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DETERMINAÇÃO AMPEROMÉTRICA DE CÉRIO (III) USANDO SOLUÇÃO DE ÁCIDO 2,7-DINITROZO-1,8-DI-HIDROXINAFTALENO-3,6-DISSULFÔNICO

AMPEROMETRIC DETERMINATION OF CERIUM (III) USING 2,7-DINITROZO-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID SOLUTION

АМПЕРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦЕРИЯ(III) РАСТВОРОМ 2,7-ДИНИТРОЗО-1,8-ДИГИДРОКСИНАФТАЛИН-3,6-ДИСУЛЬФОКИСЛОТЫ

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RESUMO

O cério e seus compostos são amplamente utilizados na produção de dispositivos eletrônicos e semicondutores, razão pela qual essas substâncias entrarão no meio ambiente com mais frequência no futuro. Há uma necessidade de métodos expressos eficazes que sejam capazes de determinar as quantidades residuais de cério e outros elementos de terras raras com alta precisão para controlar e estudar o possível impacto negativo dos compostos de cério nos ecossistemas. O objetivo deste trabalho de pesquisa foi elaborar um método expresso capaz de produzir resultados precisos e confiáveis sobre o teor de cério em águas residuais na presença de outros elementos de terras raras. A elaboração do método expresso foi realizada com base no método de titulação amperométrica estudando o efeito de várias soluções tampão na determinação de cério. Além disso, o efeito dos íons estrôncio, lutécio, ferro, ítrio, samário, nióbio, hólmio, praseodímio, gadolínio e érbio na precisão de aquisição dos íons cério (III) em amostras de água de processo foi estudado. Com base nos resultados da pesquisa, foi apresentado um método para a determinação amperométrica de cério (III) aplicando ácido 2,7-dinitroso-1,8-diidroxinaftaleno-3,6-dissulfônico em um microeletrodo de disco de platina rotativo. O método de análise extração-amperométrica foi proposto para a análise de água de processo. As concentrações ideais de eletrólitos de fundo e misturas de tampão, bem como os valores de voltagem, foram determinados; a constante de estabilidade do complexo foi calculada; foi definido o limite inferior do teor de cério determinado. Nenhuma influência de interferência de íons estranhos na determinação de íons de cério (III) foi observada. O método desenvolvido para a determinação de cério (III) tem um design de hardware mais simples do que o método descrito anteriormente de espectrometria de massa de descarga luminescente de corrente contínua pulsada, mas tem um limite de detecção mais alto.

Palavras-chave: *Titulação amperométrica, ácido 2,7-dinitrozo-1,8-di-hidroxinaftaleno-3,6-dissulfónico, potencial de meia onda, eletrólitos de fundo, extração*.

ABSTRACT

Cerium and its compounds are widely used in the production of electronic devices and semiconductors, which is why these substances will enter the environment more often in the future. There is a need for effective express methods that can determine the trace amounts of cerium and other rare earth elements with high accuracy to control and study the possible negative impact of cerium compounds on the ecosystems. The objective of this research paper was to elaborate on an express method capable of producing accurate and reliable results on the content of cerium in wastewaters in the presence of other rare earth elements. The elaboration of the express method was carried out based on the amperometric titration method studying the effect of various buffer solutions on cerium determination. Moreover, the effect of strontium, lutetium, iron, yttrium, samarium, niobium, holmium, praseodymium, gadolinium, and erbium ions on acquisition accuracy of the cerium (III) ions in samples of process water was studied. The research results presented a method for the amperometric

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determination of cerium (III) applying 2,7-dinitroso-1,8-dihydroxynaphthalene-3,6-disulfonic acid on a rotating platinum disk microelectrode. The extraction-amperometric method of analysis was proposed for the analysis of process water. The optimal concentrations of background electrolytes and buffer mixtures and the voltage values, were determined; the stability constant of the complex was calculated; the lower limit of the determined cerium content was defined. No interfering influence of foreign ions on the determination of cerium (III) ions was observed. The developed method for determining cerium (III) has a simpler hardware design than the previously described method of pulsed direct current glow discharge mass spectrometry but has a higher detection limit.

Keywords: *amperometric titration, 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid, half-wave potential; background electrolytes, extraction.*

