DETERMINATION OF PHOSPHATE CONTENT IN WATER USING ORGANIC CHROMOGENIC COMPOUNDS

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Phosphorus compounds are introduced into natural waters in significant quantities as a result of anthropogenic activities. Agriculture and inadequate wastewater treatment are the main sources of phosphorus compounds. Increased levels of phosphorus compounds in water bodies lead to unbalanced eutrophication and significant changes in ecosystems. Therefore, monitoring phosphate levels is very important for maintaining the normal state of aquatic ecosystems. Spectrophotometry is one of the most widely used methods for measuring phosphate concentration. In the article, we reviewed existing spectrophotometric methods for determining the phosphate content in water and proposed a new method based on the use of a complex of metal indicators with metals. The principle of the method is based on the change of the metal complex with the metal indicator as a result of interaction with phosphate ions. Phosphate ions bind cations of metals such as zirconyl, since its phosphates have a very low solubility. The indicator released as a result of the destruction of the complex has a different color than the complex with a zirconyl cation. We experimentally tested the feasibility of using such metal indicators as chromazurol S, 8-oxyquinoline, arsenazo I, arsenazo III. The highest efficiency was demonstrated by the complex of chromazurol S with zirconyl ions, which is reflected in a clear change in color from purple to shades of crimson, red and orange for different phosphate concentrations. In the indicator system, we used a solution of chromazurol S with a concentration of 0.005 M and a solution of zirconyl nitrate with a concentration of 0.01 M. The ratio of the volumes of the solutions is 1:1. The proposed method of determination requires a significantly smaller amount of reagents than molybdate method.

Keywords: *aquatic environment, chromazurol S, indicator system, phosphate, water pollution*

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1. Introduction

Phosphorus compounds are introduced into natural waters in significant quantities as a result of anthropogenic activities. For undisturbed waters, phosphorus concentrations are usually below 0.025 mg P/L, but in most freshwater bodies of water, phosphorus concentrations are above 0.05 mg P/L (Shaum, 2018).

Agriculture and inadequate wastewater treatment are the main sources of phosphorus compounds (Sellal et al., 2024; Zahoor et al., 2023).

Phosphorus is an essential element for normal plant growth (Shaum, 2018). Therefore, various types of phosphate fertilizers are widely used in agriculture. Atmospheric runoff leaches phosphates from the soil and enters groundwater and surface water (Patel, 2025).

Wastewater, especially municipal and food industry wastewater, contains a large amount of phosphorus compounds, as they are

part of many detergents, food additives, etc. (Goswami et al., 2021). In the case of insufficiently efficient operation of treatment plants, phosphorus compounds in the composition of treated wastewater are discharged into water bodies. In addition, pit latrines, which are still found in rural areas, can pollute groundwater with phosphorus compounds that leach from excrements (Graham & Polizzotto, 2013).

Minor phosphate impurities in drinking water do not harm human health, and are sometimes even specifically added to drinking water to reduce lead leaching from old lead-containing pipes (Ascott et al., 2016). But aquatic ecosystems are much more sensitive. Increased levels of phosphorus compounds in water bodies lead to unbalanced eutrophication and significant changes in ecosystems (Hedayatzadeh et al., 2024). Therefore, monitoring phosphate levels is very important for maintaining the normal state of aquatic ecosystems.

Spectrophotometry is one of the most widely used approaches for measuring phosphate levels. The most frequently applied methods include usage of molybdovanadate and ammonium molybdate (Badamasi et al., 2019). As a result of the interaction of these compounds with phosphates, a yellow heteropolyacid is formed. It is also possible to use sodium molybdate instead of ammonium molybdate (Lin et al., 2024). Among these, the spectrophotometric molybdenum blue method is the most useful. This method involves the reaction of orthophosphate with an excess of molybdate in an acidic medium to form molybdophosphoric acid, which is then reduced to produce molybdenum blue (Badamasi et al., 2019). Tin (II) chloride, ascorbic acid and antimony potassium tartrate are used as reducing reagents. This method is quite accurate, but requires a large number of various reagents, which makes it not very convenient for use in field conditions. Therefore, the development of other spectrophotometric methods for detecting phosphates is relevant.

The use of a combination of metal indicators with metal cations is one of the promising directions, since phosphates are able to destroy these complexes, which leads to a change in color.

2. Materials and Methods

As chromogenic compounds we used chromazurol S, 8-oxyquinoline, arsenazo I and arsenazo III in the form of 0.005 M water solutions. Zirconyl nitrate hydrate (Acros Organics) was used as source of zirconyl ions in the form of solution with concentration 0.01 M.

We prepared solutions with different ratios to test the color change of chromogenic compounds in the presence of zirconyl ions. We added 1 ml of indicator solution and different volumes (0.0, 0.05; 0.125; 0,25; 1.0; 1.5; 2.0; 3.0 ml) of zirconyl nitrate solution to 50 ml volumetric flasks. Then we made up the mixture to the mark, mixed it, and measured the spectra of the resulting mixtures using a UV/vis spectrophotometer.

In the indicator system, we used a solution of chromazurol S with a concentration of 0.005 M and a solution of zirconyl nitrate with a concentration of 0.01 M. The ratio of the volumes of the solutions was 1:1. To test the effectiveness of the indicator system, we used model waters with different phosphate contents (from 0.5 to 40 mg P/L). We determined the color for creating a color scale for a solution thickness of 1 cm.

3. Results and Discussion

Chromogenic compounds such as 8-oxyquinoline, arsenazo I, arsenazo III demonstrated unsatisfactory efficiency. Although the addition of zirconyl nitrate solution caused a shift and change in peak intensity (Fig. 1), these changes were visually inconspicuous.

