

Indirect Spectrophotometric Determination of Phosphorus Content in Steels and Alloys Based on Separation of 12-Tungstophosphate with Butyl Acetate and Absorption of Tungsten Phenylfluoronate

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Received: January 31, 2026; Accepted: July 30, 2026

DOI: 10.17721/moca.2026.38-47

A method for indirect extraction-spectrophotometric determination of phosphorus using the formation of 12-tungstophosphate (12-TPC) heteropoly complex has been developed. The conditions for the formation and extraction separation of the 12-TPC with butyl acetate were studied. 12-TPC is formed and extracted over a wide pH range — from 0.05 to 0.4 M (as H⁺)—at a tungstate concentration of 2 mM. After separation, tungsten in the composition of 12-TPC is determined by the absorption of its complex with phenylfluorone. The apparent molar absorption coefficient significantly exceeds the known methods and equals to $3.3 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$ at 515 nm. Calibration range for phosphorus is from 3 to 30 $\mu\text{g L}^{-1}$ with LOD of $1.0 \mu\text{g L}^{-1}$ and correlation coefficient of 0.9998. The method is simple to implement, rapid, highly sensitive and has good reproducibility. The possibility of eliminating the interfering influence of a number of elements that may be present together with phosphorus in alloyed steels, namely chromium, nickel, vanadium, molybdenum, and tungsten, has been studied. A method for analyzing steel and other alloys containing these elements has been developed and verified by analyzing standard samples.

Keywords: spectrophotometry, phosphorus determination, analysis of steels, extraction

Непряме спектрофотометричне визначення вмісту фосфору в сталях і сплавах, яке ґрунтується на відділенні 12-вольфрамофосфату бутилацетатом і поглинанні фенілфлуоронату вольфраму

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Надійшла: 31 січня 2026 р.; Прийнята: 30 липня 2026 р.

DOI: 10.17721/moca.2026.38-47

Розроблено метод непрямого екстракційно-спектрофотометричного визначення фосфору з використанням утворення 12-вольфрамофосфорного гетерополікомплексу (12-ВФК). Досліджено умови утворення й екстракційного розділення 12-ВФК з бутилацетатом. 12-ВФК утворюється й екстрагується в широкому діапазоні значень рН — від 0,05 до 0,4 М (як H⁺) — при концентрації вольфраму 2 мМ. Після відділення вольфрам у складі 12-ВФК визначається за поглинанням його комплексу з фенілфлуороном. Метод характеризується дуже низькою межею виявлення. Уявний молярний коефіцієнт світлопоглинання значно перевищує відомі методи і дорівнює $3,3 \times 10^5 \text{ моль}^{-1} \text{ л см}^{-1}$ при 515 нм. Діапазон концентрацій фосфору для градувального графіка становить від 3 до 30 мкг/л з LOD 1,0 мкг/л і коефіцієнтом кореляції 0,9998. Метод простий у виконанні, швидкий і має хорошу відтворюваність. Досліджено можливість усунення заважаючого впливу ряду елементів, які можуть бути присутніми разом із фосфором у легованих сталях, а саме: хрому, нікелю, ванадію, молибдену та вольфраму. Розроблено методику аналізу сталі та інших сплавів, що містять ці елементи, яку було перевірено з використанням аналізу стандартних зразків.

Keywords: спектрофотометрія, визначення вмісту фосфору, аналіз сталей, екстракція

Introduction

Phosphorus is often found together with tungsten in ores and their processing products. It degrades the quality of tungsten-containing materials, in particular tungsten oxide, which is used in electrical engineering. Tungsten is used as an alloying component in a number of alloys. All this makes it important to determine phosphorus against the background of tungsten. Determining its low content presents particular difficulties.

Heteropoly complexes (HPCs) are widely used in chemical analysis as analytical forms for the determination of central atoms of HPC or reagents when they are used for the determination of substances that behave as reducing agents [1–4]. They play a special role in analytical chemistry, since their participation makes it possible to use unique amplification reactions, one of the types of reactions for enhancing the analytical signal [5, 6]. In the formation of saturated HPCs with the Keggin structure, the central ion binds 12 ligand ions (Mo, W). The high stoichiometric ratio of ligand atoms to the central ion leads to additional amplification of the analytical signal during indirect determination.

More than 70 elements of the Periodic Table can act as central atoms in HPC [1, 7]. The ligand sphere of monoligand and multiligand HPC structures of the Keggin type consists of addenda atoms (molybdenum, tungsten, and vanadium). Almost all spectrophotometric methods for the determination of phosphorus are based on the formation of HPCs, mainly 12-molybdophosphate (12-MPC) and 11-molybdovanadophosphate [8–13]. The presence of tungsten causes difficulties associated with the formation of 12-tungstophosphate (12-TPC) or mixed heteropoly complexes, which hinders the main photometric reaction [14]. In addition, at high concentrations, poorly soluble polymeric forms of tungstate are formed, and phosphorus co-precipitates with tungstic acid. All this forces analysts to use preliminary phosphorus separation on collectors. These additional operations complicate the analysis process, reducing the reliability of the determination. The determination of phosphorus using the reaction of reduced 12-MPC formation in various materials is greatly interfered also by elements such as tungsten, vanadium, titanium, as well as large amounts of chromium and nickel.

