Propericizaine as a Selective and Sensitive Reagent for the Spectrophotometric Determination of Microgram Amounts of Platinium in Minerals

A.Thimme Gowda

Haranahalli Ramaswamy Institute of Higher Education. Behind Akshavani, Salagame Road,
Hassan-573201, Karnataka, India.
ankapuratgowda@rediffmail.com

Abstract

Propericiazine(PPC) is proposed as a new sensitive and selective reagent for the spectrophotometric determination of microgram amounts of platinum. PPC forms a pink complex with platinum(IV) at room temperature (26 ± 2^{0} C) in hydrochloric acid - sodium acetate buffer medium containing copper (II) ions. The complexation is complete within 10 min. The complex exhibits an absorption maximum at 520 nm with a molar absorptivity of 1.204 X10^4 liters mol^{-1}cm^{-1}. Beer's law is obeyed over the concentration range 0.5-12.2 ppm of platinum. A 50-fold molar excess of the chromogenic regent is necessary for the development of maximum colour Intensity. Job's method of continuous variation, the molar ratio method, and the slope- ratio method indicate a 1:1 composition for the complex. The effects of pH, time, temperature, reagent concentration, order of addition of reagents and interference for various ions are reported. The reagent has been used successfully for the determination of platinum in minerals and alloys.

Keywords: Spectrophotometry, Platinum, Propericiazine

---

1 Introduction

Beamish and Van Loon [1] have discussed the disadvantages of several spectrophotometric methods proposed for the determination of platinum. Many methods involve either heating the solution or allowing it to stand for a long time for maximum colour development. For example, acenaphthenequinone monoxide [2], 1-phenyl-3-(thibenzyl) - thiourea [3], 3, 4 – diaminobenzoic acid [4], o-hydroxythiobenzhydrazide [5], phthalimide bis (thiosemicarbazone) [6], 2, 3′ – diaminodiphenyl disulphide [7], 2 – pyridyl – 2 – thienyl β –ketoxime [8], and 4 – (2-pyridylazo) resorcinol [9], require heating for periods varying from 10 min to 5 hr. Reagents such as 2 – aminophenol – 4- sulphonic acid [10], 2,3 – quinoxalinedithiol [11], promethazine hydrochloride [12], selenocyanato mercury (II) ion [13] and di – thiooxamide [14] require 20 min. to 20 hr. at room temperature in order to develop maximum colour. Other reagents such as $SnCl_2$ [15], 4-nitrosodimethylaniline [16],5-(4-dimethylaminobenzylidine)rhodanine [17]. o–phenylenediamino [18], thiobenzhydrazide [19], and phenanthrenequinone monosemicarbazone [20] cannot tolerate interferences from base and other platinum group metals.

In this paper, we report an investigation of the complexation reaction between platinum (IV) and propericiazine (PPC). We have developed a method, using PPC as a sensitive colouring reagent, for the spectrophotometric determination of platinum(IV) in solution in the presence of large amounts of other metal ions.

2 Materials and Methods

2.1 Reagents

Platinum (IV) solution: A known weight of platinum wire (99.99% pure) was dissolved in hot aqua regia and the solution was evaporated almost to dryness. The residue was treated with 5 ml of concentrated hydrochloric acid and evaporated to a small volume. This treatment was repeated 5 times in order to destroy any nitroso complexes formed. The resulting residue after final evaporation was then dissolved and diluted to 1 liter with 1 M hydrochloric acid. Appropriate dilutions of the stock solution were made as needed.

Propericiazine solution: A 0.5% (m/v) solution of PPC was prepared in doubly distilled water and stored in an amber bottle in a refrigerator.

Cu (II) solution: An aqueous solution of Cu(II) (0.1 M) was prepared from copper (II) sulphate (Analar).

Buffer solutions: Walpole buffer solutions in the pH range of 0.65-5.2 were prepared using 1 M sodium acetate and 1 M hydrochloric acid.

