

An optode membrane for determination of gold using a simple light-emitting diode-based device

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Abstract A selective optode based on immobilization of 5-(*p*-dimethylaminobenzylidene)rhodanine on a triacetylcellulose membrane was developed for quantitative determination of Au(III). The determination procedure was performed using a simple light-emitting diode (LED)-based device as a new effort to overcome low reproducibility and repeatability problems which usually accompany optode-based determinations. The results obtained were compared with those of conventional spectrophotometric methods. The response characteristics of the sensor including dynamic range, reproducibility, response time, and lifetime are discussed in detail. This sensor was used for the determination of Au(III) in ore and electroplating liquid effluent samples with satisfactory results in comparison with flame atomic absorption spectroscopy as standard method. Under the optimum conditions, the calibration plot was linear in the concentration range of 0.3–6.0 $\mu\text{g cm}^{-3}$. The relative standard deviations for five replicate determinations of 1.0 $\mu\text{g cm}^{-3}$ Au(III) and the corresponding limits of detection were 1.76% and 0.12 $\mu\text{g cm}^{-3}$, respectively.

Keywords UV–Vis spectroscopy · Sensors · Gold · Light-emitting diode

Introduction

Because of their advantages such as easy fabrication, good sensitivity and selectivity, and low cost, the applications of

optical chemical sensors have grown rapidly over the past two decades. In optochemical sensors (called optrodes) [1] or optodes, the sensing element consists of reagent dyes immobilized on organic or inorganic matrices. Reaction of these reagents with the analyte changes the absorbance [2], fluorescence [3], or reflectance [4] behavior of the sensitive layer applied for the determination of various analytes, e.g., metal ions [5–9]. In other words, an indicator acts as a transducer for the chemical species that cannot be determined directly by optical means.

Because of the wide industrial applications as well as its role in economic activities, gold is one of the most important noble metals. Regardless of the type of detection method, separation and preconcentration of gold ions prior to its determination is usually an essential step [10]. Various techniques are generally employed for the separation and preconcentration of gold ions from different matrices [11, 12]. Most of these methods usually have drawbacks such as high costs of equipment and assays, time-consuming processes, and complicated operations. Therefore it seems that optodes with the aforementioned useful advantages might overcome these difficulties. To the best of our knowledge, there is no previous report of this idea.

The immobilization of sensing reagents onto the membranes is an important step in the development of optodes. Chemical immobilization on an appropriate support [13], physical entrapping in polymeric matrices [14–16], and adsorbing on the surface of support material [17, 18] are three commonly applied strategies; among them the last is the simplest. A common procedure for preparation of a sensor membrane is treatment of transparent triacetylcellulose membranes produced from waste photographic film tapes, removing the colored gelatinous layer, and immobilizing the sensing reagent on it [19]. To enhance adsorption of the reagent on the triacetylcellulose support

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in some cases the surface of the support was abraded with grindstone.

5-(*p*-Dimethylaminobenzylidene)rhodanine (PDR, Fig. 1) in an acidic solution reacts with some metal ions. Because PDR and its metal complexes are only slightly solubility in water and many solvents, it can be used in the operation of optical sensors. Optical sensors based on PDR have been used already for the determination of silver and palladium [20, 21]. The results obtained indicated that PDR is very sensitive to Au(III) [21, 22].

The present work reports the preparation and characterization of a sensing membrane (optode) based on the

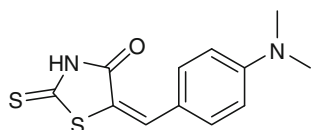


Fig. 1 Structure of 5-(*p*-dimethylaminobenzylidene)rhodanine (PDR)

