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DETERMINATION OF MINERAL ACIDS CONCENTRATION FROM MIXTURES BY CONDUTOMETRIC TITRATION

BY

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Abstract. In this study, a conductometric titration method is proposed for the quantitative determination of two mineral acids (HCl and H_3PO_4), both individually and from mixture. Conductometric titration assumes the experimental measuring of electrical conductivity of the analyzed solution as a function of added titrant volume, and depends by the concentration of all ions present in this solution. A solution of $AgNO_3$ (0.1 N) was used as titrant. Both mineral acids react with $AgNO_3$ and form low soluble compounds (AgCl and Ag_2HPO_4), and these reactions are the basis of their determination by conductometric titration. If, HCl can be analyzed in this way with high accuracy, regardless of whether is in mixture or not, the determination of H_3PO_4 acid is more difficult due to the high solubility of Ag_2HPO_4 precipitate. Thus, the neutralization of H_3PO_4 acid with NaOH (0.1 N) solution before to start the conductometric measurements is necessary, for that his quantitative determination to be possible. Therefore, the conductometric titration with $AgNO_3$ can be used for the determination of HCl and H_3PO_4, both individually and from mixtures, but this is possible only after neutralization of the mineral acids with a strong base solution.

Keywords: mineral acids; mixtures; condutometric titration; $AgNO_3$ titrant; aqueous solution.

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1. Introduction

Mineral acids have various utilizations in many industrial activities. The manufacturing of fertilizers, explosives and plastics, or as pickling agents in electroplating processes is only few examples where mineral acids, such as HCl and H_3PO_4 are used both individually and in mixtures, in industrial activities (Bernardes *et al.*, 2004; Gutberlet *et al.*, 2015; Lee *et al.*, 2015). From this reason, the finding of simple and accurate method for the determination of such mineral acids concentration is still considered important for the monitoring of industrial processes.

According with their definition, mineral acids are strong inorganic acids that are complete dissociated in aqueous solution (Liteanu and Hopîrtean, 1972). In consequence, in aqueous solution the concentration of mineral acids is equal with the concentration of protons ($c_{HX} = c_{H^+}$), and on this relation is based the determination of mineral acids through acido-basic titration methods (Sârghie *et al.*, 2005; Bejan *et al.*, 2006). The acido-basic titration methods, both in classical and instrumental version, suppose the titration of mineral acids solution with the solution of strong bases (frequently being used NaOH solution), until at equivalence. Even if this method permit the determination of most mineral acids with high accuracy, is useless when it is necessary the determination of mineral acids from mixtures. This because by titration with strong bases solutions it is determined the total acidity of analyzed samples, without being able to differentiate the mineral acids present in the mixture.

In order to solve this drawback, various instrumental methods (such as potentiometric (Driver and Perdue, 2015; Sfaelou *et al.*, 2015), spectrophotometric (Li and Dong, 2004; Rocha *et al.*, 2013), chromatographic (Onal *et al.*, 2013), etc.) have been developed based on the quantitative determination of the anions from the structure of mineral acids. Unfortunately, most of such methods are expensive, require long work time and laborious experimental protocols.

Conductometry is an instrumental method of analysis which supposes the experimental measurement of electrical conductivity of analyzed solution (Dăneţ, 1996). This parameter depends by the concentration of all kinds of ions present in solution, and therefore the measurement of electrical conductivity of solutions is commonly used in laboratories for to assume the ions content of analyzed samples (Prenesti *et al.*, 2004). However, direct conductometric analysis has limited applications due to its non-selectivity (Christian, 1994), and from this reason in the conductometric titration is preferred in most of cases.

In case of mineral acids, the utilization of conductometric titration for their analysis suppose the addition of small volumes of a strong base solution (most frequently used is 0.1 N NaOH solution), and the equivalence point is obtained graphically from titration curves. Unfortunately, when mineral acids are in the mixture, the utilization of NaOH solution for conductometric titration will permit the determination of total acidity of analyzed solution, without to be possible the individual determination of each mineral acid. In order to solve this problem other titrant must be found, so that the selectivity of conductometric titration in the analysis of such samples to be significantly improved.

In this study, a solution of $AgNO_3$ (0.1 N) was used as titrant for the determination of HCl and H_3PO_4 mineral acids by condutometric titration. Both mineral acids react with $AgNO_3$ and form low soluble compounds (AgCl and Ag_2HPO_4), and these reactions are the basis of their determination. Both mineral acids can be analyzed in this way with high accuracy, but only after their neutralization.

