Journal of Applied Sciences

ISSN 1812-5654

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Journal of Applied Sciences 7 (16): 2389-2392, 2007
ISSN 1812-5654

Simple Method for Simultaneous Determination of Carbonate, Sulfite and Hydroxide in Solution

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Abstract: A method is proposed for the simultaneous determination of carbon dioxide and sulphur dioxide in a complex matrices. The method involves salvation of the tow gases in Sodium Hydroxide solution followed by simultaneous determination of the three species (carbonate, sulfite and hydroxide) using conductometric and potentiometric titration. What set this method apart from other determination methods it's simplicity.

Key words: Carbonate, sulfite, hydroxide, conductometry, potentiometry

INTRODUCTION

Acid components such as sulphur oxides (SO_2, SO_3), Carbon oxides (CO_2, CO) and their anion counterparts are very important in environmental pollution, specially in air pollution as well as in water pollution. One of the most popular method used in the analysis of these oxides base on the conversion of them into their anions counterparts.

Thermal analysis was one of the methods used for the characterization many chemical species such as $Zn(SCN)_2.4Zn(OH)_2.0.5\ H_2O$, Within the frame of the research area studied. The gases evolved during the thermal decomposition were absorbed in hydroxide solution and hence the program of analyzing the formed mixture (excess hydroxide, carbonate and sulphite).

The simultaneous determination of acid anhydrides (CO_2, SO_2, NO_2 or Cl_2) using potentiometric, volumetric and conductometric titrations was not mentioned in the literature, although they present sometimes in the same solution. Many existing literature data are concerned only with the separate determination of CO_2 (or $OH^- + CO_3^{2-}$) and SO_2 respectively. But for carbonate the most widely used methods are the volumetric (Maria do Carmo *et al*., 1997) coulometric (Edward and Huffman, 1977) and the potentiometric (Gab and Hulanicki, 1989; Holzinger *et al*., 1997) ones. For sulfite the mentioned technique are the volumetric specially iodometric (Kilroy, 1980) and spectrophotometric (Kass and Ivaska, 2001).

Simultaneous determination of the species mentioned above was mentioned earlier in the literature. Terashima (1978) has reported the rapid simultaneous determination of carbon and sulphur, using infrared absorption detectors. Carbon and sulphur are frequently determined in geological material often by combustion in an induction furnace. Lee (1980) determined sulphur and total carbon simultaneously in samples of geological material by using a Leco induction furnace. The analyses are accomplished by initial removal of sulphur dioxide using absorption and titration, followed by collection of carbon dioxide in a gravimetric absorber.

Carbon dioxide and Sulphur dioxide are both present in wine. Linares *et al*. (1989) proposed a method for simultaneous determination of these species in wine through preseparation of the analytes with a flow through gas-diffusion unit. The analytes are sensed by two detectors in series, a potentiometric detector responsive for the both analytes and a photometric detector for SO_2 only. A Pye Unicam SP6-500 single-beam spectrophotometer was used. The error of this method was about 7% and less.

However, These methods requires sophisticated and expensive apparatus which would not be available in most chemical laboratories. Our proposed method is simple, fast, accurate and does not require expensive apparatus. The experiments could be made in any poor laboratory and this method could be used as a practical application for students.

MATERIALS AND METHODS

The experimental determinations have been carried out with solutions of various concentrations: as an example for one determination the following reagents were used: solution of NaOH (0.100 mol L^{-1}); Na_2CO_3 (0.101 mol L^{-1}); Na_2SO_3 (0.107 mol L^{-1}) and HCl (0.100 mol L^{-1}) as a titrant where prepared as described in the literature (Small *et al*., 1975).

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In order to prevent the oxidation of the sulfite in the presence of air 5% glycerol was added to the solution. Samples of 100.00 mL obtained by diluting a mixture of compounds in different ratios were titrated.

The titrations have been carried out with multi parameter analyzer C-831 for simultaneous measurements of pH and conductivity (pH range -2: +16, resolution 0.01-0.001 pH, Conductivity: 0.1: 0.001 µS cm^{-1}).

