Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Author's personal copy

Microchemical Journal 99 (2011) 486–491

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Determination of nickel in cigarettes smoke by molecular fluorescence ☆

María Carolina Talio [b], Marta O. Luconi [a], Liliana P. Fernández [a,b,*]

[a] Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Argentina
[b] Instituto de Química de San Luis (INQUISAL-CONICET), Chacabuco y Pedernera, 5700 - San Luis, Argentina

ARTICLE INFO

Article history:
Received 22 June 2011
Received in revised form 30 June 2011
Accepted 30 June 2011
Available online 8 July 2011

Keywords:
Nickel determination
Smoke cigarettes
Chemical enrichment
Solid surface fluorescence
Urinary nickel contents

ABSTRACT

Smoking represents the main avoidable cause of disease and death in the world. Cigarette smoke contains over 4700 chemical compounds including 60 known carcinogens. The inhalation of tobacco smoke is one of the most significant sources of nickel exposure for occupationally unexposed population. The aim of this work was to evaluate nickel contents present in cigarette smoke by using an automatic sample preparation step and solid surface fluorescence. A total of 250 cigarettes (brands available in Argentine) were smoked in a smoking device applying vacuum and forcing the mainstream smoke to pass through a filter holder containing a Nylon membrane treated with eosin dye (eo). Nickel present in smoke cigarette was selectively retained by eo as an association compound. Chemically enriched nickel on nylon membranes was subsequent quantified by spectrofluorimetry ($\lambda_{em} = 545$ nm, $\lambda_{exc} = 515$ nm), reaching quantitative recovery with a detection limit of 1.56 ng L^{-1} and quantification limit of 5.52 ng L^{-1}. The calibration sensitivity using zeroth order calibration was 1 10^{12} ng L^{-1} ($r^2 = 0.9992$) for the methodology with a linear range of 5.52 to 5.17 10^4 ng L^{-1} Ni(II). Standard addition method was satisfactorily applied to nickel determination in mainstream smoke cigarettes of twenty brands. Results can be good correlated with urinary nickel contents coming from fifty subjects with different levels of addiction.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Today, in San Luis (Argentine), 33.4% of adults are smoker [1] and the beginning age is between 12 and 13 years old, with a similar consumption to adults. From 2009, we are visiting San Luis teenager schools and realizing prevention activities on tabaquism theme, in concordance with the Global Survey on Smoking in Adolescents, developed by World Health Organization (WHO), Centers for Disease Control and Prevention (CDC) and Canada Public Health Association (CPHA). Experimental results obtained in our laboratory are efficacious tool for creating consciousness in these mentioned workshop activities.

Cigarettes are probably the single most significant source of toxic chemical exposure and chemically mediated illness in humans [2]. The World Health Organization forecasts cigarettes will kill nearly 10 million people per year globally by the year 2020.

Cigarette smoke contains over 4700 chemical compounds including 60 known carcinogens [3]. No threshold level of exposure to cigarette smoke has been defined but there is conclusive evidence to indicate that long-term (years) smoking greatly increases the likelihood of developing numerous fatal conditions.

Active or passive smoking harms nearly every organ of the body and diminishes a person's overall health, being substantial the increase in cardiovascular diseases [4–6] Smoking is a leading cause of cancer and death from cancer. It causes cancers of the lung, esophagus, larynx (voice box), mouth, throat, kidney, bladder, pancreas, stomach, and cervix, as well as acute myeloid leukemia [7]. Active exposure to cigarette smoke causes the vast majority of Chronic Obstructive Pulmonary Disease (COPD) cases and contributes to increased incidence of related pulmonary diseases such as asthma and allergic rhinitis [8].

For over three decades, tobacco industries have done efforts in order to decrease the exposition levels to tobacco toxics; an example of this is the market launch of light brands with lower nicotine contents and the implementation of filter ventilation provided by a zone of microscopic holes, around the circumference of the filter [9].

General population is exposed to nickel from various sources. Significant sources of nickel exposure for occupationally unexposed population are foods and the inhalation of tobacco smoke [10–12]. Tobacco plant contains nickel and several other toxic metals, most probably absorbed from the soil, fertilizing products or from pesticides [13,14]. Nickel accumulates in the tobacco plant (0.64–1.15 μg/g) and the concentration in the tobacco increases dramatically through the manufacturing process via the additives used to cure the tobacco (0.078–5 μg g^{-1}) [15].