All other reagents were of analytical grade.

2.2 Apparatus

A Beckman Model DB spectrophotometer with stoppered silica sells of 1-cm optical path was used for all absorbance measurements. An Elico L_1-10pH meter was used for pH measurements.

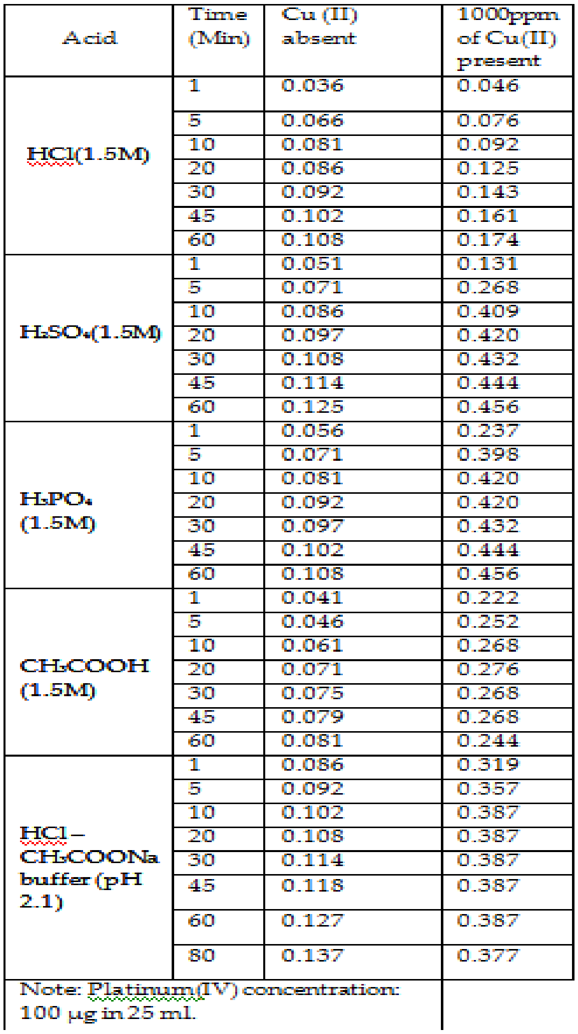
2.3 Procedure for the Determination of Platinum (IV)

To an aliquot of the sample solution containing 12.5-305 µg of platinum(IV) were added 5 ml of sodium acetate –hydrochloric acid buffer of pH 2.1, 1 ml of 0.1 M Cu(II) solution and 3.0 ml of 0.5% PPC solution. The solution was diluted to 25 ml with doubly distilled water, mixed thoroughly, and the absorbance measured at 520 nm against a reagent blank solution after 10 min. The platinum concentration of the sample solution was determined using a standard calibration curve.

3 Results and Discussion

PPC is soluble in water, giving a colourless solution. Preliminary experiments showed that PPC reacts with platinum (IV) slowly at room temperature (26±2°C) in hydrochloric, sulphuric, phosphoric, or acetic acid or hydrochloric acid-sodium acetate buffer to form a pink complex. PPC formed a complex with platinum (IV) rapidly in the presence of copper (II), which appeared to act as a catalyst. The sensitivity and stability of the pink platinum-PPC complex depended on the nature and concentration of the medium. The absorbance was found to increase with increasing concentration of sulphuric or phosphoric acid. Hydrochloric acid favoured the react reaction between copper (II) and PPC. The reaction was less sensitive in acetic acid. Nitric acid could not be used as it oxidized PPC even in the absence of copper (II). The results in table 1 show the constant absorbance readings obtained after a reaction time of 10 min in hydrochloric acid- sodium acetate buffer medium. This buffer medium was, therefore, selected for further studies.(Table-1)

Table 1. Effects of acids, Buffer Solution, Time and Copper Ions on the Absorbance of Platinium-PPC Complex (absorbance at λ = 520 nm)



