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Ion Flotation and Flame Atomic Absorption Spectrophotometric Determination of Nickel and Cobalt in Environmental and Pharmaceutical Samples Using a Thiosemicarbazone Derivative

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THIOPHENE-2-Carboxaldhyde-4-Phenyl thiosemicarbazone (TAPT), a NS containing ligand, combines with Ni (II) and Co (II) each individually and in combination, to form complexes in aqueous solution. These complexes could be successfully separated by a surfactant mediated methodology using oleic acid (HOL) surfactant. The concentration of the separated analytes was determined by flame atomic absorption spectrometry (FAAS). The different parameters affecting the flotation efficiency such as pH, the concentration of TAPT and surfactant, temperature and sample volume, were optimized. The interference from different cations and anions was studied. Beer's law was obeyed over a concentration range of 0.5 - 4.0 ppm. The analytical detection limits were 2.5 and 2.8 ng/L for of Ni (II) and Co (II), respectively. The recoveries of Ni (II) and Co (II) from the synthetic mixtures and water samples are > 96 % and the relative standard deviations (RSD) were below 1.2%. The proposed method was successfully applied to the determination of nickel and cobalt in environmental water samples as well as the determination of cobalt in B12 vitamin samples. The mechanism of flotation is proposed.

Keywords: Thiosemicarbazone, FAAS, Nickel, Cobalt, Flotation.

Introduction

Water is a vital element in each of our lives on the earth. It is used almost in all human activities; however its return to its original sources after usage usually causes pollution. This pollution unfortunately will make a lot of countries suffer difficulties in reserve of pure water [1]. Industrial effluents may have various amounts of non-biodegradable heavy metal ions, like copper, cobalt, zinc, nickel and mercury which are known as toxic and carcinogenic metals.

Nickel and cobalt are ubiquitous trace metals that occur in soil, water, air, and in the biosphere. They are used for a wide variety of purposes in modern industry. Nickel is considered as essential metal to plants [2]. Its bioavailability to organisms and related biochemical process is dependent on the compounds formed by nickel and such compounds are considered carcinogenic [3]. Exposure to nickel can lead to skin dermatitis and also in case of inhaling nickel through vapors that may cause asthma, bronchitis, lung cancer and other respiratory tract diseases. The acceptable concentration limits of nickel in water samples established by World Health Organization (WHO) is 70 µg L^{-1} [4, 5].

Cobalt is essential at trace levels to all living beings for metabolic processes [6]. Cobalt is important for living species for the synthesis of vitamin B12 complex and its deficiency usually leads to different types of anemia. On the other hand, large amounts of cobalt have several adverse effects such as vasodilation, flushing and cardiomyopathy for both human and animals [7].

It has been demonstrated that even discharging small amounts of some of these heavy metal ions leads to inevitable damage to the aquatic ecosystem, so mitigating their detrimental effects is of great importance for environmental scientists prior to discharge into water supplies Therefore, the determination of cobalt and nickel at trace level in water and environmental samples is greatly important for the public health from the environmental point of view.

Inductively coupled plasma optical emission spectrometry (ICP-OES) [8], graphite flame atomic absorption spectrometry (GFAAS) [9-11], flame atomic absorption spectrometry (FAAS) [12-16], electro-thermal atomic absorption spectrometry (ETAAS) 17,18], inductively plasma mass spectrometry (ICP-MS) [19] and other atomic and molecular methods, have been used for the determination of the trace metals [20].

Flame Atomic absorption spectrometry (FAAS) is a very sensitive analytical method with low detection limits for many heavy metals. In many cases the determination of the trace metals in water samples by FAAS is hard. This is because of the low levels of these metals in the samples and the high complexity of the sample matrices [21]. Thus, separation and pre-concentration procedures are required for elimination or minimization of matrix effects and concomitants. Several methods of separation have been reported such as precipitation, ion exchange, adsorption, electro-dialysis, liquid–liquid extraction and filtration was used [22-24]. However, these techniques are multistep, time consuming and need extensive equipment, chemicals and handling.

On the other hand, flotation is an effective separation method for removing toxic heavy metals from different environmental samples [25-40]. The flotation process has a high potential in this field because it has many advantages being very easy, fast operation, of low costs, low residual concentration of metals, small space requirements and can easily be applied to various metals at different levels [33].

In this study, thiophene-2-carboxaldhyde-4-phenylthiosemicarbazone (TAPT), (structure 1), was selected as chelating reagent and an ion flotation method combined with flame atomic absorption spectrometer (FAAS) methodology was developed for preconcentration, separation and determination of cobalt and nickel in water and drug samples. The factors affecting the flotation

efficiency such as solution pH, concentration of metal ions, organic ligand and surfactant, flotation time, sample volume, nature of surfactant, and the ionic strength will, all, be studied and optimized.

thiophene-2-carboxaldehyde-4-phenyl thiosemicarbazone
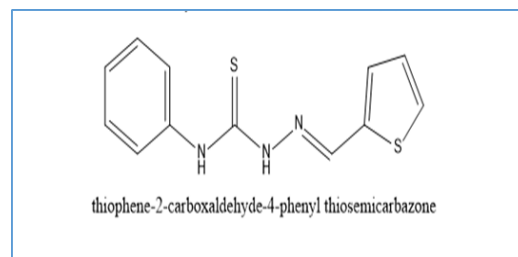
Structure 1

Experimental

Chemicals and reagents

All chemicals used were of analytical-reagent grade or the highest purity available. Doubly distilled water (DDW) was used throughout. Stock solutions (0.017 mol/L) of Ni (II) and Co (II) were prepared by dissolving 0.4049 g and 0.4037 g of $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ in 1.0 L DDW, respectively.

