

Fast Detection of Carbonate and Bicarbonate in Groundwater and Lake Water by Coupled Ion Selective Electrode



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Abstract: The content of carbonate (HCO_3^-) and bicarbonate (CO_3^{2-}) in the freshwater is an important characteristic of the geochemical environment. However, the environmental factors affect the concentration of two ions easily during the process of sampling, transportation and storage. It is a worldwide problem to determine the real content of carbonate and bicarbonate ions in the freshwater. To solve this problem, a new approach was proposed for the rapid determination of carbonate and bicarbonate ions in groundwater and lake water through a pH electrode combined with a CO_2 electrode. The results showed that the liner range of bicarbonate was 0.027–570 mg L^{-1} and that of carbonate was 1.25×10^{-8} –39.7 mg L^{-1} . In the most case, the coexisting cation, anion and weak acid (K^+ , Na^+ , Mg^{2+} , Cl^- , $\text{SO}_4^{2-} < 100 \text{ mg L}^{-1}$, HSO_3^- , NO_2^- , $\text{HOAc} < 50 \text{ mg L}^{-1}$) did not interfere with the analysis. The method was validated for real water samples and the recoveries were in the range of 95.2%–99.2% with the relative standard deviations (RSDs) of 2.6%–3.7%. The accuracy of the method was proved to be well matched with acid-base titration. However, the electrodes were temperature sensitive, so the standard solution and samples should be measured at the same temperature. In general, the method was sensitive, fast, economical, easy to carry and simple to operate, which was appropriate for rapid detection of bicarbonate and carbonate ions in freshwater in field. The method was applied in determination of bicarbonate and carbonate ions in the groundwater and lake water in Qinghai Province, China and it was found that the pH values in the groundwater samples from Haidong area were from 6.4 to 7.4, with the HCO_3^- content of 234–4096 mg L^{-1} and CO_3^{2-} content of 0.16–1.89 mg L^{-1} , and the samples from Qinghai Lake had a pH about 8.7, with the HCO_3^- content of 1.36–1.86 g L^{-1} and CO_3^{2-} content of 32.3–43.9 mg L^{-1} , which was consistent with the previous results.

Key Words: Carbon dioxide electrode; pH electrode; Carbonate; Bicarbonate; Groundwater; Lake water

1 Introduction

Carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) ions and carbon dioxide (CO_2) are the main form of carbonate compounds in the freshwater. Most of the HCO_3^- and CO_3^{2-} ions are coming from the dissolution of carbonate minerals, the decomposition of organic matter, the respiration of aquatic animals and the exchange of carbon cycling. The content of HCO_3^- and CO_3^{2-} ions could indicate the local geochemical environment, so the

determination of their content is very important. But so far, there is not an appropriate method can achieve the rapid detection in field for HCO_3^- and CO_3^{2-} ions. The acid-base titration, gas chromatography and spectrometry^[1–3] are usually used for the determination of HCO_3^- and CO_3^{2-} ions in laboratory. However, all these methods not only need big equipment, complex operation, but also need water samples to be sent to the laboratory. However, the concentration of HCO_3^- and CO_3^{2-} varies along with the change of temperature, air pressure and

Received 30 October 2015; accepted 30 November 2015

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This work was supported by the Special Funds for Scientific Research of Ministry of Land and Resources of China (No. 201411083-3), the Geological Survey Project of China (Nos. 1212011120283 and 1212010816028).

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DOI: 10.1016/S1872-2040(16)60913-1

other environmental factors. When water sample separates from water body for some time (especially groundwater sample), the concentration of HCO_3^- and CO_3^{2-} changes, in this case, the later test results deviate from their real content in water. Hence, scientists hope to find a fast and direct way to determine the content of HCO_3^- and CO_3^{2-} in the freshwater.