Acid	Time (Min)	Cu (II) absent	1000ppm of Cu(II) present
HCl(1.5M)	1	0.036	0.046
	5	0.066	0.076
	10	0.081	0.092
	20	0.086	0.125
	30	0.092	0.143
	45	0.102	0.161
	60	0.108	0.174
H_2SO_4(1.5M)	1	0.051	0.131
	5	0.071	0.268
	10	0.086	0.409
	20	0.097	0.420
	30	0.108	0.432
	45	0.114	0.444
	60	0.125	0.456
H_3PO_4 (1.5M)	1	0.056	0.237
	5	0.071	0.398
	10	0.081	0.420
	20	0.092	0.420
	30	0.097	0.432
	45	0.102	0.444
	60	0.108	0.456
CH_3COOH (1.5M)	1	0.041	0.222
	5	0.046	0.252
	10	0.061	0.268
	20	0.071	0.276
	30	0.075	0.268
	45	0.079	0.268
	60	0.081	0.244
HCl – CH_3COONa buffer (pH 2.1)	1	0.086	0.319
	5	0.092	0.357
	10	0.102	0.387
	20	0.108	0.387
	30	0.114	0.387
	45	0.118	0.387
	60	0.127	0.387
	80	0.137	0.377
Note: Platinum(IV) concentration: 100 µg in 25 ml.			

3.1 Spectral Characteristics

The absorption spectra of platinum - PPC complex, reagent blank, and platinum (IV) solution are presented in Fig. 1. The complex exhibits maximum absorbance at 518- 522 nm. The absorption spectra of platinum(IV) solution and the reagent blank under similar conditions show that they do not absorb appreciably at this wavelength, thus providing an excellent condition for platinum(IV) determination. All subsequent studies were made at 520 nm.

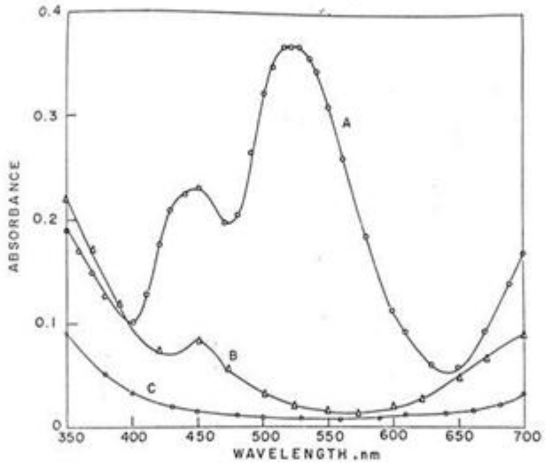


Figure 1. Absoption Spectra

(A) Platinum-PPC complex
(Pt: 6ppm, 3ml of 1% ppc, 1000ppm Cu(II), pH2.1: NaAc-HCl, λ:520nm)
(B) Reagent blank
(3ml of 1% ppc, 1000ppm Cu(II), pH2.1: NaAc-HCl, λ:520nm)
(C) Platinum (IV)
(Pt: 6ppm,), pH2.1: NaAc-HCl, λ:520nm)

3.2 Optimal Conditions of Colour Development

Effect of pH: The effect of pH on the absorbance of the complex was studied by using hydrochloric acid - sodium acetate buffer with solutions containing 100 µg of platinum(IV), 3ml of 0.5% PPC, and 1 ml of 0.1M copper(II) sulphate in 25- ml volumetric flasks. The optimal pH range was found to be 0.65-3.61. The absorbance of the complex decreased above pH 3.61. A buffer medium of pH 2.1 was, therefore, chosen for all further studies.

