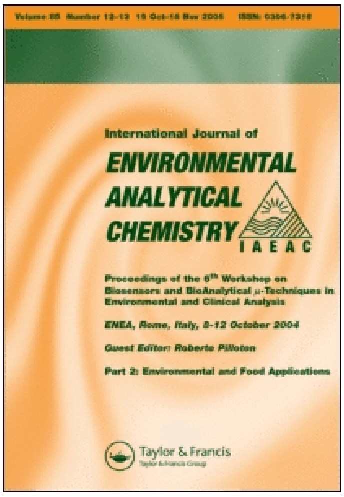

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of ultra-trace amounts of nickel in environmental samples by atomic absorption spectrometry with <i>in-situ</i> trapping of volatile species in an iridium-palladium coated graphite furnace

Hanwen Sun[a]; Ran Suo[ab]
[a] College of Chemistry and Environmental Science, Key Laboratory of Analytical Science and Technology of Hebei Province, Hebei University, Baoding, China [b] Department of Food Science, Agricultural University of Hebei, Baoding, China

To cite this Article Sun, Hanwen and Suo, Ran(2008) 'Determination of ultra-trace amounts of nickel in environmental samples by atomic absorption spectrometry with <i>in-situ</i> trapping of volatile species in an iridium-palladium coated graphite furnace', International Journal of Environmental Analytical Chemistry, 88: 11, 791 — 801

To link to this Article: DOI: 10.1080/03067310801961860

URL: http://dx.doi.org/10.1080/03067310801961860

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 11, 15 September 2008, 791–801

Determination of ultra-trace amounts of nickel in environmental samples by atomic absorption spectrometry with *in-situ* trapping of volatile species in an iridium–palladium coated graphite furnace

Hanwen Sun[a]* and Ran Suo[ab]

[a]*College of Chemistry and Environmental Science, Key Laboratory of Analytical Science and Technology of Hebei Province, Hebei University, Baoding, China;* [b]*Department of Food Science, Agricultural University of Hebei, Baoding, Baoding, China*

(*Received 30 October 2007; final version received 4 February 2008*)

A sensitive and accurate method is described for the determination of ultra-trace nickel in environmental samples with *in-situ* trapping of volatile species in iridium-palladium coated graphite furnace atomic absorption spectrometry. The effects of the conditions for the generation and collection of volatile nickel species, such as medium acidity, potassium borohydride concentration, enhancement reagent concentration, reaction temperature, as well as graphite tube coating, carrier gas flow rate and trapping time were investigated. Phenanthroline was selected as the enhancement reagent due to its good enhancing effect, and iridium–palladium coating was used for the *in-situ* trapping of volatile nickel species at 300°C. Under the optimal conditions, the calibration curve was linear from 0.21 up to $30.0\,\mathrm{ng\,mL^{-1}}$ with correlation coefficient of 0.9991, the detection limit ($S/N = 3$) was $0.21\,\mathrm{ng\,mL^{-1}}$ for 4 mL sample volumes and the relative standard deviation for 11 determinations of Ni at $10\,\mathrm{ng\,mL^{-1}}$ was 3.5%. The results found by the proposed methods are accordant with the certified values of water, soil and tea certified reference materials. The proposed methods have been applied for the determination of ultra-trace Ni in tap, river and wastewater, as well as rice and soil samples, with recoveries ranging from 97.3 to 100.5%.

Keywords: volatile species generation; *in-situ* trapping; graphite furnace atomic absorption spectrometry; nickel; environmental samples

1. Introduction

Nickel is an essential element for some microorganisms and higher plants and plays an important role in their life. However, in high doses it may be an extremely toxic element. For instance, a great deal of research results show that nickel pollution in soil can lead to serious impacts on soil microorganisms [1] and plants [2]. Therefore, the detection and quantification of nickel in environmental samples are important analytical tasks.

Hydride generation sample introduction for atomic absorption spectrometry and for other atomic spectrometric techniques has a number of advantages in the determination of volatile hydride forming elements. Thus, this technique has become one of the most

