

DEVELOPMENT OF THE METHOD FOR QUANTITATIVE DETERMINATION OF THE COMPOSITION OF Ag@Fe₃O₄ MAGNETIC NANOCOMPOSITE

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The method for quantitative determination of the components of the Ag@Fe₃O₄ nanocomposite has been developed; it allows simultaneously determining silver and iron in one sample without the stage of taking the aliquot for individual determinations of these components. The method proposed comprises: the use of a considerably smaller quantity of the substance in the test sample; elimination of the need to prepare and standardize the solution of the indicator for silver determination; reduces the labour intensity of the process by saving time and expensive reagents; eliminates the stage of separation of the mixture components, etc. The basis of the method proposed is two conjugated detection procedures – Ag determination by Volhard's method and Fe (III) determination in magnetite by the method of iodometry. It has been shown that this method allows determining silver without adding the indicator since the second component is magnetite containing bivalent and trivalent iron. The experiment is performed by the action of nitric acid on the sample of Ag@Fe₃O₄ powder. The acid, in its turn, helps silver to pass into solution and to oxidize Fe²⁺ ions to Fe³⁺ being an indicator in this determination. With the simultaneous presence of silver and iron in one sample at first silver is quantified, a pale pink colour of the solution above the precipitate appears only after all the silver has been titrated, that means the completeness of its precipitation. The experiment is completed with determination of Fe (III) by iodometry. To assess the validity of determinations the results have been confirmed by instrumental methods that are consistent with the results of the titrimetric method developed for quantitative determination of components in magnetically controlled nanocomposites. The relative error of the titrimetric determination does not exceed 0.1-0.2%.

РОЗРОБКА СПОСОБУ КІЛЬКІСНОГО ВИЗНАЧЕННЯ СКЛАДУ МАГНІТНОГО НАНОКОМПОЗИТУ Ag@Fe₃O₄

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Ключові слова: наночастки; композитні магнітокеровані системи; кількісне визначення

Розроблено спосіб кількісного визначення компонентів наноконкомпозиту Ag@Fe₃O₄, який дозволяє одночасно визначати срібло та залізо в одному зразку без проведення стадії відбору аліквот для окремих визначень цих компонентів. Запропонований спосіб призначений: для виконання експерименту використання наважки досліджуваного зразка значно меншої маси; усунення необхідності готувати та встановлювати титр розчину індикатора для визначення срібла; зниження трудомісткості процесу за рахунок економії часу та дорогих реактивів; передбачає виключення стадії розділення компонентів суміші та ін. В основі запропонованого способу лежать дві поєднані методики виявлення – визначення Ag методом Фольгарда та визначення Fe (III) у магнетиті методом йодометрії. Показано, що даний спосіб дозволяє проводити визначення срібла без додавання індикатора, оскільки другий компонент магнетит містить дво- та тривалентний ферум. Виконання досліді проводять дією на зразок порошка Ag@Fe₃O₄ нітратною кислотою, яка, у свою чергу, переводить срібло в розчин, а іони Fe²⁺ окиснює до Fe³⁺, які й виконують роль індикатора в даному визначенні. За сумісної присутності срібла та заліза в одному зразку першим кількісно визначають срібло, блідо-рожеве забарвлення розчину над осадом з'являється тільки після того, як увесь аргентум відтитровано, що визначає повноту його осадження. Дослід завершують визначенням Fe (III) методом йодометрії. Для оцінки достовірності визначень результати підтверджені інструментальними методами, які узгоджуються з результатами розробленого титриметричного способу кількісного визначення компонентів у магнітокерованому наноконкомпозиті. Відносна похибка титриметричного визначення не перевищує 0,1-0,2%.

