Spectrophotometric Method of the Determination of Gold (III) by Using Imipramine Hydrochloride and Promethazine Hydrochloride

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Imipramine hydrochloride [IPM·HCl] and promethazine hydrochloride [PMT·HCl] were used for the spectrophotometric determination of gold (III) in the aqueous solution. The halides complexes of gold (III) created a coloured coupling with the studied drugs which were extractable in chloroform. These new compounds were characterised by IR, UV-VIS spectra and thermal and elemental analysis. Rapid and sensitive spectrophotometric method for the determination of gold (III) in the aqueous solution is described. The absorbance was found to be linear function of the gold (III) concentration in the range from 0.2 to 20 x 10^{-1} mg. The ratio of complex $[AuX_4]^-$ to the organic cation from drug in the obtained compounds was determined as 1:1. The method was satisfactorily applied to the analysis of gold (III). A great advantage of the proposed method is that the trace amounts of gold (III) can also be examined.

Key words: Imipramine hydrochloride, Promethazine hydrochloride, Gold(III) halides complexes.

Introduction

One of the aims of contemporary analytical chemistry is the elaboration of more rapid, sensitive and efficient methods of determination of compounds and elements. It is known, that the derivatives of the 5H-dibenz[b,f]azepine and phenotiazine are created with some metals complexes, the coloured coupling (Dembinksi 1977; Tarasiewicz *et al* 1999; Misiuk 1999; Ramappa 1999). There are imipramine hydrochloride and promethazine hydrochloride in these groups. These compounds are used as the psychotropic drug in the medicine (Pawelczyk 1986). However, they were used most often for the determination of trace amount of some metals (Dembinski 1983; Puzanowska-Tarasiewicz 1998; Dembinski and Szydlowska-Czerniak 1999).

Many analytical procedures are used for determination of Gold (III). They are gravimetric (Donova and Siftar 1993), titrimetric (Abramovic B.F. *et al* 1999), voltammetric (Basu *et al* 1980) and spectrophotometric methods (Prakash *et al* 1986; Rakhmatuullaeu and Giyaru 1989; Patroescu *et al* 1989; Gurjeva and Savvin 1989). Moreover, the new methods of gold (III) determination are used, often. However these methods, such as electrochemical (Karolczyk 1996), AAS (Zaikm *et al* 1989) and neutron scattering (Ivanenko *et al* 1989), are expensive.

The aim of the present paper is to elaborate quick and well method of determination of gold (III) in the aqueous solutions. Au (III) forms negatively charged anionic complexes with the halides (Cl, Br, I). Anionic gold(III) halide complexes with promethazine [10-(2-dimethylaminopropyl) - phenothiaz-

ine] and imipramine [{5-(3-dimethylaminopropyl)-10, 11-dihydro-5H-dibenz [b, f] azepine}] in the hydrochlorides form can be used for a new complexing agents (Gowda and Ramappa 1976). The obtained compounds were intensively coloured and thermal stable, so they can be applied in a spectrophotometric and weight methods of gold(III) determination. The obtained coupling will be characterised by IR and UV-VIS spectra and elemental and thermal analyses.

Experimental

Reagents: Imipramine hydrochloride (99%) -aqueous solution: 0.1 x 10^{-1} mol and 1.0 x 10^{-4} mol, Promethazine hydrochloride (99%) aqueous solutions: 0.1 x 10^{-1} mol and 1.0 x 10^{-4} mol, Promethazine hydrochloride (99%) and imipramine hydrochloride (99%). These were purchased from Aldrich and used without purification.

The concentration of the gold as $[AuCl_4]^-$ was 3.2931 x 10^{-2} mol.

Gold atomic absorption standard solution: 1 µg of Au in 5 wt.% HCl, Potassium iodide - solution 10%, Potassium bromide - solution 10%. All used chemicals were analytical grade purchased from POCH Gliwice.

