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Micelle-mediated extraction of cobalt and its spectrophotometric determination in rocks, soils, sediments and sea-bed polymetallic nodules

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ABSTRACT

The surfactant sensitized bottle-green complex (1:2:1) formed of cobalt-thiocyanate-cetyltrimethylammonium bromide is suitably extracted into an organic solvent, ethylacetate, at a pH range, 6-8 and the absorption measurements were carried out at 630 nm (λ_{max}). The Beer's law is obeyed in the range from 0.05 to 10 µg per mL. The molar absorptivity and Sandell's sensitivity of the present system were found to be 2.2 x 10^3 L.mol^{-1}cm^{-1} and 0.026 µg cm^{-2}, respectively. No other element forms complex of similar colour with thiocyanate at this pH range. The method was applied to a number of samples like rock, soil, sediment, polymetallic nodules etc., as well as Certified Reference Materials and the values were found highly satisfactory. The interference of Fe^{3+} which formed a reddish complex at acidic pH (<7) was eliminated when the complex was extracted at pH 8.0. The method is highly useful for the determination of cobalt in geological samples having its concentration from µg/mL to percentage level. As the method has been made highly selective for spectrophotometric determination of cobalt, it might be applied to almost all types of geological sample of diverse matrices.

Capsule Summary: Determination of cobalt in micellar medium by surfactant sensitised extraction spectrophotometry was performed and the method adopted was highly efficient for the determination of cobalt in all types of geological matrices.

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INTRODUCTION

Cobalt is an important element because it is essentially required in the metabolic activities of plants and animals (Palit et al., 1994). Cobalt is an integral part of Vitamin, Cobalamine (Ahmed et al., 2003). Industrially it is also used in the manufacture of important alloys which are having different applications in science and technology (Banerjee et al.,1968) . Trace determination of cobalt in such diverse samples including biological ones is very important. Although cobalt is best analyzed by AAS and ICP-AES, still for certain specific applications, its spectrophotometric determinations are carried out. There are innumerable methods for the spectrophotometric determination of cobalt (Marczenko, 1976), mention may be made of α-nitroso-β-naphthol and nitroso-R-salt. Apart from that, there are many more sensitive methods reported in literature (Gavazov et al., 2007; Trohimenko and Zaporohzets, 2013; Ahmed and Hossan, 2008; Ahmed and Uddin, 2007; Gharehbaghi et al., 2008; Ombaka and Gichumbi, 2011; Kuliyev Kerim et al., 2016; Anusuya and Krishna Reddy, 2018; Hayashi et al., 1978; Kitson, 1950 ; Paleologos et al., 2002 ; Ramchandra Reddy et al., 2004), but unfortunately because of their poor selectivity, these are not, in general, used for accurate determination of the metal in diverse samples of complex matrices such as rocks, minerals, soils etc. Although the nitroso-R-salt and α-nitroso-β-naphthol methods are still being used for the determination of cobalt in various samples, because of their less sensitivity and selectivity, they are not suitable for trace determination of cobalt in these samples.

In the course of our studies on the micelle-mediated extraction of metals like Fe (Tarafder and Thakur, 2005), Ti (Tarafder and Thakur, 2008), Mo (Das and Gambhir, 2014) etc., we have come across a facile reaction of cobalt with thiocyanate and CTAB (cetyltrimethylammonium bromide). Usually the binary Co-SCN complex in aqueous solution does not display any colour, and therefore in aqueous medium cobalt cannot be estimated spectrophotometrically using thiocyanate. However, when the binary Co-SCN complex is extracted into certain organic solvent like ethylacetate, a greenish colour is displayed in the organic solvent. The intensity of the extracted complex colour is proportional to the concentration of cobalt. The molar absorptivity of the binary Co-SCN complex being $5x10^2$ $L.mol^{-1}cm^{-1}$. However, this very reaction when conducted in the presence of CTAB, the molar absorptivity (Ɛ) of the ternary complex increases four-fold. Here, CTAB increases the rate of reaction of SCN^- with Co^{2+} by way of providing micellar medium. Unlike the systems developed for metals like Fe, Ti and Mo, the sensitivity of Co-SCN-CTAB system is not much high (Ɛ=$2.2x10^3$ L. $mol^{-1}cm^{-1}$). In this context it is pertinent to mention here that Brown and Steinbach (1959) had in the past reported a spectrophotometric method for the determination of cobalt by extraction of Co-SCN-Acetylacetone ternary system.