The determination of phosphorus in ferrotungsten and high-alloy steels containing large amounts of W, Cr, and Ni is preceded by its separation from interfering components [15–17]. The method of separating tungsten by hydrolysis is not suitable due to the co-precipitation of phosphate ions with tungstic acid. Losses of phosphorus adsorbed by tungstic acid precipitate in some cases amount to 40% of its content in the analyzed sample [16]. The method of separating phosphorus [16, 17] from tungsten by precipitation on a mixed collector of calcium and iron

hydroxide, including reprecipitation of the precipitate, is very time-consuming. In steels containing chromium and nickel, phosphorus is precipitated with ammonia using a collector—iron hydroxide—after oxidation of chromium(III) to chromate ion [16]. For more complete separation from these components, the hydroxide precipitate is reprecipitated.

There are known methods for the determination of phosphorus in tungsten-containing materials without separating the base, using the formation of tungsten-phosphorus and mixed HPCs of tungsten, phosphorus, molybdenum, and vanadium [15, 18–21]. When determining phosphorus in materials based on elements capable of entering the coordination sphere of HPC (vanadium, tungsten, molybdenum), it is advisable to use the formation of mixed complexes involving the base element.

In [18], phosphorus was determined by the absorption of 12-TPC in the ultraviolet region, where it, like other HPCs, has intense absorption bands caused by the $O \Rightarrow W$ charge transfer. The absorption bands of 12-TPC and isopolytungstates coincide ($\lambda_{\max} = 265 \text{ nm}$), which complicates spectrophotometric determination. Therefore, it is necessary to separate the excess tungstate. It has been found that quantitative and selective extraction of 12-TPC with amyl alcohol is possible in the pH range 0.7–2.0. At $\text{pH} < 0.7$, the solutions lose their aggregate stability. The method can be used to determine phosphorus in WO_3 . The detection limit is $8 \times 10^{-4} \%$ and $\text{RSD} = 7\text{--}10\%$. A 20-fold excess of silicon does not interfere. The need to work in the ultraviolet region and insufficient sensitivity ($40 \mu\text{g L}^{-1}$) are the main disadvantages of this method.

The method proposed in [19] is the closest to the one we have developed in this work. Re-extraction of the 12-TPC with alkali and obtaining a colored tungsten complex (VI) in the re-extract with thiazolyl pyrocatechol allowed to proceed to measurements of absorbance in the visible region of the spectrum and to lower the detection limit of phosphorus by using a multiplication reaction (in 12-TPC, the P:W ratio is 1:12). The method was tested on fairly simple samples of tungsten trioxide and powdered tungsten. RSD in the determination of $\approx 10 \mu\text{g}$ of phosphorus was 7–10 %. The calibration curve was constructed from 7.5 to $160 \mu\text{g L}^{-1}$ of P. The molar absorptivity of the method based on the use of thiazolyl pyrocatechol is quite low for multiplication methods ($\epsilon_{500} = 5.1 \cdot 10^4$) and is significantly inferior to those described in the literature [12, 22, 23].

To increase the sensitivity of phosphorus determination, another traditional analytical chemistry technique was used. It is based on the formation of ion associates between HPC and basic organic dyes. In [20], the interaction of 12-TPC with crystal violet, a dye with one of the highest molar coefficients among triphenylmethane and other colored organic substances, was studied. When studying the extraction

of ion associates of crystal violet with 12-TPC and isopolytungstates, it was found that most solvents extract both substances equally. Only butyl acetate practically does not extract the dye and at the same time floats the 12-TPC-dye ion associate well. Double extraction with butyl acetate and double washing with 5 mL of 0.1 M H_2SO_4 solution ($\text{pH} \approx 0.6-0.7$) were used for re-extraction of co-extracted tungstate ions. Behr's law was observed in the range of $10-140 \mu\text{g L}^{-1}$ of phosphorus.

Work [21] describes a similar method based on the formation of 12-TPC ion associates with antipyrine dyes. In strongly acidic solutions, turbidity appears, which is associated with the polymerization of tungstate and the release of tungstic acid. When the acidity is reduced to 0.03–0.50 M H_2SO_4 , no precipitation of tungstic acid is observed, but a stable emulsion is formed during extraction. Quite effective destruction of the emulsion is achieved by keeping it for 15 minutes. This increases the duration of the analysis. According to the second method, it is recommended to add 2 mL of acetone, which leads to the destruction of the emulsion within 1 min, but introduces an error in the analysis results, since the dye is partially extracted into the organic phase. From pH 0.7, an increase in the absorbance of the extracts is observed, indicating the formation of tungsten(VI) compounds with dyes. At $\text{pH} > 3.5$, the absorbance of the solutions is constant.