A 6.3×10^{-2} mol/L stock solution of oleic acid (HOL) was prepared from the food grade product with sp. gr. 0.895 (from J.T. Baker chemical Co.) by dispersing 20 ml of the oleic acid in 1.0 L of kerosene. Solutions of other foaming reagents (0.05%) were prepared by dissolving appropriate amounts of surfactants; Triton X (TX 100) in water, cetyl trimethyl ammonium bromide (CTAB) in 95% ethanol, sodium palmitate (NaPL) and sodium stearate (NaST) in 99.7% propano1. Vitamin B12 ampules, were analyzed to determine the cobalt content in each drug sample using the proposed methodology. Exactly 1 mL, of each drug sample was taken, and heated in 5 mL concentrated HNO_3 for dissolution. The cold solution was filtered, collected in a 50 - mL calibrated flask and completed to the mark with DDW.

Apparatus

Two flotation cells (a cylindrical tube with 15 mm/6cm inner diameter and 290 mm/45cm length and both with a stopcock at the lowest and a stopper at the top) were the same type as previously defined [38]. These two cells were used to study the experimental variables affecting the efficiency of flotation. Elemental analyses (C, H, N) were performed with a Perkin- Elmer 2400

series II analyzer at the Micro Analytical Center at Cairo University, Egypt. Infrared spectra of the studied ligand and its isolated complexes were recorded as KBr discs on Mattson 5000 FTIR spectrophotometer (400-4000 cm^{-1}).

Traces of Ni (II) and Co (II) were determined by flame AAS using Perkin- Elmer 2380 atomic absorption spectrometer at 232 and 242.5 nm, respectively. The pH was controlled with 1.0 M HCl and/or 0.5 M NaOH and measured with a digital pH meter (Hanna Instruments, model 8519).

Preparation

Preparation of thiophene-2-carboxaldhyde-4-phenylthiosemicarbazone (TAPT)

Thiophene-2-carboxaldhyde-4-phenylthiosemicarbazone(TAPT)was synthesized as described elsewhere [40] by refluxing the mixture of 4-Phenyl-3-thiosemicarbazide and 2-thiophenaldehyde after adding 0.5 mL of glacial acetic acid. The purity of the reagent was checked by C, N and H analysis and infrared spectrometry. The product is crystalline (m.p.189°C), sparingly soluble in ethanol and/or methanol but easily soluble in acetone, DMF and DMSO. Stock solution 1x10^{-3} mol/L was prepared by dissolving 0.02614 g of TAPT salt in 100 mL of acetone.

Recommended method

A suitable known amount (5x10^{-5} mol/L) of Ni (II) and Co (II) each individually or in combination was mixed with 2 mL of 2x10^{-3} mol/L TAPT followed by the addition of 3 mL of DDW. After adjusting the pH with 2 mL of 1.0 mol/L NaOH and/or 0.5 mol/L HCl to the required value, the solution was transferred to the flotation cell and made up the volume to 10 mL with DDW. The cell was shaken well for few seconds to ensure complexation. Then, 2 mL of 2x10^{-4} mol/L HOL, which is still below the critical micelle concentration (CMC), were added. The cell was then inverted upside down twenty times by hand for complete flotation. The scum layer was collected, eluted with 2 mL of 1.0 mol/L HNO$_3$ and aspirated directly to the flame to determine Ni (II) and Co (II) individually at 232 and 242.5 nm, respectively.

The flotation efficiency (F %) was calculated in the scum layer from the relation:

$$F \% = (C_f/C_i) \, x100$$

Where C$_i$ was the initial concentration of analyte in the mother liquor before flotation and C$_f$ was the concentration of analyte after flotation in the scum layer.

As an alternative, the flotation efficiency (F, %) of Ni (II) and Co (II) in mother liquor was determined from the relation:

$$F= (C_i\text{-}C_f) / \, C_i \times100\%,$$

Where C_i and C_f denote the initial and final concentrations of analyte in the mother liquor, respectively.

Calibration curves were constructed in the concentration ranges 0.5 - 4.0 mg/L and the concentrations of Ni (II) and Co (II) ions were determined by FAAS at 232.0 and 242.5 nm, respectively. It is worthy to note that at selected wavelength, the instrumental detection limits of Ni (II) and Co (II) were 0.25 and 0.28 µg/L, respectively.

Results and Discussion

Flotation-separation and FAAS determination of nickel and cobalt

Effect of pH

The effect of pH on flotation efficiency of 5x10^{-5} mol/L analyte was investigated in the range of (2.0-9.0) in the presence and in the absence of (2.0x10^{-3}mol/L) chelating agent (TAPT) using 3.0x10^{-4} mol/L HOL at room temperature. In the absence of TAPT, Fig. 1a shows that maximum value of F % for Co (II) and Ni (II) was 25% in the pH range of 2.0 - 9.0. On the other hand, Fig. 1b, in the presence of TAPT, shows that the flotation efficiency of Co (II) and Ni (II) sharply rises from zero to nearly 100% at pH 5.0 and remains constant up to pH 6.0, and then it decreases. The marked decrease in F% at low pH is due to competition of hydrogen ion with analyte for reaction with TAPT. All further measurements were carried out at pH 5.5.