The sensitivity of the method was poor (Ɛ=0.9-$1.0x10^3$ L. $mol^{-1}cm^{-1}$) and at the same 3time iron was found to interfere seriously. In this method, the possibility of loss of cobalt by way of its adsorption onto $Fe(OH)_3$ could not be ruled out during the elimination of iron by precipitation. Similarly, in the method reported by Lorenzo Ferreira et al 1989 , the sensitivity of the method could not be improved substantially on extraction of Co-thiocyanate complex into MIBK in the presence of ephedrine (Ɛ=$4.3x10^3$ L. $mol^{-1}cm^{-1}$).

Also, as pointed out in the paper, iron and Cu seriously interfered in the determination of cobalt. The method reported by Hayashi et al 1978 for the determination of cobalt by the extraction of Triton-X 100 sensitized Co-thiocyanate complex is also not much sensitive(Ɛ=$1.77x10^3$ L. $mol^{-1}cm^{-1}$)[sensitization ability of Triton-X in this case was found to be poor]. Besides, like other surfactant sensitized methods for cobalt determination, this method too, is not free from serious interference of Cd, Fe, Cu, Zn and Ni. Pujar and Nagaraj (1989) reported a spectrophotometric method for the determination of cobalt in vitamin B-12 and synthetic alloys based on the extraction of Co-SCN-CTAB ternary complex into chloroform. The method claimed high sensitivity (Ɛ=$2.2x10^4$ $L.mol^{-1}$ cm^{-1} and SS= 0.008 μg cm^{-2}). It seems their claim is not correct because the reported Ɛ and Sandell's Sensitivity were not in agreement. Moreover, while re-investigating this method in our laboratory, we could not reproduce the claimed sensitivity. Besides, while applying the method to geological samples of diverse matrices, the method awfully failed due to the serious interference of iron.

However, this particular system, otherwise being very specific to cobalt, is very useful for the accurate determination of the metal ion over a wide range of concentration in samples having diverse matrices like rocks, soils, sediments, minerals,sea bed polymetallic nodules, etc after eliminating iron interference.

The present report encompasses details of the systematic studies carried out on the development of a highly selective spectrophotometric method for the determination of cobalt by CTAB micelle-mediated extraction of Co-thiocyanate complex into organic solvent.

MATERIAL AND METHODS

Chemicals, reagents and apparatus

A double beam spectrophotometer (Model-SPECORD 250 plus, analytikjena, Germany) equipped with 1 cm quartz cells was used for the absorbance measurements. The pH values of the reaction solutions were measured by using ELICO (LI-120) pH meter.

All the reagents used were of Analytical reagent grade. Stock Co solution (1mg/mL): A 0.25 g Co as metal was weighed into a 250 mL beaker and was dissolved in 20 mL 1:1 diluted HNO_3 and diluted to 250 mL in a volumetric flask. A working standard solution (100 μg/mL) was made by transferring 10 mL of the stock solution into a 100 mL volumetric flask followed by the addition of 5 ml concentrated nitric acid and then diluting the solution to 100 mL with distilled water. Reagents used were; (i) potassium thiocyanate (ii), HCl (iii), HNO_3 (iv), hydrofluoric acid (v) and cetyltrimethylammonium bromide and solvents used for liquid-liquid extraction studies were; (i) ethylacetate (ii) butylacetate (iii) benzene (iv) hexane (v) carbontetrachloride and (vi) chloroform etc.

Procedure

Dissolution of samples: The dissolution of rock and sediment samples was brought about either by $HF-HNO_3$ or by NH_4HF_2-H_2SO_4 treatment. A 0.5 g sample was taken in a platinum dish, and treated with 5 mL HF. The HF treatment was repeated two times. After evaporation, the residue was treated with 5 mL HNO_3 till dryness.The HNO_3 treatment was repeated. The solution was finally made up to 100 mL with distilled water in a volumetric flask by maintaining 5% HCl.

