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# Elimination of Dissolved Sulfide Interference in the Flow-Injection Determination of Sigma-CO<sub>2</sub> by Addition of Molybdate

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## Elimination of dissolved sulfide interference in the flow injection determination of $\Sigma\text{CO}_2$ by addition of molybdate

**Abstract**—A previously described flow injection method for the analysis of  $\Sigma\text{CO}_2$  included the addition of  $\text{ZnCl}_2$  to some samples before analysis in order to precipitate dissolved sulfide (which interferes with the method) as  $\text{ZnS}$ . However, the use of  $\text{Zn}^{2+}$  in samples with high concentrations of dissolved sulfide causes the coprecipitation of  $\text{ZnCO}_3$ , and in our experience with this technique,  $\text{ZnCO}_3$  also precipitates even in the absence of dissolved sulfide. The addition of molybdate effectively complexes dissolved sulfide without interfering with the determination of  $\Sigma\text{CO}_2$  by this technique.

Determining total dissolved inorganic C ( $\Sigma\text{CO}_2 = \text{CO}_{2(\text{aq})} + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$ ) in aqueous samples is frequently essential in biogeochemical investigations, particularly those involving the remineralization of organic matter. Yet until recently there was no rapid analytical technique for its determination. Hall and Aller (1992) introduced a simple and fast flow injection method that could be used effectively with small samples (5  $\mu\text{l}$  or less). Briefly, this method uses the differential solubility of  $\Sigma\text{CO}_2$  as a function of pH to convert dissolved  $\Sigma\text{CO}_2$  to  $\text{CO}_2(\text{g})$  when a sample is injected into an acid stream (10–30 mM HCl). This acidic carrier solution passes over a gas-permeable membrane, on the other side of which is a basic flow stream (5–10 mM NaOH). The  $\text{CO}_2(\text{g})$  passes through the membrane and dissolves in the NaOH solution, which then flows into a conductivity detector where the resulting conductivity depression of the carrier stream is measured. Additional details of this method are described by Hall and Aller (1992).

As Hall and Aller (1992) noted, there are interferences in this method from other acid-volatile compounds, most notably dissolved sulfide. They initially recommended dealing with this sulfide interference by adding 50  $\mu\text{l}$  of a 0.5 M  $\text{Zn}^{2+}$  solution to 1 ml of sample to precipitate the dissolved sulfide as  $\text{ZnS}$ . This method, however, proved to have its drawbacks, and Hall and Aller (pers. comm.) noted that coprecipitation of  $\text{ZnCO}_3$  might occur in highly sulfidic samples. The use of mercury salts or  $\text{H}_2\text{O}_2$  as alternatives to  $\text{ZnCl}_2$  was suggested instead.

Our experience with this technique indicated that  $\text{ZnCO}_3$  is precipitated from samples containing dissolved  $\Sigma\text{CO}_2$  even in the absence of dissolved sulfide. The toxicity of mercury salts, with the accompanying problem of disposing of solutions so contaminated, encouraged us to search for a less toxic alternative. The critical requirements for an effective additive were that it not have a significant conductivity response of its own and that it effectively precipitate or complex dissolved sulfide without removing  $\Sigma\text{CO}_2$  from solution. Based on these criteria, two candidates, molybdate ( $\text{MoO}_4^{2-}$ ) and  $\text{Fe}^{3+}$  were chosen for empirical testing.

Four different salt solutions (0.5 M  $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ , 0.5 M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.5 M  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ , all added at the ratio of 50  $\mu\text{l ml}^{-1}$  sample, and 0.25 M  $\text{HgCl}_2$ , 100  $\mu\text{l ml}^{-1}$  sample) were added to solutions containing varying quantities of  $\text{NaHCO}_3$  (8.9 and 25 mM) and  $\text{Na}_2\text{S}$  (3 and 2.5 mM) and to pore waters of Chesapeake Bay sediments. Our flow injection system consisted of a diffusion cell (fitted with Teflon plumber's tape) made to Hall and Aller's (1992) specifications, a Dionex CDM-II conductivity detector, and two pumps (a Rainin Rabbit HPLC pump and a Rainin Rabbit Plus peristaltic pump). The original reagent strengths were modified, due to the sensitivity of our detector, to 5 mM NaOH and 10 mM HCl and the corresponding flow rates to 0.35 and 0.7  $\text{ml min}^{-1}$ . Standards were made from reagent-grade  $\text{NaHCO}_3$  in distilled deionized water. For all of the metals, the precision of the determination was unaffected as long as the additives were well mixed with the sample solution.

Figure 1 illustrates our results. All of the metals were effective in decreasing the response of a  $\Sigma\text{CO}_2$ -free, 3 mM solution of dissolved sulfide to between 3% (for  $\text{Fe}^{3+}$ ) and 17% (for  $\text{MoO}_4^{2-}$ ) of its original value. Precipitates (presumably metal sulfides) were formed with  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Hg}^{2+}$  solutions, but not with the  $\text{MoO}_4^{2-}$  solution. In the latter case, this suggests the formation of a  $\text{MoS}_4^{2-}$  complex (Tonsager and Averill 1980).