РАЗРАБОТКА СПОСОБА КОЛИЧЕСТВЕННОГО ОПРЕДЕЛЕНИЯ СОСТАВА МАГНИТНОГО НАНОКОМПОЗИТА Ag@Fe₃O₄

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Ключевые слова: наночастицы; композитные магнитоуправляемые системы; количественное определение

Разработан способ количественного определения компонентов наноконкомпозита Ag@Fe₃O₄, который позволяет одновременно определять серебро и железо в одном образце без проведения стадии отбора аліквот для отдельных определений этих компонентов. Предложенный способ предназначен: для выполнения эксперимента использования навески исследуемого образца значительно меньшей массы; устранения необходимости готовить и устанавливать титр раствора индикатора для определения серебра; снижения трудоемкости процесса за счет экономии времени и дорогих реактивов; исключает стадию разделения компонентов смеси и др. В основе предложенного способа лежат две сопряженные методики обнаружения – определение Ag методом Фольгарда и определение Fe (III) в магнетите методом йодометрии. Показано, что данный способ позволяет проводить определение серебра без добавления индикатора, поскольку второй компонент магнетит содержит двух и трехвалентное железо. Выполнение опыта проводят действием на образец порошка Ag@Fe₃O₄ азотной кислотой, ко-

торая, в свою очередь, переводит серебро в раствор, а ионы Fe^{2+} окисляет до Fe^{3+} , которые и выполняют роль индикатора в данном определении. При совместном присутствии серебра и железа в одном образце первым количественно определяют серебро, бледно-розовая окраска раствора над осадком появляется только после того, как все серебро оттитровано, что означает полноту его осаждения. Опыт завершают определением Fe (III) методом йодометрии. Для оценки достоверности определенных результаты подтверждены инструментальными методами, которые согласуются с результатами разработанного титриметрического способа количественного определения компонентов в магнитоуправляемых наноккомпозитах. Относительная погрешность титриметрического определения не превышает 0,1-0,2%.

Magnetic nanoparticles and composites on their basis are the most studied and widely used nanoscale materials for medicine and pharmacy, and it is associated with their remote control by applying an external magnetic field [1]. Appropriate sizes, low toxicity and stable magnetic characteristics [2, 3] make it possible to use them for biomedical research at the cellular level [4, 5].

The world science and industries are constantly working to improve new methods for the synthesis of nanosized particles of silver and create a great number of products for their application in various fields [6]. Physicochemical and biomedical properties of silver nanoparticles allow including them virtually in any materials without the loss of valuable features. Combining several materials with useful properties into one system creates new opportunities when developing drugs of a new generation. Applying silver to the magnetite surface in the form of islets [8] leads to formation of the composite of the “core-shell” type [7], and silver as a modifying agent gives the system the ability to be controlled by the external magnetic field with the simultaneous antibacterial effect. This multifunctional system is one of the layered magnetic composites [9], which in recent years are profoundly studied for using in biomedical and pharmaceutical purposes.

When studying composites of the given composition the question of quantitative determination of the system components using expedient, economical, and rapid methods arises.

To determine the qualitative and quantitative composition the classical volumetric and gravimetric methods of analysis are used [10]. The disadvantage of gravimetric methods is a significant time of the research conducting (from several hours to several days). Being inferior in accuracy to gravimetry, the titrimetric methods differ by rapidity and are characterized as kinetic methods for the quantitative determination of the composition that are the most common in analytical practice. Currently classic methods are gradually giving way to highly sensitive instrumental ones, but they, in turn, have a number of disadvantages when determining ultra-small amounts of components. However, titrimetry and gravimetry remain unsurpassed in accuracy: the relative error of the titrimetric determination rarely exceeds 0.1-0.2%, while the error of many instrumental methods is 2.5%. Therefore, classical methods remain to be standard for quantifying the reliability of determinations.

The study of nanoscale objects, improvement of the quality of the existing objects and creation of the new ones involves improvement of the instrumental base, the use of modern express methods of research.