Effect of TAPT and analyte concentration

The effect of TAPT concentration on the flotation % of 5x10^{-5}mol/L of Ni(II) and Co (II) at pH 5.5 was investigated in the range of (3.0 -20.0) x10^{-5} mol/L using 3.0x10^{-4} HOL. The results in Fig. 2 show that the F% of nickel and cobalt increased with an increase in TAPT concentration up to 1.0x10^{-4} mol/L which is two times the concentration of analyte. The F% was kept constant with the increase of the concentration of the chelating agent. A finding that facilitates the determination of the studied analytes in media with unknown levels of these analytes.
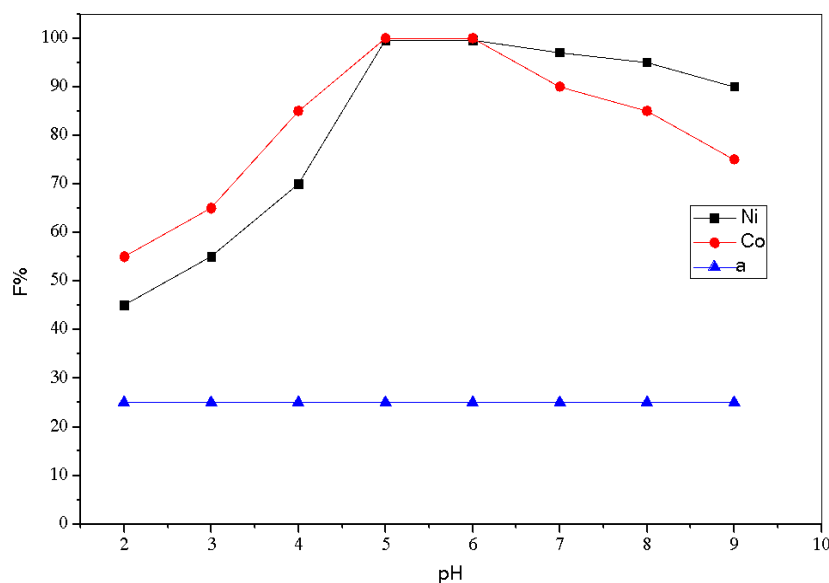
Fig. 1. Effect of pH on the flotation efficiency of 5×10^{-5} mol/L of Ni (II) and Co (II) (a) in the absence of TAPT ; (Ni, Co) in the presence of 2.5×10^{-4} mol/L TAPT using 2.0×10^{-4} mol/L HOL at room temperature, (n=5.)
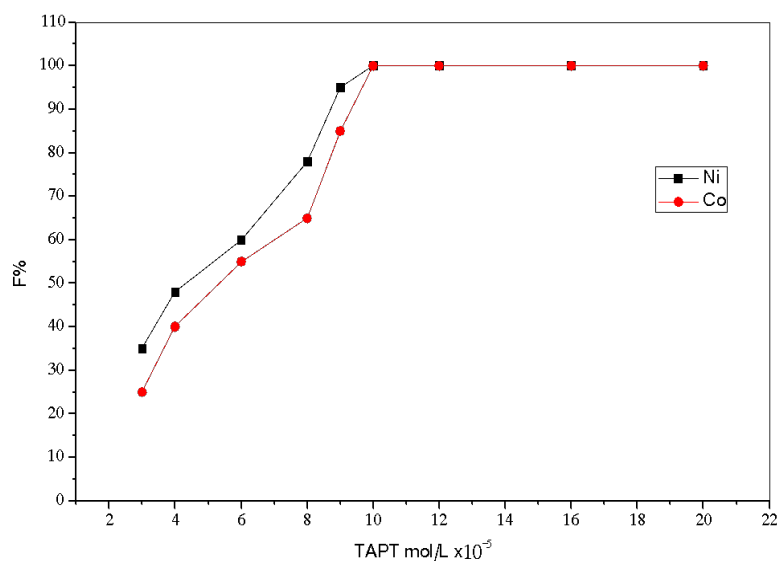

Fig. 2. Effect of TAPT concentration on the flotation efficiency of 5×10^{-5}mol/L of Ni (II) and Co (II) at pH 5.5 using 2.0×10^{-4} mol/L HOL at room temperature, (n=5).

To confirm the previous ratio, a series of experiments was carried out by changing the metal concentration. The obtained data showed that complete flotation occurs at the same previous ratio of 1:2 (M: L). Above such ratio increasing analyte concentration leads to a decrease in the flotation efficiency. This reflects that an insufficient amount of ligand is present for complete complexation and indirect flotation.

Accordingly, a concentration of 1.0×10^{-4} mol/L TAPT was selected for the subsequent work.

Effect of different types of surfactants

In order to study the influence of the type of surfactant on the flotation efficiency of 5×10^{-5} mol/L of analytes with 1×10^{-4} mol/L TAPT at pH 5.5, various ionic and polar surfactants individually and in combination were tested. The results are

given in Table 1. As it can be noticed, nonionic surfactants such as TX-100 and also cationic CTAB foamed very well and form a copious white scum at the top of the aqueous phase, but the analytes were not separated by flotation and remained in the aqueous solution.

On contrast, the anionic surfactants were more effective than the other ones. As it is obvious from Table 1, the F% of Ni (II) and Co (II) upon using HOL was almost 100 %. Nickel and cobalt can also be floated by the anionic surfactants NaOL and NaPL although to some lower extent. Considering our experience that the application of more than one surfactant gives an unnecessarily too copious scum which is very difficult to elute

by conc. HNO$_3$. Thus, HOL was chosen as the most appropriate surfactant for the subsequent experiments.

Effect of oleic acid (HOL) concentration

Various experiments were carried out to study the effect of HOL concentration on the floatability of 5x10^{-5} mol/L analyte in the absence (Fig. 3, curve a) and in the presence of 1.0x10^{-4} mol/L TAPT (Fig. 3, curve b), at pH 5.5. As shown in Fig. 3, curve b, the flotation efficiency of Ni (II) and Co (II) increases to its maximum value and remains constant over a wide range of HOL concentration (1-8) x 10^{-4} mol/L. Hence, 2 × 10^{-4} mol/L of HOL was fixed throughout all subsequent experiments.

TABLE 1. Applicability of different foaming reagents for ion flotation of each analyte using; (5.0x10^{-5}mol/L analyte in the presence of 1.0x10^{-4} mol/L TAPT) at pH 5.5 at room temperature (n=5).

