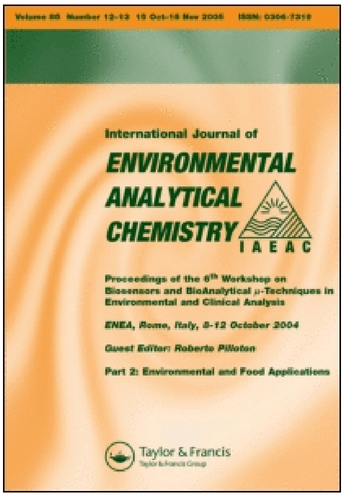

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A COLORIMETRIC METHOD FOR TRACE LEVEL DETERMINATION OF COBALT IN NATURAL AND WASTE WATER SAMPLES

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A colorimetric method which can be used to determine concentrations of cobalt as low as 0.1mg/L in natural and waste water samples is developed. This method involves the complexation of cobalt with 1-nitroso-2-naphthol-3,6,disulfonic acid disodium salt at the pH of 6.0, and the measurement of the absorbance of the colored complex at 520 nm. The interference by other metals as well as common anions was also investigated. Under the conditions employed, cobalt determination was found to be free of any interference by various metal ions and anions. The effect of digestion process using the E.P.A procedure 3030E was also investigated. On synthetic samples, the results on the determination of cobalt in digested and undigested samples were same within experimental error showing the digestion procedures did not hinder the applicability of the method to environmental samples. The method was then applied to actual waste water samples to determine the concentration of cobalt. Greater than 98% recovery of cobalt was obtained using the method developed, and better than 96% agreement between the concentrations of cobalt determined using this method and the atomic absorption spectroscopy was obtained. The method is applicable for the detection of cobalt at concentrations in environmental samples as low as 0.1 mg/L with greater than 95% accuracy, and is proposed to be used as a standard method for a rapid on-site analysis of cobalt in water and waste water samples.

Keywords: Cobalt analysis; colorimetric method; waste water

INTRODUCTION

Cobalt is widely used in industry for a variety of purposes with world wide consumption of cobalt reaching approximately 25,000 metric tons per year.[1] The largest consumption of cobalt is in the metallic form in the manufacturing of permanent magnetic alloys.[2] Various cobalt catalysts are used in a variety of industrial processes.[3–10] Another important use of cobalt is in the form of salts as highly effective driers for lacquers, enamels and varnishes. Different combina-

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tions of cobalt salts are used as ceramic pigments.[11,12] Invisible ink, cosmetics and high antiknock gasolines are other industrial uses of cobalt salts.[13]

Such industrial activities can lead to the presence of cobalt in industrial waste waters and leachates at concentrations which could be higher than the limits set by the regulatory agencies. Title 22 California code of regulations sets the Soluble Threshold Limit Concentration (STLC) of 80 mg/L and Total Threshold Limit Concentration (TTLC) of 8000 mg/L for cobalt and its compounds.[14] In the case of copper mining alone, up to 450,000 kg of cobalt has been recovered annually from copper leach solutions.[3,4] Toxic concentrations of cobalt have been reported in natural waters (rivers, lakes, bays, etc.) in the proximity of various industrial sites.[15] A study in Egypt showed that an average cobalt concentration of 100 μg/L was found at El Manzala lake.[16] Similar studies have also been conducted in Germany,[17] India[18] and Cuba.[19] In all of these cases, the industrial activities in the area were responsible for the contamination of the natural and waste waters with hazardous concentrations of cobalt found in ground and natural waters. Considering its toxicity, cobalt is now included among the 17 metals specified by United States Environmental Protection Agency (US E.P.A) as hazardous when its concentration exceeds the limits set by the Title 22, and other federal regulations. Therefore, any waste waters, sludge, waste extracts and soil samples which may be considered contaminated, are required to be analyzed for all these 17 metals including cobalt.[14]

In commercial environmental laboratories, the concentration of metals in water and soil samples is generally determined using Atomic Absorption (AA), Inductively Coupled Plazma (ICP) and colorimetric methods.[20,21] However, when a faster on-site analysis is required, only the colorimetric method, due to its simplicity and convenience, can be useful for a rapid quantitative analysis. The emergence of new waste water and soil treatment technologies has led to a growing demand for a faster and simpler method for the monitoring of the treatment process. Therefore, in recent years, there has been a great deal of interest by the E.P.A in the development of such faster methods of analysis. One such commonly used methods is the E.P.A method 7196 which involves the analysis of Cr(VI) in water and waste water samples using colorimetric method.[20,21]