АННОТАЦИЯ

Церий и его соединения широко применяются при производстве электронных устройств, и полупроводников, из-за чего данные вещества в дальнейшем будут всё чаще попадать в окружающую среду. Для контроля и изучения возможного негативного влияния соединений церия на экосистемы требуются эффективные экспресс-методы, способные с высокой точностью определять микроколичества церия и других редкоземельных элементов. Цель работы заключалась в разработке экспресс-метода, способного давать надежные и достоверные результаты по содержанию церия в сточных водах в присутствии других редкоземельных элементов. Разработку экспресс-метода проводили на основе метода амперометрического титрования с исследованием влияния различных буферных растворов на определение церия. Кроме того, исследовали влияние ионов стронция, лютеция, железа, иттрия, самария, ниобия, гольмия, празеодима, гадолиния и эрбия на точность обнаружения ионов церия(III) в образцах технологических сточных вод. По результатам исследований представлена методика амперометрического определения церия(III) с использованием 2,7-динитрозо-1,8-дигидроксинафталин-3,6-дисульфокислоты на вращающемся платиновом дисковом микроэлектроде. Для анализа технологических сточных вод предложен экстракционно – амперометрический метод анализа. Установлены оптимальные концентрации фоновых электролитов и буферных смесей, а также значения напряжения, рассчитана константа устойчивости комплекса и определена нижняя граница определяемого содержания церия. Мешающее влияние посторонних ионов на определение ионов церия(III) не наблюдалось. Разработанный метод определения церия (III) отличается более простым аппаратным оформлением, чем описанный ранее метод импульсной постоянной токовой масс-спектрометрии с тлеющим разрядом, но обладает более высоким пределом обнаружения.

Ключевые слова: *амперометрическое титрование, 2,7-динитрозо-1,8-дигидроксинафталин-3,6-дисульфокислота, потенциал полуволны, фоновые электролиты, экстракция.*

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1. INTRODUCTION:

The chemical industry, medicine, and the electric power industry are currently developing rapidly, increasing the need to develop express methods for determining the micro concentrations of rare and rare earth metals. The development of new technologies for the processing of sludge containing rare earth metals (REM) and materials based on them is especially relevant as global consumption of these elements increases with the growth in the production of electronics and microelectronics (Gwenzi *et al*., 2018; Romero-Freire *et al*., 2019). Cerium and its compounds are used to manufacture electronic devices, semiconductors, luminophores, heat-resistant ceramics and optical glasses, catalysts, pigments, batteries, superconductors, and UV filters, neutron accelerators (Zefirov and Knunjanc, 1995). Besides, the use of cerium can be mentioned in the corrosion protection of aluminum in marine environment (H. Allachi *et al.,* 2010; M.A. Osipenko *et al.,* 2019), in batteries (Lianbang Wang *et al.,* 2020), for purification of various gases (Ye Shan *et al.,* 2020), for detecting phosphates in water (Meng Liu *et al.,* 2020). Cerium compounds are used in medicine (S. Rajeshkumar and Poonam Naik, 2018) and to treat cancer (Fatemeh Kadivar *et al.,* 2020).

Thereby, the microgram quantities of cerium will increasingly frequently be released into the environment; and to prevent that, various treatment methods are under development (Ebrahim Allahkarami *et al.,* 2019; James McNeice *et al.,* 2020; A.G. Morozova *et al.,* 2020; Xin-jun Bao *et al.,* 2020). The need for purification is justified by a negative impact from cerium onto the plants, including the food crops (Sanghamitra Majumdar *et al.,* 2014; Sanghamitra Majumdar *et al.,* 2016; Wei Zhang *et al.,* 2016; Anuja Koul *et al.,* 2018; Yu Wu *et al.,* 2019; Jiu-Qiang Xiong *et al.,* 2020; Cyren M. *et al.,* 2020).

One of the main problems is that determining cerium in complex biological objects at environmentally significant concentrations is rather complicated in hardware terms. For example, trace amounts of cerium were previously studied in the shoots of four plant species, including cucumber, tomato, soy, and pumpkin (Dan *et al*., 2016). In this study, we used the method of single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS), which requires expensive and sophisticated equipment to implement. Together with that, in the study of Dan Y. *et al*. (2016), the size and distribution of particles, the concentration of particles, and dissolved cerium by size are determined. This study is the first one that reports and demonstrates dissolved cerium in the shoots of plant seedlings. The degree of absorption and accumulation by plants depends on the type of plants, which requires further systematic study of these mechanisms, which, in turn, requires a long analysis period (Stowers *et al*., 2018). In the study of Singh, Hussain, Singh, and Singh (2019), it is shown that the effect of cerium oxide nanoparticles ranging in size from 30 to 75 nm in concentrations of 20 and 100 mg/l on plants may be more favorable for the growth and metabolism of tomato plants than the effect of CeO_2 in equivalent concentrations.

The study of Wang Y., *et al*. (Wang *et al*., 2019) shows that CeO_2 nanoparticles can activate plant (in this case, rice) antioxidant defense systems to counteract oxidative stress caused by such pollutants as NaCl and $CdCl_2$. This leads us to the conclusion that, despite the ambiguous effect of cerium on plants, control over the distribution of cerium in natural objects and the development of methods for its detection are relevant nowadays.

Studies are being conducted worldwide based on the use of specific analytical reagents for the development of sensitive and selective methods for the determination of trace amounts of rare and rare earth metals in ores, sludges, and technological wastes. There is a method that allows determining trace amount of cerium by the potentiometric method with Schiff base N,N bis-(Furan-2-ylmethylene)-1,4-phenylene diamine (BFMPDA) (Moustafa and Abd-Allah, 2011a) and with 1,4-bis(2`-carboxyphenylazomethine)phenylene (Moustafa and Abd-Allah, 2011b) in dioxane medium and also to calculate the stability constants of the resulting complexes.