It has been stated that nickel in a burning cigarette might form the volatile, gaseous compound, nickel tetracarbonyl, and thereby be introduced into the respiratory tract [16]. The most common ill health effect in humans to nickel has been allergic reactions or skin rash. Some

☆ "In memoriam" of Dr. Adriana Masi, prominent researcher,dear colleague and friend,who passed away prematurely,as a consequence of public insecurity,killed by a shot in the head at the door of her house.

* Corresponding author at: Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Argentina. Fax: +54 2652 430224.
E-mail address: lfernand@unsl.edu.ar (L.P. Fernández).

0026-265X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.microc.2011.06.028

Author's personal copy

people sensitive to nickel can suffer asthma attacks, chronic bronchitis, and reduced lung function. Cancers of the lung and nasal sinus have been witnessed in people breathing dust containing high levels of nickel.

Because of the matrix complexity of cigarette smoke, separation procedures must be applied previous to the metal determination. The traditional preconcentration and separation methods for metal ions are liquid–liquid extraction, coprecipitation and ion-exchange. These methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems [17].

Nowadays, solid phase extraction (SPE) has come to the forefront compared to other preconcentration and/or separation techniques, as it offers several advantages such as flexibility, higher enrichment factors, absence of emulsion, low cost (because of lower consumption of reagents), speed and simplicity. Additionally, SPE is attractive as it reduces consumption of and exposure to toxic solvents [18], representing an environmentally friendly alternative [19–21].

Traditionally, nickel trace determination has been performed by electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma atomic emission (ICP-AES) or ICP-mass spectrometry with a previous SPE step [22–27]. Many researchers are interested in improving the selectivity of the sorbents used in SPE. Several solid materials as filter papers, silica gel, exchange resins, aluminium oxides, poly(vinylalcohol), C18 membranes, cyclodextrines, among others, have been successfully employed as supports for SPE in nickel determination [28,29]. Recently, Nylon has proved to be an adequate support for luminescent detection of organic compounds [30–34]. Experimental results have shown that this support possesses good selectivity, low background signal and can be used without previous treatment.

In this work, the separation/chemisorption of nickel on nylon membranes previously treated with eo is proposed for subsequent quantification by molecular fluorescence. The study was carried out analysing the different factors which influence on the chemisorption step and fluorescent signal of the nickel-eo association and was applied to nickel determination in mainstream smoke cigarettes coming from 20 commercials brands. The incidence of filter ventilations and smoke pH in mainstream nickel levels was investigated.

In previous investigations, Ni(II) has been determined using a similar method [35]. In this opportunity, a very complex sample is confronted, the cigarette smoke. Additional efforts must be done in order to optimizing regular experimental variables related with chemisorption and determination steps, as well as extra studies associated with samples characterization.

2. Experimental

2.1. Reagents

Nylon membranes (Millipore, Sao Paulo, Brazil) 0.45 μm pore size and 47 mm diameter were used in chemisorption studies. Tris (Mallinckrodt Chemical Works, NY, USA) solution 1 10^{-2} mol L^{-1} was prepared by weighting and subsequent dilution with ultrapure water and adjusted to the desired pH, with aqueous $HClO_4$ (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works, NY, USA). Ni (II) solutions 1.7 10^{-4} mol L^{-1} were prepared by dilution of 100 μg mL^{-1} standard solution plasma-pure (Leeman Labs, Inc.) Eosin solution 1 10^{-4} mol L^{-1} (H.E - Daniel Ltd., England) was weekly prepared by dissolution of the appropriate amount in ultrapure water.

All used reagents were of analytical grade.

2.2. Apparatus

Fluorescence measurements were made using a Shimadzu RF-5301 PC spectrofluorometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. A combined glass electrode and a pH meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940 were used for pH adjustments. A Gilson Minipuls 3 peristaltic pump with PVC pumping tubes coupled to an in-line filter holder 47 mm (Millipore) was used for filtrating samples/standard solutions. All used glass materials were previously washed with a 10% v/v HNO_3 water solution and then with ultrapure water.

