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**SIMPLE METHODS FOR QUANTITATIVE
DETERMINATION OF SULPHATE IONS FROM AQUEOUS
MEDIA WITH INDUSTRIAL APPLICATIONS**

BY

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Abstract. In this study, two simple methods (conductometric titration and turbidimetric method) have been used for the quantitative determination of sulphate ions from aqueous media. Both methods are based on the reaction between sulphate ions and BaCl_2 , when a white precipitate (BaSO_4) is obtained. The main advantage of this reaction is that the formation of the BaSO_4 precipitate occurs almost under any experimental conditions. Therefore, the two methods were comparatively examined to establish their applicability limits in the quantitative determination of sulphate ions. Thus, several important analytical parameters, such as usable concentration range, detection limit, precision, selectivity, etc., were evaluated based on the experimental results, in each case. The results included in this study show that these two methods complement each other, and allow the determination of sulphate ions from a wide range of industrial samples.

Keywords: Sulphate determination; conductometric titration; turbidimetric method; aqueous solution; industrial applications.

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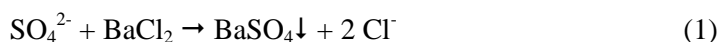
1. Introduction

Sulphate ions are used in many industrial processes, both as raw materials (mining and metallurgy industrial activities) and as auxiliary materials (in electroplating industry, chemical industry, building materials industry, etc.) (Ercikdi *et al.*, 2009). Therefore, in many of these industrial processes, the concentration of sulphate ions is an important parameter that must be determined easily and with high precision (Caceres *et al.*, 2015). On the other hand, wastewaters resulting from such industrial activities also contain sulphate ions in different concentrations, and their determination is of real interest, technological and environmental point of view.

For this reason, the determination of sulphate ions is often done in industrial laboratories, and the obtained concentration values are then used to regulate the production activity. Under these conditions, in the selection of the analysis method which will be used at industrial level, besides the analytical performances, other features such as simplicity in use, rapidity and low cost need to be considered.

From analytical point of view, four categories of methods of analysis can be used for sulphate ions determination, namely: gravimetry, spectrophotometry, potentiometry and ion chromatography (van Staden and Taljaard, 1996; Kumar *et al.*, 2001; del Rio *et al.*, 2010; Cihacek *et al.*, 2015). The last three methods are instrumental analysis methods and, even if they have very good analytical performance, these methods require costly laboratory equipment and reagents, long time of sample preparation and laborious methodologies (Dean, 1995).

Unlike these, gravimetry is a chemical method of analysis, which is much easier to use, because require only common laboratory devices and does not involve high costs (Bejan *et al.*, 2006). The gravimetric method of sulphate ions determination is based on the precipitation reaction with BaCl₂:



when a white precipitate of BaSO₄ is formed, which can be gravimetrically analyzed. Although, the gravimetric method is mentioned in Romanian standard for sulphate analysis (STAS 8601-70), its use is not always handy because it requires a long working time and relatively high concentrations of sulphate ions.

In this study two simple methods have been examined for the quantitative determination of sulphate ions from aqueous media, namely: conductometric titration and turbidimetric method. Both methods are based on the reaction between sulphate ions and BaCl₂ (see Eq. (1)), which makes that the main advantages of the gravimetric method to be maintained, but eliminates the long working time for precipitation processing by instrumental measurement of the analytical signal. The most important analytical parameters, such as

usable concentration range, detection limit, precision, selectivity, etc., have been evaluated based on the experimental results, for each method, to highlight their applicability and limitations.

2. Experimental

Stock solution of $0.1 \text{ mol}\cdot\text{L}^{-1}$ Na_2SO_4 was prepared by dissolving solid sodium sulphate in distilled water. All the working solutions were obtained by dilution from this stock solution. The solution of BaCl_2 ($0.1 \text{ mol}\cdot\text{L}^{-1}$) was prepared also by dissolving of solid reagent in distilled water. All other chemical reagents used in this study (HCl ($1 \text{ mol}\cdot\text{L}^{-1}$), Na_2CO_3 ($1 \text{ mol}\cdot\text{L}^{-1}$) and NaNO_3 ($0.1 \text{ mol}\cdot\text{L}^{-1}$)) were of analytical grade and were used without further purifications.

