Article

Study of the possibilities of determining mobile sulfur by physical-chemical and chemical methods in various substrates in the presence of orthanilic K

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Abstract: The article presents the results of testing the developed method for determining mobile sulfur in wood ash and various soil substrates. Determination of sulfur in sulfate form in presence of orthanilic K is possible due to the indicator's ability to form coloured complexes with Ba^{2+} ion. We examined the ranges of volumetric and photometric determination. The accuracy of the analysis was determined by comparison with a certified method. We present optimal conditions for the successful determination of the mobile sulfur with the titration and with spectrophotometric method. The results of experiments confirming the capabilities of the method under study are presented.

Keywords: mobile sulfur; orthanilic K; spectrophotometry; complexometric titration

1. Introduction

Sulfur is one of the key elements of agriculture, playing an important role in plant nutrition. It is involved in the formation of chlorophyll, the synthesis of oil, and the production of protein. Sulfur forms disulfide bonds in polypeptide chains during the formation of the spatial structure of proteins [1]. Moreover, sulfur has a significant impact on the nitrogen absorption in plants [2].

The main global reservoirs of sulfur are the atmosphere and the lithosphere. Most sulfur is locked up in underground rocks and minerals or buried deep beneath ocean sediments. Large volumes of sulfur gases are released into the atmosphere through volcanic eruptions or the processing of fossil fuels [3]. Reactive sulfur emissions from fossil fuel combustion degrade air, soil, and water quality, affecting ecosystems hundreds of miles away from the source of pollution. There is also a serious risk of acid rain due to lower pH [4]. Lack of sulfur leads to a deterioration in the quality and quantity of the crop, which, for example, is expressed by the loss of natural colour of the plants green mass [2]. A lack of this element is observed both in soils throughout Russia [5–7] and abroad [2,8,9]. Therefore, environmental monitoring of mobile sulfur is of no small importance for maintaining soil fertility and environmental situation in general. Today, such determination is carried out with a certified method using turbidimetric analysis. It is possible to determine mobile sulfur in the presence of the orthanilic K indicator in aqueous solutions using photometric and volumetric analysis. The article explores the possibility of this type of analysis for ash, soil and mixed substrates.

2. Materials and methods

The determination of mobile sulfur was conducted using three methods:

turbidimetry (certified method) [10], photometric and volumetric analysis. The photometric algorithm was developed based on the work of Senyavin and Myasoedov [11], where the conditions of such determination in water were described. The volumetric algorithm was developed in accordance with the Federal Environmental Protection Document [12]. We applied both algorithms to the soil extracts and found some of the required conditions for the algorithms to be suitable. Those conditions are to be discussed fully in this article.

For turbidimetric analysis the calibration curve method is used. Different volumes of standard Na_2SO_4 solution are placed in 250 cm^3 measuring flasks. Potassium chloride is used as a solvent. An equivalent volume of barium chloride precipitating solution is added to each solution in the series. The colloidal suspension forms 10 min after the procedure mentioned above, only after this time absorbance of the suspensions can be measured. Starch is used as a suspension stabilizer. A mixture of potassium chloride with a precipitating solution in an equivalent volume is used as a comparison solution. The process of analysing soil extracts is carried out in a similar way. The only difference is that instead of standard solutions, an extract of the analysed substrate is examined. The analysis is carried out with a cuvette length of $l = 5$ cm and a wavelength of $\lambda = 520$ nm. The process of preparing all necessary solutions is described in the document [10].

Photometric determination can presumably be carried out at two wavelengths $\lambda_1 = 580$ nm and $\lambda_2 = 635$ nm with a cuvette length of $l = 1$ cm. This analysis is also carried out using the calibration graph method. The following reagents are added sequentially to a 10 cm^3 measuring flask: 0.16 cm^3 of orthanilic K, 0.4 cm^3 of urotropine buffer solution with pH $= 4.0$, 6 cm^3 of ethanol, 0.12 cm^3 of $BaCl_2$ solution, the required volume of Na_2SO_4 standard solution prepared in accordance with [10] and the required volume of KCl solution to completely fill the flask. The absorbance of the solutions can be than measured. A solution of potassium chloride is used as a comparison solution. When analysing soil substrates, the standard solution is replaced by an extract of the substrate under study. The comparison solution stays the same.

For volumetric analysis a 1 cm^3 sample of the extract is taken and diluted with 9 cm^3 of distilled water. Thus, the aliquot volume is 10 cm^3 at a tenfold dilution. This dilution factor should be taken into account during the calculation. The pH of the aliquot should be around 4.15 cm^3 of ethanol and 0.6 cm^3 of orthanilic K solution should be then added to the aliquot. This mixture is titrated with a $BaCl_2$ solution until the colour changes from purple to light blue.