Apparatus: Spectrophotometer UV-VIS-Shimadzu 1601 PC; Spectrophotometer IR; -Spectrum 2000 FT Perkin Elmer; Derivatograph - MOM-OD-102; Spectrometer AAS Philips PV 9100X.

Preparation and composition of the halide complex of gold (III) with the drugs: The 100 ml of the 3.293 x10^{-2} mol x 1^{-1} tetrachloroaurate (tetrabromoaurate, tetraiodoaurate)

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were added to the 10 ml of 2 x 10^{-1} mol of sulphuric acid and 100 mol of 0.1 x 1^{-1} mol imipramine hydrochloride (or promethazine hydrochloride). The drugs were added by small portions the reaction solutions were intensively mixed, the precipitates were formed very quickly. The colours of these compounds changed from the dark brown to the light brown, The obtained precipitates were filtered, washed with distilled water and recrystallized from methanol. The pured precipitates were studied by the elemental analysis and the IR spectroscopy.

Results and Discussion

Elemental analysis: The results of the elemental analysis are presented in the Table 1. Element analysis established the composition of the obtained compounds. The ratio of the organic cation from the drug to the gold (III) complex in the obtained precipitates was 1:1. On the basis of elemental analysis, obtained coloured compounds have the formulas [IPM H]·[AuX$_4$] and [PMT H]·[AuX$_4$], where X = Cl, Br, I.

The IR spectra. Infrared spectra were analysed to establish the character of interaction between components of the obtained species (Wojtkowiak and Chabanel 1984). These spectra were obtained using the pressed pellets of the investigated compounds with potassium bromide (ratio 3/300) and as the thin films on the polyethylene plate. The clear differences are in the range of far IR. Figure 1 presents spectra of the promethazine hydrochloride, imipramine hydrochloride and their couplings with the tetrabromoaurate complex, for example. As results from these spectra the characteristic bands of the drugs have the different positions and intensity. However, in the case of their couplings with the tetrabromoaurate ion, the spectra are the same practically. This in fact indicates, that the strong bands in this range comes from [AuBr$_4$]$^{-}$ (Puddephatt 1978).