Ion selective electrode (ISE) is a kind of non-destructive electrochemical sensor, which shows many unique features compared with other analytical methods. It is compact, cheap, sensitive, easy to carry and unaffected by color or turbidity, and available for continuous measurement. In late 1990s, Goswami^[6] first reported a kind of photochemical electrode to measure the dissolved CO_2 in seawater. Then Tabacco^[7] realized the determination of dissolved CO_2 of low concentration in seawater. Zhu^[8] and Cai^[9] improved the technique and realized the measurement of two-dimensional CO_2 distributions in marine sediments. Over the past 20 years, the use of ion selective electrode for the determination of dissolved CO_2 in seawater was reported several times^[4–8]. However, few are reported on the study of CO_2 , CO_3^{2-} and HCO_3^- in groundwater and lake water. In this study, based on the chemical reactions of CO_2 , CO_3^{2-} and HCO_3^- in water ($\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$, $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$)^[10], a new method was established for the rapid determination of carbonate and bicarbonate ions in groundwater and lake water by using pH electrode and CO_2 electrode.

2 Experimental

2.1 Instruments and reagents

A pH electrode (PB-10 Sartorius) coupled with a temperature compensation device was used to determine the acidity of samples. CO_2 detection was performed with a CO_2 electrode (Scientific Orion Thermo 9502). Before use, the two electrodes were activated in the blank water for 24 h. Magnetic stirrer (WiseStir MSH-20D) and magnetons were also used in the experiment.

Sodium bicarbonate (NaHCO_3 , Sinopharm Chemical Reagent Co., Ltd) and sodium citrate (Sinopharm Chemical Reagent Co., Ltd) were analytically pure. The pH buffer solutions (4.01, 6.86, and 9.18) were from Sinopharm Chemical Reagent Co., Ltd. Ionic-strength adjustment buffer or ISA buffer (0.50 M sodium citrate solution) and internal filling solution (0.005 M sodium bicarbonate solution) were self-made products.

Blank water was deionized water and it was confirmed without carbonate and bicarbonate ions.

2.2 Preparation of electrodes

Before determination, CO_2 electrode was calibrated with a

series of standard NaHCO_3 solutions at different concentration levels (10, 5.0, 1.0, 0.5 and 0.1 mM) and the standard curve $E\text{-lg}C_T$ was drawn. At the same time, pH electrode was calibrated in the pH buffer (pH 4.01, 6.86 and 9.18) and another standard curve $E\text{-lg}[H^+]$ was given.

2.3 Sample collection

In July 2105, several groundwater samples from Haidong area and some lake water samples from Qinghai Lake were collected in Qinghai province. Sampling and preservation conditions referred to the National Environment Protection Standard of the People's Republic of China-Water quality-Guidance on sampling techniques^[11]. The main information of the samples was shown in Table 1.

2.4 Experimental procedure

The pH of water sample (100 mL) in a 150-mL beaker was measured by the pH electrode under stirring at steady rate of 120 rpm. Then the pH of the sample was adjusted to 4.8 ± 0.1 ^[12] by ISA buffer solution for determination of CO_2 by a CO_2 electrode. When the change of the reading was less than 0.6 mV min^{-1} ^[13,14], the voltage values were recorded. After that, the electrodes were rinsed with blank water until the blank potential occurred for the next measurement.

3 Results and discussion

3.1 Measuring principle of carbonate and bicarbonate ions

The determination of CO_3^{2-} and HCO_3^- is mainly base on the principle of ISE, whose potential is linearly dependent on the logarithm of the ionic activity in solution according to the Nernst equation as $E = E^\circ + S \lg C$. E is measuring potential. E° is standard potential and is unique for each measured ion. S is electrode slope, and C is the ion activity which is approximate to the ion concentration in the dilute solution.

Table 1 Sampling information of groundwater and lake sample

Type	No.	Geographic coordinate	Sampling date
Groundwater	1	N36°466'E101°889'	2015.07.21
	2	N36°466'E101°891'	2015.07.21
	3	N36°454'E101°868'	2015.07.21
	4	N36°425'E101°956'	2015.07.22
	5	N36°496'E102°139'	2015.07.22
	6	N36°499'E102°126'	2015.07.23
	7	N36°393'E101°910'	2015.07.23
Lake water	8	N36°589'E100°507'	2015.07.24
	9	N36°587'E100°512'	2015.07.24
	10	N36°592'E100°505'	2015.07.24
	11	N36°656'E100°476'	2015.07.24
	12	N36°633'E100°447'	2015.07.24

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