



Solidified floating organic drop microextraction (SFODME) for simultaneous separation/preconcentration and determination of cobalt and nickel by graphite furnace atomic absorption spectrometry (GFAAS)

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ABSTRACT

Solidified floating organic drop microextraction (SFODME), combined with graphite furnace atomic absorption spectrometry (GFAAS) was proposed for simultaneous separation/enrichment and determination of trace amounts of nickel and cobalt in surface waters and sea water. 1-(2-Pyridylazo)-2-naphthol (PAN) was used as chelating agent. The main parameters affecting the performance of SFODME, such as pH, concentration of PAN, extraction time, stirring rate, extraction temperature, sample volume and nature of the solvent were optimized. Under the optimum experimental conditions, a good relative standard deviation for six determination of 20 ng l^{-1} of Co(II) and Ni(II) were 4.6 and 3.6%, respectively. An enrichment factor of 502 and 497 and detection limits of 0.4 and 0.3 ng l^{-1} for cobalt and nickel were obtained, respectively. The procedure was applied to tap water, well water, river water and sea water, and accuracy was assessed through the analysis of certified reference water or recovery experiments.

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1. Introduction

The trace amount of nickel and cobalt, are indicated to be either essential or toxic depending on their concentration range. For instance, due to studies on chicks and rats (the latter of which are relatively close to human genetically) nickel is apparently essential for proper liver function, or cobalt is at the core of a vitamin-B12. On the other side, some of nickel and cobalt compounds are carcinogenic [1–3]. Thus it is clear that determination of cobalt and nickel, at trace level, in water and environmental samples is of great significance from the public health and environmental point of view [4].

Modern instrumental methods including spectrometry, ICP-MS, ICP-AES, AAS, etc. [5–7], have been used for determination of traces of metal ions in various media. However, in these determinations, low concentration levels of analytes and high levels of matrices are the main problems [8,9]. To solve these problems, a separation/preconcentration step prior to analysis is required. Up to now, several methods have been designed for separation/preconcentration of cobalt and nickel from various matrices, including, solid-phase extraction (SPE) [5,10,11], liquid–liquid extraction (LLE) [12], ion-exchange [13], flotation [14],

cloud point extraction [15], etc., are among the most widespread used methods. Although relatively good analytical performance can be obtained with the above-mentioned pretreatment techniques, inconveniences such as, lengthy separation, large consumption of reagent, multi-stage, and unsatisfactory enrichment factor can be listed as their disadvantages.

LLE is among the classical pretreatment technique that has been widely employed in analytical chemistry [16,17]. Although it offers high reproducibility and high sample capacity, it suffers from several limitations, such as use of large volume of solvent, time and labor intensity, and tendency for formation of emulsion.

More recently, study activities have been placed on miniaturizing the traditional LLE procedure by reducing the organic solvent to aqueous phase ratio, resulting in the development of microextraction techniques such as, drop-in-drop system [18] single-drop microextraction (SDME) [19,20] homogenous liquid–liquid microextraction [HLLME] [21,22] solid-phase microextraction (SPME) [23,24], and dispersive liquid–liquid microextraction (DLLME) [4,25,26]. The main advantages of these techniques are; the negligible volume of solvents and their ability to detect analytes at very low concentration. However, it should be noted that overwhelming majority of research work on microextraction are concentrated on the analysis of organic analytes and there are only few reports on the use of microextraction techniques for preconcentration and separation of inorganic species [4,20]. Recently; a new liquid–liquid microextraction method namely, solidified float-

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Table 1
Temperatures programs of GFAAS for determination of Co and Ni.

Steps	Cobalt			Nickel		
	Temp. (°C)	Time (s)	Argon flow rate (l min ⁻¹)	Temp. (°C)	Time (s)	Argon flow rate (l min ⁻¹)
Drying	85	5	3	85	5	3
Drying	95	40	3	95	40	3
Drying	120	10	3	120	10	3
Ashing	800	10.5	3	800	11.5	3
Atomization & read command	2400	3.1	0	2300	3.1	0
Tube cleaning	2400	2	3	2300	3	0

ing organic drop (SFODME), which is a modified solvent extraction method, was proposed for extraction and determination of organic analytes [27]. It has the advantages of simplicity, low cost, minimum organic solvent consumption and achievement of high enrichment factor. We extend its application to inorganic analysis [28].