When performing titrimetric and photometric determinations, additional purification of the extract is required by passing it through the cationite KU-2-8.

3. Results and discussion

Azo dyes are organic compounds containing R–N=N–R' groups in their molecular structure. Aryl radical is usually present in there. Azo dyes can be considered as members of the commercially useful group of azo compounds, i.e. compounds based on C–N=N–C [13]. Azo dyes are widely used in leather goods, textile and food industries. About 70% of all industrial dyes belong to this group [14].

In addition, azo dyes can exhibit anti-corrosion properties and are used as corrosion inhibitors in metal alloys, as well as in water-based electrolytes [15].

Orthanilic K is an azo dye belonging to the orthanilic group. In analytical chemistry, these reagents are widely used due to their ability to form complexes, which results in an analytical signal in the form of a colour change. Indicators of this group are used as complexometric indicators [16,17], and for anion determination [18,19]. The proposed structure of compounds of this group is presented by Dedkov et al. [17]. Complexation reactions with the reagents of the orthanilic group have been studied in [17,18,20–22].

Arabov [22] provides a review of the spectrophotometric characteristics of orthanilic group reagents. It has been shown that orthanilic K has advantages in photometric analysis. The reagent has the largest range of working wavelengths, as well as a high molar absorption coefficient, which suggests the possibility of determining the component in a wider range of concentrations. The reagent is also applicable in volumetric analysis for the determination of sulfates in water. In our study we test the possibility of working with this indicator when analysing soil extracts in the presence of potassium chloride.

3.1. Reaction mechanism

The chemistry underlying the method being studied, is the ability of orthanilic K to form complexes of 1:1 composition with the Ba^{2+} ion. In this case, the colour of the indicator changes from purple to light blue. The proposed scheme of complex formation is presented in the **Figure 1**.
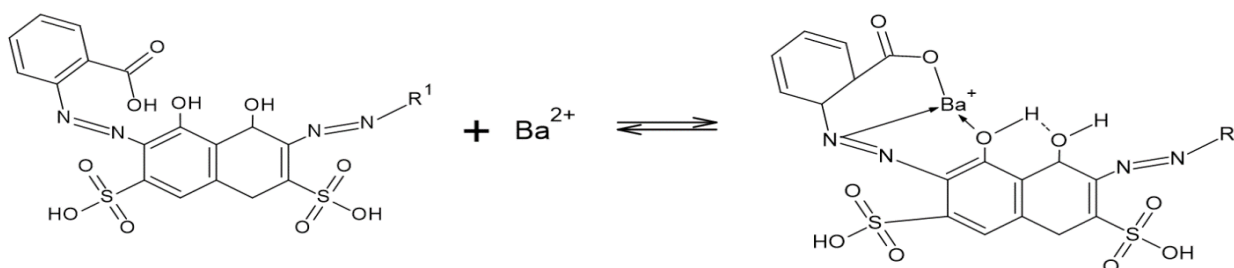

Figure 1. Formation of a complex of Ba^{2+} with orthanilic K.

If sulfur in the form of sulfate appears in the system, this complex is destroyed, giving a reverse color change (**Figure 2**). This reaction underlies the previously studied photometric determination. This explains the inverse dependence of the solution absorbance on the sulfur concentration: A ↓C(S) ↑, as well as the negative impact of dilution on the results quality.

During the volumetric determination, the reaction presented in **Figure 1** occurs. Barium ions are added as a titrant to a system containing sulfur in the form of sulfates. Initially, the reaction of barium sulfate formation takes place: $Ba^{2+} + SO_4^{2-} = BaSO_4$, with the solution retaining its purple color. The equivalence point is fixed by the beginning of complex formation, which occurs as soon as there are no SO_4^{2-} ions left in the system.
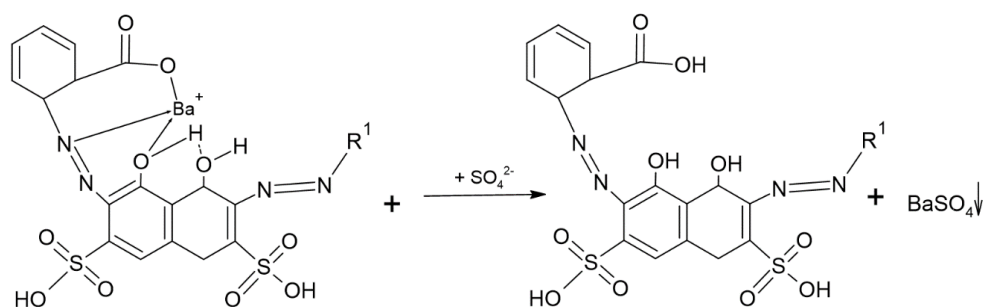
Figure 2. Ba^{2+}-orthanilic K complex destruction under the influence of sulfate ions.

