



January 2007

Volume 3 Issue 4-6

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 3(4-6), 2007 [109-113]

Cobalt Determination In Fresh Waters Using Flow Injection With Luminol Chemiluminescence Detection



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Received: 22nd September, 2006

Accepted: 7th October, 2006

Web Publication Date : 21st December, 2006



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ABSTRACT

A simple and rapid and portable flow injection method is reported for the determination of Co(II) in fresh waters based on luminol CL detection in the absence of added oxidant. The detection limit (3s) was 0.1 nM with a sample throughput 60 h⁻¹. Under the optimum conditions the method provided a linear range for Co(II) between 1.0 - 10 nM ($r^2=0.9986$) with relative standard deviations (R.S.D) ($n = 4$) in the range 1.2 - 2.1%. The effect of interfering cations (Na⁺, Ca(II), Mg (II) , Zn(II), Cu(II), Fe(II), Fe(III) and anions (Cl⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, NO₂⁻) were studied on luminol CL system for Co(II) determination. The method was applied to spiked fresh water samples and the satisfactory recoveries were obtained (97±0.10% - 105±0.10%). © 2007 Trade Science Inc. - INDIA

KEYWORDS

Flow injection analysis;
Chemiluminescence;
Cobalt;
Fresh water.

INTRODUCTION

Cobalt is an essential micronutrient for aquatic organism e.g, it acts as a cofactor in the vitamin B₁₂ complex and is an essential element in some metalloproteins. The oceanic concentrations of cobalt are extremely low and it has been suggested that the element may act as a co-limiting nutrient for marine phytoplanktons^[1]. Cobalt is known to accu-

mulate in manganese nodules. It is only toxic to plants and mammals at relatively high concentrations (>17 uM) which are rarely observed in the aquatic environment^[2].

Cobalt is not a high reactive metal and is stable in air at normal temperature. It reacts with most organic and inorganic acids to form simple cobalt salts. Cobalt has major uses in petrochemicals and plastic industries as both hetero and homogenous catalyst.

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The cobalt available to all living organisms must have its origin in rocks and minerals.

The pollution of water with transition metals has increased dramatically in recent years as a consequence of the expansion of industrial activities. Transition metal ions are toxic when their concentration in water exceeds certain levels. Therefore, a rapid and convenient method for their simultaneous analysis in natural water samples has attracted much attention.

Chemiluminescence is the production of light by a chemical reaction in solution CL has many analytical applications^[3] and the advantage of CL include high sensitivity, a wide linear dynamic range and simple instrumentation. For analytical applications the rapid and transient nature of solution phase CL emission requires a rapid and reproducible mixing of sample and reagent for which FI is well suited^[3,4].

CL reactions are oxidative involving a range of organic molecules^[5]. The best known of these being luminol (5-amino, 2,3-dihydrophthaline-1,4-dione). The chemiluminescent oxidation of luminol to 3-aminophthalate with blue light emission (425 nm) by hydrogen peroxide, oxygen, hypochlorite, permanganate or perchlorate in an alkaline medium (pH 10-11) was reported in 1928^[6]. The reaction catalyzed by enzyme such as peroxidase and by number of divalent ions such as Cu(II), Co(II), Mn(II) and Fe(II) or ferricyanide is practically efficient^[7] e.g Burguera et al.^[8] reported a flow injection CL method for the determination of Co(II) and sulfide, detection limit for Co(II) were 0.1 and 0.6 pg with a 10 and 100 μ L sample loops, respectively. The relative standard deviation for 1 ng of cobalt was 1.5% ($n=5$). Olsson used a micropoxidase-catalyzed luminol reaction to determine hydrogen peroxide^[9].

Commonly used laboratory techniques for sub-nanomolar Co and Fe determination include electrothermal atomic absorption spectrometry (ETAAS) following filtration and extractive complexation^[10] and inductively coupled plasma mass spectrometry (ICP-MS)^[11]. ICP-MS and ETAAS are impractical because the instrumentation is bulky, expensive and sensitive and the preferred methods for Co and Fe are based on voltametry^[12,14], catalytic spectrophotometry^[15] and flow injection with liquid phase

Chemiluminescence detection (FI-CL)^[16-24] There is a need, however to develop a portable, onboard analytical methods owing to the problems of sample instability and contamination during transport and storage.

In the present work we describe a simple, portable FI-CL method for the rapid and selective determination of Co by its catalytic effect on the oxidation of luminol in the absence of added oxidant^[25] in fresh waters.

