Gold nanorods and a nanocomposite material based on them: analytical possibilities for spectrophotometric determination of total catecholamines

M V Gorbunova, A O Shlenova, R V Klimenko, S V Gutorova, V V Apyari and S G Dmitrienko

Department of Chemistry, Lomonosov Moscow State University, Leninskie gory, 1/3, Moscow 119991, Russia

E-mail: masha13_1992@mail.ru

Abstract. Gold nanorods and nanocomposite material based on them were synthesized and used as spectrophotometric reagents for determination of catecholamines. Approaches to the determination of total catecholamines content are discussed. Use of radar charts for evaluation of the error of catecholamines determination and for selection of the appropriate standard substance is proposed. Developed spectrophotometric techniques were used for determination of total catecholamines in a model mixture, urea samples and diluted blood serum. Accuracy of the techniques was proved by the standard addition method and by results of HPLC analysis.

1. Introduction
In recent years, there has been a steady tendency to study nanoobjects of non-spherical shape, for example, gold nanorods (AuNRs) characterized by several modes and several bands of surface plasmon resonance (SPR). The existing correlation between the composition, geometrical dimensions of AuNRs and their SPR-spectra provides a possibility of developing methods for spectrophotometric determination of various compounds that cause changes in these parameters. Thus, it was established that catecholamines reduce silver ions in the presence of gold nanorods in glycine buffer solution medium [1, 2]. Metallic silver covers longitudinal faces of AuNRs, changing particle shape. As a result, a hypsochromic shift of both maxima in the absorption spectrum of AuNRs is observed. This is a basis for spectrophotometric determination of this class of compounds.

As far as deposition of nanoparticles on a solid matrix contributes to their stabilization and, in some cases, improves their ease of use, synthesis and study of nanocomposite materials is also promising. Among various matrices for nanocomposite materials, polyurethane foam (PUF) has proven itself as a material of high strength, low cost and ease of use [3, 4].

Catecholamines (CAs) perform various vital functions in humans and animals: regulating stress, psychomotor activity, emotions, learning, sleep, memory [5, 6]. Epinephrine, norepinephrine and dopamine are of particular importance as far as these substances are directly produced by organisms. Abnormal concentration of these substances in the human body could serve as a marker of various diseases. Since biological objects, as a rule, contain mixture of catecholamines, the development of techniques for determining their total content is very topical.

Determination of CAs is mostly carried out by high-performance liquid chromatography with an electrochemical detector, fluorescence and chemiluminescence methods, mass spectrometry. A
combined method for determination of CAs by HPLC or capillary electrophoresis in tandem with mass-spectrometric detection is widely used [7, 8]. It is advisable to develop methods that allow to increase analysis speed and reduce its cost; spectrophotometric methods meet these criteria. The analysis of literature data indicates that in most cases the detection limits of CAs using the spectrophotometric method are 0.1-1 μg mL⁻¹, which is insufficient for biological fluids. Use of metal nanoparticles instead of “classical” spectrophotometric reagents leads to significant decrease in the detection limits down to ~ 0.01 μg mL⁻¹ [9]. Therefore, study of nanoparticles in relation to solving problems of the spectrophotometric determination of catecholamines seems relevant.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate (chemically pure) and silver nitrate (pure) were used for preparation of AuNRs. Sodium borohydride (analytical grade) and ascorbic acid (chemically pure) were used as reducing agents, cetyltrimethylammonium bromide (CTAB, analytical grade) was used as a stabilizer of AuNRs. Epinephrine, norepinephrine hydrochloride and dopamine hydrochloride (all of analytical grade) were used as subjects of the study (figure 1). The substances stock solutions were prepared by dissolving their weighed portions in deionized water. Epinephrine was dissolved in 0.01 mol L⁻¹ HCl. The stock solutions were frozen and kept in a refrigerator. Working 0.2 mmol L⁻¹ solutions were prepared from the stock solutions immediately before use. Glycine buffer (pH 9.5) was prepared by addition of 74.8 mL of 0.1 mol L⁻¹ glycine (7.51 g of glycine and 5.85 g of NaCl in 1 L) to 25.2 mL of 0.1 mol L⁻¹ NaOH. Phosphoric acid (H₃PO₄), octane-1-sulfonic acid sodium salt, acetonitrile (all of analytical grade) were used for preparation of chromatographic eluent.

