SIMULTANEOUS SEPARATION/PRECONCENTRATION OF NICKEL AND COBALT BY DISPERSIVE LIQUID-LIQUID MICROEXTRACTION PRIOR TO DETERMINATION BY FAAS

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Abstract

In this work, an efficient microextraction method was applied to the separation and preconcentration of Ni (II) and Co (II), namely dispersive liquid-liquid microextraction (DLLME). The influences of analytical parameters, including pH, extraction solvent volume, disperser solvent type and its volume, concentration of chelating agent, on the quantitative recoveries of nickel and cobalt were investigated. Under the optimized conditions, the detection limits were 1 µg L^{-1} and 3.5 µg L^{-1} for Ni and Co, respectively. The proposed method was applied to the determination of these elements in food samples with satisfactory results. The accuracy of the method was studied by analyzing certified reference materials.

Keywords: Cobalt, nickel, DLLME, certified reference materials, foods, FAAS

Introduction

The impact of trace elements on environment and man’s health has fostered the development of analytical techniques and instrumentation capable of measuring concentrations lower than the parts per million levels or less.

Cobalt is a natural earth element present in trace amount in soil, plants and our diets, which is an essential mineral, although the body only needs a small amount. Cobalt is an element that occurs naturally in many different chemical forms throughout the environment that has properties similar to those of iron and nickel. Small amounts of cobalt are essential for good health. Cobalt is a relatively rare element of the earth’s crust, composing approximately 0.001% of the earth's crust, which is essential to mammals in the form of cobalamin (vitamin B_{12}).

Natural sources of cobalt in the environment are soil, dust, sea water, volcanic eruptions and forest fires. People are commonly exposed to small amounts of cobalt naturally present in the air they breathe, the water they drink, and the food they eat. Very small amounts of cobalt in people's diets are necessary for good health.

Cobalt is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles the uptake by plants and animals is higher and accumulation in plants and animals may occur. The natural background air concentration of cobalt is in the order of 1 pg/m^3, but concentrations up to 40 ng/m^3 have been reported in urban areas. In occupational settings, workers are exposed to cobalt compounds by inhalation of dusts. The main industrial use of cobalt is for the manufacture of alloys and hard metals. The concentration of cobalt in soil varies widely, generally ranging from about 1 to 40 ppm, with an average level of 7 ppm. Soils containing less than about 3 ppm of cobalt are considered cobalt-deficient because plants growing in them do not have sufficient cobalt to meet the dietary requirements of cattle and sheep. On the other hand, soils near cobalt-containing mineral deposits, mining and smelting facilities, or industries manufacturing or using cobalt alloys or chemicals may contain much higher levels of cobalt. The concentration of cobalt in surface and groundwater is generally low, between 1 and 10 ppb in populated areas; concentration may be hundreds or thousands times higher in areas that are rich in cobalt-containing minerals or in areas near mining or smelting operations.

As an essential biochemical element, cobalt is mainly stored in red blood cells with smaller amounts in kidney, liver pancreas and spleen. Research indicates that cobalt helps with the repair of the myelin sheath, increases the effectiveness of glucose transport from the blood into body cells, and increases the assimilation of iron and the building of red blood cells. Cobalt is also an important agent of Vitamin B_{12}; it increases the body's ability to absorb it. Because of its low absorption rate and high excretion rate, cobalt toxicity is not common, but an excess can lead to enlargement of the thyroid gland.

Cobalt is toxic in large amounts and chronic ingestion of Co in the daily diet can cause toxic effects. Toxicological effects of cobalt include vasodilatation, flushing and cardiomyopathy in humans and animals. The respiratory system is the main target organ on inhalation exposure to cobalt, with a higher risk of fibrosing alveolitis and lung cancer in the hard metal industry, where workers are exposed to cobalt metal mixed with tungsten carbide particles. Other target organs include the hematopoietic system, the myocardium, the thyroid gland, and possibly the reproductive system.

The adult human body contains approximately 1 mg of cobalt, 85% of which are in the form of vitamin B_{12}. Human dietary intake of cobalt varies between 5 and 50 µg/day, and most of the cobalt ingested by humans is inorganic, vitamin B_{12} representing only a small fraction (Nordberg G.F., Fowler B.A., Nordberg M. and Friberg L.T., 2007).