---

*Corresponding author. Email: hanwen@hbu.edu.cn

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310801961860
http://www.informaworld.com

successful and convenient methods for the determination of such elements [3]. Feng and colleagues expanded the scope of chemical vapour generation for noble and other transition metals [4]. Volatile nickel species could be generated by reaction in an aqueous solution [5,6]. The generation technique of volatile species has been applied for Ni determination by inductively coupled plasma atomic emission spectrometry (ICP) [7]. Pohl reviewed the advances in chemical vapour generation via reaction with sodium tetrahydroborate [8]. To increase the efficiency of vapour generation some organic reagents have been used. The use of L-cysteine as enhancing agent was described for hydride generation of As, Sb, Bi, Sn and Ge [9]. Thiourea [10–12] and didodecyldimethylammonium bromide [13] were used as enhancing agent of hydride generation for Cd, and phenanthroline for Cu [14] as well as DDTC for Au [15]. In our previous works, the enhancing effects and possible mechanism of different types of organised media, including cationic surfactants and anionic surfactants, on the generation of volatile zinc species were investigated by atomic fluorescence spectrometry [16]. 8-Hydroxyquinoline and phenanthroline individually showed excellent performance for the simultaneous vapour generation of Zn and Cd [17]. The efficiency data from individual reports on chemical vapour generation of transition and noble metals were reviewed, the efficiencies reported do not exceed 30% [18].

Some of the main problems associated with conventional hydride procedures are that the analyte hydrides are diluted by the co-evolved hydrogen and carrier gas, thereby decreasing the sensitivity of the determination. Drasch and colleagues first reported the concept of *in-situ* trapping of a volatile hydride in a preheated graphite furnace with subsequent atomisation [19]. Matusiewicz and Sturgeon reviewed atomic spectrometric detection of hydride formed elements following *in-situ* trapping within a graphite furnace [20]. Volatile species generation of Ag, Cu, Cd and Zn and *in-situ* trapping in a pre-heated graphite tube were described [21]. Flow-injection *in-situ* trapping of volatile species of gold in graphite furnace have been reported [22–24]. This technique offers substantial advantages over conventional furnace or quartz tube analytical techniques, including simplicity of operation, flexible use of sample volumes, high sensitivity and a considerable increase in the relative detection power as a result of the *in-situ* concentration. Otherwise, the carbonyl generation combined with *in-situ* preconcentration technique has been used for graphite furnace atomic absorption spectrometry (GFAAS) to determine Ni in water reference materials [25,26] and in marine samples [27] with low detection limits.

To our knowledge, volatile nickel species generation with *in-situ* trapping in graphite furnace has not yet been reported. The main purpose of this work was to develop a sensitive and accurate methodology suitable for the determination of ultra-trace Ni levels in environmental samples with *in-situ* trapping of volatile species in an iridium-palladium coated graphite furnace.

2. Experimental

2.1 *Instrumentation*

The determinations were performed with a Perkin-Elmer 1100B graphite furnace atomic absorption spectrometer equipped with a HGA-700 graphite atomiser and a deuterium lamp background corrector (Beijing Haiguang Instrument Co., China). Integrated absorbance over a 4 s atomisation time was used. The Ni hollow cathode lamp was operated at 6 mA. The most sensitive line (232.0 nm) with a 0.2 nm band pass was typically used.

A flow injection-hydride generation system (Shenyang Zhaofa Automation Analysis Institute, China) was used for the generation of volatile nickel species (Figure 1). An AFS-230 double-channel non-dispersive atomic fluorescence spectrometer (Beijing Haiguang Instrument Company, China) was used for investigating the optimal conditions of volatile nickel species generation at a fluorescence line of 232.0 nm. A flow injection-hydride generation system was used for *in-situ* trapping volatile nickel species in the graphite furnace. The inner surface of the gas–liquid separator was alkylation-treated with a 5% (v/v) toluene solution of dimethyl dichlorosilicane (DMCS) in order to set up hydrophobic surface and decrease adsorption activity. A 40 mm long quartz capillary was used for sampling.

2.2 *Reagents*

A Ni standard solution (National Steel Material Yest Center, Beijing, China) with a Ni concentration of 1000 μg mL^{-1} in 5% HCl was diluted with double distilled water (DDW) to provide a calibration solution of 10 μg mL^{-1}. Working standard solutions were prepared daily by further adequate dilution. Hydrochloric and nitric acid were of Suprapure grade (Merck, Darmstadt, Germany). All other chemicals (phenanthroline, 8-hydroxyquinoline, etc.) were at least of analytical-reagent grade. DDW, obtained from a quartz distillation apparatus, was used throughout. The iridium modifier solution (2.50 mg mL^{-1}) was prepared by dissolving 0.5973g $(NH_4)_3IrCl_6$ in 10 mL of 0.1 mol L^{-1} HNO_3 and diluting to 100 mL with DDW. The palladium modifier solution (1.00 mg mL^{-1}) was prepared by dissolving 0.8336g $PdCl_2$ in 10 mL of 0.1 mol L^{-1} HNO_3 and diluting to 500 mL with DDW. KBH_4 (Merck) solutions (10–40 mg mL^{-1}) were prepared fresh daily by dissolving the appropriate amount of KBH_4 in 0.1% NaOH and filtered through a 0.45 μm membrane filter.