Commercially available polyether-type polyurethane foam (PUF) was used as a matrix for nanocomposites. Tablets of PUF of 16 mm in diameter (20 ± 2 mg) were cut with a metal punch from an industrial sheet of the polymer. To remove impurities, the PUF tablets were placed in acetone and shaken for 10 minutes. The procedure was repeated twice, after which the tablets were dried under stream of air.

2.2. Instruments

Absorption spectra of solutions were recorded by SF-103 spectrophotometer (Akvilon, Russia). Diffuse reflection in the visible region was recorded using an Eye-One Pro mini-spectrophotometer (X-Rite, USA). Chromatographic determination of catecholamines was performed using a Tsvett Yauza chromatograph (NPO Khimavtomatika, Russia) with an amperometric detector (E = +0.8 V). The chromatographic column “Eclipse XDB-C18” (Agilent) and guard column Security Guard C18 were used. Eluent contained acetonitrile and 0.1% H₃PO₄ in water (10:90, v/v) with addition of sodium 1-octanesulfonate (0.3 mmol L⁻¹). The flow rate was 0.4 mL min⁻¹. The eluent was degassed in a Bransonic 1510R-DTH ultrasonic bath (USA). Sample volume was 20 μL, injection was performed with a loop. Deionized water was obtained from the purification system Millipore Simplicity (Millipore, Germany). A mechanical shaker and a magnetic stirrer were also used.
2.3. Synthesis of AuNRs and the nanocomposite

AuNRs were synthesized according to the method previously reported by Nikoobakht and El-Sayed [10] with some modifications. A detailed scheme of synthesis is described in [2].

The nanocomposite material based on polyurethane foam and AuNRs was obtained by sorption modification of polyurethane foam [4]. Samples of the nanocomposite were modified with silver nitrate. To do this, the nanocomposite was placed into 5 mL of 0.001 mol L⁻¹ AgNO₃, pressed with a glass rod, shaken for 10 minutes and dried between sheets of filter paper.

2.4. General procedure

To study the interaction of colloidal solutions of AuNRs with catecholamines, 0.3 mL of AuNRs, 20 µL of 0.01 mol L⁻¹ AgNO₃, 0.1 mL of glycine buffer solution and 0 – 0.5 mL of 25 µmol L⁻¹ catecholamines solution were added into a test-tube. The total volume of all components was 2.5 mL. The absorption spectra of the obtained mixtures were measured after 3 minutes.

Interaction of the nanocomposite modified with silver nitrate with catecholamines was studied by placing nanocomposite into 5 mL of solution containing 1 – 100 µmol L⁻¹ catecholamines and 1 mL of glycine buffer solution. It was shaken on a mechanical shaker for 30 minutes. Then the nanocomposite was removed and dried between sheets of filter paper. The diffuse reflection coefficients (R) of the obtained nanocomposite were measured in a range of 400 – 730 nm with the 10 nm increment. Then, the values of the Kubelka-Munk function (F) were calculated from the formula: \( F = \frac{(1-R)^2}{2R} \), here \( R \) is the diffuse reflection coefficient. The plotted spectra \( F \) versus \( \lambda \) were used to estimate changes in state of AuNRs in the phase of polyurethane foam.

3. Results and discussion

3.1. Interaction of catecholamines with AgNO₃ in AuNRs colloidal solution and AuNRs nanocomposite

The interaction of catecholamines with silver ions in the presence of AuNRs or the nanocomposite is accompanied by a hypsochromic shift of the SPR bands and an increase of their intensity (figure 2). These effects are visually detected as change of color of the AuNRs solution from pale purple to bright green and color of the nanocomposite from pale purple to grey. The shift of the maxima (Δ\( \lambda \)) can be considered as a characteristic of completeness of the interaction.

A supposed scheme of the interaction includes oxidation of CAs catechol group by silver ions into ortho-quinonoid structure and subsequent deposition of metallic silver onto the surface of AuNRs (figure 3).

Dependencies of the shift of maxima on concentration of individual epinephrine, norepinephrine, dopamine and their equimolar mixture are represented in figure 4. Initial parts of these dependencies can be used as calibration graphs for determination of CAs. Some analytical characteristics of CA determination are listed in table 1. Determination of catecholamines with the use of colloidal solution of AuNRs is characterized by higher sensitivity in comparison with the use of nanocomposite material. Moreover, lower volumes of the analyzing samples are required. Nevertheless, nanocomposite material is characterized by higher selectivity to determination of CAs in the presence of inorganic ions that could be caused by its matrix influence. Ease of use could also serve as an argument for determination of CAs by nanocomposite material.
Figure 2. Absorption (a) and diffuse reflectance (b) spectra of AuNRs before (1) and after (2) interaction with catecholamines.