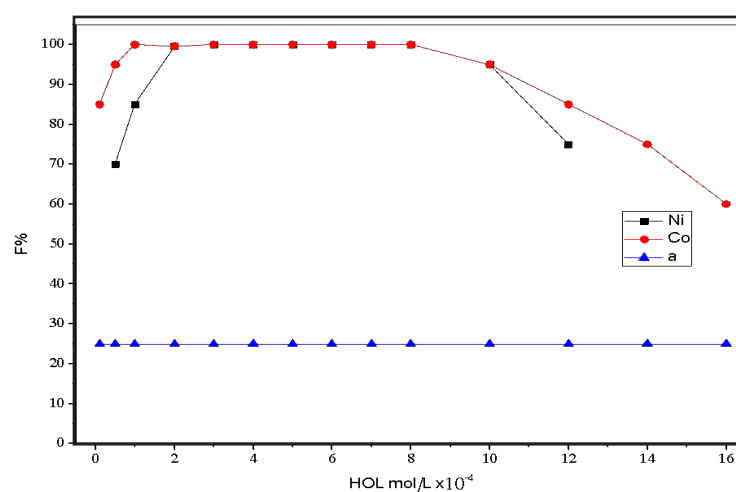| Surfactant	F%	
	Ni(II)	Co(II)
TX-100	Foam, no flotation	Foam, no flotation
CTAB	Foam, no flotation	Foam, no flotation
NaST	92.5	92.5
HOL	99.5	99.0
NaPL	88.0	75.0
NaST/HOL	98.3	98.5
NaPL/HOL	96.0	97.0
NaPL/ NaST	94.1	93.5

Fig. 3. Effect of HOL concentration on the flotation efficiency of 5x10^{-5}mol/L Ni (II) and Co (II) at pH 5.5; (a) in absence of TAPT; (Ni, Co) in the presence of 1.0x10^{4-} mol/L TAPT at room temperature, (n=5).

Effect of temperature:

In order to study the optimum temperature required for quantitative flotation of 5×10^{-5} mol/L of analyte each individually or in combination with 1.0×10^{-4} mol/L TAPT at pH 5.5, a series of experiments was conducted over a wide temperature range (20 – 100°C) using 2.0×10^{-4} mol/L HOL. The floatability % of the complexes formed was not markedly affected in the 20 – 60°C range, as shown in Fig. 4. Therefore, subsequent studies were carried out at room temperature.

Flotation time and stability of Ni (II)-TAPT and Co (II)-TAPT complexes within the scum layer

Flotation time could be defined as the interval time related to the introduction of all reagents [Ni (II), Co (II), TAPT, HOL and buffer] into the flotation cell and the start of flotation. The effect of flotation time for the flotation efficiency of Ni (II) and Co (II) was examined over a time period range of 0.0 – 60.0 min whilst the other parameters were kept constant. It had been found out that maximum flotation (100%) could possibly be obtained within 2 min (Fig. 5). A time period of 5 min was chosen for subsequent experiments as the flotation time. Because of this, the flotation separation procedure isn't time consuming. To confirm the stability of Ni (II)-TAPT and Co (II)-TAPT complexes after 5 min, additional tests had been performed from 5 min to 72 hours. It had been demonstrated that the absorban*ce* of the floated Ni (II)-TAPT and Co (II)-TAPT complexes in the scum layer as well as the separation efficiency % didn't change approximately for 48 hr.
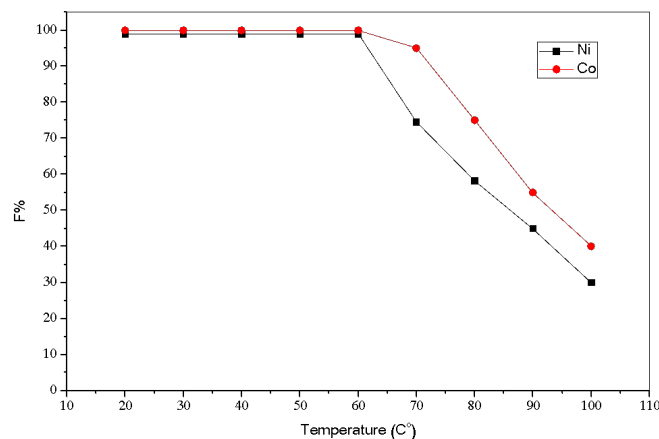
Fig. 4. Effect of temperature on flotation efficiency of 5×10^{-5} mol/L of analytes in the presence of 1.0×10^{-4} mol/L TAPT using 2.0×10^{-4} mol/L HOL at pH 5.5,(n=5).
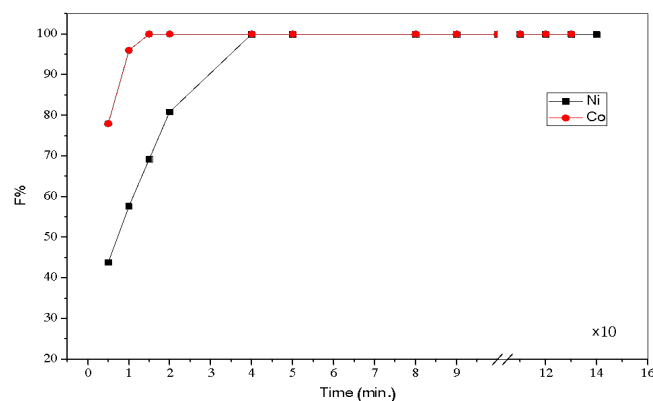

Fig. 5. Effect of time on the flotation efficiency of 5×10^{-5} mol/L of analyte in the presence of 1.0×10^{-4} mol/L TAPT using 2.0×10^{-4} mol/L HOL at pH 5.5 at room temperature, (n=5).

Effect of sample volume

A series of experiments was conducted to float a fixed concentration of each anlyte (5×10^{-5} mol/L), individually and in combination, from different aqueous volumes using suitable large flotation cells under the recommended conditions. The data presented in Fig. 6 shows that 5×10^{-5} mol/L of Ni (II) and Co (II) can be quantitatively separated from different aqueous volumes up to 1.0 L; after which, the floatability decreases by 25% at 1.5 L. Accordingly, with this methodology, 8.6×10^{-7} mol/L of Ni (II) and 6.8×10^{-7} mol/L of Co(II) could be pre-concentrated, separated and quantified from different aqueous volume up to 1.0 L upon adding five milliliters of 2.0×10^{-4} mol/L HOL with a preconcentration factor of 100.

Influence of the viscosity of scum layer

The obtained scum layer, after flotation, was very viscous. Therefore, proper elution of the surfactant-rich phase before aspiration to the flame of the atomic absorption spectrophotometer was necessary. The effect of different eluting solvents on analytical signals of Ni (II) and Co (II) was investigated. The results revealed that maximum signal was obtained by the use of 2.0 mL of 1.0 mol/L HNO_3. Thus, 2 mL of 1.0 mol/L HNO_3 was selected for further experiments.