Masking with organic oxoacids also failed to achieve separation of HPC and isopoly complexes. On the contrary, tungsten extraction in the presence of citric and other oxoacids even increased. Attempts to determine phosphorus in the form of ion associates of tungstomolybdophosphate mixed HPCs with dyes were also unsuccessful. The best results were obtained using the third option: conditions for complete formation of 12-TPC were created in the re-extract, the ion associate of 12-TPC with a dye was formed and floated with a mixture of acetone and toluene, and the film was dissolved in acetone.

It has been found that 12-TPC is quantitatively formed in a wide acidity range from pH 2 to 0.6 M H_2SO_4 . The optimal extraction range for 12-TPC with butyl acetate was in the range of 0.5–1.0 M H_2SO_4 ($1-2 \text{ M H}^+$) [19]. Thus, it is possible to carry out both stages—the formation of HPC and its extraction—simultaneously, which is very convenient. It is worth recalling that at comparable reagent concentrations, the formation of the molybdenum analogue of 12-molybdophosphoric acid cannot be obtained quantitatively at any pH. The detection limit was $16 \mu\text{g L}^{-1}$ of phosphorus. This is quite high sensitivity, but it can be achieved using a more common and simpler method based on the reduction reaction of 12-molybdophosphate. In terms of sensitivity, this method is significantly inferior to the one based on the formation and flotation of ion associates of molybdenum HPCs with organic dyes. Thus, for silicon, a detection limit of $1 \mu\text{g L}^{-1}$ was achieved [24].

Methods based on the formation of 12-TPC are promising for determining phosphorus in materials containing tungsten, vanadium, molybdenum, and other metals that have a strong interfering effect. This substance is very stable compared to its molybdenum analogue and many mixed HPCs. As a result, there is no need to introduce a large excess of reagent, and its concentration is easy to adjust. Even high concentrations of the above-mentioned interfering elements are not capable of affecting the equilibrium of 12-TPC formation. This approach can be implemented to determine phosphorus in a number of samples with very complex compositions. Unfortunately, the authors of works [18–21] focused on the possibility of eliminating the interfering effect of tungsten alone. In addition, few studies have been conducted on the analysis of complex samples containing various combinations of interfering elements.

This work develops a new indirect amplification method for determining phosphorus, based on the selective extraction of 12-TPC with butyl acetate and the formation of an intensely colored tungsten complex with phenyl fluorone in the presence of non-ionic surfactants in the re-extract after the destruction of 12-TPC. The reasons for the insufficient efficiency of the extraction separation of excess molybdate or tungstate during amplification methods have been clarified. It has been shown that the proposed method allows the determination of phosphorus in the presence of high concentrations of tungsten and other metals, which usually have a significant interfering effect and require complex and lengthy preliminary separation.

Experimental part

Chemicals. All chemicals used were analytical reagent grade or higher and were not further purified. Double-distilled water was used throughout the study. Sodium tungstate $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, grade “chemically pure”. The preparation was pre-purified according to the following procedure using recrystallization. For this, 250 g of the starting material was dissolved in 400 mL of water and filtered. To precipitate sodium tungstate, ~300 mL of ethanol was added. To prepare a 0.1 M solution of sodium tungstate, 3.2985 g of preparation is dissolved in 100 mL of deionized water. The initial solution of potassium dihydrogen phosphate with a concentration of 0.01 M was prepared by dissolving an exact sample of pre-recrystallized and dried for 3 hours at 120°C KH_2PO_4 brand “chemically pure”. Sulfuric acid “extra pure” (Merck) was used for the acidification.

Apparatus. The absorbance of the solutions was measured using an SF-46 UV-visible spectrophotometer LOMO with glass cuvettes with an optical path length of 10 mm. Spectra in the ultraviolet and visible parts of spectrum were recorded on spectrophotometer SPECORD M-40. The pH of the solutions was monitored on an ionomer EV-74 using

glass and silver chloride electrodes.

Procedure for orthophosphate determination. In a 25 mL flask, mix an aliquot of orthophosphate solution corresponding to a concentration of 0.1 to 1.0 $\mu\text{mol L}^{-1}$, 5 mL of 0.01 M Na_2WO_4 , 5 mL of 0.5 M H_2SO_4 , and bring the volume to 25 mL. The 12-TPC was extracted with 5 mL of butyl acetate in a 100 ml separating funnel. It was shaken 100 times. The aqueous phase was separated, and the organic phase was poured through the top into a separate glass. The funnel was thoroughly washed using a mixture of NH_3 and butyl acetate. Re-extraction was carried out with 5 mL of NH_3 (1 : 10) by shaking 50 times. The aqueous phase was separated, and the ammonia in it was then neutralized with a previously selected amount of acid, 2.5 mL of 1 M H_2SO_4 , and the volume of the re-extract was brought to 25 mL.

