

In conclusion, the resource (food)-feedback model of bioturbation, Eq. 3, not only predicts the existence of a finite-depth bioturbated zone in sediments, but substitution of currently available parameter values into this model indicates that the mean mixing depth should be a worldwide constant of 9.7 cm, independent of water depth or sedimentation rate. This result agrees with the data compilations in Fig. 1 and in Boudreau (1994). If this paper had dealt with a problem of physics or chemistry where predictive theories are the norm, then the model and calculations presented here would be valuable, but not overly remarkable; however, the natural sciences, and particularly geochemistry and ecology, are singularly lacking in successful quantitative theories. The complexities of the phenomena studied in these fields is thought to preclude simple and predictive explanations. This paper also illustrates the fallacy of such a belief.

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References

- ALLER, R. C. 1982. The effects of macrobenthos on chemical properties of marine sediments and overlying water, p. 53–102. *In* P. L. McCall and M. J. S. Tevesz [eds.], *Animal-sediment relations*. Plenum.
- BERNER, R. A. 1980. *Early diagenesis: A mathematical approach*. Princeton Univ. Press.
- BOSWORTH, W. S., AND L. J. THIBODEAUX. 1990. Bioturbation: A facilitator of contaminant transport in bed sediment. *Environ. Prog.* **9**: 211–217.
- BOUDREAU, B. P. 1986. Mathematics of tracer mixing in sediments: I. Spatially-dependent, diffusive mixing. *Am. J. Sci.* **286**: 161–198.
- . 1994. Is burial velocity a master parameter for bioturbation? *Geochim. Cosmochim. Acta* **59**: 1243–1249.
- . 1997. *Diagenetic models and their implementation*. Springer-Verlag.
- GUINASSO, N. L., AND D. R. SCHINK. 1975. Quantitative estimates of biological mixing rates in abyssal sediments. *J. Geophys. Res.* **80**: 3032–3043.
- JUMARS, P., L. M. MAYER, J. W. DEMING, J. A. BAROSS, AND R. A. WHEATCROFT. 1990. Deep-sea deposit-feeding strategies suggested by environmental and feeding constraints. *Phil. Trans. R. Soc. London* **A331**: 85–101.
- , AND R. A. WHEATCROFT. 1989. Responses of benthos to changing food quality and quantity, with a focus on deposit feeding and bioturbation, p. 235–253. *In* W. H. Berger, V. S. Smetacek, and G. Wefer [eds.], *Productivity of the oceans: present and past*. Report of the Dahlem Workshop. Wiley-Interscience.
- MCCALL, P. L., AND M. J. S. TEVESZ. 1982. The effects of benthos on physical properties of freshwater sediments, p. 105–176. *In* P. L. McCall and M. J. S. Tevesz [eds.], *Animal-sediment relations*. Plenum.
- MIDDELBURG, J. J., K. SOETAERT, AND P. M. J. HERMAN. 1997. Empirical relationships for use in global diagenetic models. *Deep-Sea Res.* **44**: 327–344.
- RHOADS, D. C. 1974. Organism-sediment relations on the muddy sea floor. *Oceanogr. Mar. Biol. Ann. Rev.* **12**: 263–300.
- , AND L. F. BOYER. 1982. The effects of marine benthos on physical properties of sediments: A successional perspective, p. 3–52. *In* P. L. McCall and M. J. S. Tevesz [eds.], *Animal-sediment relations*. Plenum.
- SMITH, C. R. 1992. Factors controlling bioturbation in deep-sea sediments and their relation to models of carbon diagenesis, p. 375–393. *In* G. T. Rowe and V. Pariente [eds.], *Deep-sea food chains and the global carbon cycle*. Kluwer.
- THOMANN, R. V., W. MERKLIN, AND B. WRIGHT. 1993. Modeling cadmium fate at superfund site: Impact of bioturbation. *J. Environ. Eng.* **119**: 424–442.
- TROMP, T. K., P. VAN CAPPELLEN, AND R. M. KEY. 1995. A global model for the early diagenesis of organic carbon and organic phosphorus in marine sediments. *Geochim. Cosmochim. Acta* **59**: 1259–1284.
- WESTRICH, J. T., AND R. A. BERNER. 1984. The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested. *Limnol. Oceanogr.* **29**: 236–249.
- WHEATCROFT, R. A., P. A. JUMARS, AND A. R. M. NOWELL. 1990. A mechanistic view of the particulate biodiffusion coefficient: Step lengths, rest periods and transport directions. *J. Mar. Res.* **48**: 177–207.

