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Theoretical and Analytical Aspects of Carbonic Species Determination in Rain, Ground, Geothermal and Petroleum Waters

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ABSTRACT

We present the acid-base titration procedure for the determination of carbonic species in four types of waters: *a. rainwater containing low concentration of dissolved species and low alkalinity, b. ground and surface water which contains mainly carbonic alkalinity, c. geothermal water which has carbonic and other alkalinities,* and *d. petroleum waters which have high concentration of salts and no contact with the present atmospheric CO_2.*

The calibration of standards is crucial. The NaOH solution mostly contains a small amount of CO_2 dissolved. Therefore, the standardization of NaOH solution is performed with titrating up to the carbonic acid equivalence point (H_2CO_3EP) instead of pH = 7.0.

The Gran titration method for rainwater is performed with adding a small amount of NaOH (or HCl) and then titrating with HCl (or NaOH). The NaOH standard solution must be free from dissolved CO_2.

The H_2CO_3EP alkalinity method requires the subtraction of other alkalinities (such as boric, silicic) from the total alkalinity in order to obtain a representative carbonic alkalinity for geothermal waters. This method is also applicable for ground waters. The preliminary results for the determination of carbonic species in petroleum waters show the existence of very little or no carbonic alkalinity in them. However, the proposed method requires a complete analysis of all parameters which contribute to the H_2CO_3EP alkalinity including dissolved gases like H_2S.

1. INTRODUCTION

The environmental problems: *global warming, flooding, dryness, etc.* associated with the emission of CO_2 due to burning of fossil fuel have been well recognized in late 1960s. Carbon dioxide (CO_2) plays a fundamental role in governing the geological and environmental processes on the Earth. The distribution of carbonic species (H_2CO_3, HCO_3^- and CO_3^{2-}) in natural waters permits the examination of CO_2 exchange between atmosphere and waters, the evaluation of the buffering mechanisms and the definition of their acid-base neutralizing capacity, etc. In geothermal systems, the concentration of *CO_2* controls the fluid *pH* and pressure in the reservoir. Similarly, to understand the incrustation of calcite in the geothermal reservoir and production wells during exploitation demands a detailed knowledge of CO_2 chemistry at high temperature and pressure.

From the analytical point of view there exist four principle types of natural water: *a. rainwater containing low concentration of dissolved species and low alkalinity, b. ground and surface water which contains mainly carbonic alkalinity, c. geothermal water which has carbonic and other alkalinities,* and *d. petroleum waters which have high concentration of salts and no contact with the present atmospheric CO_2.*

Verma (2005) presented the theoretical and experimental aspects of techniques to measure carbonic species in the first three types of waters. Here we will revise mainly the analytical procedures for measuring carbonic species concentrations in geothermal and petroleum waters.

2. IAEA COMPARISON OF HCO_3^- ANALYSIS IN GEOTHERMAL WATERS

With interlaboratory comparisons of isotopic analysis ($\delta^{18}O$ and δD) of natural waters the International Atomic Energy Agency (IAEA), Vienna has created successfully a worldwide network of laboratories for good quality analysis (Parr and Clements, 1991). The chemical and isotopic data are complementary to understand the geochemistry of natural water system. Therefore, the IAEA has also conducted various interlaboratory comparisons for geothermal waters within the framework of the project "*Coordinated Research Program on the Application of Isotope and Geochemical Techniques in Geothermal Exploration*". The results are reported in the internal reports as followings: (i) 22 laboratories from 19 countries (Giggenbach et al. 1992), (ii) 15 laboratories from 7 countries (Gerardo-Abaya et al. 1998), (iii) 26 laboratories from 10 countries (Alvis-Isidro et al. 1999), (iv) 35 laboratories from 16 countries (Alvis-Isidro et al. 2000), (v) 38 laboratories from 23 countries (Alvis-Isidro et al. 2002) and (vi) 31 laboratories from 18 countries (Urbino and Pang 2004).

