ELSEVIER

Analytica Chimica Acta 357 (1997) 99–102

ANALYTICA
CHIMICA
ACTA

Long pathlength absorbance spectroscopy: trace analysis of Fe(II) using a 4.5 m liquid core waveguide

Robert D. Waterbury, Wensheng Yao, Robert H. Byrne*

University of South Florida, Department of Marine Science, St. Petersburg, FL 33701, USA

Received 11 June 1997; received in revised form 15 August 1997; accepted 27 August 1997

Abstract

A Liquid Core Waveguide (LCW) can be used to extend the sensitivity of conventional absorbance spectroscopy by two or more orders of magnitude. Analysis of dissolved iron concentrations with a 4.47 m pathlength LCW made of Teflon AF-2400 provides a 0.2 nmol dm^{-3} detection limit and a linear response between 0.5 and 10 nmol dm^{-3}. No preconcentration is required in this analysis. The analytical procedures employed in long pathlength absorbance spectroscopy are amenable to miniaturization and autonomous operation. © 1997 Elsevier Science B.V.

Keywords: Iron; Analysis; Absorbance spectroscopy; Long pathlength spectroscopy; Liquid core waveguide

1. Introduction

The importance of iron in biological and geochemical systems [1,2] has sustained an intense interest in the development of sensitive and robust techniques for analysis of iron in natural waters. In spite of the abundance of iron in the earth's crust, the low solubility and high reactivity of ferric iron, in addition to the obligate role of iron in metabolic processes, limits dissolved concentrations in most natural aqueous systems to nanomolar levels. Analytical methods developed for the determination of iron include colorimetry [3,4], controlled-potential coulometry [5], and chemiluminescence analysis [6–11]. Among the reagents which have been used for colorimetric analysis, ferrozine (FZ) has gained wide acceptance due to its high solubility and the high selectivity of FZ for ferrous iron [3]. In spite of the simplicity of colorimetric analysis with ferrozine and the relatively high molar absorptivity of the ferrous–ferrozine complex (2.79×10^4 dm^3 mol^{-1} cm^{-1}) [3], colorimetric analysis with conventional spectrometers and 10 cm pathlength absorbance cells have a detection limit larger than 10 nmol dm^{-3}. Preconcentration techniques have been developed to improve detection limits [12–14]. However, this has resulted in greater analytical complexity and large sample volume requirements.

The sensitivity of absorbance spectroscopy can be improved by extending optical pathlength. Liquid core waveguides provide for long optical pathlengths by constraining light propagation within a liquid medium which has a higher refractive index (RI) than the surrounding solid tubing [15]. The first LCW [16,17] employed glass tubing (RI ~1.5) and a high refractive index liquid, bromobenzene (RI = 1.56).

---

*Corresponding author. E-mail: robert@caesar.marine.usf.edu

PII S0003-2670(97)00530-8

Subsequent applications [18,19] have also been confined to liquids with higher refractive indices than that of water (RI $\sim$1.33). There are very few materials which have an index of refraction less than that of water and even fewer which are chemically stable and inert. However, an amorphous fluoropolymer form of Teflon designated AF-2400 (Dupont), has an RI of $\sim$1.29 and many of the desirable chemical properties of Teflon [20]. An LCW constructed of Teflon AF-2400 with a water core provides total internal reflection for light rays intersecting the water/tubing interface at 19° or less, or a numerical aperture (NA) of 0.32.

In this work, use of a Teflon AF-2400 LCW is demonstrated for analysis of iron in aqueous solutions. The methods outlined in this work can also be used to extend the spectrophotometric detection limits of many other chemical species.

2. Experimental

An overview of the experimental setup for quantification of dissolved iron by long pathlength absorbance spectroscopy is shown in Fig. 1. The heart of the setup is a Teflon AF-2400 LCW (Biogeneral), with an inner diameter of 280 μm and an outer diameter of 530 μm. A 4.47 m length of LCW was coiled and placed in a 10 cm diameter chamber to prevent ambient light coupling into the LCW. A custom 'T' was designed to interface the LCW to an optical fiber (Polymicro Technologies 150 μm core diameter), and standard 5 mm ID silicon tubing (Fig. 1). This 'T' allowed insertion of the optical fiber in the Teflon AF-2400 tubing. Sample solutions entered and exited the LCW through an annular gap between the fiber and tubing. A CCD array spectrometer (Ocean Optics S1000-TR-1) and fiber-coupled tungsten halogen lamp (Ocean Optics LS-1) provided spectral absorbance measurements. Continuous sampling was achieved with a peristaltic pump (Ismatec, model 78016-30) at a flow rate of $\sim$ 0.3 cm^3/min. In order to avoid formation of bubbles in the system, the pump was active only during periods of sample introduction. Bubbles inadvertently introduced to the system are, however, easily flushed out by continuous pumping of sample.