The differences of the IR spectra in the higher range for the drugs and the studied coupling pointed on formation the new systems. Figure 2 presents IR spectra for imipramine hydrochloride and imipramine tetrabromoaurate. The characteristic bands for third order amine C$_3$N (weak in the range 2200-2500 cm^{-1}), are difficult to identify, but their hydrochlorides have the strong bands at 2500-2600 cm^{-1}. Others characteristic bands are marked by different bands. The bands characteristic for the drug hydrochloride are shifted towards lower energetic region in IR spectra of the coupling [IPM][AuBr$_4$] and their intensity which is lower. This effect is connected with the appearance of the strong interactions: Au-Br.....H-N-CH$_2$. Hydrogen bond which occurs in the crystal lattice reduces the N-H bond strength causing the above mentioned band shift. The spectroscopic investigations indicate that formation of these new compounds is the results of the exchange of chloride ion in drug for the greater gold (III) halide complex.
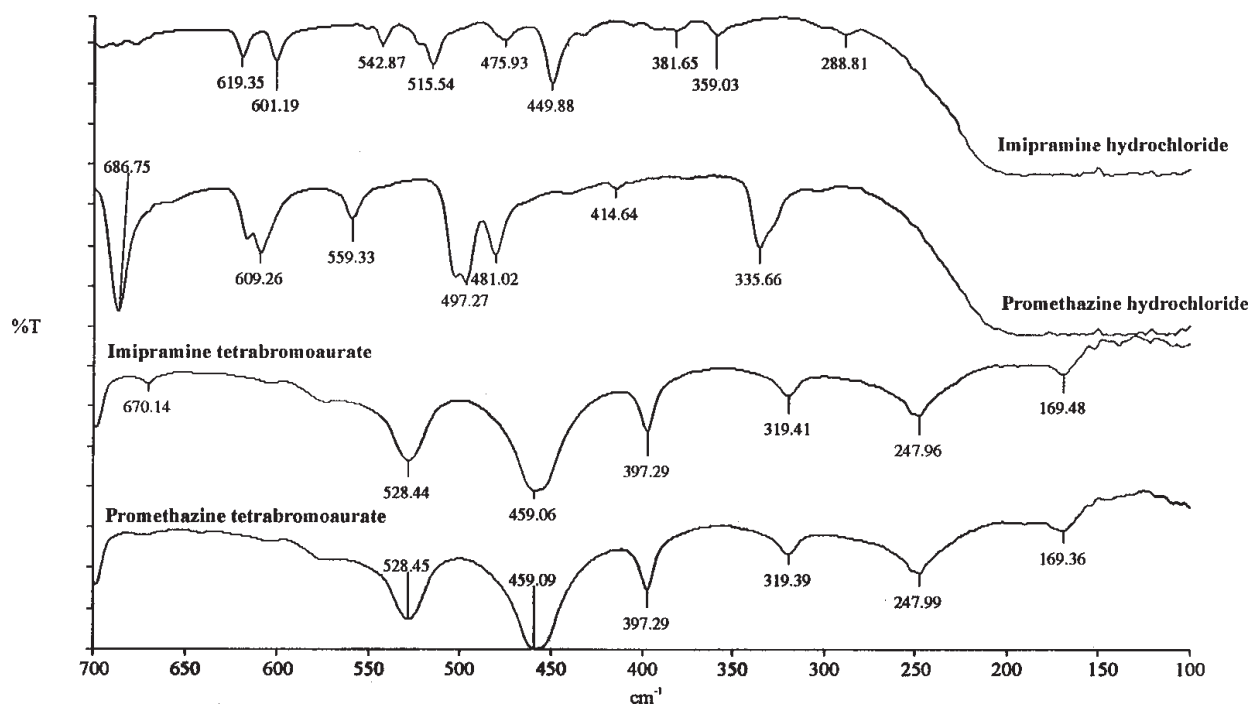
Fig. 1 IR spectra for imipramine hydrochloride, imipramine tetrabromoaurate, promethazine hydrochloride and promethazine tetrabromoaurate (thin film on PE).
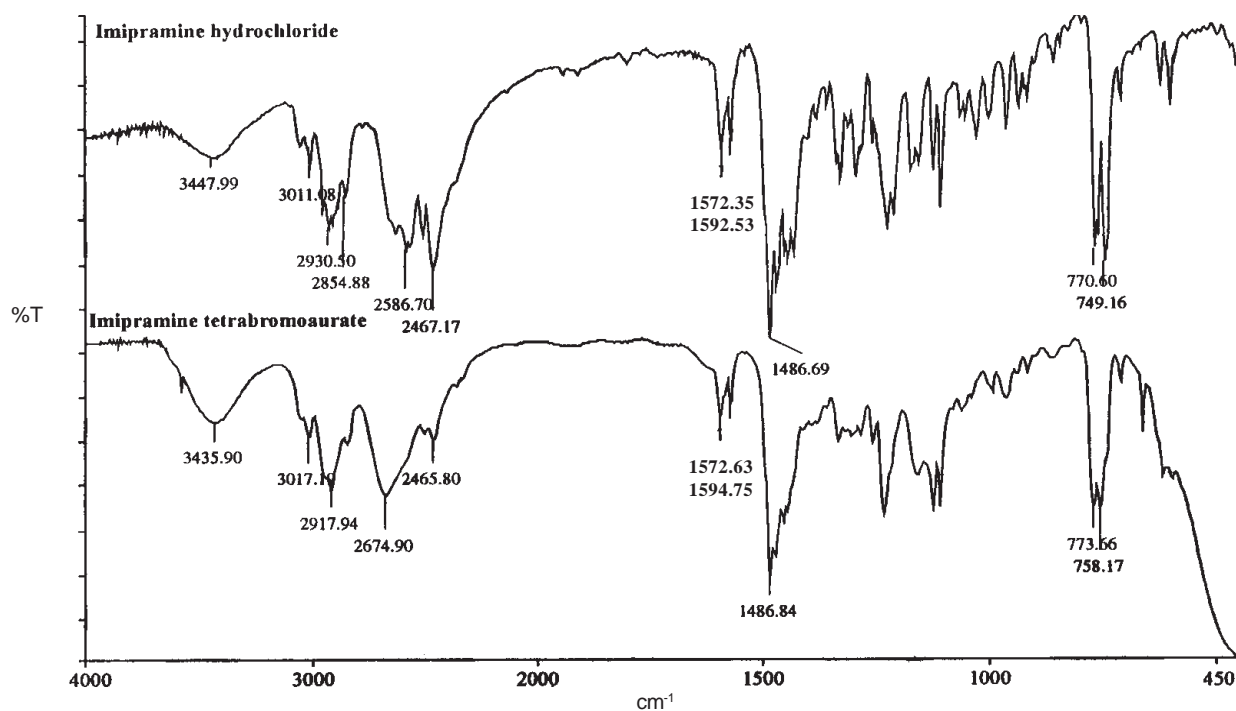
Fig. 2 IR spectra for imipramine hydrochloride and imipramine tetrabromoaurate.