There is also a spectrofluorimetry method to study the content of cerium with N-acetyl-4-aminophenol (paracetamol) at the ultra-trace level (Jamaluddin, Prosenjit, and Tazul, 2019). This method is based on the oxidation of paracetamol in the presence of a slightly acidic (0.05 – 0.15M H_2SO_4) water solution with fast oxidizing agent cerium (IV) for direct spectrofluorimetric determination of paracetamol. As well there is a method for determining cerium (III) and manganese (II) by the spectrophotometric method using iodine-based on Dushman reactions (Ungureanu, Duca, Humelnicu, and Bourceanu, 2018). Reactions are based on redox processes; the solution potential depends on the concentration of the determined element.

The extraction method using extragent DX-510A of β-diketones class which was studied by the electroflotation method, was previously developed for extraction and separation of cerium (III), (IV) and copper (II) ions from the water solutions (Meduntseva *et al*., 2015; Volkova, Gaydukova, Brodskiy, and Kolesnikov, 2015). The maximum degree of extraction of cerium (III) ions is achieved by separating cerium (III) from lanthanum (III) in an extraction system using nitric acid solutions at pH 4.0, and lanthanum (III) at pH 7.0 (Gayfullina *et al*., 2015). To increase extraction, the extraction process is carried out several times.

The method of pulsed direct current glow discharge mass spectrometry is described in the literature. Using this method (PGD-TOF-MS) 24 elements (As, B, Ce, Co, Dy, Fe, K, La, Lu, Mg, Mn, Na, Nb, Nd, P, Pr, Rb, S, Sb, Si, Sm, Th, Ti, and U) in ore samples were studied (Ganeev *et al*., 2019; Jaison, Kumar, Telmore, and Aggarwal, 2009; Jaison *et al*., 2009). The samples were prepared by pressing powdered samples into aluminum tablets with 10 mm diameter to determine cerium. The detection limits of the developed method were within the range $2–4 \cdot 10^{-6}$ mass % depending on the element. Some elements prevent the determination of cerium.

The literature data shows that the development of a technique with high sensitivity, accuracy, and a wide range of determined concentrations is required. Thus, the amperometric method stands out by simplicity of hardware and methodological implementation, comparative rapidity of analysis (Shaydarova, Chelnokova, Ilina, Gedmina, and Budnikov, 2017).

This study aimed to develop a new express and highly sensitive amperometric methods for determining the mass concentrations of cerium (III) with a synthesized reagent 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid in objects various in nature at the level of micro quantities with improved metrological characteristics (accuracy, reproducibility, expansion of the range of determined contents, selectivity).

2. MATERIALS AND METHODS:

The influence of the potential supplied to the indicator electrodes (0.25-1.0 V) on the shape of the curves, and the results of amperometric titration (AT) of cerium (III) using 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution was examined.

As a rule, the concentration of reagents must significantly exceed the number of metals to be determined. The titrant was added in small portions 30 µl with a precision piston microburette, so dilution of the test solution could be neglected (Lurye, 2012). Standard cerium (III) solutions were made by dissolving precise salt samples $CeCl_3·6H_2O$ (99% of basic substance) by known methods: 0,35461 grams of the CeCl3·6H2O salt samples were weighed up using the analytic scales, and brought up to the mark by bidistilled water in the 1 l measuring flask. The concentration of the resulting solution amounted to 0,001 M or 141 µg/ml of cerium (Geyrovskiy, Kuta, Geyrovskiy, and Kuta, 1965).

The solutions of 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid were made by dissolving the sample 0,1 g in bidistilled water 100 ml with a concentration equal to 0.1%. Solutions of buffer mixtures and metals were prepared from the relevant salts and acids. The universal buffer mixture was prepared in the 1 l measuring flask from phosphoric, acetic and boric acids, with 0,04 M of each by the procedure as follows: 2,33 ml of acetic acid of 1,05 g/ml density, 2,48 g of boric acid and 2,45 ml of phosphoric acid of 1,755 g/ml density was poured into the measuring flask, and was adjusted upto the mark by bidistilled water. pH of the universal buffer mixture amounted to 1,81.

The solutions of background electrolytes as below were also used in the study: 0,2 M solution of potassium phthalic acid (40,846 g of salt was dissolved in a 1 l measuring flask, with pH 2,20; (content of the main substance being 99,8 %)), 0,1 M solution of potassium citrate (21,014 g of citric acid monohydrate was added to 200 ml of 1 n. potassium hydroxide solution and brought upto the mark in the 1 l measuring flask (citric acid monohydrate, basic substance content being 99,5%)); 0,1 n. of aminoacetic acid solution (7,507 g of aminoacetic acid was added to 5,85 g sodium chloride and brought up to the mark in the 1 l measuring flask (aminoacetic acid, content of the main solution being 98,5%)).

The bidistilled water obtained using the distiller Heal Force CR-RO30 (China) was used for the experiment. The electrical conductivity of bidistilled water was 0.475 mSm/m. The piston microburette of 2.0 ml allowing to dose the titrant with an accuracy up to 0.001 ml was used for titration with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution. The manual ammeter “Expert – 001 A” pH-meter pH/mV/TEMP Meter P25 EcoMet (Korea) was used for AT.