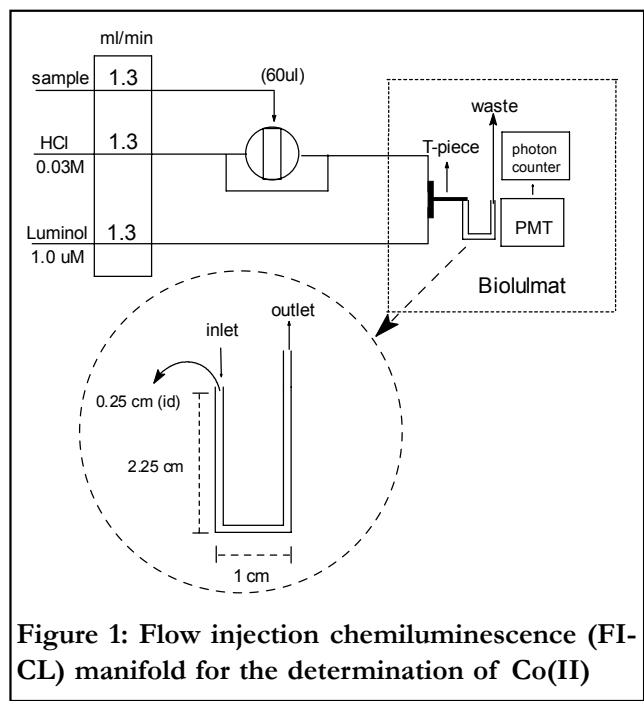
EXPERIMENTAL

Reagents

All plastic ware used during the experiments and for storage of reagents and standards was pre-cleaned with 20% HCl for a week, thoroughly rinsed with deionised water, stored in plastic bags to prevent contamination and used as required. All chemicals were of analytical-reagent grade, supplied by Merck BDH, England, unless stated otherwise. A Co(II) stock (0.001 M) was prepared by dissolving 0.0291 g of Co(II) $\text{NO}_3 \cdot 6\text{H}_2\text{O}$ in 100 ml of HCl solution (0.1 M) and subsequent standards were prepared daily by serial dilution of the stock with HCl solution (0.03 M). Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione, Sigma) stock solution (0.01 M) was prepared by dissolving 0.177 g in dilute sodium hydroxide solution followed by sonicating for 30 min. A working luminol solution was prepared by diluting the required volume in borate solution (0.1 M) and adjusting to pH 12 with sodium hydroxide solution. Standard solutions (1000 mg L^{-1}) of Na^+ , Ca(II), Mg (II), Zn(II), Cu(II), Mn(II), Fe(II), Fe(III) were prepared in HCl solution (0.1 M) and NO_3^- , NO_2^- and SO_4^{2-} and PO_4^{3-} were prepared in water and subsequent standards of each covering the range required were by serial dilution of the stock solutions with HCl solution (0.03 M).

Instrumentation and procedure

The flow injection chemiluminescence manifold used for this study is shown in figure 1. A peristaltic pump (four channels, Ismatic, Switzerland) was used to propel the sample and reagent solutions at a flow rate of 1.3 mL/min. A rotary injection valve



(Rheodyne 5020, UK) was used to inject Co(II) standards (60 μL) into the HCl (0.03M) stream and was merged at a T-piece with the CL reagent stream. The merged streams pass through a home-built U-shaped glass flow cell (2.5 x 55 mm, volume, 270 μL) placed directly in front of a side window photomultiplier tube (Biolumate junior, LB 9509, Berthold Technology, Germany). This instrument counts the photon generated in given period of time and display the result on the screen as relative light units (RLU). At the time of sample injection the start button is pressed and 30 sec is given to allow the streams to merge and produce light in front of the PMT and recorded as RLU. The whole instrument is battery powered and portable, can be used easily onsite.

RESULTS AND DISCUSSIONS

Optimization of FI manifold

The experimental conditions for the determination of Co(II) using luminol CL system, various parameters were investigated including buffer pH, reagent concentrations, sample volume and reagent flow rates. A univariate strategy was adopted in order to understand the effect of each variable on the reaction chemistry and system response. All these studies were performed with 0.1 μM Co(II) solution.