Presently the most commonly used methods for the analysis of cobalt in environmental laboratories are the Atomic Absorption or the Inductively Coupled Plasma methods. There is no colorimetric method, similar to the Method 7196 for Cr(VI) analysis, which can be used to analyze cobalt at concentrations commonly found in environmental samples. 2-nitroso-1-naphthol and its related salts has been used as the complexing agent for the quantitative determination of cobalt in biomaterial, alloys, and rocks[22,23] using colorimetric methods. Those studies were designed to determine cobalt concentrations at much higher (percent) level. In addition, the results of some of those earlier studies are contradictory to each other. Nevertheless, the earlier methods have never been applied to any waste water, and contaminated soil samples for cobalt determination. This paper describes the deveolpment and utilization of a colorimetric method for the determination of cobalt as low as 0.1 mg/L in water and waste water samples. As the E.P.A. protocols require that the environmental samples be digested prior to their analyses for metal ions, the method was tested for its applicability to waste, and ground water, and soil samples after those samples were digested using E.P.A. method 3030E. It was also tested for any interference by other metals and common anions. The method developed was then tested on synthetic as well as real environmental samples following the E.P.A. Protocols.

EXPERIMENTAL

Materials

The water used in all experiments was deionized water passed through an ion-exchange resin. All chemicals in this study were of very high purity and were tested for any traces of cobalt before use. 1-Nitroso-2-naphthol-3,6-disulfonic acid disodium salt hydrate (hereinafter referred to as NRS) was purchased from Aldrich Chemical Company. Cobalt (II) chloride, magnesium nitrate hexahydrate, potassium phosphate dibasic, sodium sulfate anhydrous, sodium oxalate, potassium oxalate and stannic chloride pentahydrate were purchased from J.T Baker Chemicals and used as received. Silver nitrate was ACS reagent grade and was purchased from Spectrum Chemical Mfg. Corp. Bismuth nitrate pentahydrate was purchased from Allied Chemicals. Copper metal, fine granule and sodium acetate trihydrate were Mallinckrodt products. Ferric chloride, Chromium trioxide, cadmium metal, lead nitrate, zinc metal (30 mesh), nickel metal (325 mesh) were used to prepare the stock solutions of these metals.

A 1% Nitroso R salt (NRS) solution was prepared and used throughout the studies. The pH measurements were carried out using Beckman ϕII pH meter calibrated with 4 and 7 Mallinckrodt standard buffer solutions. Absorption measurements were made using Perkin Elmer Lambda 14 Spectrophotometer. Whenever needed, Perkin-Elmer Model 3300 Atomic Absorption Spectrophotometer and the corresponding hollow cathode lamps were used in the flame AA mode for the analysis of metals.

Methods

Method Development

As the method under development was to be used for the analyses of environmental samples, it was necessary to follow E.P.A guidelines throughout various stages of method development.[21]

Complex Formation: Cobalt (II) chloride was used as a source of cobalt to study its complexation with Nitroso R Salt. A cobalt stock solution of 0.0200 M was prepared in 1.2 M HCl. Several sets of Co(II) solutions with known concentration (0.1 – 5.0 mg/L range) were prepared, by adding appropriate volumes of the stock solution to a 100 mL volumetric flask. 10 mL of 3.7 M sodium acetate was added to each of these solutions. The pH of the solutions was adjusted as desired and then 2 mL of 1% NRS aqueous solution was added. The solution volume in each flask was increased to approximately 80 mL using deionized water and the solutions were heated for one hour in a water bath at 85–90 °C. Immediately after heating, 10 mL of concentrated HCl was added to each flask. The solutions were allowed to cool down to the room temperature and made up to the mark using deionized water. The absorbance of these solutions was measured at 520 nm. A blank solution which contained all the components except cobalt was also prepared and was treated the same way by following the procedure mentioned above. This solution was always used as a blank along with sample solutions.

In order to check for complete complex formation, three ion exchange columns (10 cm long, 1.5 cm diameter) were prepared using DOWEX 1-X8, 200 mesh anion exchange resin. Columns were then charged with 40 mL of 4 M HCl. A triplicate of 3.00 mg/L solution of Co(II) was prepared and the complexation with NRS was carried out by following the procedure described above. A 50.0 mL aliquot of this complexed solution was introduced to each column. Then 30 mL of 4 M HCl was used for each column to elute any uncomplexed cobalt(II) present. The eluted solutions were then heated gently to evaporate down to approximately 2 mL and 50 mL of deionized water was added to each sample. The complex formation procedure was repeated on these samples to observe any formation of Co-NRS complex.