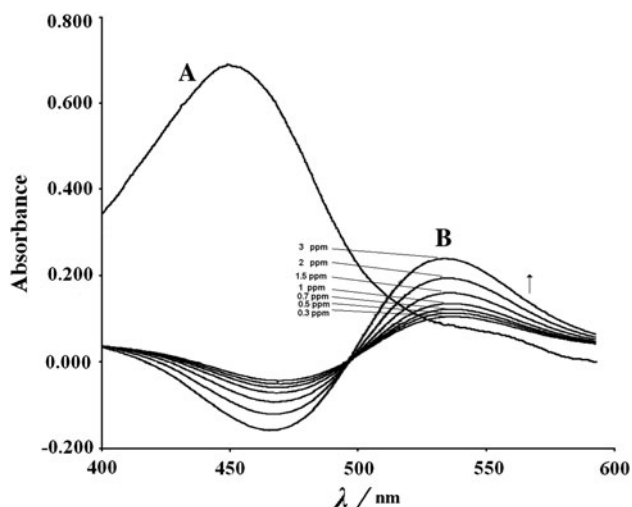


Fig. 2 Absorption spectra of PDR in the absence (a) and in the presence (b) of varying concentrations of Au(III) ions (0.5–5 $\mu\text{g cm}^{-3}$)

immobilization of PDR on a triacetylcellulose membrane for determination of gold ions in real samples.

Because of the small size, exceptional stability, low cost, low power consumption, and robust nature of LEDs, several researchers have utilized LEDs to replace the traditional spectrophotometric light sources [23–27]. The absence of a reported LED-based evaluation of optodes sparked our interest in devising a simple and low-cost detection system. The proposed device is composed of readily accessible components such as a light-dependent resistor (LDR) as a detector, LED as a light source, and a plastic semi-micro cuvette as an optode container. The presented optode in combination with the proposed detection device was successfully applied for the determination of gold in real samples.

Results and discussion

Spectral characteristics and LED selection

The absorption spectrum of PDR immobilized on triacetylcellulose membrane shows a maximum absorbance wavelength at 450 nm. As shown in Fig. 2, the formation of the Au–PDR complex on the surface of the membrane causes a new peak to appear at 530 nm. In accordance with the mechanisms proposed in the literature [28–30] for some other ligands, a similar one may be proposed for PDR with activated membrane as in Fig. 3. With due attention to the maximum wavelength of the complex, a green LED, emitting a continuous spectrum ranging from 520 to 605 nm ($\lambda_{\text{max}} = 565 \text{ nm}$), was used as a light source.

Abrasion of membrane surface

The preliminary studies showed that the smooth surface of the membrane is not capable of adsorbing enough PDR. Replacing the smooth surface with an abraded one leads to

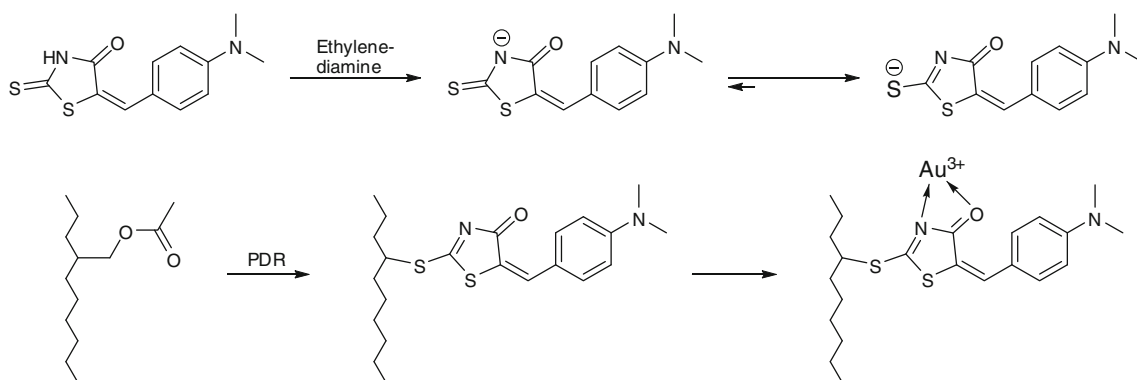
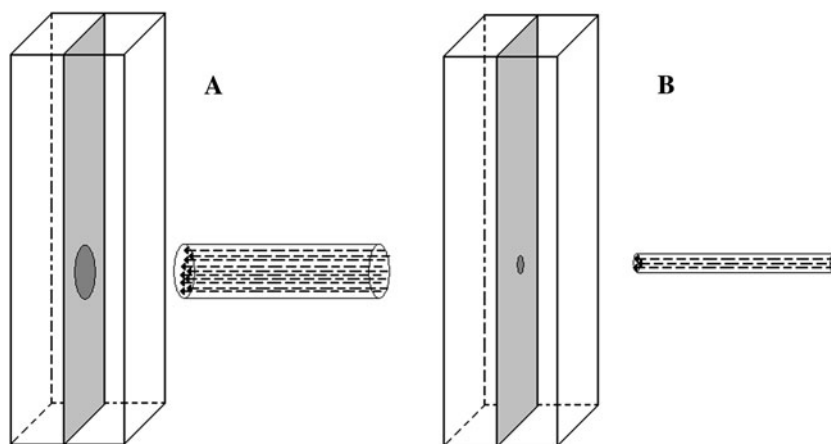