Britton-Robinson universal buffer mixture was prepared using Lurye method (Lurye, 2012): a solution of the mixture of acetic, boric, and phosphoric acids (0.04M in respect of each) was prepared in a 1 L measuring flask. Then it was brought to the mark by bidistilled water. The remaining buffer solutions were prepared according to known methods. The solutions of potassium phthalate (99.8% of basic substance), potassium citrate (potassium citrate monohydrate, 99.5% of basic substance), and aminoacetic acid (98.5% of basic substance) were used in the study as background electrolytes.

To determine the effect of other ions on the determination of cerium (III) ions, the substances shown in Table 1 were used. For bringing ions in, 0.01 M salt solutions were prepared. A sample of the required mass was weighed on an analytical balance and dissolved in a 250 ml measuring flask. The weighing error was ± 0,00001 g. All the substances used were produced by Merck company (Germany). Technical waters used in the study were previously analyzed by the atomic absorption method using an AA spectrometer Shimadzu 6200.

Method for determination of cerium was: 2 ml of a standard solution of cerium was added to a measuring cup, 1 ml of a Britton-Robinson universal buffer mixture with pH 3.55 was added, and distilled water was added to reach 10 ml of volume. Then it was titrated with a 0.1 % solution of 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid and the cerium concentration was determined by the equivalence point.

For statistical estimation of the accuracy of the developed method for cerium (III) determination using 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution with two platinum indicator electrodes, AT of its various amounts was carried out with multiple (at least 4 times) repetition of each determination under the following optimal conditions: 2.0 ml of 0.04 M universal buffer solution (pH 3.55), the potential difference ΔE = 0.75 V, the total volume of the examined solution was 10 ml.

2.1. Influence of voltage

The development of AT methods should start with taking polarogram of the corresponding ion. The polarogram is taken on the electrode which is supposed to be titrated in the future, and in the same medium. The potential of the indicator electrode should be set more negative (on 0.1-0.3). The composition and acidity of the examined solution at a selected potential value can lead to the release of impurities present in the solution or hydrogen recovery. The correctness of the choice of potential can be easily checked as follows: a solution which should serve as the background for the proposed titration is placed in the titration cup; a solution containing the ion which should give an electrode reaction is placed in the burette. The selected potential is set on the indicator electrode. The polarogram is usually taken on the background on which the titration will take place. Amperometric indication of the titration endpoint (TEP) of ions of various metals with two indicator electrodes must be carried out at a voltage of 0.30-1.10 V. The current-voltage curves of 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid on a platinum disk microanode in the presence of various background electrolytes in an aqueous solution indicate the optimal voltage for the complex formation of cerium ions should be (ΔE) 0.75 V (Spiridonov, Lopatkin, Spiridonov, and Lopatkin, 1970).

2.2. Logarithmic analysis

The number of electrons emitted during cerium electrooxidation was determined from the slope of the line chart showing dependence on E when studying the mechanism of the electrode complex formation process of cerium with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid. The half-wave potential of the obtained complex compounds was determined at different concentrations of the reagent in the optimal value of the buffer mixtures by adding surfactants, and the values of current-voltage curves of the ABC polarographs (made in Russia) and the three-electrode cell were taken.

2.3. Statistical processing

Statistical processing of the obtained results was carried out by calculating the standard deviation and relative standard deviation. The standard deviation was determined by the equation:

$$S = \sqrt{\frac{\sum_{n=1}^{n}(x_i - \bar{x})^2}{n-1}} \qquad (1)$$

Where S is standard deviation,

$\bar{x}$ – arithmetic mean of n measurements

x_i – measurement result

n – number of measurements

The relative standard deviation was determined by the equation:

$$S_r = \frac{S}{\bar{x}} \qquad (2)$$

where S_r is relative standard deviation.

3. RESULTS AND DISCUSSION:

The results obtained from cerium (III) AT using 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution with various buffers are shown in Figure 1. For a statistical assessment of the method's accuracy, amperometric titration of various amounts of cerium was conducted under optimized conditions. The titration results are shown in Table 2. The developed method was also tested by the analysis of process water. Extraction with TBF was used to separate cerium from other metals (Bukin and Igumnov, 2002; Simonova, 2019). The results of cerium (III) extraction-amperometric determination using 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution with the presence of foreign ions are shown in Table 3.

When developing AT techniques with one or two solid indicator electrodes in any (aqueous, non-aqueous and mixed) medium, it is necessary to know the peculiarities of the voltammetric behavior in it on the corresponding electrode of not only the detected ions, but also the reagent used and its metal complexes. This is necessary in order to correctly select the optimal titration conditions and the potential difference applied to the indicator electrodes. $E_{1/2}$ becomes more negative with increasing pH for electrode recovery processes involving hydrogen ions in the potential-determining stage. Conversely, the effect of pH on $E_{1/2}$ unambiguously indicates the participation of hydrogen ions in the potential-determining stage.