2. Experimental

2.1. Materials

The chemical reagents: HCl, H_3PO_4, NaOH and $AgNO_3$ were analytical grade and were used without purification. Distilled water, obtained from a commercial distillation system, was used for the preparation and dilution of all solutions required in the experiments. 0.1 N HCl solution was obtained by measuring a exact volume of 36% HCl solution, and diluting to 1000 mL with distilled water. 0.1 N H_3PO_4 solution was prepared similarly using a 40% H_3PO_4 solution. NaOH and $AgNO_3$ solutions was obtained by weighing a know quantity of solid reagent, dissolving and dilution to 1000 mL with distilled water. All the obtained solutions were then standardized, according with well known procedures (Sârghie *et al.*, 2005), in order to determine their exact concentration.

The conductometric measurements were performed with a pH/ion meter MM 347 type, equipped with a combined glass electrode (for pH measurements) and a conductometric bell cell (cell constant 1.50 cm^{-1}). A 150 mL Berzelius glass was used as conductometric cell and a 10 mL burette (with 0.1 mL divisions) was used for titrant addition. All the experiments were performed at room temperature (20 ± 1°C).

2.2. Methods

Volumes between 1.0 and 3.0 mL of HCl and H_3PO_4 (0.1 N) were measured and transferred into Berzelius glass, and directly diluted with distilled water until about 100 mL. In experiments were the neutralization is necessary, before to start the titration 0.1N NaOH solution was added until the required pH value was obtained. Portions of 0.5 mL of 0.1 N $AgNO_3$ solution was added from burette. After each addition of $AgNO_3$, the solution was homogenized and the electrical conductibility was measured. The conductometric experiments were stopped only after at least five values after equivalence point were recorded. The exact equivalence volume was obtained from conductometric titration curves, and the mineral acids concentration was calculated using equivalence law.

3. Results and Discussions

According with the theory, in conductometric titration can be used any kind of chemical reaction, such as: acid-base, complexation or precipitation (Ye *et al.*, 2015; Garcia and Schultz, 2016), with the condition that during of titration, significant changes of solution conductibility to take place. From this reason, in case of HCl and H_3PO_4 determination, $AgNO_3$ was chosen as titrant. In presence of $AgNO_3$ both mineral acids form low soluble compounds, and the difference of solubility between these makes that the decrease of conductibility to be different, which makes it possible their determination in mixtures.

3.1. Conductometric Titration of HCl and H_3PO_4 without Neutralization

The determination of HCl by conductometric titration with $AgNO_3$ is based on the reaction:

$$(H^+ + Cl^-) + (Ag^+ + NO_3^-) \rightarrow AgCl\downarrow + (H^+ + NO_3^-) \qquad (1)$$

and the conductometric titration curve obtained experimentally is presented in Fig. 1.

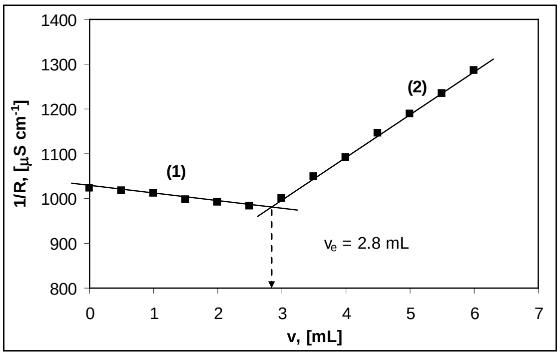

Fig. 1 − Conductometric titration curve of HCl with $AgNO_3$.

As can be seen from Fig. 1, the conductometric titration curve, obtained by plotting electrical conductibility as a function of volume of $AgNO_3$ added to the analyzed solution is formed from two linear portions, with different slopes. The first line segment (1) describes the behaviour of titration system until equivalence, where the electrical conductibility of solution slowly decreases due to the formation of low dissociated AgCl precipitate. The second line segment (2) indicates the behaviour of titration system after equivalence, when the electrical conductibility of solution increase proportional with $AgNO_3$ solution added in excess. The AgNO3 volume at equivalence point is obtained from the intersection of the two linear portions, and this value is used for the determination of HCl concentration, according with the usual analytical calculation procedures (Bulgariu, 2010).