Fig. 3 Possible schemes of reaction of PDR with activated membrane

Fig. 4 Schematic comparison between beam diameters of light from a LED (a) and a commercial spectrophotometer (b)



an increased adsorbing efficiency. This advantage stems from the fact that the abraded surface possesses many small pores that retain the sensing reagent. Although this plays an advantageous role in optode preparation, it leads to increased surface nonuniformity and decreased reproducibility and repeatability. Utilizing a LED-based detection system is an effort to overcome the decreased reproducibility and repeatability. The beam divergence (beam diameter) of an electromagnetic beam is a measure for how fast the beam expands far from the beam waist. As shown schematically in Fig. 4, LEDs emit a much more divergent beam than the common spectrophotometers. In other words, a much wider area of the sensor membrane surface is exposed by the LED emission which helps to overcome the poor reproducibility and repeatability caused by non-uniformity of the membrane surface (Table 1).

A wide range of grindstones are available which have a European Manufacturers of Abrasive Products (FEPA)-assigned code according to their particle size. Grindstones with smaller particle sizes have higher code numbers. Results obtained for the spectrophotometric determination show that although the macrogrit grindstones have higher response values, their repeatability is lower than the that of the microgrits (Table 1). The precision of the results obtained from a LED-LDR detection system for macrogrits proved to be better than those of the spectrophotometers and is similar to that of the microgrits.

Table 1 Results obtained for the determination of $2 \mu\text{g cm}^{-3}$ of Au(III) using membranes abraded with different grindstones ($n = 5$)

Grindstone	Commercial spectrophotometer		LED-LDR system	
	Mean (absorbance)	RSD (%)	Mean (resistance)	RSD (%)
P180	0.186	4.90	0.47	1.76
P320	0.155	4.42	0.33	1.52
P1000	0.142	1.47	0.28	1.15

The practical experiences showed that the preparation of an optode using macrogrit grindstones is faster and easier than microgrit. In this work the P180 grindstone was selected as the abrasive material. Hence, it seems that the simplicity and much lower costs of the proposed method combined with enhanced repeatability and precision of results may well compensate the probable higher sensitivities of the photometric methods.

Optimization of some parameters affecting the optode preparation

Because of the lipophilic character of PDR, we searched for a suitable organic solvent to dissolve PDR and immobilize it on triacetylcellulose. Five membranes prepared according to the procedures described earlier were treated with solutions of PDR (0.015 M) in five different solvents, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), ethanol, acetonitrile, and ethylenediamine. Use of ethylenediamine as solvent led to the best results.

The influence of the PDR concentration in ethylenediamine was studied in the range 0.0004–0.03 M and the results obtained showed that the sensitivity increases with the concentration up to 0.023 M and remains constant thereafter.

The effect of time on the immobilization of PDR was also investigated. For this study, the activated membranes were immersed in a solution containing 0.023 M PDR for different periods of time (from 1 to 15 min). Because of the chemical effect of ethylenediamine on triacetylcellulose, the membrane was deformed and became unusable after 10 min. Hence an 8- to 10-min period was selected as working time.

Optimization of parameters affecting Au-PDR complex formation

The influence of solution pH on the Au-PDR complex formation was studied in the pH range of 2.0–7.0. The

