Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 108 (2008) 774–778
Food Chemistry
www.elsevier.com/locate/foodchem

Analytical Methods

Automatic determination of nickel in foods by flame atomic absorption spectrometry

M.C. Yebra *, S. Cancela, R.M. Cespón

Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, 15782-Santiago de Compostela, Spain

Received 9 January 2007; received in revised form 16 October 2007; accepted 8 November 2007

Abstract

A new sensitive and low cost flow injection method that combines acid extraction, preconcentration and flame atomic absorption spectrometric determination of nickel in food samples at μg/g levels is described. The dynamic acid extraction step was carried out by using a continuous ultrasound-assisted extraction system. The acid extract was preconcentrated on-line on a minicolumn packed with a chelating resin (Serdolit Che, with iminodiacetic groups) and nickel was eluted with diluted hydrochloric acid, being continuously monitored by flame atomic absorption spectrometry. An experimental design (Plackett-Burman $2^6 \times 3/16$) is used to optimise the methodology proposed. The method allowed a total sampling frequency of 13–28 samples per hour. Good precision of the whole procedure (1.9–3.6% expressed as relative standard deviation) and a detection limit of 0.12 μg/g, for 60 mg of sample were achieved. The method was successfully applied to the determination of trace amounts of nickel in food samples.

Keywords: Ultrasound-assisted acid extraction; Minicolumn preconcentration; Flow injection analysis; Nickel; Food analysis

1. Introduction

Foods have been found to be the main source of nickel intake by man. Though nickel is a moderately toxic element as compared with other transition metals, it is known that can lead to serious problems, including respiratory system cancer. Moreover, nickel can cause a skin disorder known as nickel-eczema, and some nickel-sensitive patients present systemic (cutaneous and/or digestive) symptoms related to the ingestion of high nickel-content foods. Therefore, the knowledge of the nickel-content in foods could be of a great interest for the dietary control of these patients (Schiavino et al., 2006).

Ultrasonic radiation is a powerful aid in the acceleration of sample pre-treatment and a operation such as ultrasonic extraction is emerging as an alternative to traditional sample digestion with concentrated acids. Thus, ultrasounds have been applied to assist the acid extraction of several metals from different solid samples (Luque de Castro & Priego Capote, 2007).

Several techniques have been used to determine nickel in food samples, such as inductively coupled plasma-optical emission spectrometry (ICP-OES) (LaBrecque et al., 2004), inductively coupled plasma-mass spectrometry (ICP-MS) (Lee, Muraoka, Oshima, & Motomizu, 2004), differential pulse cathodic stripping voltammetry (DPCSV) (Karadjova, Girousi, Iliadou, & Stratis, 2000), differential pulse adsorptive voltammetry (DPAV) (Paneli & Voulgaropoulos, 1991), potentiometry (Pinilla-Gil & Ostapczuk, 1993) and graphite furnace (GFAAS) or flame atomic absorption spectrometry (FAAS) (Cabrera, Fuensanta, Gimenez, Olalla, & Lopez, 2003; Jorhem, Sundstrom, & Engman, 2001). From among all, FAAS is a widely used analytical technique because of its low cost, but its sensitivity is usually

* Corresponding author. Fax: +34 981595012.
E-mail address: qncayebi@usc.es (M.C. Yebra).

0308-8146/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2007.11.019

insufficient for the low concentrations of nickel in food samples. Thus, several solid phase preconcentration methods involving chelating resins were proposed to improve the sensitivity of nickel determinations: by using an iminodiacetate resin (Warnken, Tang, Gill, & Santschi, 2000), a chelating resin obtained by chemical modification of Amberlite XAD-16 with 1,2-diphenyl-ethanolamine (Maheswari & Subramanian, 2003), Amberlite XAD-7 impregnated with xylenol orange (Tewari & Singh, 2000) or by using the chelating resin Toyopearl AF-Chelate 650 M (Beck, Franks, & Bruland, 2002).

In this paper, we describe a flow injection (FI) method combining continuous ultrasound-assisted extraction, preconcentration using a commercial chelating resin (Serdolit Che) and nickel determination by FAAS. Thus, the whole manifold combines the three processes (acid extraction, preconcentration and detection), allowing the direct treatment of a solid sample within the FI system. The method was applied to food samples.