In case of H_3PO_4, the titration reaction can be written as:

$$(2H^+ + HPO_4^{2-}) + 2\,(Ag^+ + NO_3^-) \rightarrow Ag_2HPO_4\downarrow + 2\,(H^+ + NO_3^-) \qquad (2)$$

and the obtained conductometric titration curve is illustrated in Fig. 2.

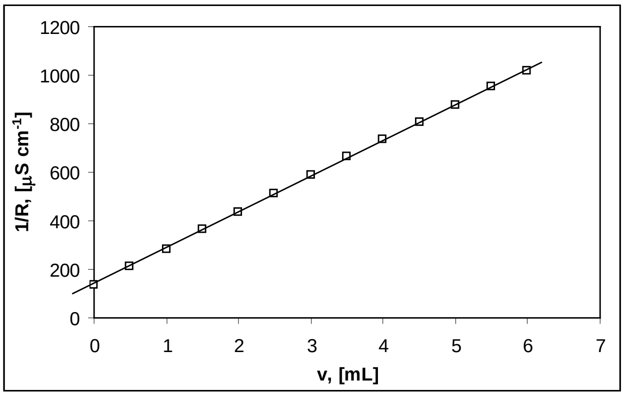

Fig. 2 − Conductometric titration curve of H_3PO_4 with $AgNO_3$.

It can be observed from Fig. 2 that in case of H_3PO_4 titration with $AgNO_3$, the electrical conductibility of analyzed solution linearly increases with the increasing of volume of titrant. Under conditions the determination of H_3PO_4 it is not possible, because the equivalence point can be established.

This behaviour can be explained as follow: during of titration on relatively low decrease of solution electrical conductibility due to the precipitation of Ag_2HPO_4 is overlapping the high concentration of H^+. The protons have the highest equivalent conductibility, compared with the other ions from solution (Dean, 1995), and therefore their presence make that the small variation of electrical conductibility due to the precipitation of Ag_2HP_4 it can not be observed.

In order to solve this drawback, the neutralization of protons from solution is required, and this can be done by adding NaOH, before to start the conductometric titration.

3.2. Conductometric Titration of HCl and H_3PO_4 after Neutralization

The minimization of protons contribution to the measured electrical conductibility of analyzed solution can be achieved by their neutralization, and this supposes the adding of strong base solution. In these experiments, a solution of 0.1 N NaOH was used for the neutralization, and the volume of solution required for this must be added before to start the conductometric titration.

The neutralization of HCl suppose his transformation in NaCl, which it is a salt without hydrolysis that has a pH = 7.0. Therefore, in analyzed solution which contains HCl, NaOH was added until the pH value, measured experimentally was 7.0. Then, the solution was conductometric titrated with $AgNO_3$, according with the chemical reaction:

$$(Na^+ + Cl^-) + (Ag^+ + NO_3^-) \rightarrow AgCl\downarrow + (Na^+ + NO_3^-) \qquad (3)$$

and the obtained conductometric titration curve is presented in Fig. 3.

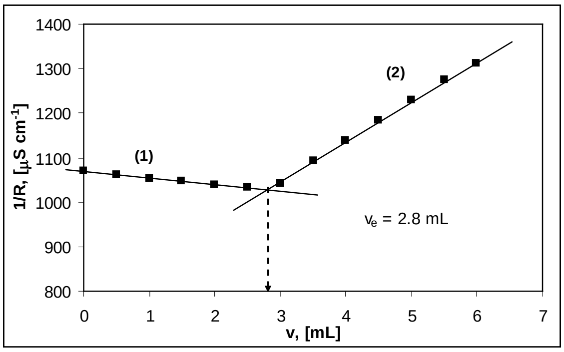

Fig. 3 − Conductometric titration curve of HCl with $AgNO_3$, after neutralization.

As is shown in Fig. 3, after neutralization the shape of conductometric titration curve remains unchanged (Fig. 1). The first line segment (1) indicates the decrease of solution conductibility due to the formation of AgCl precipitate, while the second line segment (2) show the increase of solution conductibility due to the excess of $AgNO_3$ added after equivalence. Therefore we can say that the neutralization does not affect the accuracy of this method, and that HCl can be easily analyzed by conductometric titration, even after this supplementary step. In Table 1 are summarized the experimental results obtained for HCl determination by conductometric titration in absence and in presence of neutralization step.

In case of H_3PO_4, considering the values of dissociation constants, his neutralization occurs until to the formation of Na_2HPO_4, which correspond to a calculate pH value of 8.27.