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Determination of dissolved vanadium in natural waters by flow injection analysis with colorimetric detection

Abstract—A flow injection technique for the determination of dissolved vanadium in natural waters has been developed. The technique utilizes the vanadium-catalyzed oxidation of Bindschedler's green leuco base by bromate with tiron and tartrate as reaction activators. The reaction product is quantified colorimetrically. A chelator column of immobilized 8-hy-

droxyquinoline reduces matrix effects but can be eliminated if samples with a constant matrix are being analyzed. By using the chelator column, 1 ml of sample can be analyzed in <10 min with a detection limit of 0.2 nM. The method has been used successfully for the determination of dissolved vanadium in river and estuarine waters.

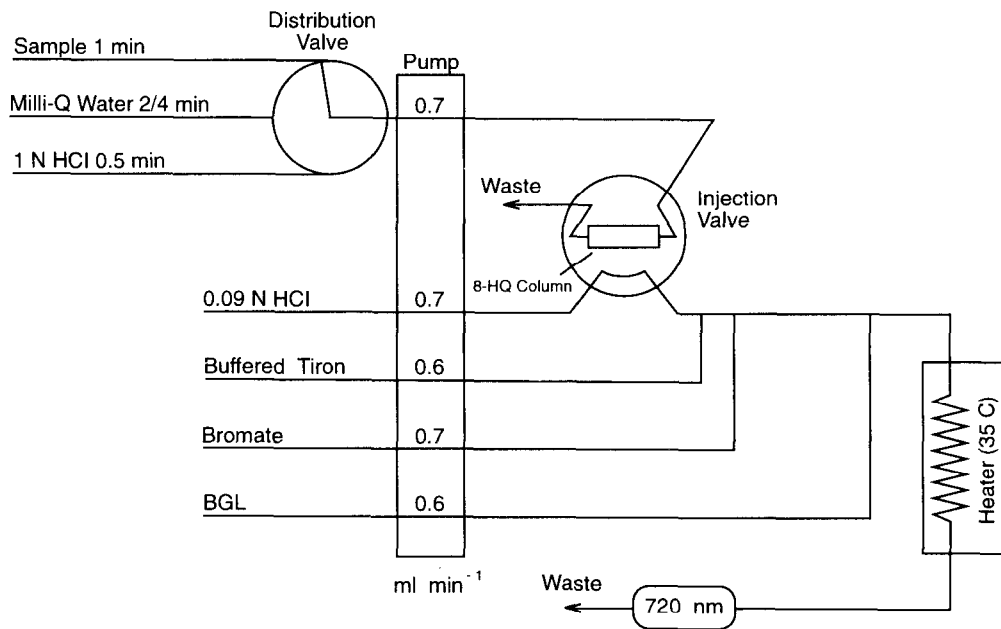


Fig. 1. Schematic diagram of the FIA colorimetric V analysis system.

Dissolved vanadium is found in nanomolar concentrations in natural waters (e.g. Collier 1984; Shiller and Boyle 1987). Redox chemistry, biological activity, and weathering all appear to play roles in determining this concentration range (Collier 1984; Shiller and Boyle 1987; Emerson and Huested 1991). Thus, there is the potential for studies of vanadium geochemistry to shed light on these processes. However, all of the studies cited above have used a time-consuming method for the determination of dissolved vanadium—coprecipitation followed by atomic absorption spectrophotometry. With a more rapid analysis technique, the understanding and use of vanadium geochemistry might proceed apace.

Because of the common availability of spectrophotometers as well as the ease with which one can build inexpensive colorimetric detectors for flow systems (e.g. Betteridge et al. 1978), we elected to pursue the development of a colorimetric flow injection analysis (FIA) method for determination of dissolved V. There are a variety of colorimetric V methods described in the literature. One frequently mentioned method is the gallic acid/persulfate colorimetric technique of Fishman and Skougstad (1964). However, even when modified to give better reproducibility (Weiguo 1983), the method requires a 40-min color-development time and 5-cm cuvettes for a detection limit of 4 nM. Kawashima and Nakano (1992) reviewed bromate-based catalytic colorimetric methods for V determination; these methods are generally rapid but also frequently suffer from iron interferences. Sugiyama and Hori (1992) described a continuous-flow system utilizing the catalytic effect of V on the bromate oxidation of Bindschedler's green leuco base (BGL). They reported a detection limit of 21 pM, without preconcentration, for the determination of V using a continuous-flow analysis system.