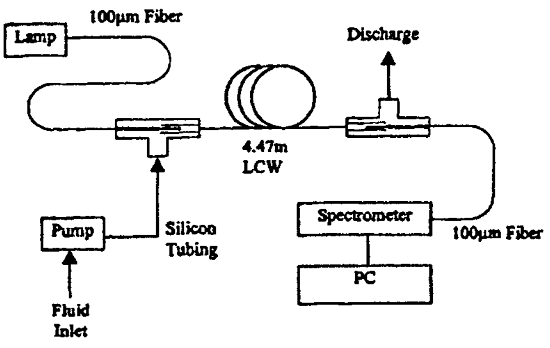

Fig. 1. Overview of LCW experimental setup.

All reagents were analytical-reagent grade unless otherwise noted and were used without further purification. Water was obtained as ion-exchanged Millipore Super Q (18 MΩ). Ferrozine (Sigma) reagent was prepared as a 0.01 M solution. Buffer solution (pH = 5.5) consisted of a 1 : 8 ratio of 6.9 M HCl and 5 M HAc/ammonia [21]. Ammonia and HCl used were trace-metal grade obtained from J.T. Baker. Fe(II) stock solution was prepared in 0.01 M HCl from ammonium iron(II) sulfate. Serial dilutions of the stock solution were used to construct a calibration curve. Each sample solution (100 cm^3) contained the desired amount of Fe(II), 0.2 cm^3 ferrozine reagent and 0.2 cm^3 buffer solution. Absorbance measurements of each sample were made relative to a reference solution containing no ferrozine reagent but identical to the sample solution in all other respects. All absorbance measurements were obtained at ambient laboratory temperatures. The absorbance peak of the Fe(II)-ferrozine complex (Fe(FZ)$_3$) at 562 nm was used for the determination of Fe(II) concentration. The Fe(FZ)$_3$ absorbance maximum coincides with the (480–700 nm) transmission window of water, thus minimizing the extent of light absorption by water. Absorbances were referenced to a non-absorbing wavelength (700 nm) in order to compensate for instrumental drift. Analysis of aqueous solutions for total dissolved iron (Fe(III) + Fe(II)), rather than Fe(II) alone, can be accomplished by including a reductant (such as hydroxylamine hydrochloride) in the mixed buffer solution [3]. Analysis of Fe(II) in the presence of Fe(III) may produce a slow reduction of Fe(III) by the Ferrozine reagent [22]. The work of Hong [23] indicated that the extent of Fe(III) reduction was on the order of 10% after a 10 min reaction period and approached a limiting value on the order of 25% for long time periods.

3. Results and discussion

The simple analytical apparatus and protocol used in this investigation provides a linear absorbance response for dissolved iron concentrations between 0.5 and 10 nmol dm^{-3}

$$\text{Absorbance} = (0.0071 \pm 0.0009) + (0.0106 \pm 0.0002) \times [\text{Fe(II)}]\ (\text{nM})$$

with $r^2 = 0.999$ ($n = 6$). The Fe(FZ)$_3$ molar absorbance obtained using a 4.47 m pathlength for a 5 nmol dm^{-3} Fe(II) sample was 2.71 × 10^4, in good agreement with the value, 2.79 × 10^4, determined with a conventional spectrophotometric cell [3]. The Fe(FZ)$_3$ molar absorbance obtained with a 2.75 m (LCW), based on six replicate measurements of a 5 nmol dm^{-3} Fe(II) sample (Fig. 2) was (2.76 ± 0.12) × 10^4. The Fe(II) detection limit for the Fig. 1 experimental apparatus, defined as three times the standard deviation of the measurement blank (deionized water + reagents), was 0.2 nmol dm^{-3}.

The sample size requirement for LCW analysis is very low. The internal volume of the LCW is ≈0.062 cm^3 per meter. As such, a typical 4.5 m LCW analysis requires < 0.3 cm^3. The practical upper limit pathlength for LCW analysis appears to be substantially larger than 4.5 m (i.e. 10–20 m). Light throughput is not a limiting analytical parameter for pathlengths of this magnitude. Pathlengths > 4.5 m were not used in our study due to flowrate limitations. Slow flow rates through 4.5 m × 280 µm tubing lead to transition times between samples on the order of 10 min. Transition times can be markedly reduced using larger bore LCWs. Increasing the LCW diameter to 560 µm reduced the transition times to ≈2 min.