Effect of foreign ions

The effect of interfering ions on the flotation % of Ni (II) and Co (II) ions under the optimum conditions was examined. These foreign ions were selected on the basis that they are normally present in fresh and saline waters. Table 2 showed that most of the tested foreign cations did not interfere in the recovery of analytes. The effect of some other foreign ions that have little interfering effects, was completely removed by increasing the concentration of TAPT.

The analytical characteristics

Under optimum conditions that are described in the suggested procedure, the calibration curves show good linearity over the range 0.5 - 4.0 mg/L of both analytes. The analytical detection limit of a standard aqueous solution is 2.5 and 2.8 ng/L for Ni(II) and Co(II), respectively, with a relative standard deviation (n = 8) of 1.1 and 0.6 % for Ni (II) and Co (II), respectively. The analytical characteristics of this method is shown in Table 3.

Flotation Mechanism

The suggested flotation mechanism of analytes is based on the following points: the analyte reacts with the thiosemicarbazone derivative (TAPT) to form a 1:2 complex in aqueous solution. The most characteristic features of the IR spectrum of TAPT (Fig. 7&8, curve a) are as follow: it exhibits ν(N-H) band at 3140 cm^{-1} and also the bands at 1546 and 835 cm^{-1} are attributed to ν(C=N) and ν(C=S) vibrations, respectively.

Careful comparison of the IR spectra of the Ni-TAPT and Co-TAPT complexes, isolated from the aqueous solution and surfactant layer (Fig. 7&8) (curve b& c), respectively with that of TAPT shows that the ligand behaves as a bidentate
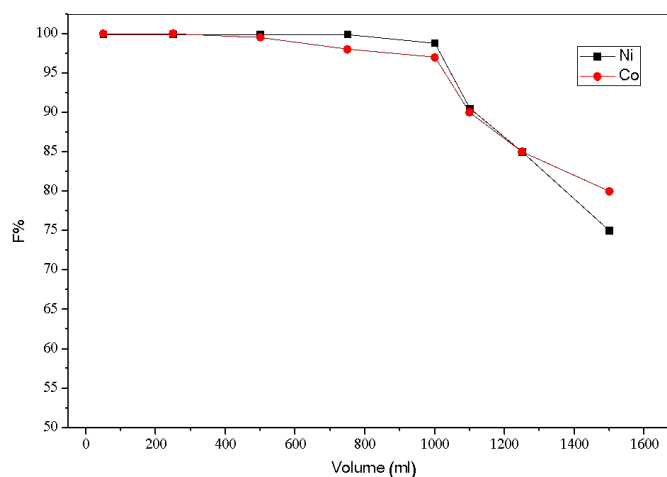

Fig. 6. Effect of volume on the flotation efficiency of 5×10^{-5} mol/L of analyte in the presence of 1.0×10^{-4} mol/L TAPT and 2.0×10^{-4} mol/L HOL, at pH 5.5 at room temperature, (n=5).

TABLE 2. Tolerance limits for the determination of 5.0x10^{-5}mol/L Ni (II) and Co (II), (n=5).

Foreign ions	Concentration (mg/L)	F%	
		Ni(II)	Co(II)
Pb^{+2}	5.0	99.5	98.3
Pd^{+2}	5.0	96.9	96.0
Zn^{+2}	5.0	97.1	97.3
Mn^{+2}	10.0	99.5	98.3
Hg^{+2}	5.0	98.5	97.6
Ba^{+2}	10.0	99.5	98.3
Cr^{+2}	10.0	99.5	98.4
Cu^{+2}	3.0	99.5	98.4
Fe^{+3}	3.0	99.5	97.4
Au^{+3}	3.0	96.0	97.6
Bi^{+2}	3.0	99.3	98.3
Al^{+3}	3.0	99.3	98.3
Na^+	230.0	97.5	99.8
Cl^-	177.5	99.9	99.9
CH_3CO	295.0	98.5	98.2
NO_2^-	230.0	99.8	99.8
NO_3^-	310.0	99.9	99.9
$S_2O_3^-$	440.0	93.2	99.0
CO_3^-	300.0	97.0	98.0

TABLE 3. Analytical characteristics of the method.

Parameter	Ni(II)	Co(II)
Linear range (mg/L)	0.5- 4.0	0.5-4.0
RSD % (n=3)	1.1	0.6
LOD (ng/L)	2.5	2.8
Enrichment factor	5.03	5.0
Correlation coefficient	0.9969	0.9772
Regression equation*	A = 1.4714 c + 0.2518	A = 1.3493 c - 0.2707
Sample volume (ml)	10	10

*A=Absorbance, C=concentration

ligand in the thione form and coordinates through the C=N and C=S groups.

These bonding sites are suggested based on the following evidence: i) the shift of n(C=N) and n(C=S) to a lower frequency; ii) the appearance of a new band at 422-420 and 500-530 cm^{-1}, for Ni(II) and Co(II) assignable to v (Ni-N) and n(Ni-S), respectively; iii) The obviously increase in frequency of v(N–N) band from 1205 cm^{-1} supports the coordination of imine N atom [36]. Moreover, the solid-state electronic spectra of TAPT ligand, exhibit two bands in the 344 nm