2. Experimental

2.1. Instrumentation

A Perkin–Elmer Model 5000 atomic absorption spectrometer (Perkin–Elmer, Shelton, CT-USA) fitted with a nickel hollow cathode lamp was used. The instrument was set at 232.0 nm. The FI system (Fig. 1) comprises two Gilson Minipuls 3 peristaltic pumps (Gilson, Villiers Le Bel, France) fitted with Viton tubes, an ultrasonic bath with an ultrasound power of 40 KHz (Selecta, Barcelona, Spain), six Rheodyne injection or switching valves (Rohnert Park, USA), a glass minicolumn (100 mm × 3 mm i.d., Omnifit, Cambridge, UK). The ends of minicolumn were plugged with filter paper (Whatman 541). Minicolumns for the preconcentration step were prepared by filling Viton tubes (10 cm length and 1 mm i.d.) with 50 mg of chelating resin.

2.2. Reagents

Ultrapure water of 18.2 MΩ cm resistivity, obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA.) was used for the preparation of the reagents and standards. Hydrochloric acid, nitric acid (Scharlau Chemie, Barcelona, Spain), ammonium acetate (Merck, Germany) and 1000 μ/mL nickel standard solution (Merck, Darmstad, Germany) were reagent grade. Serdolit Che (Serva Electrophoresis GmbH, Heidelberg, Germany) with iminodiacetic acid groups was used as chelating resin.

2.3. Sample preparation and procedure

Mussel samples were grinded, homogenized and freeze-dried (−40 °C). The rest of samples were cut in small pieces, dried at 50 °C, triturated and pulverized in a porcelain mortar. After sieving, fractions with a particle size less than 30 μm were taken.

Samples of 50–60 mg were directly weighed into the glass minicolumn. Then, the minicolumn was connected to the continuous device (Fig. 1). First, the extraction unit circuit (2 mL) was loaded with the acid leaching solution (3 M nitric acid for legume samples and 1.5 M nitric acid for the other samples). Once this circuit was closed by means of SV1, the leaching solution circulates through the minicolumn subjected to ultrasound energy during 3 min (meat and cereal samples), 2.5 min (seafood samples), 1.5 min (legume and dried fruit samples) and 0.5 min (cheese samples). The flow rate of the leaching solution was 3.5 mL/min. Then, the switching valve (SV2) was switched to its opposite position and the acid extract was homogenized in the mixing coil. After this, the acid extract channel converged with a buffer solution stream (16 M ammonium acetate for legume samples and 8 M ammonium acetate for the other samples) in order to obtain a pH value >4.5. The mixture was homogenized in a second mixing coil and then, was passed through