Thermal analysis: For the purpose to establish the thermal stability of the obtained couplings they were made thermal studies. The conditions of these studies are as follow: the nitrogen atmosphere with the heating rate 2.5°C x min⁻¹, the temperature range from 20 to 500°C, the weight of the samples -5 mg. The sensitivity of DTA and DTG was 1/3. In Figure 3, for example, the thermal curves of [PMT·H] · [AuBr₄] are presented.

All the curves have the similar runs. The runs of TG and DTG point that created couplings are about to stable [PMT.H]. [AuCl₄] -230 ; [PMT·H] · [AuBr₄] - 220 °C; [PMT·H] · [AuI₄]-200 °C; [IPM·H] · [AuCl₄] -215 °C; [IPM·H]·[AuBr₄] - 205 °C; [IPM·H] · [AuI₄] - 190 °C. The thermal degradation takes place at the different temperature depends on the gold (III) complex and the kind of drug.

The DTA curves of the studied compounds are more complicated. The large exothermic peaks which are before the melting and degradation temperature probably point all the intramolecular processes. The peaks at 215°C for presented coupling point the melting point, what confirms the study on the Betius table.

Analysis of UV-VIS spectra: For the purpose of the useful application of the obtained compounds to the spectrophotometric method for determination of the gold (III), it was made the spectra in the range of UV-VIS. The spectroscopic studies were made for the coloured coupling of psychotropic drug with the chloride complexes of gold (III) as the solutions in chloroform. In Figure 4, for example, the spectra of imipramine hydrochloride and tetrabromoaurate complexes with imipramine, are presented.

