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Development of a selective and pH-independent method for the analysis of ultra trace amounts of nitrite in environmental water samples after dispersive magnetic solid phase extraction by spectrofluorimetry

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ABSTRACT

This paper describes an innovative and rapidly dispersive magnetic solid phase extraction spectrofluorimetry (DMSPE-FL) method for the analysis of trace amounts of nitrite in some environmental water samples. The method includes derivatization of aqueous nitrite with 2, 3-diaminonaphthalene (DAN), analysis of highly fluorescent 2, 3-naphthotriazole (NAT) derivative using spectrofluorimetry after DSPME. The novelty of our method is based on forming NAT that was independent with the pH-responsive and was adsorbed on MMWCNT by hydrophobic attractions in both acidic and basic media.

The extraction efficiency of the sorbent was investigated by extraction of nitrite. The optimum extraction conditions for NO_2^- were obtained as of extraction time, 1.5 min; 10 mg sorbent from 160 mL of the sample solution, and elution with 1 mL of acetone/KOH. Under the optimal conditions, the calibration curves were obtained in the range of 0.1–80 μg L^{-1} (R^2=0.999) and LOD (S/N=3) was obtained in 34 ng L^{-1}. Relative standard deviations (RSD) were 0.6 % (five replicates at 5 μg L^{-1}). In addition, the feasibility of the method was demonstrated with extraction and determination of nitrite from some real samples containing tap, mineral, sea, rain, snow and ground waters, with the recovery in standard addition to real matrix of 94–102 % and RSDs of 1.8–10.6%.

1. Introduction

Nitrite (NO_2^-) is an abundant anion in the environment, which is widely used as an additive and corrosion inhibitors in food and environmental systems [1]. NO_2^- is classified as an environmentally hazardous species because of its toxicity to human life and aquatic animals when present above the permissible concentration level [2]. Besides, it is found that NO_2^- can induce methemoglobinemia and form highly carcinogenic *N*-nitrosoamines through the reactions with various amines and amides [3], which results in the potential toxicity of NO_2^-. NO_2^- is also a versatile chemical agent that has found numerous applications, ranging from dye manufacture to food preservation [4]. Moreover, the determination of nitrite in natural waters is important because NO_2^- is harmful to human health. At present, the US EPA considers the maximum contaminant level that is allowed for nitrite in drinking water is 1.0 mg L^{-1} [5]. Thus, its quantitative analysis is significant in environmental security and public wellness.

To date, several techniques, including fluorescence [3], spectrophotometry [6], sequential injection technique [7], photometric method [8] high-performance liquid chromatography (HPLC) [9], ion-pair HPLC [10], ion chromatography [11], capillary electrophoresis [12] gas chromatography [13], electrochemical methods [14,15] and kinetic methods [16–17] have been developed for the determination of NO_2^-. Some of them involve time-consuming, high cost and tedious procedures. Therefore, in that location is even an urgent demand for simple, sensitive and specific assays for NO_2^-. Among these methods, spectrophotometry and spectrofluorimetry are widely utilized because of common availability of instrumentations and simplicity of operations. Compared with spectrophotometry, spectrofluorimetric method is more sensitive and less subject to interference. Fluorometric methods have been widely employed for sensitivity analysis of NO_2^-. These methods involve the derivatization reaction of NO_2^- with 2,3-diaminonaphthalene (DAN) to form 2,3-naphthotriazole (NAT). Several methods using HPLC with fluorescence detection were developed for the measurement of NO_2^- in water, urine, plasma and cell culture medium [18–21]. Nevertheless, most fluorimetric HPLC