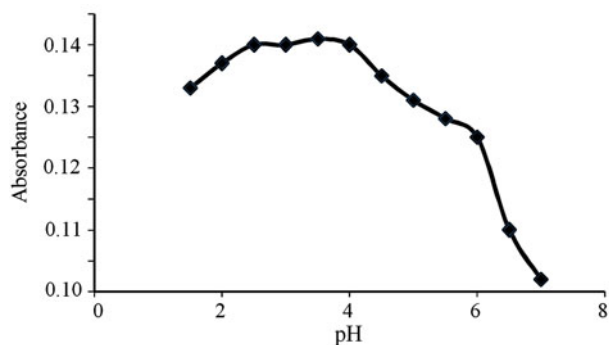


Fig. 5 Effect of pH on the response of the membrane in the presence of $2 \mu\text{g cm}^{-3}$ Au(III) at 530 nm

activated membrane was immersed in a solution containing $2 \mu\text{g cm}^{-3}$ Au(III). Then the membrane was washed with water, dried, and the signal of the complex deposited on the surface of the optode was measured. As can be seen in Fig. 5, a maximum value of the sensor response was obtained at pH 3.5 (phthalate buffer) which was then selected for further studies. To obtain the optimum buffer concentration, its influence was studied in the range 0.02–0.50 M. The results obtained showed that the sensitivity increases up to 0.10 M, remains constant until 0.40 M, and decreases slightly thereafter. Because phthalate is an organic compound, increasing its concentration causes an increase in the organic characteristics of the solution which results in desorption of PDR from the membrane surface. Hence, 0.10 M was selected as the optimized concentration.

Investigation of LED light stability

According to our investigations [24] and others [31], after turning on a LED the signal intensity decreases by 3–4% after reaching the maximum value. Relative standard deviations (RSDs) for determination of a standard sample ($2 \mu\text{g cm}^{-3}$ solution of Au(III)) at different standing times after turning on the LED were studied. The RSD decreased to less than 3 after 1.5 min. Hence all determinations were made at 1.5 min after turning on the LED.

Response time, stability, and lifetime

An important analytical feature of any sensor is its response time. Figure 6 shows the response of the optode using four different concentrations of Au(III). In this work, the optode film was found to reach 95% of the final signal at 4–6 min, depending on Au(III) concentration.

Reproducibility of the optode (no changes among membranes prepared on different days) was evaluated by performing four determinations for each of seven different membranes. The RSD for determination of a $2 \mu\text{g cm}^{-3}$

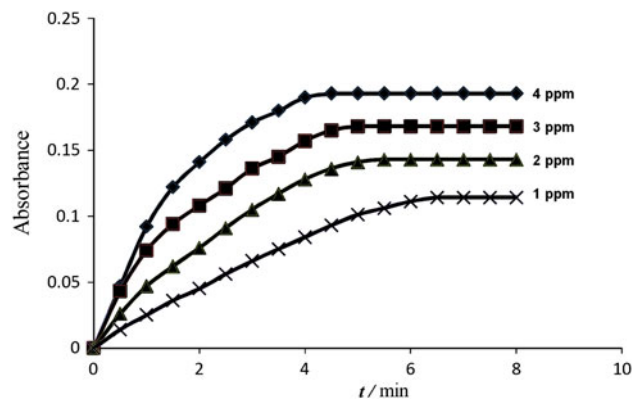


Fig. 6 Response time of the proposed optode at different concentrations of Au(III) ions

solution of Au(III) was 2.08% which indicated a satisfactory reproducibility.

The lifetime of the optode film in buffer solution (pH = 3.5) was studied. The signal was recorded over 10 days, during which the signal of the membrane did not reduce below 95% of that of a fresh membrane. The film in the buffer solution was also exposed to sunlight for 24 h, without the signal dropping below 95% of that of a fresh membrane. The prepared membranes were kept under water to prevent them from drying out. The stability of the film response was investigated over 4 weeks under these conditions and the results showed that the film was stable over this period. The stability of the film in the open air was also investigated; however, the stability did not last more than 1 h, and the film's yellow color changed to red. It seems that the PDR was oxidized in open air.

Optode regeneration

The reversible color change of the membrane is an important characteristic of a suitable optode. Some reagents including EDTA, I^- , SCN^- , CN^- , and $\text{S}_2\text{O}_3^{2-}$ were studied as regenerating reagents. It was concluded from the preliminary experiments that cyanide is the best reagent for this purpose, requiring a very short time for regeneration (less than 10 s) at a low concentration (0.001 M).

To evaluate the repeatability of the sensor, successive runs using a single sensor were performed. The result was repeatable for up to 10 successive runs and the RSD of sensor response for $4 \mu\text{g cm}^{-3}$ was 2.11%.

