Cobalt Determination in Natural Waters Using Cation-Exchange Liquid Chromatography with Luminol Chemiluminescence Detection

Edward A. Boyle,* Brent Handy, and Alexander van Geen

Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A method has beed developed for the analysis of cobalt in natural waters by cation-exchange liquid chromatography using luminol chemiluminescence detection. Cobalt can be determined directly in freshwater samples on 500-μL samples with a detection limit of 20 pmol/kg; larger samples provide proportionately lower detection limits. Seawater samples can be analyzed on 100-mL samples following APDC solvent extraction; the detection limit of this method is 5 pmol/kg. The precision of the method is ±5%. The method should also be applicable to the analysis of V, Cu, and Fe in natural waters. Equipment is low in cost and transportable and can be used in the field.

Rapid and accurate analysis of trace metals in natural waters is essential to the study of earth surface geochemical transfer processes. Very little information is available on the distribution of cobalt in natural waters and the processes controlling its earth-surface geochemical behavior. The low concentration levels at which cobalt occurs in natural waters (10^{-11} to 10^{-9} mol/kg) leads to significant problems with analysis and contamination. In seawater, the limited available data indicate that cobalt is particle-reactive and that its distribution shows a rough similarity to manganese (probably because of its coprecipitation in manganese oxyhydroxides) (*1*, *2*). Little if any reliable data are available on cobalt behavior in freshwater systems.

In recent years, natural water trace-element analysis has been dominated by various methods of flameless atomic absorption spectroscopy (FAAS) because of its sensitivity, specificity, and multielement capability. Atomic absorption has disadvantages for certain applications; however: (1) the most capable instruments are relatively large, ruling out practical use in field work; (2) although FAAS is capable of analyzing many elements, analysis is usually done one element at a time; and (3) the cost is high, exceeding $75 000 for the most capable instruments. There are some methods which overcome these limitations; the most successful alternative approach has been gas chromatography of volatile metal chelates with electron-capture detection (*3*); this technique is sensitive, portable, and low in cost (about $10 000 for a very good instrument). But many metal chelates are unstable at the high temperatures required for sufficient volatility, and methods which appear to work at high concentration levels often fail at lower concentration levels. Direct chemiluminescence analyses with adequate sensitivity have been proposed for the analysis of cobalt in natural waters (*4–6*), but special care must be taken to avoid interferences in these methods.

Liquid chromatography (LC) shares many of the advantages of gas chromatography, with the additional advantage that analysis can be done at room temperature where problems of column denaturation and chelate decomposition are minimal. Because available LC detection methods are not very sensitive (hence requiring an impractical degree of preconcentration for analysis of metals occurring at 10^{-10} M and lower), this technique has not been routinely applied to metal analysis in natural waters. Some previous workers have suggested that the trace-metal-catalyzed chemiluminescence (CL) reaction of luminol (2-aminophthalhydrazide) could be used as a highly sensitive LC detector for metals (*7*, *8*). Initial work using this detection method was not encouraging. Metal chelates do not catalyze the reaction, so it is necessary to keep the metal in inorganic form (or possibly to decompose chelates upon elution). Chloride-complex anion chromatography was tested, but low column efficiencies and poor separation were obtained (perhaps because the LiCl eluent is so viscous), and concentrated HCl eluent rapidly degrades silica HPLC columns. Recently, improved methods of trace-metal cation-exchange chromatography using weakly complexing eluents have been developed (*9–12*). Since weak complexes do not severely depress chemiluminescence, it seemed appropriate to reexamine the use of LC/CL for trace metal analysis.

A number of specific problems had to be overcome to provide a successful method: (1) metal contamination from pumps had to be eliminated; (2) it was necessary to design a detector that provides high sensitivity with minimal noise; (3) reagent purification techniques had to be developed to reduce background chemiluminescence to a minimum; (4) a uniform and pulse-free postcolumn reagent introduction system was required. In this report, an LC/CL method for the analysis of cobalt on small (≤100 mL) natural water samples is described; preliminary tests suggesting probable extension of the method to Cu, V, and Fe analysis are described briefly.