and 260 nm regions. An intense band at *ca.* 344 nm is attributed to the n→π* transitions of C=S group, C=N group and thiophene ring, which are overlapped. The π→π*transitions of the thiophene ring and thiosemicarbazone imine function are observed at *ca*. 260 nm. These two bands are shifted to lower energies (bathochromic shift) after complexation [37]. The appearance of new band at 420 - 416 nm, and μ_{eff} = diamagnetic-4.5 for Ni (II) and Co (II), respectively. All the above observations suggest a square planar structure for the complex [Ni (TAPT)$_2$].Cl$_2$ and octahedral for [Co(TAPT)$_2$Cl$_2$].
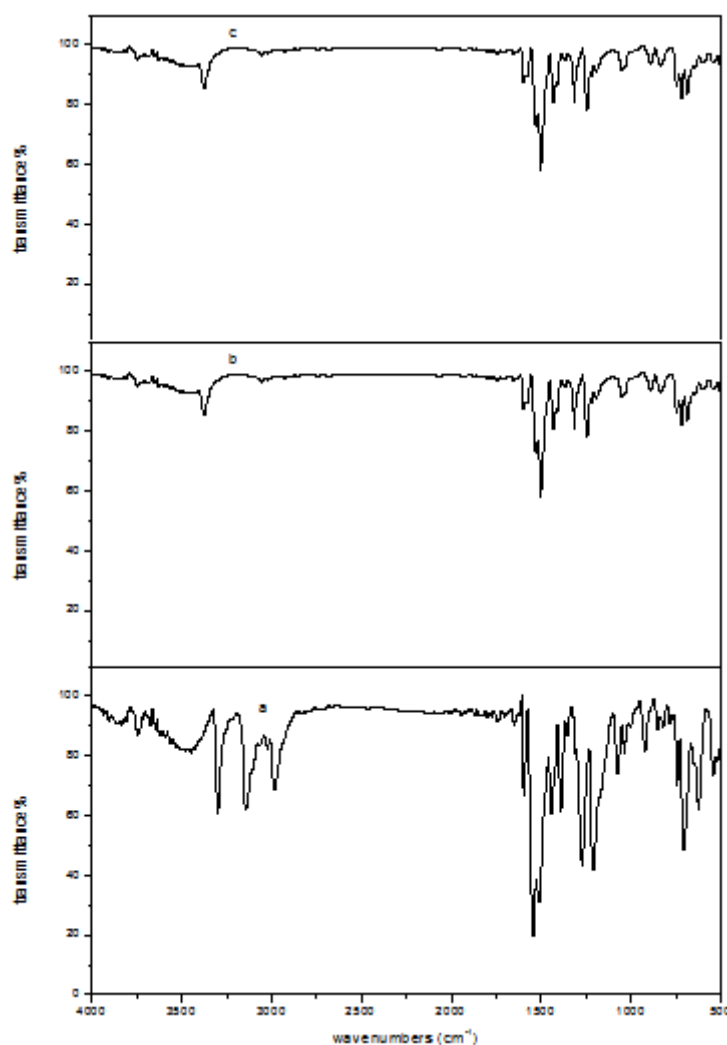
Fig.7. FTIR spectra of (a) The reagent TAPT; (b) Ni–TAPT complex and (c) Ni–TAPT–HOL floated complex.

The infrared spectra of the complexes isolated from the surfactant layer (after thorough washing) have no absorption bands corresponding to the oleic acid surfactant (Fig. 7c & 8c). The floated species have the same color as that obtained in the aqueous solution. The data in Fig. 4 shows that increasing the temperature above 60 ºC decreases the separation percentage, reflecting that the physical force between HOL and the Ni-TAPT complexes are destroyed by heating. All these findings reflect the fact that there is no coordinate or hydrogen bond contribution between HOL and the Ni-TAPT and Co -TAPT complexes. In conclusion, all of the mentioned studies confirm that the flotation mechanism of Ni(II)-TAPT and Co(II)-TAPT complexes using HOL surfactant is physical in nature;

a sublate structure of the floated complexes is presented in Fig. 9.

Applications

Natural water sample

The developed procedure for the determination of Ni (II) and Co (II) using a flotation methodology and FAAS was applied to several natural water samples. The recoveries % of spiked known additions to different water samples are greater than 98% and the RSD (n=5) is less than 1.2%, as shown in Table 4.

Analysis of pharmaceutical samples

The flotation followed by FAAS determination was applied to determine Co (II) in some vitamin B12 samples. The experimental results agreed well with the given reported values (Table 5).
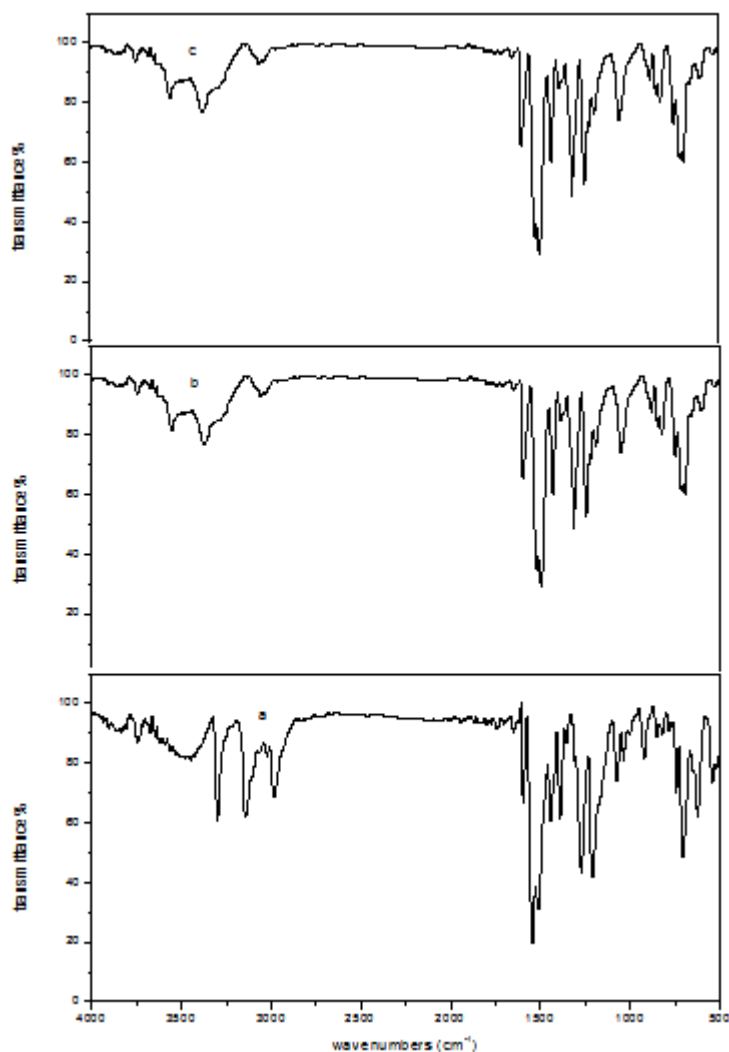
Fig. 8. FTIR spectra of (a) The reagent TAPT; (b) Co–TAPT complex and (c) Co–TAPT–HOL floated complex. The measurements were carried out in KBr discs.

