO_3^{2-}, SO_4^{2-} do not interfere in the determination of Pd (II) and Pt (II). Its found that Zn^{++}, Ag^{+}, Cr^{+++} do not interfere, whereas Ni^{++}, Cu^{++}, Pb^{++}, Co^{++}, Fe $^{+++}$, Mn $^{++}$ interfere seriously. However, their interferences are masked efficiently by addition of 0.5- 2.0 ml of 0.1 M of tartaric acid and 0.5- 1.5 ml of 0.1 M of sodium cyanide, respectively .

Table 4:-Effect of foreign ions

Foreign ions	Amount added µg/ml	Interferences with Pd(II)	Interferences with Pt(II)
Ni^{++}	100	+22.1	+12.1
Cu^{++}	=	+24.3	+29.5
Pb^{++}	=	30.5	14.3
Co^{++}	=	+38	+32
Fe^{+++}	=	+52	+43
Mn^{++}	=	+17	+15
Ag^{+}	=	+1.7	+2.1
Cr^{+++}	=	-1.2	+2.1
Cl^{-}	=	-0.4	+1.8
$CO_3^{=}$	=	+2.3	0.0
NO_3^{-}	=	+1.03	+0.95
$SO_4^{=}$	=	+1.4	+2

Composition of the complexes and free energy

The FT- IR bands of the (APAR) and its palladium (Π) and platinum (II) complexes with their probable assignment are given in Table 5. The IR Spectrum of the ligand shows band a broad at 3425 cm^{-1} ,which can be attributed to the phenolic OH group . However ,the *v* (N=N) stretching band in the free ligand is observed at 1580 cm^{-1} .This band has been shifted to lower with low intensity 1550 cm^{-1} and 1540 cm^{-1}frequency values upon complexation suggesting chelation via the (M-N) [12-14] . The band of phenolic of (C-O) in the free ligand is observed at 1240 cm $^{-1}$ This band is shifted to low in tensity 1230 cm $^{-1}$` and 1225 cm $^{-1}$ .The IR Spectrum of the ligand revealed a sharp band at 1645 cm^{-1} due to *v* (C=N)of the N pyrozol azo nitrogen .The band of (C=O) has been shifted to lower frequencies in the complexes indication to that it has been affected upon chelation to the metal ion[12] .The bonding of oxygen to the metal ion is provided by the occurrence of bands at 517-525 cm^{-1} as the result of *v* (M-O) [15] .

Table .5:Selected IR .bands of APAR Complexes

Compound	υ C=N	υ N=N	υ C-O Phenolic	υ O-H	H υ C-H Aromatic	υ M-N	υM-O
APAR	1645 (S)	1580 (m)	1240 (m)	3425 (m)	------	-------	-------
Pd(APAR)	1620 (s)	1550 (m)	1230 (m)	3320 (m)	3030 (m)	425 (w)	525 (w)
Pt(APAR)	1618 (s)	1540 (m)	1225 (m)	3150 (m)	3025 (w)	430 (w)	517 (w)

s=strong , m= medium , w=weak

The compoisition of complexes was studied in the excess of reagent solution by the mole – ratio and job' s methods. A break at a 1:1 (M:L) mole ration suggested the formation of both complexes where M=Pd(II),Pt(II) and L=APAR under the given condition .Fig (9,10,11,12). The calculated according to the equation [16] .Also the free energy changes (G) were calculated according to the following equation ; $\Delta G = -2.303\ RT \log K_f$ Where R= gas constant =8.3 J/degree .mole ,T =absolute temperature =C° +273 .Using the above equation ΔG were found to be -16170 K.J.mole and -52.3 K.J.mole Pd and Pt respectively .The negative values of ΔG indicates that the reaction of both complexes are spontaneous .On the basic of the FT.IR ,stoichiomstric and conductivity data, the structures of complexes can be suggested as the following (Fig 13).

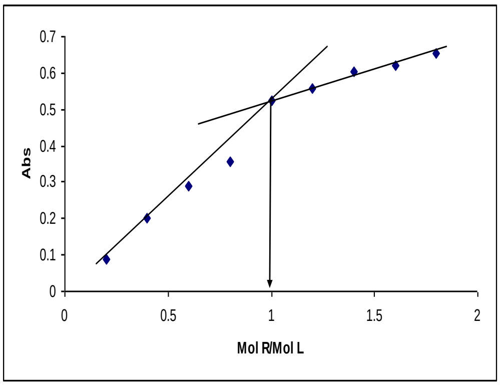


Fig 9: Mole ratio of reagent to sample for the Pd(II) complex .