RESULTS AND DISCUSSION

The study of the investigated mixture was preceded by determinations concerning the mixture: $OH^{-}+CO_3^{2-}$, $OH^{-}+SO_3^{2-}$, $CO_3^{2-} + SO_3^{2-}$, respectively. For an accurate interpretation of the obtained results, the coexistence domains of the different species present in the solution have been also considered (Fig. 1).

The favorable results obtained validated the study of the mixture for the three components. The pH-metric and conductometric titration curves for one of the determinations carried out are present in Fig. 2.

From the pH-metric curve one reads tow equivalence volumes: the first corresponds for the titration of excess NaOH and Na_2CO_3 to $NaHCO_3$, respectively. The second corresponds to titration of $NaHCO_3$ and Na_2SO_3 to H_2CO_3, $NaHSO_3$, respectively.

For the quantitative determination of the three components found in the system, a third equivalence volume obtained by the separate titration of hydroxide in equivalence quantity that in which the two gases were absorbed.

Under these circumstances the proposed method allows for the direct quantitative determination of the mixture components avoiding a second titration.

- The first one corresponds to the titration of NaOH excess (V_1) by the equation: $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O$
- The second one corresponds to the titration of Na_2CO_3 to $NaHCO_3$ (V_2) by the equation: $Na_2CO_{3(aq)} + HCl_{(aq)} \rightarrow NaHCO_{3(aq)} + NaCl_{(aq)}$.
- The third one volume corresponds to the titration of $NaHCO_3$ and Na_2SO_3, to H_2CO_3 and $NaHSO_3$, respectively (V_3) by the equations:

$$NaHCO_{3(aq)} + HCl_{(aq)} \rightarrow H_2CO_{3(aq)} + NaCl_{(aq)}$$

$$Na_2SO_{3(aq)} + HCl_{(aq)} \rightarrow NaHSO_{3(aq)} + NaCl_{(aq)}.$$

By subtracting the last two volumes one obtains the volume corresponding to the titration of Na_2SO_3 to $NaHSO_3$ (V_4), thus:

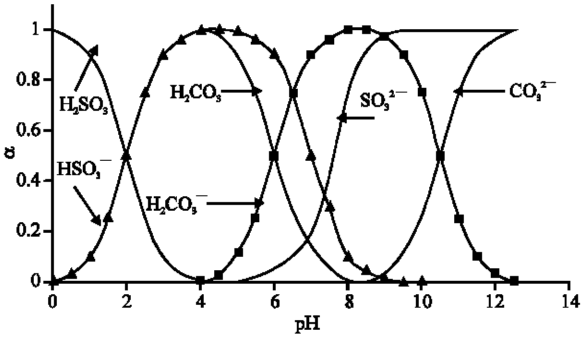

Fig. 1: Molar fractions of the species H_2SO_3, HSO_3^{-}, SO_3^{2-}, H_2CO_3, HCO_3^{-} and CO_3^{2-} versus pH

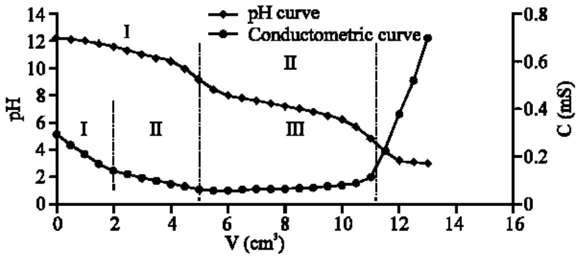

Fig. 2: pH-metric and conductometric titration curves of 20 mmol NaOH + 30 mmol Na_2CO_3 + 0.33 mmol Na_2SO_3 with 0.100 M HCl

$$V_4 = V_3 - V_2$$

As it may be seen from the Table 1, the experimental results are very close to the theoretical ones, thus proving that the proposed method is acceptable for such determination.