Based on the analysis of classical and modern sources of literature data [11-13] on the use of the methods for quantitative determination of silver and iron with their simultaneous presence in the same sample by express gravimetric and titrimetric methods are almost unknown. Modern instrumental methods of determining the quantitative content of the components in the objects of study (X-ray diffraction analysis (XDA) [12], atomic absorption spectrometry (AAS) [13], etc.) are not always available since they require the use of specific equipment and skills, the purchase of expensive reagents, the use of special software for processing results, etc.

Currently, quantitative determination of silver and iron in one sample is carried out separately by suitable methods [14, 15].

The aim of the work is to develop an express and simple method for quantitative determination of the composition of $Ag@Fe_3O_4$ magnetic nanocomposite.

According to the method developed for quantitative determination of the composition of $Ag@Fe_3O_4$ nanocomposite it has the following essential advantages. They are: determination of silver and iron in one sample; determination of silver does not require the indicator since iron is a part of magnetite; preparation of the titrants does not take much time, they are prepared from the titration standard with the known concentrations; titration takes place in the acidic medium to prevent hydrolysis of iron (III) with formation of coloured products of hydrolysis; when determining iron (III) the colour becomes visible already in the concentration of 6.4×10^{-6} mol/L [17], and the indicator is quite sensitive in relation to thiocyanate ions.

The method proposed is performed according to the experimental procedure developed: place 0.0200 g (accurate weight) of $Ag@Fe_3O_4$ into a conical flask with glass stopper, add 10 ml of 6 M nitric acid, and boil to complete removal of a brown gas. Cool the solution, add 50 ml of deionized water and mix thoroughly. Titrate with 0.01M solution of KSCN, it is accompanied by formation of a white precipitate $AgSCN$ ($K_{sp} = 1.1 \times 10^{-12}$ mol/L – practically insoluble [18]) until a pink colour of the solution appears (formation of insoluble iron complexes) and record the end point.

Table 1

Determination of the correction factor for the titre of 0.1 M solution of KSCN

The volume of 0.1M solution of AgNO ₃ , ml	The volume of 0.1M solution of KSCN, ml	K ₁
20.00	19.95	0.9930
20.00	19.95	0.9930
20.00	20.00	0.9905
Mean \bar{K}		0.9922
Standard deviation SD _K		0.0008
Relative standard deviation RSD _K , %		0.08
Relative confidence interval of the mean Δst (%)		0.18
Compliance with the requirements of the SPbU Δ _{st} ≤ 0.2%		0.18 ≤ 0.2

Table 2

Determination of the correction factor for the titre of 0.1 M solution of Na₂S₂O₃

The volume of 0.033M solution of KBrO ₃ , ml	The volume of 0.1M solution of Na ₂ S ₂ O ₃ , ml	K ₁
10.00	19.63	1.0437
10.00	19.65	1.0426
10.00	19.65	1.0426
Mean \bar{K}		1.0430
Standard deviation SD _K		0.0006
Relative standard deviation RSD _K , %		0.06
Relative confidence interval of the mean Δst (%)		0.11
Compliance with the requirements of the SPbU Δ _{st} ≤ 0.2%		0.11 ≤ 0.2

After that add 1 ml of concentrated hydrochloric acid and 0.3 g of potassium iodide to the test solution, mix thoroughly, close with a glass stopper and leave for 10-15 min in a dark place. Then wash the stopper on the flask with deionized water and titrate the liberated iodine with 0.05M sodium thiosulphate solution until a pale yellow colour of the solution appears. After that add 2-3 drops of starch solution (the solution becomes blue), and the titration is continued with vigorous stirring to discoloration of the solution above the precipitate. Record the end point.

The results of determination of the correction factors to the titres of 0.1 M solutions of potassium thiocyanate and sodium thiosulphate are given in Tab. 1 and 2.

As can be seen from Tab. 1 and 2, both titrated solutions meet the requirements of monograph 4.2.2. "Titrated solutions" of the SPbU, ed. 1 [14], as well as the requirements for precision of the molarity specified. It allowed obtaining correct and accurate results.