Method selectivity

One of the most important characteristics of an optical membrane sensor is its relative response towards the primary ion over other ions present in the solution. The effect

of various cations and anions on the determination of Au(III) was examined. The ions tested were added individually to a $1 \mu\text{g cm}^{-3}$ Au(III) solution and the signal was measured. The tolerance limits of ions within relative errors of 5% are shown in Table 2. Under the applied conditions, no interference was observed from most of the ions tested except for some heavy metal ions and mostly for Pd^{2+} , Hg^{2+} , and Ag^+ . The interference from such heavy metal ions can be minimized by using EDTA (0.01 M) as a masking agent, and addition of potassium bromide (0.01 M) proved to be most effective for Ag^+ .

Analytical parameters

Under the optimum conditions, the calibration graphs were obtained for Au(III) determination by using a series of standard solutions. The calibration graph was linear in the range of $0.3\text{--}6 \mu\text{g cm}^{-3}$ of Au(III) concentration. The RSD calculated for nine replicate determinations of $1 \mu\text{g cm}^{-3}$ of Au(III) was 1.76%. The limit of detection (LOD) based on the International Union of Pure and Applied Chemistry (IUPAC) definition ($C_{\text{LOD}} = 3S_b/m$, where S_b is the standard deviation of blank, and m denotes the slope of the calibration line) was $0.12 \mu\text{g cm}^{-3}$.

For the conventional spectrophotometric method, linearity of the calibration graph was in the range of $0.3\text{--}4.5 \mu\text{g cm}^{-3}$ of Au(III). The RSD for $1 \mu\text{g cm}^{-3}$ Au(III) was 1.20% based on nine replicated measurements

Table 2 Tolerable concentration ratios for the determination of $1 \mu\text{g cm}^{-3}$ of Au(III) with the proposed method (relative error $\pm 5\%$)

Ion added	Tolerable concentration ratio
Na^+ , K^+ , Ba^{2+} , CO_3^{2-}	800
Mg^{2+} , Ca^{2+} , SO_4^{2-} , Be^{2+} , Al^{3+} , F^- , Mo^{4+} , citrate	400
V^{4+} , Sr^{2+} , Ga^{2+} , La^{3+} , I^- , PO_4^{3-}	250
^a Hg^{2+} , Co^{2+} , Cr^{3+} , $\text{C}_2\text{O}_4^{2-}$	200
^b Ag^+ , Pb^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Bi^{3+} , Cd^{2+}	100
^a Pd^{2+} , Hg^{2+}	15
Ag^+ , Pd^{2+}	0.5

^a Masked by EDTA (4×10^{-4} M)

^b Masked by KBr (0.01 M)

and the estimated LOD value was $0.09 \mu\text{g cm}^{-3}$. The membrane used was abraded with a P1000 grindstone.

Analytical applications

The method was applied to the determination of Au(III) in real samples. The method was validated using an ore sample and an electroplating liquid effluent sample. The results obtained by the proposed procedure were compared with those obtained by the flame atomic absorption spectroscopy (FAAS) standard method and conventional spectrophotometric method (Table 3). To compare both methods the Student's t test with a 95% threshold level was used. Five replicate samples were separately analyzed by FAAS, the spectrophotometric optode-based method, and the proposed method. The calculated t (t_c) indicates that the methods are not significantly different and the results agree within the experimental error.

Experimental

Apparatus and reagents

A Shimadzu UV-1650 PC (Japan) double beam spectrophotometer was used for all spectral measurements and a Shimadzu 2554 (Japan) spectrofluorimeter was used to obtain the LED light emission spectrum. A Shimadzu AA-6300 flame atomic absorption spectrophotometer was used for comparing the results.

All chemicals were of analytical reagent grade or the highest purity available purchased from Merck (Darmstadt, Germany). All solutions were prepared using doubly distilled water. A Au(III) solution of $1,000 \mu\text{g cm}^{-3}$ was prepared by dissolving 0.145 g of $\text{H}[\text{AuCl}_4] \cdot x\text{H}_2\text{O}$ (49% Au) in a few cubic centimeters of water and making up to 10 cm^3 in a graduated flask. A solution of KCN ($0.001 \mu\text{g cm}^{-3}$) was prepared and used. A phthalate buffer solution (pH 3.5) was prepared by mixing potassium phthalate ($0.1 \mu\text{g cm}^{-3}$) and HCl ($0.1 \mu\text{g cm}^{-3}$); the pH of the solution was monitored using a pH meter. A solution of PDR of $0.023 \mu\text{g cm}^{-3}$ in ethylenediamine was prepared and used.

