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COMPARISON OF VOLUMETRIC METHODS OF SULPHATES DETERMINATION IN WATER AND WASTES

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In the paper following methods of sulphates determination are described and compared: indirect determination according to Polish Standards, direct titration by barium perchlorate in the presence of different indicators (thorin, thorin+methylene blue, sulphonazo III).

Direct method with sulphonazo III was chosen to be the best. Described procedure was used for sulphates determination in several water and sewage samples.

Preliminary separation of cations on the ion exchanger is also described.

W pracy przedstawiono i porównano następujące metody oznaczania siarczanów: pośrednią według Polskiej Normy oraz bezpośrednie miareczkowanie za pomocą nadchloranu baru w obecności różnych wskaźników (toryna, toryna+błękit metylenowy, sulfonazo III).

Jako optymalną wybrano metodę bezpośrednią z użyciem sulfonazo III. Opisaną procedurę zastosowano do oznaczania siarczanów w wodach i ściekach.

Opisano również wstępne oddzielanie przeszkadzających w oznaczeniu kationów na kolumnie jonowymiennej.

The determination of sulphates in water and wastes up to now presents some difficulties. Interlaboratory studies performed by Department of Analytical Chemistry, Technical University, Cracow [1–3] show rather big discrepancies.

The compleximetric determination of sulphates according to Polish Standards [4] consists of several stages and is troublesome.

Some of the volumetric methods of SO_4^{2-} determination with different end point detection require various sample preparation [5–11] and are applied for determination of sulphates in waters and wastes.

In this paper the determination of sulphates according to Polish Standards [4,12] as well as titration with barium perchlorate in the presence of sulphonazo III [13–15], thorin [12,16–19] and mixed indicator (thorin+methylene blue) [12,18] have been checked and compared.

EXPERIMENTAL

Reagents, solutions and apparatus

Sulphuric acid (d=1.84 g l^{-1}), barium perchlorate, sodium sulphate, sodium chloride, ammonium chloride, sodium carbonate, sodium thiosulphate, potassium fluoride, disodium hydrogen phosphate, potassium bromate, *n*-propanol. All reagents were of analytical grade (POCh, Gliwice).

Sulphonazo III (Chemapol), thorin (Fluka).

Dowex 50W [H^+] (Fluka) – strongly acidic cation exchanger, 50–100 mesh, humidity=53%, break through capacity=5.3 mmol g^{-1} of dry exchanger.

Sodium sulphate, about 0.005 mol l^{-1} standardized gravimetrically, Barium perchlorate, about 0.005 mol l^{-1} standardized by titration using sulphonazo III or thorin as indicator,

Disodium ethylenediaminetetraacetate, about 0.02 mol l^{-1} standardized by compleximetric titration.

Magnesium chloride, about 0.02 mol l^{-1} standardized by compleximetric titration.

Thorin indicator, 0.2 g of substance was dissolved in 100 ml of water, Mixed indicator, 0.8 g of thorin, 0.16 g of methylene blue and 0.29 g of potassium bromate were dissolved in 1 l of water. Sulphonazo III indicator, 1 g of substance was dissolved in 100 ml of water.

For preparation of all solutions triple distilled water was used.

Automatic burette EK-15 (Metrohm, Switzerland) pH-meter N-517 (Meratronik, Poland).

MEASUREMENTS

1. Sulphates determination according to Polish Standards

The principle of recommended determination depends on the titration of EDTA excess with standard solution of $MgCl_2$ (0.025 mol l^{-1}) after precipitation of SO_4^{2-} ions (1–20 mg in 100 ml) with $BaCl_2$ solution and then dissolution of $BaSO_4$ in the mixture of NH_3 (10 mol l^{-1}, 5 ml) and EDTA (0.025 mol l^{-1}, 15 ml).

The determination of sulphates in standardized sodium sulphate solution containing 9.35 mg SO_4^{2-} has been carried out according to Polish Standard [4]. Two series of 7 determinations were performed. The obtained results were 7.16 and 7.29 mg with standard deviation 0.46 and 0.10 mg respectively. For both series the blank 0.14 mg was taken into account, but a negative error approx. 20% is significant.

The procedure consists of several stages and the sources of negative errors may be the following:

– non-quantitative precipitation or separation of barium sulphate (effect of temperature, filter or solution composition),

– incomplete dissolution of barium sulphate precipitate in the excess of EDTA (effect of EDTA excess, temperature, heating time, pH and the amount of added ammonia),

– the substitution reaction by titration of EDTA excess with the magnesium salt solution (log β_{MgEDTA} =8.69, log β_{BaEDTA} =7.76).

The effect of individual parameters has been analyzed. The completeness of precipitation may be influenced by filtration of precipitate after cooling of solution using two filter papers, and the precipitation from mixed water–propanol solution. When the precipitation was carried out exactly according to the standard procedure, the negative error was -11.7%. When the 1+1 water–propanol solution was used the error decreased to -5.9%, but if additionally two hard filter papers were used, the error was -3.1% only.