In this study, the possibility of multi-element enrichment by SFODME was considered. 1-(2-Pyridylazo)-2-naphthol (PAN), the classical organic reagent for spectrophotometric determination of transition metal ions was selected as chelating reagent and a new SFODME method combined with graphite furnace atomic absorption spectrometer (GFAAS) was developed for separation, enrichment and determination of cobalt and nickel in water samples. Factors affecting the extraction efficiency, such as solution pH, concentration of organic ligand, extraction time, sample volume, nature of organic solvent, and ionic strength were studied and optimized.

2. Experimental

2.1. Reagents and standard solutions

The reagents used throughout this study were of the highest purity available and at least of analytical reagent grade. The standard stock solutions of nickel(II) (1000 mg l⁻¹) and cobalt(II) (1000 mg l⁻¹) were prepared by dissolving proper amount of Ni(NO₃)₂·6H₂O (Merck), CoCl₂ (Merck) in 1% nitric acid solution. Standard solutions of cobalt and nickel were prepared daily by appropriate dilution of stock solutions. Deionized water was used throughout in sample preparation and all solutions were stored in pre-cleaned polypropylene (Nalgene, Lima, OH, USA) containers. 1-Undecanol was obtained from Merck (Darmstedt, Germany) and used as extracting solvent. PAN was obtained from Merck (Darmstedt, Germany) and the solution of PAN in 1-undecanol (6.8 × 10⁻⁴ mol l⁻¹) was prepared by dissolving proper amount of PAN in 1-undecanol.

2.2. Instrumentation

The analysis was performed using Varian Zeeman Spectra atomic absorption spectrometer, Model 220Z equipped with autosampler. Varian spectra-AA hollow cathode lamps for Ni and Co were used as light sources which operated, respectively, at current of 4 and 7 mA, wavelength of 232 and 242.5 nm with a spectra bandwidth of 0.2 nm, as recommended by manufacturers. The sample injection volume was 10 μl in all experiment. The instrumental parameters and temperature program for graphite atomizer are given in Table 1.

2.3. Extraction procedure

The pH of the sample solution with a concentration of Ni and Co, in the range of 5–50 and 5–60 ng l⁻¹, respectively, was adjusted to ~7 using 1% nitric acid or ammonium hydroxide. 10 ml of this

solution was transferred into ~11 ml vial containing a stirrer bar and 20 μl of PAN in 1-undecanol (6.8 × 10⁻⁴ mol l⁻¹) was added. The magnetic stirrer was turned on and the solution was mixed for 30 min at 1000 rpm. In this step Ni and Co ions react with PAN and extracted into 1-undecanol. After the extraction time was out, the sample vial was transferred into an ice bath and organic solvent was solidified after 5 min. The solidified solvent was then transferred into a conical vial where it melted immediately (Fig. 1). Primarily the extract was diluted to 500 μl with ethanol and was transferred to the cup of autosampler of GFAAS for quantization, whereas for obtaining the performance data and analysis of real samples, 10 μl of the extract was manually injected into graphite furnace atomic absorption spectrometer.

3. Results and discussion

In order to demonstrate the capability of SFODME for simultaneous separation and preconcentration of metal ions, the chromogenic reagent 1-(2-pyridylazo)-2-naphthol which is widely used for determination of heavy metal ions [28–31] was selected as the chelating agent. The preliminary experiments revealed that Co and Ni could be simultaneously extracted into small volume of solution of PAN in 1-undecanol. Next the different parameters affecting the formation of complex, extraction and analysis process was optimized in a univariable approach. Furthermore, the percent of extraction and enhancement factor were calculated according to Eqs. (1) and (2) as described before [28]:

$$\text{Percent of extraction} = \left(\frac{C_0 V_0}{C_{\text{aq}} V_{\text{aq}}} \right) \times 100 \quad (1)$$

$$\text{Enrichment factor} = \frac{C_0}{C_{\text{aq}}} \quad (2)$$

where V and C are the volume and concentration and the suffixes O and aq indicate organic and aqueous phase, respectively. C_0 was calculated from the calibration graph of standard solution of interested metal–PAN complex in ethanol.