Figure 1 presents a relation between the laboratory number and concentration of HCO_3^-, analyzed in thirteen samples during the IAEA interlaboratory comparison program. It can be observed that there is wide spread in the analysis. Figure 2 presents a whisker plot between the concentration of HCO_3^- and % S.D. (coefficient of variation) for each sample after removal of outliers. There are two groups of analysis: a) overall 10% analytical uncertainty which is independent of concentration and b) analytical uncertainty increases with decreasing concentration with ~25% for 50 ppm and ~60% for 25 ppm of HCO_3^-. There is a considerably high analytical uncertainty for the measurements of HCO_3^-; however, each participating laboratory had good reproducibility. Therefore, we initiated a project to understand theoretical and experimental aspects of the analysis of carbonic species in natural waters (Verma, 2004, 2005, 2008) concluding the calibration of acid- base standards.

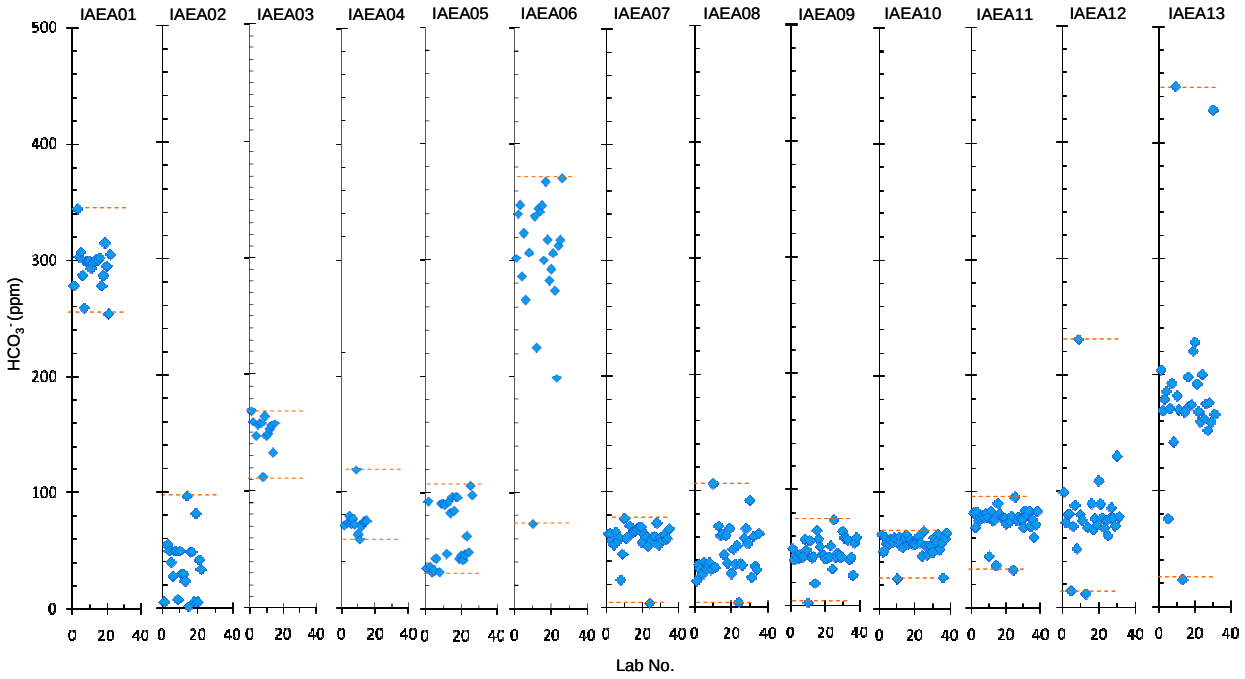

Figure 1: A relation between the laboratory number and concentration of HCO3- analyzed in the thirteen samples as part of the IAEA interlaboratory comparison program during 1982 and 2004. The dashed lines indicate the lower and upper bounds of the results.

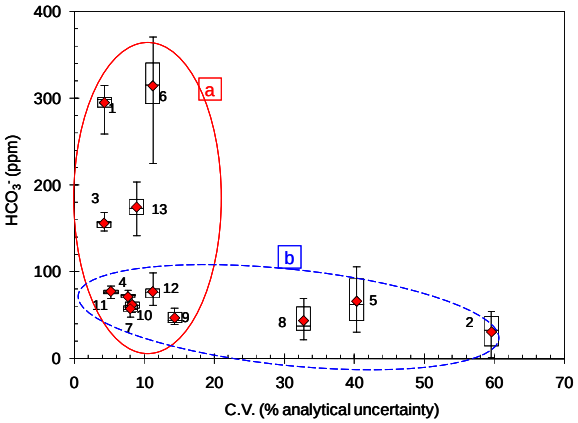

Figure 2: Whisker plot for the concentration and analytical uncertainty of HCO3-, analyzed in thirteen samples (Figure 1). There are two groups of analysis: a) 10% analytical uncertainty which is independent of concentration and b) analytical uncertainty increases with decreasing concentration.