Table 1
The results of the elemental analysis

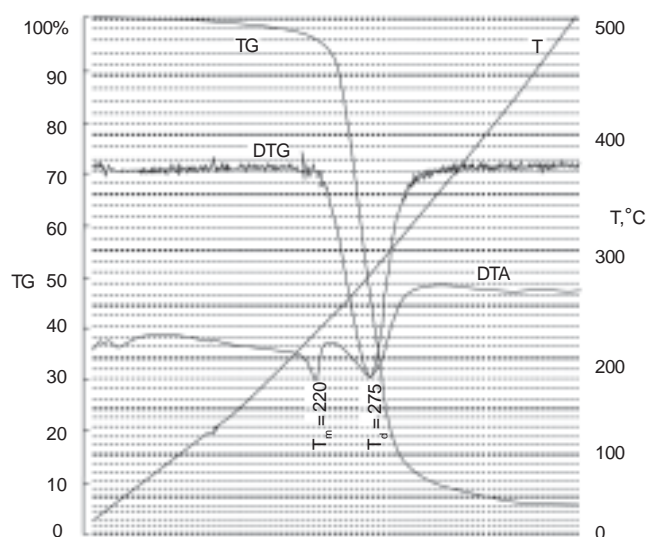| Compounds	C % calc.	det.	H % calc.	det.	N % calc.	det.	S % calc.	det.
[PMT·H] [AuCl₄]	32.70	32.85	3.37	3.42	4.49	4.51	5.13	5.11
[PMT·H] [AuBr₄]	25.45	25.50	2.62	2.68	3.49	3.60	3.99	4.08
[PMT·H] [AuI₄]	20.61	21.01	2.12	2.10	2.83	2.90	3.23	3.20
[PMT·H] [AuCl₄]	36.79	36.82	4.03	4.05	4.52	4.48	-	-
[PMT·H] [AuBr₄]	28.59	28.65	3.13	3.15	3.51	3.54	-	-
[PMT·H] [AuI₄]	23.13	23.93	2.54	2.61	2.84	2.86	-	-

Fig. 3 The thermal curves of the imipramine tetrabromoaurate.

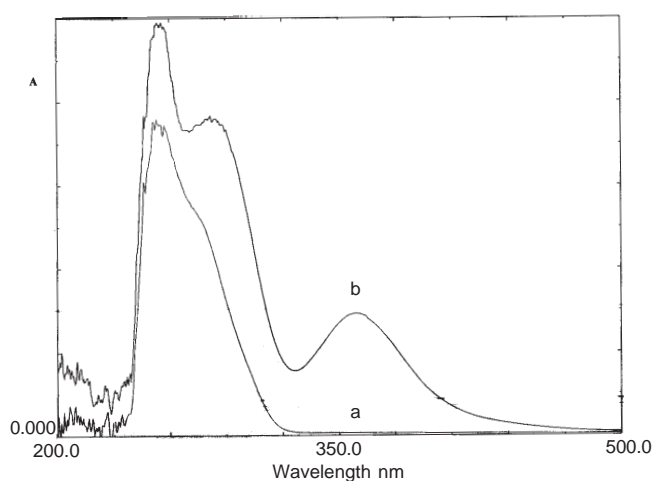**Fig. 4** UV-VIS spectra of imipramine hydrochloride (a) and imipramine tetrabromoaurate (b) (solution in $CHCl_3$).

The spectra in VIS region shows only one absorption band for all investigated compounds. This band is connected probably with the ligand - metal charge transfer (Lever 1984).

Determination of calibration curve: The solutions for the determination of the calibration curves were made for the gold (III) concentration from 0.02 to 20 x 10^{-1} mg. The gold (III) was in the form of tetrachloroaurate ion. Into the measuring flask were added 0.05 - 0.5 ml of 3.2931 x 10^{-2} mol; 0.05 - 0.5 ml of 3.2931 x 10^{-4} mol and 0.05 ml of 3.2931 x 10^{-6} mol; solution of tetrachloroaurate and 2 ml of the sulphuric acid (the concentration 2 x 10^{-1} mol). Next, it was introduced 2 ml of the drug solution (the concentration 1 x 10^{-4} mol). The contents were refilled with water to 10 ml and then was ex-

tracted with few portions of chloroform. In three times repeated extraction (each 2 extracts were filled up to 10 ml with chloroform. The chloroform solutions of studied couplings were stable for 48 hours.

The absorbance was measured at 517 nm for the promethazine coupling and at 667 nm for imipramine and was found to be a linear function of gold (III) chloride complexes in the range of 0.02 to 20 x 10^{-1} mg for promethazine hydrochloride and in the range 0.2 to 20 x 10^{-1} mg for imipramine hydrochloride. The molar absorptivity is found as $\varepsilon = 3.66$ x 10^{4} 1 x mol^{-1} for [PMT·H]·[$AuCl_4$] and $\varepsilon = 1.20$ x 10^{3} 1 x mol^{-1} x cm^{-1} for [IPM·H] [$AuCl_4$]. The data were elaborated using a linear least squares method (y = 36613.41x - 0.01247, correlation coefficient = 0.9947 for promethazine and y = 1197.35x - 0.02057, correlation coefficient = 0.9922 for imipramine).