In the case of reversible processes, the hydrogen concentration is found by the Nernst equation. Kinks are often observed on the curves of the dependence of $E_{1/2}$ on pH. If the recovered form is protonated, then the incline of the almost rectilinear section after the kink is greater than before it with an increase in pH, and the pH of the kink corresponds to the pKa of the recovered form. If, on the contrary, the oxidized form is protonated, the $E_{1/2}$ – pH curve consists of line segments, the incline of which decreases with increasing pH, and the kink corresponds to the pKa of the oxidized form. If both the oxidized and reduced forms are able to protonate or if one or both forms are polybasic acids (bases), then the dependence of $E_{1/2}$ on pH is a polyline, each kink of which corresponds to one of the pKa values. In a wide range of pH changes, the dependence of $E_{1/2}$ on pH is expressed by an S-shaped curve: in a strongly acidic medium, $E_{1/2}$ ceases to depend on pH, since the entire depolarizer is in protonated form. In an alkaline medium, $E_{1/2}$ usually does not depend on pH; in this case, the recovery process takes place with the participation of only one proton donor – water. The vast majority of the electrochemical transformations of organic compounds on a platinum electrode in protogenic media involve adding or removing protons. Most often, the source of protons is the hydroxonium ions present in the solution, but any other proton donors can function as such a source. Proton transfer can take place either before electron transfer, or after it. Before the actual electrochemical stage, the addition of protons affects the $E_{1/2}$ value of both a reversible and an irreversible process.

Electrooxidation of 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid in different media is studied while determining metals in AT. Half-wave potential of 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid in acidic medium equals ($E_{1/2}$) 0.72 V. Chemical mechanism of reagent electrooxidation is shown in Figure 2.

Nernst equation shows that the half-wave potential of the solution is directly proportional to the concentration of the titrant being determined. Therefore, a straight line is observed up to the equivalence point during amperometric titration as a result of complex formation of the studied metal with an organic reagent, and a curve grows after the equivalence point, confirming the electrooxidation of the organic reagent.

The background electrolyte affects the complex formation reaction; therefore, we studied the effect of the nature and concentration of background electrolytes and buffer mixtures in this work. We studied the effect of the nature and concentration of background electrolyte and buffer mixture on the results of cerium (III) AT using 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution. Results of titration using universal buffers with pH 1.12 showed that cerium (III) is titrated well enough in strongly acidic environments (pH 1.18-4.2), and in neutral and basic ones it forms low-strength complex compounds with the used reagent and, accordingly, is not titrated well enough (Figure 1).

Based on the polarogram curves, the half-wave potential and the dependence of the logarithmic value of the reagent were found, the composition of the complex was found, and the conclusion was made about the complex formation of cerium with a solution of 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid. The obtained data is shown in Table 4 and in Figure 3.

Figure 3 shows that complexes of Me:Reagent=2:1 compound are obtained by AT of cerium (III) ions with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid. The graph showing their dependence is given in Figure 4. The dependence of the half-wave potential on the concentration of the complexing reagent can be calculated by the stability constant of the complex and its compound by the Lingane method (Lurye, 2012):

$$
\begin{aligned}
&(E_{1/2})comp - (E_{1/2})reagent = \\
&= \frac{RT}{nF}\ln\sqrt{\frac{D}{D^*}} - \frac{RT}{nF}\ln K - \frac{RT}{nF}\ln\left[X^{m-}\right]^p
\end{aligned}
\qquad (3)
$$

The calculated value of the complex stability constant equals $1.6 \cdot 10^4$.

The mechanism of cerium and reagent complex formation shows that there is the complex and after the equivalence point up to the equivalence point 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid electrooxidizes.

3.1. Statistical evaluation of the accuracy

Table 2 and Figure 5 show different amounts of cerium (III) with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution titration, processed following the rules and procedures known in the literature of mathematical statistics (Kutlimurotova, Mahmadoliev, and Smanova, 2018). As Table 3 and Figure 5 show, the found amounts of Ce (III) correspond to its introduced contents and do not go beyond the confidence interval. This once again confirms the high accuracy of the developed amperometric method for determining cerium (III) with a relative standard deviation (S_r) not exceeding 0.014 and a lower limit of the determined contents equal to 0.7 mcg/ml. Complex characteristics are shown in Table 5.

3.2. Process water analysis

Cerium is found in process water together with scandium, yttrium, uranium, thorium, and lanthanides. As mentioned above, cerium was separated from other metals by extraction with TBF. Due to the large separation coefficient (> 1000), extraction of cerium (IV) can be single. The best results in the separation of cerium from REE are shown with extraction of 40% TBF in kerosene from 4M HNO_3. The separation of REE into groups using TBF can be conducted at a relatively low acidity of the solution (7 - 9M HNO_3), at which the separation and distribution coefficients are quite high. It is possible to divide the REE of the yttrium subgroup into separate groups and individual elements from more acidic solutions (12 – 13M HNO_3). The results are shown in Table 3. In the extraction-amperometric determination of cerium (III), the interfering effect of samarium, holmium, lutetium, and neodymium was not observed.

