

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI

Publicat de

Universitatea Tehnică „Gheorghe Asachi” din Iași

Volumul 65 (69), Numărul 1, 2019

Secția

CHIMIE și INGINERIE CHIMICĂ

SIMPLE AND RAPID SPECTROPHOTOMETRIC DETERMINATION OF Au(III) IONS USING RHODAMINE B AS COLOUR REAGENT

BY

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Received: February 12, 2019

Accepted for publication: March 25, 2019

Abstract. In this study a simple spectrophotometric method is proposed for the rapid determination of Au(III) ions from aqueous solution. The proposed method use Rhodamine B as colour reagent, and the reaction occurs immediately in strong acid media (2 N HCl solution). The purple complex shows a maximum of adsorption at 520 nm, against a blank solution. The method allows the determination of Au(III) ions in a concentration range of 1.5 – 3.5 $\mu\text{g}\cdot\text{mL}^{-1}$, with a molar absorptivity of $8.71\cdot 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and a detection limit of 0.18 $\mu\text{g}\cdot\text{mL}^{-1}$. Although the method exhibits a relatively good selectivity over other heavy metals (Pb(II), Cu(II) and Cd(II)) which may be present in different real samples, the constituents of water samples drastically interfere with the determination of ions Au(III) by the proposed spectrophotometric method, which makes this method can only be used for the analysis of laboratory solutions.

Keywords: Au(III) determination; Rhodamine B; aqueous solution; spectrophotometry; simple analysis method.

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1. Introduction

Gold is one element which is very important in many industrial activities. This is the main reason why numerous studies in the literature present different uses of Au(III) ions with potential applicability in various industrial sectors (Marsden and House, 2006; Cui and Zhange, 2008).

One of the problems that need to be solved before starting experimental studies is finding a suitable analysis method for determination of Au(III) ions, both in terms of its analytical performance and cost of analysis.

In determination of Au(III) ions various analytical methods, including potentiometry (Christian, 1994), flame and electrothermal atomic absorption spectrometry (Medved *et al.*, 2004), optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS) (Pyrzynska, 2005; Emre *et al.*, 2016; Nagaraja *et al.*, 2017) can be applied for a large variety of samples. Unfortunately, many of these methods, even if they have excellent analytical performance, are either time consuming or require complicate and costly laboratory instruments. Therefore, the development of simple, rapid and inexpensive analytical methods that can be used for Au(III) ions determination is still an area of high interest, because such methods can solve this problem, at least at the level of laboratory studies.

Spectrophotometry is one of the most recommended methods for the determination of metal ions from aqueous solution. Simplicity in work, low cost and the possibility of determination of relative higher concentrations in comparison with ICP-OES or ICP-MS are some important advantages of spectrophotometric methods (Zuoto and McCreedy, 1999; Tang *et al.*, 2004; Tao *et al.*, 2017). Although there is a great variety of organic reagents that can be used for Au(III) determination by spectrophotometry, including dithizone, methiomeprazine hydrochloride, 5-(4-sulphophenylazo)-8-aminoquinoline, phenothiazine, etc. (Zuoto and McCreedy, 1999; Wu *et al.*, 2004; Fazli *et al.*, 2009), many of these lead to the formation of water insoluble complexes, and required organic media.

In this study is proposed a simple and rapid spectrophotometric method for Au(III) ions determination which does not require organic media. This method is based on the color reaction between Au(III) ions and Rhodamine B, when in strong acid media, a purple complex is formed. The reaction between Au(III) ions and Rhodamine B was first used to identify gold ions (Ripan *et al.*, 1963), but the good spectrophotometric characteristics of the formed complex allowed the development of a quantitative analysis method. Therefore, the volume of HCl used to obtain the strong acid media and the volume of Rhodamine B required to form the purple complex have been optimized, and the quantitative parameters required for the characterization of the proposed spectrophotometric method have been calculated from the experimental data. The proposed method has a moderate selectivity, but a good accuracy and

sensitivity, and can be used for the quantitative determination of Au(III) ions at least from laboratory solutions.

2. Experimental

Stock solution of $50 \text{ mg}\cdot\text{L}^{-1}$ of AuCl_3 was purchased from Sigma-Aldrich, and was used without any purification. All the working solutions were prepared from stock solution by dilution with distilled water. The solution of Rhodamine B was obtained dissolving 0.05 g of solid reagent in 25 mL ethanol (96%), and the solution was kept for at most 5 days. The strong acid media was obtained by adding an exact measured volume of 2N HCl solution. The other reagents used in this study were also of analytical grade and were used as received.