Interferences

Interference by other metals: The metal used to check for any interference were Fe, Cr, Ni, Cu, Ag, Ca, Bi, Sn, Zn, Cd and Pb. All the interferents were tested individually as well as together. The concentration of each metal in the solution which was tested for interference ranged from 10 mg/L to 50 mg/L, whereas the concentration of cobalt in such solutions was 1.2 mg/L. These solutions were then treated for complex formation according to the procedure described earlier. Addition of 10 mL of concentrated hydrochloric acid immediately after one hour of heating helped to decompose any complex formed between NRS and other metals. In all these experiments, a solution which contained the same concentration of cobalt as in the mixtures was also prepared. The concentration of the cobalt determined in this solution was compared with the concentrations of cobalt obtained in the mixture.

***Interference by anions*:** A series of solutions containing cobalt and three important anions, $SO_4{}^{2-}$, $PO_4{}^{3-}$, $C_2O_4{}^{2-}$ were prepared to check for any interference by these metals. Approximate ratios of 1:10 and 1:50 for cobalt to anion were used. Anions were studied for individual as well as combined interference. A solution of cobalt with the same concentration as in the mixtures was also run in all experiments for comparison purposes.

Effect of Digestion

The effect of digestion was studied on both synthetic as well as real samples. In both cases, the digestion method 3030E, recommended by the E.P.A for water and waste water was followed.[20,21] For synthetic samples, a triplicate of 11.80 mg/L of Co(II) solution was prepared from the stock solution and digested using Method 3030E. The digestion procedure involved the addition of 5 mL concentrated nitric acid and gentle evaporation of the solution on a hot plate to the lowest volume possible before precipitation. Each sample was then diluted to 50.00 mL and then analyzed for cobalt using the method developed. A triplicate of a set of the dilute solutions with cobalt concentrations of 0.12, 0.59, 1.18 and 2.35 mg/L was also prepared and digested according to method 3030. After digestion was complete, the concentration of cobalt was determined for each sample by complexing with NRS as described earlier. Similar approach was used for real environmental samples as well.

RESULTS AND DISCUSSION

Method development

The formation of the red Co-NRS complex was investigated at different initial concentrations (0.1 to 10 mg/L) of cobalt. Figure 1 shows the visible absorption spectra of Co-NRS complex and pure NRS solution. In an earlier study[24] where 2-nitroso-1-napthol was used as the complexing agent, inconsistent results were obtained. In that study, the absorbance of the solution was measured at 418 nm and Beer's law was not found to be applicable. By examining the two spectra, we found that 418 nm is not the appropriate wavelength to measure the absorbance of the complex formed. At 418 nm, the excess NRS present in the solution will make a larger contribution to the overall absorbance of the solution. In that case, a smaller absorbance of Co-NRS complex will be masked by this large absorbance due to the excess NRS present and will lead to incorrect results. It is evident from Figure 1 that the absorbance contribution of the Co-NRS complex increases significantly near 520 nm and the contribution from excess NRS is minimal. Therefore, 520 nm was determined to be the appropriate wavelength to monitor the complex formation. By following the absorbance of Co-NRS solution at 520 nm, excellent agreement between different sets of solutions which contained a wide range of initial cobalt concentrations was obtained, and Beer's law was found to be applicable.

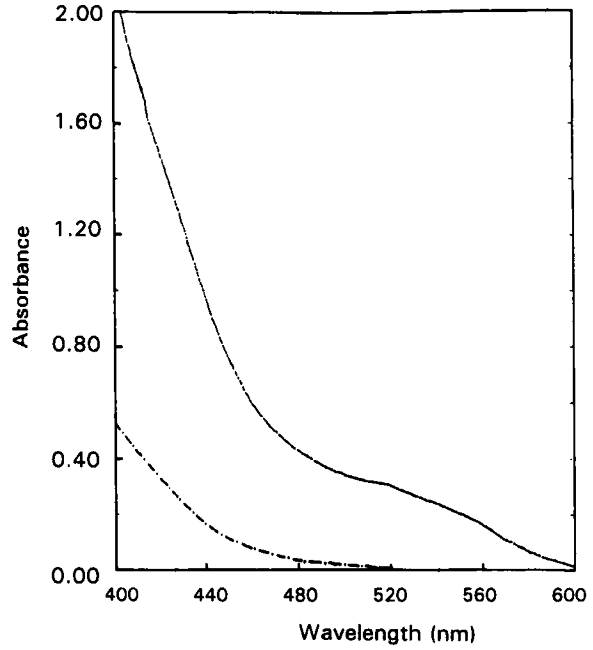

FIGURE 1 The Visible Absorption Spectra of Co-NRS Complex (.....) and Pure NRS (-.-.-) After the Addition of Concentrated HCl