The concentration of tungstate ions in re-extract was determined using the phenylfluoronate method. During the determination, 2 mL of 0.5 M H_2SO_4 , 1 mL of 1% neonole, 0.5 mL of 0.4 mM alcoholic solution of phenylfluorone, and 4 mL of the aliquot of the analyzed solutions (the total volume of the photometrically measured solution was 7.5 mL in all experiments). The absorbance was measured in a 1 cm cuvette at 515 nm relative to the reagent solution.

Method for the analysis of stainless steel for phosphorus content. Standard sample No. 53-D was selected as the object of analysis, containing P – 0.021%, V – 0.274%, Ni – 0.32%, Cr – 12.09%, Mo – 0.47%. Place 0.502 g of stainless steel in a 250 mL glass beaker, add 30 mL of a mixture of hydrochloric and nitric acids (1:3). Dissolve with moderate heating. After dissolution, a small amount of black precipitate remains at the bottom. Add 20 mL of HClO_4 (conc.) and evaporate until abundant white vapors are released, cover the beaker with a watch glass and continue heating until the color of the salts changes from green to orange-red. After cooling, dissolve in 25 mL of warm water and dilute to 50 mL. During the analysis, the solution must first be acidified and then tungstate must be added. The analysis was then carried out as described above. This is due to the formation of poorly soluble tungstates in a weakly acidic environment.

Determination of phosphorus in carbon steel and copper alloys. A sample of steel (copper alloy) weighing 0.1-0.5 g is dissolved in 10 mL of concentrated nitric acid. After complete dissolution of the sample, add a solution of 0.2 M potassium permanganate solution (25 g L^{-1}) until a brown precipitate of MnO_2 is formed and boil for 2-3 minutes. A solution of sodium nitrite (50 g L^{-1}) is added dropwise to the boiling solution until the MnO_2 precipitate dissolves and boiled until nitrogen oxides are removed, evaporated to dryness. The dry residue is dissolved in 10 ml of conc. HCl and again evaporated to dryness. If a significant amount of arsenic is present in the steel sample, dissolve the salts in 10 mL of conc. HCl, add 0.1 g of NH_4Br ,

evaporate to dryness (arsenic is distilled off in the form of AsCl_3), repeat the treatment. Add to the dry residue 5.0 ml of conc. HCl and heated to a clear solution. Cool, adjust the volume to 25 mL.

An aliquot of the sample solution neutralized to pH 1.5-2.0, containing from 0.075 to 1.5 μg of phosphorus, which corresponds to the concentration range from 0.1 to 2.0 $\mu\text{mol L}^{-1}$, is placed in a 25 ml flask. Further determination is carried out as described above in the amplification method.

Results and discussion

Heteropoly complexes play a special role in analytical chemistry, as they enable the use of unique amplification reactions—a type of reaction that enhances the analytical signal [5, 6]. In the formation of saturated heteropoly complexes with a Keggin structure, the central ion binds 12 ligand ions (Mo, W). The high stoichiometric ratio of ligand atoms to the central ion leads to additional amplification of the analytical signal during indirect determination.

Analysis of factors determining the absorbance of blank experiment. A review of the literature has allowed us to establish that trioxyfluorones are among the most sensitive reagents for the determination of molybdenum and tungsten [25, 26]. At the same time, the selectivity of the method for determining tungsten plays a secondary role in this case. We chose trioxyfluorides as reagents for the determination of tungsten because of their wide availability and the simplicity of the reaction. The use of cationic or non-ionic surfactants makes it possible to avoid the use of organic solvents and achieve maximum molar absorption coefficients of $1 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$ and above. These factors are the most important when developing amplification methods. We have confirmed the high efficiency of using inexpensive and readily available nonionic surfactants for solubilisation and modification of molybdenum(VI) and tungsten(VI) complexes with phenylfluorone. The molar absorption coefficients obtained in this way are comparable to those obtained using cationic surfactants.

Under the optimal conditions found the molar absorption coefficients of molybdenum [22] and tungsten complexes with phenylfluorone in a neonol medium (an analogue of the well-known surfactant Triton X-100) were 1.4×10^5 and $1.0 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$ at 524 and 515 nm, respectively (Fig. 1). Based on these values, the calculated values of the effective molar absorption coefficients for the indirect determination of phosphorus (V) in the form of 12-molybdophosphate and 12-tungstophosphate were $12 \times 1.4 \times 10^5 = 1.68 \times 10^6$ and $12 \times 1.0 \times 10^5 = 1.2 \times 10^6 \text{ mol}^{-1} \text{ L cm}^{-1}$. With such high molar coefficients, the detection limit of amplification extraction spectrophotometric methods should be around 1 nmol L^{-1} and below.