The spectrophotometric experiments were performed in 25 mL volumetric flasks, by adding 0.5 – 5.0 mL of Rhodamine B solution (0.1%), 1.0 – 3.0 mL of 2 N HCl solution (to reach the strong acid media) and variable volume of $50 \text{ mg}\cdot\text{L}^{-1}$ of Au(III) solution (0.4 – 1.6 mL). Each time, the solutions were diluted to the mark with distilled water and mix. The absorbance was measured at different wave length (320 – 600 nm), after 10 min of stand by. The spectrophotometric measurements were done with Digital Spectrophotometer S 104 D type (1 cm glass cell), against distilled water or blank solution, depending of the experiment.

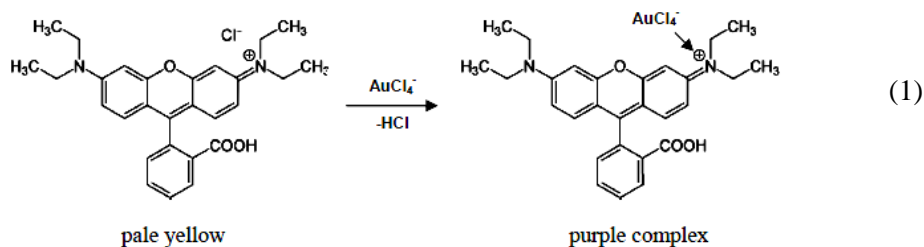
The selectivity coefficients were calculated as the ratio between Au(III) ions concentration and interfering ions concentration, which gives a 5% (0.05) absorbance change. This value was selected taking into account the technical performance of the spectrophotometer used for the absorption measurements. Validation of the proposed method was performed with tap water from the “Gheorghe Asachi” Technical University laboratories, where the Au(III) ions concentration was adjusted to a well-know value using the stock solution. After spectrophotometric analysis, the Au(III) content in these samples was determined using a prepared calibration curve.

3. Results and Discussion

The spectrophotometric method proposed in this study for Au(III) determination in aqueous media is based on the identification reaction between Au(III) ions and Rhodamine B (Ripan *et al.*, 1963), when in strong acid media, a purple complex is formed, according with Eq. (1).

Under these conditions, it is expected that the formation of purple complex between Au(III) ions and Rhodamine B to depends by:

- i) volume of HCl used to obtain the reaction media;
- ii) volume of Rhodamine B solution, which is the color reagent;
- iii) concentration of Au(III) ions from aqueous solution.



All these three factors have been analyzed one by one to obtain the optimal conditions for forming the colored complex, which can then be used in quantitative determinations.

3.1. Determination of the Optimum Volume of 2N HCl Solution

In order to obtain the optimal volume of HCl solution required for the formation of purple complex, three samples were prepared using constant concentration of Au(III) ions ($2 \mu\text{g}\cdot\text{mL}^{-1}$), constant volume of 0.1% Rhodamine B (2 mL) and various volume of 2 N HCl solution (1.0 – 3.0 mL). The VIS spectra recorded for each sample after 10 min of stand by, against distilled water are presented in Fig. 1.

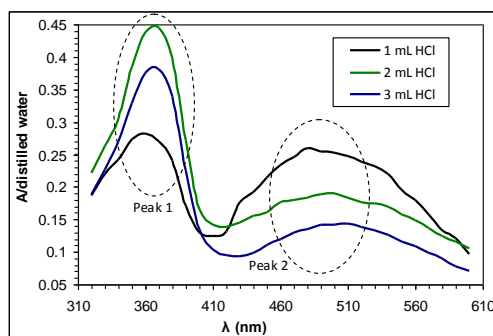


Fig. 1 – VIS spectra of Au(III)-Rhodamine B purple complex at different volumes of 2N HCl solution.

As can be seen from Fig. 1, the VIS spectra have two absorption bands. First band (Peak 1) has the maximum of absorption at 370 nm and correspond to Rhodamine B dye (which is in excess) (Dean, 1995), while the second band (Peak 2) correspond to the purple complex of Au(III) ions, and has the maximum of absorption at 510 nm. Therefore, only the variation of absorbance for the second absorption band will be taken into account, in selecting the optimum conditions.

