

DETERMINATION OF SULPHIDE BY POTENTIOMETRIC TITRATION

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abstract: Sulphide anion was determined indirectly, by potentiometric titration. For this purpose, a known concentration of Ce^{4+} and sulphide ions was added into the electrochemical cell. Ce^{4+} remained in the cell after his reduction by the sulphide ions was titrated with a Fe^{2+} solution having a known concentration. The difference between total Ce^{4+} and the titrated Ce^{4+} corresponds to the amount of Ce^{4+} reduced by the sulphide ion. The proposed method is reproducible, fast and allows the determination of sulphide ion in waters.

keywords: sulphide, potentiometric determination

Introduction

The sulphide ion is found in various waters and often arises the problem of quantitative analysis. Regarding the methods used in the analysis of the sulphide from waters can be applied well-known techniques in analytical chemistry, depending on the variable amount of sulphide. For this purpose classical and instrumental methods of analysis can be used.

The sulphide determination can be made using volumetric methods [1], spectrophotometric methods [2-7] and electrometric methods [9-13]. Among all electrometric methods those frequently used are direct or indirect potentiometric methods.

In this paper indirect determination of sulphide ion was achieved by potentiometric titration.

Experimental

Apparatus and reagents

For measuring the electromotive tension an electrochemical cell was used containing a platinum electrode as indicator electrode and a calomel-saturated electrode as the reference electrode. The electrochemical cell was connected to a pH-meter/millivoltmeter MV-84 Clahmann - Grahnet. The solution was stirred with a magnetic stirrer.

For the determinations the following solutions were used:

- $10^{-1}N$ $Ce(SO_4)_2$ solution in $10^{-1}N$ H_2SO_4 , provided by Merck;

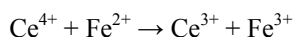
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- 10^{-2} N Na_2S solution in 10^{-1} N H_2SO_4 , provided by Merck;
- 10^{-1} N $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ solution, provided by Merck.

All reagents used in our studies were of analytical purity. The solutions were obtained in bidistilled water.

Results and Discussion

Potentiometric determinations were made in an electrochemical cell containing a platinum electrode and a calomel-saturated electrode. The Ce^{4+} solution was titrated with a Fe^{2+} solution. The reaction that takes place is:



In the electrochemical cell were also added S^{2-} ions. After the reduction of one part of the initial amount of Ce^{4+} , the Ce^{4+} remained was titrated with Fe^{2+} .

From the titration curve the equivalence volume was calculated. Knowing the Ce^{4+} initial concentration, the amount of Ce used to oxidize S^{2-} ions can be calculated by difference and the sulphide amount present in solution can be implicitly calculated.

In order to verify of the Ce^{4+} solution's titre, 5 ml 10^{-1} N Ce^{4+} solution was titrated with 10^{-1} N Fe^{2+} solution. In the titration cell was also added 20 ml 10^{-1} N H_2SO_4 solution. The titration curve is presented in the Fig. 1.

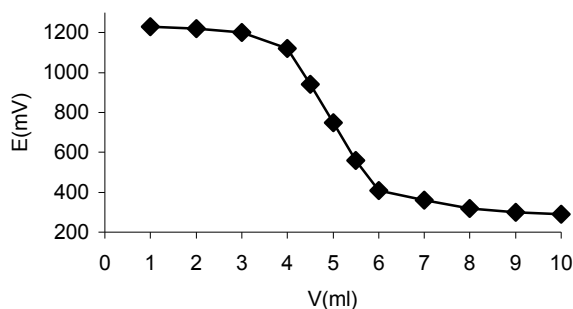


Fig. 1: Potentiometric titration curve of Ce^{4+} with Fe^{2+} ($c_{\text{Ce}^{4+}} = 10^{-1}$ N; $c_{\text{Fe}^{2+}} = 10^{-1}$ N).

From this figure 5 ml equivalence volume was obtained.

a) The time influence

The time influence on Ce^{4+} reduction by S^{2-} was studied. For this purpose, 5 ml 10^{-1} N Ce^{4+} solution, 10 ml 10^{-2} N S^{2-} solution and 10 ml 10^{-1} N H_2SO_4 solution were added into the electrochemical cell. From the potentiometric titration curves presented in Fig. 2, Fig. 3, Fig. 4 and Fig. 5 the equivalence volumes were determined at 10 minutes, 20 minutes, 25 minutes, 30 minutes after adding S^{2-} solution into the electrochemical cell.

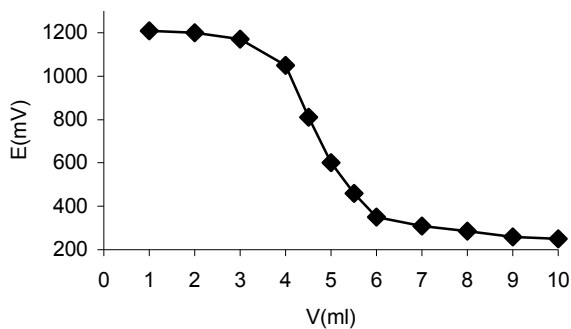


Fig. 2: Potentiometric titration curve of Ce^{4+} and S^{2-} with $10^{-1}N Fe^{2+}$ solution at 10 minutes after adding S^{2-} ($V_c=4.75$ ml)