A water certified reference material (GBW08607), a soil certified reference material (GBW07402) and a tea certified reference material (GBW 08505) were purchased from the National Standard Material Research Center (Beijing, China).

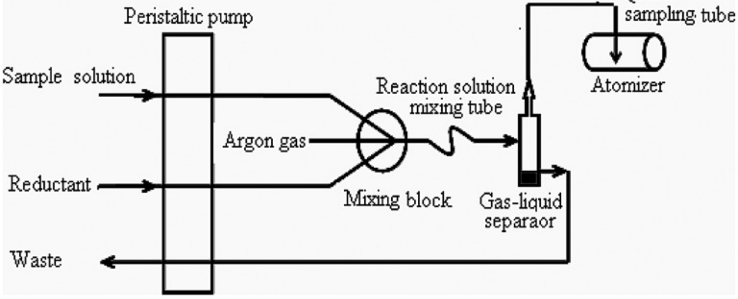

Figure 1. Basic flow diagram for the sample injection-hydride generation *in-situ* trapping in the graphite furnace.
Notes: Reductant flow rate, 4.0 mL min^{-1}; sample solution flow rate, 8.0 mL min^{-1}; argon gas flow rate for AFS, 200 mL min^{-1}; argon gas flow rate for in-situ trapping, 100 mL min^{-1}.

2.3 *Coating procedure*

The coating procedure was based on that described by Haug and Liao [28]: 50 µL of a mixture of 0.05% m/v Pd and 0.05% m/v Ir in 0.1 M nitric acid was injected into the graphite tube, slowly dried at 110–130°C for 50 s and heated at 1200°C for 30 s and 2000°C for 3 s. The complete injection and heating cycle were repeated; thus, the total mass on the graphite tube was 50 µg Pd and 50 µg Ir. The same procedure using a 0.1% m/v of Ir or Pd solutions gave 100 µg of Ir or Pd in the graphite tube, respectively.

2.4 *Generation of volatile nickel species*

The sample solution containing 0.15 mol L^{-1} HCl and 2.0 mg mL^{-1} phenanthroline was introduced by means of a peristaltic pump. The flow rate of the sample solution was selected as 8 mL min^{-1} with higher sensitivity through the compasion in the range of 5–12 mL min^{-1}. A 20 mg mL^{-1} KBH_4 solution was pumped through another passage at 4 mL min^{-1} into the Y mixing block. The volatile nickel species generated in the mixing tube were separated at the gas–liquid separator and transported to the graphite furnace by a stream of argon, used as carrier gas (100 mL min^{-1}).

A quartz capillary was used for the insertion of the gases into the graphite tube and the trapping temperature was set at 300°C. After collecting the gases for 40–120 s (depending on the analyte content), the atomiser was purged with argon in order to ensure complete flushing of the reaction gases from the graphite furnace. The quartz capillary was removed and the determination of the collected analyte was performed using the furnace temperature program shown in Table 1.

2.5 *Sample pre-treatment*

A 20 mL sample of waste, river or tap waters was acidified with 1–2 mL 1% nitric acid and then filtered through a 0.45 µm membrane filter. The soil samples were collected from the cultivated layer (0–20cm) in farmland near a wastewater treatment plant. The soil as well as rice samples were air-dried, ground, and passed through 80 mesh sieve. A 0.5 g sample was digested with 10 mL aqua regia for 10 h, followed by the addition of 5 mL perchloric acid and gentle heating on an electric hot-plate to dryness. Then, 5 mL 1% nitric acid were added, and the solution was heated and centrifuged. The obtained solution was transferred into a 25 mL volumetric flask and diluted to the volume with DDW.

Table 1. Furnace temperature program.

Step	Temp (°C)	Ramp (s)	Hold time (s)	Internal gas (mL min^{-1})	Read	Action
1	150	10	10	300		Dry
2	300	10	40–120	100		Trapping
3	300	1	10	300		Ar flush
4	1050	10	10	300		Pyrolysis
5	2500	0	4	0	Yes	Atomise
6	2600	1	1	300		Clean

Final sample solutions were adjusted to contain 0.30 mol L^{-1} HCl for the generation of volatile nickel species. The sample blank was prepared in the same way.

3. Results and discussion

3.1 *Optimisation of volatile nickel species generation conditions*

3.1.1 *Effect of acid medium and reductant concentration*

For operational convenience, the optimisation of the conditions for the generation of volatile nickel species was carried out with atomic fluorescence detection. The effect of the type of acid and concentration on the Ni responses was studied for a sample flow rate of 8.0 mL min^{-1}, KBH_4 concentration of 10 mg mL^{-1} and its flow rate of 1.0 mL min^{-1}. The most sensitive atomic fluorescence line (230.0 nm) of analyte was chosen for the investigation. The same experimental conditions (i.e., acid concentration and flow rates) were applied for sample introduction and volatile Ni generation.