EXPERIMENTAL SECTION

Apparatus. (*1*) *Pump Modification.* "Nonmetallic" LC pumps are available at present (although they were not upon initiation of this study). But it is not certain that they are free of metal contamination to the extent required by a highly sensitive detector. Most materials contain metal impurities which are released into aqueous samples, particularly at low pH. Given extreme conditions of pressure and friction inherent in high-pressure pumps, a reliable contamination-free pump might be difficult to construct. The design described in this report allows *any* LC pump to supply pressurized metal-free eluent, since it does not rely on the contamination characteristics of the pump. A dual-loop isolation system was constructed by using $^1/_{16}$ in. i.d. Teflon tubing and two six-port rotary injection valves (Cheminert) connected in series (Figure 1). The eluent is loaded into a 15-mL loop nearest the outlet end of the series; distilled water is loaded into a 15-mL loop nearest the pump. 2-Propanol (colored with methylene blue for visibility) is pumped into the top of the distilled water loop (a Gilson Model 603 pump with an Apple II+ controller was used in this work). 2-Propanol is used to minimize metal solubility and to maintain separation of the fluids through density contrast. The 2-propanol displaces distilled water from its loop, which in turn displaces eluent. A pressure relief valve is incorporated into

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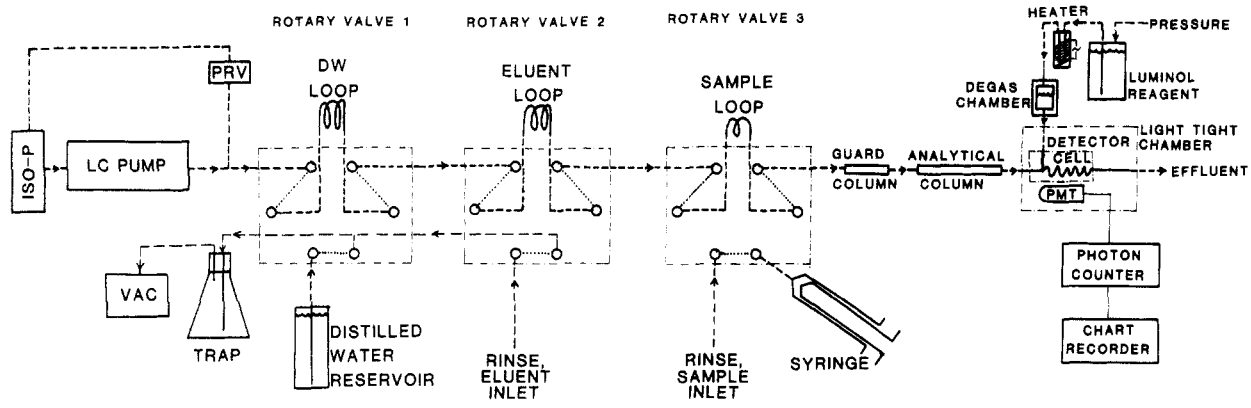

Figure 1. Trace metal liquid chromatographic system using chemiluminescent detection. Optional premixing system (not shown) can be placed within the light-light chamber just before the detector cell to optimize for elements where peak chemiluminescence lags initial mixing. The distilled water and eluent loops are horizontaly mounted to take advantage of density stratification to keep solutions separated. Rotary valves are shown in the "run" positions as used for chromatograms.

the 2-propanol inlet to prevent pressure from exceeding the 1000 psi limit of the Teflon tubing and rotary valves (although the valves are rated at 500 psi, they worked well up to 1000 psi). The eluent is directed into another six-port rotary injection valve which serves as the sample introduction loop. The size of the sample loop can be varied; in this work loops from 50 to 500 μL were used. The sample injector is connected to a guard column followed by the analytical column and detector.