The conductometric titration experiments were performed in a 100 mL conductometric glass cell, by adding 1.5 mL of sulphate ions solution (0.1 and $0.01 \text{ mol}\cdot\text{L}^{-1}$) and dilution to about 80 mL with distilled water in conductometric cell. Volumes of 0.2 mL of $0.1 \text{ mol}\cdot\text{L}^{-1}$ BaCl_2 were added from 10 mL burette. After each addition, the solution was homogenized and the electrical conductivity ($1/R$, $\mu\text{S}\cdot\text{cm}^{-1}$) was measured with a Hach conductometer (MM 374 type). The conductometric measurements were stopped only after the recording of at least six points after the equivalence point. The volume of BaCl_2 consumed at equivalence was calculated from the titration curve.

The analysis of sulphate ions by turbidimetric method was done using the calibration curve. This was obtained by adding 3.0 mL $0.1 \text{ mol}\cdot\text{L}^{-1}$ BaCl_2 solution and exact measured volumes of $0.01 \text{ mol}\cdot\text{L}^{-1}$ sulphate solution (0.5 – 3.0 mL) in a 50 mL volumetric flasks. The samples were diluted with distilled water and the turbidity was measured after 5 min of stand by at 490 nm using a Digital Spectrophotometer S 104 D (1 cm glass cell) against distilled water. The selectivity of turbidimetric method was evaluated using the selectivity coefficients. These were calculated as the ratio between sulphate ions concentration and interfering ions (CO_3^{2-} or NO_3^-) concentration, which gives a 5% turbidity change. The validation of the turbidimetric method was done using two samples of real water, sampled from Danube River and tap water from the “Gheorghe Asachi” Technical University laboratories. Before to be used for analysis the water samples were filtrate to quantitative filter paper to remove all the solid impurities.

3. Results and Discussion

As it was mentioned above, both methods proposed in this study for the sulphate ions determination from aqueous media are based on the precipitation reaction with BaCl_2 , when a white precipitate is obtained (see Eq. (1)). This precipitate has a low solubility ($P_s = 1.1\cdot 10^{-10}$) (Dean, 1995) over the entire pH

range of the aqueous solution, which is an important advantage from the point of view of industrial analyzes.

3.1. Determination of Sulphate Ions by Conductometric Titration

In general, the conductometric titration is based on the measurement of the electrical conductivity variation of an electrolyte solution to the addition of known volumes of titrant solution (Bulgariu, 2011). The titration curve obtained from graphical representation of the experimental results is used for the determination of the equivalence point.

Any titration reaction can be used in the conductometric measurements, with the conditions that during titration, a significant variation of the electrical conductivity of the solution occurs. It is also the case of precipitation reactions (such as the reaction described in the Eq. (1)), when the formation of low soluble precipitate causes a decrease in the electrical conductivity of the analyzed solution (Garcia and Schutlz, 2016).

The experimental conductometric curve obtained at the titration of $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ SO}_4^{2-}$ solution with $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ BaCl}_2$ solution is presented in Fig. 1.

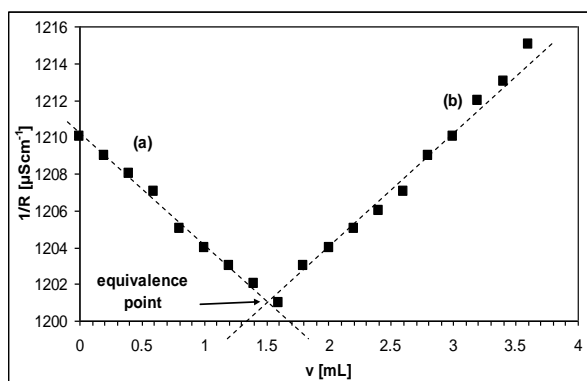


Fig. 1 – Conductometric titration curve of sulphate ions ($0.1 \text{ mol}\cdot\text{L}^{-1}$) with BaCl_2 solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$).

As can be seen from Fig. 1, the titration curve is composed by two distinct segments. First segment (a) represents the decrease of electrical conductivity until at equivalence point and is caused by the formation of BaSO_4 precipitate, while the second segment (b) indicate a increase of the electrical conductivity of the solution, due to the addition of titrant excess. The intersection point of these two segments show the point of equivalence, and the volume of titrant consumed until at this point is 1.51 mL, in this case. The calculated sulphate concentration based on the equivalence law using the volume of equivalence determined in Fig. 1, is $9.6641 \text{ mg SO}_4^{2-}\cdot\text{L}^{-1}$,

corresponding to an experimental error of + 6.4%. The relatively low value of the experimental error suggests that conductometric titration could be an alternative method for the determination of sulphate ions from aqueous media.