It was noticed that the fluorescence intensity was higher in the HCl concentration range of 0.15–0.32 mol L^{-1}, containing 2.0 µg mL^{-1} phenanthroline, and decreased when the concentration was above 0.32 mol L^{-1}. In HNO_3 medium, the fluorescence intensity was constant within the 0.28–0.32 mol L^{-1} range, but only 60% of that in HCl medium. For concentrations down to 0.15 mol L^{-1}, the intensity and higher than 0.32 mol L^{-1}, the fluorescence signal decreased. Thus, the HCl medium was chosen, at a concentration of 0.30 mol L^{-1} as suitable for the generation of volatile nickel species.

A series of KBH_4 solutions were prepared covering the 0.25 to 40 mg mL^{-1} concentration range. The flow rates of both the acidified sample and reductant solutions were 8 and 1.5 mL min^{-1}, respectively. The Ni signal increased continuously with increasing reductant concentration up to 15 mg mL^{-1}, and in the range of 15–25 mg mL^{-1}, the signal reached the higher intensity. Beyond 25 mg mL^{-1}, the Ni signal experienced only slight variations and offered no practical advantages for supporting the increase of the reductant concentration. In addition, a significant increase of the blank signal was observed as this reagent concentration increased. Thus, a KBH_4 concentration of 20 mg mL^{-1} was selected as the most convenient. The influence of the KBH_4 flow rate on Ni intensities was further investigated with a sample flow rate of 8.0 mL min^{-1}. The increase in the KBH_4 flow rate caused a growth in intensities of Ni signal up to 4.0 mL min^{-1}. Above 4.0 mL min^{-1} the intensity rapidly decreased, which was related to the decrease of the reaction time and the production of a larger amount of hydrogen in the reaction chamber. So the favourable flow rate was selected as 4.0 mL min^{-1} for KBH_4 solution.

In the light of comparison tests, argon flow rate should be changed from 200 mL min^{-1} for AFS to 100 mL min^{-1} for *in-situ* trapping GFAAS, and the above selected other conditions for AFS can be applied for *in-situ* trapping GFAAS with higher sensitivity.

3.1.2 *Effect of enhancement reagent and reaction temperature*

The presence of an appropriate reagent was necessary to enhance the chemical vapour generation. In our previous work [17], the enhancing effect of some organic reagents such as phenanthroline, 8-hydroxyquinoline, ferron, thiourea, L-cysteine, EDTA and ascorbic acid was investigated and compared. It was found that 8-hydroxyquinoline and phenanthroline individually showed excellent performance for the simultaneous vapour generation of Zn and Cd. The enhancement reagents could form complexes with Zn and Cd. In the light of the above study, the present work investigated the enhancing effect of these organic reagents for vapour generation of Ni. It was also found that phenanthroline and 8-hydroxyquinoline were the most effective for the generation of volatile nickel species. The complexes (ML) of phenanthroline or 8-hydroxyquinoline with Ni should produce a reactive transient intermediate $H \cdots M \cdots L$ with KBH_4, which changed the thermodynamic reaction constant and facilitated the generation of M–H bond [17]. In the absence of a complexing reagent, the initial stages of chemical reduction of metallic ions in solution must proceed through the formation of single atoms, followed by the rapid formation of clusters with other atoms until the continued coalescence produced observable precipitates or evidence of stable sol formation [29].

Figure 2 shows that the Ni signal was poor in the absence of the enhancement reagent, whereas it improved 25 times in the presence of phenanthroline, and 12 times in the presence of 8-hydroxyquinoline. Therefore, phenanthroline was used as enhancement reagent, and $2.0\,\mu g\,mL^{-1}$ was selected as optimal concentration.

In the present work, no significant signal was observed when the experiment was carried out at laboratory temperatures below 10°C. In order to evaluate the effect of temperature on vapour generation, the sample vessel and mixing coil were immersed in a water bath and the temperature was varied between 10 and 90°C. The results showed that the efficiency of vapour generation was poor at lower temperatures, but increased by 10% at 60°C. However, no further enhancement was shown at temperatures over 65°C. Certainly, the higher temperature facilitated the kinetic process of the Ni vapour generation, while much higher temperature caused the hydride reaction products to decompose before phase separation could be accomplished. For simplicity, the measurements were carried out at ambient temperature (18–25°C). The effect of reaction temperature on signal in the absence of the enhancement reagent was also tested, and the result showed that temperature did not influence the efficiency of vapour generation.