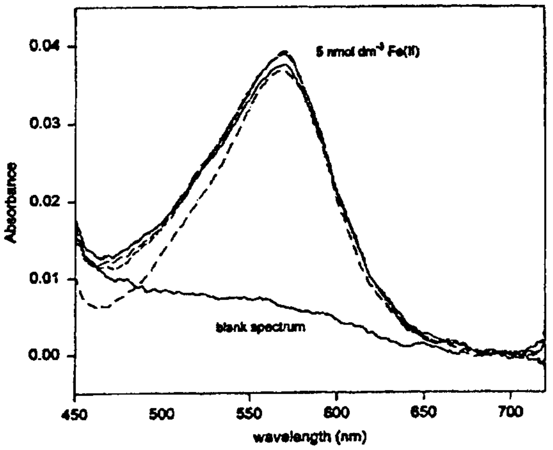

Fig. 2. Six replicate measurements of a 5 nmol dm^{-3} Fe(II) sample using a 2.75 m long LCM. The relative standard deviation obtained in this analysis was 5%. Also shown in the figure is a blank spectrum consisting of water + buffer + Ferrozine.

Most analytical environments are replete with potential sources of iron contamination. One of the most significant advantages of LCW absorbance spectroscopic iron analysis is its substantial simplicity. Only one step, addition of combined reagent to a sample, is a prerequisite to absorbance measurement. The absence of preconcentration steps considerably lessens the potential for sample contamination. Due to concerns about potential contamination of samples, our analyses were performed without filtration. Omission of a filtration step is the likely cause of an eventual loss of AF-2400 waveguiding properties for the 280 µm ID tubing over a period of two-to-three days. This behavior appears to be due to the presence of particulates adhering to the liquid core interface rather than chemical alteration since Teflon AF-2400 tubing is inert [20] to the types of chemicals used in our analyses. It should be noted that we have not experienced such waveguiding problems with larger bore tubing (560 µm ID), probably due to increased sample flushing rates.

4. Conclusions

The technique presented in this work can be used to markedly extend the detection capabilities of many existing solution-based measurements obtained via absorbance spectroscopy. The analytical apparatus required for this analysis is very simple and robust. The overall analysis is quite amenable to miniaturization and autonomous in-situ analysis. The spectrometer used in this analysis has a volume of 15 × 15 × 5 cm^3, and the 4.5 m LCW can be accommodated in a volume on the order of 25 cm^3. We are currently constructing an LCW module for autonomous operation in the upper ocean.

Acknowledgements

The authors wish to thank Ilia Koev of Biogeneral and Robert Altkorn of Northwestern University for their beneficial discussions. This work was supported by the Office of Naval Research under contract # N00014-96-1-5011.

References

[1] J.H. Martin, S.E. Fitzwater, Nature (London) 321 (1988) 341.
[2] S.R. Taylor, S.M. McLennan, in: The Continental Crust: Its Composition and Evolution, Blackwell Scientific Publications, Brookline Village, MA, 1985.
[3] L.C. Stookey, Anal. Chem. 42 (1970) 779.
[4] S.O. Pehkonen, Y. Erel, M.R. Hoffmann, Environ. Sci. Technol. 26 (1992) 1731.
[5] T.D. Waite, F.M.M. Morel, Anal. Chem. 56 (1984) 787.
[6] W.R. Seitz, D.M. Hercules, Anal. Chem. 44 (1972) 2143.
[7] L.L. Klopf, T.A. Nieman, Anal. Chem. 55 (1983) 1080.
[8] M.A. Nussbaum, H.L. Nekimken, T.A. Nieman, Anal. Chem. 59 (1987) 211.
[9] V.A. Elrod, K.S. Johnson, K.H. Coale, Anal. Chem. 63 (1991) 893.
[10] H. Obata, H. Karatani, E. Nakayama, Anal. Chem. 65 (1993) 1524.
[11] D.W. O'Sullivan, A.K. Hanson, D.R. Kester, Mar. Chem. 49 (1995) 65.
[12] H. Hong, D.R. Kester, Limnol. Oceanogr. 31 (1986) 512.
[13] D.W. King, J. Lin, D.R. Kester, Anal. Chim. Acta 247 (1991) 125.
[14] Z. Yi, G. Zhuang, P.R. Brown, R.A. Duce, Anal. Chem. 64 (1992) 2826.
[15] L. Wei, K. Fujiwara, K. Fuwa, Anal. Chem. 55 (1983) 951.
[16] J. Stone, J. Quantum Electronic 8 (1972) 386.
[17] J. Stone, App. Phys. Lett. 20 (1972) 239.
[18] F. Tsunoda, A. Nomura, J. Yamada, S. Nishi, Appl. Spectro. 44 (1990) 1163.
[19] K. Hong, L.W. Burgess, SPIE Proc. 2293 (1994) 71.
[20] W.H. Buck, P.R. Resnick, Dupont Technical Product Information, 1993.
[21] W.M. Landing, S. Westerlund, Mar. Chem. 23 (1988) 329.
[22] J.W. Murray, G. Gill, Geochim. Cosmochim. Acta 42 (1978) 9.
[23] H. Hong, Ph.D. Dissertation, University of Rhode Island, 1984.