Because of the apparent ease, rapidity and sensitivity of the Sugiyama and Hori (1992) BGL-bromate method, we used it as the basis of our own FIA method. Initial investi-

gation of the method demonstrated that it is sensitive to variations in salinity and pH, in accord with previous workers' findings. However, we were unable to achieve the previously reported sensitivity. Therefore, we decided to modify the BGL-bromate method by adding an additional activator and adapting the technique for a FIA system incorporating a preconcentration column to eliminate interferences (e.g. Sakamoto-Arnold and Johnson 1987).

Previous work indicated that both sulfosalicylic acid (Nakano et al. 1986) and tiron (Hwang et al. 1985) can enhance the rate of bromate-based V catalytic methods. Preliminary work in our laboratory indicated superior results with tiron, and so the method was optimized with this reagent. The use of tiron improved sensitivity by ~20-fold. In addition, the method as described by Sugiyama and Hori (1992) utilizes a tartrate buffer; tartrate has previously been identified as an activator of V-catalyzed reactions (Bontchev 1972).

Figure 1 shows the reaction manifold that was constructed using 0.8-mm-i.d. PTFE tubing throughout, except for the pump manifold, which has PVC tubing. A Rainin Rabbit peristaltic pump propelled the various flow streams. The injection and distribution valves were formed by combining electrically activated Teflon 3-way valves (Bio-Chem Valve) that were controlled by an Onset Tattletale 4A microcontroller. The reaction coil was constructed by wrapping 300 cm of Teflon tubing around an inexpensive cartridge heater (Omegalux No. C406/120). The heater was maintained at ~35°C by a 12.6-V AC transformer. An additional 50-cm mixing coil was placed in the manifold immediately before the BGL entry point. The concentration column consisted of a 1.5-mm-i.d. piece of Teflon tubing filled with ~1 cm of polymer-immobilized 8-hydroxyquinoline (Landing et al. 1986) held in place with small plugs of Teflon wool. Colorimetric detection at 720 nm utilized a 1-cm path length flow cell in a Perkin-Elmer Lambda 2 spectrophotometer. However, the method provides a high enough

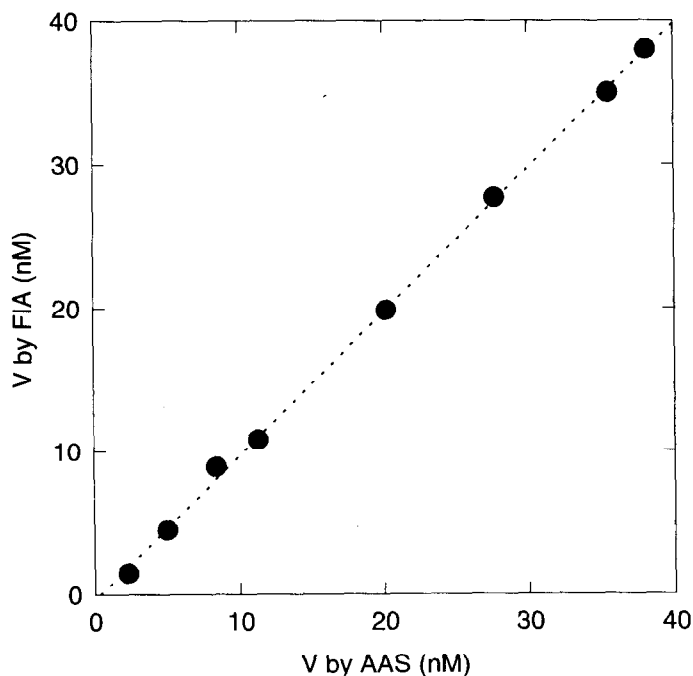


Fig. 2. Comparison of dissolved V analysis in filtered, acidified river samples as determined by colorimetric flow injection (this work) and graphite furnace atomic absorption following preconcentration by Co-APDC coprecipitation (e.g. Shiller and Boyle 1987). Dotted line is linear regression.

signal that a simple colorimetric detector (e.g. Betteridge et al. 1978) should provide adequate sensitivity. Note that the order of addition of reagents in the manifold is important. In particular, if the bromate and buffered tiron are mixed before the acid stream, precipitation in the flow stream is likely to result.