Effect of Cu(II) concentration: It was observed that PPC formed a complex with platinum(IV) after 10min in the presence of copper(II), which did not react with PPC but appeared to act as a catalyst. The optimal copper concentration was found to be 500-2000 ppm. With less than 500 ppm of copper (II) present, the development of the maximum colour was very slow. Above 2000 ppm of copper(II), the absorbance value slightly increased with increase in the concentration of copper(II) (Table 2). Hence, a concentration of 1000 ppm of copper(II) was chosen for all further work.

Table 2. Effect of Copper (II) Concentration on Formation of the Complex[a]

Copper(II) (ppm)	Absorbance at 520 nm[b]	Copper(II) (ppm)	Absorbance at 520nm[b]
0	0.102	1200	0.387
100	0.215	1500	0.387
300	0.357	2000	0.387
500	0.387	2300	0.392
700	0.382	2500	0.409
1000	0.387	3000	0.420

[a] Platinum(IV) concentration: 100 µg in 25ml hydrochloric acid- sodium acetate buffer of pH: 2.1.
[b] Absorbance recorded after 10 min

Effect of reagent concentration: The effect of PPC concentration was investigated by measuring the absorbance at 520 nm of solutions containing 4 ppm of platinum (IV) and varying amounts of the reagent in pH 2.1 buffer. A 50-fold molar excess of the reagent over platinum was required for maximum absorbance. A total of 1.5 ml of 0.5% reagent solution in a final volume of 25 ml sufficed for solutions containing less than 4 ppm of platinum (IV) (Table 3).

Effect of time and temperature: The maximum colour of the complex developed in 10 min after mixing the reagents. An essentially constant absorbance was obtained for over atleast 40 min. There was no appreciable change in the absorbance or colour of the complex if the order of addition of the reactants was varied. The formation of the complex was investigated at temperature in the range of 5-68^{0}C. The absorbance values were not affected by temperature in the range of 10-52^{0}C. Above 52^{0}C the absorbance gradually decreased with an increase in temperature.

Table 3. Effect of Reagent Concentration on the Absorbance of the Complex

Molar excess of PPC over Platinum [a]	Absorbanc at 520nm [b]	Molar excess of PPC over Platinum	Absorbanc at 520nm [b]
10	0.229	60	0.387
20	0.268	70	0.387
30	0.292	80	0.393
50	0.387		

[a] Platinum (IV) concentration =4 ppm.
[b] Absorbance recorded after 10 min.

3.3 Beer's law and sensitivity of the reaction

Beer's law was obeyed in the range 0.5-12.2 ppm of platinum. The optimal concentration range for the effective spectrophotometric determination of platinum, evaluated by Ringbom's [21-22] was 0.8-11.8 ppm. For log $I_0/I = 0.001$ (where I_0 is the intensity of monochromatic radiation falling on absorbing species and I is the intensity of monochromatic radiation transmitted by absorbing species), the sensitivity of the reaction, calculated from Beer's law data, was 16.20 ng cm^{-2}. The molar absorptivity, €, of the complex is 1.204 X 10^{4} liters mol^{-1} cm^{-1}.

3.4 Precision and accuracy

The precision and accuracy of the method were studied by analyzing solutions containing known amounts of platinum(IV) in the absence of other possibly interfering metals. The results are presented in Table 4.

3.5 Stoichiometry of the platinum(IV) - PPC complex

The stoichiometry of the complex was found by job's method of continuous variation with equimolar solutions [23-24], the molar –ratio method [25], and the slope-ratio method [26]. Job's method showed the stoichiometric ratio of platinum - PPC to be 1:1 and this was confirmed by the molar- ratio and slope-ratio methods, too. The stability constant of the complex, evaluated by the molar-ratio method was log K= 5.63 ± 0.1 at 27^{0}C.

Table 4. Precision and Accuracy in the Determination of Platinum

Amount of platinum (IV) (ppm)		Relative error (%)	SD (ppm)
Taken	Found [a]		
1.00	1.01	+1.00	0.0055
2.00	2.006	+0.30	0.0035
3.00	2.98	-0.66	0.0109
4.00	3.99	-0.25	0.0028
5.00	5.08	-1.60	0.0110
6.00	5.91	-1.50	0.0072

[a] Average of 10 determination.