TABLE 1: Ranges investigated and optimized conditions for FI-CL manifold parameters (n=4)

Parameter	Range	Optimized
Borate buffer (0.1M) PH	10-13	12
HCl (M)	0.1-0.05	0.03
Luminol(M)	1×10^{-9} - 1×10^{-4}	1×10^{-6}
Flow rate (mL min ⁻¹)	0.6-1.5	1.3
Injection volume (μL)	30-150	60

The efficiency of luminol chemiluminescence is particularly dependent on reaction conditions. In the proposed FI-CL system, borate buffer pH was investigated in the range of 10 - 13. Maximum CL emission was observed at pH 12.0 (TABLE 1). Sodium hydroxide solution of different concentrations was also characterized to check the response of luminol (1.0 μM) for cobalt determination. Maximum CL signal was observed at 0.1 M sodium hydroxide, but this CL signal was lower (50 - 60%) as compared to borate buffer (pH 12). Therefore borate buffer (0.1 M, pH 12) was selected and used for subsequent studies. The effect of luminol concentration was then studied over the range 0.001 - 10 μM using the optimized borate buffer (0.1 M, pH 12) (TABLE 1) CL signal increased up to 10 μM . At 10 μM concentration of luminol, non-reproducible CL signals with high blank values were observed and therefore 1.0 μM , luminol concentration was selected for further studies. The effect of HCl on the determination of cobalt was investigated in the range 0.1 - 0.005 M. There was an increase in CL response up to 0.03 M was observed and further increase in HCl concentration reduced the signals. Therefore, 0.03 M HCl was used as a sample carrier stream.

The effect of flow rate on luminol CL intensity and reagent streams was studied over the range 0.6 - 1.5 mL min⁻¹ in terms of CL response, speed of analysis and reagent consumption. At a flow rate of 1.3 mL min⁻¹ (used for all subsequent experiments), maximum CL intensity was observed with a steady and reproducible background (TABLE 1). The effect of the sample volume on CL response was studied in the range of 30 - 150 μL . Maximum CL response was obtained at 60 μL (TABLE 1) and was used for all further studies.

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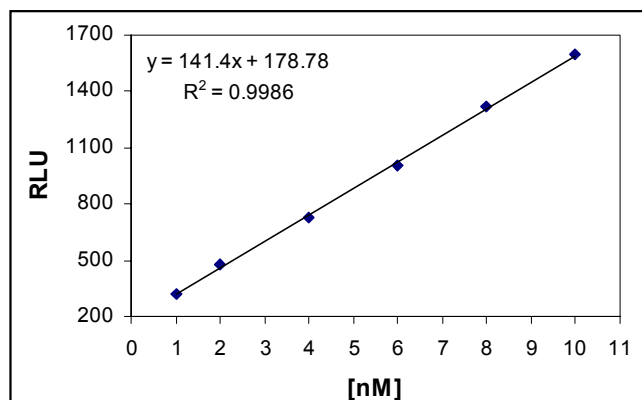


Figure 2: Calibration graph for the determination of Co(II)

Analytical figures of merit

Under the optimized conditions, a calibration graph of CL intensity versus Co(II) over the range of 1.0 - 10.0 nM was obtained as shown in figure 2. The correlation coefficient (r^2) was 0.9986 ($n = 6$) and the regression equation was $y = 141.4x + 178.78$ [$y =$ CL response (RLU), $x =$ concentration (nM)]. The limit of detection was 0.1 nM Co(II) with a sample throughput 60 h⁻¹.

Interferences

The influence of foreign species was investigated by analyzing a standard mixture solution of 1×10^{-8} M Co(II), to which the amount of interfering species were added, such as Na⁺, Ca(II), Mg(II), Zn(II), Pb(II), Cu(II), Fe(II), Fe(III), NO₃⁻, NO₂⁻, SO₄²⁻ and PO₄³⁻. Tolerable limit of foreign species was taken as relative error not greater than 5%. The experimental results showed that, Fe(II), Fe(III), Cu(II) were main cationic interferences. And other common species such as Na⁺, Ca(II), Mg(II), Zn(II), Pb(II), SO₄²⁻, PO₄³⁻ and NO₃⁻, NO₂⁻, had no effects under the concentration range present in fresh waters. The concentration of Fe(III) and Fe(II) and Cu(II) found to be low in fresh waters samples (Cu(II) 1.5×10^{-9} M, Fe(II) 1.1×10^{-8} M by graphite furnace atomic absorption spectrometry reference method). Therefore do not interfere.

Application to water samples

Samples were collected from three different sources, filtered through a membrane filter of 0.45- μ m pore size, adjusted the concentration to 0.03M

TABLE 2: Measurement of Co(II) in fresh waters samples

Sample No.	Added (nM)	Recovery (%)
A.	5	98.1
	10	104.2
B.	4	99.1
	8	102.1
C.	3	98.5
	9	105.1
D.	7	103.6
	15	104.9

HCl, spiked with Co(II), analyzed by the recommended procedure. As shown in TABLE 2, all samples analyzed provide satisfactory recoveries.