All materials that come in contact with the eluent are either Teflon, Kel-F, or acrylic. These materials are not subject to friction and wear that would be expected from a conventional HPLC pump. The dead volume of the loop system also minimizes pressure pulsations from the pump. Filling the loops is a minor nuisance which can be minimized by using larger loops (hence requiring fewer refills) or programmed automatic injection valves. Small isolation loops are convenient for experimentation with modifications of the eluent.

(2) *Chemiluminescence Postcolumn Reaction Cell and Detector.* Design goals for the reaction cell were (1) minimize boundary-layer dead volume, (2) maximize the flux of photons into the photomultiplier tube without degrading resolution, (3) produce efficient mixing in order to maximize reaction rate and to minimize signal fluctuations due to inhomogeneities, and (4) allow for different rates of peak luminescence following initial mixing (since preliminary work indicated that the cobalt reaction occurred almost instantaneously while the copper reaction peaked after initial mixing).

Principal features of the cell design are illustrated schematically in Figure 2. Efficient mixing is produced by adaptation of the rotary mixing design described in ref 13, where liquids are introduced off-center into a cylindrical chamber; centrifugal action forces the fastest-moving fluid toward the walls of the container and boundary-friction-retarded fluid to move toward the center. Several cylinders are placed in series as close to the photomultiplier tube as the shutter will allow. An optional premixing chamber using the same mixing principle (not illustrated) can be used for reactions which peak some time after mixing, with a delay loop of $^1/_{64}$ in. i.d. Teflon tubing (to minimize peak spreading).

The cell is constructed by self-cementing several pieces of acrylic together with chloroform. Piece 1 has six cylindrical $^3/_{64}$ in. holes drilled into it. Connecting passages ($^1/_{64}$ in. wide) are made by milling channels between the cylindrical holes. Pieces 2 and 3 are then cemented together to seal the detector. Tapped Plexiglas fittings (pieces 4, 5, and 6) are cemented onto connecting holes to allow for flanged Teflon tubing connections (Cheminert). The final outside dimensions of the detector cell are $^1/_2$ in. width and 1 in. length. The CL chamber is mounted onto a larger piece of Plexiglas (not shown) to allow insertion into the housing of the photomultiplier tube.

(3) *Detector.* Photon counting provides lower base-line noise and higher sensitivity than could be obtained with the direct current mode on a Pacific Instruments Model 126D photon counter with 1P28 photomultiplier tube. The dark count rate was 200 counts per second (cps), which was much lower than

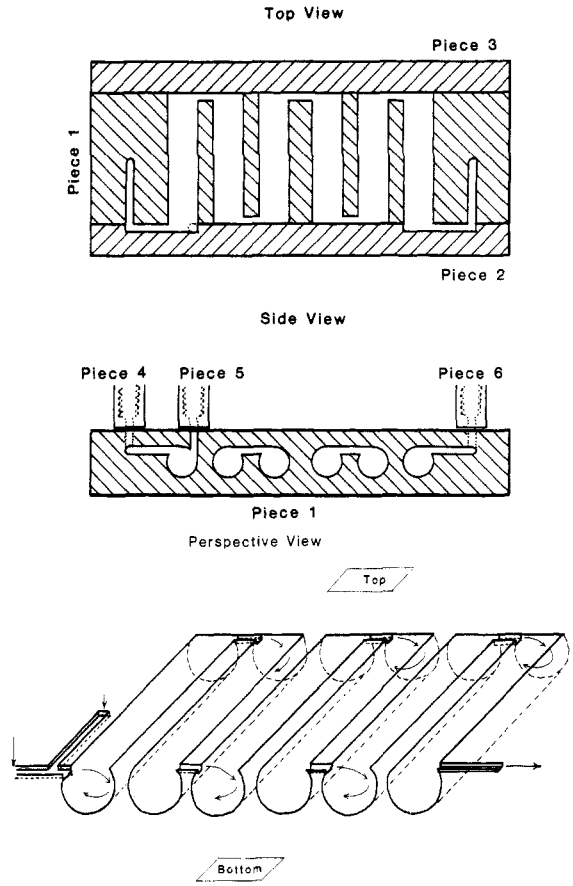

Figure 2. Schematic views of the chemiluminescence detector cell. Drawings are not to scale.