On the other hand, nickel is a very abundant natural element. Nickel makes up about 0.01 to 0.02 % of the Earth's crust. It ranks about 22nd among the chemical elements in terms of abundance in the Earth's crust. Similarly to many other trace elements, nickel is ubiquitous in the environment being present in natural waters and practically all soils and foods. Food is the major source of nickel exposure, with an average intake for adults estimated to be approximately 100-300 µg per day. Individuals also may be exposed to nickel in occupations involved in its production, processing, and use, or through contact with everyday items such as nickel-containing jewelry and stainless steel cooking and eating utensils, and by smoking tobacco. Nickel is found in ambient air at very low levels as a result of releases from oil and coal combustion, nickel metal refining, sewage sludge incineration, manufacturing facilities, and other sources. (Cempel M and Nikel G., 2006)

Nickel can pose a health hazard to certain individuals. The most common health problem is called nickel allergy. Some people are more likely to develop nickel allergy than are others. People who are sensitive to nickel may develop a skin rash somewhat like poison ivy. The rash becomes itchy and may form watery blisters. Nickel is present in dozens of products. So it is easy for sensitive people to develop nickel allergy. Nickel can cause more serious health problems too. For example, people who are exposed to nickel fumes (dust and gas) breathe in nickel on a regular basis. Long term nickel exposure may cause serious health problems, including cancer.

The International Agency for Cancer Research, concluded in 1990 that nickel compounds were human carcinogens, and most animal data *in vivo* and genetic toxicology data *in vitro* before that time suggested that the insoluble particulate nickel species were the most carcinogenic; however, more recent human epidemiology and experimental data are pointing to the water-soluble nickel compounds as perhaps of equal hazard.

Several novel microextraction techniques are being developed in order to improve the quality and the sensitivity of the analytical methods. The cloud point extraction (CPE) (Ojeda C.B, Rojas F.S., 2009, 2012), the homogeneous liquid–liquid extraction (HLLE) (Ebrahimzadeh, H., Yamini, Y., Kamare, F., Shariati, S., 2007; Ghiasvand, A. R., Shadabi, S., Mohagheghzadeh, E., Hashemi, P., 2005); the liquid phase microextraction (LPME) (Ahmadi, F., Assadi, Y., Hosseini, M.R.M., Rezaee, M., 2006; Zanjani, M.R.K., Yamini, Y., Shariati, S., Jonsson, J.A., 2007), and the solid phase microextraction (SPME) (Djozan, D., Assadi, Y., Haddadi, S.H., 2001; Djozan, D., Assadi, Y., 2004) are fairly new methods of sample preparation. They are employed in the separation and preconcentration of environmental contaminants in different matrices and can solve some of the problems, encountered with the conventional pretreatment techniques. Recently, a new liquid-liquid microextraction method namely, dispersive liquid-liquid microextraction (DLLME) was proposed (Rezaee, M., Assadi, Y., Hosseini, M.R.M., Aghaee, E., Ahmadi, F., Berijani, S., 2006). This method has been applied for the determination of trace organic pollutants and metal ions in the environmental samples (Ojeda C.B., Rojas F.S., 2009, 2011). DLLME is based on a ternary component solvent system like homogeneous liquid-liquid extraction and cloud point extraction. In this method, the appropriate mixture of extraction solvent and dispersive solvent is injected into an aqueous sample rapidly with a syringe, and a cloudy solution is formed. The analyte in the sample is extracted into the fine droplets of extraction solvent. After extraction, phase separation is performed by centrifugation.

This work presents the development of a procedure for the separation/preconcentration of cobalt and nickel from diverse samples and its determination by FAAS. This procedure is based on DLLME after complexing these metal ions with 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide (DPTH).

Experimental

Standard solutions and reagents

Stock standard solution for Ni(II) and Co(II) (1000 mg L^{-1}) were supplied by Merck, Darmstadt, Germany. Standard solutions were prepared by appropriate dilution of the stock solutions daily.