3.3. Comparison with the methods used

The detection limit of the proposed method is $70 \cdot 10^{-6}$ mass %, which is inferior to the method of pulsed direct current glow discharge mass spectrometry with a detection limit of $2–4 \cdot 10^{-6}$ mass % depending on the determined REE (Ganeev *et al*., 2019; Jaison *et al*., 2009; Kumar *et al*., 2013). However, unlike the latter method, the method of amperometric titration requires less hardware implementation and allows us to determine the content of cerium (III) ions in the process water.

4. CONCLUSIONS:

The developed method for the determination of cerium (III) can be used in metallurgical and chemical production, as well as for environmental monitoring of industrial facilities. The method allows determining the cerium (III) content in samples of ores and alloys, controlling the concentration of cerium in process water during production, and wastewater before and after treatment. The simple hardware implementation of the method and the relative simplicity of the analysis do not require serious retraining of laboratory personnel when introducing this method to industrial enterprises.

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Table 1. *Substances for studying the influence of other ions.*

Substance	The content of the main component/purity qualification
$ScCl_3$	99%
$FeCl_3$	98%
$YCl_3 \cdot 6H_2O$	99%
$NdCl_3$	99.99%
$HoCl_3$	99%
$PrCl_3$	99%
$ErCl_3 \cdot 6H_2O$	99.999%
$Lu(NO_3)_3 \cdot 6H_2O$	99.9%
$Sm(NO_3)_3 \cdot 6H_2O$	99.99%
$Gd(NO_3)_3 \cdot 6H_2O$	99.9%

Table 2. *Results of amperometric titration of different amounts of cerium (III) with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution under optimized conditions*

No.	Added Ce(III), μg	Found Ce(III), μg ($\bar{X} \pm \Delta X$; P=0,95)	S	S_r
1	1.40	1.49±0.02	0.021	0.014
2	14.00	14.22±0.05	0.043	0.003
3	28.00	28.38±0.06	0.052	0.002
4	42.00	42.31±0.06	0.048	0.001
5	56.00	56.36±0.08	0.069	0.001

Note: S – standard deviation, S_r – relative standard deviation

Table 3. *Results of 14 mcg of cerium (III) extraction-conductometric determination (D=0.8) (P = 0.95; n=5)*

Extractant	**Titrant**	**Foreign cation [x]**	**Added [x], μg**	$\frac{[x]}{[Ce]}$	**Found Ce(III), μg ($\bar{X}$ ±ΔX)**	**S**	**Sr**
40 % TBF kerosene 4M HNO_3	2,7-dinitrozo-1,8-dihydroxy naphthalene-3,6-disulfonic acid	Sc(III)	2.5	0.17	14.12±0.19	0.17	0.012
		Lu(III)	3.8	0.27	14.06±0.16	0.14	0.010
		Fe(III)	5.7	0.40	14.08±0.22	0.19	0.013
		Y(III)	6.8	0.48	14.07±0.14	0.12	0.008
		Sm(III)	8.2	0.58	14.04±0.08	0.07	0.005
		Nd(III)	9.8	0.70	14.06±0.12	0.11	0.008
		Ho(III)	10.5	0.75	14.07±0.15	0.13	0.009
		Pr(III)	18.0	1.28	14.09±0.17	0.15	0.011
		Gd(III)	22.4	1.60	14.08±0.10	0.09	0.006
		Er(III)	28.0	2.00	14.05±0.09	0.08	0.005

Note: S – standard deviation, S_r – relative standard deviation

Table 4. *The calculated data of the stability constant of the cerium with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution complex*

Cation	**HR**	**C_{HR}, mole fraction**	**lgC_{HR}**	**$E_{1/2}$ of the complex, V**	**K**	**P number of reagents**
Cerium(III)	2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid	0.001	-3	-0.29	$1.6 \cdot 10^4$	0.5
		0.01	-2	-0.22		
		0.1	-1.3	-0.15		
		0.2	-1	-0.14		
		0.5	-0.69	-0.16		

Note: HR – titration reagent; C_{HR} – reagent concentration; lgC_{HR} – logarithm of concentration; $E_{1/2}$ of the complex – half-wave potential of the complex, B; K – complex stability constant; P number of reagents – see Figure 3.

Table 5. *Certain characteristics of the complex Ce (III) with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid*

Cation	**HR**	**C_{HR}, mole fraction**	**Contents of the complex**	**K**	**Ionic strength, mol/L**
Ce^{3+}	2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid	0.01	2:1	$1.6 \cdot 10^4$	0.1

Note: HR – titration reagent; C_{HR} – reagent concentration; contents of the complex – the ratio of the determined metal and reagent in the complex; K – complex stability constant; Ionic strength – ionic strength of solution.