The soil sample (1.0 g) was weighed into a 250 mL Teflon high-pressure microwave acid digestion system and

Table 1: Details of interference studies carried out for the determination of 5 mg/L cobalt

Elements/ions studied	Tolerance limit*, (mg/L)
Na^+, K^+, Rb^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Fe^{3+}, Cl^-, Br^-, I^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, $C_2O_4^{2-}$, CH_3COO^-	>5000
Mn^{2+}, Ni^{2+}, Bi^{2+}, Pb^{2+}, Zn^{2+}, Th^{4+}, REEs	200
Mo^{6+}, w^{6+}, Nb^{5+}, V^{5+}, Ti^{4+}, UO_2^{2+}	50

*less than 2% error

10 mL aqua-regia was added to it. The system was operated at full power for 30 minutes in the microwave digester. The digested material was evaporated to incipient dryness. Then, 50 mL of 5% hydrochloric acid was added and heated close to boiling in order to leach the residue. After cooling, the residue was filtered and washed two times with a small volume of 5% hydrochloric acid. The filtrates were quantitatively collected in a 100 mL volumetric flask and diluted to the mark with distilled water. The sea bed polymetallic nodule sample solutions were prepared by HF and HCl treatment, and made up the volume in a 100 mL volumetric flask by maintaining 5% HCl (Maxwell, 1968).

Extraction and spectrophotometric measurements

A 1 mL sample aliquot containing Co up to 50 µg was taken in a 125 mL separating funnel. To it was added 5 mL of 10% KCNS solution, mixed well and adjusted the pH to around 6.0. To this solution, were added 10 mL of ethylacetate and 1 mL of 0.5% CTAB (cetyltrimethylammonium bromide). Mixed well. The mixture was shaken vigorously for three minutes and set aside for 5 minutes in order to allow for phase separation. Then, 1-2 drops of dilute (1:1) ammonia was added in order to raise the pH of the aqueous phase to 8.0 and again, shaken the mixture for a while. While the reddish Fe-CNS complex instantaneously vanished, the bottle green complex of cobalt (Co-SCN-CTAB) persisted in ethylacetate phase. The aqueous layer was drained out and the absorbance of the organic phase was measured at 630 nm (λ_{max}) against the reagent blank processed similarly without containing any cobalt.

RESULTS AND DISCUSSION

Spectral studies

In order to have an idea of the electronic spectra of the complex formed, absorbance of the ternary complex having increasing concentration of Co was plotted against increasing wavelength in the range, 350-800 nm. The wavelength of maximum absorption was found at 630 nm. Fig. 1 shows the spectra of the complex against process blank as well as that of the blank against ethylacetate.

Effect of pH

The influence of pH on the extraction, complex formation and colour development was studied. Under the optimized conditions of other variables like concentration of the complexing agent (potassium thiocyanate), the surfactant concentration (CTAB) and the appropriate solvent (ethylacetate), the pH of the reaction medium was varied over a wide range i.e., from 0 to 12. However, it was observed that the maximum absorbance coupled with better stability of the complex formed was found to remain constant up to a pH of 8.5. A plot of pH vs. absorbance has been shown in the Fig. 2.

Effect of potassium thiocyanate concentration

In order to obtain maximum absorbance of the complex formed, the concentration of the reagent, potassium-thiocyanate was varied over a wide range, i.e., from 0.1% to 50%. A 5 mL of 0.5% of the reagent was sufficient for obtaining maximum absorbance. Thiocyanate complexes of many metals are generally weak, and at lower concentration of CNS-, the Co-complex is unstable, but in presence of excess of the reagent (due to law of mass action) the ternary complex once formed remains stable for long. That is the reason, a higher concentration (10% soln.) was recommended than that actually required for attaining maximum sensitivity. Fig. 3(a) shows the effect of the thiocyanate concentration on the extraction of cobalt species.

Effect of surfactant concentration

The surfactant, cetyltrimethylammonium bromide (CTAB) was found to provide a micellar medium for the reaction to take place between thiocyanate and the metal ion. Usually, the binary Co-SCN complex in aqueous solution does not display any colour, and therefore in aqueous medium, cobalt cannot be estimated spectrophotometrically using thiocyanate. However, when the binary Co-SCN complex is extracted into certain organic solvent like ethylacetate at pH range, 6-8, a greenish colour is displayed in the organic solvent, the intensity of colour being proportional to the concentration of cobalt. The molar absorptivity of the binary Co-SCN complex being 5 x 10^2 $L.mol^{-1}cm^{-1}$.