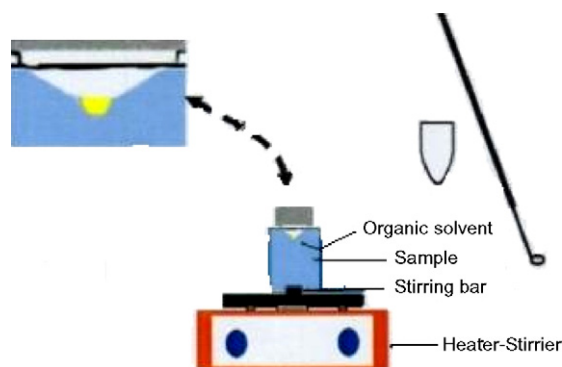


Fig. 1. Schematic diagram of the proposed SFODME apparatus.

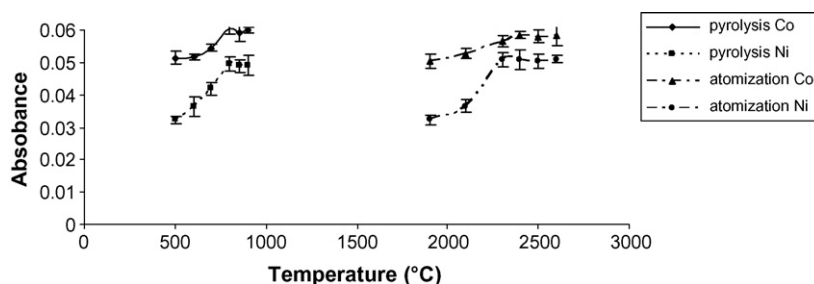


Fig. 2. Effect of pyrolysis and atomization temperature on absorption of $10 \mu\text{g l}^{-1}$ of cobalt and nickel.

3.1. Selection of organic solvent

The extracting solvent for SFODME has to fulfill the following requirement;

1. It must have low volatility in order to be stable in extraction period.
2. It must have low water solubility in order to have good extraction efficiency.
3. Its melting point must be near room temperature (in the range of $10\text{--}30^\circ\text{C}$).
4. It also must not interfere in the analytical techniques used for determination of analytes.

Accordingly, several extracting solvents, including 1-undecanol (m.p. $13\text{--}15$) 2-dodecanol (m.p. $22\text{--}24$), 1,10-dichlorodecane (m.p. $14\text{--}16$) and n-hexadecane (m.p. 18) were investigated. 1-Undecanol was found to give the best extraction efficiency, with 2-dodecanol the extraction efficiency was about 75% of 1-undecanol, while 1,10-dichlorodecane and n-hexadecane produced high background during the analysis with GFAAS which interfere with determination of analytes. Thus, in the present study, 1-undecanol was selected as extracting solvent.

3.2. Optimization of furnace time and temperature program

At the primary step of the ongoing study, it was demonstrated that the time and temperature program suggested by manufacturers could not be efficient in this method, and the magnitude of background signal was high. In order to maximize the absorption of the interested metal ions and eliminate the background signal during the pyrolysis step, optimization of time and temperature program of GFAAS during the process was performed, and the final results are given in Table 1. The optimal pyrolysis and atomization temperature for Ni were 800 and 2400°C and for Co were 800 and 2300°C , respectively (Fig. 2). Under these established conditions the proper results achieved and no modifier is required.

3.3. Effect of pH

Extraction of metal ions by SFODME involves complex formation with sufficient hydrophobicity to be extracted into small volume of organic phase. It is obviously indicated that pH of the sample solution is one of the essential factors affecting the formation of metal complex and its extraction. The effect of pH on the complex formation and extraction of cobalt and nickel were studied in the range of $1\text{--}9$ using nitric acid or ammonium hydroxide. The results illustrated in Fig. 3 reveals that the recovery is nearly constant in the pH range of $6.5\text{--}7.5$. The progressive decrease in extraction of interested metal ions at low pH is due to competition of hydrogen ion with analytes for reaction with PAN. Accordingly, a pH of ~ 7 was selected for subsequent work and real sample analysis.