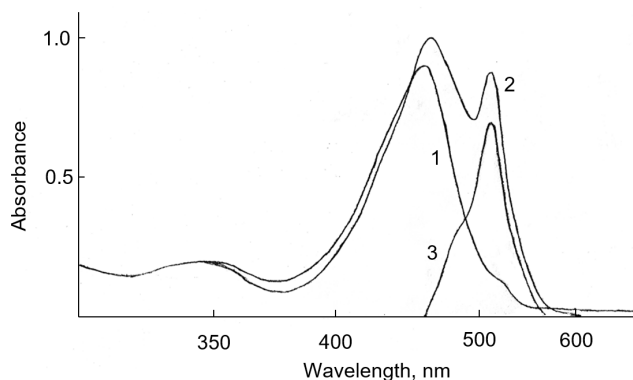


Fig. 1. Absorption spectra of phenylfluorone (1), complex formed between tungsten(VI) and phenylfluorone (2) and the difference spectrum (3) in the presence of neonole. Conditions of photometric reaction: tungsten(VI) concentration – 7.0 μM , neonole AF 9-12 concentration – 0.33%, pH – 0.78, phenylfluorone concentration – 0.033 mM, $l = 1$ cm.

Consequently, the main reserve for increasing sensitivity lies in improving the technique of conducting amplification reactions. There are several reasons why it is difficult to achieve so high sensitivity. Amplification techniques are multi-stage. An error can be introduced at each stage, which in total can significantly reduce the overall reproducibility of the determination. The measurement result in spectrophotometry is obtained as the difference between the absorbances of the analyte solution and the blank solution. If the absorbance of the blank experiment is high and subject to strong random fluctuations, the number of significant digits in the obtained analytical signal value may decrease to zero (the law of subtraction of large, close numbers). In this case, it becomes meaningless to further increase the path length of the cuvette, the degree of preconcentration, or the molar absorption coefficient. Therefore, it is precisely the analysis and elimination of the causes of the high value and fluctuations in absorbance of the blank solution that can suggest ways to improve amplification techniques.

The ratio of tungstate concentration to phosphorus concentration during the amplification process and HPC reaches $10^4:1$. Even if it is possible to separate most of the tungstate and reduce this ratio to 1:1, the determination error will be 100%. This example demonstrates the significant impact of all factors that contribute to the presence of excess tungstate in the final photometric solution.

Absorbance of the blank in amplification methods is determined by several factors. One of them is the presence of impurities of the element being determined or its analogues in the reagents used. Considering that reagents are introduced in relatively high concentrations, even small impurities in the reagents can sharply increase blank absorbance. Two methods have been proposed to combat this phenomenon, both of which have proven to be highly effective.

1. Preliminary purification of reagents. It is very important to significantly reduce the influence of impurities in the acid and sodium tungstate used. In such a highly sensitive procedure as amplification, it is recommended to use acids of the highest possible purity. There are few and contradictory indications regarding phosphate concentration values in purified water. Our data indicate that the upper limit for phosphorus content in distilled and double-distilled water is no more than 10 nmol L^{-1} . Such a low content of phosphate ions should not interfere with the determination. As regards molybdate or tungstate, the use of their non-recrystallised salts is unacceptable. These reagents contain impurities of poorly soluble metal tungstates, as well as phosphorus and silicon compounds at a level of $10^{-3}\%$. The content of phosphorus and silicon impurities was evaluated using a developed amplification method. It was found that a single recrystallisation from an aqueous-alcoholic solution is sufficient to obtain reagents of the required purity.

2. Preliminary extraction of heteropolytungstate (molybdate). The second method of removing phosphate impurities from the reaction mixture is more versatile and effective. It is based on purifying the reagent—an acidified tungstate (molybdate) solution—during the extraction of heteropolytungstates (molybdates) formed from phosphate in the reagents used. In addition, if this extraction is carried out in a separating funnel, the result of such an experiment will also indicate the purity of the glassware. The extraction can be repeated several times to achieve the required minimum blank value. In this way, all interfering impurities in all reagents are removed. It was found that after the first washing, the absorbance value of the blank test becomes acceptable, and after the second washing, the further decrease in absorbance practically stops.

It has been suggested that the relatively high residual absorbance of the blank solution, which remains even after all the above precautions have been taken, is the result of the sorption of small amounts of tungstate by the walls of the vessel. Washing with water or acid solution cannot ensure complete desorption of tungstate. It has been found that rinsing with a diluted ammonia solution reduces the absorbance of the blank solution to practically zero. The presence of an aqueous phase emulsion in the organic phase also has some effect on the blank experiment value, which requires the extraction system to be held for a certain time for complete phase separation. Compliance with all precautions made it possible to reduce the absorbance of the blank solution to ~ 0.01 units ($l = 5$ cm, $\epsilon_w = 1.0 \times 10^5$), which corresponds to a tungstate concentration of 20 nmol L^{-1} .

The choice of extractant. The choice of extractant for the amplification method, as in other extraction-spectrophotometric methods, depends, firstly, on how

high the distribution constant of the complex of the substance being determined is, and, secondly, on how selective its extraction will be. Isopolymolybdates(VI) and isopolytungstates(VI) are less easily extracted than phosphorus Keggin HPCs. For the amplification method, it is very important that the distribution constant of isopolytungstate(molybdate) is as low as possible, and the ratio of the distribution constants of HPC and isopolyanion is as high as possible.