When added to stock solutions of  $\text{NaHCO}_3$ , with and without dissolved sulfide, dilution and sulfide-corrected peak area were little affected by molybdate (97–98% of the response of untreated solutions), but reduced by up

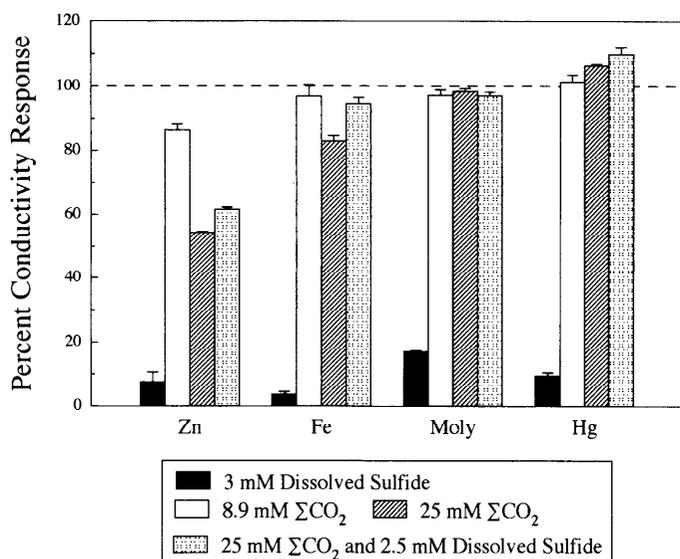


Fig. 1. Percentage of the original  $\Sigma\text{CO}_2$  or sulfide conductivity response for solutions treated with  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{MoO}_4^{2-}$ , and  $\text{Hg}^{2+}$ . The ideal additive would have a near-zero response for the 3 mM dissolved sulfide solution and a near 100% response for the remaining solutions. Percentages were determined as the dilution-corrected conductivity response of a solution with the metal added, normalized to the conductivity of the solution alone without metal. In the case of the mixed  $\Sigma\text{CO}_2$  and dissolved sulfide solution, normalization was done to the conductivity of the 25 mM  $\Sigma\text{CO}_2$  standard alone, without added metal or dissolved sulfide. Control experiments in which 50 or 100  $\mu\text{l}$  of distilled deionized water were added to  $\Sigma\text{CO}_2$  standards in place of the metal solution yielded dilution-corrected responses that were 99–100.4% of the conductivity response of the standard alone.

to half with 0.5 M  $\text{Zn}^{2+}$ . Ferric iron reduced the peak area by  $\sim 20\%$  at high concentrations of  $\Sigma\text{CO}_2$  in the absence of dissolved sulfide, whereas the addition of  $\text{HgCl}_2$  resulted in a small unexplained increase in peak area (101.5–109.8% of the response of untreated solutions), possibly due to volatilization of the mercury.

When these metal solutions were added to pore-water and incubation samples from Chesapeake Bay sediments (Lustwerk and Burdige unpubl. data), samples treated with  $\text{Fe}^{3+}$  produced a large amount of yellow precipitate (presumably  $\text{FeSO}_4$ ). Larger filters and consequently larger sample sizes were required for these solutions when compared to samples treated with other metals.

For the flow injection determination of  $\Sigma\text{CO}_2$ , the addition of 50  $\mu\text{l}$  of 0.5 M  $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$   $\text{ml}^{-1}$  sample is considered the best alternative to zinc chloride for sulfide removal because of its negligible effect on  $\Sigma\text{CO}_2$  peak area. Ferric chloride reduces the conductivity response ( $\sim 20\%$ ) at high  $\Sigma\text{CO}_2$  concentrations and produces an inconvenient amount of precipitate in sulfate-bearing solutions. Mercuric chloride is toxic, possibly volatile in the acid stream, and creates numerous disposal problems.

Although molybdate has the highest residual sulfide response (17% of original value for 3 mM dissolved sulfide), samples likely to have high sulfide concentrations

are also likely to be high in  $\Sigma\text{CO}_2$ . In our experiments, this residual sulfide translates to an "apparent"  $\Sigma\text{CO}_2$  concentration of 0.18 mM, given that dissolved sulfide produces a conductivity response only half that of  $\Sigma\text{CO}_2$  (Hall and Aller 1992). Natural samples from Chesapeake Bay sediments with comparable dissolved sulfide concentrations contain 12–25 mM  $\Sigma\text{CO}_2$  (Burdige and Homstead 1994; Lustwerk and Burdige unpubl. data); for these samples the signal from the residual sulfide constitutes 1–2% of the  $\Sigma\text{CO}_2$  response.

We note one effect not mentioned by Hall and Aller (1992). The conductivity response is inversely dependent on the flow rate of the basic flow stream: a doubling of this flow rate results in a halving of the peak area. However, changing the flow rate of the acidic flow stream has little effect. These observations suggest that the kinetics of the reaction  $2\text{OH}^- + \text{CO}_2(\text{g}) \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$  is the rate-controlling step for the method. If membrane diffusion were limiting, decreasing the flow rate of the basic flow stream would increase the peak width while peak area remained constant. In addition, variations in the flow rate of the acidic stream should produce a greater effect than we observed. Because dissolution of  $\text{CO}_2(\text{g})$  in the basic flow stream is not instantaneous, some of the dissolution may take place after the solution has passed through the conductivity cell. Precision and sensitivity may thus be increased by decreasing the flow rate of the basic flow stream or increasing the length of tubing between the diffusion cell and the conductivity cell.

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