*Polish Journal of Chemical Technology, 9, **1,** 33 — 35, 2007, 10.2478/v10026-007-0009-8*

A quick method to determine the content of sulfates in silicic and aluminosilicate fillers

Barbara Sołtysik

Institute of Inorganic Chemistry, ul. Sowinskiego 11., 44-101 Gliwice, Poland, phone: +48 32 231 30 51, fax: +48 32 231 75 23, e-mail: basiasol@poczta.onet.pl

The paper presents the possibility of using barium-selective electrode to a potentiometric determination of sulfates in silicic and aluminosilicate fillers. The results of sulfates potentiometric titration in silicic and aluminosilicate fillers are described. A statistical interpretation of the results was carried out. The recommended method is based on the end-point detection of sulfates potentiometric titration in hydro-alcoholic medium by means of barium chlorate(VII) titrant. The potentiometric titration, which uses an ion-selective electrode as the indicator for the end-point was applied as the analytical technique. The parameter ranges for accurate sulfates determination in model solutions and the method of samples' preparation for analysis were investigated.

Keywords: sulfates, potentiometric titration, silicic fillers, aluminosilicate fillers.

INTRODUCTION

In case of both silicic fillers and fuller's the earth presence of sulfates results in lowering the quality of products. That is why a prompt assessment of sulfates' content is particularly essential[1, 2]. The current – a recommended gravimetric method – is time-consuming, whereas an application of classical titration method leads to some discrepancies (an error resulting from a subjective localization of the end-point of titration). Ion-selective electrodes give a possibility of a more objective determination of the end-point of titration in comparison with the visual method (end-point of sediment emergence, change of colour). The electrodes also give the possibility of a more exact determination (analytical error < 0.5%) which is comparable with the gravimetric method[3].

Useful numerous hints concerning the application of such electrodes in sulfates' titrimetric analysis of industrial products, as well as information concerning their membrane synthesis, are presented in the articles by Läubli et al[4] and Gaujali et al[5]. Lead or barium ion-selective electrodes are mainly used in the process of potentiometric titration of sulfates. A detailed characteristic of barium electrodes (membranes content, selectivity coefficients, work conditions, etc.) is presented in the review by Umezawa et al[6].

All the chemical reactions used in the potentiometric analysis should fulfill the following requirements: they must be performed promptly and in a stoichiometric manner, only in a specified direction, possible to the total conversion. In order to fulfill the above, only substances which present a possibly lowest solubility product should be considered. Also, the reactions should have an individual ion-selective electrode[7]. Theoretically, the analytical error below 0.1% should emerge in the outcome after the fulfillment of the above specified requirements. However, it is not possible to fulfill all of these conditions in reality due to the unsatisfactory selectivity of measurement electrodes and a simultaneous action of disturbing ions in the process of potentiometric titration.

The choice of a proper type of electrode can be suppressed not only by the presence of ions disturbing the process. The choice also depends on the expected range of concentration. This problem can only be solved by means of a proper preparation of the samples used for the analysis[8].

The work focused on the elaboration of an appropriate, fast and – simultaneously – a precise method of determining the concentration of sulfates in Arsil-type silicic and aluminosilicate fillers using barium ion-selective electrodes. The recommended method is based on the end-point detection of potentiometric titration (with barium chlorate (VII) titrant) in the samples after the extraction of sulfates. In this method, the ion-selective electrode works as the end-point marker of titration. Due to numerous benefits of this method, such as its simplicity and accuracy, and possibility of obtaining results in a short period of time, it is especially recommended in an internal control of silicic fillers and fuller's earth production, as well as in the control of end products of the above technologies.

EXPERIMENTAL

Apparatus

Ion-meter (720 A ORION) with a barium-selective electrode (manufactured by „DETEKTOR"), and Ag/AgCl reference electrode (manufactured by „DETEKTOR"), and a magnetic stirrer were used for the investigations. Figure 1 shows a scheme of the apparatus used for potentiometric titration of sulfates.

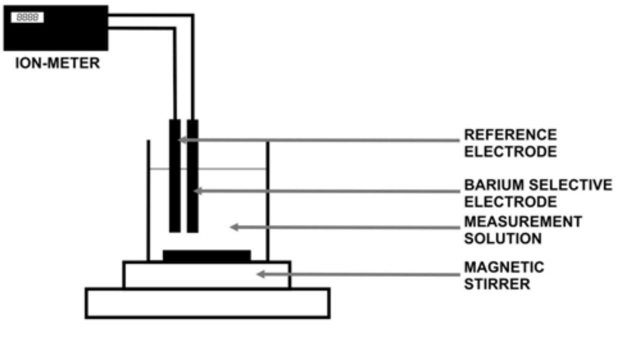

Figure 1. The potentiometric titration of sulfates' system

Reagents and solutions

Stock solution of sodium sulfate and model solutions: Na^+, K^+, Ca^{2+}, Fe^{3+}, Al^{3+}, PO_4^{3-}preparated according to Polish Standards (PN-81/C-06503). *Chemical analysis. Preparation of solution for calorimetry and nephelometry.*

ISA-buffer – magnesium 6-hydrat chloride; 0.1 mol/dm^3 solution.

