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The Concentration and Separation of a Trace Amount of Cobalt(II) in Sea Water as Its 1-Nitroso-2-naphtholate by Extraction Chromatography

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Synopsis. The behavior of a trace amount of cobalt(II) in extraction and back extraction has been examined with 1-nitroso-2-naphthol in carbon tetrachloride, and the results have also been applied to the concentration and separation of a trace amount of cobalt(II) in sea water as its 1-nitroso-2-naphtholate by extraction chromatography.

Extraction chromatography has been proved to be a powerful technique in the mutual separation of various metals,[1] because the extraction and back extraction may repeatedly accompany it during the process in the chromatographic column. However, this technique has not yet been applied to the concentration and separation of trace amounts of metals in natural waters. In this investigation, the behavior of a trace amount of cobalt(II) in extraction and back extraction with 1-nitroso-2-naphthol in carbon tetrachloride has been examined in detail, and the results have also been applied to the concentration and separation of a trace amount of cobalt(II) in sea water by using a Kel-F column, with 1-nitroso-2-naphthol in carbon tetrachloride as the stationary phase.

Experimental

The experimental procedures for the liquid-liquid extraction and the extraction chromatography were the same as have previously been described.[2,3] 1-Nitroso-2-naphthol was purified by recrystallization from cold petroleum ether. The behavior of cobalt(II) in extraction and extraction chromatography was checked by using a ^{60}Co tracer. The chromatographic column was prepared as follows: to 6.0 g of Kel-F powder of 42—80 mesh, a 15-ml portion of a solution containing 10^{-2} M 1-nitroso-2-naphthol in carbon tetrachloride was added. The mixture was then stirred until it became homogeneous. After having then stood for one night, the mixture was poured into a column which had been filled with a pre-equilibrated eluting solution of pH 3.8. The chromatographic column bed thus prepared (20—22 cm in height) was washed with 50—200 ml of the eluting solution of pH 3.8 at the flow rate of 1.0 ml/min in order to eliminate the excess organic solution. A solution containing a trace amount of cobalt(II) ($<10^{-5}$ M) with the ^{60}Co tracer was then poured onto the column, and the cobalt was collected on the column by passing through an aqueous solution of pH 3.8 at a flow rate of 0.6—4.0 ml/min. The cobalt was strongly held in the stationary phase, but was finally washed down as cobalt chelate in carbon tetrachloride by passing 30 ml of acetone through the column, because the cobalt was not eluted even with a concentrated HCl solution.

Results and Discussion

First of all, the behavior of a trace amount of cobalt(II) in extraction and back extraction has been studied with 10^{-5}—10^{-2} M of various chelating agents in carbon tetrachloride. The results (Fig. 1) revealed that 1-nitroso-2-naphthol gave rise to an extraction behavior of cobalt(II) similar to that of STTA;[4] that is, the back extraction of the cobalt chelate extracted did not occur at all even when the organic phase was shaken with an aqueous solution of 12 M HCl and of 1 M NaOH, by both of which other interfering ions, such as iron(III), nickel(II), and copper(II), and the free ligand could be stripped out from the organic phase. This abnormal behavior of cobalt chelates seems to be caused by the formation of certain inert complexes such as trivalent cobalt chelates.[5] The quantitative extractability of cobalt(II) (trace—10^{-4} M) is attained in about one minute's shaking, and the volume of the initial aqueous solution seems to have no effect on the extraction recovery of cobalt(II), even at a fourteen-fold volume of the organic phase (Fig. 2). On the basis of the experimental results described above, the chromatographic behavior of a trace amount of cobalt(II) was

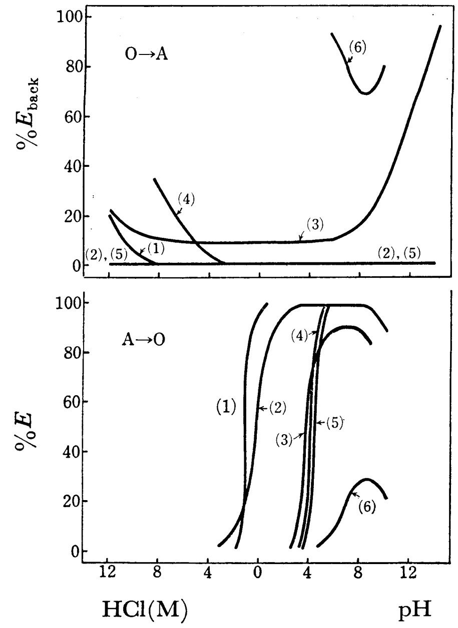

Fig. 1. Effect of pH or HCl(M) on the extraction and the back extraction of a trace amount of cobalt(II). $10^{-5}-10^{-2}$M chelating agents–carbon tetrachloride system.