3.6 Nature of the complex

The nature of the complex was studied by passing an aliquot of the complex through the cation-exchange resins Amberlite IR-120(H^{+}) and Dowex 50W-X8. The complete removal of the colour of the solution by the ion-exchange resins indicated that the complex was cationic species.

3.7 Interference Study

In order to assess the possible analytical applications of the proposed method the effects of foreign ions that often accompany platinum were studied. For these studies different amounts of ionic species were added to 150 μg of platinum (IV) solution contained in 25-ml volumetric flasks and the colour was developed as outlined in the procedure.

An error within ±2% in the absorbance reading was considered tolerable. Platinum (6 ppm) can be determined in the presence of large amounts of cadmium(II), zinc(II), selenium(IV), aluminium(III), cobalt(II), nickel(II), titanium(IV), sulphate, nitrate, citrate, tartrate, fluoride, bromide, EDTA, or oxalate; 200ppm of rhodium(III) or iridium(III); or 40 ppm of osmium(VIII). Interference from iron(III), palladium(II), and ruthenium(III) can be reduced using citrate, dimethylglyoxime, and EDTA as masking agents (table 5). Among anions iodide and thisulphate interfered seriously (Table 5).

Table 5. Interference of Foreign Ions in the Determination of Platinum

Ion added	Tolerance limit [b] (ppm)	Ion added	Tolerance limit [b] (ppm)
Zn (II)	4000	Ti(IV)	250
Cd (II)	4000	W(VI)	100
Al (III)	1200	Rh(III)	240
Co (II)	600	Ir(III)	240
Ni (II)	600	Fluoride	1000
Fe(III)	1.0	Bromide	3000
Fe (III)	40.0 [c]	Iodide	0.3
Pb (II)	100		
Au(III)	0.5	Nitrate	10000
Pd(II)	3.5[d]	Sulphate	10000
Ru(III)	6.2	Phosphate	5000
Ru(III)	34.0[e]	Thiosulphate	0.2
Os(VIII)	100	Oxalate	1500
Ag(I)	1.8	Citrate	2000
Cr(III)	80	Tartrate	1200
Se(IV)	700	DMG	180
Te(IV)	150	EDTA	1400

[a] platinum (IV) concentration = 4 ppm.

[b] Amount causing an error of less than 2%

[c] In the presence of 1500 ppm of citrate.

[d] In the presence of 150 ppm of dimethylglyoxime.

[e] In the presence of 1200 ppm of EDTA.

4 Applications

Analysed samples of platinum-iridium (10-40% iridium), platinum-tungsten (4% tungsten), and platinum –nickle (40-55% nickel) alloys, platinum-rhodium (10-20% rhodium) thermocouple alloy, and nevjanskite mineral (8-12% platinum, 62-65 % iridium, 13-14% osmium, 2-3 % rhodium, and 1% ruthenium) were not available. Therefore, synthetic mixtures containing platinum and other metals corresponding of these alloys and nevjanskite were prepared and the platinum content was determined by following the standard procedure. The results are given in Table 6.

Table 6. Determination of Platinum in Synthetic Mixtures Corresponding to Alloys and Nejanskite