A significant role plays the quantitativeness of $BaSO_4$ dissolution in the excess of EDTA. Changing one parameter and keeping the other according to Polish Standard it was observed that the extension of heating time of the precipitate above 10–12 min does not influence the result of determination. On the other hand the amounts of EDTA and ammonia significantly affect the results (Table 1). It must be remembered that dissolution of $BaSO_4$ precipitate occurs at pH 8.

Table 1. Effect of EDTA excess and amount of added ammonia on the results of compleximetric determination of sulphates (n=7, 9.35 mg SO_4^{2-})

Volume of EDTA ml	Volume of NH_3 ml	Rel. error %
15	5	-22.0
20	5	-11.7
25	5	-4.7
35	5	-4.5
15	3	-32.2
15	5	-23.4
15	7.5	-20.3
15	10	-18.5
15	2×7.5	-15.4

Finally the possibility of occurrence of the magnesium substitution reaction was tested. For this purpose the expected excess of EDTA solution was added to the solution of barium perchlorate and after adjusting pH to 9–10 was titrated by Mg^{2+} salt solution. The results indicated that the substitution reaction occurs causing the losses of sulphates of *ca.* 0.19 mg SO_4^{2-} (2%).

All those experiments indicate that the indirect compleximetric determination of sulphates in waters is time-consuming and requires very carefully defined experimental conditions. The negative errors may be reduced by filtration of the cool solution with barium sulphate precipitate through double hard filter paper, by dissolution the precipitate in 25 ml of *ca.* 0.02 mol l^{-1} EDTA solution, by addition of ammonia in two 7.5 ml portions and by heating the precipitate with the filter papers during 10–12 min.

In such conditions sulphates were determined in pure salts solutions. It was stated that for sulphate range 18.71–4.68 mg determination errors were still negative but equal to 3%. For lower SO_4^{2-} amounts discrepancies were higher and for 0.5 mg SO_4^{2-} results were the same as blank values.

2. Direct titrimetric determination of sulphates with thorin and mixed indicator

Basing on experiments carried out in pure salts solutions optimal conditions for titration were chosen: water+*n*-propanol mixture (1+4), pH range 3.4–4.6, 2–3 drops of each indicator. During titrations colour changes for thorin from yellow to pink, for mixed indicator from gray-green to gray-blue. It was also stated that decreasing of *n*-propanol amount causes the significant positive error of determination.

This procedure was applied for determination of sulphates in pure salt solutions containing 9.35–0.04 mg of SO_4^{2-} ions. It was observed that the error strongly depends on sulphates amount: -7% for 9.35 mg and +75% for 0.04 mg. For the range 2.3–0.5 mg SO_4^{2-} (10 ml sample) the error is 5%. It is worth to mention that for smaller or bigger amounts of SO_4^{2-} ions the precision is poor and the colour change is not distinct.

Thorin and mixed indicator are not specific for barium ions. Therefore the separation of other cations before the titrimetric determination of sulphates is necessary. For this purpose a cation exchanger Dowex 50 W was applied. The column of 12 mm diameter and 5 cm height of bed was used. The 100 ml sample was passed through the column. The eluate was collected after rejecting the initial 40 ml. The 10 ml of eluate were taken for each determination, the pH was controlled and adjusted to 3.5–4.5 by ammonia or perchloric acid solutions. Next the indicator was added as well as 40 ml of *n*-propanol and the titration was carried out using standardized barium perchlorate solution up to the colour change.

This procedure was applied for the determination of sulphates in pure salt solutions of different SO_4^{2-} contents and also in the samples of "synthetic water" containing other ions (Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Cl^-, F^-, CrO_4^{2-}, PO_4^{3-}, Br^-) in amounts occurring in natural waters. It has been stated previously that the above mentioned ions in such amounts do not influence the SO_4^{2-} determination. The results obtained are presented in Table 2.

Table 2. Results of SO_4^{2-} determination (n=3–5) in the presence of thorin and mixed indicator after separation on ion exchange column

Taken SO_4^{2-} mg	Model solution Na_2SO_4		"Synthetic water"	
	Found SO_4^{2-} mg	Relative error, %	Found SO_4^{2-} mg	Relative error, %
3.74	3.51	-6.1	3.55	-4.3
2.34	2.22	-5.1	2.28	-2.6
1.87	1.80	-3.7	1.84	-1.6
0.94	0.92	-2.1	0.93	-1.1
0.75	0.73	-2.7	0.75	0
0.47	0.48	+2.1	0.49	+4.3
0.37	0.40	+8.1	0.41	+10.8

Described method is not convinient for serial analysis due to high alcohol consumption. The colour change at the titration end point is also indistinct and its observation needs some practice.