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methods developed require a complicated sample preparation procedure to remove matrix components, and a guard column was also taken. These additional preparation steps may introduce contamination by environmental nitrite. In addition, the fact that NAT is stable and has a higher fluorescence intensity at alkaline conditions of pH 8.5–11.5 is not compatible with the stability of normal reversed phase HPLC columns [22]. Thus, a special column or adsorbent is needed for analysis of nitrite in alkaline conditions. Likewise, the extremely low concentrations in environmental samples and the matrix interferences make determination of NO_2^- challenging tasks. Because of this, there is a critical demand for rapid and simple preparation techniques, especially extraction techniques, for evaluating and monitoring NO_2^- from different water samples at trace level. Solid-phase extraction (SPE) is an efficient sample pretreatment method, routinely used for the extraction of compounds from liquid or solid matrices. SPE approach, in which adsorbents have been treated as media for the retaining of target compounds, followed by selective elution, has been broadly utilized due to the advantages of fewer organic solvents, no emulsion formation like in liquid–liquid extraction, and short time, etc. [23–24]. The selection of appropriate adsorbent is a vital component to obtain good recovery and high enrichment factor in SPE procedure.

Many different adsorbents have been used in SPE. Among them, carbon nanotubes (CNTs) have attracted great attention due to their unique properties [25–28]. The hydrophobic and π–π electron donor–acceptor interactions between CNTs and other molecules make it a good candidate for use as SPE adsorbents [27]. Nevertheless, due to their hydrophobic nature and nano-size, carbon nanotubes can make resistance against the liquid flow when used as SPE adsorbents and therefore, gets to the SPE procedure inefficient, especially when aqueous solvents containing suspended particles are used. As a new alternative mode of SPE, dispersive magnetic solid-phase extraction (DMSPE) shows such features as high extraction yield, short extraction time and easy operation [29]. The performance of this technique could be considerably improved by using nanoparticles as solid phase adsorbent [28]. Magnetic nanoparticles (MNPs) are nowadays one of the most important trends in science and applications, including analytical chemistry, biotechnology and pharmacy [30–35]. In this way and to solve the elution problem of CNTs adsorbents mentioned above; CNTs have been modified with magnetic particles by a chemical process, which were further used as adsorbents of magnetic solid-phase extraction (MSPE) [36–39]. The prepared magnetic CNT can be well dispersed in water and easily separated from the medium with the help of a magnet.

Taking into account the properties of the MMWCNT and the sensitivity of spectrofluorimetry, a study was undertaken to develop a sensitive, specific and reliable analytical technique that could be applied to a variety of environmental water samples (tap, mineral, sea, rain, snow and ground) to enable the precise determination of nitrite at trace levels. For this purpose, two procedures were estimated (pre and post derivatization). The procedures offer several significant advantages over the other techniques available, such as higher sensitivity, reliability, short extraction time and selectivity in isolation. At first procedure (post derivatization), the nitrite ions were adsorbed on MMWCNT, and then the extracted anions were eluted by NaOH. After, DAN was added to form NAT, and at final NaOH was added again to stable NAT and reach a high fluorescence intensity. In fact, this extraction procedure takes a long time. At second procedure (pre derivatization) the nitrite anions were first derivatized as NAT by using DAN under acidic conditions. Then NAT was adsorbed on MMWCNT in the range pH of 1.5–11.0. Subsequently, the extracted NAT was washed from the surface of the adsorbent with KOH/acetone, then collected using an external magnetic field and determined by spectrofluorimetry. This procedure provides a fast extraction and overcomes the problem of using HPLC columns in alkaline media or pre- or post-column derivatization which takes too much time and using toxic reagent in HPLC.

To the best of our knowledge, dispersive magnetic solid phase extraction spectrofluorimetry (DMSPE-FL) has not been employed previously in the extraction and determination of trace amounts of nitrite from aqueous samples.