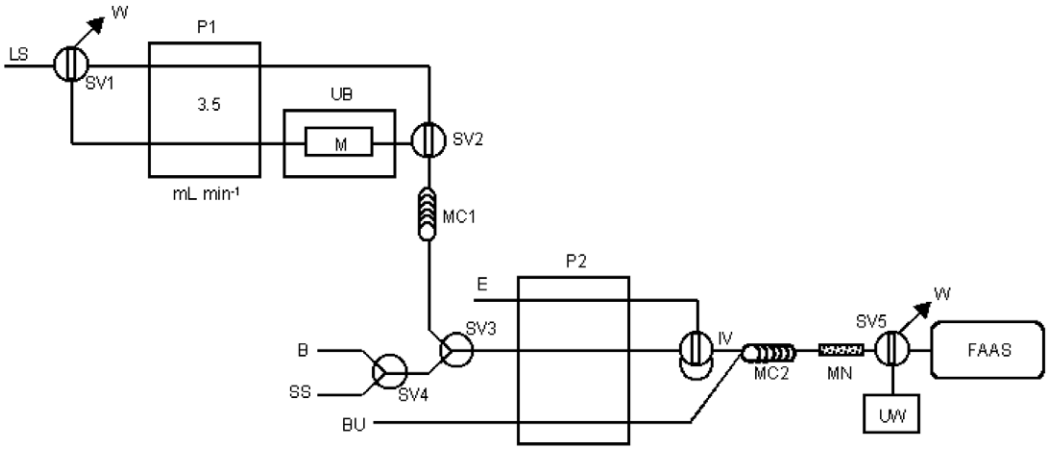

Fig. 1. Flow injection manifold for the whole procedure (continuous acid extraction and preconcentration devices) for nickel determination in food samples. P1 and P2: peristaltic pumps; LS: leaching solution; W: waste; UB: ultrasonic bath; M: minicolumn containing the sample; SS: standard solution; B: blank; IV: injection valve; E: eluent (HCl: 3 mol/L); BU (buffer: ammonium acetate); SV1–SV5: switching valves; MC1 and MC2: mixing coils; MN: minicolumn containing the chelating resin (Serdolit Che or Chelite P); UW: ultrapure water and FAAS, flame atomic absorption spectrometer.

the preconcentration minicolum, at a flow rate of 2 mL/min, where Ni(II) was retained quantitatively by formation a metal chelate. Then, it was eluted by injection of 133.2 μL of 3 M hydrochloric acid into a water carried stream, which swept it to the detector, where was continuously monitored. As is shown in Fig. 1, standard solutions containing up to 0.040 μg/mL of nickel in the same acid medium as the leaching solution were introduce into the FI system.

3. Results and discussion

3.1. Optimisation of the nickel preconcentration step

A Plackett-Burman $2^6 \times 3/16$ factorial type III resolution design with one center point and involving 13 non-randomised runs was built for optimisation of the nickel preconcentration step (Statgraphics Plus V.5.1). This factorial design was applied to a standard solution containing 0.04 μg/mL of nickel, which was measured on-line by FAAS with a FI system similar to that depicted in Fig. 2. The variable response was percent Ni recovery. The following factors were considered as variables: sample pH, sample flow rate, eluent concentration (hydrochloric acid), eluent flow rate, eluent volume and minicolumn diameter. The lower and upper levels for each studied variable are listed in Table 1. From the results of these analytical data it can be concluded that nickel preconcentration-elution process appeared to be affected positively by one statistically significant factor: eluent concentration. As the Plackett-Burman design only provides the tendencies to the optimum values of the variables, these factors were fine-tuned outside the framework of the design. The optimum conditions for nickel preconcentration-elution were listed in Table 1. An ammonium acetate buffer solution was proposed in order to achieve the optimum pH (4.5–5.5) for nickel retention. In order to carry out on-line this pH increase, a study of concentration, volume and flow rate of the ammonium acetate buffer solution was developed. So, an 8 or 16 M concentration (according to the acid concentration required in the extraction step), 0.5 mL and 0.4 mL/min, were selected as a compromise for the ammonium acetate channel.

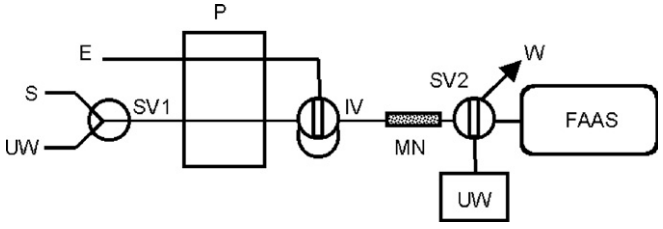

Fig. 2. Flow injection manifold for nickel preconcentration. P: peristaltic pump; SV1 and SV2: switching valves; IV: injection valve; MN: minicolumn containing the chelating resin Serdolit Che; W: waste; UW: ultrapure water; FAAS: flame atomic absorption spectrometer.