Determination of the quantitative content of silver and iron in Ag@Fe₃O₄ magnetic composite was performed in 5 parallel tests, for which homogeneity of the sample of the results for quantitative determination of the components in the mixture was checked. The calculated values Q₁, Q₅ for both components in separate determinations (Tab. 3) and components in one sample (Tab. 4) do not exceed the tabular values Q(P₁, n) [14]. It has been found that the results of the experiment are clear of gross error.

Table 3

The test for homogeneity of the sample of the results for quantitative determination of silver and iron in Ag@Fe₃O₄ composite (in a separate determination)

Parameters	Quantitative determination of silver					Quantitative determination of iron				
	1	2	3	4	5	1	2	3	4	5
x _i , %	37.09	37.14	37.17	37.19	37.22	52.16	52.63	54.15	54.17	55.14
R	0.13					2.98				
Q ₁	0.38					0.16				
Q ₅	0.23					0.33				
Q(P ₁ , n)	0.64					0.64				

Table 4

The test for homogeneity of the sample of the results for quantitative determination of silver and iron in Ag@Fe₃O₄ composite (in one sample)

Parameters	Quantitative determination of silver					Quantitative determination of iron				
	1	2	3	4	5	1	2	3	4	5
x _i , %	36.72	36.97	37.48	37.48	37.49	53.10	53.88	54.53	54.64	55.31
R	0.77					2.21				
Q ₁	0.32					0.35				
Q ₅	0.01					0.30				
Q(P ₁ , n)	0.64					0.64				

Table 5

Metrological characteristics of the average result of quantitative determination of silver by thiocyanometry

n	Sample weight	The volume of KSCN 0.01 M titrant	The silver content in % (Xi, %)
1	0.0200	6.90	37.14
2	0.0199	6.85	37.22
3	0.0199	6.85	37.19
4	0.0200	6.85	37.09
5	0.0200	6.9	37.17
Mean, Xi (%)			37.16
Standard deviation, s			0.0497
Dispersion, s ²			0,0081
Relative standard deviation (in relation to the average result), sr			0.0013
Relative standard deviation, RSD ₀ (%)			0.13
Standard deviation of the average result			0.0222
Relative standard deviation of the average result			0.0006
Relative standard deviation of the average result in %, RSDx (%)			0.05981
Confidence probability, P			95 %
The numerical value of Student's coefficient t (95%, 4)			2.7764
The half-width of the confidence interval of the average result Δx			0.06
The half-width of the relative confidence interval of the average result Δx,r			0.0017
The relative uncertainty of the average result, %			0.17

Table 6

Metrological characteristics of the average result of quantitative determination of iron (III) by iodometry

n	Sample weight	The volume of Na ₂ S ₂ O ₃ 0.05 M titrant	The content of iron (III) in % (Xi, %)
1	0.0206	4.06	55.14
2	0.0207	4.00	54.17
3	0.0201	3.75	52.16
4	0.0199	3.85	54.15
5	0.0202	3.80	52.63
Mean, Xi (%)			53.65
Standard deviation, s			1.2248
Dispersion, s ²			1.5003
Relative standard deviation (in relation to the average result), sr			0.0228
Relative standard deviation, RSD ₀ (%)			2.28
Standard deviation of the average result			0.5478
Relative standard deviation of the average result			0.0102
Relative standard deviation of the average result in %, RSDx (%)			1.021
Confidence probability, P			95 %
The numerical value of Student's coefficient t (95%, 4)			2.7764
The half-width of the confidence interval of the average result Δx			1.52
The half-width of the relative confidence interval of the average result Δx,r			0.02835
The relative uncertainty of the average result, %			2.83

Metrological characteristics of the average results are presented in Tab. 5 (for silver), 6 (for iron) and 7 (for silver and iron in one sample); it has been shown that the method gives reproducible results.