Babko, Shkaravsky, and Ivashkovich [27] proposed using a separation coefficient to evaluate the differentiating power of an organic solvent with respect to the separation of iso- and heteropoly compounds. It is equal to the ratio of the distribution coefficients of these substances to the solvent. According to these authors, the highest separation coefficient in the 12-molybdophosphate–isopolymolybdate system is observed during extraction with complex esters ($\gamma > 1000$ in propyl acetate at pH 0.2), while alcohols have the lowest differentiating ability ($\gamma < 50$ in butanol). The degree of tungstate extraction under the amplification method conditions was determined to be 0.022 for methyl isobutyl acetate and 0.012 for butyl acetate. This means that when using MIBK and butyl acetate, one wash of the organic phase is sufficient to reduce the concentration of tungstate to a value that will no longer affect the result of the amplification determination.

The best extractants for 12-tungstophosphoric acid are alcohols, ketones, and esters [28–37]. At the same time, esters are the most selective extractants. When using them, it is possible to separate tungsten heteropolyacids of silicon, arsenic, and germanium. Also, very important in this work, the separation of iso- and heteropolywolframates is very effective. Like HPCs, isopolytungstates are best extracted with alcohols and less easily with ethers and ketones [29].

12-TPC has very high stability. Its stability constant, determined in the work of Lunk and Litke [38], is 2.4×10^{12} for the equilibrium scheme:



Such high stability of 12-TPC allows introducing a smaller excess of reagent necessary for complete complex formation. This makes it easier to separate excess tungstate ions.

Effect of acidity and tungsten(VI) concentration.

The distribution of 12-TPC between the aqueous and organic phases depends simultaneously on the pH and concentration of tungsten(VI). When studying the effect of solution acidity and tungstate concentration on the degree of formation and extraction of 12-TPC, the studied tungstate concentration ranges were from 0.8 mM to 2.2 mM, and the acidity ranged from pH 3 to 1 M H_2SO_4 .

Although the conditions for the formation of 12-TPC have been studied previously, there are still contradictions in the recommendations. In [20], it is stated that the pH range for the formation of 12-TPC is 0.5–0.9, while in [21], a wider range of acidities from

pH 2 to 0.6 M H_2SO_4 is recommended. As can be seen from Fig. 2, 12-TPC is formed and extracted over a wide pH range, from 0.05 to 0.4 M (as H^+). At the same time, the extraction percentage reached 31%. 0.2 M acidity was chosen as optimal.

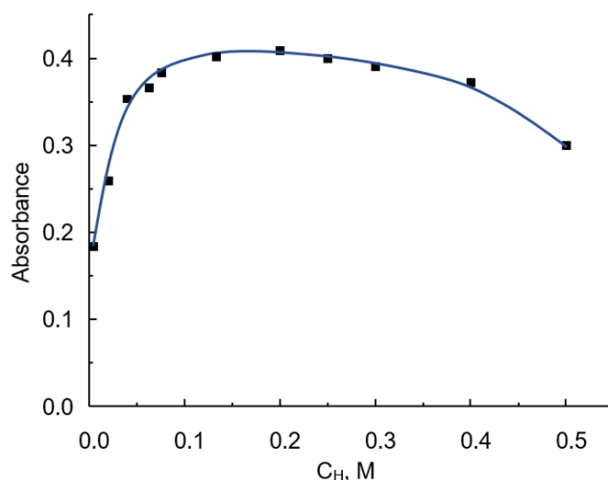


Fig. 2. Effect of sample solution acidity on the absorbance of tungsten(VI) phenyl fluoronate in reextract. Sample phase – 25 mL, butyl acetate volume – 5 mL, reextract volume – 25 mL, phosphate concentration – 2 μM , tungstate concentration – 2 mM. Conditions of photometric reaction. Aliquot volume – 2 mL, total volume – 5.5 mL, neonole AF 9-12 concentration – 0.2%, sulfuric acid concentration – 0.1 M, phenyl fluorone concentration – 0.2 mM, $\lambda = 515 \text{ nm}$, $l = 1 \text{ cm}$.

A 1.4 mM sodium tungstate concentration is sufficient to achieve the maximum possible extraction of 12-TPC (Fig. 3). A 2 mM tungstate concentration was chosen as optimal. It was also found that the extraction percentage of tungstate under these conditions does not exceed 0.5%.

Investigation of interference from elements accompanying phosphorus in steels. It has been shown that a 1000-fold excess of nickel, 100-fold excess of silicon, molybdenum and vanadium do not interfere. Chromium(III) interferes to the phosphate determination starting from 100-fold excess. However, 10000-fold excess of chromium(VI) does not have influence on the phosphate determination. During the analysis, most of the chromium is oxidized to chromate. This eliminates the influence of this element on the determination of phosphorus in steels.