Table 1
Factor levels, estimated effects and optimum conditions for each variable

Variable	Low	Upper	Estimated effect	Optimum
pH	1	7	13.0833	4.5–5.5
Sample flow rate (mL/min)	0.5	4.0	−10.3167	2.0
Eluent concentration (M)	0.1	3.0	21.65	3.0
Eluent volume (μL)	70.4	190.0	8.31667	133.2
Eluent flow rate (mL/min)	3.0	5.0	−12.6833	3.0
Minicolumn diameter (mm)	1.0	2.0	4.61667	1.0

3.2. Optimisation of the continuous ultrasonic acid extraction of nickel

A Plackett-Burman $2^6 \times 3/16$ experimental design was used again. This factorial design was applied to 60 mg of food samples. The studied variables and their lower and upper levels were: nitric acid concentration (0–3 M), hydrochloric acid concentration (0–3 M), sonication time (0.5–5 min), leaching volume (2–5 mL), flow rate of the extraction system (3.5–5.0 mL/min) and leaching temperature (20–70 °C). From the results obtained it was proven that sonication time and nitric acid concentration were the significant variables for meat, legume and cereal samples. For seafood and dried fruit samples, the significant variable was sonication time, while for cheese samples; the significant variable was nitric acid concentration. To simplify the analysis, 0 M hydrochloric acid, room temperature, 2 mL of leaching solution and a flow rate of 3.5 mL/min were selected since these parameters were not statistically influential factors. In order to increase the sampling frequency, a possible reduction of the sonication time was studied. Thus, 3 min was enough to obtain a quantitative extraction of nickel in meat and cereal samples. Seafood samples required a sonication time of 2.5 min, while 1.5 min was an adequate sonication time for dried fruit and legume samples. The less sonication time was obtained for cheese samples that only need 0.5 min for quantitative nickel extraction. Finally, the use of less concentrated nitric acid was studied. Only legume samples require 3 M HNO_3. In the other food samples, 1.5 M was enough to obtain a quantitative nickel extraction. Sample particle sizes between 30 and 100 μm were tested to study the influence of this variable, and the results obtained indicated that the extraction process it is not affected within the size range studied. As a sample amount of 60 mg was used to optimise the continuous extraction system with good results, greater sample amounts were studied. Nevertheless, it was observed that amounts greater than 60 mg produced great pressure in the continuous extraction system causing sample losses.

3.3. Features of the method

The analytical parameters of the proposed method are summarised in Table 2. To evaluate the nickel determination for possible sample matrix interferences, a standard addition method was performed. As can be seen in Table

Table 2
Analytical parameters of the proposed method

Calibration plot	$A = 0.49C + 6 \times 10^{-6}$; A, absorbance signal; C, concentration expressed as μg/mL					
r^2	0.9999					
LOD (μg/g)	0.12 (for 60 mg of sample)					
Sample	Seafood	Meat	Cereal	Legumes	Dried fruit	Cheese
Nickel concentration (μg/g)	0.80	0.91	0.78	0.86	0.90	0.61
Relative standard deviation (%) ($n = 11$)	3.6	2.9	2.4	1.9	3.0	2.1
Addition calibration graph (Ni added: between 0 and 0.015 μg/mL; $n = 7$)						
Slope	0.49	0.49	0.49	0.49	0.49	0.49
Intercept	11.9×10^{-3}	12.9×10^{-3}	10.8×10^{-3}	12.7×10^{-3}	12.9×10^{-3}	8.9×10^{-3}
r^2	0.995	0.996	0.995	0.996	0.995	0.996
Sample throughput (samples/h)	14	13	13	19	19	28