Table 1
Values of HCl Concentration Obtained by Conductometric Titration

HCl added [mol L^{-1}]	without neutralization		with neutralization	
	HCl found, [mol L^{-1}]	Error, [%]	HCl found, [mol L^{-1}]	Error, [%]
0.1015	0.0983	–3.15	0.1045	2.95
0.2030	0.2095	3.21	0.2068	1.87
0.3045	0.3126	2.66	0.3126	2.66

In consequence, 0.1 N NaOH solution was added to the analyzed solution which contains H_3PO_4, until the measured pH value was close to 8.27, and then the conductometric titration was started, according with the chemical reaction:

$$(2Na^+ + HPO_4^{2-}) + 2\,(Ag^+ + NO_3^-) \rightarrow Ag_2HPO_4\downarrow + 2(Na^+ + NO_3^-) \qquad (4)$$

The conductometric titration curve, recorded under these conditions, is illustrated in Fig. 4. Unlike the conductometric titration curve recorded without the preliminary neutralization of H_3PO_4 (Fig. 2), in this case it can be observed that the conductometric titration curve is composed from two line segments. In the first line segment (1), the electrical conductibility of solution is almost constant due to the formation of low dissociated Ag_2HPO_4 precipitate, while in the second line segment (2), the electrical conductibility of solution increase, proportional with $AgNO_3$ solution added in excess.

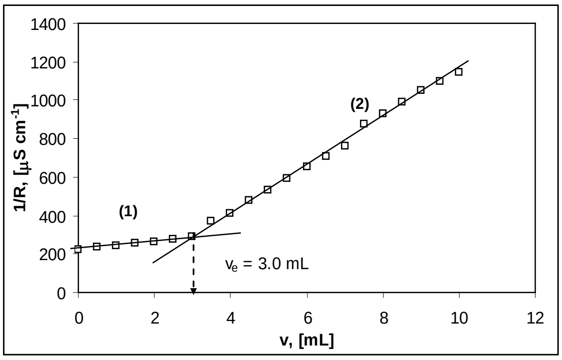

Fig. 4 − Conductometric titration curve of H_3PO_4 with $AgNO_3$, after neutralization.

From the intersection of these two line segments can be determined the volume of titrant at equivalence point, which then is used for the calculation of the H_3PO_4 concentration, in analyzed solution. In Table 2 are presented the experimental results obtained for H_3PO_4 determination by conductometric titration, in absence and in presence of neutralization step.

Table 2

Values of H_3PO_4 Concentration Obtained by Conductometric Titration

H_3PO_4 added [mol L^{-1}]	without neutralization		with neutralization	
	H_3PO_4 found [mol L^{-1}]	Error [%]	H_3PO_4 found [mol L^{-1}]	Error [%]
0.1024	not possible	–	0.1064	3.91
0.2048	not possible	–	0.2095	2.29
0.3072	not possible	–	0.3104	1.04

The results presented in Tables 1 and 2 clearly show that after neutralization, both mineral acids (HCl and H_3PO_4) can be analyzed by conductometric titration, and the errors of determination are lower than the maximum value (5%), imposed by analytical criteria.

3.3. Conductometric Titration of Mineral Acids Mixture

Starting from the experimental observations presented above, for the determination of HCl and H_3PO_4 from mixtures, 3.0 mL of solution which contains both mineral acids (1.5 mL HCl and 2.5 mL H_3PO_4), was transferred into Berzelius glass, diluted with distilled water to about 100 mL and then neutralized with NaOH solution (0.1 N) until the measured pH value was close to 8.27. In this way, it is sure that both mineral acids from mixture were neutralized. After neutralization the solution was conductometric analyzed by titration with 0.1 N $AgNO_3$ solution. The conductometric titration curve obtained by graphical representation of experimental results is presented in Fig. 5.

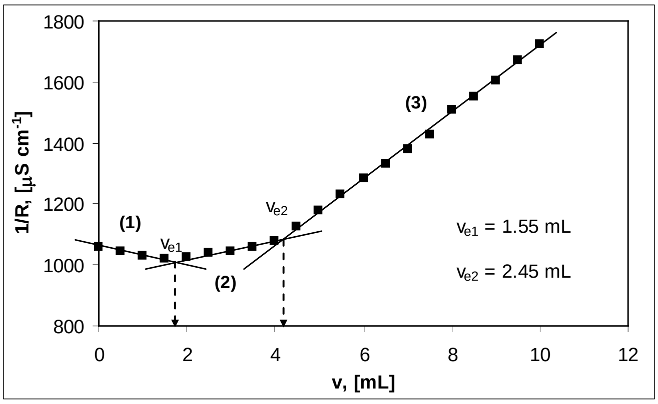

Fig. 5 – Conductometric titration curve of HCl and H_3PO_4 mixture with $AgNO_3$, after neutralization.