Performance of the method. The results of the calibration graph construction indicated very good reproducibility of phosphorus determination results. The correlation coefficient was 0.9998. The equation of the calibration graph was $A = 0.146 \pm 0.002 + (2.24 \pm 0.04) \times 10^5 \times C_{\text{P}}$, where phosphorus concentration is expressed in mol L^{-1} . The tangent of the slope angle of the calibration graph is 224000. If dilution is taken into account in the analysis, then $\varepsilon_{515}^{\text{app}}$ is $2.24 \times 10^5 \times 7.5/4$

$= 3.9 \times 10^5$, which is $3.9 \times 10^5 / 1.2 \times 10^6 \cdot 100 = 33\%$ of the theoretically possible.

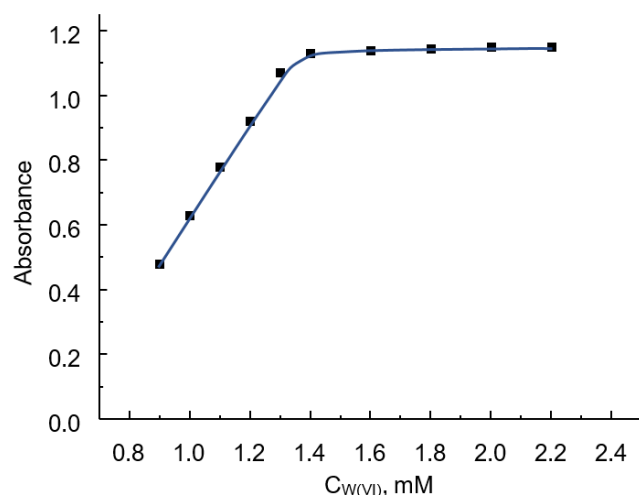


Fig. 3. Effect of sodium tungstate concentration on the absorbance of tungsten(VI) phenyl fluoronate in reextract. Sulfuric acid concentration in sample solution – 0.25 M, phosphate concentration – 6 μM . Other conditions are the same as in Fig. 2

A comparison of the developed method with existing methods in the literature indicates that the proposed method surpasses them in sensitivity (Table 1). Moreover, provided that the ratio of the aqueous and organic phases is increased, it has considerable potential for further increasing sensitivity.

Analysis of real samples. The accuracy and reproducibility of the proposed method were evaluated by analyzing several standard reference samples

containing phosphorus and a number of other metallic elements.

Table 2. Verification of the accuracy and reproducibility of the indirect phosphorus determination method using the formation of 12-TPC in reference sample No. 53-D ($P = 0.95$, $n = 5$).

A_{515}	$C_p, \%$	$S(S_r)$	$\bar{x} \pm \Delta, \%$
0.390	0.0210	0.0004	$0.0211 \pm$
0.400	0.0215	(0.020)	0.0005
0.390	0.0210		
0.400	0.0215		
0.380	0.0205		

The results of the standard sample analysis confirm the accuracy of the proposed method. The true value of 0.021% P falls within the confidence interval of 0.0206 to 0.0216. The methodology is characterized by high reproducibility – the relative standard deviation is 2%. The quantification limit of the method is much lower than 0.001% P, which is more than sufficient for determining phosphorus in any stainless steel samples. It should be emphasized that, as a rule, the precision of determination is no worse, and in the range of low phosphorus concentrations, it is better than in existing methods for determining this element.

The developed method for the determination of phosphorus was also tested in the analysis of carbon steel and copper alloys (Tables 3 and 4). The results of the analysis of a number of standard reference samples of carbon steels and brass indicate high sensitivity and reproducibility of phosphorus determination using the proposed method.

Table 1. Comparison of amplification extraction-photometric methods for phosphorus determination.

Analytical form at the final stage. Conditions for determination	Method characteristics	References
WO_4^{2-} , extraction pH 0.7 – 2.0	$\epsilon_{265} = 2.6 \cdot 10^4$, LOD = 40 $\mu\text{g L}^{-1}$	[18]
Complex of W(VI) with thiazolylpyrocatechin, extraction pH 1 – 2	$\epsilon_{500} = 5.1 \cdot 10^4$, 12–100 $\mu\text{g L}^{-1}$	[19]
Ion associate (crystal violet) $_2$ HPW $_{12}\text{O}_{40}$, pH 0.5 – 0.9	$\epsilon_{590} = 2.1 \cdot 10^5$, 10–140 $\mu\text{g L}^{-1}$	[20]
Ion associate of 12-TPC with chrompyrazole, extraction acidity 0.5 – 1.0 M H_2SO_4	$\epsilon_{590} = 1.8 \cdot 10^5$, LOD = 16 $\mu\text{g L}^{-1}$	[21]
Complex of Mo(VI) with phenylfluorone in presence of non-ionic SAS	$\epsilon_{524} = 1.7 \cdot 10^6$, $\epsilon_{\text{app}} = 7.8 \cdot 10^5$, LOD = 0.6 $\mu\text{g L}^{-1}$	[22]
Complex of Mo(VI) with sulfonitrazo DAF	$\epsilon_{560} = 1.56 \cdot 10^5$, LOD = 10 $\mu\text{g L}^{-1}$	[23]
Complex of W(VI) with phenylfluorone in presence of non-ionic SAS, acidity range 0.05 – 0.4 M	$\epsilon_{515} = 1.2 \cdot 10^6$, $\epsilon_{\text{app}} = 3.9 \cdot 10^5$, 3–30 $\mu\text{g L}^{-1}$, LOD = 1 $\mu\text{g L}^{-1}$	Present work