However, this very reaction when conducted in the presence of CTAB, the molar absorptivity (Ɛ) increased four-fold. Here, CTAB increases the rate of reaction of SCN^- with Co^{2+} by way of providing micellar medium. The binary Co^{2+}-(SCN^-) complex is a neutral one, hence no counter cation is required for its extraction into an organic solvent. Therefore, it is construed that CTA^+ of CTAB does not act as a counter cation, rather it sensitizes the colour reaction of Co^{2+} with KSCN by providing micellar medium only.

Table 2: Comparison of results obtained for cobalt determination by the proposed method vis-à-vis those obtained by AAS (n=3)

S. No	Nature of samples	Sample codes	Co (ppm) by proposed method	Co (ppm) by AAS	Literature value
1.	Rock-Syenite	SY-3*	15 ± 0.4	15	12
2.	Rock-Gabbro	MRG-1*	90 ± 3.0	91	86
3.	Sea-bed Polymetallic nodule	NML-Polymetallic nodule*	1370 ±28	1360	1400
4.	Soil	RT-912	29 ± 0.8	30	-
5.	Soil	RT-924	31 ± 0.7	32	-
6.	Soil	RT-936	42 ± 0.8	44	-
7.	Soil	RT-939	26 ± 0.6	25	-
8.	Soil	RT-940	<10	<10	-
9.	Soil	RT-1032	<10	<10	-
10.	Soil	RT-1033	12 ± 0.3	11	-
11.	Sediment	RT-1034	19 ± 0.5	18	-
12.	Sediment	RT-1035	29 ± 0.7	30	-
13.	Sediment	RT-1036	11 ± 0.2	<10	-
14.	Sediment	RT-1037	14 ± 0.3	14	-
15.	Rock	RT-1038	<10	<10	-
16.	Rock	RT-1039	12 ± 0.2	11	-
17.	Rock	RT-1040	<10	<10	-
18.	Rock	RT-1041	21 ± 0.5	22	-
19.	Rock	RT-1042	16 ± 0.4	14	-
20.	Rock	RT-1532	35 ± 0.7	34	-
21.	Rock	RT-1533	14 ± 0.3	15	-

*Certified Reference Materials

In order to see its impact on the colour formation and subsequent extraction into the organic solvent, its concentration was varied in the range, 0.1 to 2% (m/v). It was found that 1 mL of 0.5% aqueous solution of the reagent was found to be sufficient for obtaining maximum absorbance of the extracted species. However, in order to allow for reagent impurity, a 1 mL of 1% solution was recommended. Fig. 3(b) shows the effect of the concentration of CTAB in the colour formation and extraction of the ternary complex.

Choice of solvents

A number of polar and non-polar solvents were tried for the extraction of ternary complex of cobalt(II), with thiocyanate and CTAB. The best result, in terms of facile extraction and its better stability in the organic solvent as well as maximum absorbance of the complex formed was found with ethylacetate.

Effect of equilibrium time, temperature and electrolyte on the complex formation and its extraction

The equilibrium time for the extraction of the complex was found to be two minutes. The maximum absorbance of the complex and its stability was found to be in the temperature range, 20-40° C. In order to verify the degree of extraction and the colour formation, various electrolytes were separately used. These electrolytes used were NaCl, $NaNO_3$, NH_4Cl, Na- acetate etc. It was found that the colour formation and extraction of the complex into organic solvent was independent of electrolyte addition.

Beer's law, molar absorptivity, Sandell's sensitivity and precision

The Beer's law of the system was obeyed in the range 0.05 to 10 ppm of cobalt (Fig. 4). The regression equation of the linear calibration curve was Y = 1.09x + 0.05 with correlation coefficient ($R^2 = 0.98$). The molar absorptivity of the complex at the λ_{max} (630 nm) was found to be 2.2×10^3 L. mol^{-1}cm^{-1}. The Sandell's sensitivity of the method was 0.026 µg cm^{-2}. The detection limit (3σ of the blank) of the method being 0.03 µg mL^{-1}. The precision of the method in terms of RSD was found in the range, 2 to 3%.