2. Experimental

2.1. Chemicals and materials

MMWCNT nanocomposite was prepared according to our previous study [40]. All chemicals used were of analytical-reagent grade. All aqueous solutions were prepared using the ultra-pure Milli-Q purification system. Ammonium ferric sulfate, ammonium ferrous sulfate, ammonium hydroxide, acetone, potassium hydroxide, sodium hydroxide, hydrochloric acid was purchased from Merck (Darmstadt, Germany). DAN was purchased from Sigma-Aldrich (St. Louis, MO, USA). Standard nitrite and other solutions used for the experiments as well as for the interference study were prepared by sequential dilution of 1000 mg L^{-1} of standard solutions (Merck) in ultra-pure water. The pH of solutions was adjusted by 1 mol L^{-1} NaOH and HCl solution.

DAN solution (0.0002 mol L^{-1}) was prepared by dissolving 15.8 mg of DAN in 1.6 mol L^{-1} HCl solution and stored in the darkness at 4 °C. This solution was stable for three months in a refrigerator.

A 500 μg L^{-1} of NAT solution was prepared daily by adding 1 mL of nitrite solution (5 mg L^{-1}) and 0.5 mL of DAN solution and staying for 5 min. Then 1 mL of KOH (1 mol L^{-1}) was added, and final volume of the solutions was adjusted at 10 mL using deionized water.

2.2. Apparatus

All fluorescence measurements were made using a Perkin-Elmer LS 50 spectrofluorimeter equipped with xenon discharge lamp and quartz cell. Instrument excitation (375 nm) and emission (415 nm) slits both were adjusted to 15 nm. The pH of solutions was determined and adjusted using a pH meter model 823 Metrohm with a combined glass-calomel electrode. Magnetic separation was performed with a strong magnet with 1 Tesla magnetic fields include the dimensions of the magnet employed ($10 \times 3 \times 2$ mm^3). A Heidolph motor stirrer (Schwabach, Germany) was applied for stirring of solutions with a glassware stirrer. An adjustable sampler (100–1000 μL) was prepared from Eppendorf (Hamburg, Germany).

2.3. Sample preparation

Six sets of water samples were separately obtained from Tehran province in Iran. All samples were filtered through a membrane filter of 0.45 μm and stored at 4 °C prior to extraction in polyethylene flasks. Sampling of sea water was conducted from three different areas of the Caspian Sea. Seawater samples were collected at a depth of 0.5 m below the surface using 1 L polycarbonate bottles that had been previously rinsed with diluted hydrochloric acid (HCl, 0.1 mol L^{-1}). The collected seawater samples were kept in a cooler box, and were brought back to the laboratory and stored in the dark at 4 °C until analysis. Tap water samples were obtained after flowing for 15 min in our laboratory. Ground water was collected from University of Tehran. Mineral water (Sabalan Brand) was purchased from a local supermarket.

Rain and snow water was collected from the roof of our department (department of chemistry, University of Tehran) on February 2014 in an open homemade collector made of polyvinyl chloride (PVC) and then transferred into 1 L precleaned polypropylene containers. For analysis of real samples, 45 mL of each one was taken and 0.5 mL of DAN solution (0.0002 mol L^{-1} in 1.6 mol L^{-1} HCl) was added. After 5 min, 1 mL of KOH introduced in each bottle and MMWCNT was dispersed and the total volume was adjusted to 50 mL, and the extraction was done as follows.

2.4. Procedure

The reaction of nitrite with DAN was performed by two procedures, Pre and post derivatization DMSPE.

Procedure (I): In the post derivatization method, 48 mL of sample solutions containing 5 μg L^{-1} of nitrite ions was taken in a 50 mL conical capped tube and the pH of sample solutions was adjusted at 4 by drop wise addition of 0.5 mol L^{-1} HCl. 1 mL of MMWCNT suspension (containing 10 mg of the adsorbent in ultra-pure water) was dispersed into the sample solution and final volume of the solutions was adjusted at 50 mL using deionized water. Later on, a 1.5 min agitation using a glassware stirrer (1000 rpm), the extracted nitrite anions were treated with a magnet to separate the MMWCNT nanocomposite adsorbents from the result. After about a few seconds, the solution became limpid and the supernatant solution was completely decanted. 0.2 mL of NaOH (1 mol L^{-1}) as eluent solution was added to the isolated adsorbent, and the obtained mixture was shaken up and again exposed on the strong magnet, and the clear solution of eluent was removed using a sampler and injected into a quartz cell. Subsequently, 0.5 mL of DAN solution was added and derivatization was completed within 5 min to form NAT. For higher fluorescence intensity, 0.3 mL of NaOH (5 mol L^{-1}) was added again and the total volume of 1 mL in the cell was located in spectrofluorimeter to obtain related spectra.