In order to confirm that all the cobalt present in the solution has been used to form a complex with NRS, a Co-NRS complex solution was prepared using 3.00 mg/L of Co(II) solution. The complexed red solution was then passed through an ion-exchange column and then eluted with 4 M hydrochloric acid to collect any uncomplexed cobalt(II). The complexed cobalt was found to stay at the top of the column in the form of a red band of approximately 5 mm thickness. The concentration of the uncomplexed cobalt, if any, in the eluted solutions was determined. No red Co-NRS complex was observed and no appreciable absorbance was obtained at 520 nm. A portion of the eluted sample was also analyzed using atomic absorption spectroscopy and no cobalt was found to be present in the eluted sample. In a control experiment, where 10.0 ppm solution of cobalt was introduced to the column, eluted with 4 M HCl, and complexed with NRS, greater than 96% recovery of cobalt was achieved. The results of the 3 trials showed that for initial cobalt concentrations of 0.50 and 3.0 mg/L, the concentrations of cobalt recovered were 0.48 and 2.9 mg/L showing that the complexation was more than 95% complete.

The effect of pH on the complex formation was also investigated. Figure 2 shows a plot of the molar absorptivity values at 520 nm for the red Co-NRS complex against pH. The molar absorptivity which can be an indication of a higher degree of complexation was shown to change with pH. As shown in Figure 2, the maximum molar absorptivity value was found at the pH of 6.0. Therefore, this pH was considered to be the most suitable pH for complex formation and was used in all subsequent experiments. In the present method, HCl was added after the addition of NRS and heating the solution. In contrast to the earlier studies,[25] no precipitates were formed. The Co-NRS complex formed was found to be stable in strong acidic media. Addition of concentrated hydrochloric acid is also advantageous with the point of view that it helped in decomposing any complex formed by other metals.

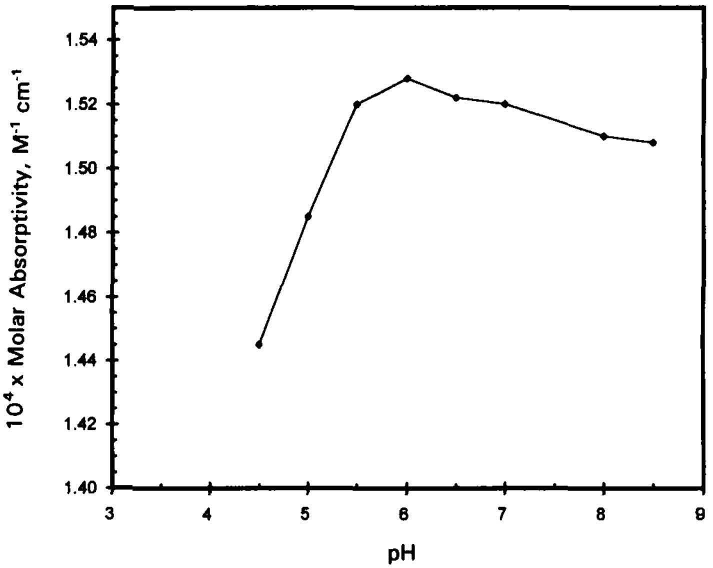

FIGURE 2 Plot of Molar Absorptivity of Co-NRS Complex at 520 nm Against the pH

Since this method was developed for environmental analysis, it was necessary to determine the appropriate range of concentrations for standard solutions. In order to get the absorbance of the standard solutions in the range of 0.1–0.7, which is usually recommended by E.P.A for colorimetric methods,[20,21] the concentration range needed to prepare standards which gave absorbance in the desired range using a 1 cm^2 cell was between 0.5 and 3.0 mg/L. The detection limit[26] of this method was determined to be 0.1 mg/L. It was also found that in order to achieve complete complex formation and color development, it was necessary to heat the solutions using a water bath at 80–90 °C after the addition of sodium acetate and the complexing agent.