Figure 3. A supposed scheme of interaction.
Figure 4. Dependencies of the shift of maxima of colloidal solution of AuNRs (a) and nanocomposite material (b) on concentration of individual epinephrine (1), dopamine (2), norepinephrine (3) and their equimolar mixture (4).

Table 1. Analytical characteristics of the determination of catecholamines (n = 3, P = 0.95).

|                         | epinephrine | norepinephrine | dopamine | equimolar mixture |
|-------------------------|-------------|----------------|----------|-------------------|
| Using the colloidal solution of AuNRs | y = 23.2x   | y = 23.5x       | y = 31.8x | y = 26.0x          |
| LOD, µg mL⁻¹           | 0.02        | 0.01            | 0.02     | 0.02              |
| Linear range, µg mL⁻¹  | 0.05 – 0.27 | 0.04 – 0.15     | 0.05 – 0.25 | 0.05 – 0.25      |
| Using the nanocomposite | y = 1.39x   | y = 1.82x       | y = 1.66x | y = 1.55x         |
| LOD, µg mL⁻¹           | 0.07        | 0.05            | 0.05     | 0.05              |
| Linear range, µg mL⁻¹  | 0.2 – 1.8   | 0.1 – 1.5       | 0.1 – 1.7 | 0.1 – 1.7         |
3.2. Determination of total catecholamines

In the case of some diseases progressions, a sharp change in the content of individual catecholamines is observed. Thus, in blood samples of patients with Alzheimer’s disease, 10-fold decrease in the content of dopamine may be observed [11]. Biological fluids of patients with Addison’s disease are characterized by 10-fold decrease in adrenaline levels [12]. For patients with pheochromocytoma, on the contrary, 10-fold rise of adrenaline production is peculiar [13]. Such changes in the content of individual catecholamines affect the overall content of catecholamines.

Since the sensitivity coefficients in the calibration graph equations for catecholamines, both in the case of colloidal solution of nanorods and nanocomposite, differ slightly (table 1), it is possible to use them to estimate the total content of catecholamines. Epinephrine, norepinephrine, dopamine, and their equimolar mixture were considered as possible standards for evaluation of CAs total content. Several mixtures containing these CAs in various proportions were analysed (tables A1, A2). The total content of catecholamines was calculated according to the equations of the calibration graphs presented in table 1 and compared with the added quantity.

In this paper, plotting a radar chart is proposed as a technique for estimation of the error in determining total content of CAs and selection of a standard system, in terms of which the total content should be expressed to minimize the error. The radar chart displays the module of relative error in the analysis of model mixtures. In this case, the mixtures were in order of increasing error by one of the standard substances (equimolar mixture). The resulting radar charts are shown in figure 5. Errors of the analysis are minimal for a standard (or standards) giving the smallest area of the diagram.

The advantages of the radar chart are ease of data interpretation and selection of the best standard; ease of estimating the minimum and the maximum error in determining sum of analytes within the studied samples (the closest and the furthest vertex of the obtained polyhedron) and the percentage of mixtures that can be analysed within the specified error (according to the angle of rotation of the radius vector, within of which the polyhedron does not exceed a circle characterizing this error). Moreover, the radar chart allows to evaluate compositions of real objects for which the smallest or the largest errors are achieved by using a particular standard.

As can be seen from figure 5, the standards giving the smallest error for the total content of CAs determined using colloidal solution of AuNRs are epinephrine and norepinephrine. Diagrams of these substances are practically equal and have the smallest area. In case of the nanocomposite material, dopamine or norepinephrine should be used as the standards: error in determination of the total amount does not exceed 0.2. The absence of obvious mutual influence of different catecholamines on each other allows to determine their total content.

![Radar Chart](image)

**Figure 5.** Relative error modulus (δ) of determination of the total amount of CAs with the use of colloidal solution of AuNRs (a) and nanocomposite material (b) in terms of epinephrine, norepinephrine, dopamine and the equimolar mixture.
To estimate a possibility of practical application of the proposed method, the analysis of a model mixture containing epinephrine (E), norepinephrine (NE), and dopamine (DA) in the ratio E:NE:DA = 1:7:32 (the average ratio of CAs in daily urine of a healthy adult) as well as inorganic ions in the following ratio "total content of CA: ion concentration": 1:100 Na⁺, 1:100 K⁺, 1:100 Mg²⁺, 1:100 Ca²⁺, 1:50 SO₄²⁻, 1:50 NO₃⁻, 1:450 Cl⁻ was performed. The results of the determination represented in table 2 indicate that the method can be used to determine the total content of CAs in mixtures containing 50 – 450-fold excess of common inorganic ions. As a standard substance for representing the total content of CAs, both individual catecholamines and their mixture can be considered.