High purity water (resistivity 18.2 MΩ cm) obtained by a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout this work.

2,2’-Bis(di-2-pyridinyl-methylene)-thiocarbohydrazone (DPTH) solution in DMF was prepared by dissolving solid reagent samples prepared and purified by the authors (Bonilla Abascal J., García de Torres A., Pavón J.M.C. 1983).

All the other reagents including extractants and disperser solvents were analytical-grade reagents, as well as the reagents mentioned above.

The acetate buffer solution was prepared to adjust pH values for the extraction of Ni and Co.

NaCl solutions were prepared by dissolving appropriate amounts of NaCl in deionized water.

Instrumentation

Phase separation was achieved with a centrifuge Selecta Centromix in 15 mL calibrated conical tubes. A Varian Model SpectrAA 50 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the analysis with the appropriate nickel and cobalt hollow cathode lamps. The operating parameters were set as recommended by the manufacturer. Atomic absorption measurements were carried out in an air-acetylene flame. The following conditions were used: absorption line Ni: 232.0 nm; slit widths: 0.2 nm; and lamp currents: 4 mA. Absorption line Co: 240.7 nm; slit widths: 0.2 nm; and lamp currents: 7 mA.

Sample analysis

The accuracy of the method for determination of nickel and cobalt content was checked by analyzing the reference standard material TMDA 54.4, Estuarine water (CRM LGC6016), Eau de mer (CASS-5), Riverine water (SLRS-5). These samples were analyzed by standard addition method and in the case the content of these analytes were under detection limits of the method, recovery studies were carry out.

The proposed method was also evaluated by analysis of Ni and Co in several spiked food samples. The Co and Ni concentrations in all the original samples were below the detection limit. For this purpose, standard solutions containing Co and Ni were added in 0.3–1.2 g of diverse foods, and the resulting materials were mineralized by reflux digestion, then evaporate to eliminate excess of acid, adjusted pH and diluted at convenient volume. Standard addition method was used in all instances.

DLLME procedure

For DLLME under optimum conditions, 10 mL analyte solution containing variable amounts of nickel and cobalt, 2 mL acetate buffer solution, pH 5.4, 1 mL of 0.05% DPTH solution in DMF as chelating agent was placed in a 15 mL screw cap glass test tube. Then, 1 mL of methanol (as disperser solvent) and 0.3 mL of chloroform (as extraction solvent) were rapidly injected into a sample solution by using a microsyringe. A cloudy solution was formed in the test tube and separation of the phases was achieved by centrifugation at 3800 rpm for 5 min. After this process, the organic phase was sedimented in the bottom of the conical test tube. After removal of the whole aqueous solution, the extraction phase was evaporated in a water bath to 60ºC and then diluted with HNO_3 0.1 M and aspirated into the FAAS.

Results and discussion

In order to obtain a high preconcentration factor, the effect of different parameters affecting the complex formation and extraction conditions, such as kind of extraction and disperser solvent and their volume, pH, concentration of the chelating agent, and salt addition, was optimized. One variable at a time optimization was used to obtain the optimum conditions for the DLLME.

pH study

The separation of metal ions by DLLME involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of the sedimented phase, thus, obtaining the desired preconcentration. pH plays a unique role on metal chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of nickel and cobalt from the samples was studied in the range of 3.0–8.0 by using acetate or phosphate buffer. The results reveal that the absorbance is nearly constant in the pH range of 4.5–6 for Ni and 5.0-5.5 for Co. Thus, the value of pH 5.4 was selected for the following experiments. Also, the influence of 0.2 M acetate buffer solution amount was investigated for variation of volume added from 1 to 4 mL. The extraction efficiency diminished between 3-4 mL. A volume of 2 mL was selected as the optimum value for subsequent work.

Effect of chelating reagent (DPTH) concentration

The effect of DPTH concentration on the absorbance was examined using increasing volumes of 0.05% DPTH from 0.5 to 2 mL. The results showed that the change of DPTH concentration in the studied range has effect on analytical signals (Figure 1), thus the volume of 1 mL, corresponding to its maximum value, was used in other experiments.