Procedure (II): In the pre derivatization method, NAT solution was first prepared by derivatizing nitrite anions using DAN in acid media followed by adding KOH for more stability and higher fluorescence intensity. The extraction operation was performed within 1.5 min by adding 0.5 mL of NAT solution (500 μg L^{-1}) in 50 mL of sample solutions containing 1 mL of MMWCNT (10 mg), no further needed to adjust pH. As the procedure (I), the extracted NAT was separated by magnet, eluted using 1 mL of acetone/KOH (70/30 v/v) and measured by spectrofluorimetry.

3. Results and discussion

Several parameters (i.e., eluent type and volume, the amount of sorbent, sample volume, adsorption and desorption times, and ionic strength) were optimized to achieve the best extraction efficiency of nitrite using MMWCNTs sorbent. Each experiment was run in triplicates. Double-distilled water spiked with 5.0 μg L^{-1} of NO_2^- was used for optimization of the extraction parameters.

3.1. Influence of pH

The pH of the sample solution plays an important role in the adsorption process of the target compounds onto the MMWCNTs by affecting the existing form of the target compounds and charge species and density onto the adsorbent surface. Since pH_{pzc} (the pH at which the adsorbent has a net zero surface charge) of the MMWCNTs is about 5.5, surface charge of the MMWCNTs is positive in the acidic condition, so an anionic species such as nitrite can be adsorbed onto it. Thus, in this work, the influence of pH on the extraction efficiency was investigated by two different procedures as mentioned above. For procedure (I), the effect of solution pH on the extraction of nitrite was checked in the range of 2.0–10.0. It was seen that when the pH was below 4.0, the fluorescence intensity decreased with the decrease of pH. It is known that nitrite anions are not stable in strong acidic medium and can undergo the following transformation. The decrease in intensity at lower pH <4.0 may be attributed to the conversion of NO_2^- to NO and NO_3^-. On the other hand, because the pK_a of HNO_2 was 3.3, most nitrite anions were protonated in this acidic solution [41]. The extraction efficiency was constant between pH 4.0 and 5.5. By increasing the pH from 6 to 10 the adsorption efficiency decreased due to the repulsion between the negative charge of nitrite ions and adsorbent surface. Therefore, pH of 4.0 was selected as the optimum pH. For procedure (II), the effect of solution pH on the extraction of nitrite was checked in the range of 1.5–11.0. The varying sample pH could not affect on extraction efficiency. This is due to the hydrophobicity structure of NAT and MWCNT. CNT has the ability to establish π–π interactions as well as excellent Van der Waals interactions with other molecules, in particular, with hydrophobic ones [27]. So, hydrophobic and π–π interactions between naphthyl and hexagonal rings of carbon atoms in MWCNT lead to adsorb NAT on the surface of adsorbent without attention to varying pH. Besides, it was clear that a solid interaction between MWCNTs and these organic compounds was made because the lone pair electrons of the nitrogen atoms increase the electron cloud density of the benzene rings and then bring out stronger π–π interactions with the large π-electron system of MWCNTs.

In comparison, between the two procedures, both had same extraction efficiency, but the procedure (I) was time-consuming and adjustment of pH was necessary. In procedure (II), there was no need to adjust pH and use buffer, so for the further studies, we followed the optimization by procedure (II).