3. CO_2 CHEMISTRY

A summary on the basic aspects of CO_2 chemistry related to the acid-base titration procedures for the determination of carbonic species in different types of water has been presented in Verma (2005). A diprotic acid like H_2CO_3 has three equivalence points H_2CO_3EP, $NaHCO_3EP$, and Na_2CO_3EP, associated with the dissolution of H_2CO_3, $NaHCO_3$, or Na_2CO_3, respectively. The three types of alkalinity, alk, alk1, and alk2 with the respective equivalence points are defined as

$$alk = [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}] \quad (1a)$$

$$alk1 = [OH^-] - [H^+] - [H_2CO_3] + [CO_3^{2-}] \quad (1b)$$

$$alk2 = [OH^-] - [H^+] - [H_2CO_32] - [HCO_3^-] \quad (1c)$$

The fundamental importance of these definitions of alkalinity is that the addition or removal of H_2CO_3, $NaHCO_3$, or Na_2CO_3 does not change alk, alk1, or alk2, respectively; whereas the pH of the solution decreases (or increases). It has been observed that there is a continuous addition or removal of atmospheric CO_2 during the acid-base titration (Verma, 2005). Similarly, a NaOH solution acts as a pump to suck the atmospheric CO_2. Thus it is difficult to obtain a pure NaOH solution (i.e. without dissolved CO_2 in it). This is one of the reasons why analysis of carbonic species is performed by measuring the H_2CO_3 alkalinity (alk).

4. ANALYTICAL PROCEDURE FOR CARBONIC SPECIES DETERMINATION

The acid-base titration is the only reliable method for the determination of carbonic species in natural waters. The basic aspects of CO_2 chemistry discussed in the previous section will be used to improve the analytical methods. Previously, the calibration of standards will be presented, which is fundamental in obtaining accurate results.

4.1 Calibration of Standards

In the acid-base titration we use the known concentration solutions of HCl and NaOH as standards. First step is to prepare approximately the same concentration solutions of HCl, NaOH and Na_2CO_3. The weight of dry Na_2CO_3 can be measured with sufficient accuracy, permitting the preparation of known concentration solution of Na_2CO_3. However, this is not true for HCl and NaOH solutions

The concentration of HCl and NaOH solutions is calibrated with a titration procedure. Figure 3 shows the titration of Na_2CO_3 0.05002N and NaOH ~0.05N with HCl ~0.05N. The backward titration is conducted with NaOH ~0.05N. It can be observed that 25 ml of Na_2CO_3 is titrated with 24.28

ml of HCl. Thus the concentration of HCl is 0.05150N (=25x0.05002/24.28).