CONCLUSION

The proposed FI-CL method for Co(II) determination is simple and cheap and portable as compared to atomic absorption spectroscopy and ICP-MS methods described in the literature. The method described is rapid (60 h⁻¹ sample throughput) with a limit of detection of 0.1 nM. The method is based on enhancement of the luminol CL reaction with no added oxidant and does not need a preconcentration column. The method was applied to water samples with satisfactory results.

REFERENCES

- [1] G.A.Knauer, J.H.Martin, R.M.Gordon; Nature, **297**, 49-51 (1982).
- [2] G.N.Schrauzer; Cobalt-In: Merian E(Ed) 'Metals and their Compounds in the Environment, Occurrence, Analysis and Biological Relevance', VCH, Heidelberg, 879-892 (1991).
- [3] P.Fletcher, K.N.Andrew, A.C.Calokerinos, S.Forbes, P.J.Worsfold; Luminescence, **16**, 1-23 (2001).
- [4] P. J.Worsfold, E.P.Achterberg, A.R.Bowie, R.Sandford, V.Cannizzaro. in A.Gianguzza, A.Pelizzeti, S.Sammartana; (eds). Chemistry of Marine Water and Sediments; Chapter 16, Springer, Berlin, 394-396 and references cited therein (2002).
- [5] J.S.Woodhead, I.Week, A.K.Cambell, M.E.T.Ryall, R.Hart, A.Richardson, F.McCapra, M.Serio, M.Pazzagli; Editors 'Luminescent Assays Perspectives in Endocrinology and Clinical Chemistry', Raven

Full Paper

- Press, New York, 79 (1982).
- [6] S.G.Shulman; (eds.) 'Molecular Luminescence Spectroscopy', Part 3, Chap 1, Chemical Analysis Series, 77 (1993).
- [7] J.W.Briks; (Eds.) 'Chemiluminescence and Photo-Chemical Reaction Detection in Chromatography', VCH., New York, (1989).
- [8] J.L.Burguera, A.Townshend, S.Greenfield; Anal.Chim. Acta, 114, 209-214 (1980).
- [9] B.Olesson; Anal.Chim.Acta, 136, 113-119 (1982).
- [10] K.W. Bruland, R.P. Franks, G.A.Knauer, J.H.Martin; Anal.Chim.Acta, 105, 23-245 (1979).
- [11] J.F.Wu, E.A.Boyle; Anal.Chim.Acta, 367, 183-191 (1998).
- [12] M.GledHill, C.M.G.Van den Berg; Mar.Chem., 50, 51-61 (1995).
- [13] E.L.Rue, K.W.Bruland; Mar.Chem., 50, 117-138 (1995).
- [14] M.Vaga, C.M.G.VandenBreg; Anal.Chem., 69, 874-881 (1997).
- [15] C.I.Measure, J.Yuan, J.A.Resing; Mar.Chem. , 50, 3-12 (1995).
- [16] R.T.Powell, D.W.King, W.M.Landing; Mar.Chem., 50, 13-20 (1995).
- [17] K.Isshiki, E.Nakayama; Talanta, 34, 277-281 (1987).
- [18] C.M.Sakamoto. Arnold, K.S.Johanson; Anal.Chem., 59, 1789-1794 (1987).
- [19] T.Yamane, K.Watanabe; Anal.Chim.Acta, 207, 331-336 (1988).
- [20] H.Obata, H.Karatani, E.Nakayama; Anal.Chem., 65, 1524-1528 (1993).
- [21] A.R.Bowie, E.P.Achterberg, R.F.C.Mantoura, P.J.Worsfold; Anal.Chim.Acta, 361, 189-200 (1998).
- [22] J.T.M.Djong, J.Dendas, U.Bathmann, M.H.C.Stool, G.Kattner, R.f.Nolting, H.J.W-de Baar; Anal.Chim.Acta, 377, 113-124 (1988).
- [23] Y.Masaaki, T.Komatsu, S.Nakahara, M.Yamada, S.Suzuki; Anal.Chim.Acta, 155, 259-262 (1983).
- [24] S.Nakahara, M.Yamada, S.Suzuki; Anal.Chem.Acta, 141, 255-262 (1982).
- [25] L.L.Klopf, T.A.Nieman; Anal.Chem., 55, 1080-1083 (1983).