Unless specified, solutions were prepared from reagent-grade chemicals and water purified first by distillation and then by deionization in a Barnstead E-pure system (referred to as Q-water here). HCl was sub-boiling distilled. We were unable to locate a supply of BGL. However, the oxidized dye Bindschedler's green (BG) was obtained from Pfaltz and Bauer and reduced to the leuco base by stoichiometric addition of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$). Care should be exercised in this reduction as excess dithionite in the reagent will inhibit the reaction (2 mol of BG is reduced by 1 mol of dithionite). The BGL was prepared as a 5×10^{-4} M solution and was filtered prior to use. If kept in the dark at 4°C , it is stable for at least 1 week. The solution should be translucent, and the pH is adjusted to ~ 3.6 prior to use. The buffer activator is a combined solution of 0.15 M tartaric acid and 2% (wt/vol) tiron; it was filtered and then adjusted to pH 3.9 prior to use. A 4.8% (wt/vol) KBrO_3 solution was prepared daily. Reagents were degassed with helium immediately prior to use. The final pH of the flow stream should be 3.8 for optimum sensitivity.

To obtain optimum V extraction by the immobilized 8-hydroxyquinoline column, samples were adjusted to a pH between 8 and 9 prior to analysis. pH adjustment was accomplished using clean ammonium hydroxide prepared by bubbling ammonia in Q-water.

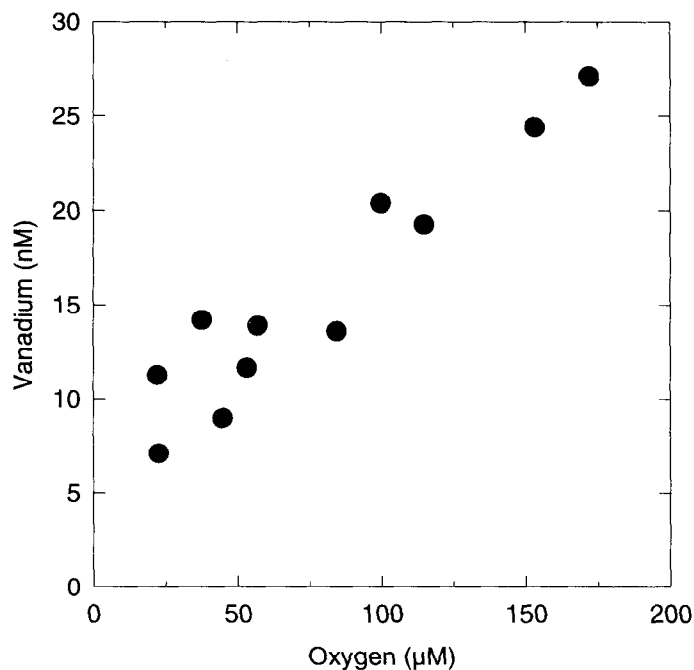


Fig. 3. Dissolved vanadium vs. oxygen in bottom waters of the Louisiana Shelf, July 1991.

Operation of the FIA system proceeds as follows. With the injection valve in the load position, cleaning acid (1 N HCl) is passed through the chelating column for 30 s to remove residual metals. Q-water is then passed through the column for 2 min to wash away residual acid. Sample or standard is then loaded for an appropriate amount of time—1 min for typical environmental concentrations (10s of nM)—after which an additional Q-water wash of 4 min removes residual salts from the chelator column. Finally, the injection valve is switched to the inject position allowing the 0.09 N HCl to elute the V into the reagent manifold. After 70 s the valve was switched back to the load position and the cycle repeated.

Using the above conditions (i.e. 1 min sample load), only ~ 1 ml of sample is consumed and an analysis cycle takes ~ 8.7 min. The detection limit (based on $3 \times$ the SD of the blank) was 0.2 nM. Four injections of 9.7 and 38.4 nM standards gave relative SDs of 0.7 and 0.2%, respectively.

Sugiyama and Hori (1992) examined the effects of possible interfering species on the BGL-bromate method. Major ions at seawater concentrations affected the reaction; however, our use of the chelator column eliminates this problem. Although we have not examined the effect of various strong complexing agents on the analysis, we would expect that any complexer that binds V with a strength ≥ 8 -hydroxyquinoline would interfere with the analysis. Of redox active species, only Fe was reported to interfere with the method at concentrations typically found in oxic waters (Sugiyama and Hori 1992). However, the addition of tiron reduced this interference and we found that $>1 \mu\text{M}$ Fe could be present in the reaction mixture with no significant effect on the absorbance of a 25 nM V sample. This interference test was performed without

the chelator column. We also found that seawater levels of Mo (105 nM) and 1 μ M Mn likewise did not interfere with the determination of V. Addition of a V(IV) spike to a sample produced the same result as addition of a V(V) spike; however, the oxidation of V(IV) is very rapid at the pH used for the chelator column extraction.