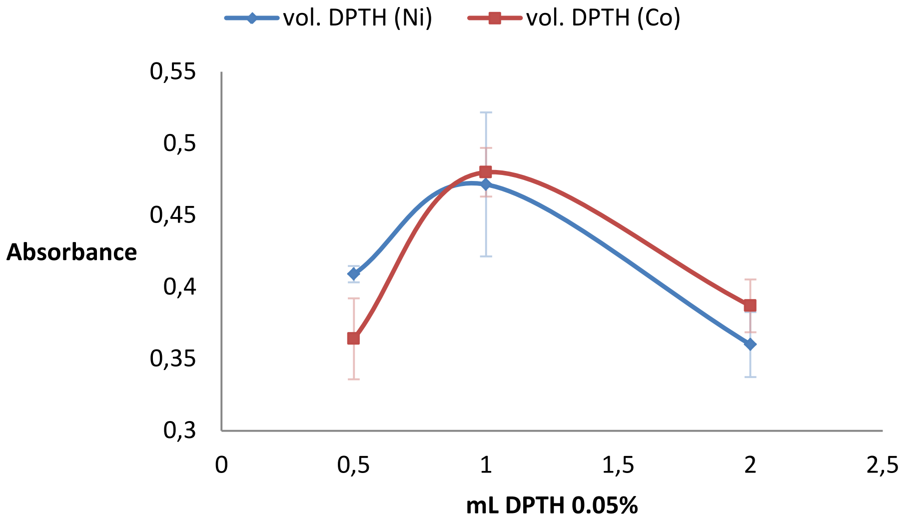


Figure 1. Influence of reagent volume

Effect of ionic strength

For investigating the influence of ionic strength on performance of DLLME, various experiments were performed by adding different amounts of NaCl (0–3% (w/v)). Other experimental conditions were kept constant. Ionic strength had a negative effect upon percent recovery and sensitivity for Ni extraction.

Effect of DLLME parameters

Effect of type and volume of extractant

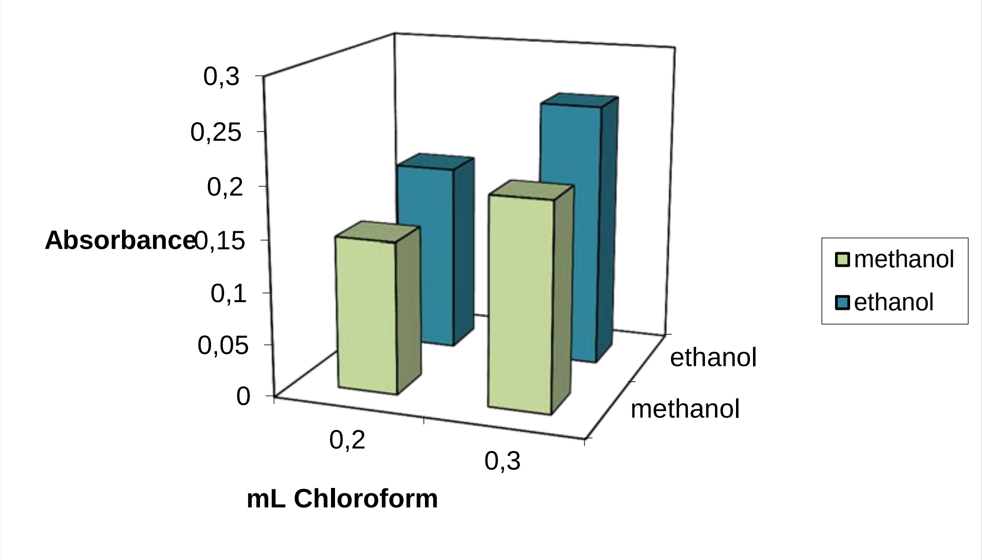
Careful attention should be paid to the selection of the extraction solvent. It should have a higher density than water, extraction capability of the interested compounds and low solubility in water. Chloroform, carbon tetrachloride and dichloromethane were compared in the extraction of nickel and cobalt. Results showed that the maximum extraction recovery was obtained by using chloroform.