In order to test the limits of conductometric titration as analysis method for sulphate ions determination, two separated experiments were performed. In first experiment, it was added 2.0 mL of 1N HCl solution ($\text{pH} \approx 0.5$), while in the second experiment, a solution of sulphate ions of $0.01 \text{ mol}\cdot\text{L}^{-1}$ was analyzed. The conductometric titration curves are illustrated in Fig. 2.

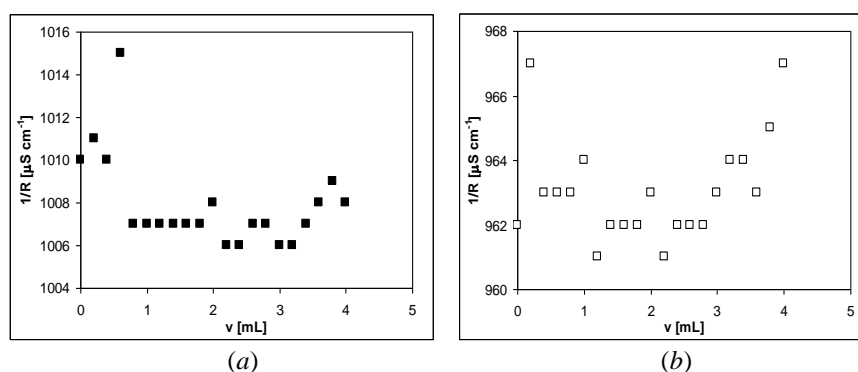


Fig. 2 – Conductometric titration curves of (a) sulphate ions ($0.1 \text{ mol}\cdot\text{L}^{-1}$) in presence of HCl solution, and (b) sulphate ions ($0.01 \text{ mol}\cdot\text{L}^{-1}$).

The obtained experimental results have clearly shows that when in the analyzed sample is present a mineral acid (as HCl), which has high conductivity (Fig. 2a), or when the concentration of sulphate ion is lower (Fig. 2b), the variation of the electrical conductivity is irregular, and the point of equivalence cannot be determined precisely. Therefore, the determination of sulphate ions by conductometric titration can be used only when their concentration is high (around $0.1 \text{ mol}\cdot\text{L}^{-1}$ ($9600 \text{ mg}\cdot\text{L}^{-1}$)) and in the absence of inert electrolytes, which drastically limits the practical applicability of this method.

3.2. Determination of Sulphate Ions by Turbidimetric Method

Most of the disadvantages of conductometric titration can be minimized if the turbidimetric method is used to determine the sulphate ions (Santelli *et al.*, 1995). The turbidimetric method of sulphate ions determination is based on the same precipitation reaction (see Eq. (1)), with the difference that in this case the turbidity is measured experimentally, which is directly proportional to the amount of precipitate formed (in agreement with Lambert-Beer law). The experimental measurement of the turbidity is made at the specific wavelength, which was selected based on the VIS spectrum recorded for a solution of sulphate ions, with well known concentration after addition of BaCl_2 (Fig. 3).

It can be observed from Fig. 3 that on entire VIS spectral domain the BaSO_4 precipitate does not have any absorption bands, and this behaviour is characteristic of the white precipitates. Under these conditions, the wavelength that can be used for the turbidity measurements is 490 nm, in agreement with the recommendations from literature (Bîlbă and Bulgariu, 2005).

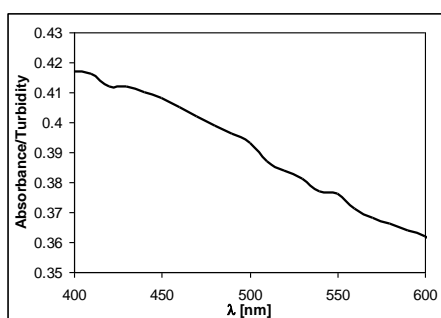


Fig. 3 – VIS spectra of sulphate ions solution ($0.01 \text{ mol}\cdot\text{L}^{-1}$) after addition of BaCl_2 .

In addition, because the turbidimetric method is a direct method of analysis, a calibration curve is required for the experimental determinations. In Fig. 4 is illustrated the calibration curve obtained as described in the Experimental section, using six standard solution with different concentrations of sulphate ions. The most important analytical parameters (linear concentration range, limit of detection, limit of quantification, precision, etc.), calculated on the basis of the experimental calibration curve are summarized in Table 1.