To examine the efficiency of vapour generation, the waste liquid obtained after vapour generation under the optimal conditions was heated to dryness and the residue was dissolved with 0.1% nitric acid. The remaining Ni in the waste liquid was determined

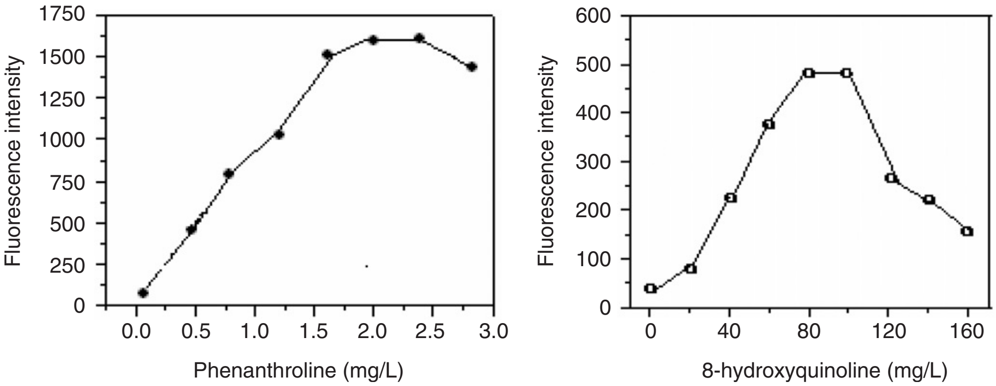

Figure 2. Effects of phenanthroline and 8-hydroxyquinoline on the Ni fluorescence signal.
Notes: Ni: $20\,\mu g\,L^{-1}$, $8.0\,mL\,min^{-1}$; HCl: $0.30\,mol\,L^{-1}$; KBH_4: $20\,g\,L^{-1}$, $4.0\,mL\,min^{-1}$; Argon gas flow rate: $200\,mL\,min^{-1}$.

by GFAAS. A 73% of the vapour generation efficiency was obtained based on the original quantity and the remaining quantity of Ni. Otherwise, to examine the transport efficiency of the generated volatile nickel species, the inner surface of reaction tube, gas–liquid generator and transport tube were washed with 0.1% nitric acid, and the content of Ni in the washing solution was determined by GFAAS. A 20% loss efficiency of Ni was observed, based on the original quantity and the lost quantity of Ni. Considering the generation and transport, a 53% total efficiency for volatile nickel species was obtained.

3.2 *Effect of different coatings of graphite tube on* in-situ *trapping*

The volatile nickel species generated were introduced into graphite tube surface for *in-situ* collection. The effects of the modification of the graphite tubes by coating them with iridium, palladium or iridium–palladium, as well as the different trapping temperatures for collecting the analyte were investigated. Figure 3 shows the analytical signal obtained for different coatings as a function of the temperature, in the range of 100–700°C. It is shown that the temperature of collection is a parameter that significantly affects the collection efficiency but not critically with respect to the investigated coatings. The losses at higher trapping temperatures may be explained by early volatilization of the trapped species. It was also noted that the collection efficiency for graphite tubes without coating was much lower than that for graphite tubes with coating. The palladium-coated graphite tube showed the highest collection efficiency, however, it needs re-coating before each collection. The iridium-coated graphite tube exhibited better stability, however, to get higher collection efficiency the trapping temperature should be 600°C. The iridium–palladium coated graphite tube showed higher collection efficiency and better stability, and the same coating could be used up to 300 times. So iridium–palladium coating (50 µg Ir + 50 µg Pd) was chosen for *in-situ* trapping volatile nickel species, and for the subsequent work a temperature of 300°C was selected for better efficiency and convenience.

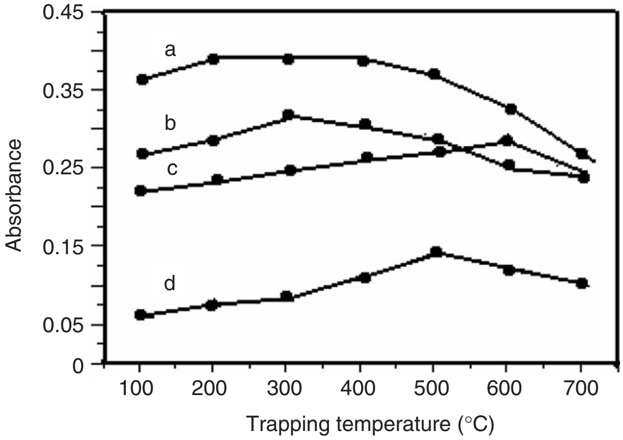

Figure 3. Effect of different coatings on the *in-situ* collection efficiency of volatile nickel species.
Notes: (a) palladium coating; (b) iridium–palladium coating; (c) iridium coating; (d) without coating; Ni: 20 ng mL^{-1}, 8.0 mL min^{-1}; HCl: 0.30 mol L^{-1}; KBH$_4$: 20 mg mL^{-1}, 4.0 mL min^{-1}; Argon gas flow rate: 100 mL min^{-1}; Trapping time: 30 s.