Effect of diverse ions

Effect of foreign ions on the determination of cobalt by the prescribed procedure was studied thoroughly. Most elements which form thiocyanato complexes generally do not absorb at 630 nm (λ_{max} for Co-SCN-CTAB complex).

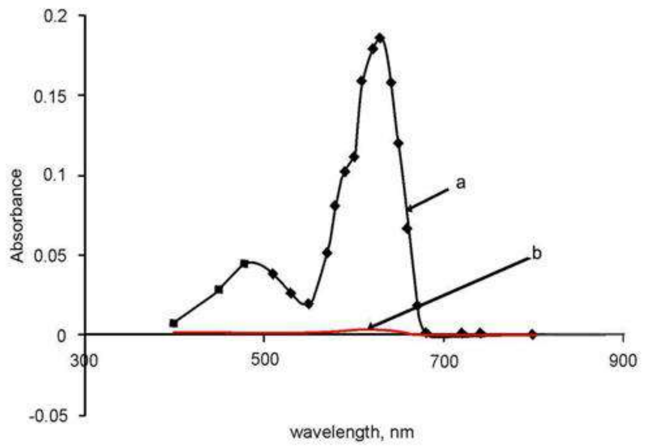

Fig. 1: Absorption spectra of (a) cobalt complex against reagent blank (b) process blank against ethylacetate

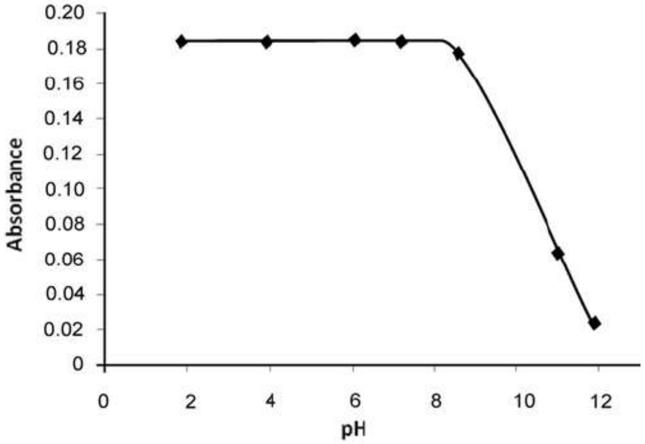

Fig. 2: Effect of pH on the extraction of cobalt species

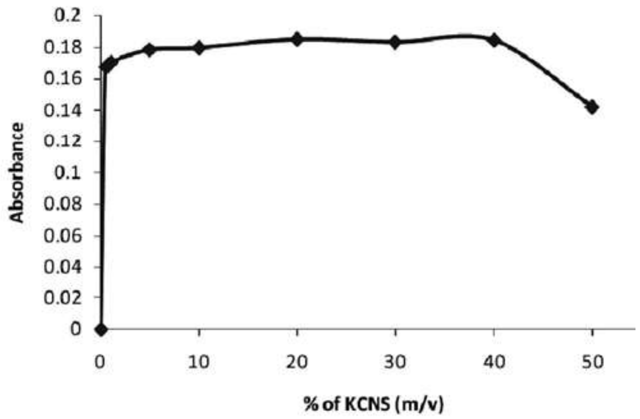

Fig. 3(A): Effect of thiocyanate concentration on the extraction of cobalt species

Hence, their interferences have not been encountered while determining cobalt. However, iron, being a major element in rocks and soil samples, forms strong thiocyanato complex in the acidic pH (up to a pH of 6.5), thereby interfering in the determination of cobalt, although its λ_{max} (495 nm) is wide apart from that of Co-SCN-CTAB complex (while cobalt forms a bottle-green complex, iron forms a purple complex with thiocyanate). Interference of iron is eliminated by raising the pH to 8.0, where thiocyanate complex of iron is broken down (while the colour of Fe-SCN-CTAB complex readily vanishes, the colour of cobalt–thiocyanate complex remains intact). Other than iron, no interference was encountered in the determination of cobalt by this proposed technique. As such, the proposed method for cobalt-determination is highly selective because no other element forms complexes of similar colour with thiocyanate. Details of the interference studies are given in Table 1.