spontaneous emission by the luminol reagent (2000 cps). The observed base-line noise level was comparable to the theoretical counting statistics for this background (± square root of 2000); hence background emission is a principal limitation on scale expansion and detection limit.

(4) *Postcolumn Reagent Pump.* To eliminate contamination and pulsation, air was pumped into a sealed 1-L polypropylene container with a peristaltic pump. The resulting overpressure forces reagent into the reaction cell. Use of the peristaltic pump requires a waiting period to attain steady-state overpressure. Alternatively, a regulated gas cylinder could provide instantaneous overpressure. A similar strategy has been employed elsewhere (*14*).

(5) *Column and Guard Column.* Dionex HPIC-CG2 guard and HPIC-CS2 analytical columns were used in this work. The ability of this system to resolve a variety of metals has been documented in the manufacturers literature (*15*). A few other columns were

tested during this work, but the Dionex column provided best separation at a given flow rate.

The total cost of pumps, valves, photon counter, and columns used in this work is of the order of $10 000.

Reagents. Reagent background luminescence determines the system noise, hence limiting scale expansion and detection limit. Background luminescence can be lowered by minimizing metallic impurities. Residual chemiluminescence may occur even in catalyst-free systems; it is not clear how closely our precautions approach that limit. Standard oceanographic trace metal precautions were employed in preparation of reagents and cleaning of apparatus and bottles (see references quoted in ref 16).

(*a*) *Boric Acid/Potassium Hydroxide Buffer.* Reagent grade boric acid (7.5 g) is dissolved with 6.5 g of reagent grade potassium hydroxide per liter of distilled water. This solution is filtered through a 0.4-μm Nuclepore filter. This formula provides pH 10.8 buffer; the sensitivity for various metals is a function of the pH which therefore may be varied to optimize for particular elements. For example, in this eluent system, cobalt sensitivity may be increased a factor of 5 by increasing the pH of the buffer to 12 (*17*).

(*b*) *Luminol.* Luminol (2-aminophthalhydrazide) is purified by dissolution in a minimum volume of NaOH solution and precipitation by rapidly mixing into dilute HCl. This purification procedure was adequate for work described here and not always necessary for some batches of luminol; a more thorough discussion of luminol purification procedures can be found in ref 18.

(*c*) *Citric Acid/Oxalic Acid/Lithium Eluent.* Reagent grade citric acid and oxalic acid were prepared by slowly passing saturated solutions through a Chelex 100 ion-exchange column. The resin was cleaned in 6 N HCl, flushed with distilled water, and settled into the exchange column. The first acidic fractions of the eluent were discarded. Purified reagents were mixed and diluted with distilled water to produce a solution 0.1 M in oxalic acid and 0.075 M in citric acid; this solution was buffered to pH 4.1 by addition of concentrated LiOH solution. pH testing was done on small subsamples of the reagent to prevent metal contamination by the pH electrode. Eluent was prepared from this concentrated solution by mixing 1:10 with distilled water.