Table 3
Nickel content in samples of different food groups

Sample	Nickel concentration (μg/g)		Sample	Nickel concentration (μg/g)	
	Conventional method[a]	Present method		Conventional method[a]	Present method
Seafoods			*Cheeses*		
Mussel 1	0.80 ± 0.00	0.77 ± 0.01	Sheep cheese	0.46 ± 0.01	0.45 ± 0.01
Mussel 2	0.97 ± 0.03	1.04 ± 0.03	Fresh cheese	0.57 ± 0.01	0.54 ± 0.00
Mussel 3	0.74 ± 0.02	0.75 ± 0.01	Cream cheese	0.57 ± 0.01	0.57 ± 0.01
Mussel 4	0.84 ± 0.01	0.83 ± 0.00	Slice cheese	0.61 ± 0.01	0.61 ± 0.00
Clam 1	0.43 ± 0.01	0.41 ± 0.01	Mozzarella	0.49 ± 0.01	0.49 ± 0.01
Clam 2	0.46 ± 0.01	0.46 ± 0.01	Grated cheese	0.42 ± 0.01	0.42 ± 0.01
Tuna	0.50 ± 0.01	0.51 ± 0.00	Yoghurt	0.84 ± 0.01	0.84 ± 0.00
Cockle	0.63 ± 0.02	0.61 ± 0.00	Curd	0.86 ± 0.00	0.85 ± 0.00
Crab	0.57 ± 0.01	0.58 ± 0.00	*Cereals*		
Prawn	0.72 ± 0.02	0.72 ± 0.01	Wheat flour	0.67 ± 0.02	0.67 ± 0.01
Hake	0.52 ± 0.02	0.52 ± 0.01	Corn flour	0.95 ± 0.01	0.95 ± 0.01
Razor-shell	0.52 ± 0.02	0.55 ± 0.01	Wholemeal flour	0.67 ± 0.02	0.67 ± 0.01
Sardine	0.55 ± 0.01	0.57 ± 0.00	Semolina	0.41 ± 0.02	0.43 ± 0.01
Scallops	0.48 ± 0.01	0.46 ± 0.01	Breadcrumbs	0.66 ± 0.01	0.667 ± 0.01
Meats			Wafer-thin slice	0.51 ± 0.01	0.52 ± 0.01
Chicken	0.63 ± 0.01	0.64 ± 0.01	Biscuits	0.61 ± 0.01	0.64 ± 0.02
Turkey	0.74 ± 0.02	0.76 ± 0.00	Breakfast cereals	0.78 ± 0.01	0.78 ± 0.01
Pork	0.61 ± 0.01	0.63 ± 0.01	Spaghetti	0.56 ± 0.01	0.57 ± 0.01
Calf	0.92 ± 0.01	0.91 ± 0.00	Noodle	0.56 ± 0.01	0.55 ± 0.01
Mutton	0.72 ± 0.01	0.71 ± 0.01	Rice	0.54 ± 0.01	0.54 ± 0.01
Rabbit liver	0.91 ± 0.01	0.94 ± 0.00	*Dried fruits*		
Mutton kidney	1.10 ± 0.03	1.08 ± 0.02	Nut	0.55 ± 0.01	0.56 ± 0.01
Legumes			Pistachio	0.63 ± 0.01	0.62 ± 0.01
Chickpea 1	0.59 ± 0.01	0.58 ± 0.01	Chestnut	0.90 ± 0.01	0.92 ± 0.00
Chickpea 2	0.55 ± 0.01	0.55 ± 0.00	Almond	0.52 ± 0.01	0.53 ± 0.01
Broad bean	0.49 ± 0.01	0.48 ± 0.00	Hazelnut	0.48 ± 0.02	0.48 ± 0.01
Lentil	0.86 ± 0.01	0.88 ± 0.00	Peanut	0.75 ± 0.02	0.75 ± 0.01

[a] Conventional off-line sample digestion method with concentrated nitric acid, preconcentration step previously optimised by using the chelating resin Serdolit Che and determination by FAAS.

2, the slopes of these addition calibration graphs were comparable to that achieved by the calibration graph, demonstrating that nickel determination is free of matrix interferences in the samples studied. Validation of the method was performed by using certified reference materials (BCR186 Pig Kidney and BCR189 Wholemeal Flour, Community Bureau of Reference, Brussels, Belgium, with indicative concentrations of 0.42 and 0.38 μg/g Ni). The nickel-contents obtained (mean ± SD, $n = 3$) were 0.44 ± 0.01 and 0.38 ± 0.01 μg/g for BCR186 and BCR189, respectively, which agrees with the indicative values.

3.4. Analysis of samples

The proposed methodology was applied to determine nickel in several food samples. The results obtained were compared with those achieved by a conventional off-line sample digestion method with concentrated nitric acid, the preconcentration step previously optimised by using the chelating resin Serdolit Che and determination by FAAS. The results, expressed as μg/g and their standard deviation ($n = 3$) obtained by these two methods are shown in Table 3. To compare the results, the Paired *t*-test

($P = 0.05$) (Miller & Miller, 1984) was applied and it was concluded that both methods do not give significantly different values for the nickel concentration and thus, the agreement between the two methods is satisfactory.