Table 3. Verification of the accuracy and reproducibility of phosphorus determination results in reference sample No. 151 (certified phosphorus content value 0.0173%).

Amplification method			Method of molybdophosphate heteropoly blue		
C_p , %	$S(S_r)$	$X_{cp} \pm \Delta$, %	C_p , %	$S(S_r)$	$X_{cp} \pm \Delta$, %
0.0173			0.0168		
0.0172	0.00017	$0.01726 \pm$	0.0172	0.0008	0.0164 ± 0.0009
0.0174	(0.008)	0.00020	0.0153	(0.046)	
0.0171			0.0159		
			0.0166		

* Contents of other elements, %: C – 0.18; Mn – 0.53; S – 0.014; Si – 0.31; Cr – 0.89; Ni – 0.14; Cu – 0.23; B – 0.004; Mo – 0.05; V – 0.03; Ti – 0.02; As – 0.02.

Table 4. Verification of the accuracy and reproducibility of phosphorus determination results in various analysis objects using an amplification technique ($P = 0.95$; $n = 4$).

Sample	C_p , % (certified)	$C_p \pm \Delta$, % (found)	S_r
Brass, RS M114*	0.12	0.117 ± 0.003	0.024
Open-hearth rail steel, RS № 199**	0.027	0.028 ± 0.002	0.08

Certified content of other components:

* Cu – 94.82; Al – 1.02; Sb – 0.0095; Bi – 0.006; Fe – 0.035; Zn – 3.27; Pb – 0.088.

** C – 0.65; Mn – 0.77; Si – 0.19; S – 0.025; As – 0.117; V – 0.04; Ti – 0.002.

Conclusions

12-tungstophosphate heteropoly complex is much more stable than its molybdenum counterpart. Therefore, its formation does not require a large excess of reagent. This approach is promising for determining phosphorus not only in tungsten-containing samples but also in a number of other complex samples. The shortcomings of previously proposed methods for the indirect determination of phosphorus in the form of 12-TPC, as well as their insufficiently high sensitivity, necessitated the search for more suitable methods for completing the determination. As noted earlier, when choosing an analytical form for an element for which indirect determination is carried out, it is not the selectivity of the reaction that is important, but only its sensitivity. From this point of view, the reagents listed in Table 1 are not entirely a good choice. In addition, the proposed reagents are poorly accessible, and the reactions are slow. As in the case of molybdenum, one of the best reagents for tungsten are trioxofluorones. Along with the very high molar coefficient of tungsten(VI) complexes with trioxofluorones, such reactions are very fast and highly reproducible.

A positive aspect of using 12-TPC is the ability to reduce the reagent concentration required for complete complex formation to 1.5 mM by an order of magnitude. Furthermore, it has been shown that the recovery rate of isopolytungstates does not exceed 0.2%. This significantly simplifies the method, as even a single wash of the extract is not necessary for

determining phosphorus in the concentration range from 0.1 to 1.0 μM . This makes the determination more rapid and improves reproducibility. Based on previous studies, cleaning the separatory funnel with a mixture of ammonia and butyl acetate is proposed, which allowed the absorbance of the blank solution to be reduced to virtually zero.

It has been shown for the first time that the reaction of 12-TPC formation can be successfully used to analyze steel samples containing not only tungsten, but also large amounts of chromium, nickel, molybdenum, titanium, and vanadium. This suggests that such methods are a viable alternative to methods based on the formation of molybdenum HPCs, especially in the case of analyzing samples with a high content of multicharge metal ions. The method is faster and easier to perform. The stage of the extract washing is eliminated. The method has a much higher sensitivity than known methods for determining phosphorus in tungsten-containing materials (Table 1). The sensitivity of the method can be significantly improved using modern approaches, such as employing an external liquid waveguide capillary cell [9, 39] or increasing the degree of preconcentration through modern microextraction methods [30, 40]. Attempts to use green solvents may also hold promise [41].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships

that could have appeared to influence the work reported in this manuscript.

Data availability

The data are available upon request.

Acknowledgments

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V01-00106 (Andrii Vyshnikin).

Authors' contribution

Mohammed, Al-Shwaiyat - data validation, writing (original draft); Anna, Gres - data validation, formal analysis, writing (original draft); Andriy, Vishnikin - conceptualization, methodology, writing (review and editing).

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