Extraction equilibrium and tentative composition of the complex extracted

The equilibrium studies for Co-SCN-CTAB system are given below. The mechanism by which Co^{2+} ion was extracted from aqueous phase into ethylacetate in the presence of the cationic surfactant, CTAB follows the reaction shown below:

$$Co^{2+}(aq)+wKCNS(aq)+xCTAB(aq)=\{Co(SCN)_w{}^{(2-w)}.(CTAB)_x\} +wK^+ \quad (1)$$

$$K_{ex(w,x)}=[Co(SCN)_w{}^{(2-w)}.(CTAB)_x]_o[K^+]^w/[Co^{2+}]_{aq} [SCN]_{aq}{}^w\,[CTAB]^x{}_{aq} \quad (2)$$

$$K_{ex}(_{w,x})=D[K^+]^w/[SCN]_{aq}{}^w\,[CTAB]^x{}_{aq} \quad (3)$$

Where, $D=[Co(SCN)_w{}^{(2-w)}.(CTAB)_x]_o/[Co^{2+}]_{aq}$

Equation (3) can be written as

$$\log K_{ex(w,x)}= \log D-w\log[SCN]_{aq}-x\log[CTAB]_{aq}+x\log[K^+] \quad (4)$$

Analyzing the experimental values of the distribution ratio (D) as a function of equilibrium pH and extractants concentration at constant values of other parameters, allows the estimation of the number of extractant molecules associated with the extracted metal.

The composition of the Cobalt-thiocyanate-CTAB ternary complex was found out by curve-fitting method (Sillen, 1951). In order to know the number of molecules of thiocyanate participating in the formation of Cobalt-thiocyanate-CTAB complex extractable in the organic solvent, different logarithmic concentrations of the reagent, thiocyanate were plotted against log D values. A slope of 1.74 close to the integer 2 was obtained (Fig. 5). This shows that two molecules of thiocyanate participated in the complex formation. Similarly, in order to know the number of molecules of CTAB participating in the formation of Cobalt-thiocyanate-CTAB complex extractable in the organic solvent, different logarithmic concentrations of the reagent, CTAB were plotted against log D values. A slope of 0.903 close to the integer 1 was obtained (Fig. 6).

