Potentiometric titrations

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Abstract
The concentration of different carbonate species in 3 samples of mineral waters was determined both by manual titrations and automatic potentiometric titrations. The potentiometric titration gave more precise results. The pH of the three samples was determined to be 7.8, 7.92 and 7.68 in respectively Evian, Valser and Swiss Alpina.

Introduction
Titration is the most suited way to measure the speciation of carbonate ions in water. The equilibrium of these ions can be described by the following equations:

\[
\begin{align*}
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+
\end{align*}
\]

The carbonate ion is only present in traces, unlike the two other species. In this experiment, the concentrations of carbonate species are determined first by manual titration and then by an automatic potentiometer. Finally, another method, the “ion selective potentiometry” is explored, using a carbonate selective electrode.

Methodology

3.1 Manual titrations
A solution of 0.1 M HCl is filled into a burette. Then, 10 mL of 0.1 M NaOH and 10 mL of mineral water is pipetted to the titration beaker containing 20-30 mL of Millipore water. A few drops of phenolphthalein indicator are finally added to the mixture and it turns red. The solution is then titrated to the first equivalence point, when it turns colourless. At this moment, a few drops of bromocresol green indicator are added and it turns blue. The titration is then continued to the second equivalence point when it turns yellow.

3.2 Potentiometric titration
The methodology given by the protocol [1] was followed without any modifications, except that the TRIS-HSO₄ buffer was at pH 8.0 instead of 8.6.

Results

4.1 Manual titrations
The volumes of HCl required to reach each stoichiometric point allow us to determine, knowing the concentration of HCl, the number of moles of total carbonate species. The following relation is derived in the notebook:

\[
n_{\text{tot}} = n_{\text{H}_2\text{CO}_3} + n_{\text{HCO}_3^-} = n_{\text{HCl}}^{(2)} - n_{\text{HCl}}^{(1)}
\]

And the concentration \(c = \alpha \cdot c_{\text{tot}}\) of each species can be found from their fractions defined by:

\[
\alpha_{\text{H}_2\text{CO}_3} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{\alpha_1}[\text{H}^+] + K_{\alpha_1}K_{\alpha_2}}
\]
with $[H^+] = 10^{-pH}$ and $c_{tot}$ the total concentration of carbonate species present in solution.

**Table 1: The equivalence volumes of HCl determined by manual titrations and the pH of the water samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>$V_{eq 1}$ [mL]</th>
<th>$V_{eq 2}$ [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evian</td>
<td>7.8</td>
<td>11.7</td>
<td>12.7</td>
</tr>
<tr>
<td>Valser</td>
<td>7.92</td>
<td>11.8</td>
<td>12.3</td>
</tr>
<tr>
<td>Alpina</td>
<td>7.68</td>
<td>11.7</td>
<td>12.6</td>
</tr>
</tbody>
</table>

The carbonate species’ concentration calculations give us the following results:

**Table 2: Concentration of carbonate species in mineral waters determined by manual titration**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[H_2CO_3]$ mg/L</th>
<th>$[HCO_3^-]$ mg/L</th>
<th>$[CO_3^{2-}]$ mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evian</td>
<td>20.3±0.3</td>
<td>588.6±9.0</td>
<td>1.71±0.03</td>
</tr>
<tr>
<td>Valser</td>
<td>7.7±0.1</td>
<td>296.4±4.5</td>
<td>1.13±0.02</td>
</tr>
<tr>
<td>Alpina</td>
<td>23.8±0.4</td>
<td>524.7±8.0</td>
<td>1.16±0.02</td>
</tr>
</tbody>
</table>

### 4.2 Potentiometric titration

The data collected by the automatic titration is analysed. The same calculations are used to determine the fraction and then the concentration of each species. The equivalence point is found by using the tangents method (deriving the function of pH over added $V_{HCl}$) for each mineral water. The following results were obtained:

**Figure 1: Potentiometric titration of Evian**
Table 3: Concentration of carbonate species in mineral waters determined by automatic titration

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\text{H}_2\text{CO}_3]$ mg/L</th>
<th>$[\text{HCO}_3^-]$ mg/L</th>
<th>$[\text{CO}_3^{2-}]$ mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evian</td>
<td>9.7</td>
<td>282.5</td>
<td>0.82</td>
</tr>
<tr>
<td>Valser</td>
<td>5.0</td>
<td>189.7</td>
<td>0.73</td>
</tr>
<tr>
<td>Alpina</td>
<td>14.8</td>
<td>326.5</td>
<td>0.72</td>
</tr>
</tbody>
</table>