Table 2. The results of determination of the total content of catecholamines in a model mixture with inorganic ions in terms of different standards (n = 3, P = 0.95).

| Standard substance | Epinephrine (E) | Norepinephrine (NE) | Dopamine (DA) | Mixture (E:NE:DA = 1:1:1) |
|--------------------|-----------------|--------------------|---------------|---------------------------|
| Using the colloidal solution of AuNRs | Added, µM | 1.00 | 1.05 ± 0.08 | 1.03 ± 0.07 | 0.76 ± 0.06 | 0.93 ± 0.07 |
| | Found, µM | 6.2 ± 0.9 | 4.7 ± 0.7 | 5.2 ± 0.8 | 5.5 ± 0.8 |
| RSD, % | 3 | | 3 | 6 |
| Using the nanocomposite | Added, µM | 5.0 | | | |
| Found, µM | 6.2 ± 0.9 | 4.7 ± 0.7 | 5.2 ± 0.8 | 5.5 ± 0.8 |
| RSD, % | 6 | | 6 | | |

3.3. Analysis of biological fluids

3.3.1. Determination of catecholamines in urine samples. The proposed approach was tested for determination of CAs in urine. Standard addition method was used for the analysis. For CAs determination by colloidal solution of AuNRs, 0.25 mL of urine and a mixture of catecholamines (E:NE:DA = 1:7:32) were added into the reaction mixture (0.30 mL of AuNRs colloidal solution, 0.10 mL of glycine buffer solution (pH 9.5), 0.02 mL of 0.01M AgNO₃, V = 2.50 mL). Total added CAs were 0/1/2/3 µM. For determination by the nanocomposite material, 3.00 / 0.30 mL of urine and a mixture of catecholamines (A:NA:DA = 1:7:32) were added into the reaction mixture (1.00 mL of glycine buffer solution (pH 9.5), V = 5.00 mL). Total added CAs were 0/5/10/15 µM. Then a tablet of the nanocomposite material modified with AgNO₃ was put, pressed with a glass rod, shaken on a mechanical shaker for 30 minutes and dried between sheets of filter paper.

As an independent method for estimating correctness of the determination, reversed-phase HPLC with amperometric detection was used. The mobile phase consisted of acetonitrile and 0.1% H₃PO₄ in water (10:90, v/v) with addition of sodium 1-octanesulfonate (0.3 mM), the flow rate was 0.4 mL min⁻¹. The results of CAs determination using gold nanorods and chromatography in urine samples are represented in table 3. Good agreement of the results obtained by various methods indicates their correctness.
Table 3. The results of determination of the total content of catecholamines in urine samples with the use of colloidal solution of AuNRs, nanocomposite material and HPLC.

|                     | Sample 1, μM     | Sample 2, μM     |
|---------------------|-----------------|-----------------|
| Using the nanocomposite | 10 ± 2 (RSD 9)  | 14 ± 5 (RSD 5)  |
|                     | 9.9 ± 0.4 (RSD 5) | 14 ± 1 (RSD 10) |
| Using the colloidal solution of AuNRs | – | 14 ± 0.7 (RSD 6) |
| HPLC                | epinephrine: 7 ± 3 (RSD 20) | epinephrine: 10.0 ± 0.7 (RSD 10) |
|                     | norepinephrine: 1.4 ± 0.2 (RSD 8) | norepinephrine: 1.3 ± 1.1 (RSD 40) |
|                     | dopamine: 1 ± 0.7 (RSD 40) | dopamine: 3 ± 4 (RSD 70) |

3.3.2. Determination of catecholamines in blood serum. Standard addition method was used for evaluation of a possibility of CAs determination in serum samples. 0.10 and 0.25 mL of blood serum were added into reaction mixtures containing colloidal solution of AuNRs and nanocomposite respectively. The dependencies of Δλ on the total concentration of catecholamines in the system were preliminarily measured. According to the results represented in table 4, the developed methods are applicable for the determination of CAs in serum at the level of 0.5 and 5 μM by using colloidal solution of AuNRs and nanocomposite material respectively.