Acides: hydrochloric acid, concentrated, and 6% solution; nitric acid, concentrated; hydrofluoric acid, concentrated; sulphuric acid, 33% solution.

Ammonia, 12,5% solution. Sodium hydroxide; 10% solution. Barium chlorate(VII); 0.1 mol/dm^3 standardized gravimetrically. 2-propanol.

All the reagents were analytically-reagent graded.

Distilled water was used for the preparation of all the solutions.

Potentiometric titration for model sulfates solutions

To begin with, the accuracy of barium ion-selective electrode was examined. As a result, it was stated that in the range of barium concentration $10^{-5} \div 10^{-1}$ mol/dm^3 (sulfates $10^{-4} \div 10^0$ mol/dm^3) the signal of the electrode changed approximately 28 ± 2 mV/decade of barium ions concentration (sulfates). It meant that the electrode worked in accordance with Nernst equation, which meant that it worked properly. Magnesium chloride was used as an ISA buffer.

The model analysis of potentiometric titrimetry of sulfates was conducted in the basic hydro-alcoholic solution of sodium sulfate. Barium chlorate(VII) titrant was used – a solution of 0.1 mol/dm^3 in 35% 2-propanol. The performance of titration in water solutions was not successful, either. All the attempts at sulfates' precipitation were performed in the 3.0 ÷ 3.5 pH range.

A potentiometric titration of model sulfate solution was performed, as well as the titration in the medium composed of the following ions: Na^+, K^+, Ca^{2+}, Fe^{3+}, Al^{3+} (the matrix content of the primary sample) and PO_4^{3-}. They were introduced in molar ratio of 1:1 in relation to the designed component. The „disturbing" influence of phosphates was eliminated since they were removed from the tested solution by precipitation with magnesium carbonate. The results of this experiment are presented in Table 1.

Table 1. The results of sulfates' determination in model solutions using potentiometric titration

Model solutions	Assumed SO_4^{2-} mg	Detected SO_4^{2-} mg	Relative error, %
SO_4^{2-}	20.00	19.98	-0.10
SO_4^{2-}, Na^+	20.00	19.97	-0.15
SO_4^{2-}, K^+	20.00	19.97	-0.15
SO_4^{2-}, Ca^{2+}	20.00	19.98	-0.10
SO_4^{2-}, Fe^{3+}	20.00	19.95	-0.25
SO_4^{2-}, Fe^{3+}, Al^{3+}	20.00	19.92	-0.40
SO_4^{2-}, Fe^{3+}, Al^{3+}, PO_4^{3-}	20.00	21.93	+9.65
SO_4^{2-}, Fe^{3+}, Al^{3+}, PO_4^{3-} (precip.)	20.00	20.64	+3.20

Potentiometric titration for sulfates in silicic and aluminosilicate fillers

On the basis of the research performed on the model solutions, the samples of real silicic fillers and fuller's earth were prepared for the analysis of sulfates' content.

In case of Arsil-type fillers two methods were chosen:

- to remove silica (in nitric and hydrofluoric acid medium), and next to dissolve the remains in hydrochloric acid.
- to extract sulfates to water without the removal of silica.

For fuller's earth, two methods were taken into account:

- the extraction of analyte to the solution of hydrochloric acid with the separation of trivalent cations with ammonia.
- the extraction of analyte to the solution of hydrochloric acid without of the removal of trivalent cations.

In the analyte samples prepared in this way, pH was adjusted to 3.0 ÷ 3.5 and potentiometric titriation was performed in hydro-alcoholic medium with 0.1 mol/dm^3 barium chlorate(VII) solution. On the basis of titrametric results, the curves of titration were drawn and the end-point was determined graphically. Next, the content of $X_{SO_4^{2-}}$ sulfates was calculated using the following equation (percentage):

$$X_{SO_4^{2-}} = \frac{V_{PK} * c_t * M * 100}{1000 * n}$$

VPK – volume of titrant in the end-point for titration, cm^3;
c_t – concentration of titrant, mol/dm^3;
M – molecular mass of 1 mole SO_4^{2-};
n – weighed portion of silicic/aluminosilicate filler sample, g.

The analysis of sulfates using the gravimetrical method was performed for comparison purposes and the relative error was determined in relation to both results. The statistical interpretation of results was also performed. Due to the number of analyzed samples (the content of sulfates was determined 10 times), the t-Student distribution was selected. The analytically determined results (relative errors and relative standard deviations) are presented in Table 2 and Table 3.

DISCUSSION

Consequently, it can be stated that the ion-selective barium electrode works in accordance with Nernst's law in the concentration ranges of: barium $10^{-5} \div 10^{-1}$ mol/dm^3 and sulfates $10^{-4} \div 10^0$ mol/dm^3. The electrode is selective in sodium, potassium and lime cation medium. Trivalent cations, especially aluminum, slightly influence its potential. The electrode is not selective in phosphate medium, because it is co-precipitated with the analyzed sulfates.