The final mixing ratio varies somewhat depending on the elution behavior of the column. Elution can be controlled in three ways: (1) Varying the eluent pH: Higher pH results in faster elution, because a higher proportion of the complexing agents are in their ionized form (which increases the proportion of metals complexed in solution relative to those adsorbed onto the column). The useful range of variation is pH 3.9–4.5. (2) Using a more aggressive cation: Cesium elutes peak about twice as fast as lithium. (3) Varying the concentration of the eluent: Increasing the concentration of the eluent results in faster elution. The elution rate of a given metal was observed to be a highly nonlinear function of the final concentration; a small percentage decrease in total concentration led to very large increases in elution time. While we have not explored the mechanism responsible for this nonlinearity, it may be due to the exchange stoichiometry of univalent Li for divalent metals, which should introduce a dependence on the $[Li]^2$:metal ratio. The relative elution of different metals also depends on the concentration of the eluent. Modifications of the basic elution scheme should be undertaken with caution.

Procedure. Luminol reagent is prepared daily by dissolving 100 mg of luminol in 1 L of buffer solution and adding 200 μL of 30% H_2O_2. This reagent is stable over at least a day; adding H_2O_2 at the outset allows background CL due to impurities to diminish before reagent is introduced into the reaction cell. The reagent flow pump is started and allowed to run for at least 15 min to attain steady-state overpressure. Typical reagent flow is 1.5 mL/min, but this may be varied to optimize sensitivity. If reagent flow is too low, sensitivity is reduced due to lowered pH and luminol concentration; if reagent flow is too high, sensitivity is reduced due to dilution of the peak. The signal is not overly sensitive to flow rate near the optimum mixing ratio.

The distilled water loop is filled by applying vacuum when the rotary valve is in position to draw distilled water into the loop. Vacuum is used to eliminate contamination that a pump might introduce. While the distilled water loop is being filled, the eluent loop is rinsed with dilute (0.1 N) pure HCl and filled with eluent (again, using a vacuum to draw both into the loop). The sample loop is rinsed with dilute HCl and then filled with the sample; a demountable syringe provides the vacuum for this step to allow for more control when filling the loop with very small samples. Each valve is place in closed position after the loops are filled (i.e., the valves are positioned between click-stop positions), and the vacuum is turned off. Valves are turned to their flow-through positions, and the LC pump is started (a flow rate of 1.0 mL/min results in a pressure of about 450 psi). The photon counter is set to a 3-s damping time constant (which is chosen to be close to the 2-s residence time of fluid in the detector) and the signal is monitored on a chart recorder. At the end of the chromatogram, the LC pump is stopped and valves are placed in closed (intermediate) positions to prevent flow of the 2-propanol into the column. A timer should be incorporated into the system to prevent flow of 2-propanol into the clean loops.

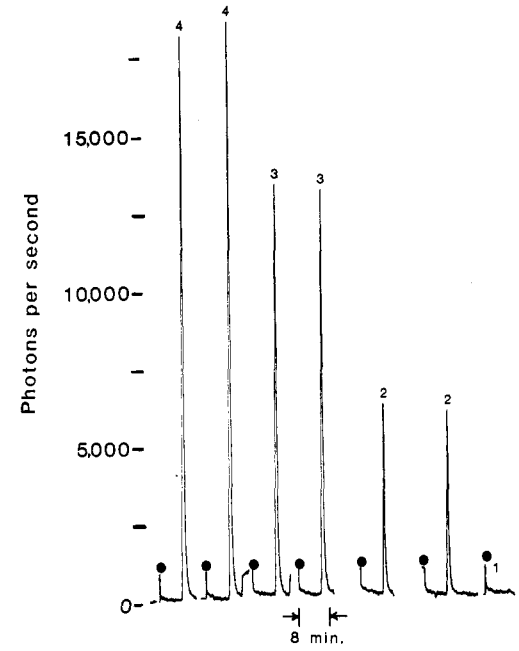

Figure 3. Chromatograms of dilute cobalt standards using the conditions outlined in the text. Note that the true base-line luminescence was 2000 cps; in this figure the vertical scale is shifted to subtract background luminescence. Peak 1 is 0.02 N HCl blank, peaks 2 are 13 nM Co in 0.02 N HCl, peaks 3 are 26 nM, and peaks 4 are 39 nM. Black dots signify beginning of chromatograms.