3.3 *Effect of the carrier gas flow rate and trapping time*

Figures 4 and 5 show, respectively, the influence of the carrier gas flow rate and trapping time on the Ni signal. The results show that the integrated absorbance of Ni decreased with the increase of the flow rate. Therefore, an argon flow rate of 100 mL min^{-1} was used throughout subsequent experiments. Concerning the trapping time, it was noted that maximum adsorption efficiency was reached for a collection of 120 s, and this was selected in the present work in order to ensure maximum sensitivity.

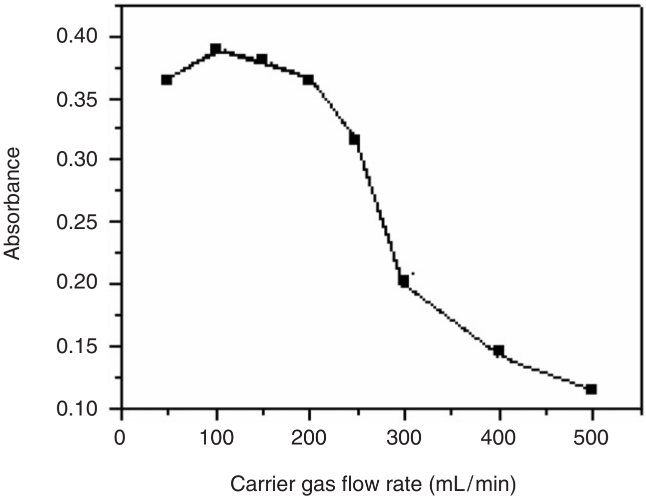

Figure 4. Effect of carrier gas flow rate on *in-situ* collection efficiency.
Notes: Ni: 20 ng mL^{-1}, 8.0 mL min^{-1}; HCl: 0.30 mol L^{-1}; KBH_4: 20 mg mL^{-1}, 4.0 mL min^{-1}; Trapping time: 30 s.

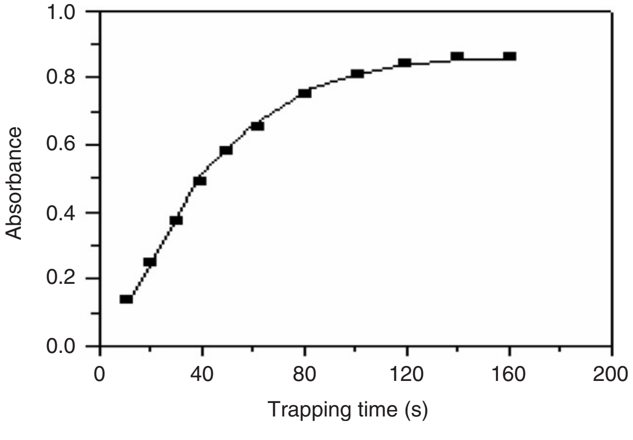

Figure 5. Effect of trapping time on collection efficiency of volatile nickel species in graphite tube with iridium–palladium coating.
Notes: Ni: 20 ng mL^{-1}, 8.0 mL min^{-1}; HCl: 0.30 mol L^{-1}; KBH_4: 20 mg mL^{-1}, 4.0 mL min^{-1}; Argon gas flow rate: 100 mL min^{-1}.

3.4 *Analytical performance*

The calibration curve, obtained by triplicate measurements, is described by the equation: $A = (0.037 \pm 0.001)C + (0.003 \pm 0.001)$, that was linear from 0.21 up to 30.0 ng mL^{-1}, with a correlation coefficient of 0.9991. The limit of detection, defined as the concentration giving a signal equal to three times the standard deviation of the blank signal ($n = 11$) was 0.21 ng mL^{-1} for a 4 mL sample volume and 10.5 ng g^{-1} for a 0.5 g of rice and soil sample. The precision of the procedure, calculated as the RSD of 11 determinations at the 10 ng mL^{-1} level, was 3.5%. The detection limit of the proposed method was higher than those of carbonyl generation with *in-situ* pre-concentration–GFAAS [25–27], cloud point extraction–GFAAS (0.12 ng mL^{-1}) [30] and ion-exchange–GFAAS (0.0102 ng mL^{-1}) [31] as well as activated carbon preconcentration–vapour generation–ICP (0.06 ng mL^{-1}) [32], and lower than those of slurry sampling–GFAAS (44 ng g^{-1}), [33 direct sampling–GFAAS (2 ng g^{-1}) [34], solid sampling–GFAAS (20 ng g^{-1}) [35], line-source and high-resolution continuum-source–GFAAS (70 ng g^{-1}) [36], vapour generation–ICP (0.5 ng mL^{-1}, 1.8 ng mL^{-1}) [6,7], and vapour generation–ICP/MS (6.1 ng mL^{-1}) [37].