To compare the methods for the simultaneous and separate quantitative determination of silver and iron (III) Fischer test *F* was calculated. Its comparison with the tabular value of the distribution percentage point *F* (*P*, *v*₁, *v*₂) [14] shows that the discrepancy between the values *S*₁² and *S*₂² is not significant in both cases – for silver and iron, respectively (*S*₁² and *S*₂² – are dispersions of separate and simultaneous determinations), the reproducibility of both series are the same (dispersions are homogeneous).

The data of the results of the study of Ag@Fe₃O₄ nanocomposite obtained earlier by the methods of XDA and AAS [19] were compared with the results of quantitative determination of silver and iron by titrimetry. Analysis of the results of the content of mag-

netite in the sample took into account the gravimetric form (magnetite) and the analyte (iron III), for this purpose the analytical factor – 1.37 was determined [20].

Tab. 8 gives the comparative characteristics of the results obtained by different methods. The discrepancy between the percentage of the main components in the composite does not exceed 7-10% for magnetite and 10-20% for silver.

The results of determination of the quantitative content of Ag@Fe₃O₄ nanocomposite by the method proposed confirm the given core/shell molar ratio of 1 : 0.5 previously determined [21]. Therefore, this method can be recommended for use when developing the quality control methods for the substance mentioned above.

Experimental Part

The quantitative determination of silver and iron in the Ag@Fe₃O₄ nanocomposite under research by

Table 7

Metrological characteristics of the average result of quantitative determination in the simultaneous presence of silver and iron (III) in one sample

n	Sample weight	The volume of KSCN 0.01 M titrant	The volume of Na ₂ S ₂ O ₃ 0.05 M titrant	The silver content in % (Xi, %)	The content of iron (III) in % (Xi, %)
1	0.0201	6.95	3.85	37.48	55.31
2	0.0203	6.75	3.90	37.37	54.53
3	0.0199	6.80	3.90	37.15	54.64
4	0.0200	6.95	3.85	37.49	53.88
5	0.0202	6.95	3.80	37.48	53.10
Mean, Xi (%)				37.39	54.29
Standard deviation, s				0.1450	0.8374
Dispersion, s ²				0.0210	0.7012
The numerical value of Fisher test F (99%, 5)				15.98	
Fischer test, F				2.5963	2.1397
Relative standard deviation (in relation to the average result), sr				0.0039	0.0154
Relative standard deviation, RSD ₀ (%)				0.39	1.54
Standard deviation of the average result				0.0644	0.3745
Relative standard deviation of the average result				0.0017	0.0069
Relative standard deviation of the average result in %, RSDx (%)				0.1734	0.6897
Confidence probability, P				95%	
The numerical value of Student's coefficient t (95%, 4)				2.7764	
The half-width of the confidence interval of the average result Δx				0.18	1.04
The half-width of the relative confidence interval of the average result Δx,r				0.0048	0.0192
The relative uncertainty of the average result, %				0.48	1.92

the kinetic method was performed using two approaches: 1) separately, in individual samples; 2) simultaneously in one sample.

Silver was determined using thiocyanometry by Volhard's method [16]. The indicator in this method is Fe³⁺ ions, which forms soluble, red complex ions ([Fe(SCN)₄]⁻, [Fe(SCN)₃], [Fe(SCN)]²⁺, [Fe(SCN)₂]⁺) with SCN⁻ ions in the end point of titration. The thiocyanate complexes of iron (II) are not formed to the end point since thiocyanate ions, first of all, bind to AgSCN.

Before starting the experiment the control experiments were carried out. The first experiment for determination of silver – the sample contained magnetite nanoparticles and other necessary components except silver. The second experiment for determination of iron – the sample contained silver nitrate and the necessary components except iron.