Now in order to determinate the equivalent volumes by the differentiation methods, which known as the most precise graphic methods, the variation of the electromotive force (voltage) was also recorded during the titration. Since the titration reactions of carbonate and sulfite are not symmetric, the first order derivative is not enough for accurate results. Therefore the second derivative has been used which vanishes at the point corresponding to the equivalence volume.

Taking into account that during the calculation of the two derivatives one value is subsequently lost, a biunique correspondence in the graphic representation exists no more, thus the equivalence values are uncertain. Therefore it is assumed to work with a first average of the titrant volumes (for the first order derivative) and respectively a new average of the values from the first average V, (for the second order derivative). Figure 3 and 4 show the assumed analytical method.

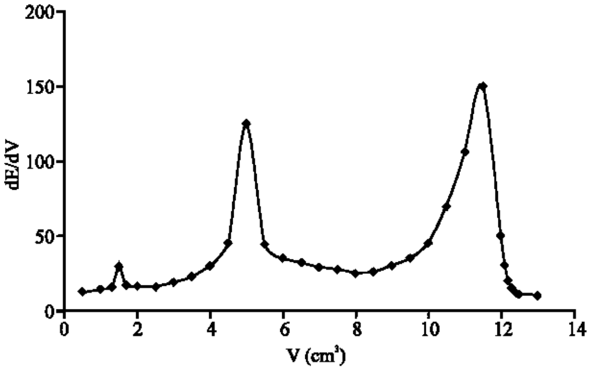

Fig. 3: The first order derivative of the potential for the titration represented in Fig. 2

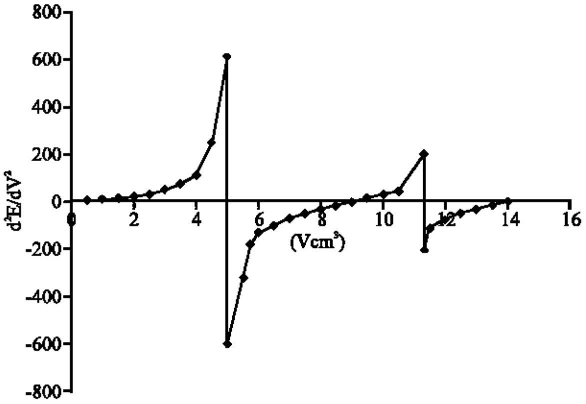

Fig. 4: The second order derivative of the potential for the titration from Fig. 2

Table 1: The actual amount of the species in the prepared samples and their experimentally determined value

	Prepared (% mmol)			Determined (% mmol)		
Sample	OH^-	CO_3^{2-}	SO_3^{2-}	OH^-	CO_3^{2-}	SO_3^{2-}
1	20.0	45.0	35.0	19.5	44.0	35.0
2	20.0	50.0	30.0	20.0	49.0	29.0
3	30.0	35.0	35.0	28.0	36.0	35.0
4	30.0	40.0	30.0	29.5	40.5	30.2
5	30.0	30.0	40.0	29.5	30.0	40.0

The values of two equivalence volumes (5.00 and 11.30 mL) support the improved alternative method. This improved alternative has been checked with samples of variable contents of the compounds. Some of other results are presented in Table 1.

As it may be seen from the Table 1, the experimental results are very close to the theoretical ones, thus proving that the proposed method is acceptable for such determination.

Among the major impurities which may potentially interfering in the analysis of acid components and their counterparts anions are sulfates and phosphates. However it was found that the concentration of such substances in natural waters very low and as a result they may do not affect the results of this study (Sekara and Lechner, 1974). Nevertheless this method will be applied in our next research to study this phenomena.

CONCLUSIONS

The simultaneous determination of carbonate, sulfite and hydroxide proved to be possible through conductometric and potentiometric titrations. In contrary to the difficulty for the determination of low concentration acid components using conventional titrimetry and ion-selective electrode method, we may ascertain that the proposed method is simpler, faster and more accurate. In addition, spectrophotometry does not determine these acid components simultaneously (Nonomura and Hobo, 1998). By this method, the determination of sulfur dioxide and carbon dioxide with the excess of hydroxide is possible through one single titration.

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