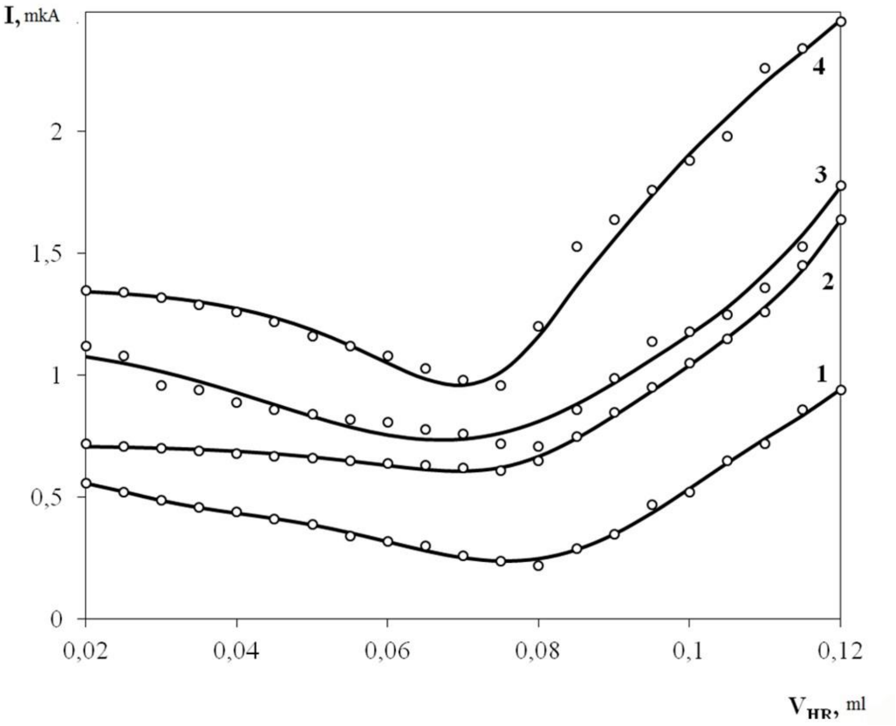

Figure 1. *The impact of different in nature background electrolytes on the shape of curves of cerium (III) amperometric titration with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution: 1 – potassium phthalate (pH 2.20); 2 – potassium citrate (pH 1.68); 3 – aminoacetic acid (pH 1.50); 4 – universal buffer (pH 1.81).*

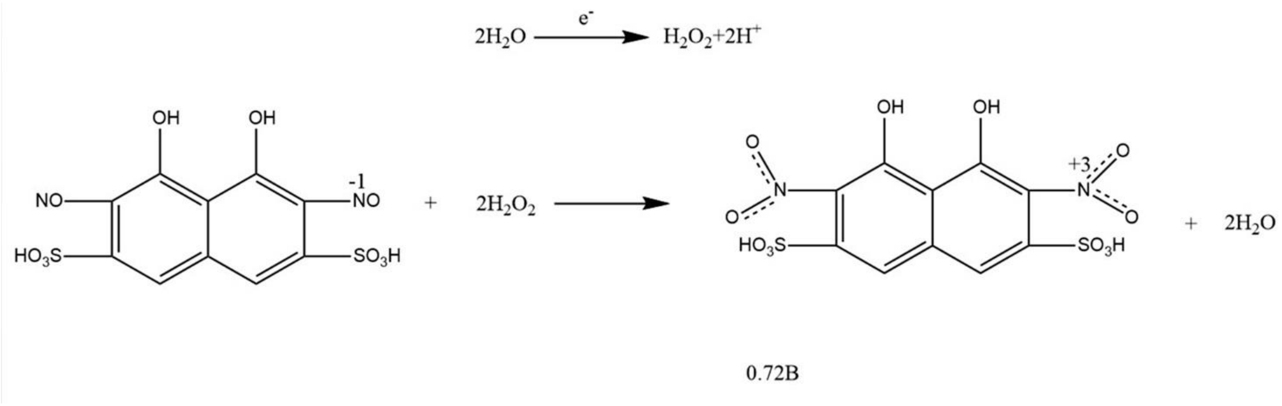

Figure 2. *Chemical mechanism of 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid electrooxidation*