To establish the accuracy of the proposed method, the determination of Ni was performed in certified reference materials. The results are given in Table 2 and indicate that the proposed method is reliable.

3.5 *Application to environmental samples*

The possible interfering effect of transition metals (Cd, Co, Cu, Cr, Fe, Mn, Zn), hydride forming elements (As, Ge, Pb, Sb, Se, Sn, Te), and Hg on the Ni signal has been examined previously [7]. It has been demonstrated that generation of volatile nickel species is markedly free of interferences. Although any interference study was not undertaken in the present work, it became obvious from the present data that no systematic errors occurred due to the presence of any of the matrices. The slopes of the calibration curves performed with aqueous calibration solutions and those of the analyte addition curves were compared and no remarkable differences were observed between them, showing that no matrix interference occurred. Also, the Ni spiked before the digestion procedure was recovered quantitatively. Therefore, analyses could be performed using external calibration with aqueous calibration. However, to eliminate any possible matrix effects, due to the unknown composition of the investigated real samples, only the method of analyte addition was used.

In this way, samples of tap, river and wastewaters, rice and soil samples collected in Baoding (P.R. China) were analysed. In addition, recovery experiments of different amounts were also carried out, and the results are shown in Table 3.

Table 2. Comparison of the found and certified values in the determination of Ni in some certified reference materials.

Reference material	Certified value (μg g^{-1})	Found value (X ± SD, $n = 5$) (μg g^{-1})
Water (GBW08607)	0.500 ± 0.010	0.508 ± 0.011
Soil (GBW07402)	4.00 ± 1.92	4.00 ± 0.08
Tea (GBW08505)	7.61 ± 0.48	7.54 ± 0.31

Table 3. Determination of Ni in environmental samples ($n=5$).

Sample	Content in sample (ng mL^{-1})	Added value (ng mL^{-1})	Average recovery (%)
Tap water-1	1.51 ± 0.23	1.00, 1.50, 2.00	98.1
Tap water-2	1.83 ± 0.29	1.00, 1.50, 2.00	100.5
River water-1	4.85 ± 0.19	4.00, 4.50, 5.00	99.6
River water-2	4.52 ± 0.15	4.00, 4.50, 5.00	98.0
Wastewater-1	17.3 ± 0.1	10.0, 15.0, 20.0	98.1
Wastewater-2	31.1 ± 0.1	10.0, 15.0, 20.0	99.8
Rice-1*	0.65 ± 0.09	0.50, 0.60, 0.70	97.3
Rice-2*	0.61 ± 0.11	0.50, 0.60, 0.70	98.1
Soil-1**	20.65 ± 0.02	10.0, 20.0, 30.0	99.4
Soil-2**	23.97 ± 0.02	10.0, 20.0, 30.0	100.4

Notes: *Content in rice samples and added quantity expressed in μg kg^{-1}; **Content in soil samples and added quantity expressed in mg kg^{-1}.

Recoveries in the range of 97.3–100.5% were found reasonable for the investigated concentration levels.

4. Conclusions

The proposed method has good sensitivity for the determination of Ni in environmental samples. Phenanthroline is an effective enhancement reagent for generation of volatile nickel species with good enhancing effect, and iridium–palladium coating of the graphite furnace was effective for trapping volatile nickel species. This technique offers substantial advantages over conventional furnace or quartz tube analytical techniques, including simplicity of operation, flexible use of sample volumes, high sensitivity and a considerable increase in the relative detection power. The detection limit of the proposed method is famous for the determination of ultra-trace Ni. The accuracy of the procedure was confirmed by analysing the certified reference materials. This approach provides a viable alternative to the conventional GFAAS technique.

Acknowledgement

We express thanks to the Natural Science Foundation of Hebei Province (China), for much support to the studied subject.

References

[1] X.D. Cai, R.L. Qiu, and G.Z. Chen, Ecol. Sci. **23**, 273 (2004).