3.2. Influence of amount of adsorbent and sample volume

To study the effect of adsorbent quantity on the extraction efficiency of nitrite, different amounts of sorbent in the range of 5–15 mg was added to the solution. Based on the obtained results, quantitative recovery of nitrite could be obtained using 10 mg of sorbent. This is due to a higher surface area to a volume ratio of CNTs. Therefore, satisfactory results can be achieved with fewer amounts of MMWCNT.

To achieve better extraction efficiency and higher preconcentration factor with shorter operational time, the effect of the sample volume was studied using a series of different volume of aqueous solutions (50–200 mL) spiked with a fixed amount of 5 μg of nitrite and 10 mg of the sorbent. It was seen that for solution volumes more than 160 mL, recoveries decreased and insufficient recovery was obtained. Thus, 160 mL was considered to be the optimal sample volume.

3.3. Influence of extraction time

The conditions of adsorption time were also investigated. To increase the precision and sensitivity of the extraction method, it is necessary to select an exposure time that guarantees the equilibrium between aqueous phase and sorbent. Thus, the extraction times were varied in the range of 1–5 min. It was observed that after 1.5 min, the fluorescence intensity of the nitrite had no significant variation. Therefore, the extraction time of 1.5 min was selected for further studies.

3.4. Effect of salt content

To investigate the effect of salinity on the recoveries of the nitrite ions, concentration of NaCl in sample solution was varied in the range of 0–10 % (w/v). Based on the results obtained in this study; the addition of salt between 0 and 5% had no significance and beneficial effect on the analytical signals, but in higher concentration, a slightly negative effect on the DMSPE efficiency was occurring. It is because the aqueous solution viscosity would increase with the addition of salt, which resulted in a difficult mass transfer and low extraction efficiency. Furthermore, the addition of salt would reduce the interaction of analyte with adsorbent surface; thus reduce the extraction efficiency. Hence, no salt was added in subsequent experiments.

3.5. *Influence of desorption conditions*

To find the best eluent to desorb the analytes from the sorbent, different solvents (methanol, ethanol, acetone, acetonitrile, and 1-propanol) were examined. Among them, acetone was found to be the superior solvent in comparison with other solvents for desorption of nitrite ions from the surface of the MMWCNTs. Considering that NAT is stable and has a higher fluorescence intensity at alkaline conditions, thereby, alkali eluents were selected for evaluation of the desorption process. As it can also be seen in Fig. 1, desorption ability for 30/70 (v/v) KOH (1 mol L^{-1}) in acetone was superior to that of the other eluents. Therefore, it was used as eluent in further experiments.

Likewise, for selecting the optimal volume of the eluent for quantitative desorption of nitrite, a minimum volume that we could use in spectroflourimetry was 1 mL. At higher volumes of the eluent, the fluorescence intensity of the nitrite ions decreased due to dilution effect. So, 1 mL of eluent was applied in the subsequent experiments.

The effect of desorption time on the recovery of NO_2^- was investigated in the range of 1–3 min, and no significant effect was observed when the time of desorption was greater than 1 min. Thus, the time of 1 min that was sufficient for quantitative desorption of nitrite from adsorbent was selected for the subsequent experiments.

3.6. *Reusability studies*

Since adsorption of the nitrite on the MMWCNTs is a reversible process, it is possible for regeneration or activation of the adsorbent to reuse. The objective of regeneration is to restore the adsorption capacity of exhausted adsorbent. The further studies indicated that the MMWCNTs can be restored by the acetone/water and reused for twelve successive extraction processes without loss of analytical performance.