Table 3 Results obtained for the determination of Au(III) in real samples with FAAS, conventional spectrophotometry, and the proposed method

Real samples	FAAS		Spectrophotometry		LED-LDR system	
	[Au(III)] ($\mu\text{g cm}^{-3}$)	RSD (%)	[Au(III)] ($\mu\text{g cm}^{-3}$)	RSD (%)	[Au(III)] ($\mu\text{g cm}^{-3}$)	RSD (%)
Ore sample	0.914	1.60	0.910	4.71	0.927	4.20
Electroplating liquid effluent sample	3.606	0.80	3.616	2.42	3.631	1.83

Preparation of the optical membrane

The optical sensor was prepared by immobilizing PDR on the triacetylcellulose membrane. For this purpose, the transparent triacetylcellulose membranes were produced from waste photographic films that had been previously treated with commercial sodium hypochlorite (0.01 M) to remove colored gelatinous layers and abraded with grindstone (a 10 × 10 cm film for 5 min). The membranes were cut in 5 × 1 cm pieces and treated with a solution of PDR (0.023 M) in ethylenediamine for 8 min at ambient temperature; they were then washed with water to remove the excess reagent. The optode membrane was stored in water when not in use.

Construction of the detection device

Figure 7 shows a schematic diagram of the constructed device. A common green-color LED (Shenzhen Mingxue Optoelectronic Co., Ltd., China), emitting a continuous spectrum ranging from 520 to 620 nm, bandwidth 25 nm, and maximum wavelength of 565 nm, operated by two 1.5-V dry batteries, was used as light source and a cheap common light-dependent resistor (LDR) (Xiamen Xinpu-long Semiconductor Co., Ltd., China) as a detector. Two holes were drilled, a small one at the center of the front side (2-mm diameter) and another hole (3 × 4 mm) at the center of the back side of the optode container (a plastic semi-micro cuvette with path length 4 mm). The LED and LDR were glued with some silicone glue on the first and second holes, respectively, such that the tips of the LDR and LED were positioned on the center of the holes. All outer surfaces of the cuvette, LED, and LDR were coated with a layer of black oil color. Light emitted from the LED passed through the plastic cuvette containing the optode and transmitted light intensity was detected with the LDR. A digital multimeter (Mastech MS8201, China) connected to the LDR poles was used for the resistance reading.

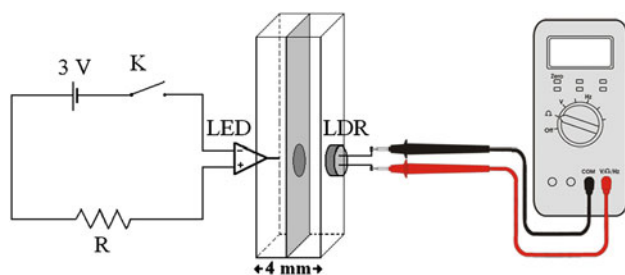


Fig. 7 Schematic diagram of the constructed device

Analytical procedure

The membrane was placed in the phthalate buffer (pH 3.5) for 100 s to reach equilibrium. The LED was turned on; the sensing film was placed into the optode container after standing for 1.5 min and the resistance of the LDR was then measured. Another membrane which had been prepared in the same way and placed in the sample containing an appropriate concentration of Au(III) ions was then placed in the optode container and the resistance of the LDR was again measured. The analyte content of the sample was then calculated from the difference of two values obtained.

The resistance measured is proportional to the absorbed light intensity and hence proportional to the concentration of the analyte [26]. The absorption of the light emitted by the LED increased with the quantity of Au(III) adsorbed on the membrane. The detector (LDR) resistance increases as the radiation intensity decreases.

Preparation of ore sample

Crushed ore sample (5 g) was transferred into a 250-cm³ beaker containing 50 cm³ concentrated hydrochloric acid. The beaker was covered and heated gently on an electric heater to dissolve the sample. The mixture was filtered, the residue mixed with 5 g of sodium peroxide, 2 g of sodium hydroxide, and fused (in a porcelain crucible) at 700 °C. The fused sample was washed with distilled water into a 250-cm³ beaker and 50 cm³ concentrated hydrochloric acid was added. The mixture was heated to decrease the volume and then diluted with distilled water. Evaporation followed by distilled water addition was repeated several times until a pH below 4 was reached. The remaining solution was transferred into a 100-cm³ graduated flask and filled up to the mark with distilled water.