The method is sensitive enough so that if samples with the same matrix and pH are to be analyzed, the chelator column can be eliminated. Some adjustment of the pH of the reagents may be necessary in this case. For instance, in analyzing acidified seawater samples we used 0.02 N HCl as the carrier and adjusted the buffer to pH 4.0. A 250- μ l injection loop provided adequate sensitivity. For direct seawater analysis, standards should be made in V-free seawater, which can be made by running seawater through a column of immobilized 8-hydroxyquinoline.

We have used our V analysis system (with chelator column) to analyze a wide variety of river and estuarine samples. Fig. 2 shows a comparison between dissolved V in acidified river samples analyzed by this FIA method and by a preconcentration atomic absorption spectroscopy (AAS) method (Shiller and Boyle 1987). The slope of the regression line is not significantly different from 1, and there is no significant offset between the two sets of analyses.

Figure 3 shows an application of the technique to the study of V removal in oxygen-depleted estuarine waters. The figure shows dissolved V vs. O₂ in bottom waters of the Louisiana Shelf. The depletion of dissolved V in apparent conjunction with O₂ removal is consistent with the more particle-reactive nature of V(IV) than V(V) (e.g. Emerson and Husted, 1991).

The V analysis system described here is robust, easy to set up, and could therefore be used in the field. To date we have analyzed dozens of river samples and several estuarine transects. Results comparable to preconcentration AAS methods have been obtained rapidly and at low cost.

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References

- BETTERIDGE, D., E. L. DAGLESS, B. FIELDS, AND N. F. GRAVES. 1978. A highly sensitive flow-through phototransducer for unsegmented continuous-flow analysis demonstrating high-speed spectrophotometry at the parts per 10⁹ level and a new method of refractometric determinations. *Analyst* **103**: 897-908.
- BONTCHEV, P. R. 1972. Catalytic reactions—II. Activation. *Talanta* **19**: 675-685.
- COLLIER, R. W. 1984. Particulate and dissolved vanadium in the North Pacific Ocean. *Nature* **309**: 441-444.
- EMERSON, S. R., AND S. S. HUESTED. 1991. Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. *Mar. Chem.* **34**: 177-196.
- FISHMAN, M. J., AND M. W. SKOUGSTAD. 1964. Catalytic determination of vanadium in water. *Anal. Chem.* **36**: 1643-1646.
- HWANG, J. M., J. C. TSUNG, AND Y. M. CHEN. 1985. Catalytic spectrophotometric determination of vanadium by flow injection analysis. *J. Chin. Chem. Soc.* **32**: 405-410.
- KAWASHIMA, T., AND S. NAKANO. 1992. Flow-injection analysis of trace elements by use of catalytic reactions. *Anal. Chim. Acta* **261**: 167-182.
- LANDING, W. M., C. HARALDSSON, AND N. PAXEUS. 1986. Vinyl polymer agglomerate based transition metal cation chelating ion-exchange resin containing the 8-hydroxyquinoline functional group. *Anal. Chem.* **58**: 3031-3035.
- NAKANO, S., C. YAMADA, M. SAKAI, AND T. KAWASHIMA. 1986. Catalytic determination of nanogram amounts of vanadium by the oxidative coupling reaction of 4-aminoantipyrine with *N,N*-dimethylaniline. *Anal. Sci.* **1986**: 61-65.
- SAKAMOTO-ARNOLD, C. M., AND K. S. JOHNSON. 1987. Determination of picomolar levels of cobalt in seawater by flow injection analysis with chemiluminescence detection. *Anal. Chem.* **59**: 1789-1794.
- SHILLER, A. M., AND E. A. BOYLE. 1987. Dissolved vanadium in rivers and estuaries. *Earth Planet. Sci. Lett.* **86**: 214-224.
- SUGIYAMA, M., AND T. HORI. 1992. Air-segmented continuous-flow analysis for vanadium based on a catalytic reaction with Bindschelder's green leuco base. *Anal. Chim. Acta* **291**: 186-196.
- WEIGUO, Q. 1983. Determination of trace vanadium in water by a modified catalytic-photometric method. *Anal. Chem.* **55**: 2043-2047.

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