3.2. Determination conditions

It is known that orthanilic K is applicable in a limited pH range in acidic solutions. In photometric analysis, the desired pH is maintained with a buffer solution. In the case of volumetric analysis, it is proposed to maintain acidity by adjusting the pH with sodium hydroxide solution. Ethanol is used as a solvent. Barium chloride solution is used to detect the analytical signal in both cases.

At first, we studied subtleties of photometric determination. It has been found that suitable wavelengths are: $\lambda_1 = 580$ nm, $\lambda_2 = 635$ nm. An algorithm for photometric analysis is presented and data from the first series of experiments is obtained in our previous work [23]. Before proceeding with further research, we assessed the reliability of the results obtained. For the accuracy control, a comparison method was used.

The photometric determination results were compared with the results determined with the certified method under the same conditions. Requirements for permissible error values were based on the hypothesis that the photometric method works no worse than the one certified. That means that the analysis error does not exceed 7.5% rel.

The reliability of the results was assessed by the method of operational control: $K_\kappa \leq K$.

$$K_\text{к} = |\bar{x} - X| \leq K = \sqrt{\Delta_1{}^2 + \Delta_2{}^2} \tag{1}$$

where K_κ: the result of the control procedure, and K is the control standard. The results are presented in **Table 1**.

Table 1. Results of the first series of experiments to test the conditions of photometric analysis with the calculation of repeatability control.

Object under study	Method				
		Using Orthanilic K			
	Certified Method C(S), ppm	$\lambda_1 = 580$ nm		$\lambda_2 = 635$ nm	
		C(S), ppm	$K_\text{к} \leq K$	C(S), ppm	$K_\text{к} \leq K$
Soil	10.1 ± 0.8	9.1	$1.0 = 1.0$	11.2	$1.1 = 1.1$
Soil after planting wheat	5.8 ± 0.4	5.6	$0.2 < 0.6$	8.0	$2.2 > 0.1$
Wood ash	519 ± 39	475	$44 < 53$	385	$134 > 48$
Wood ash after planting wheat	237 ± 18	201	$36 > 23$	248.5	$12 < 26$
Soil-ash mixture 2:1	109.1 ± 8.2	107	$2 < 11$	127.5	$18 > 16$

When assessing the reliability of the data, it was concluded that the $\lambda_2 = 635$ nm wavelength was unsuitable. Further studies were carried out only at wavelength $\lambda_1 = 580$ nm.

The volumetric algorithm is developed on the basis of the methodology for water analysis, which includes aqueous extracts titration. Since the extractant for soil analysis is the solution of potassium chloride, it is necessary to check the possibility of the analysis in its presence and identify its optimal content, which does not negatively affect the results of the analysis. In addition, the range of concentrations in which the volumetric technique provides suitable results is of some interest. In order to find those conditions a series of standard solutions was analysed. The results are presented in **Figure 3**.
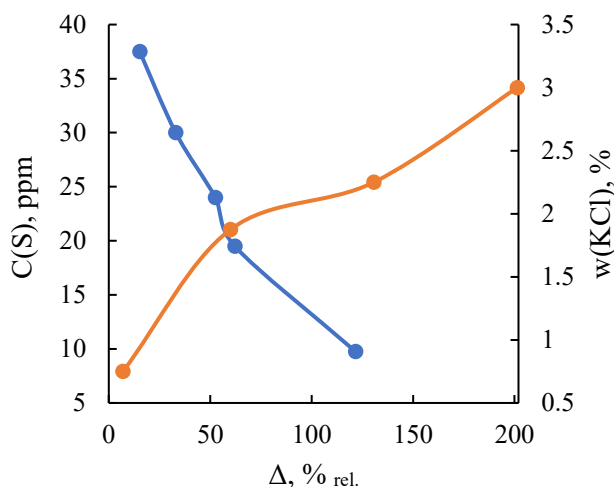

Figure 3. Dependence of the concentration of mobile sulfur (ppm) and the percentage of chlorine-potassium extract in the volume of an aliquot on the relative error of determination, %.

Based on the graph presented in **Figure 3**, the suitable conditions for titrimetric determination were identified. The volumetric algorithm was developed on the basis of a water analysis technique, which is the presumed reason for the adverse effect of the potassium chloride presence in an aliquot. It is important to note that no negative effect of the KCl content in the solution on the accuracy of photometric analysis was noticed. This may be due to the replacement of the reference solution from distilled water to a potassium chloride solution, which was also used as an additional solvent.

Thus, the limits of determination have been identified using two methods, where photometric determination is possible in the concentration range of mobile sulfur from 0.25 ppm to 25 ppm. The titrimetric determination is possible from 37.5 to 700 ppm of sulfur content. The upper limit was determined by calculation, based on the data of the methodology on which the study was based.