To examine the effect of extraction solvent volume, solutions containing different volumes (0.4–0.7 mL) of chloroform were subjected to the same DLLME procedure. When the volume of extraction solvent was increased, the volume available for the measurement also increased, but the enrichment factors decreased. Thereby, in the following studies, the optimum volume of 0.3 mL was selected for the extraction solvent.

Effect of type and volume of disperser solvent

The role of a disperser is dispersion of an extraction solvent into aqueous sample to make extensive contact area between them and facilitating the mass transfer of analyte from water to organic solvent which causes considerable acceleration in the extraction of analytes. Miscibility of disperser solvent with extraction solvent and aqueous phase is the main point for selection of disperser solvent. Therefore in this section the ability of ethanol and methanol was investigated. The results (figure 2) show light differences between disperser solvents containing 0.2 and 0.3 mL chloroform (extraction solvent). As can be seen from this figure better results were obtained by using 0.3 mL chloroform and ethanol as disperser solvent. Then, extraction of analytes was carried out by using 0.5 to 1.5 mL of ethanol and in figure 3 are shown the results obtained. A 1 mL ethanol was selected for subsequent studies.

a)



b)

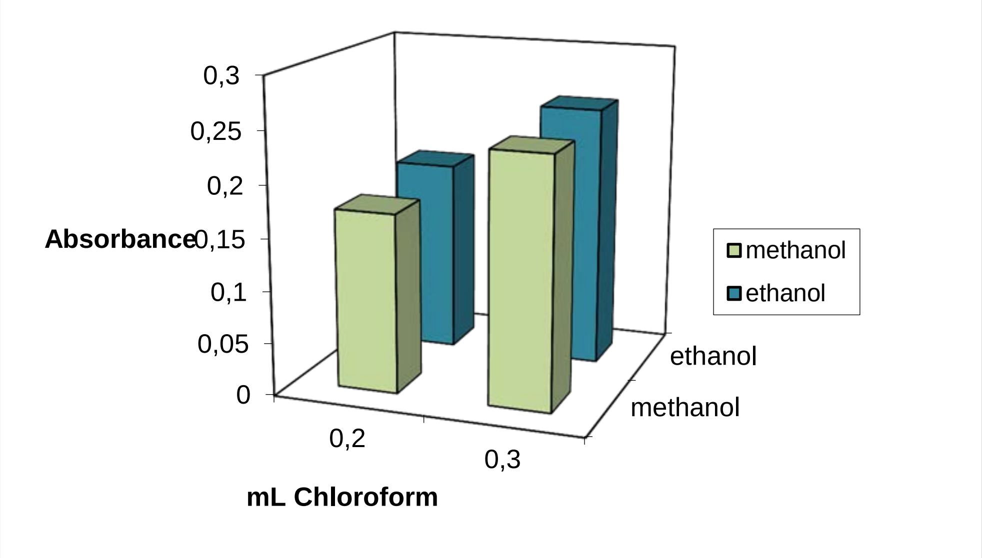


Figure 2. Influence of disperser solvent: a) Ni signal b) Co signal

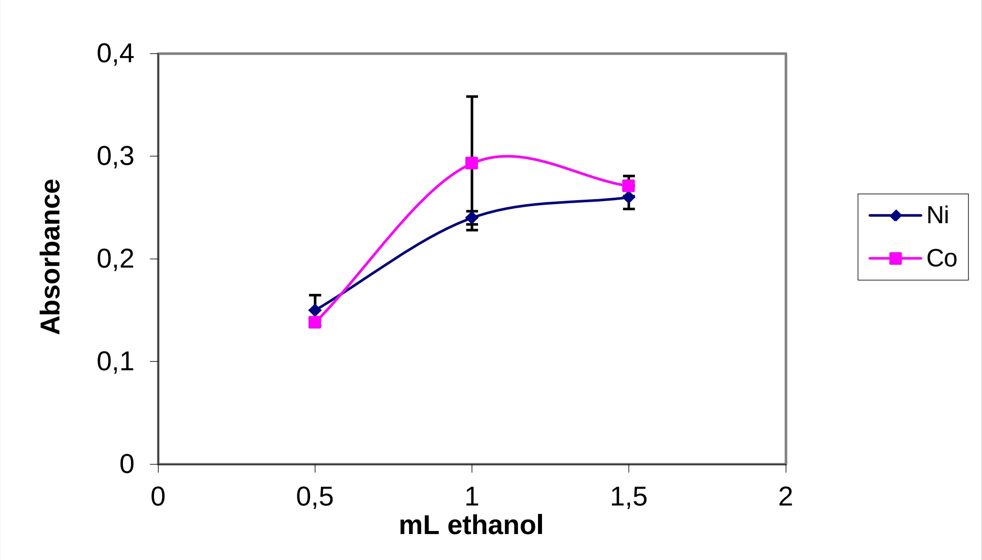


Figure 3. Influence of disperser volume

Interferences

Because DPTH is a versatile chelating agent, interferences may occur due to the competition of other heavy metal ions and their subsequent co-extraction with Co(II)/Ni(II). For this purpose, the effect of typical potential interfering ions was investigated. The tolerance limit was defined as the concentration of added ion that caused less than ± 5% relative error in the determination of Ni and Co. About 500-fold excess of Fe^{3+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, K^+, I^-, F^-, $SO_4^=$ and HCO_3^- do not affect Ni signal and Co. Cd^{2+}, Hg^{2+}, Cr^{3+}, Ba^{2+}, Mn^{2+} and Al^{3+} do not interfere at 100-fold excess. Cu^{2+}, Bi^{3+}, Zn^{2+} can be tolerated at 50-fold excess.

Analytical figures of merit