The VIS spectra presented in Fig. 1 clearly show that the absorbance of the second absorption band decreases with increasing volume of 2N HCl solution added. This is probably due to the fact that in the formation of purple complex, HCl has only the role of ensuring the existence of gold ions as anionic species (AuCl_4^-), thus facilitating interaction with the dye molecule. When the concentration of HCl is too high, the equilibrium of purple complex formation is moved to the left, according with Eq. (1). Under these conditions, a volume of 1 mL 2N HCl solution was considered the best choice and was used in all subsequent experiments.

3.2. Determination of the Optimum Volume of 0.1% Rhodamine B Solution

Rhodamine B is a organic dye with low solubility in water, and quite hardly soluble in ethanol (Merouani *et al.*, 2010). This is the main reason why the Rodamina B solution can not have a concentration greater than 0.1%. The optimal volume of 0.1% Rhodamine B solution was determined by measuring the absorbance of five samples containing a different volume of reagent solution (0.5 – 5.0 mL), and constant concentration of Au(III) ($2 \mu\text{g}\cdot\text{mL}^{-1}$) and 2N HCl solution (1 mL). The experimental VIS spectra, recorded against distilled water after 10 min of stand by are illustrated in Fig. 2.

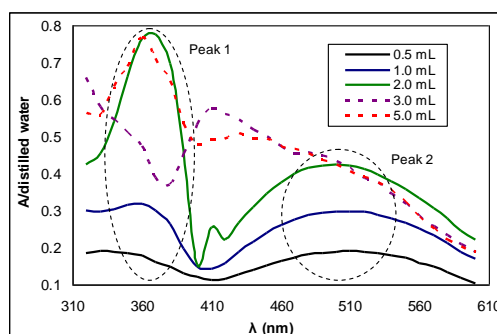


Fig. 2 – VIS spectra of Au(III)-Rhodamine B purple complex at different volumes of 0.1% Rhodamine B solution.

It can be observed from Fig. 2 that the absorbance of the band from 510 nm (Peak 2) increases with the increasing of volume of Rhodamine B solution up to 2.0 mL. Adding higher volumes of Rhodamine B solution (3.0 or 5.0 mL) causes precipitation of the Au(III)-complex and the recorded VIS spectra are significantly changed (Fig. 2). Therefore, a volume of 2 mL of 0.1% Rhodamine solution was considered sufficient to react with Au (III) ions from the aqueous solution and to provide an excess of reagent (Peak 1) so that this reaction would be quantitative.

3.3. Influence of Au(III) Ions Concentration

Fig. 3 shows the VIS spectra recorded at different initial concentration of Au(III) ions, and constant volume of 2N HCl solution (1.0 mL) and 0.1% Rhodamine B (2.0 mL). In order to minimize the intensity of Peak 1, all the spectra were recorded against a blank solution (M), which has the same composition, but without Au(III) ions.

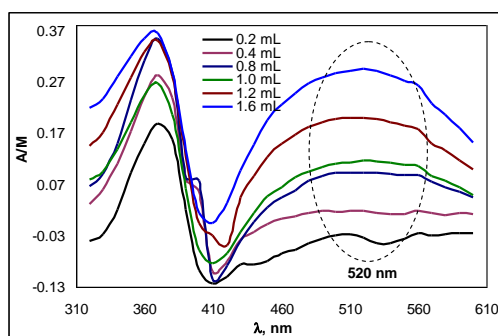


Fig. 3 – VIS spectra of Au(III)-Rhodamine B purple complex at different concentrations of Au(III) ions.

With the exception of the first two spectra (which have negative absorbance), all the others have a maximum absorbance at 520 nm, against a blank solution, that increases with increasing concentration of Au(III) ions in the solution. Therefore, the reaction between Au(III) ions and Rhodamine B dye can be successfully used for quantitative analysis of Au(III) ions in aqueous solution.

3.4. Characterization of the Spectrophotometric Method

First step in the characterization of the spectrophotometric method is the calculation of the qualitative parameters. The qualitative parameters: maximum absorption wave length (λ_{\max} , [nm]), spectral bandwidth ($\Delta\lambda_{1/2}$, [nm]) and molar absorption coefficient (ϵ , [$\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$]) provide information about the nature of the absorbent specie, and the values of these parameters calculated from the VIS spectra from Fig. 3, are summarized in Table 1.