Table 4. The results of catecholamines determination in blood serum with the use of colloidal solution of AuNRs and nanocomposite material (n = 3, P = 0.95).

|                     | Using the colloidal solution of AuNRs | Using the nanocomposite |
|---------------------|--------------------------------------|-------------------------|
| Added, μM           | 0.5                                  | 5                       |
| Found, μM           | 0.5 ± 0.1                            | 5 ± 1                   |
| RSD                 | 8                                    | 2                       |

4. Conclusions
Interaction of catecholamines with silver nitrate in the presence of colloidal solution of AuNRs and a nanocomposite material has been examined. This interaction is accompanied by a hypsochromic shift of the maxima in the SPR-spectra of AuNRs, the magnitude of this shift can serve as a characteristic of completeness of the reaction. The possibility of using epinephrine, norepinephrine, dopamine and their equimolar mixture as standards in the determination of the total content of catecholamines has been studied. To estimate the errors in determination of catecholamines and select the best standard, the use of radar charts has been proposed. The polyhedrons area correlates with value of the error, and the angle of rotation of the radius vector, within which the diagram does not exceed a circle characterizing the given error, serves to determine the percentage of mixtures, the analysis of which can be made within this error. The standards giving the smallest error in determination of the total content of CAs with the use of colloidal solution of AuNRs are epinephrine and norepinephrine. For the determination by the nanocomposite material, dopamine or norepinephrine should be used as the standards. Analysis of model mixture confirmed applicability of the developed method for the determination of the total content of CAs. The developed method can be applied to the analysis of urine and blood serum.

Acknowledgments
This work was financially supported by the Russian Science Foundation (grant N 18-73-10001).
Appendices

Table A1. Mixture compositions and results of the determination of the total content of catecholamines in these mixtures using colloidal solution of gold nanorods in terms of individual compounds and their equimolar mixture.

| No of mixture | Mixture composition (E:NE:DA), µM | Total content of catecholamines (µM) in terms of: |
|---------------|----------------------------------|--------------------------------------------------|
|               |                                 | Epinephrine (E) | Norepinephrine (NE) | Dopamine (DA) | Mixture (1:1:1) |
|               |                                 | $y = 23.2x$     | $y = 23.5x$         | $y = 31.8x$   | $y = 26.0x$    |
| 1             | 0.25:0.625:0.125                | 1.13            | 1.11                | 0.82          | 1.00           |
| 2             | 0.125:0.625:0.25                | 1.14            | 1.12                | 0.83          | 1.01           |
| 3             | 0.4:0:4:0.2                     | 1.09            | 1.07                | 0.79          | 0.97           |
| 4             | 0.5:0:0:5                       | 1.04            | 1.03                | 0.76          | 0.93           |
| 5             | 0.2:0:4:0.4                     | 1.04            | 1.02                | 0.76          | 0.93           |
| 6             | 0.025:0.175:0.8                 | 1.04            | 1.02                | 0.76          | 0.92           |
| 7             | 0.25:0:5:0.25                   | 1.03            | 1.02                | 0.75          | 0.92           |
| 8             | 0:0:5:0.5                       | 1.02            | 1.00                | 0.74          | 0.91           |
| 9             | 0.25:0:25:0.5                   | 0.97            | 0.96                | 0.71          | 0.87           |
| 10            | 0.125:0.25:0.625                | 0.95            | 0.94                | 0.69          | 0.85           |
| 11            | 0.25:0:125:0.625                | 0.92            | 0.91                | 0.67          | 0.82           |
| 12            | 0.5:0:5:0                       | 0.92            | 0.90                | 0.67          | 0.82           |
| 13            | 0.5:0:25:0.25                   | 0.91            | 0.89                | 0.66          | 0.81           |
| 14            | 0.4:0:2:0.4                     | 0.90            | 0.89                | 0.66          | 0.80           |
| 15            | 0.625:0.25:0.125                | 0.90            | 0.88                | 0.65          | 0.80           |
| 16            | 0.25:0.625:0.125                | 1.13            | 1.11                | 0.82          | 1.00           |

Table A2. Mixture compositions and results of the determination of the total content of catecholamines in these mixtures using nanocomposite in terms of individual compounds and their equimolar mixture.