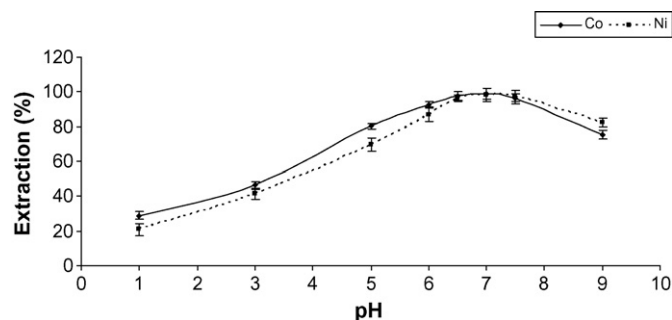


Fig. 3. Effect of pH on extraction of Co and Ni by SFODME method. Extraction conditions: water sample volume, 10 ml ; amount of metal ions, 20 ng l^{-1} ; organic solvent volume, $20 \mu\text{l}$.

3.4. Effect of PAN concentration

The effects of PAN concentration on the recoveries of analytes were evaluated in the range of $6.8 \times 10^{-7}\text{--}2.0 \times 10^{-3} \text{ mol l}^{-1}$. The results are shown in Fig. 4 and showed that the recovery of cobalt and nickel were increased with an increase in PAN concentration up to $6.8 \times 10^{-4} \text{ mol l}^{-1}$ and kept constant up to $2.0 \times 10^{-3} \text{ mol l}^{-1}$. It is worth mentioning that the presence of too excess amount of the ligand causes a decrease in extraction which is due to the fact that high concentration of PAN may cause saturation of extracting solvent which resulted in its extraction into aqueous phase. In this study a concentration of $6.8 \times 10^{-4} \text{ mol l}^{-1}$ of PAN was chosen for subsequent experiments.

3.5. Extraction time and temperature

Extraction time is an important factor influencing the extraction efficiency and speed of analysis. In order to have a good precision, sensitivity and speed, it is necessary to select an extraction time

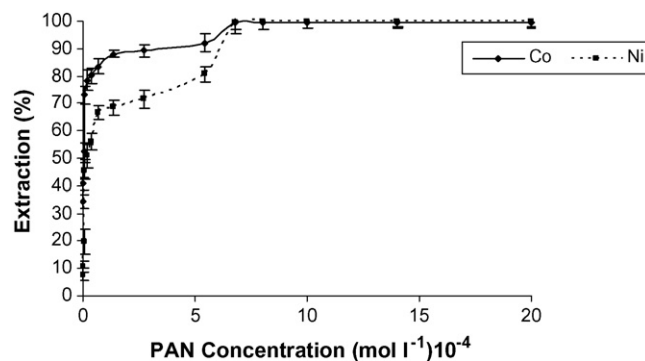


Fig. 4. Effect of PAN concentration on extraction of Co and Ni by SFODME method. Extraction conditions: water sample volume, 10 ml ; amount of metal ions 20 ng l^{-1} ; organic solvent volume, $20 \mu\text{l}$, sample pH ~ 7 .

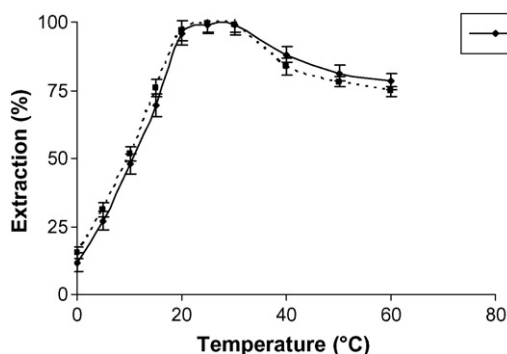


Fig. 5. Effect of temperature on extraction of Co and Ni by SFODME method. Extraction conditions: water sample volume, 10 ml; amount of metal ions 20 ng l^{-1} ; organic solvent volume, $20 \mu\text{l}$; PAN concentration, $6.8 \times 10^{-4} \text{ mol l}^{-1}$, sample pH ~ 7 .

that guarantees the achievement of equilibrium between aqueous and organic phase and maximum extraction of analytes. The effect of extraction time was investigated with the time varying from 5 to 90 min at a stirring rate of 1000 rpm. The results displayed that after 30 min, quantitative recovery (>95%) of both analytes is possible. An optimum stirring period of 30 min was selected.