Application to synthetic mixtures

An aliquot of 10 ml of aqueous sample solution containing different compositions of foreign metal ions (Cd (II), Zn (II), Mn (II) and Cu (II), Fe (III), Au (III) and different amounts of the analytes, 5 x10^{-3} mol/L of TAPT and 1.0x10^{-4} HOL. The flotation procedures were performed under the previously mentioned optimum conditions and the recovery of the analytes were determined. Table 6 showed that there were high recoveries of the analytes from samples containing different synthetic mixtures.

Comparison of ion flotation with other methods

Determination of nickel and cobalt in water samples by the proposed combined ion flotation-FAAS using TAPT chelating agent and HOL surfactant, was compared with other methods recently reported (Table 7). As it can be seen the proposed flotation-FAAS method is greatly comparable to the previously repo

Conclusion

The ion flotation separation method using HOL as a surfactant and TAPT as chelating agent was successfully employed for determination of cobalt and nickel in environmental samples by FAAS. The method proposed here is simple, rapid, inexpensive and has good reproducibility. This study offers a nonpolluting technique for the pre-concentration and determination of trace metals.
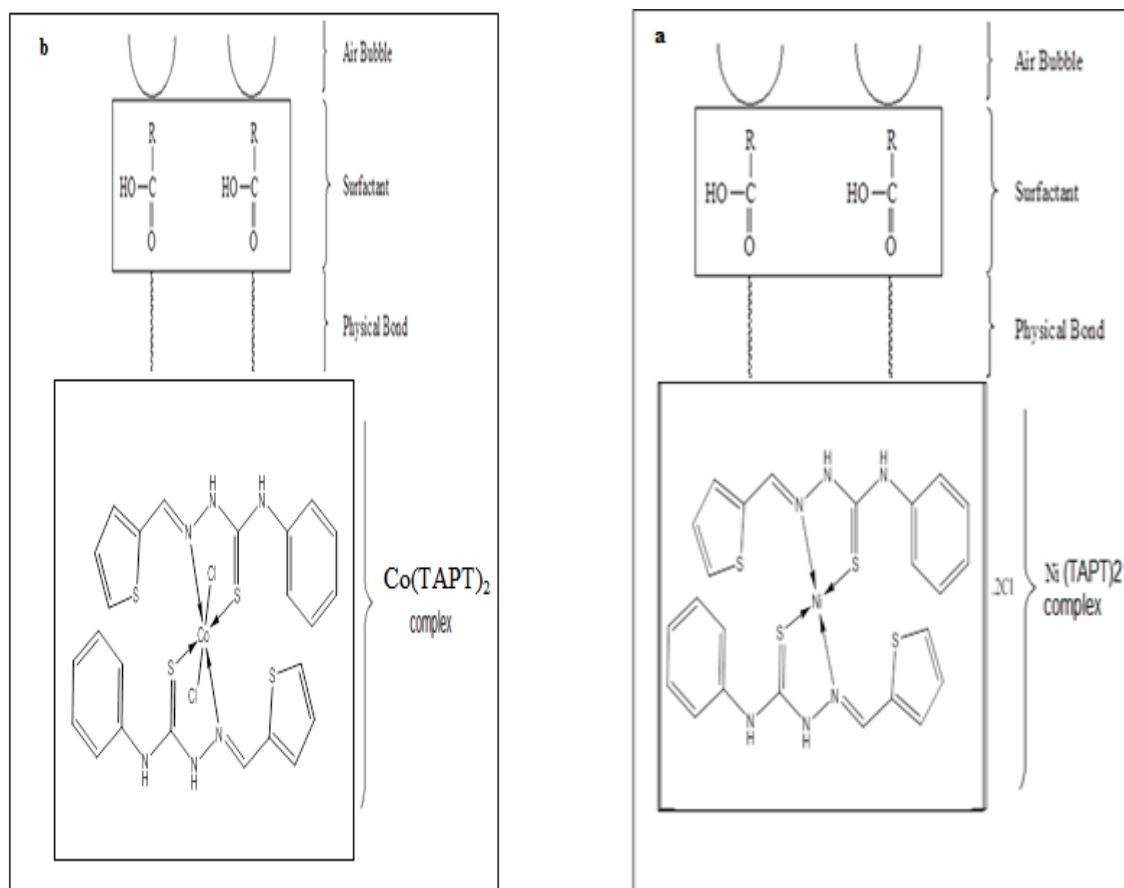
Fig. 9. Mechanism of flotation; (a) [Ni (TAPT)$_2$]Cl$_2$ complex; (b) [Co(TAPT)$_2$Cl$_2$].

TABLE 4. Recovery of Ni (II) and Co (II) spiked in natural water samples after flotation using 2x10^{-3}mol/L TAPT and 1.0x10^{-4} mol/L HOL at pH 5.5 at room temperature.