Table 1
The Values of Qualitative Parameters of Proposed Spectrophotometric Method

$c_{\text{Au(III)}}$, [$\mu\text{g}\cdot\text{mL}^{-1}$]	1.6	2.0	2.4	3.2
λ_{\max} , [nm]	520	520	520	520
A_{\max}/M	0.093	0.116	0.206	0.294
$\Delta\lambda_{1/2}$, [nm]	144.28	148.12	152.06	156.14
ϵ , [$\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$]	$5.58\cdot 10^5$	$5.71\cdot 10^5$	$5.84\cdot 10^5$	$6.24\cdot 10^5$

Similar values of the qualitative parameters (Table 1) clearly shows that in presence of Rhodamine B, Au(III) ions form the same complex, regardless of their initial concentration. In addition, Au(III) ions react immediately with Rhodamine B in strong acid media, and the absorbance can be measured after 10 min of stand by. All these features suggest that the formation of purple complex between Au(III) and Rhodamine B can be the starting point in developing a quantitative spectrophotometric method of analysis.

In order to prove the quantitative application of this method in Au(III) determination, the calibration curve was obtained using six solution with known concentration of Au(III) ions, according with the procedure described in Experimental section (Fig. 4). The Lambert-Beer law is obeyed from 0.5 – 3.5 $\mu\text{g}\cdot\text{mL}^{-1}$), at 520 nm against a blank solution.

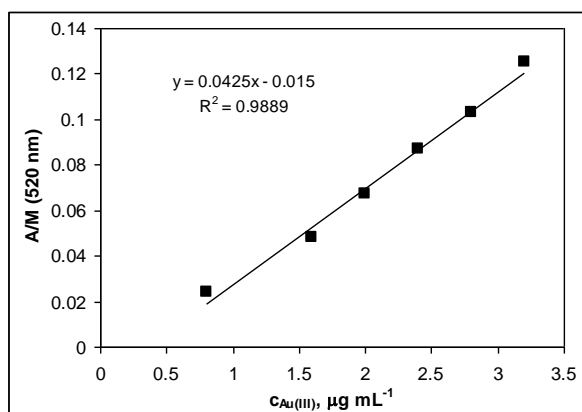


Fig. 4 – Calibration curve of the spectrophotometric method.

The main quantitative parameters of the proposed spectrophotometric method, such as calibration sensitivity (the slope of calibration curve), detection limit (calculated as three times of standard deviation), limits of quantification (calculated as ten times of standard deviation) and precision (RDS, [%]) are summarized in Table 2.

Table 2
The Analytical Characteristics of the Proposed Method

Analytical parameter	At 520 nm
Calibration sensitivity	0.0425 $\text{mL}\cdot\mu\text{g}^{-1}$
Correlation coefficient	0.9889
Linear dynamic range	0.5 – 3.5 $\mu\text{g}\cdot\text{mL}^{-1}$
Limit of detection (3σ)	0.081 $\mu\text{g}\cdot\text{mL}^{-1}$
Limit of quantification (10σ)	0.2726 $\mu\text{g}\cdot\text{mL}^{-1}$
Precision	2.68%

The quantitative parameters (Table 2) shows that the proposed spectrophotometric methods have a sufficiently wide linear dynamic range, a low detection limit and relatively high precision, and can be used for the quantitative determination of Au(III) ions from aqueous media.

Another aspect to be considered in characterizing the applicability of this method of analysis is its selectivity towards Au(III) ions, compared with other interfering ions. For this purpose, are used the selectivity coefficients ($a_{Au, j}$), which are defined as the ratio between Au(III) ions concentration (c_{Au} , [$\mu\text{g}\cdot\text{mL}^{-1}$]) and the interfering ions concentration (c_j , [$\mu\text{g}\cdot\text{mL}^{-1}$]), which give a 5% absorbance change in a reference solution.

In this study, the concentration of Au(III) ions in the reference solution was $2.4 \mu\text{g}\cdot\text{mL}^{-1}$, and Pb(II), Cu(II) and Cd(II) ions were selected as the interfering ions. The values of the selectivity coefficients, calculated for each interfering ion based on the experimental absorbance values (Fig. 5), measured at 520 nm against a blank solution, are summarized in Table 3.

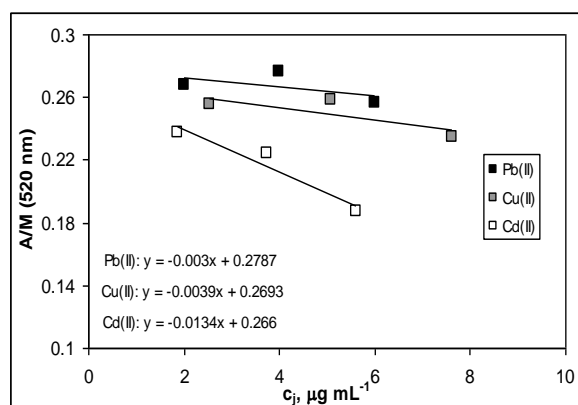


Fig. 5 – Experimental dependences used in the calculation of the selectivity coefficients.