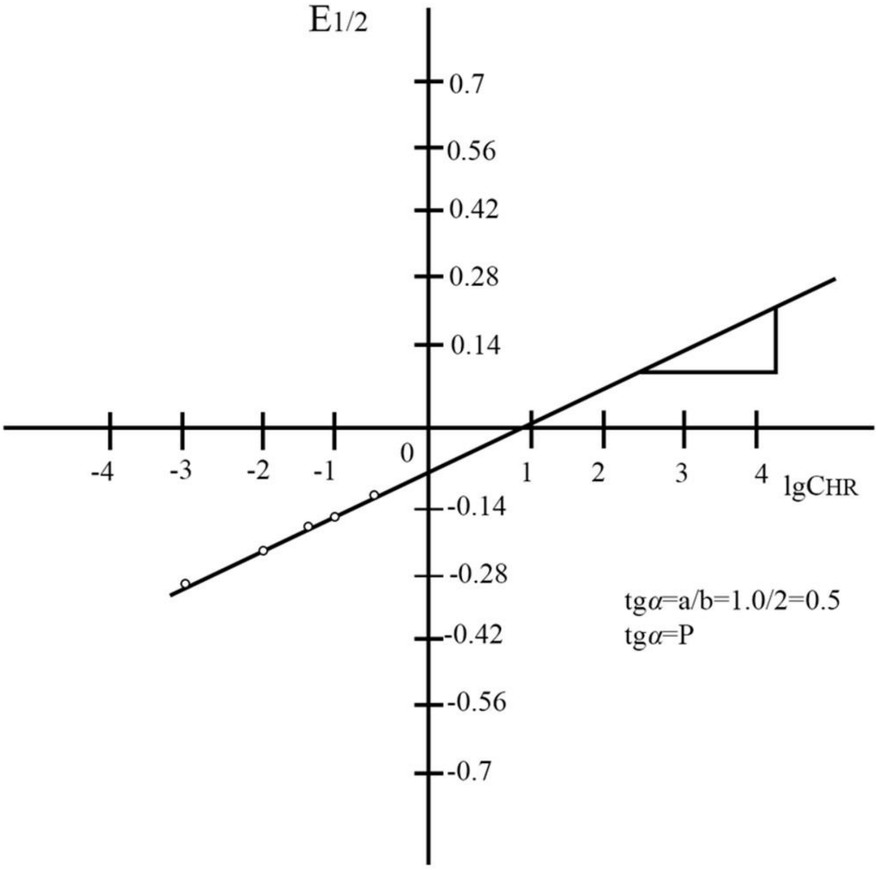

Figure 3. *Finding the stability constant value of the cerium (III) with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid solution*

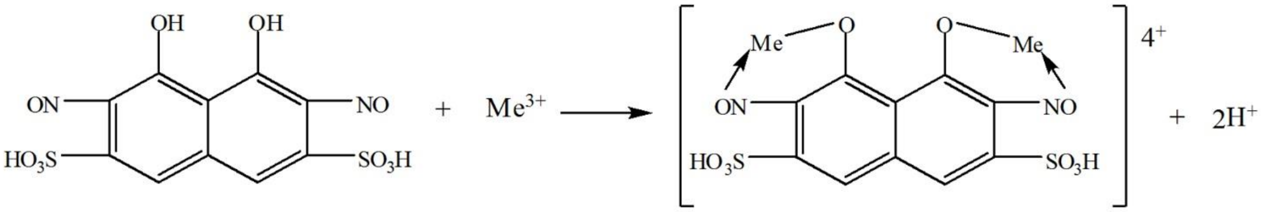

Figure 4. *Scheme of the interaction of metal ions with 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid*

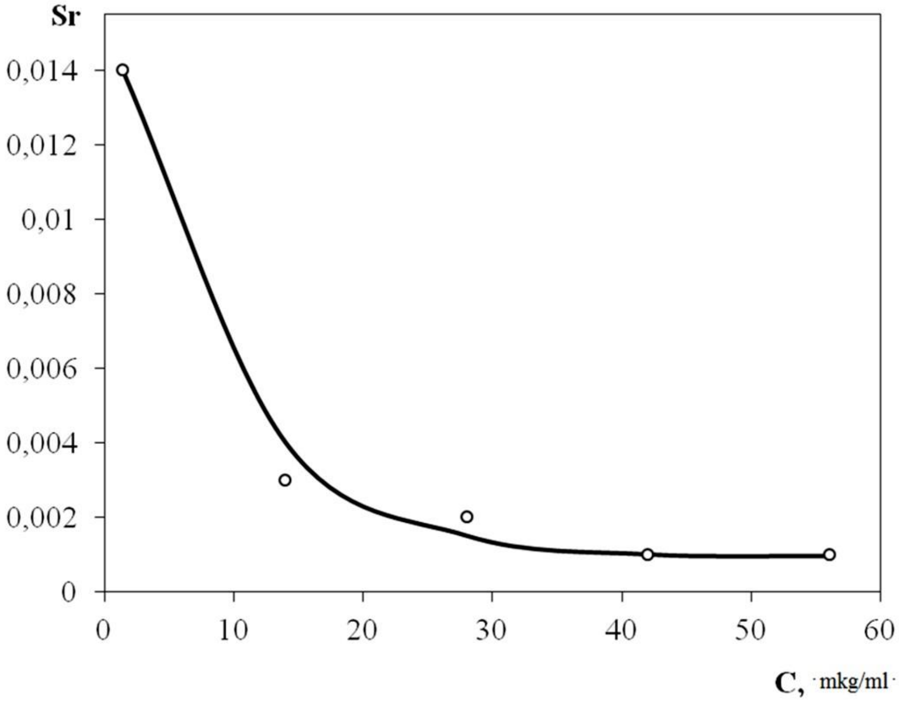

Figure 5. *Curves of the dependence of the relevant standard deviation (Sr) values on the determined element contents (CCe) using the reagent 2,7-dinitrozo-1,8-dihydroxynaphthalene-3,6-disulfonic acid*