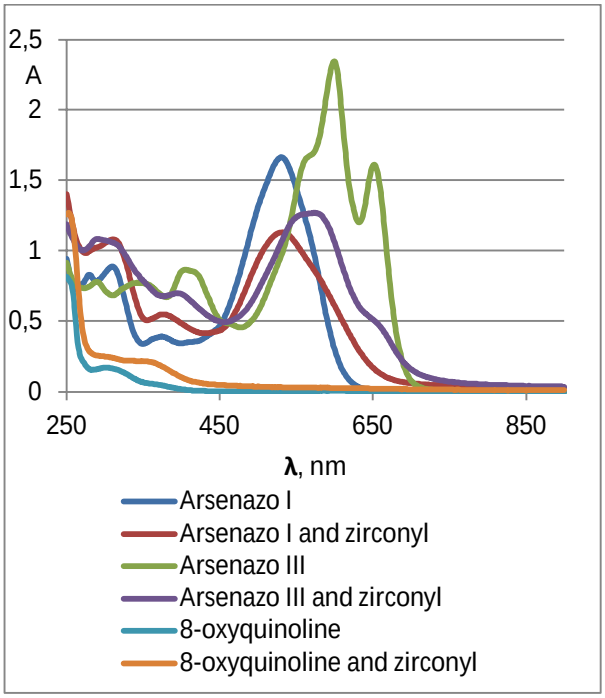

Fig 1. *Changes in the spectra of various chromogenic compounds in the presence of zirconyl ions*

In the case of arsenazo I, the solution changed color from pink to purple, in the case of arsenazo III, the color changed from blue to purple, and in the case of 8-oxyquinoline, no visual changes were observed at all.

Chromazurol S changes color very strongly in the presence of zirconyl ions (Fig. 2), which is promising for the development of an indicator system for the detection of phosphates.

Fig 2. *Color changes of chromazurol S in the presence of different concentrations of zirconyl ions*

The determination of phosphates (PO_4^{3-}) was carried out using chromazurol S and zirconium salt ($ZrO(NO_3)_2$). In this method, zirconyl initially formed a stable complex with chromazurol S, which led to a change in the color of the solution from orange to blue-violet. However, in the presence of phosphate ions, they interacted with zirconyl, forming phosphate with a very small solubility. As a result of this reaction, chromazurol S passed into a non-bonded form, which is reflected in the color change (Fig. 3).

Fig 3. *Color change in the presence of different concentrations of phosphate ions (mg/L)*

The chemical mechanism of the process can be represented by the following main stages:

1. Dissociation of chromazurol S and formation of the previous complex. In a weakly acidic medium (pH 3.5-4.5), chromazurol S dissociated with the formation of a tricharged anion, which was coordinated with the zirconyl ion through carboxylate and sulfonate groups.

2. Selective interaction with phosphate ions. Phosphate ions displaced chromazurol S from the inner coordination sphere of zirconyl ions, forming strong phosphate compounds with zirconyl ions.

The sensitivity of this indicator system could be altered by varying the ratio of chromazurol S and zirconyl.

4. Conclusions

Phosphate pollution of natural waters is a major problem, as it leads to unbalanced eutrophication and, as a result, the death of some species of aquatic organisms. Therefore, frequent monitoring of phosphates in water is extremely important to maintain a healthy ecosystem. The use of a combination of metal indicators with metal cations is one of the promising directions in phosphate detection, because phosphates are able to destroy these complexes, which leads to a change in color.

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ВИЗНАЧЕННЯ ВМІСТУ ФОСФАТІВ У ВОДІ З ВИКОРИСТАННЯМ ОРГАНІЧНИХ ХРОМОГЕННИХ СПОЛУК

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Сполуки фосфору потрапляють у природні води у значних кількостях в результаті антропогенної діяльності. Основними джерелами сполук фосфору є сільське господарство та недостатньо ефективне очищення стічних вод. Підвищений вміст сполук фосфору у водоймах призводить до незбалансованої евтрофікації та значних змін в екосистемах. Тому моніторинг рівня фосфатів дуже важливий для підтримки нормального стану водних екосистем. Спектрофотометрія є одним із найбільш широко використовуваних методів для вимірювання концентрації фосфатів.У статті розглянуто існуючі спектрофотометричні методи визначнння вмісту фосфатів у воді та запропоновано новий спосіб, який базується на використанні комплексу металоіндикаторів з металами. Принцип методу грунтується на зміні комплексу металу з металоіндикатором в результаті взаємодії з фосфат-іонами. Фосфат іони зв'язують катіони цирконілу, оскільки їх фосфати мають дуже низький добуток розчинності. Індикатор, вивільнений в результаті руйнування комплексу, має інше забарвлення, ніж комплекс з цирконіл-іоном. Експериментально перевірено доцільність використання таких металоіндикаторів як хромазурол С, 8-оксихінолін, арсеназо І, арсеназо ІІІ. Найвищу ефективність продемонстрував комплекс хромазуролу С з цирконіл-іонами, що відображається у чіткій зміні забарвлення з фіолетового на відтінки малинового, червоного та оранжевого для різних концентрацій фосфатів. В індикаторній системі було використано розчин хромазуролу С з концентрацією 0,005 М та розчин цирконіл нітрату з концентрацією 0,01 М. Співвідношення об'ємів розчинів 1:1. Запропонована методика визначення потребує значно меншої кількості реактивів, ніж молібдатний метод.

Ключові слова: *водне середовище, забруднення води, індикаторна система, фосфати, хромазурол С*