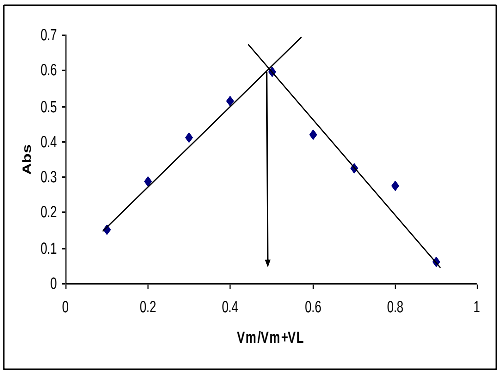


Fig 10: Job's method of the Pd(II) complex .

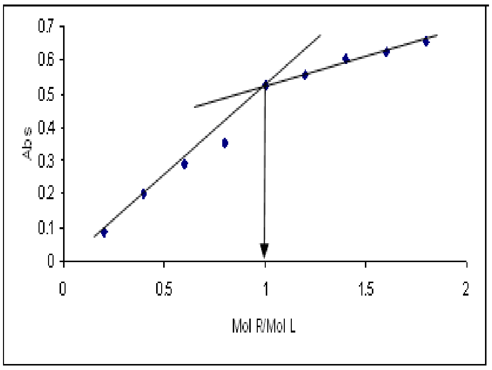


Fig 11: Mole ratio of reagent to sample for the Pt (II) complex .

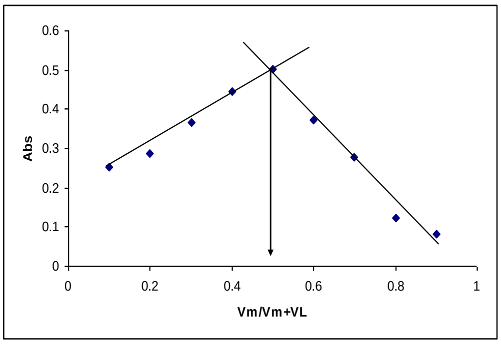
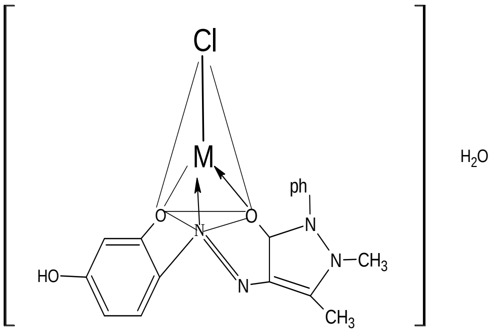


Fig 12:- Job's method of the Pt(II) complex .



Where M = pd $^{2+}$, pt $^{2+}$

Fig. 11: The proposed structural formula of metal complexes

Application

The digest samples were analyzied by atomic absorption and UV-visible spectrophotometeric methods[17] .The results abtained are given in Table (6).

Table 6. Determination of Pd(II) and Pt(II) in dust of Iraq

Sample	atomic absorption µg.g^{-1} Pd(II) Pt(II)	This work µg.g^{-1} Pd(II) Pt(II)
AL –Najaf dust	0.009 0.082	0.008 0.093
AL –Muthana dust	0.008 0.065	0.007 0.073

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التقدير الطيفي المايكروي للبلاديوم الثنائي والبلاتين الثنائي بأستعمال البايرزولون ازو ريزور سينول

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الخلاصة:

تم تطوير طريقة طيفية جديدة سريعة وحساسة في تقدير الكميات الضئيلة من ايونات Pd(II) و Pt (II) باستعمال الكاشف 4- (4 ̎ – بايرازولون ازو) ريزوسينول واعتمدت الطريقة على عملية التعقيد الحاصل بين ايونات Pd و Pt والكاشف حيث تكونت معقدات ذائبة لها أعلى امتصاص عند الاطوال الموجية595 نانوميتر و464 نانوميتر لمعقدات البلاديوم والبلاتين على التتابع وكانت قيم معامل الامتصاص المولاري للمعقدات 1.11×10^{4} مول$^{-1}$سم$^{-1}$ لتر 1.35×10^{4} مول$^{-1}$ سم$^{-1}$ لتر لكل من معقد البلاديوم الثنائي والبلاتين الثنائي وتراوح مدى العلاقة الخطية بين الامتصاص والتركيز بين 0.2 -1.4 جزء بالمليون لمعقد البلاديوم ولمعقد البلاتين0.2-3.2 جزء بالمليون كذلك تم دراسة انتقائية الطريقة عن طريق التداخلات الأيونية الموجبة والسالبة وكانت ثوابت استقرار المعقدات المحضرة هي 0.5×10^{5} لمعقد البلاديوم و 0.4×10^{4} لتر مول$^{-1}$ لمعقد البلاتين . تم إجراء تطبيق للطريقة التحليلية بالاعتماد على تقدير كمية الايونات قيد الدراسة في عينات من غبار محافظة النجف الاشرف ومحافظة المثنى وتم اخذ هذه العينة من المناطق التي تعرضت للقصف لبيان مدى تلوث المحافظات قيد الدراسة بهذه الايونات .