[2] Z.L. Xie, B.L. Yang, G.Z. Bao, and D.M. Dong, J. Jilin University (Earth Science Edition) **36**, 599 (2006).

[3] J. Dedina and D.L. Tsalev, *Hydride Generation Atomic Absorption Spectrometry* (Wiley, Chichester, 1995).

[4] Y.L. Feng, J.W. Lam, and R.E. Sturgeon, Analyst **126**, 1833 (2001).

[5] P. Pohl and W. Zyrnicki, Anal. Chim. Acta **429**, 135 (2001).

[6] X.W. Guo, B. Huang, Z. Sun, R. Ke, Q. Wang, and Z.B. Gong, Spectrochim. Acta, Part B **55**, 943 (2000).

[7] J. Marrero and P. Smichowski, Anal. Bioanal. Chem. **374**, 196 (2002).

[8] P. Pohl, Tren. Anal. Chem. **23**, 21 (2004).

[9] H.W. Chen and Q.H. He, Chin. J. Anal. Chem. **28**, 368 (2000).

[10] X.W. Guo and X.M. Guo, Anal. Chim. Acta **310**, 377 (1995).

[11] X.W. Guo and X.M. Guo, J. Anal. At. Spectrom. **10**, 987 (1995).

[12] X. Yu, Z.H. Liao, and Z.C. Jiang, J. Wuhan University **43**, 751 (1997).

[13] A. Sanz-Medel, M.C. Valdés-Hevia, N. Bordel, and M.R. Fernández, Anal. Chem. **67**, 2216 (1995).

[14] H.Y. Zhou, S.K. Xu, and Z.L. Fang, Spectroscopy and Spectr. Anal. **20**, 525 (2000).

[15] X.G. Du and S.K. Xu, Fresenius J. Anal. Chem. **370**, 1065 (2001).

[16] H.W. Sun, R. Suo, and Y.K. Lu, Anal. Chim. Acta **457**, 305 (2002).

[17] H.W. Sun and R. Suo, Anal. Chim. Acta **509**, 71 (2004).

[18] T. Matoušek, Anal. Bioanal. Chem. **388**, 763 (2007).

[19] G. Drasch, L.V. Meyer, and G. Kauert, Fresenius J. Anal. Chem. **304**, 141 (1980).

[20] H. Matusiewicz and R.E. Sturgeon, Spectrochim. Acta, Part B **51**, 377 (1996).

[21] A.S. Luna, H.B. Pereira, I. Takase, R.A. Gonçalves, R.E. Sturgeon, and R.C. de Campos, Spectrochim. Acta B **57**, 2047 (2002).

[22] G. Ertaş and O.Y. Ataman, Applied Spectroscopy **58**, 1243 (2004).

[23] G. Ertaş and O.Y. Ataman, Applied Spectroscopy **60**, 423 (2006).

[24] H.B. Ma, X.F. Fan, H.Y. Zhou, and S.K. Xu, Spectrochim. Acta B **58**, 33 (2003).

[25] D. Erber and K. Camman, Analyst **120**, 2699 (1995).

[26] M. Johansson, R. Hansson, J. Snell, and W. Frech, Analyst **123**, 1223 (1998).

[27] R.E. Sturgeon, S.N. Willie, and S.S. Berman, J. Anal. At. Spectrom **4**, 443 (1989).

[28] H.O. Haug and Y.P. Liao, Spectrochim. Acta, Part B **50**, 1311 (1995).

[29] N. Panichev and R.E. Sturgeon, Anal. Chem. **70**, 1670 (1998).

[30] Z.M. Sun, P. Liang, Q. Ding, and J. Cao, J. Hazard. Mater. B **137**, 943 (2006).

[31] J.H. Wang and E.H. Hansen, Anal. Chim. Acta **435**, 331 (2001).

[32] S. Cerutti, S. Moyano, J. Marrero, P. Smichowski, and L.D. Martinez, J. Anal. At. Spectrom. **20**, 559 (2005).

[33] M. González, M. Gallego, and M. Valcárcel, Talanta **48**, 1051 (1999).

[34] M.N. Matos Reyes and R.C. Campos, Talanta **70**, 929 (2006).

[35] M.M. Silva, I.C.F. Damin, M.G.R. Vale, and B. Welz, Talanta **71**, 1877 (2007).

[36] M.G.R. Vale, I.C.F. Damin, A. Klassen, M.M. Silva, B. Welz, A.F. Silva, F.G. Lepri, D.L.G. Borges, and U. Heitmann, Microchem. J. **77**, 131 (2004).

[37] X.C. Duan, R.L. McLaughlin, I.D. Brindle, and A. Conn, J. Anal. At. Spectr. **17**, 227 (2002).