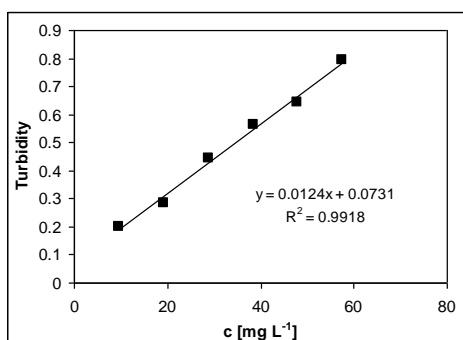


Fig. 4 – Experimental calibration curve obtained for the determination of sulphate ions by turbidimetric method.

As can be seen from Fig. 4, the linear dependence between turbidity and sulphate ions concentration is respected for the entire experimental concentration range ($10 - 70 \text{ mg}\cdot\text{L}^{-1}$). This means that the turbidimetric method

can be successfully used to determine the low concentration of sulphate ions, as compared to the conductometric titration. The possibility of using the turbidimetric method to determine the low concentrations of sulphate ions can be viewed from two perspectives: (a) as an advantage, represented by the analytical performance of the method, and (b) as a disadvantage, because in the case of solutions containing high concentrations of sulphate ions it is necessary to dilute the samples before analyze.

Table 1
The Analytical Characteristics of the Turbidimetric Method

Analytical parameter	At 490 nm
Calibration sensitivity	0.0124 L·mg ⁻¹
Correlation coefficient	0.9918
Linear dynamic range	10 – 70 mg·L ⁻¹
Limit of detection (3σ)	0.1153 mg·L ⁻¹
Limit of quantification (10σ)	0.3843 μg·mL ⁻¹
Precision	1.96%

On the other hand, the quantitative parameters (Table 1) shows that the turbidimetric methods have a low detection limit, a sufficiently wide linear concentration range, a and relatively high precision, and can be used for the quantitative determination of sulphate ions from aqueous media.

The influence of various interfering ions that can affect the determination of sulphate ions by the turbidimetric method has been also quantitatively evaluated. This evaluation was done using the selectivity coefficients ($a_{sulphate, j}$), which are defined as the ratio between sulphate ions concentration ($c_{sulphate}$, mg·L⁻¹) and the interfering ions concentration (c_j , mg·L⁻¹), which give a 5% turbidity change, in a reference solution (with constant concentration of sulphate ions) (Christian, 1994). In this case, the sulphate ions concentration in the reference solution was 19.20 mg·L⁻¹, and NO₃⁻ and CO₃²⁻ ions were selected as interfering ions. These was selected as interfering ions because are present in the most real water samples. The values of the selectivity coefficients, calculated for each interfering ion from experimental turbidity measurements (Fig. 5) are presented in Table 2.

The values of selectivity coefficients indicate that the presence of nitrate ions doest not interfere in the sulphate determination by turbidimetric methods, compared with carbonate ions, which interfere still at a low concentrations. According with the data from Table 2, the nitrate ions concentration can be more than 8 times higher than the sulphate ions concentration to cause a 5% turbidity change, and this variation in mainly due to the increase of ionic strength of solution. In case of carbonate ions, the 5% turbidity variation is obtained at a much lower concentration (7.21 mg CO₃²⁻·L⁻¹),

and is caused by the formation of the white precipitate of BaCO_3 , after the addition of the BaCl_2 reagent.

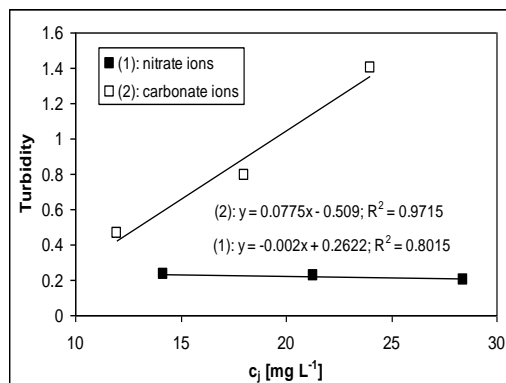


Fig. 5 – Experimental dependences between turbidity and interfering ions concentration.

Table 2
The Selectivity Coefficients

Interfering ion	$c_{\text{sulphate}} [\text{mg}\cdot\text{L}^{-1}]$	$c_j [\text{mg}\cdot\text{L}^{-1}]$	$a_{\text{sulphate}, j}$
NO_3^-	19.20	160.12	0.12
CO_3^{2-}	19.20	7.21	2.66

This means that the turbidimetric method cannot be used for analysis of industrial samples that contains beside sulphate ions and important concentration of carbonate ions. In such conditions, it is recommended that the determination of sulphate ions to be done by conductometric titration (if the concentration of sulphate ions is higher than $0.1 \text{ mol}\cdot\text{L}^{-1}$), or by turbidimetric method but only when the carbonate ions have been removed by other specific method (Sipos *et al.*, 2000; Zhao *et al.*, 2005).