The effect of temperature on extraction was studied by varying the temperature between 15 and 60°C ; the results of which is shown in Fig. 5 and revealed that the extraction are quantitative (>95%) from 20 to 30°C ; but a further increase in temperature cause a slight decrease in recovery, which might be due to increase in solubility of organic phase at higher temperature as well as degradation of complex. The decreases in extraction at temperature lower than 20 may be due to improper dispersion of the organic phase at low temperature. Thus based on these results and as it was more convenient, the further experiments were done at room temperature.

3.6. Stirring rate

Effective mixing of the aqueous and organic phases is essential for the overall procedure as based on the penetration theory of mass transfer of solute, the aqueous-phase mass-transfer coefficient increase with increasing the stirring rate [20]. Hence, in this work various stirring rate were studied and for the prevailing experimental conditions a stirring rate of 1000 rpm proved to be adequate for analysis.

3.7. Effect of sample volume

An important parameter which influences the preconcentration factor is sample volume. An increase in the ratio of volume of aqueous phase to organic phase will result in significant increase in the enrichment factors. But an increase in sample volume may cause a decrease in extraction efficiency in a given time. The effect of sample volume on extraction of 0.2 ng of nickel and cobalt from different sample volume (10–50 ml), in a proper size vial, was investigated. The results (Fig. 6) showed that the extraction was quantitative (recovery >95%) with the aqueous phase volume in the range of 10–20 ml, and a decrease was observed with further increase in sample volume. Therefore based on organic phase volume ($20 \mu\text{l}$) and the maximum sample volume that the extraction was quantitative (20 ml) a preconcentration factor of 1000 was determined. However a sample volume of 10 ml was selected for further experiment as the enrichment was sufficient. Based on the slope of calibration standard curve with microextraction and without microextraction, an enrichment factor of 502 and 497 for Co and Ni were determined, respectively.

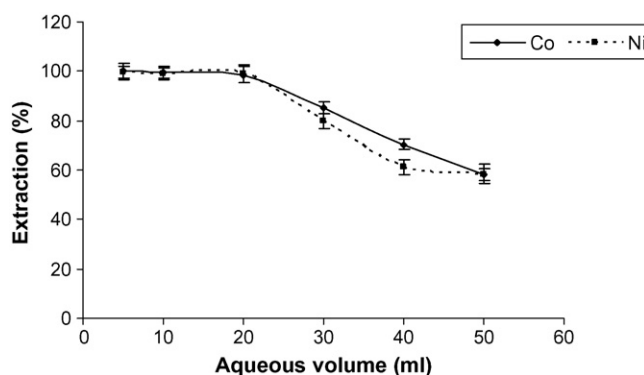


Fig. 6. Effect of volume of aqueous phase on extraction of Co and Ni by SFODME method. Extraction conditions: amount of metal ions 20 ng l^{-1} ; organic solvent volume, $20 \mu\text{l}$; PAN concentration, $6.8 \times 10^{-4} \text{ mol l}^{-1}$, sample pH ~ 7 .

3.8. Effect of foreign ions

In order to consider the suitability of the method for determination of Co and Ni in saline matrices the effect of concentration of NaCl on extraction was investigated by varying its concentration within the range of 0– 1 mol l^{-1} . The results showed that addition of salt has no significant effect on extraction efficiency and extractions of both species were quantitative. Thus the method is suitable for separation and determination of interested ions in saline solutions such as sea water.