Potentiometric titrametry of sulfates is conducted in the optimal medium at the range of pH 3.0 ÷ 3.5 with 2-propanol (35%) added to the analytical solution. Barium chlorate(VII) titrant was also used. Potentiometric titrametry of sulfates in the optimal analytical conditions is possible with 0.1% accuracy.

The preparation of samples of silicic and aluminosilicates fillers for potentiometric sulfates analysis was based on the analytical extraction performed by means of hydrochloric acid and it did not involve arduous silica removal in the hydrofluoric acid medium. It also did not involve the separation of trivalent cations.

The content of sulfates in the silicic and aluminosilicate fillers can be determined precisely using potentiometric

Table 2. A comparison of the potentiometric titration method with the gravimetric method in silicic fillers (* = relative error for potentiometric titration 1; ** = relative error for potentiometric titration 2)

Method	Silicic filler			
	1	2	3	4
	Sulfates content, % mass.			
Potentiometric titration with silica removal (1)	1.35÷1.38 $\bar{x}$ = 1.37	3.19÷3.20 $\bar{x}$ = 3.19	2.39÷2.40 $\bar{x}$ = 2.39	1.18÷1.21 $\bar{x}$ = 1.20
Potentiometric titration without silica removal (2)	1.37÷1.38 $\bar{x}$ = 1.38	3.19÷3.20 $\bar{x}$ = 3.20	2.36÷2.39 $\bar{x}$ = 2.38	1.20÷1.21 $\bar{x}$ = 1.21
Gravimetric method	1.38	3.20	2.39	1.21
Relative error referred to gravimetric method, %	-0.72 * 0.00 **	-0.31 * 0.00 **	0.00 * -0.42 **	-0.83 * 0.00 **
Relative standard deviation	0.0117 * 0.0051 **	0.0043 * 0.0022 **	0.0029 * 0.0067 **	0.0133 * 0.0059 **

Table 3. Comparison of the potentiometric titration method with the gravimetric method in aluminosilicate fillers (* – relative error of potentiometric titration without Fe^{3+} and Al^{3+} cations elimination)

Method	Aluminosilicate filler I	Aluminosilicate filler II
	Sulfates content, % mass.	
Potentiometric titration	0.225÷0.236 $\bar{x}$ = 0.231	0.241÷0.252 $\bar{x}$ = 0.248
Potentiometric titration without Fe^{3+} and Al^{3+} cations elimination	0.231÷0.238 $\bar{x}$ = 0.234	0.247÷0.255 $\bar{x}$ = 0.251
Gravimetric method	0.232	0.249
Relative error referred to gravimetric method, %	-0.431 +0.862 *	-0.402 +0.803 *
Relative standard deviation	0.016 0.010 *	0.013 0.012 *

titration after non-complicated preparation of samples. The accuracy of this method is comparable with the conventional, gravimetrical one.

CONCLUSIONS

As a result of the tests it was stated, that barium ion-selective electrode used for the purpose of potentiometric analysis of sulfates content in silicic and aluminosilicate fillers proved to be useful. This method of determining the sulfates' content was developed on the basis of the tests performed in the Institute of Inorganic Chemistry in Gliwice. The method allows to carry out a quick, accurate, and simple (and therefore convenient) determination of the of content sulfates. It can speed up analytical controls in technologies requiring frequent analyses of the content of sulfates.

LITERATURE CITED

(1) Gallus-Olender J.: Oznaczanie zawartości siarczanów w napełniaczu krzemionkowym Arsil; Instrukcja analityczna IChN w Gliwicach.

(2) Stechman M., Różycka D., Mateńko H., Legutko M.: Badania nad modyfikacją technologii otrzymywania ziemi bielącej, Sprawozdanie IChN nr 4122/1997 w Gliwicach, niepublikowane, Gliwice **1997**.

(3) Camman K.: Zastosowanie elektrod jonoselektywnych, Wydawnictwo Naukowo; Techniczne Warszawa **1977**.

(4) Läubli M. W., Dinten O., Pretsch E., Simon W., Vögtle F., Bongardt F., Kleiner T.: Anal. Chem., **1985**, 57, 2756.

(5) Gaujali M. R., Mizani F., Prirelahi H.: Canadian Journal of Analitycal Sciences and Spectroscopy, **2002**, 47, 157.

(6) Umezawa Y., Bühlmann P., Umezawa K., Tohda K., Amemiya S.: Pure Appl. Chem., 2000, 72, **2022**.

(7) Lalikow J. S.: Fizykochemiczne metody analizy, Państwowe Wydawnictwa Techniczne Warszawa **1956**.

(8) Williams W. J.: Oznaczanie anionów, Państwowe Wydawnictwo Naukowe Warszawa **1985**.