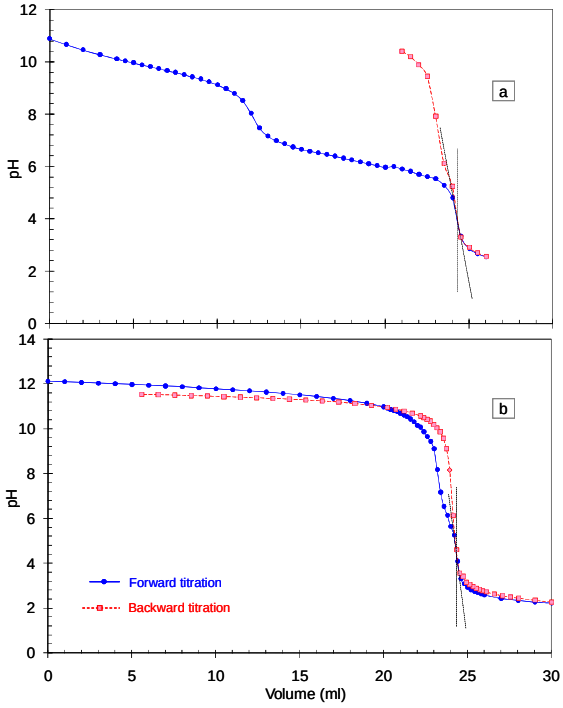

Figure 3: Titration curves for the calibration of standards: a) 25 ml Na2CO3 0.05002N and b) 25 ml of NaOH (~0.05 N). The forward titration is performed with HCl 0.05 (~0.05 N), while NaOH (~0.05 N) is used for backward titration. It can be observed that there is a small amount of CO2 even in the fresh NaOH solution. However, the dissolution of atmospheric CO2 does affect the concentration of NaOH, if the titration is conducted to the H2CO3 acid equivalence point.

The titration of NaOH with HCl is shown in Figure 3(b). If there is no CO_2 in the NaOH solution, the equivalence point will be at pH=7.0. As NaOH solution always has a small amount of dissolved CO_2, it is titrated to H_2CO_3EP. It can be seen in Figure 3(b) that 25 ml of NaOH is titrated with 24.35 ml of HCl, thus the concentration of NaOH is 0.05016N (=24.35x0.05150/25). The procedure was repeated three times and the averaged values are taken as the concentration of standards.

4.2 Analysis of Rainwater

The concentration carbonic species in rainwaters is determined with the Gran titration method. Verma (2005) revised the method and recommended the use of Gran functions, F_1 and F_4 for it. For this method a small amount (say 1 ml) of HCl (or NaOH) is added to a specified amount of rainwater sample (say 25 ml), and then it is titrated with NaOH (or HCl). In this procedure the NaOH solution should be free from dissolved CO_2; otherwise the results of analysis will have some uncertainty depending on the amount of dissolved CO_2.

4.3 Analysis of Groundwater

The analytical procedure for the determination of bicarbonate and carbonate in ground and surface waters has been well established by chemists and hydrologists since the beginning of the last century (Verma, 2005). For this method the sample is titrated with an acid (HCl) to pH = 8.3 and pH = 4.5 (or 3.8) in order to determine carbonate and bicarbonate, respectively. Verma (2005) modified the method by considering the end points as the points of inflexion corresponding to $NaHCO_3$EP and H_2CO_3EP in the whole titration curve. As pointed out earlier there is a time dependent liberation of CO_2 during the titration with HCl. It affects $NaHCO_3$EP, but there is no alteration of H_2CO_3EP. Similarly, a fast titration does not provide sufficient time to release CO_2. Thus the titration time is very important for location of $NaHCO_3$EP. The total alkalinity determination method proposed for geothermal water is also applicable to ground waters which have pH higher than 8.3 (i.e. presence of carbonate).

4.4 Analysis of Geothermal Water

Verma (2005) proposed an analytical method for the determination of carbonic species in geothermal waters. It consists of the determination of total alkalinity (alk) with respect to H_2CO_3EP. In the presence of boric and silicic species, alk is expressed as

$$\begin{aligned} \text{alk} &= [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \\ &\quad + [H_3SiO_4^-] \\ &= [OH^-] - [H^+] + C_T(\alpha_1 + 2\alpha_2) + C_{TB}(\alpha_{1B}) + C_{TSi}(\alpha_{1Si}) \end{aligned} \quad (2)$$

where square brackets [ ] represent the molal concentration of the species. C_T, C_{TB} and C_{TSi} are the total concentration of carbonic, boric and silicic acids, respectively. Knowing the initial pH, silica (C_{TSi}), boron (C_{TB}) and total alkalinity (alk), the concentration of total dissolved CO_2 (C_T) is calculated through the above equation. With the values of C_T and initial pH, we calculate the concentration of individual carbonic species through equation (2).

A limitation of this approach was suggested for waters which have initial pH higher than 10. The measurement of pH through an electrode is not very accurate for water at pH>10 due the interference of Na^+. An error of ± 0.1 in pH produces considerable error in the concentration of carbonate and bicarbonate at pH>10.

4.5 Analysis of Petroleum Water

Table 1 presents the chemical analysis of three formation water samples, derived from a petroleum reservoir. A pure water sample was recovered from Well B, while an emulsion mixture of crude oil and water was extracted from well A and C. The water sample A showed a natural separation process between both phases during storage in the lab, whereas the centrifuge technique with addition of toluene had to be applied for the recuperation of water sample C.