Determination of the composition of nanoparticles was started with quantitative determination of silver. The accurately weighed quantity of the sample

Table 8

The comparison of the results of the quantitative content of silver and iron (III) in Ag@Fe₃O₄ nanocomposite

Method	Analytical signal	The content of components, %	Accuracy of measurements, %
XDA	The phase composition ¹ Fe ₃ O ₄ JCPDS # 88-315 Ag JCPDS # 87-717	The phase content, w % 67 33	±2.5%
AAS	Analytical lines ² Fe # 248.3 nm, calculated with reference to Fe ₃ O ₄ Ag # 328.1 nm	Content, % 51±2 69.87±2 29.6±1.5	3-5%
Titrimetry	The end point ³ Fe – discoloration of the solution, calculated with reference to Fe ₃ O ₄ Ag – precipitate AgSCN	Content, % 54.29±2.0 74.38±2.0 37.17±0.3	0.01%÷0.02%

Notes: 1. The number of substance according to the X ray card-file in the JCPDS (the Joint Committee of Powder Diffraction Standards) database of powder diffraction standards, PDF2. 2. Resonance lines (absorption signal) in the spectral range that is characteristic for the element. 3. The colour change of solutions, precipitation.

(0.0200 g) was quantitatively placed to a volumetric flask (250 ml) adding 6M nitric acid and boiled to complete dissolution of $\text{Ag}@Fe_3O_4$; the process was accompanied with intensive evolution of a brown gas.

After the gas evolution the solution containing ions of silver and iron (III) was cooled, and deionized water was added. The titrant, potassium thiocyanate, was prepared according to the instructions from the titration standard of the molarity specified – 0.1 M. For the experiment 0.05M potassium thiocyanate solution prepared by dilution of the stock solution was used. The product of analysis obtained as a result of dissolution was titrated with 0.05M KSCN solution, and a white precipitate AgSCN was formed. The titration was stopped when a stable pale pink colour of the solution appeared; it indicated the complete precipitation of silver ions. To the resulting solution 1 ml of the concentrated hydrochloric acid was added by a micropipette, then potassium iodide was added, thoroughly mixed, closed with a glass stopper and left for 10-15 min in a dark place. Then the stopper on the flask was washed with deionized water, and the liberated iodine was titrated with sodium thiosulphate solution ($\text{Na}_2\text{S}_2\text{O}_3$ solution was prepared according to the instructions for the titration standard of the molarity specified – 0.1 M, diluted to the required concentration, and its titre was determined). In the process of titration, when approaching the point of the analytical signal, the solution had a pale yellow colour, then the solution of starch was added (the solution became blue). The titration was continued with vigorous stirring to disco-

loration of the solution above the precipitate. The necessary calculations of the quantitative content of the components were performed.

Titration solutions of potassium thiocyanate and sodium thiosulphate were prepared according to the requirements of the State Pharmacopoeia of Ukraine (SPhU, ed. 1) [14]. To obtain correct results, in accordance with the requirements of the SPhU, the test for molarity of titrated 0.1 M potassium thiocyanate solution and assessment of uncertainties in the concentration of the standard solution were carried out. Determination of the correction factor (K) to the titre of 0.1 M potassium thiocyanate solution was performed for each aliquot of 0.1 M silver nitrate solution (Tab. 1).

The test for molarity of titrated 0.1 M sodium thiosulphate solution and assessment of uncertainties in the concentration of the standard solution were carried out according to the method of the SPhU, ed. 1 [14] (Tab. 2).

Conclusions

The affordable, simple, efficient, sensitive and reliable method for quantitative determination of the composition of the magnetic nanocomposite of $\text{Ag}@Fe_3O_4$ type has been developed. Using it silver and iron (III) can be identified in a single sample; and it can be recommended for use when developing the quality control methods for $\text{Ag}@Fe_3O_4$. The content of silver (37.17 ± 0.3) and iron (III) (calculated with reference to $Fe_3O_4 - 74.38 \pm 2.0$) confirms the given molar ratio of the core/shell.

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