| No of mixture | Mixture composition (E:NE:DA), µM | Total content of catecholamines (µM) in terms of: |
|---------------|----------------------------------|--------------------------------------------------|
|               |                                 | Epinephrine (E) | Norepinephrine (NE) | Dopamine (DA) | Mixture (1:1:1) |
|               |                                 | $y = 1.39x$     | $y = 1.82x$         | $y = 1.66x$   | $y = 1.55x$    |
| 1             | 0.125:0.875:4                   | 5.5             | 4.2                 | 4.6           | 4.9            |
| 2             | 2:2:1                           | 5.5             | 4.2                 | 4.6           | 4.9            |
| 3             | 1.25:2.5:1.25                   | 5.6             | 4.3                 | 4.7           | 5.0            |
| 4             | 2.5:1.25:1.25                   | 5.7             | 4.3                 | 4.8           | 5.1            |
|   |   |   |   |   |
|---|---|---|---|---|
| 5 | 1.25 : 1.25 : 2.5 | 6.1 | 4.7 | 5.1 |
| 6 | 2.5 : 2.5 : 0 | 6.3 | 4.8 | 5.3 |
| 7 | 1 : 2 : 2 | 6.5 | 5.0 | 5.4 |
| 8 | 2.5 : 0 : 2.5 | 6.7 | 5.1 | 5.6 |
| 9 | 2 : 1 : 2 | 6.8 | 5.2 | 5.7 |
| 10 | 0 : 2.5 : 2 | 7.1 | 5.4 | 6.0 |

References

[1] Liu J M, Wang X X, Cui M L, Lin L P, Jiang S L, Jiao L and Zhang L H 2013 A promising non-aggregation colorimetric sensor of AuNRs–Ag⁺ for determination of dopamine Sens. Actuat. B 176 97 – 102
[2] Gorbunova M V, Apyari V V, Dmitrienko S G and Garshew A V 2016 Formation of core-shell Au@Ag nanorods induced by catecholamines: a comparative study and an analytical application Anal. Chim. Acta 936 185 – 194
[3] Apyari V V, Arkhipova V V, Gorbunova M V, Volkov P A, Isachenko A I, Dmitrienko S G and Zolotov Yu A 2016 Towards the development of solid-state platform optical sensors: aggregation of gold nanoparticles on polyurethane foam Talanta. 161 780 – 788
[4] Gorbunova M V, Matveeva M A, Apyari V V, Garshew A V, Volkov P A, Dmitrienko S G and Zolotov Yu A 2017 Sorption of gold nanorods on polyurethane foam as a way to obtain a nanocomposite material with a surface plasmon resonance for chemical analysis purposes Nanotechnologies in Russia 12 185 – 192
[5] Pussard E, Neveux M, Guigueno N 2009 Reference intervals for urinary catecholamines and metabolites from birth to adulthood Clin. Biochem. 42 536 – 539
[6] Whiting M J and Doogue M P 2009 Advances in biochemical screening for pheochromocytoma using biogenic amines Clin. Biochem. Rev. 30 3 – 17
[7] Tsunoda M 2006 Recent advances in methods for the analysis of catecholamines and their metabolites Anal. Bioanal. Chem. 386 506 – 514
[8] Bergquist J, Ściubisz A, Kaczor A and Silberring J 2002 Catecholamines and methods for their identification and quantitation in biological tissues and fluids J. Neurosci. Methods 113 1 – 13
[9] Gorbunova M V, Gutorova S V, Berseneva D A, Apyari V V, Zaitsev V D, Dmitrienko S G and Zolotov Y A 2018 Spectroscopic methods for determination of catecholamines: a mini-review Appl. Spectrosc. Rev. DOI 10.1080/05704928.2018.1470980
[10] Nikoobakht B and El-Sayed M A 2003 Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method Chem. Mater. 15 1957 – 1962
[11] Fonteh A N, Harrington R J, Tsai A, Liao P, Harrington M G 2007 Free amino acid and dipeptide changes in the body fluids from Alzheimer's disease subjects Amino Acids 32 213 – 24
[12] Bornstein S R, Breidert M, Ehrhart-Bornstein M, Kloos B, Scherbaum W A 1995 Plasma catecholamines in patients with Addison's disease Clin. Endocrinol. 42 215 – 8
[13] Eisenhofer G, Keiser H, Friberg P, Mezey E, Huynh T T, Hiremagalur B, Ellingson T, Duddempudi S, Eijsbouts A, Lenders J W 1998 Plasma metanephrines are markers of pheochromocytoma produced by catechol-O-methyltransferase within tumors J. Clin. Endocrinol. Metab. 83 2175 – 85