Figure 4 shows the whole titration curves for 25, 25 and 20 ml of A, B and C samples, respectively. The initial pH is 6.99, 7.74 and 7.12, respectively. The values are close to the reported values in Table 1, except for sample B. It was observed that the stabilization of pH-meter reading took longer time for these waters. Probably, it is a consequence of high salinity. We are still working on it.

If we consider the titration to pH=4.3 (groundwater method) to obtain alkalinity, it consumes 21, 27 and 10 ml of HCl 0.05150N for respective sample. Thus the resulting concentrations of HCO_3^- would be 2639, 3393 and 1751 ppm, respectively. Considering the point of inflection in backward titration curve as H_2CO_3EP and the presence of only carbonic alkalinity, the concentration of HCO_3^- resulted in 704, 2010 and 691 ppm, respectively.

Table 1: Analysis of three formation water samples, derived from a petroleum reservoir.

Sample	Elec. Cond.	TDS	pH	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	B	Cl^-	Br^-	SO_4^{2-}	SiO_2
	(mS/cm)	ppm											
A	124.5	98820	7.07	26.0	29200	1270	563	4320	78.2	61100	405	965	107
B	128.8	96290	6.41	32.8	23400	3270	928	8210	99.0	58300	522	331	107
C	128.2	122710	7.34	22.8	50200	1810	767	8130	96.7	60000	453	436	128

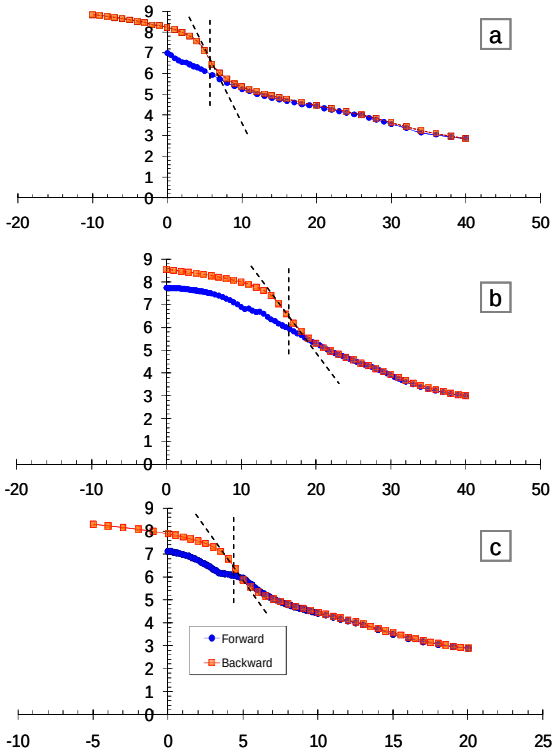

Figure 4: Titration curve for petroleum waters: a) 25 ml, b) 25 ml and c) 20 ml of samples A, B and C, respectively.

A comparison between the titration curves in Figures 3(a) and 4 indicates that there is no similarity. Figure 3(a) is only for carbonic alkalinity solution.

The petroleum samples had high concentration of dissolved H_2S. The liberation of H_2S produces a slight difference in the forward and backward titration. The apparent point of inflection in the backward titration curves in Figure 4 may be associated with the release of H_2S. The forward and backward titration curves are overlapping up to pH 5.5. These are preliminary results on the method to determine carbonic species in petroleum waters. There is need to analysis all the species including dissolved H_2S in order to determine the concentration of carbonic species in petroleum waters.

As natural waters mostly have pH values lower than 10, this procedure can be used without producing any significant errors except for rainwater.

5. CONCLUSIONS

The titration procedure to the carbonic acid equivalence point (H_2CO_3EP) works well for the analysis of carbonic species in groundwater and geothermal waters. Its application for the formation water obtained from petroleum reservoirs is feasible; however, there is need to perform an extensive study including the measurement of all dissolved species.

The carbon dioxide is the second important component after water in geothermal fluid. To understand the CO_2 chemistry of geothermal system the analysis of carbonic species in geothermal fluid is of fundamental importance.

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