3. Direct titrimetric determination of sulphates with sulphonazo III

The last investigated method of SO_4^{2-} determination was direct titration in the presence of another indicator namely sulphonazo III. In pure salts solutions the effect of titration conditions on the obtained results was checked. It was observed that the distinct change of indicator colour (from violet to blue) occurs in water+*n*-propanol solution in pH range 3–5.5. Below pH 3 the colour change is indistinct whereas above pH 5 the reaction is slow what can cause the positive error. The optimum pH ranges from 4 to 5.

The advantageous effect of propanol on solubility of barium sulphate was observed and water+alcohol ratio 1+1 was found to be optimum.

For checking reproducibility of results two series of titration were performed. In titration of sulphates in model solutions containing 1.44 and 3.61 mg SO_4^{2-} respectively the following results were obtained: 1.47 and 3.61 mg with relative standard deviation 0.14% and 0.23% respectively (n=8). This indicates satisfactory reproducibility. The colour reaction of sulphonazo III with barium ions is not specific. Direct titrimetric determination of sulphates requires the preliminary separation of cations. It was carried out using Dowex 50W cation exchanger and the procedure was the same as described in part 2. 10 ml samples of the eluate were adjusted to pH 4.6–4.8 with dilute ammonia and 10 ml of propanol as well as 2 drops of sulphonazo III were added. Solutions were titrated with standard barium perchlorate up to colour change from violet to blue.

Results obtained when analyzing the solutions containing of 0.72 and 1.44 mg SO_4^{2-} respectively (such amounts were expected in natural waters) were 0.72 and 1.45 mg with relative standard deviation of 0.60% and 0.95% respectively (n=7). These results were very close to those obtained by direct titration.

As in natural waters various anions may occur at different concentrations, the effect of Cl^-, CO_3^{2-}, $S_2O_3^{2-}$, Br^- and F^- (in amounts expected in water) on the results of sulphates determination was checked. No significant influence was observed.

The method was applied for the determination of sulphates in synthetic waste prepared for interlaboratory studies by Department of Analytical Chemistry, Technical University of Cracow. The obtained result was 254.9 mg l^{-1} (256.9, 254.8, 255.4, 255.4, 254.6, 252.6) and it is in good agreement with the value given by the organizers 250.0 mg l^{-1}.

Direct titration using as indicator sulphonazo III was also applied for determination of sulphates in different water samples: tap water, spring water, water from Vistula river and mineral water "Jan". The preliminary step for all samples included passing them through the ion exchanger column. Results are presented in Table 3.

Table 3. Results of sulphates (mg l^{-1}) determination in water samples

Sample	*n*	Found	St. dev.
Tap water	8	120.6	1.1
	8	119.0	0.4
	6	113.5	0.8
Spring water	7	39.7	0.5
Vistula river	7	91.3	0.3
	6	93.4	0.5
Mineral water "Jan"	5	55.8	1.9

DISCUSSION OF RESULTS AND CONCLUSIONS

The indirect procedure for sulphates determination according to Polish Standards is labour- and time-consuming and depends on several significant parameters. The precision of obtained results is poor – it is mentioned that their dispersion can reach even 20% [4]. Accuracy is also not good and the results of determination of SO_4^{2-} ions may show high negative errors. This procedure can be improved, as it was mentioned in part 1, but still has many disadvantages.

Basing on investigations carried out in pure salt solutions it was found that better results can be reached by direct titration with barium perchlorate in the presence of such indicators as: thorin, mixed indicator (thorin+methyl blue) and sulphonazo III. It is worth to mention that in these methods preliminary separation of cations on the ion exchanger is indispensable.

Comparing direct methods of sulphates determination one should state that the colour change for thorin and mixed indicator is not very distinct and needs some practice. The disadvantage of this procedure is the necessity of using large excess of propanol (1+4).

The final conclusion is that the best and recommended procedure consists in direct titration with barium perchlorate in the presence of sulphonazo III. The amount of added organic solvent is smaller (1+1), the colour change is distinct and in consequence the results are more accurate and precise. This method was checked in interlaboratory studies. Comparison of results obtained by chosen direct method and Polish Standards method is presented in Table 4.

Table 4. Results of SO_4^{2-} determination (mg l^{-1}) by: 1) direct titration in the presence of sulphonazo III; 2) Polish Standard (without improvements) in natural samples (*n*=3)

Sample	Method (1)		Method (2)		Diff. %
	x	x	x	x	
Tap water	113.0	113.3	97.0	91.0	-19.2
	113.5		95.0		
	113.5		81.0		

Deep well water	68.7	68.4	58.2	57.4	-16.1
	68.2		57.0		
	68.2		57.0		
Well water I	206.1	206.1	165.0	161.3	-21.7
	206.1		159.0		
	206.1		160.0		
Well water II	209.3	209.5	165.0	151.3	-27.8
	209.8		146.0		
	209.3		143.0		
Vistula river	105.7	105.6	91.0	90.0	-14.8
	105.3		88.0		
	105.7		91.0		

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