4.3 Potentiometric titration using carbonate selective electrode

From the values of p($\text{CO}_3^{2-}$) given by the carbonate selective electrode, it is easy to calculate the concentration of this species. Then, knowing the pH and the equilibrium constants $K_a1$ and $K_a2$ ($pK_{a1}=6.33$, $pK_{a2}=10.33$), the other carbonate species’ content is calculated. The following results were obtained:
Table 4: Concentrations determined by the ion selective electrode

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>p(CO$_3^{2-}$)</th>
<th>[CO$_3^{2-}$] mol/L</th>
<th>[CO$_3^{2-}$] g/L</th>
<th>[HCO$_3^-$] mol/L</th>
<th>[HCO$_3^-$] mg/L</th>
<th>[HCO$_2^-$] mol/L</th>
<th>[HCO$_2^-$] mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evian</td>
<td>7.8</td>
<td>4.32</td>
<td>4.79E-05</td>
<td>2.88E-03</td>
<td>0.016</td>
<td>0.99</td>
<td>5.50</td>
<td>341.1</td>
</tr>
<tr>
<td>Valsen</td>
<td>7.68</td>
<td>4.33</td>
<td>4.68E-05</td>
<td>2.81E-03</td>
<td>0.021</td>
<td>1.28</td>
<td>9.34</td>
<td>579.2</td>
</tr>
<tr>
<td>Alpina</td>
<td>7.92</td>
<td>4.39</td>
<td>4.07E-05</td>
<td>2.44E-03</td>
<td>0.010</td>
<td>0.64</td>
<td>2.69</td>
<td>166.8</td>
</tr>
</tbody>
</table>

5 Discussion

When making a graph of each specie’s evolution in function of the pH, we can observe that, at the pH of the water (between 7 and 8), the main species are the bicarbonate and the carbonic acid. The graph below uses the information collected by the potentiometric titration for the Evian sample:

![Each specie's fraction in Evian sample](image)

Figure 4: The speciation graph for the Evian sample

Now, we can compare the values obtained by the different methods to those indicated on the mineral water bottles:

Table 5: Comparison between the concentrations obtained by each method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Man [HCO$_3^-$] mg/L</th>
<th>Aut [HCO$_3^-$] mg/L</th>
<th>Sel-El [HCO$_3^-$] mg/L</th>
<th>Bot [HCO$_3^-$] mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evian</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valsen</td>
<td>588.6±9.0</td>
<td>282.5</td>
<td>0.99</td>
<td>360</td>
</tr>
<tr>
<td>Alpina</td>
<td>296.4±4.5</td>
<td>189.7</td>
<td>1.28</td>
<td>-</td>
</tr>
</tbody>
</table>

Man=manual titration, Aut=potentiometric titration, Sel-El=selective electrode, Bot=value indicated on the bottle.

Unfortunately Valsen doesn’t indicate the bicarbonate’s content on the bottle. Otherwise, we can observe that the potentiometric titration gives the most accurate results. The values obtained by the ion-selective electrode are way below the expected.
6 Conclusion
In this experiment, the concentrations of each carbonate species were determined by manual titration and then by an automatic titration. The automatic method is more precise, but is required to have the appropriate equipment in the laboratory. The manual method is less precise, but gives sufficiently good results if great precision isn’t needed. Both methods are easy and fast, even though the analysis of manual titration gives straightforward results. The carbonate-selective electrode method didn’t work very well. This might be due to the wear of the electrode or to the interaction with other ions present in the water.

7 References

8 Annexes
Copy of the notebook
Potentiometric titrations

0.1 M \rightarrow 25 \text{ mL } \text{HCl} \ 1.0 \text{ M}
0.1 M \rightarrow 10 \text{ mL } \text{NaOH} \ 1.0 \text{ M}

m = n \cdot c \cdot V = 0.1 \cdot 40 \cdot 0.25 = 1 \text{ g}

peSe = 1.050 \pm 0.000, 4\text{,}2004

\[ \text{Alpina} \]
\[ \text{pH} = 7.68 \]
\[-4.33 \]

\[ \text{Valser} \]
\[ \text{pH} = 7.92 \]
\[-4.33 \]

\[ \text{H}_2\text{CO}_3 + n \text{ HCO}_3^- = n^{'2} \text{HCO}_3^- - n' \text{ HCl} \]
\[ \text{NaOH} - n \text{HCO}_3^- \]