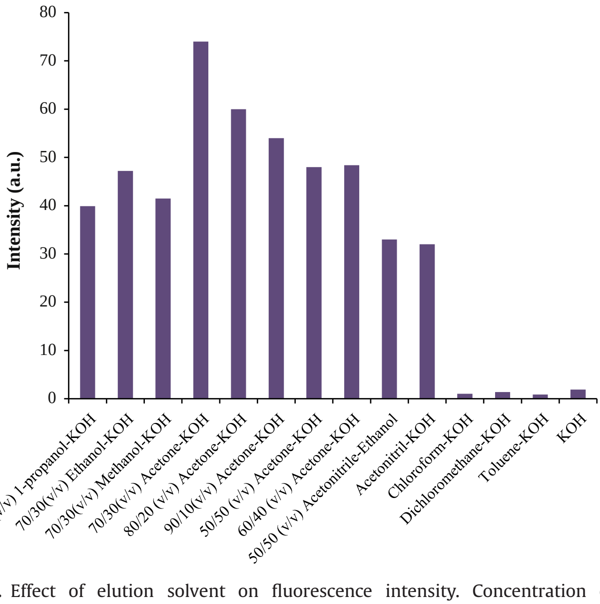

Fig. 1. Effect of elution solvent on fluorescence intensity. Concentration of nitrite = 5 μg L^{-1}, 10 mg of the MMWCNT, extraction time = 1.5 min, elution with 1 mL of KOH/acetone.

3.7. *Effect of coexisting ions*

The effect of different cations and anions on the determination of 5 μg L^{-1} of nitrite ions by the proposed method was studied. An ion was considered to be interference when it caused a variation greater than ±5% in the absorbance of the sample. 5 mg L^{-1} of Fe(III), 10 mg L^{-1} of Cu(II), 1000 mg L^{-1} of alkali, alkaline earth cations, Mn(II), Pb(II), Zn(II) and Cd(II), common anions (nitrate, chloride, and sulfate) and urea did not affect the extraction recovery. Sulfide did not interfere up to a concentration of 20 mg L^{-1}. Amino acids could be tolerated up to a concentration of 100 mg L^{-1}. The obtained results showed that under the conditions specified in the procedure, the major ions in the water samples had no obvious influence on the recovery of the target ion.

3.8. *Quantitative analysis*

Once the proposed DMSPE method based on MMWCNT sorbent was optimized, different quality parameters were evaluated to assess the method performance. Some analytical features such as preconcentration factor, linear range, coefficient of determination (R^2), limit of detection, and precision were investigated. Calibration curves were constructed using different concentrations of the nitrite ions in the range of 0.1–80 μg L^{-g}. Good linearity was observed for all analytes throughout the concentration range, with R^2 of 0.999 and equation of, $I = 12.20C + 7.475$. Good limit of detection (LOD) = 34 ng L^{-1} based on $S/N = 3$ was obtained. High sample volume of 160 mL was obtained; so preconcentration factor was 160. Precision, expressed as the relative standard deviation (RSD), was evaluated in terms of repeatability (from five independent sample preparations at 5 μg L^{-1}, intra-day RSD) was 0.6%.

The efficiency of the proposed method was evaluated by comparing the obtained results with those of other similar methods reported in the literature and given in Table 1. Considering the results, the DMSPE method proved to be a sensitive, efficient, reliable, and easy to use a technique with good LOD, precision and dynamic linear range in extraction and preconcentration of trace amounts of nitrite from aqueous samples. The exceptions were some methods in which sensitive instrument such as GC–MS and LC–MS were used. Furthermore, there is a possibility of extraction of nitrite ions from large volumes of sample in lower extraction times in comparison with conventional SPE sorbents. The proposed MMWCNT based DMSPE has some advantages in comparison with other applied extraction methods such as SPE, including lower consumption of adsorbent and eluting organic solvents and shorter extraction times.

3.9. *Application of the proposed method to real samples*

In order to assess the applicability of the suggested method for real samples an attempt was made to determine nitrite ions in different environmental water samples (tap, mineral, sea, rain, snow and ground waters). Sample preparation of real samples was performed as described in Section 2.3. The main results are given in Table 2. For verification of the accuracy of the method, the spiking recovery method was used. For spiking study, samples were split into two portions and a known amount of a standard solution of nitrite species was added in one portion.