Effect of foreign ions: Selectivity of the prepared spectrophotometric method for the determination of gold (III) was checked with the foreign ions. Results of these measurements indicate that the positive interference is caused by following ions: Cu(II), Pt(II). It was shown that the fivefold excess of the above ions influence on determination results and gives positive error 5% and more. Even fivefold and tenfold excess of such cations as: Ni(II), Co(II), Mg(II), Ca(II) and anions as: Cl^{-}, NO_3^{-}, SO_4^{2-} not interfere.

Comparison elaborated method with the AAS results: The elaborated method was tested on the gold atomic absorption standard solution: 1 µg of Au in 5% wt. HCl compared with the AAS method. The AAS method of gold (III) determi-

Table 2
Comparison determination of gold (III) with using promethazine hydrochloride and AAS method

Cotents of gold (III)				
added mg	found* mg	Standard deviation $mg \times 10^{-4}$	Relative standard deviation%	Confidence limits** mg
	a) 0.0178	5.27	2.95	0.0178 ± 6.54 x10^{-4}
0.02	b) 0.0201	1.58	0.78	0.0201 ± 1.96 x 10^{-4}
	c) 0.0199	1.58	0.79	0.0199 ± 1.96 x 10^{-4}
	a) 2.0009	1.55	0.01	2.0012 ± 1.92 x10^{-4}
2	b) 2.0005	0.95	0.01	2.0002 ± 1.18 x 10^{-4}
	c) 2.0007	1.01	0.01	2.0007 ± 1.25 x 10^{-4}
20	a) 20.0049	1.83	<0.01	20.0049 ± 0.02 x 10^{-4}
	b) 20.0017	1.27	<0.01	20.0017 ± 1.58 x 10^{-4}
	c) 20.0015	1.34	<0.01	20.0015 ± 1.66 x 10^{-4}

a) determined with IPM* HCl, b) determined with PMT* HCl, c) determined by AAS, *for five determination, **probability level 0.95

nation was made to use the cavity cathode at 242.8 nm. These results are listed in Table 2.

As shown in Table 2 the elaborated method is comparable with the AAS method in the range 0.02 to 200 x 10^{-1} mg gold concentration. The results obtained for promethazine hydrochloride were better than for impipramine hydrochloride and in excellent agreement obtained from AAS.

Conclusion. It was shown that promethazine hydrochloride and impiramine hydrochloride react with halide complexes of gold (III) in acid medium, forming intensively coloured compounds. The results of thermal studies of obtained compounds point on their thermal stability.

It has been proved that these compounds are ionic pair salt of protonated promethazine and imipramine with the $[AuX_4]^-$ in the ratio 1:1. This fact confirms the results of the elemental analysis. Moreover, the IR spectra indicates that the coupling of drugs hydrochlorides with the gold (III) halogens complexes were formed by an exchange of chloride ion in PMT·HCl or IPM·HCl for $[AuX_4]^-$ ion.

The obtained compounds can be quantitatively extracted with chloroform. Taking into account a large stability of the complex in chloroform extract. The linear dependence was found for the concentration gold (III) from 0.2 to 20 x 10^{-1} mg. The studies show that it is possible to determine imipramine and promethazine hydrochloride using halogens complexes of gold (III). The presented method of the spectrophotometric determination of gold (III) is a quick and in good agreement with the AAS method.

References

Abramovic B F, Marinkovic M M, Gaal F F 1990 Titrimetric determination of gold in some pharmaceutical preparations. *Analyst* **115** (1) 79-83.