3.3. Natural objects analysis

The correctness of the method was repeatedly studied on real objects with wide ranges of concentrations of both the determined and interfering components. Soils of various genesis, wood ash, and soil-ash mixtures 10:1 were selected as study objects.

Table 2 presents the results of two series of experiments, indicated by numbers, on separate substrates. The results show that the hypothesis about the limits of action of each algorithm is confirmed.

Table 2. Determination of mobile sulfur using three methods.

Substrate analysed	C(S), ppm				
	Certified method	Titrimetric analysis	$K_\kappa \leq K$	Photometric analysis	$K_\kappa \leq K$
Wood ash	2405 ± 180	3242.5	$838 > 299$	-	-
Nutrient soil (1)	5.4 ± 0.4	-	-	5.6	$0.2 < 0.6$
Acidic Peat (1)	231 ± 17	221.9	$9.1 < 24$	-	-
Garden soil (1)	2.7 ± 0.3	-	-	3.0	$0.3 = 0.3$
Gardenhouse soil (1)	27.5 ± 2.1	54.0	$26.5 > 4.3$	44.8	$17.3 > 3.8$
Nutrient soil (2)	33.5 ± 2.5	33.1	$0.4 < 3.5$	0.9	$32.6 > 1.8$
Acidic Peat (2)	117.5 ± 8.8	109.9	$7.6 < 12$	-	-
Garden soil (2)	9.2 ± 0.6	-	-	10.1	$0.9 < 1.0$
Gardenhouse soil (2)	70.9 ± 5.3	58.9	$12 > 6.9$	-	-

Table 3 presents the research results of a mixture of substrates with wood ash with a composition of 10:1. Based on a quantity of the analyte in the ash, calculations revealed that the expected values of the concentrations of mobile sulfur in all mixtures exceed at least 100 ppm. Therefore, photometric analysis for these objects was considered inappropriate. The next part of the experiment was carried out only by turbidimetric and titrimetric methods.

Table 3. Determination of mobile sulfur in a soil-ash mixtures (10:1) using two methods, two experiment series.

Substance analysed	C(S), ppm Certified method	C(S), ppm Titrimetric analysis	$K_\kappa \leq K$
Nutrient Soil + wood ash (1)	234 ± 18	222.3	$12 < 24$
Acidic Peat + wood ash (1)	422 ± 32	444.2	$22 < 46$
Garden Soil + wood ash (1)	233 ± 17	222.3	$10 < 24$
Greenhouse Soil + wood ash (1)	254 ± 19	266.6	$13 < 28$
Nutrient Soil + wood ash (2)	411 ± 31	444.2	$33 < 45$
Acidic Peat + wood ash (2)	676 ± 51	644	$32 < 70$
Garden Soil + wood ash (2)	148 ± 148	149.9	$2 < 16$
Greenhouse Soil + wood ash (2)	189 ± 14	177.6	$12 < 19$

It can be seen that in both series of experiments the results of operational control are satisfactory. This allows us to conclude that the titrimetric algorithm is suitable for the use on substrates with a large quantity of mobile sulfur.

Interfering components seriously affect the quality of analysis results. The results obtained through the analysis of standard solutions were much more accurate than those obtained through the analysis of the natural substrates. Interfering influences must be eliminated by passing the extract through a column with cation exchange resin.

The highest error was observed in the analysis of wood ash due to the quantity of the component being determined.

In addition, the determination of mobile sulfur in the concentration range of 25–37.5 ppm causes difficulties. Determination in this range under the above conditions is characterized by a greater error than the error of the certified method. Therefore, the use of the method in these conditions at this stage is not advisable. Finding suitable conditions, as well as expanding the range of the technique towards higher concentrations can be a direction for further research.

4. Conclusion

In the course of this study, the algorithm for analysing soil extracts using the orthanilic K indicator was developed. Depending on the content of the component being determined, a photometric or titrimetric method of analysis must be selected.

Photometric determination is possible under the following conditions: $\lambda = 580$ nm, l = 1 cm, a potassium chloride solution with a concentration of 1 M serves as a reference solution. Dilution by more than 10 times is not allowed. For volumetric determination, the KCl content in the aliquot volume should not exceed 0.75%. There are no strict time frames for conducting the analysis.

The developed algorithm has a number of advantages over the certified methodology. These include: simple preparation of solutions and the absence of strict requirements for their storage conditions, low consumption of reagents, simplicity and high speed of analysis, absence of complex instrumentation, as well as the absence of the need to strictly adhere to the development of the colouring time of solutions

This method can serve as a good alternative to the certified one. It is applicable for the analysis of soils of various origins, as well as ash and mixed substrates

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