Mixture	Pt taken (ppm)	Metal ion added (ppm)						Pt found (ppm)
		Rh	Ir	Os	Ru	W	Ni	
Pt-Ir alloy	3.5	-	1.5	-	-	-	-	3.54
	4.0	-	1.0	-	-	-	-	4.00
	4.5	-	0.5	-	-	-	-	4.49
Pt-W alloy	2.0	-	-	-	-	0.09	-	2.01
	3.0	-	-	-	-	0.14	-	3.00
	5.0	-	-	-	-	0.23	-	5.03
Pt-Ni alloy	3.0	-	-	-	-	-	2.0	3.00
	4.5	-	-	-	-	-	4.0	4.52
	6.0	-	-	-	-	-	5.5	5.96
Rh thermo- couple allo	4.0	1.0	-	-	-	-	-	4.01
	4.5	0.5	-	-	-	-	-	4.46
	6.0	1.5	-	-	-	-	-	6.05
Nevjan- skite mineral	3.0	0.8	16.0	3.5	0.3	-	-	2.98
	4.0	1.0	31.0	6.5	0.5	-	-	4.02
	5.0	1.5	32.5	7.0	0.5	-	-	

Average of 5 determinations.

5 Conclusion

Although many reagents for the colourimetric determination of platinum are known, comparatively few are well suited for the purpose. PPC is more sensitive than acenapthenequinone monoxise [2], chlorfurthizene [27], perazine [28], promethazine hydrochloride [12], and 1-(2-pyriylazo)-2-naphthol [29] which have been proposed as sensitive reagents for platinum (IV). The major advantage of the platinum –

PPC complex is that the maximum colour intensity is attained within 10 min after mixing the reagents at room temperature where as in most other methods heating or standing for a long time is necessary. The proposed method offers the advantages of simplicity, rapidity, reasonable selectivity and sensitivity, without the need for an extraction step or heating the solution.

Acknowledgments: The author thanks May and Baker Private Ltd., Mumbai, India, for supplying pure PPC as gift sample.

6 References

[1]. Beamish, F. E.; Van Loon, J. C. Recent Advances in the Analytical Chemistry of the Noble Metals, Pergaqmon, Oxford, 1972.

[2] Sindhwani, S. K.; Singh, R. P. Acenaphthenequinone monoxide as Selective Reagent for Spectrophotometric Determination of Platinum(IV) by Solvent Extraction. Talanta. 20; 248-251, 1973.

[3] Uttarwar, R.M.; Joshi, A. P. Extraction Spectrophotometric Determination of Platinum(IV) with 1-Phenyl-3-(thiobenzyl)thiourea. Z. Anal Chem. 287; 317, 1977.

[4] Keil, R. High Selective Rapid Spectrophotometric Determination of Platinum with 3, 4-Diaminobenzoic acid. Z. Anal. Chem. 254; 191-192, 1971.

[5] Gangopadhyay, P.K.; Das, H.R., Shome, S.C. The Spectrophotometric Determination of platinum(IV) with 0-hydroxythiobenzhydrazide. Anal. Chim.Acta.66; 460-463, 1973.

[6] Guzman. C.M.; Perez, B.D.; Pino, P.F. Phthalimide bis(thiosemicarbazone) as Analytical Reagent. I. Photometric Determination of Platinum. An. Quim . 70; 828-832, 1974.

[7] Bag, S. P.; Chakrabarthi, S. K. 2,2′-Diaminodiphenyl disulphide- a Sensitive Spectrophotometric Reagent for Platinum. Talanta . 24; 128-129, 1977.

[8] Beupre, P. W.; Holland, W. J.; Notenboom, H. R. Pyridine Ketoximes as Analytical Reagents XIX. Spectrophotometric Determination of Traces of Platinum with 2-pyridyl-2-thienyl-β-ketoxime. Mikrochim. Acta. 1979; I (3-4), 303-310

[9] Ivanov, V. M.; Gorbunova, G. N. The Spectrophotometric Determination of Platinum with 4-(2-pyridylazo) Resorcinol. Zh. Anal. Khim. 1980; 35, 3363-3368.