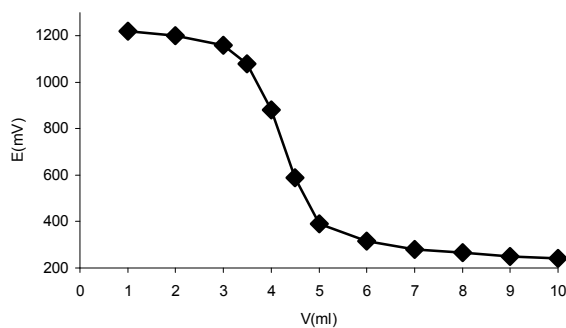


Fig. 3: Potentiometric titration curve of Ce^{4+} and S^{2-} with $10^{-1}N Fe^{2+}$ solution at 20 minutes after adding S^{2-} ($V_c=4.125$ ml)

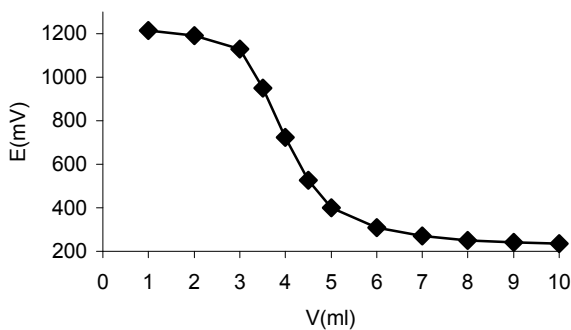


Fig. 4: Potentiometric titration curve of Ce^{4+} and S^{2-} with $10^{-1}N Fe^{2+}$ solution at 25 minutes after adding S^{2-} ($V_c=4$ ml)

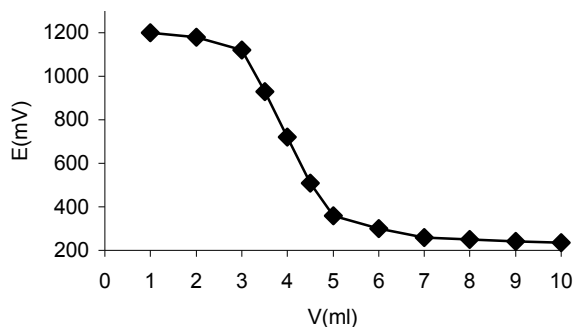
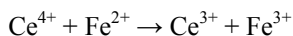
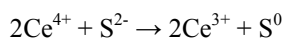


Fig. 5: Potentiometric titration curve of Ce^{4+} and S^{2-} with $10^{-1}N Fe^{2+}$ solution at 30 minutes after adding S^{2-} ($V_e=4$ ml)

The reactions that take place are:



In Fig. 6 the equivalence volume is graphically represented as a function of time.

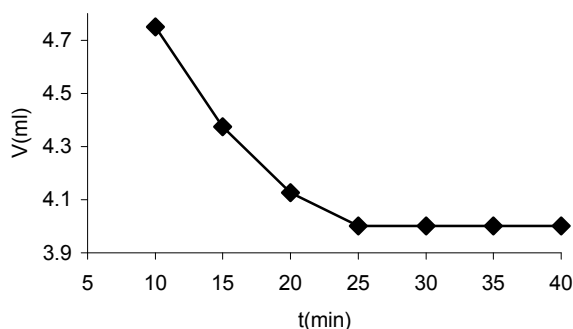


Fig. 6: Graphic representation of equivalence volume as a function of time

From this figure a constant equivalence volume (4 ml) is observed at 25 minutes after adding $10^{-2}N S^{2-}$ solution. In the following determinations 30 minutes were allowed to pass before the titrations were done.

b) The influence of sulphide concentration

5 ml $10^{-1}N Ce^{4+}$ solution, $10^{-1}N H_2SO_4$ solution and variable amounts of $10^{-2}N S^{2-}$ solution (10 ml; 5 ml; 2.5 ml; 1 ml) were introduced into the electrochemical cell. The final volume in the cell was 25 ml ($10^{-1}N H_2SO_4$ solution was added).

The variation of equivalence volume with the S^{2-} added amount was followed.

All titration were made at 30 minutes after adding S^{2-} solution.

In Table 1 the equivalence volumes obtained for variable amounts of 10^{-2}N S^{2-} solution are presented.

Table 1. The equivalence volumes (ml) of 10^{-1}N Fe^{2+} obtained at the titration of variable amounts of S^{2-}

10^{-2}N S^{2-} volume (ml)	10	5	2.5	1
10^{-1}N Fe^{2+} equivalence volume (ml)	4	4.5	4.75	4.9
S^{2-} concentration	$4 \cdot 10^{-3}\text{N}$	$2 \cdot 10^{-3}\text{N}$	$1 \cdot 10^{-3}\text{N}$	$4 \cdot 10^{-4}\text{N}$

From this study is ascertain that, using the proposed method, S^{2-} concentrations higher than $4 \cdot 10^{-4}\text{N}$ can be determined.

Conclusions

In this work the experimental conditions for potentiometric determination of sulphide anion were established. An indirect method of sulphide anion determination was used. Known concentrations of Ce^{4+} and S^{2-} were added into the electrochemical cell. The Ce^{4+} was titrated with a Fe^{2+} solution with known concentration. The difference between total Ce^{4+} and the resulted Ce^{4+} at the titration corresponds to the amount of Ce^{4+} reduced by S^{2-} .

It was observed that the titration can be done at 25-30 minutes after adding S^{2-} to the Ce^{4+} solution.

This method can be used for determination of S^{2-} concentrations higher than $4 \cdot 10^{-4}\text{N}$. The method is reproducible, fast and allows the determination of sulphide ion in waters.

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