The applicability of the turbidimetric method for sulphate ions determination was done by recovery test using two types of real water samples: one tap water, from the laboratories of “Gheorghe Asachi” Technical University of Iași, and one water sample from Danube River, without any preliminary treatment. For these experiments, 20 mL of each real water sample was transferred into eight 50 mL volumetric flasks, and different volumes (1.0; 1.5 and 2.0 mL) of stock sulphate solution ($960 \text{ mg}\cdot\text{L}^{-1}$) were added. After addition of 3.0 mL of BaCl_2 solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$), each flask was diluted with distilled water to the mark and homogenized. In each case the turbidity was measured at 490 nm against distilled water, and the concentration of sulphate ions was calculated by interpolation from the calibration curve. The recovery percent obtained for the addition of sulphate ions spikes to the two real water samples are summarized in Table 3.

Table 3
The Results of Recovery Test

Sample	$v_{\text{sulphate}}^{\text{add}}$ [mL]	$c_{\text{sulphate}}^{\text{add}}$ [mg·L ⁻¹]	$c_{\text{sulphate}}^{\text{found}}$ [mg·L ⁻¹]	Recovery percent [%]	Recovery percent* [%]
Tap water	0	0	4.71	-	-
	1.0	19.20	24.82	129.27	104.74
	1.5	28.20	33.12	117.45	100.74
	2.0	38.40	43.09	112.21	99.95
Danube River water	0	0	18.33	-	-
	1.0	19.20	36.95	192.45	96.98
	1.5	28.20	47.03	166.77	101.77
	2.0	38.40	56.87	148.09	100.36

Recovery percent* - the values of recovery percents recalculated considering the initial concentration of sulphate ions without addition of stock solution.

The obtained experimental results (Table 3) indicate that in all the cases the values of sulphate ions concentration determined by turbidimetric methods are higher than those theoretical. This is mainly due to the fact that the real water samples contain in their composition sulphate and carbonate ions, which makes the recovery percent much higher than 100%. If the values of recovery percent are recalculated considering the sulphate ions content of each water sample, then a better recovery is obtained and the turbidimetric method can be successfully used for sulphate ions determination.

Even if the turbidimetric method has excellent analytical characteristics, it is recommended to be used to determine sulphate ions from water samples where their concentration is low and does not contain carbonate ions, which can significantly affect the accuracy of the analysis results.

4. Conclusions

In this study, two simple methods, namely: conductometric titration and turbidimetric method have been used for the quantitative determination of sulphate ions from aqueous media. These methods are based on the precipitation reaction between sulphate ions and BaCl₂, a reaction that occurs almost under any experimental conditions. The obtained experimental results have shown that the conductometric titration can be used only when the sulphate concentration is high (around 0.1 mol·L⁻¹) and in the absence of inert electrolytes, which drastically limits the practical applicability of this method. Unlike this, the turbidimetric method can be used to determine sulphate ions in water samples where their concentration is low and does not contain carbonate ions, which give significant interference. However, both studied methods are simple, rapid and low-cost, and can be used in industrial laboratories.

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METODE SIMPLE PENTRU DETERMINAREA
CANTITATIVĂ A IONILOR DE SULFAT DIN MEDII APOASE CU
APLICAȚII INDUSTRIALE

(Rezumat)

În acest studiu, au fost utilizate două metode simple (titrare conductometrică și metoda turbidimetrică) pentru determinarea cantitativă a ionilor sulfat din medii apoase. Ambele metode se bazează pe reacția dintre ionii de sulfat și BaCl_2 , când se obține un precipitat alb (BaSO_4). Principalul avantaj al acestei reacții este că formarea precipitatului de BaSO_4 are loc aproape în orice condiții experimentale. Prin urmare, cele două metode au fost examinate comparativ pentru a stabili limitele lor de aplicabilitate în determinarea cantitativă a ionilor de sulfat. Astfel, mai mulți parametri analitici importanți, cum ar fi intervalul de concentrație utilizabil, limita de detecție, precizia, selectivitatea etc., au fost evaluați pe baza rezultatelor experimentale, în fiecare caz. Rezultatele incluse în acest studiu arată că aceste două metode se completează reciproc și permit determinarea ionilor de sulfat dintr-o gamă largă de probe industriale.