Studies on Interference

In previous studies,[27] it was reported that some metal ions such as iron, chromium, nickel and copper also form colored complexes with 2-nitroso-1-napthol. Iron was reported to form a green complex whereas orange complexes were reported for chromium, nickel and copper. No such interference by any of these metals was observed in the present study. We believe that if any such complex is formed between NRS and any of these interfering metals, it is immediately decomposed by the addition of strong inorganic acid. In our initial studies, we used perchloric acid, but later-on hydrochloric acid was found to be more efficient in decomposing any such complex formed between NRS and the interfering metals. Therefore, in all subsequent studies, hydrochloric acid was used as part of the general procedure. The most appropriate time for the addition of acid was also determined and was found to be immediately after the 1-hour heating prior to cooling. Different volumes of concentrated hydrochloric acid ranging from 1 mL to 20 mL were used, however 10 mL of the acid was found to be sufficient to destroy any other metal complexes formed. In the case of iron and chromium however, if the concentration of these two metals was 50 fold larger than the cobalt concentration, less than 10 mL volume of hydrochloric acid could not decompose the metal complexes. Higher volumes of hydrochloric acid were not found to make any significant difference. Table I shows the data obtained for samples containing cobalt and various metals at different cobalt to metal ratios. In all of these experiments, 10 mL of concentrated hydrochloric acid was added after heating. In the case of chromium, the absorbance of the solution slightly increased and the concentration of cobalt calculated was slightly higher than the original concentration. When Ag, Mg, Bi, Zn, Sn, Ca, Pb, Cu, Ni and Cd were studied individually as the interfering metals, the concentration of cobalt determined was within ± 0.05 mg/L of the 1.20 mg/L cobalt initially present. Some of these metals were also tested together for any interference, and the results in

Table I show that no interference was observed. Therefore, all of these metals could be considered as non-interfering. Table II shows the results on the analysis of cobalt in the presence of anions which are important from an environmental point of view. It is clear from the data in Table II that the anions studied can be considered as non-interfering.

TABLE I Results on the Recovery of Cobalt in the Presence of Various Metal Ions[a]

Metal	*[metal]*[b] *mg/L*	*[cobalt]*$_{added}$ *mg/L*	*[cobalt]*[d]$_{deter.}$ *mg/L*
Fe	9.92 – 50.00	1.20	1.01 – 1.06
Ni	10.74 – 50.04	1.20	1.19 – 1.22
Cr	9.92 – 50.00	1.20	1.27 – 1.35
Cu	9.99 – 50.00	1.20	1.16 – 1.23
Ag	10.60 – 53.12	1.20	1.16 – 1.18
Mg	10.08 – 50.14	1.20	1.18 – 1.20
Bi	10.79 – 54.08	1.20	1.18 – 1.22
Ca	9.86 – 49.41	1.20	1.16 – 1.21
Cd	9.74 – 50.23	1.20	1.18 – 1.24
P.B.	10.18 – 47.33	1.20	1.18 – 1.20
Sn	12.13 – 49.96	1.20	1.14 – 1.22
Zn	9.95 – 50.04	1.20	1.18 – 1.20
Fe,Ni,Cr,Cu	12.24 – 54.22[c]	1.20	1.26 – 1.32

[a] pH of the solutions was adjusted at 6.0 and the absorbance was measured at 520 nm. [b] Concentration range of the interferant metals used to study the combined effect of these metals. [c] The synthetic samples contained a mixture of Fe, Ni, Cr, and Cu with concentration ratio 10 to 45 times larger than the cobalt concentration of 1.2 mg/L. [d] Refer to the range of cobalt concentrations determined for the range of metal ions concentrations given in column 2, and were calculated using a calibration curve constructed with standard cobalt solutions 0.477, 0.588, 0.832, 1.19, 2.36 and 3.50 mg/L. Maximum error in individual results is 5%.

TABLE II Results for the Recovery of Cobalt in the Presence of Various Anions[a]

Anion	*[anion] mg/L*	*[cobalt]*$_{added}$ *mg/L*	*[cobalt]*[b]$_{deter.}$ *mg/L*
PO_4^{3-}	9.90	0.117	0.110
PO_4^{3-}	49.90	1.20	1.17
$C_2O_4^{2-}$	9.90	0.117	0.118
$C_2O_4^{2-}$	49.90	1.20	1.19
SO_4^{2-}	11.67	0.117	0.122
SO_4^{2-}	50.76	1.20	1.17

[a] pH of the solutions was adjusted at 6.0 and the absorbance was measured at 520 nm. [b] The concentration of cobalt in the solutions were calculated using a calibration curve constructed with a standard cobalt solutions of 0.477, 0.588, 0.832, 1.19, 2.36 and 3.50 mg/L. Maximum error in these results is 5%.