Furthermore, the extraction efficiency was investigated in presence of various cations and anions commonly existing in natural waters. The interference refers to the competition of other heavy metals ions for the chelating agent and their subsequent co-extraction with Ni and Co. The results of this investigation are given in Table 2. A species that cause a variation of more than $\pm 10\%$ in recovery of Co and Ni was consider as interfering ion. As it is shown in the table with the exception of Cd^{2+} , Zn^{2+} and Cu^{2+} which interfere at the mole ratio of 5, the other ions at the given level shows no significant interference in the determination of interested metal ions. These results indicate that the developed method is applicable. Furthermore, the interference of Cd^{2+} , Zn^{2+} and Cu^{2+} were eliminated upon addition of EDTA at a concentration of $2.0 \times 10^{-4} \text{ mol l}^{-1}$, and this was also reported by other researcher in literature [29]. These results indicate that the developed method is applicable to analysis of Co and Ni in different water samples.

Table 2

Effect of foreign ions on the recovery of Co and Ni: concentrated volume 10 ml, Co and Ni at a concentration of 20 ng l^{-1} .

Foreign ions	Molar ratio (ion/Ni or Co)	Ni ^a recovery (%)	Co ^a recovery (%)
K ⁺	1000	101 ± 5	97 ± 3
Ca ²⁺	500	99 ± 6	98 ± 3
Mg ²⁺	500	102 ± 4	100 ± 3
Ba ²⁺	500	103 ± 3	97 ± 4
Ag ⁺	250	100 ± 3	96 ± 5
Pb ²⁺	250	101 ± 4	99 ± 5
Fe ³⁺	50	107 ± 3	99 ± 6
Hg ²⁺	100	101 ± 4	100 ± 4
Cd ^{2+b}	5	96 ± 2	99 ± 4
Zn ^{2+b}	5	97 ± 3	100 ± 3
Cu ^{2+b}	5	99 ± 4	97 ± 4
F ⁻	1000	99 ± 5	100 ± 5
Br ⁻	1000	100 ± 5	100 ± 5
I ⁻	500	98 ± 6	100 ± 4
NO ₃ ⁻	1000	100 ± 5	98 ± 4
CO ₃ ²⁻	500	99 ± 4	105 ± 2
SO ₄ ²⁻	500	98 ± 2	98 ± 3
CH ₃ COO ⁻	500	98 ± 3	97 ± 5

^a Results are mean and standard deviation of three independent measurements.

^b In the presence of EDTA (2.0×10^{-4}).

Table 3
Analytical characteristics of the method.

	Co	Ni
Slope	2.5×10^{-3}	2.4×10^{-3}
Correlation coefficient (<i>r</i>)	0.9997	0.9995
R.S.D. (%) (<i>n</i> = 6)	3.6	4.6
Detection limit (ng l ⁻¹)	0.4	0.3
Quantification limit (ng l ⁻¹)	1.3	1.0
Enhancement factor ^a	502	497

^a Calculated as the slope ratio of the calibration graphs obtained with preconcentration of 10 ml solution and without preconcentration.

3.9. Analytical performance

The analytical characteristics of the developed method, including the limit of detection and quantification, reproducibility, correlation coefficient and enrichment factors were obtained by processing standard solution of Co and Ni and are summarized in Table 3. The limit of detections and quantification were determined as $3S_b/m$ and $10S_b/m$, respectively (where S_b is the standard deviation of the blank signals and m is the slope of calibration curve after extraction). For a sample volume of 10 ml, calibration graph exhibited linearity over the range of 5–60 ng l⁻¹ for Co and 5–50 ng l⁻¹ for Ni. The regression equations for the calibration curves of Co and Ni were $Y = 0.0025X + 0.0089$ with correlation coefficient (R^2) of 0.9996 and $Y = 0.0024X + 0.0012$ with correlation coefficient (R^2) of 0.9992, respectively, where Y is the absorbance and X is the concentration of analytes (ng l⁻¹) in the aqueous phase. The linearity range can be extended by lowering the preconcentration factor, i.e. by lowering the sample volume or diluting the extract to 0.5 or 1.0 ml depending on the analytes concentration in real sample. In the case of dilution of the extract, determination of analytes by GFAAS can be done by using autosampler.