Analytical figures of merit of the proposed DLLME-FAAS method were obtained under optimal conditions and summarized in table 1. For this purpose, calibration equation were obtained by this procedure for Ni with different amount of Co (between 10-500 µg L^{-1}); and the same manner calibration equation for Co were obtained with different amount of Ni (between 10-500 µg L^{-1}). In all instances the slopes obtained were similar.

Analysis of synthetic mixtures

In order to check for potential synergistic effects of the mixtures of two ions, various synthetic mixtures were readily resolved by using pertinent calibration graphs. The analytical results are listed in table 2. As it can be seen, mixtures of the two ions can be resolved with satisfactory results.

Table 1. Analytical figures of merit

	Ni	Co
Dynamic range (µg L^{-1})	10-500	10-500
Regression equation	A=0.0005[Ni]+0.0105	A=0.0004[Co]+ 0.016
R^2	0.9987	0.9995
Detection limit (µg L^{-1})	1	3.5
Determination limit (µg L^{-1})	15	13.5
Precision (% RSD) Ratio 1:1 (Ni:Co) n=6	4.62	5.38
Precision (% RSD) Ratio 1:4 (Ni:Co) n=6	5.79	5.86
Precision (% RSD) Ratio 4:1 (Ni:Co) n=6	6.11	6.15
Preconcentration factor	50	40

Analysis of standard reference materials

In order to assess the accuracy and validity of the presented procedure, the method was applied to the determination of nickel and cobalt in certified reference materials (TMDA 54.4, Estuarine water (CRM LGC6016), Eau de mer (CASS-5), Riverine water (SLRS-5), which were analyzed according to the proposed method. It was found that analytical results were in good agreement with the certified values (table 3). Contents of Ni and Co in CASS-5 and SLRS-5 were under detection limits of the method, so different amounts of these ions were added to the samples for to verify if it is possible to determine Ni and Co under the proposed procedure. Goods recoveries were obtained in all cases.

Analysis of foods

In view of the application of the method to the determination of nickel and cobalt in food samples, the ability to recover these elements from different samples spiked with nickel and cobalt were investigated. All samples were arbitrarily selected and acquired from a local superstore. For this purpose, standard solutions containing different quantities of these elements were added to samples and the resulting materials were prepared as described under Experimental. Standard additions method was used in all instances and the results were obtained by extrapolation. The results of these analyses are summarised in table 4. The recoveries for the spiked samples were in the acceptable range.