Effect of Digestion

Since the E.P.A protocols require that environmental samples should be digested prior to their analysis for metal ions, it was necessary to investigate the effect of digestion on the method developed. Digestion is a procedure which is carried out to release metal ions from any soluble and insoluble complexes of metals formed with organic ligands in the matrices of interest. Various procedures are recommended for digestion depending upon the matrix.[20,21] Our studies showed that digestion process, even at very low initial concentrations of cobalt, have no effect on the analysis method. The concentrations of cobalt obtained after digestion were all above 98% of the original cobalt concentration.

Application of the Method Developed

The method developed was first applied on synthetically prepared samples which contained cobalt and four other metals, Fe, Ni, Cr, and Cu, which in our earlier studies showed some signs of interference. Because there is usually more than one metal contaminant present in any waste water, it was necessary to explore the combined effect, if any, of the presence of these metals on the method developed. Results on these studies are also collected in Table I. The original concentration of cobalt in these solutions was 1.20 mg/L whereas the concentration of each metal in the mixture was about 10 to 50 fold. The concentration of cobalt determined was 1.26, 1.32, 1.31 and 1.30 mg/L in four different trials. These concentrations are within 10% of the original cobalt concentration of 1.20 mg/L.

Finally, the method developed was applied to waste water samples which were obtained from Montgomery Laboratory, Pasadena, California. Three different waste water samples having different matrices were studied. Analysis of these samples using atomic absorption spectroscopy showed that no appreciable concentration of cobalt was initially present. These samples were then spiked with a known concentration of cobalt, digested following E.P.A.'s prescribed method, and then cobalt analysis was carried out on a portion of the samples. During the analysis procedure, when the complexing agent was added, samples 2 and 3 turned green which showed the presence of iron. However, as soon as hydrochloric acid was added after the heating, the green color disappeared. These results again confirm the need for the addition of HCl. No such behavior was observed for sample 1.

Two different concentrations of cobalt were used to spike these samples. When a higher concentration (1.27 mg/L) of cobalt was used for spiking, the concentrations of cobalt found were 1.24, 1.23 and 1.22 mg/L for waste water samples 1, 2 and 3 respectively. When the waste water samples were spiked with a lower concentration (0.59 mg/L) of cobalt, the concentrations determined were 0.64, 0.60 and 0.62 mg/L respectively. In all of these experiments, excellent spike recoveries were achieved. The results collected in Table III show that the presence of other metals, anions and organic contaminants, if present in the matrix, as well as the treatment of the samples for the E.P.A.'s digestion process, did not interfere with the analysis of cobalt when this method was applied.

TABLE III Results on the Recovery of Cobalt in Actual Waste Water Samples[a]

Sample No.	$[\text{cobalt (II)}]^{c}_{added}$ *mg/L*	$[\text{cobalt (II)}]^{d}_{deter}$ *mg/L*
1[b]	1.27	1.2
2[b]	1.27	1.23
3[b]	1.27	1.22
1[b]	0.59	0.64
2[b]	0.59	0.60
3[b]	0.59	0.62

[a] These samples were obtained from commercial environmental laboratories and represents the waste discharge from three different industrial facilities. [b] Initially no detectable concentration of cobalt was present in these samples, pH of these solutions was adjusted to 6.0, [c] Concentration of cobalt used for spiking the samples. [d] Concentration of the solutions were calculated using a calibration curve constructed with standard cobalt solutions of 0.477, 0.588, 0.832, 1.19, 2.36 and 3.50 mg/L. Maximum error in these results is 5%.

Our results indicate that the method developed works very well for waste water and drinking water samples. It is very specific and has a high potential to be used as a standard method for the analysis of cobalt in environmental samples. The method is very specific for cobalt. Due to high molar absorptivity which is greater than 15,000 $M^{-1}cm^{-1}$ at the pH of 6, the concentrations of cobalt as low as 0.1 mg/L can be determined with greater than 95% accuracy. Although the detection limit of the method is not comparable with the ICP technique, however, it is similar to that of flame AA, and reliable results can be obtained for trace level determination of cobalt in environmental samples. The method developed can be particularly useful for a rapid on-site analysis to monitor the progress of a treatment process or the determination of an effluent coming out of an industrial discharge. Preliminary studies also show success for using this method for the analysis of cobalt in soil samples. However, in soil samples, the chemistry of each matrix is very complex, therefore, further investigations should be done before this method is applied to soil samples.

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