Table 1
Comparison of the proposed method with some of the methods reported in the literature for extraction and determination of nitrite.

Method	Sample species	LOD (μg L^{-1})	LDR (μg L^{-1})	RSD (%)	Ref.
SPE-UV/vis	Tap and river water	5.0	0–140	0.4–0.8	[42]
CE[a]-UV/vis	Spinach	800	1.6–160[b]	0.6	[43]
FIA[c]-UV/vis	Soil	22	0.05–1.6[b]	0.96	[44]
DLLME-HPLC[d]	Tap, well and river water, saliva	0.05	0.4–500	1.5–4.8	[45]
GC–MS[e]	Biological, food and environmental samples	0.02[f]	2.5–100[f]	1.0	[13]
LC–MS[g]	Biological, food and environmental samples	0.29[f]	2.5–100[f]	1.0	[13]
CPE-FO-UV/vis[h]	Tap, lake water and milk	0.5	2–230	4.0	[46]
STR-DRS[i]	Well water and meat	0.09[b]	0.29–5.0[b]	2.0	[47]
µFIA-CL[j]	Food	4.0	8–100	4.1	[48]
DSPME-FL	Tap, mineral, snow, rain sea and ground water	34[f]	0.1–80	0.6	This work

[a] CE: capillary electrophoresis.
[b] mg L^{-1}.
[c] FI: flow injection analysis.
[d] DLLME: dispersive liquid–liquid microextraction—high performance liquid chromatography.
[e] Gas chromatography–mass spectrometry.
[f] ng L^{-1}.
[g] Liquid chromatography with fluorescence detection.
[h] Cloud point extraction-fiber-optic based spectrometer.
[i] Spot test reaction-diffuse reflectance spectroscopy.
[j] Chemiluminescence.

Table 2
Determination of nitrite in different water samples by our proposed method.

Water Samples	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	RSD (%) (n=3)
Tap	0	0.20	–	1.8
	1.00	1.15	95.8	1.9
Mineral	0	2.13	–	2.4
	1.00	3.20	102.0	2.7
Ground	0	5.02	–	3.0
	1.0	5.7	94.7	3.9
Sea	0	87.22	–	9.8
	10.00	96.40	99.1	10.6
Snow (1th day snowing)	0	103.6	–	8.2
	10.0	110.5	97.3	8.7
(3th day snowing)	0	9.95	–	3.1
	1.0	10.6	96.8	3.3
Rain	0	105.1	–	4.5
	10.0	112.9	98.0	4.8

The concentration of the analytes was determined in both the spiked, C_1, and unspiked portions, C_2. The relative recovery, $\%R$, was calculated as “Eq. (1)”.

$$\%R = \frac{C_1 - C_2}{C_3} \times 100 \qquad (1)$$

where C_3 is the concentration of the analytes added to the spiked portion. As can be viewed in Table 2, the recovery values were acceptable.

4. Conclusion

A fast and sensitive method for the determination of nitrite in environmental water samples by DMSPE with fluorescence detection has been successfully developed and validated. To test the feasibility of the MMWCNT sorbent in DMSPE, it was used as an extraction sorbent for preconcentration of trace amounts of nitrite in water samples. Thus, it is considered that the proposed procedure can easily be blown up to determination of other pollutants in environmental samples. The result proved that MMWCNT based DMSPE method had a great potential in rapid preconcentration of analyses of large-volume water samples in comparison to conventional SPE sorbents due to the high specific surface area, the absence of internal diffusion resistance, operation in dispersed mode, and magnetic separation. The advantages of the proposed method based on the MMWCNT include rather easy, simple, fast, pH-independent and inexpensive synthesis method; rapid and convenient extraction operation, feasibility for large-volume samples, high sensitivity, and precision and accuracy in preconcentration and determination of environmental pollutants such as nitrite.

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