Basu A, Mazumdar M, Shome S C 1986 Voltammetric behaviour of gold at a dithiazone modified carbon-past electrode. *Fresenius Z Anal Chem* **325** (2) 181-185.

Dembinski B, Szydlowska-Czerniak A 1999 Spectrophotometric determination of palladium(II). *Pak J Sci Ind Res* **42** (6) 310-313.

Dembinski B 1977 Oznaczanie chlorowodorkow chlorpromazyny, prometazynyl tiorydazyny za pomoca kompleksu czterojodoantymonowego. *Farm Polska* **33** 15-19.

Dembinski B 1983 Ekstrakcyjno-spektrofotometryczne ozanczanie palladu (II) jako czterojodopalladanu imipraminy. *Chem Anal (Warsaw)* **28** 161-166.

Donova I, Siftar I 1993 Separation and gravimetric determination of gold and tellurium using hydrazinum. *Acta Chim Slov* **40** (4) 343-347.

Gowda H S, Ramappa P G 1976 Spectrophotometric determination of traces of gold with N-substituted phenothiazines. *Fresenius Z Anal Chem* **280** (3) 221-227.

Gurjeva R F Savvin S B 1989 Azobenzene - azorhodamine determination as new reagents for noble and heavy metals in presence of surfactants. *Zh Anal Khim* **44** (12) 2165-2170.

Ivanenko V V, Kustov V N, Anutriv V A 1989 Neutron - activation determination of elements with over-lapping resonance in neutron absorption cross-section. Determination of gold in ores with silver. *At Energ* **66** 423-424.

Karolczyk M 1996 Selective method for the determination of gold by anodic stripping voltammetry. *Fresenius J Anal Chem* **356** 480-486.

Lever A B P 1984 Inorganic Electronic Spectroscopy, Elsevier, Amsterdam pp 343-344.

Misiuk W, Spectrophotometric determination of desipramine using ammonium peroxidsulfate and the titanium (IV) thiocyanate complex. *J Trace and Microprobe Tech* **17** (4) 425-431.

Patroescu C, Pioara F, Patroescu I 1989. New spectrophotometric method for determination of gold. *Rev Chem* **40** (7) 605-609.

Pawelczyk E 1986 Chemia Lekow PZWL, Warszawa pp 71-104.

Praksh K M M S, Prabhakar L D, Reddy D V 1986 P-Nisaldehyde 4-phenyl 3-thiosemikarbazone as analytical reagent for the extractive spectrophotometric determination of gold. *Analyst* **111** (11) 1301-1306.

Puddephatt R J 1978 The Chemistry of Gold, Elsevier, Amsterdam pp 210-223.

Puzanowska-Tarsiewiez H, Tarasiewicz M, Karpinska J, Kojlo A, Wolyniec E, Kleszczewska E 1998 Analytical application of the reaction of 2- and 10-disubstitued phenothiazines with some oxidizing agents, *Chem Anal (Warsaw),* **43** 159-178.

Rakhmatullaeu K, Giyarov A. Sh 1989 Extraction - photometric determination of gold (III) with methylene blue. *Uzb Khim Zh* **3** 5-9.

Ramappa P G 1999 Biologically active metal complexes with phenothiazine and related ligands: A review. *J Ind Chem Soc* **76** (5) 235-238.

Tarasiewicz M, Puzanowska- Tarasiewicz H, Misiuk W, Kojlo A, Grudniewska A, Starezewska B, Analytical Application of the Reaction of 2- and 10-Disubstitued Phenothiazines with Some Metals Ions. *Chem Anal (Warsaw)* **44** 137-155.

Wojtkowiak B, Chabanel M 1984 Spektrochemia molekularna. PWN Warszawa pp 235-240.

Zaikm I D, Zubova O A, Borodavkina O N 1989 Solvent extraction - flame atomic absorption determination of gold in geological samples using oil sulphides. *Zh Anal Khim* **44** (7) 1221-1226.