Types of water (location)	Ni (II) Added (mg/L)	Co (II) Added (mg/L)	Recovery %		RSD, %	
			Ni(II)	Co(II)	Ni(II)	Co(II)
	2.00	4.00	99.5	99.5	1.10	0.80
Distilled water	4.00	8.00	98.4	98.4	0.90	0.90
	8.00	10.0	99.8	98.8	1.01	1.10
Tap water (Tanta city)	2.00	4.00	99.8	98.8	0.89	0.70
	4.00	8.00	98.7	98.7	0.92	0.90
	8.00	10.0	99.3	98.3	0.8	0.60
Nile water (Mansoura city)	2.00	4.00	99.4	98.4	0.78	0.80
	4.00	8.00	99.7	99.7	0.98	1.02
	8.00	10.0	98.2	98.2	1.01	0.70
Sea water (Alexandria city)	2.00	4.00	99.4	99.4	0.79	0.88
	4.00	8.00	99.6	99.6	0.82	0.93
	8.00	10.0	99.8	99.8	0.98	0.70
Ground water	2.00	4.00	98.3	98.3	1.00	0.62
	4.00	8.00	98.5	98.5	1.03	0.93
	8.00	10.0	98.2	97.2	0.98	1.04
Tap water (Meat Anter)	2.00	4.00	99.6	99.6	0.88	0.94
	4.00	8.00	99.8	99.8	0.98	0.82
	8.00	10.00	99.2	99.2	1.00	1.1

TABLE 5. Statistical evaluation for analysis of some pharmaceutical vitamin B12 samples after flotation (n=5). Comparison of experimental mean ($\overline{X}$) mg/ampule with true value (μ), by $|t|_1$ test

Sample	($\overline{X}$)	μ	S	$|t|_1$	RSD,%
No. 1[a]	0.99	1.0	0.01	0.49	1.98
No. 2[b]	0.98	0.5	0.02	0.75	2.04

[a] Betolvex (Menapharm) ampule. [b] Cobalvex ampoule.(Sigma)($\overline{X}$): experimental value, (μ) true value; $|t|_1$ for P = 0.05 and n = 5 (4 degree of freedom) = 2.78. R.S.D., %: Relative standard deviation.

TABLE 6. Recovery of Ni (II) and Co (II) from synthetic mixtures.

Synthetic mixtures composition (mg/L)	Concentration Added of each, (mg/L)	Ni(II) (mg/L)		Co(II) (mg/L)	
		founded	R%	Found	R%
$Cd^{+2}+ Zn^{+2}$	2.0	1.960	98.00	1.964	98.2
$Cd^{+2} + Cu^{+2}$	2.0	1.966	98.30	1.960	98.0
$Cd^{+2} + Zn^{+2}+ Co^{+2}$	3.0	2.980	99.30	2.925	97.5
$Fe^{+3} + Zn^{+2}+ Au^{+2}$	3.0	2.941	98.03	2.940	98.0
$Co^{+2} + Zn^{+2}+ Cd^{+2} +Au^{+2}$	4.0	3.852	97.00	3.888	97.2
$Fe^{+3}+ Zn^{+2}+ Cd^{+2} + Mn^{+2}$	4.0	3.920	98.00	3.896	97.4

TABLE 7. Comparative data from some recent studies on preconcentration-separation of Ni (II) and Co(II) ions.

Method	System	DL(ng/L)		EF		R.S.D, %		Reference
		Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)	
SFODME	GFAAS	0.3	0.4	502	497	4.6	3.6	[9]
Emulsion	GFAAS	6	10	100	100	-	-	[11]
CPE	FAAS	1090	1220	27	29	2.53	2.89	[12]
CPE	ICP-OES	-	6.3[a]	-	9.79[b]	-	2.6	[8]
CPE	ETAAS	0.5[a]	-	-	15	4.5	-	[17]
SPE	FAAS	-	800	-	43	-	-	[13]
SPE	FAAS	-	920	-	200	-	-	[14]
SPE	FAAS	-	0.75[a]		330[b]	-	0.9	[15]
DLPME	GFAAS	21	33	101	200	7.5	8.2	[10]
CME	ICP-MS	0.33	1.5	10	10	2.7	4.1	[19]
Flotation	GFASS	7.8[a]	9.0[a]	-	-	-	-	[16]
Flotation	ETAAS	-	0.7[a]	-	93[b]	-	<1	[13]
Ion flotation	FASS	2.8	2.5	100[b]	100[b]	<1.2		This work

SFODME: solidified floating organic drop micro-extraction; DLPME: dispersive liquid phase micro-extraction; CPE: cloud point extraction–flame atomic absorption; SPE: solid phase extraction–; CME: capillary micro-extraction; GFAAS: graphite furnace atomic absorption spectrometry; FAAS: flame atomic absorption spectrometry; ICP-MS: inductively plasma mass spectrometry; ETAAS: electro-thermal atomic absorption spectrometry, (a) µg/L; (b) Pre-concentration factorrted methods.

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التعويم الأيوني و التقدير بطيف لهب الامتصاص الذري للنيكل والكوبلت في عينات بيئية ودوائية باستخدام أحد مشتقات ثيوسيميكاربازون

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قسم الكيمياء ـ كلية العلوم ـ جامعة المنصورة ـ مصر.

تم عرض تقنية بسيطة للفصل عن طريق التعويم التقدير بطيف لهب الامتصاص الذري للنيكل والكوبلت في عينات بيئية ودوائية باستخدام أحد مشتقات ثيوسيمي كاربازون. في هذه الدراسة البحثية التي تستخدم فيها Thiophene-2-Carboxaldhyde-4-Phenyl thiosemicarbazone (TAPT) للتركيز المسبق لأيونات النيكل الثنائي والكوبلت الثنائي لتشكيل متراكب ملونة في محلول مائي في نطاق درجة الحموضة ٥,٠-٦,٠، وقد تم استخدام حامض الأوليك (HOL) السطحي لتعويم المتراكبات المتكونة بنجاح وبشكل كامل للطبقة العضوية. وقد تم تحديد الخصائص الفيزيائية والكيميائية للتقنية التحليلية المقترحة. تحت المعاملات المثلى، تم الحصول على الخصائص الفيزيائية ـالكيميائية التالية. تم اطاعة قانون بير حتى 4 ppm، والحد من الكشف (LOD) هي ٢,٥ و٢,٨ نج/لتر (ن = 5)، للنيكل والكوبلت على التوالي مع عامل تركيزمسبق 100 وRSD (ن = 5) هو ٢,٥٪. تم استخدام كمية زائدة من عامل مخلب TAPT لإخفاء آثار الأيونات المختلفة على كفاءة التعويم. تم تطبيق الإجراء المقترح لتقدير الكوبلت والنيكل في عينات دوائية ومائية. كما تم شرح آلية الفصل.