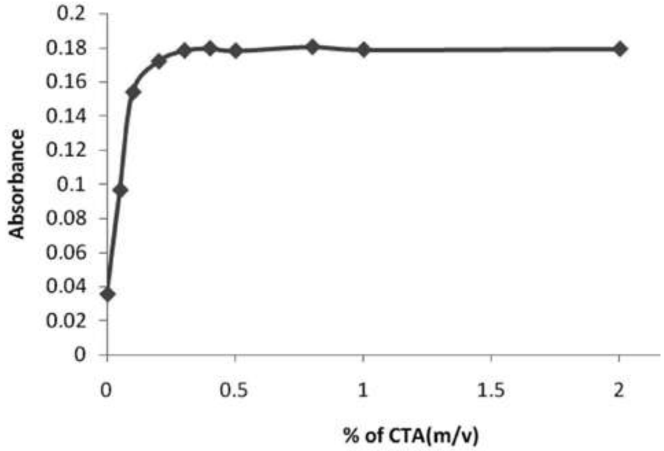

Fig. 3(B): Effect of CTAB concentration on the extraction of cobalt species

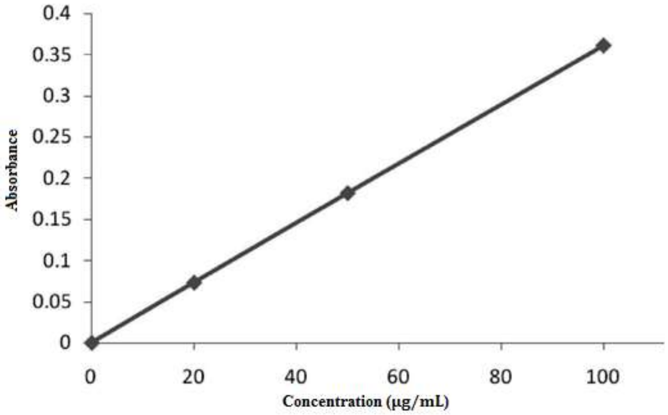

Fig. 4: Calibration graph for cobalt

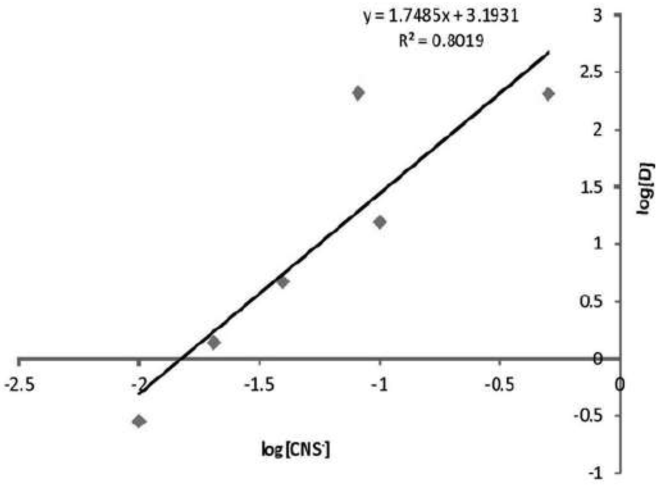

Fig. 5: Plot of log D vs. log [CNS$^-$] (curve-fitting method)

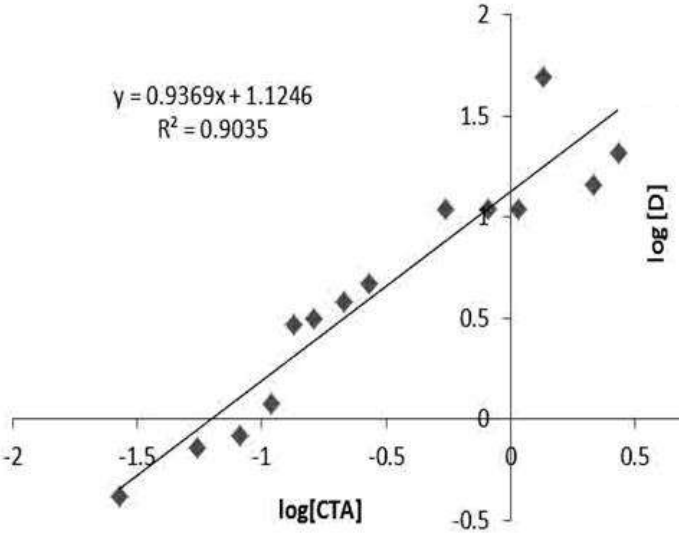

Fig. 6: Plot of log D vs. log [CTAB] (curve-fitting method)

This shows that one molecule of CTAB participated in the complex formation. Hence, the stoichiometry of the complex formed was found out to be 1:2:1. The results were further attested by Job's method of continuous variation. In this context, it is pertinent to mention here that two molecules of thiocyanate were coordinated with the metal cobalt and one mole of CTAB formed an adduct with the thiocyanate complex, which facilitated the extraction of the complex by way of providing micellar medium.

Analytical application

The extraction spectrophotometric method thus developed, is based upon the surfactant-mediated extraction of the metal. The method being highly selective has been applied to the determination of cobalt in a host of rock, soil and mineral samples including Certified Reference Material (CRMs). The results are shown in Table 2. The results obtained were compared with those obtained from AAS (samples whose certified values are not available) as well as with certified values of CRMs. Regarding method, as is evident, the results obtained are satisfactory and this method can be used for cobalt determination (Abouhiat et al., 2017; Amin, 2014; Gurumoorthy et al., 2017; Moradi et al., 2012; Wen et al., 2013; Zou et al., 2014).

CONCLUSIONS

This is a new and highly selective method for cobalt determination in geological samples having cobalt content 10 ppm and above. The striking feature of the proposed method is that unlike other thiocyanate methods and their variants where iron seriously interferes (iron forms a reddish-purple, Fe-SCN complex), in the proposed method, the interference of iron is completely eliminated by extracting the Co-SCN-CTAB complex at pH 8.0 where Fe-SCN complex gets completely broken. Thus, the method developed is highly selective for Cobalt determination in rock, soil and mineral samples.

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