Table 2. Resolution of synthetic Ni(II)-Co(II) mixtures by use of the proposed method

Ratio	**Concentration added (μg L^{-1})**		**Concentration found (μg L^{-1})**		**Concentration added (μg L^{-1})**		**Concentration found (μg L^{-1})**	
Ni:Co	**Ni**	**Co**	**Ni**	**Co**	**Co**	**Ni**	**Co**	**Ni**
1:1	50	50	56.8	49.25	50	50	45.5	50.2
1:2	50	100	56.8	94.25	50	100	43.0	91.2
1:4	50	200	54.8	196.75	50	200	48.0	202.2
1:10	50	500	50.8	474.25	50	500	53.0	510.2
10:1	100	50	82.8	49.5	100	50	93.0	51.0
1:1	100	100	86.8	95.0	100	100	95.5	92.0
1:2	100	200	90.8	192.5	100	200	95.5	210.0
1:5	100	500	106.8	487.5	100	500	108.0	499.0
4:1	200	50	204.8	43.75	200	50	180.5	59.6
2:1	200	100	194.8	91.25	200	100	185.5	107.6
1:1	200	200	234.8	206.25	200	200	193.0	179.6
1:2,5	200	500	234.8	506.25	200	500	210.5	511.6
10:1	500	50	476.8	48.5	500	50	395.5	51.2
5:1	500	100	478.8	98.5	500	100	433.0	115.2
2,5:1	500	200	474.8	197.25	500	200	458.0	169.2
1:1	500	500	478.8	498.5	500	500	460.5	496.2

Table 3. Analysis of four certified reference materials for the determination of Ni and Co with DLLME-FAAS method

Sample	**Certified value (μg L^{-1})**		**Found value (μg L^{-1})^{a}**		**% Recovery**	
	Ni	**Co**	**Ni**	**Co**	**Ni**	**Co**
TMDA 54.4	337±15,5	309±13.5	336.2±0.36	308.3±6.29	99.76	99.77
Estuarine water. CRM LGC6016	186 ± 3	26.08*	184.9±8.9	25.84 ± 0.42	99.4	99.08
	Added*		**Found (μg L^{-1})^{a}**		**% Recovery**	
	Ni	**Co**	**Ni**	**Co**	**Ni**	**Co**
Eau de mer. CASS-5	20	20	18.93±0.50	22.27±1.17	94.65	111.35
	50	50	46.93±3.01	50.60±0.92	93.86	101.2
	100	100	99.27±1.63	92.60±0.92	99.27	92.6

	200	200	192.27±2.80	200.27±0.42	96.13	100.13
Riverine water. SLRS-5	20	20	21.28±1.36	19.53±1.2	106.40	97.65
	50	50	51.48±1.84	44.53±2.34	103.68	89.06
	100	100	102.76±2.94	100.87±2.81	102.00	100.87
	200	200	197.6±13.72	190.87±0.70	98.80	95.43

[a] mean±SD; n=3
*Added in μg L^{-1}

Table 4. Analytical results for Ni and Co in food samples (Avg. ± SD of three trials)

Sample	**Added (μg g^{-1})**		**Found (μg g^{-1})**		**% Recovery**	
	Ni	**Co**	**Ni**	**Co**	**Ni**	**Co**
Rice	9.09	9.09	9.09±0.04	10.03±1.27	100	110.34
Chick pea	8.68	8.68	8.78±0.71	8.58±0.25	102.40	98.85
Lettuce	15.81	15.81	16.19±0.45	15.81±1.40	102.40	100.00
Lentil	11.10	11.10	11.62±0.06	11.26±0.14	104.68	101.44
Apple	8.45	8.45	8.25±0.10	8.70±0.68	97.63	102.96

Conclusion

Sample preparation by DLLME is a procedure that considered inside the Green Chemistry, because of the small volumes of dissolvent employed. In this work, a simple, rapid, and sensitive DLLME preconcentration technique coupled with FAAS has been developed for the determination of cobalt and nickel in spiked food samples. All variables that influence in the formation of the complexes Ni–DPTH and Co-DPTH and then application of DLLME procedure have been optimized. Employing FAAS as detection technique, the detection limit obtained is in the order of μg L^{-1} for both analytes that by the direct method of FAAS is impossible to obtain because of the low sensitivity that present.

To study the accuracy of the proposed method, certified reference materials have been analysed with good agreements.

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