As it is expected, when these two mineral acids are in mixture, neutralized HCl will react first with $AgNO_3$ solution (line segment 1), and formation of AgCl precipitate determine a slowly decrease of electrical conductibility. After complete titration of HCl, starts the titration of neutralized H_3PO_4 (line segment 2), when the electrical conductibility remains almost constant due to the formation of Ag_2HPO_4 precipitate. After the second equivalence point, the electrical conductibility linearly increases (line segment 3) due to the excess of $AgNO_3$ added into solution.

The volumes of $AgNO_3$ solution used for the titration of each mineral acid from mixture were obtained graphically, from conductometric titration curve. These values were then used for the calculation of the concentration of the two acids from mixture.

Thus, for the analyzed mixture, which according with the calculation contains 0.1523 mol L^{-1} HCl and 0.2560 mol L^{-1} H_3PO_4, after conductometric titration has been obtained 0.1573 mol L^{-1} HCl and 0.2611 mol L^{-1} H_3PO_4, respectively. This means that the error of analysis was 3.28% in case of HCl and 1.99% in case of H_3PO_4. Therefore, the conductometric titration with $AgNO_3$ can be used for the determination of HCl and H_3PO_4 from mixtures, but this is possible only after neutralization of the mineral acids with a strong base solution.

4. Conclusions

In this study, a conductometric titration method was used for the quantitative determination of two mineral acids, namely: HCl and H_3PO_4, both individually and from mixture. As titrant, a solution of 0.1 N $AgNO_3$ was used. Both mineral acids react with $AgNO_3$ and form low soluble compounds (AgCl and Ag_2HPO_4) and these reactions are the basis of their determination. If in case of HCl, the conductometric titration curve is composed by two line segments and the volume of $AgNO_3$ solution at equivalence can be ease determined, in case of H_3PO_4 the electrical conductibility increase linearly, without that the equivalence point to be visible. In order to solve this drawback, the neutralization of protons from solution is required, and this can be done by adding NaOH, before to start the conductometric titration. After neutralization both mineral acids can be analyzed by conductometric titration with high accuracy. The same procedure can be applied and for the analysis of these two mineral acids from mixture, and in this case the errors of analysis are lower than 3.3%. Therefore, the conductometric titration with $AgNO_3$ can be used for the determination of HCl and H_3PO_4, both individually and from mixtures, but this is possible only after neutralization of the mineral acids with a strong base solution.

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DETERMINAREA CONCENTRAŢIEI ACIZILOR MINERALI DIN AMESTECURI PRIN TITRARE CONDUCTOMETRICĂ

(Rezumat)

În acest studiu, este propusă o metodă de titrare conductometrică pentru determinarea cantitativă a doi acizi minerali (HCl şi H_3PO_4), atât individual cât şi din amestec. Titrarea conductometrică presupune măsurarea experimentală a conductibilităţii electrice a soluţiei de analizat în funcţie de volumul de titrant adăugat, şi depinde de concentraţia tuturor ionilor prezenţi în soluţie. O soluţie de $AgNO_3$ (0,1 N) a fost utilizată ca titrant în aceste experimente. Ambii acizi minerali reacţionează cu $AgNO_3$ şi formează compuşi greu solubili (AgCl and Ag_2HPO_4), iar aceste reacţii stau la baza determinării lor prin titrare conductometrică. Dacă HCl poate fi analizat în acest fel cu acurateţe ridicată, indiferent dacă se găseşte în amestec sau nu, determinarea H_3PO_4 este mai dificilă, datorită solubilităţii ridicate a precipitatului de Ag_2HPO_4. Astfel, este necesară neutralizarea H_3PO_4 cu o soluţie de NaOH (0,1 N), înainte de începerea măsurătorilor conductometrice, pentru ca determinarea cantitativă a acestuia să fie posibilă. Prin urmare, titrarea conductometrică cu $AgNO_3$ poate fi utilizată pentru determinarea HCl şi H_3PO_4, atât individual cât şi din amestec, dar acest lucru este posibil numai după neutralizarea acizilor minerali cu o soluţie de bază tare.