[10] Majumdar, A. K.; Sen Gupta, J. G. Spectrophotometric Determination of Platinum with 2-Aminophenol-4-sulphonic acid. An. Anal. Khim. 1960; 177, 265-268

[11] Janota, H.F.; Ayres, G. H. Simultaneous Spectrophotometric Determination of Palladium and Platinum with 2,3- quinoxalinedithiol. Anal. Chem. 1964; 36, 138-140

[12] Sanke Gowda, H.; Padmaji, K. A. Spectrophotometric Studies on Platinum-Promethazine hydrochloride Complex Microchem. J. 1980; 25, 396-402

[13] Bosch, S.F.; Rodriquez, P.D.; Guardiola, Saenz, J L. The Selenocyanatomercury(II)cation as analytical reagent: Spectrophotometric determination of platinum. Inf . Quim Anal. 1971; 25, 91-98

[14] Gawali, S. B.; Shinde, V.M. Spectrophotometric Determination of Platinum(IV) using Dithiooxamide as reagent. Z. Anal. Chem. 1976; 280, 29

[15] Ayres, G. H. Evaluation of Accuracy in Photometric Analysis. Anal. Chem. 1949; 21, 652-675

[16] Kirkland, J.J.; Yoe, J.H. Spectrophotometric Study of p-Nitrosodimethyl Aniline. Anal. chem. 1960; 26, 1340-134

[17] Piercy, F. E.; Ryan, D. E. The Colorimetric Determination of Platinum with 5-(p-Dimethylaminobenzylidine)-rhodanine. Canad. J. Chem. 1963; 41, 667-670

[18] Golla E.D.; Ayress G. H. Spectrophotometric Determination of Platinum with o-Phenylenediamine. Talanta. 1973; 20, 119-120

[19] Gangopadhyay, S.; Gangopadhyay, P. K.; Shome, S C. Extraction and Spectrophotometric Determination of Platinum(IV) with Thiobenzhydrazide. Z. Anal.Chem. 1976; 281, 143

[20] Kamil, F.; Sindhwani, S. K.; Singh, R.P. Phenanthrenequinone monosemicarbazone as Reagent for Microdetermination of Iridium(III) and Platinum(IV). Ann. Chim. (Rome). 1980; 70, 241-256

[21] Ayres, G. H.; Meyer, A. S Spectrophotometric Study of Platinum (IV) and Tin (II) chloride System Anal. Chem. 1951; 23, 299-304

[22] Ringbom, A. Accuracy of Colorimetric Determinations." Z. Anal. Chem. 1939; 115, 332-343

[23] Irving, H.; Pierce, T. B. Observations on Job's Method of Continuous Variation and its Extension to Two-Phase Systems. J. Chem. Soc. 1959; 109, 2565-2574,

[24] Job, P. Spectrographic Study of the Formation of Complexes in Solution and their Stability C. R. Hebd, Seances Acad. Sci. 1925; 180, 928-930

[25] Yoe, J. H.; Jones, A. L. Colorimetric Determination of iron with disodium 1, 2-dihydroxybenzene-3, 5-disulfonate. Ind. Eng. chem. Anal. Ed. 1944; 16, 111-115

[26] Harvey, A. E.; Manning, D. L. Spectrophotometric Methods of Establishing Empirical Formula of Colored Complexes in Solution. J. Amer. Chem. Soc. 1950; 72, 4488-4493

[27] Kerentseva, V. P.; Lipanova, M.D.; Mas' ko, L. I. Spectrophotometric Determination of Palladium and Platinum with Chlorfurthizene [the thiosemicarbazone of 3-(5-chloro-2-furyl) acrylaldehyde]." Zh. Anal. Khim. 1972; 27, 1561-1565

[28] Sanke Gowda, H.; Jagdeesh, K.S. Spectrophotometric Method for the Rapid Determination of Micro-gram Amounts of Platinum."Analyst. 1979; 104, 400-406, 1979.

[29] Ivanov, V. M.; Pigurovskaya, V. N.; Busev, A.I. Spectrophotometric Determination of Platinum and Palladium with 1-(2-Pyridylazo)-2-Naphthol in Binary System. Zavod. Lab. 1972; 38, 1311-1313,