3.10. Analysis of waters

The proposed method was applied to the determination of Co and Ni in tap water, well water, river water and sea water. Reliability was checked by spiking the sample. The results along with the recovery for the spiked sample are given in Table 4. As could be seen, the recoveries of the spiked samples are satisfactory. Furthermore, in order to verify the accuracy of the proposed method, the procedure was used to the determination of the Co and Ni in certified sea water (NASS-1). The concentration of cobalt and nickel in the sample were found to be 3.9 ± 0.3 and 260.0 ± 7 ng l⁻¹, respectively, which at 95% confidence limit, are in good agreement with the certified values of 4 ± 1 for Co and 257.0 ± 27 for Ni. Thus the

Table 4
Determination of Co and Ni in water samples: sample volume 10 ml, except for sea water samples (5 ml).

Water sample	Cobalt			Nickel		
	Added (ng l ⁻¹)	Found (ng l ⁻¹)	Recovery (%)	Added (ng l ⁻¹)	Found (ng l ⁻¹)	Recovery (%)
Tap water		6.0 ± 0.3			8.2 ± 0.2	
	10	15.9 ± 0.5	99	10	18.1 ± 0.7	99
Well water		7.5 ± 0.4			4.1 ± 0.5	
	10	17.5 ± 0.3	100	10	13.9 ± 0.3	98
River water		3.5 ± 0.5			4.4 ± 0.4	
	10	13.3 ± 0.5	98	10	14.2 ± 0.6	98
Sea water (Caspian sea)		8.5 ± 0.4			80.6 ± 1.8	
	10	18.4 ± 0.6	99	10	90.1 ± 2.2	95
NASS-1	4 ± 1^a	3.9 ± 0.3	98	257 ± 27^a	260 ± 7	101

Results are mean and standard deviation of three independent measurements.

^a Accepted value.

Table 5
Comparison of detection limit and enrichment factor.

Method	Detection Co (ng l ⁻¹)	Limit Ni (ng l ⁻¹)	Enrichment Co	Factor Ni	References
SFODME–GFAAS	0.3	0.4	502	497	Present work
Emulsion–GFAAS	6	10	100	100	[30]
DLPME–GFAAS	21	33	101	200	[4]
CPE–FAAS	1090	1220	27	29	[3]
SPE–FAAS	–	800	–	43	[31]
SPE–FAAS	–	920	–	200	[32]
Flotation–GFAAS	7.8 ^a	9.0 ^a	–	–	[33]
CME–ICP–MS	0.33	1.5	10	10	[34]

SFODME–GFAAS: solidified floating organic drop microextraction–graphite furnace atomic absorption spectrometry; DLPME–GFAAS: dispersive liquid phase microextraction–graphite furnace atomic absorption spectrometry; CPE–FAAS: cloud point extraction–flame atomic absorption; SPE–FAAS: solid-phase extraction–flame atomic absorption spectrometry; CME–ICP–MS: capillary microextraction–inductively plasma mass spectrometry.

^a $\mu\text{g g}^{-1}$.

method is reliable for determination of Co and Ni in natural water samples.

3.11. Comparison of SFODME with other methods

Determination of cobalt and nickel in the water samples by the developed solidified floating organic drop microextraction was compared with other methods [3,4,30–34] and the results are summarized in Table 5. As can be seen the SFODME had higher enrichment factor and with the exception of CME–ICP–MS, it had lower detection limit.

4. Conclusion

It has been demonstrated that solidified floating organic drop microextraction combined with GFAAS can be used for simultaneous separation/enrichment and determination of ultra trace of multi-element. Furthermore, the proposed SFODME method incorporating PAN as chelating agent, permits effective separation and preconcentration of Co and Ni and final determination by GFAAS and provide a novel route for trace determination of Co and Ni in several categories of natural waters. The results also indicate that this extraction procedure is noticeable due to its outstanding advantages which are minimum organic solvent consumption, simplicity, low cost, high enrichment factor, and rejection of matrix constituent. Future work will be directed at extraction of other metals using various ligands and assessment of the multi-element enrichment capability of the method for ultra trace determination in different matrices.

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