Chelating agents: (1) 10^{-2}M NaDDTC (sodium diethyldithiocarbamate), (2) 10^{-2}M 1-nitroso-2-naphthol, (3) 10^{-2}M cupferron, (4) 10^{-4}M dithizone, (5) 10^{-3}M STTA, (6) 10^{-2}M TTA

Shaking time: 30 min, O→A: Back extraction, A→O: Extraction

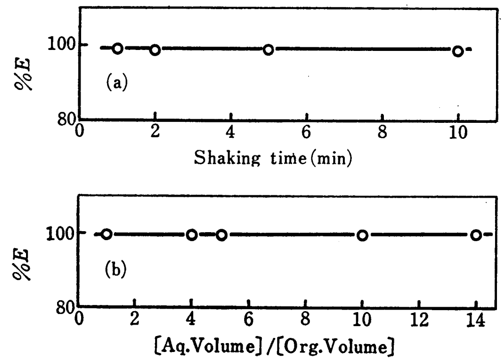

Fig. 2. (a) Effect of shaking time. (b) Effect of the volume of the aqueous phase.
Co(II): Trace—10^{-4}M, 1-nitroso-2-naphthol: 10^{-2}M, solvent: carbon tetrachloride, pH 4.0

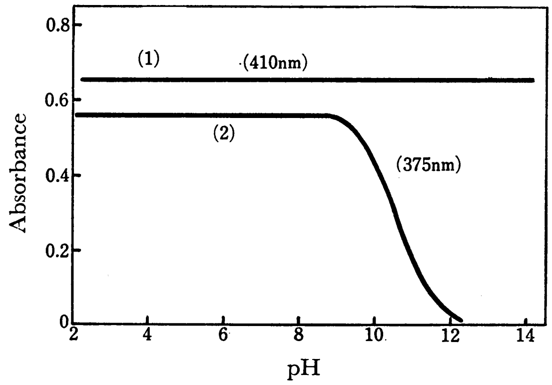

Fig. 3. Back-washing of 1-nitroso-2-naphthol and its cobalt chelate in carbon tetrachloride with an aqueous solution of different pH/acidity.
(1): 2×10^{-5}M Cobalt chelate, (2) 10^{-4}M 1-nitroso-2-naphthol.

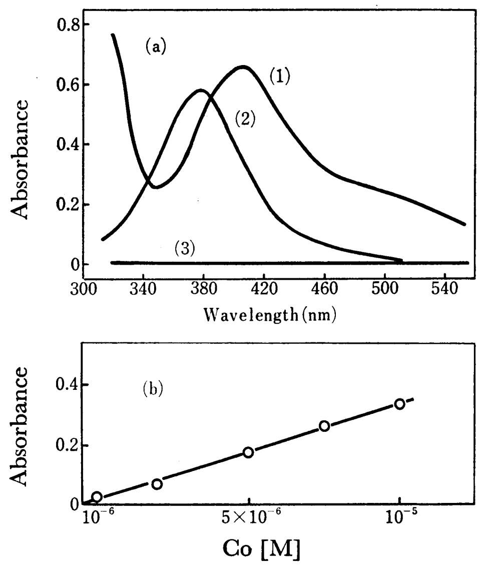

Fig. 4. (a) Absorption spectra of 1-nitroso-2-naphthol and its cobalt chelate in carbon tetrachloride after back washing of the organic phase with a solution of 1M NaOH. (1): 2×10^{-5}M Cobalt chelate after back washnig, (2): 10^{-4}M 1-nitroso-2-naphthol before washing, (3): 1-nitroso-2-naphthol of (2) after back washing.
(b) Working curve for cobalt(II) at 410 nm.

studied by means of the Kel-F column, which consists of 8.3 ml of 1-nitroso-2-naphthol in carbon tetrachloride as the stationary phase and of 3.8 ml of an eluting solution as the mobile phase; it was loaded with 50 ml of a pre-equilibrated test solution of pH 3.8 at the flow rate of 0.6—4.0 ml/min, followed by 50—1000 ml of acidified sea water of pH 3.0—4.0 containing a trace amount of cobalt(II) with a ^{60}Co tracer at the flow rate of 0.6—2.0 ml/min. When the sea water was passed through the column, it turned the upper side of the column bed pink, and the length of the band expanded to 5 cm for 400 ml of the effluent, 8 cm for 600 ml of the effluent, and 11 cm for 800 ml of the effluent. It was found that 30—40% of 1-nitroso-2-naphthol in the stationary phase flowed down for about 400—500 ml of the effluent. This fact—that is, the loss of 1-nitroso-2-naphthol from the stationary phase during the chromatographic process—is a weak point in extraction chromatography and may decrease the usefulness of the column for the concentration of a trace amount of cobalt(II) in sea water. In all cases, the cobalt in about 1000 ml of sea water and a distilled water was collected quantitatively with the use of the Kel-F column and was not eluted, not even with a concentrated HCl solution, as could have been predicted from the extraction behavior. The cobalt was finally washed down as metal chelates, together with the excess 1-nitroso-2-naphthol in carbon tetrachloride, by passing 30 ml of acetone through the column. When the organic phase was shaken with a 1 M NaOH solution, the excess of the free 1-nitroso-2-naphthol was almost entirely transferred into an aqueous solution, leaving only the cobalt chelate in the organic phase (Fig. 3). The cobalt chelate with 1-nitroso-2-naphthol could be determined selectively by measuring its absorbance in carbon tetrachloride at 410 nm with a 1 cm quartz cell (Fig. 4), as has briefly been pointed out in a previous short communications on the determination of cobalt(II) in sea water.[6] The recovery of cobalt(II) was about 97—99% under the conditions of this investigation.

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