Table 3
The Selectivity Coefficients

Interfering ion	$c_{Au(III)}$, [$\mu\text{g}\cdot\text{mL}^{-1}$]	c_j , [$\mu\text{g}\cdot\text{mL}^{-1}$]	$a_{Au(III), j}$
Pb(II)	2.40	76.23	0.03
Cu(II)	2.40	56.23	0.04
Cd(II)	2.40	17.42	0.13

The values of selectivity coefficients show that the proposed method has a relatively good selectivity towards Au(III) ions in presence of some other heavy metals that may be present in different real samples. Thus, the Pb(II) concentration may be up to 30 times higher than the Au(III) ions concentration for the absorbance to change by 0.05 units, while for Cu(II) and Cd(II) ions, this

change occurs at concentrations up to 20 times higher and 6 times higher, respectively.

But, more important than calculating the selectivity coefficients is the validation of the proposed method. In this study, the validation of this method was done using tap water from the “Gheorghe Asachi” Technical University laboratories, where the Au(III) ions concentration was adjusted to a constant value ($2.4 \mu\text{g}\cdot\text{mL}^{-1}$). All the samples were prepared according with the procedure described in the Experimental section, and the Au(III) ions concentration was determined using a prepared calibration graph. The obtained results are presented in Table 4.

Table 4
The Validation of Proposed Method

Sample	$V_{\text{tap water}}$, [mL]	$C_{\text{Au(III), added}}$, [$\mu\text{g}\cdot\text{mL}^{-1}$]	$C_{\text{Au(III), found}}$, [$\mu\text{g}\cdot\text{mL}^{-1}$]
1	5.0	2.40	4.17
2	10.0	2.40	5.27
3	15.0	2.40	5.91

As can be seen from Table 4, the constituents of water samples drastically interfere in the determination of Au(III) ions by proposed spectrophotometric method. Therefore, even if this method is simple, fast and has a good selectivity against other heavy metal ions, it can only be used for the analysis of laboratory solutions.

4. Conclusions

The spectrophotometric method based on the colour reaction between Au(III) ions and Rhodamine B is simple, rapid and occurs in aqueous media. The purple complex is formed in strong acid media (1 mL of 2N HCl solution) requires a low volume of 0.1% Rhodamine B solution (2 mL), and its absorbance can be measured after 10 min of stand by. The suitable linear dynamic range ($0.5 - 3.5 \mu\text{g}\cdot\text{mL}^{-1}$), low detection limit ($0.081 \mu\text{g}\cdot\text{mL}^{-1}$), and the relatively good selectivity towards of some other heavy metals (Pb(II), Cu(II) and Cd(II)) that may be present in different real samples, highlights the applicability of this method. Unfortunately, the constituents of water samples drastically interfere in the determination of Au(III) ions by proposed spectrophotometric method, and so can be used only for the analysis of laboratory solutions.

Acknowledgements. This paper was elaborated with the support of grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, project number PN-III-P4-ID-PCE-2016-0500.

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DETERMINAREA SPECTROFOTOMETRICĂ
SIMPLĂ ȘI RAPIDĂ A IONILOR DE Au(III) UTILIZÂND RODAMINA B
CA REACTIV DE CULOARE

(Rezumat)

În acest studiu este propusă o metodă spectrofotometrică simplă pentru determinarea rapidă a ionilor Au(III) din soluții apoase. Metoda propusă utilizează Rodamina B ca reactiv de culoare și reacția are loc imediat în mediu puternic acid (soluție HCl 2N). Complexul violet prezintă o absorbantă maximă la 520 nm, măsurată față de o probă martor. Metoda permite determinarea ionilor Au(III) într-un interval de concentrație cuprins între 1,5 – 3,5 $\mu\text{g}\cdot\text{mL}^{-1}$, cu un coeficient de absorbție molară de molară de $8,71\cdot 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ și o limită de detecție de 0,18 $\mu\text{g}\cdot\text{mL}^{-1}$. Cu toate că metoda prezintă o selectivitate relativ bună față de alte metale grele (Pb(II), Cu(II) și Cd(II)) care pot fi prezente în diferite probe reale, componenții probelor de apă intervin în mod drastic în determinarea ionilor Au(III) prin metoda spectrofotometrică propusă, ceea ce face ca această metodă să poată fi utilizată numai pentru analiza soluțiilor de laborator.