4. Conclusions

The method proposed presents the advantage of simplicity and avoids the use of expensive and sophisticated analytical instruments such as inductively coupled plasma mass spectrometry (ICP-MS). High sample throughput, good accuracy and precision, low detection limit, easy of use, freedom from interferences, safety conditions (concentrated acids and carcinogenic nitrous vapours were avoided) and automation makes this methodology very suitable for nickel determination in solid food samples.

Acknowledgements

The authors are grateful for the financial support provided by the Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA), Ministerio Ciencia y Tecnología (Project No. CAL01-043).

References

Beck, N. G., Franks, R. P., & Bruland, K. W. (2002). Analysis for Cd, Cu, Ni, Zn and Mn in estuarine water by inductively coupled plasma mass spectrometry coupled with an automated flow injection system. *Analytica Chimica Acta, 455*, 11–22.

Cabrera, C., Fuensanta, L., Gimenez, R., Olalla, M., & Lopez, M. C. (2003). Mineral content in legumes and nuts: contribution to the Spanish dietary intake. *The Science of the Total Environment, 308*, 1–14.

Jorhem, L., Sundstrom, B., & Engman, J. (2001). Cadmium and other metals in Swedish wheat and rye flours: Longitudinal study, 1983–1997. *Journal of AOAC International, 84*(6), 1984–1992.

Karadjova, I., Girousi, S., Iliadou, E., & Stratis, I. (2000). Determination of Cd, Co, Cr, Cu, Fe, Ni and Pb in milk, cheese and chocolate. *Mikrochimica Acta, 134*, 185–191.

LaBrecque, J. J., Benzo, Z., Alfonso, J. A., Codoves, P. R., Quintal, M., Gomez, C. V., & Marcano, E. (2004). Determination of selected trace elements in raw clams and commercial clam meats from the state of Miranda (Venezuela) employing ICP-OES, GF-AAS and WD-XRF. *Atomic Spectroscopy, 25*(3), 112–124.

Lee, K. H., Muraoka, Y., Oshima, M., & Motomizu, S. (2004). Determination of heavy metals and rare earth elements in environmental samples by ICP-MS after solid phase preconcentration with chelating resin fibers and anion exchanger filters. *Analytical Sciences, 20*, 183–187.

Luque de Castro, M. D., & Priego Capote, F. (2007). *Analytical applications of ultrasounds*. Amsterdam: Elsevier.

Maheswari, M. A., & Subramanian, M. S. (2003). A new chelating resin for preconcentration and determination of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) by flame atomic absorption spectrometry. *Journal of AOAC International, 86*(6), 1218–1224.

Miller, J. C., & Miller, J. N. (1984). *Statistics for analytical chemistry*. Chichester: Ellis Horwood.

Paneli, M. G., & Voulgaropoulos, A. (1991). Determination of Ni and Co using 2-quinolinethiol by adsorptive voltammetry. *Fresenius Journal of Analytical Chemistry, 341*, 71–719.

Pinilla-Gil, E., & Ostapczuk, P. (1993). Determination of nickel and cobalt by constant current potentiometry. *Fresenius Journal of Analytical Chemistry, 346*, 957–960.

Schiavino, D., Nucera, E., Alonzi, C., Buonomo, A., Pollastrini, E., Roncallo, C., De Pasquale, T., Lombardo, C., La Torre, G., Sabato, V., Pecora, V., & Patriarca, G. (2006). A clinical trial of oral hyposensitization in systemic allergy to nickel. *International Journal of Immunopathology and Pharmacology, 19*, 593–600.

Tewari, P. K., & Singh, A. K. (2000). Amberlite XAD-7 impregnated with Xylenol Orange: a chelating collector for preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) ions prior to their determination by flame AAS. *Fresenius Journal of Analytical Chemistry, 367*, 562–567.

Warnken, K. W., Tang, D., Gill, G. A., & Santschi, P. H. (2000). Performance optimisation of a commercially available iminodiacetate resin for the determination of Mn, Ni, Cu, Cd and Pb by on-line preconcentration inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta, 423*, 265–276.