RESULTS AND DISCUSSION

Standard Chromatograms and Natural Water Analysis. Chromatograms of 50-μL cobalt standards in 0.02 N HCl are shown in Figure 3. The number of theoretical plates is 1500 as estimated from elution time and half-width of the peak (*19*). The sensitivity of the peak heights is 10 000 cps per 10^{-12} mol of Co; the detection limit (defined as twice the standard deviation of base-line noise, 2000 cps) is therefore 10^{-14} mol injected at the top of the column. This Co detection limit is 2 to 3 orders of magnitude lower than the most sensitive alternative detection system (PAR postcolumn reaction with optical absorbance detection (*10*).

Since the peak elutes over approximately 0.5 mL of eluent (30 s), higher resolution columns could provide better detection limits. Fluid residence time in the detector is 2s (70 μL volume divided by 2.5 mL/min total flow of eluent and luminol reagent), so better columns could provide an order of magnitude improvement in signal with the current detector geometry. If even higher resolution columns were available, the volume of the detector could be reduced, but the gain in luminescence due to higher eluting concentrations would be offset by the decreased volume seen by the photomultiplier. Even so, the detection limit would decrease in proportion to the square root of the detector volume because of reduced background luminescence.

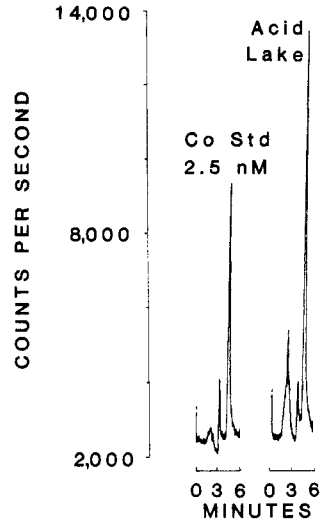

Figure 4. Chromatograms of a 500-μL freshwater sample from an acid lake in upstate New York.

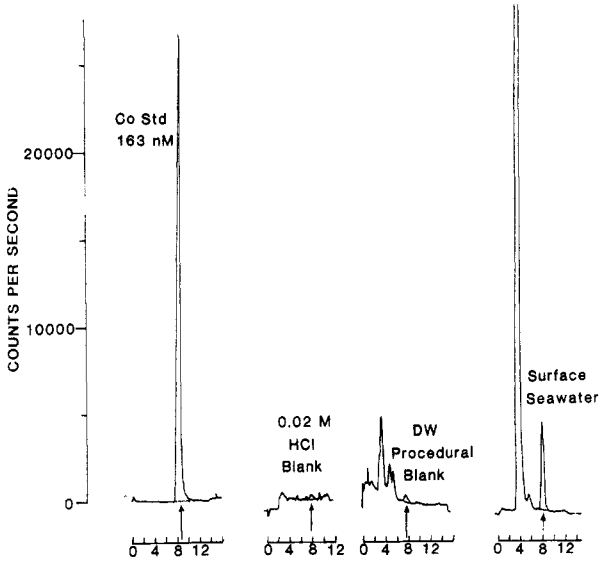

Figure 5. Chromatograms run at sea aboard the R/V *Endeavor*. Ordinate is chromatogram time in minutes. At left, a standard in 0.02 N HCl is shown, then a 0.02 N HCl system blank, followed by the chromatogram of a distilled water sample taken through the complete extraction procedure, and finally, a chromatogram of a 50-μL extract from 10 mL of surface seawater (150 pmol/kg cobalt) collected off the northeast U.S. (Table I). Arrow indicates the location of the cobalt peak.