Preparation of electroplating liquid effluent sample

The prepared electroplating effluent solution was alkaline and contained the cyanide complexing agent. The effluent (25 cm³) was transferred into a 50-cm³ beaker containing 10 cm³ of an aqua regia mixture formed by freshly mixing concentrated nitric acid and concentrated hydrochloric acid in a volumetric ratio of 1:3. The mixture was heated for 15 min and H₂AuCl₄ was extracted from the aqueous solutions with 15 cm³ methyl isobutyl ketone (MIBK). The determination was made directly on the organic extract.

References

1. Wolfbeis OS (1986) *Fresenius Z Anal Chem* 325:387
2. Ensafi AA, Fouladgar M (2008) *IEEE Sensors J* 8:347

3. Shamsipur M, Poursaberi T, Karami AR, Hosseini M, Momeni A, Alizadeh N, Yousefi M, Ganjali MR (2004) *Anal Chim Acta* 501:55
4. Kuswandi B, Vaughan AA, Narayanaswamy R (2001) *Anal Sci* 17:181
5. Fouladgar M, Ensafi AA (2010) *Sens Actuators B* 143:590
6. Tavallali H, Daneashian S (2009) *Monatsh Chem* 140:1149
7. Safavi A, Bagheri M (2005) *Anal Chim Acta* 530:55
8. Zare-Shahabadi V, Akhond M, Tashkhourian J, Abbasitabar F (2009) *Sens Actuators B* 141:34
9. Joshi JM, Pathak PN, Pandey AK, Manchanda VK (2008) *Talanta* 76:60
10. Sorouraddin MH, Saadati M (2008) *Bull Chem Soc Jpn* 81:1103
11. Nakbanpote W, Thiravetyan P, Kalambaheti C (2000) *Miner Eng* 13:391
12. Hua Q, Yang X, Huanga Z, Chena J, Yang G (2005) *J Chromatogr A* 1094:77
13. Glenn SJ, Gullum BM, Nair RB, Nivens DA, Murphy CJ, Angel SM (2001) *Anal Chim Acta* 448:1
14. Sotomayor PT, Raimundo IM Jr, Zarbin AJG, Rohwedder JJR, Alves OL (2001) *Sens Actuators B* 74:157
15. Albero MI, Ortuno JA, Garcia MS, Cuartero M, Alcaraz MC (2010) *Sens Actuators B* 145:133
16. Gholivand MB, Niroomandi P, Yari A, Joshagani M (2005) *Anal Chim Acta* 538:225
17. Ganjali MR, Zare-Dorabei R, Norouzi P (2009) *Sens Actuators B* 143:233
18. Safavi A, Bagheri M (2004) *Sens Actuators B* 99:608
19. Chamjangali MA, Soltanpanah S, Goudarzi N (2009) *Sens Actuators B* 138:251
20. Rastegarzadeh S, Rezaei V (2008) *J Anal Chem* 63:897
21. Pourreza N, Rastegarzadeh S (2004) *Can J Anal Sci Spectrosc* 49:314
22. Pourreza N, Rastegarzadeh S (2001) *Anal Chim Acta* 437:273
23. O'Toole M, Diamond D (2008) *Sensors* 8:2453
24. Sorouraddin MH, Saadati M (2010) *Sens Actuators B* 145:367
25. Sorouraddin MH, Saadati M (2010) *J Anal Chem* 65:423
26. Sorouraddin MH, Saadati M, Samadi A (2010) *J Chin Chem Soc* 57:56
27. Sorouraddin MH, Saadati M (2010) *Chemistry* 18:176
28. Tang E, Yang G, Yin J (2003) *Spectrochim Acta A* 59:651
29. Ensafi AA, Katiraei Far A, Meghdadi S (2008) *Sens Actuators B* 133:84
30. Ensafi AA, Fouladgar M (2006) *Sens Actuators B* 113:88
31. Fonseca A, Raimundo IM Jr (2004) *Anal Chim Acta* 522:223