Filtered freshwater samples can be analyzed for Co directly without prior preconcentration. In solutions with no cations or anionic complexing agents capable of elution, metals are retained at the top of the column. Peak height (or area) is then proportional to sample size and can be increased arbitrarily. In real freshwater samples with minor amounts of such eluting agents, a substantial degree of enrichment is still possible. A chromatogram of a 500-μL sample from Moss Lake, New York State (43°48′N, 74°52′W) is shown in Figure 4. The sample was also analyzed by direct injection graphite furnace atomic absorption spectroscopy after evaporative preconcentration; the GFAAS analysis (representing *total* cobalt) gave 4.1 nmol/kg compared to the LC/CL result of 3.8 nmol/kg; the difference is probably not significant. No detectable system blank appeared when 500 μL of 0.02 N HCl was run as a sample; this implies that the blank does not significantly exceed the detection limit.

This technique for the analysis of cobalt in freshwater samples will respond to the ionic form, and its labile inorganic complexes and organic complexes that are weak compared to the binding strength of the column. It will not respond to strong or irreversibly bound organic complexes. In principle the combination of this technique with methods for the destruction of strong complexes (*12*) may provide partial speciation information, at least to the extent of distinguishing these broad categories. In normal fresh surface waters, we have not yet observed interferences in total cobalt analyses, but we have found interferences due to dissolved organic carbon in the analysis of organic-rich pore waters from lake sediments. In this case, and other situations where high organic concentrations are encountered (but a total cobalt analysis is desired), it is necessary to destroy the organic matter by oxidation or irradiation treatment (*12*).

Cobalt cannot be analyzed directly in seawater. Seawater cations are more aggressive eluents than lithium citrate/tartrate, so cobalt elutes with the solvent front. For seawater analysis, cobalt must be separated from salt. In this work, a double APDC/CCl_4 solvent extraction from 100-mL samples was employed. Solvent was evaporated off and the chelate decomposed by fuming with 2 N HNO_3 on a hotplate at low heat in flowing clean air, and the residue was dissolved in 500 μL of 0.02 N HCl. Fifty microliters of this solution was analyzed. A typical chromatogram is shown in Figure 5. The recovery efficiency was 90% as monitored by standard additions. A procedural blank was determined by extracting 100 mL of distilled water; on this occasion the procedural blank was equivalent to 12 pmol/kg. Once the recovery efficiency of the extraction procedure is determined, the samples can be quantified by using standards in 0.02 N HCl, since there is no difference in peak height for concentrate matrix relative to dilute 0.02 N HCl. The detection limit is 5 pmol/kg. Resolution of the column decreases over time when running these samples due to the retention of noneluting species in the concentrates. Efficiency can be restored by passing concentrated (10×) eluent through the column and resuming analysis when the peak shape of dilute 0.02 N HCl standards returns to normal (since initial leakage of concentrated eluent from the column voids degrades peak shapes). Following this procedure, the sensitivity remains nearly constant over a period of 10 h. Occasional injection of standards is recommended to compensate for drift and resolution degradation.

Table I. Cobalt Data for Surface Seawater Obtained Aboard the R/V *Endeavor*, August 24–September 2, 1984

ID no.	latitude, longitude	temp, °C	salinity, ppt	amt of cobalt, pmol/kg
1	41°00′N 71°00′W	20.2	32.060	108
2	40°51′N 70°49′W	22.2	32.784	179
4	40°41′N 70°24′W	21.3	32.571	307
5	40°35′N 70°10′W	21.8	32.988	263
6	40°30′N 69°56′W	22.8	33.815	124
7	40°24′N 69°42′W	23.2	32.691	302
8	40°18′N 69°28′W		34.016	159
11	40°07′N 69°09′W		32.663	132
12	39°55′N 68°41′W	23.1	33.575	219, 205
18	39°22′N 67°34′W	25.4	34.879	71, 74
22	38°54′N 66°44′W	26.1	34.509	91

There are a number of other peaks in the seawater concentrate chromatogram. The peak near the solvent front is probably nonretained vanadate; a small peak (copper?) sometimes appears just before the Co peak, and another peak (Fe(II)?) follows several minutes after the Co peak. The complete extraction and analysis procedure was carried out at sea in August 1984 aboard the R/V *Endeavor* (Table I). The results of these analysis of seawater are comparable to other analysis of cobalt in surface seawater (*1*). The reproducibility was tested by duplicate analysis of a few samples

Table II. Detection Limits[a] Inferred from Multiple-Element Chromatogram Compared To Typical Seawater Values

element	peak height sensitivity, cps per nM	inferred direct detection limit (dilute soln), nM	inferred 100:1 DL, nM	seawater range, nM
V	610	0.15	0.0015	20–35
Cu	470	0.3	0.003	0.5–7
Co	3300	0.04	0.0004	0.01–0.2
Fe	320	0.3	0.003	0.1–0.5

[a] Note: detection limit (DL) is inferred as twice the standard deviation of the base-line noise; 100:1 DL is that attainable after a 100:1 preconcentration.

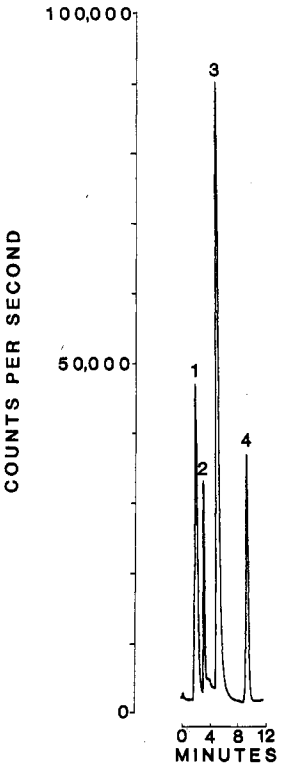

Figure 6. Chromatogram of a 500-μL solution containing (1) vanadium (74 nM), (2) copper (64 nM), (3) cobalt (26nM), and (4) ferrous iron (110 nM). For this chromatogram, the luminol reagent was at pH 10.6. Flow programming was employed; the eluent flow rate was 0.5 mL/min for the first 5 min and 2.0 mL/min for the next 7 min.

and was about 5% at 70 and 200 pmol/kg.

Potential Extension to Other Elements. This chromatographic technique is known to resolve several other trace metals, and luminol chemiluminesces in response to a number of these elements. As a test of the potential determination of other elements by this detection technique, a mixed vanadium–Cu^{2+}–Co^{2+}–Fe^{2+} standard in 0.1 M HCl solution is shown in Figure 6. Vanadium elutes just after the solvent front; copper, cobalt, and Fe(II) are easily resolved from one another, as documented previously for this column/eluent system. Calculated detection limits from this experiment are below typical quantities of these elements in 100 mL of seawater after 100:1 preconcentration (Table II).

The signal due to copper increases by a factor of 5 when solutions are heated to 60 °C; the cobalt signal is unaffected by increased temperature. Excessive heating of reagents can increase noise in the base line and signal due to degassing of the reagent in the high-velocity zones of the detector cell. This problem is eliminated by incorporating a degassing device after the heater. A short length of Goretex tubing (expanded poly(tetrafluoroethylene)) proved to be an effective degassing device.

It appears that all of these elements could be analyzed in seawater by solvent extraction followed by LC/CL of the digested extract. Alternate separation techniques (e.g., anion chromatography for vanadium or chromium species) may also be possible. As with any chromatographic method, extension to each new element or medium requires careful study to prove that interferences due to coeluting metals, anomalous chromatographic behavior, or detector suppression are not present. The above experiment must then be considered as a demonstration of the potential of the column/detector system for trace analysis of these metals in an appropriate matrix. At this time, we do not claim to be able to analyze natural waters for elements other than Co, but it is probable that further work will unlock this potential.

ACKNOWLEDGMENT

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Registry No. H_2O, 7732-18-5; Co, 7440-48-4; V, 7440-62-2; Cu, 7440-50-8; Fe, 7439-89-6; luminol, 521-31-3.

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