2.3. General procedure

a) Impregnation procedure: Nylon membranes were impregnated in batch by contact with 1 10^{-7} mol L^{-1} eo solution for 5 min. Membranes were dried at ambient temperature and reserved in dried ambient (20–25 °C) up to the chemifiltration step. Later, a dried membrane was put in the filtration holder.
b) Nickel automatic chemifiltration: Nickel standard solution (0 to 51.7 μg L^{-1}), 75 μL buffer Tris solution 1 10^{-2} mol L^{-1} (pH = 8.0), were placed in a 10 mL graduated centrifuge tube. The whole mixture was diluted to 10 mL with ultrapure water. Systems were filtrated across eo-impregnated membranes, using a peristaltic pump at 0.25 mL min^{-1} and dried at ambient temperature.
c) Chemifiltration of nickel in mainstream smoke of cigarettes: Cigarettes were smoked using a home built smoking machine connected to a vacuum pump (Fig. 1A). Mainstream smoke was conducted for 5 s across the membranes prepared as described in b) at three Ni(II) level and put into the filtration holder ($n = 4$, for each cigarette brand). The same procedure was repeated obstructing 100% of filter ventilation for cigarette brands with microperforations.
d) Nickel determination: Nickel concentration on each membrane was determined by fluorescent emission at $\lambda_{em} = 545$ nm ($\lambda_{exc} = 515$ nm), using a solid sample holder.

2.4. Filter ventilation incidence

Cigarettes containing filter ventilation were prepared by blocking 100% of microperforations with masking tape. Under this condition, Ni(II) was determined by applying the general procedure.

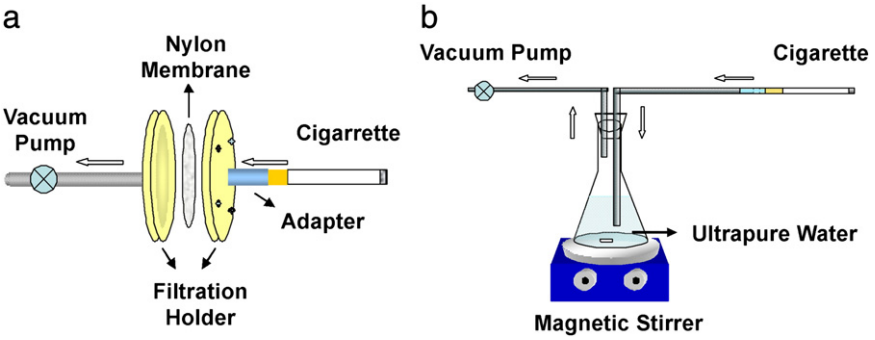

Fig. 1. a - Schematic representation of smoking machine; and b - Schematic representation of device used for determination of smoke pH.

Author's personal copy

2.5. Determination of pH in mainstream tobacco smoke

The pH value of smoke coming from each brand of cigarette was obtained by bubbling of mainstream smoke of a whole cigarette in 10 mL distilled water (Fig. 1B). The pH of obtained aqueous solution was determined using a pHmeter with a glass electrode.

2.6. Interferences study

Different amounts of ions (1/1, 1/10, 1/100 and 1/1000 Ni (II)/interferent ratio) were added to the test solution containing 30 ng L^{-1} Ni(II) and the general procedure was applied.

All burning cigarettes experiments were carried out using fume extraction system.

3. Results and discussion

In order to study the possibility of evaluating the nickel content of cigarette smoke, metal retention was investigated passing cigarette smoke through the previously prepared Nylon membranes with eo dye, as it has been indicated in a previous work [35]. Nickel retention levels for each assayed cigarette were checked measuring solid fluorescence signals at $\lambda_{em} = 545$ nm, using $\lambda_{exc} = 515$ nm.

This operative mode had two main advantages:

- First, it related with the selective Ni(II) separation of very complex matrix, the cigarette smoke;
- The other, related with the advantageous preconcentration using chemical enrichment on Nylon membrane, improving the instrumental sensitivity.

Experimental parameters that influence in SPE procedure and fluorimetric determination were optimized varying one parameter at a time, keeping constant the others. Taking into account that the brand number 12 (see Table 1) represents one of the most fashionable brands commercialized in Argentine, it was chosen for optimization assays.

Since the nickel retention mechanism represents association equilibrium between eo dye and metal, the first optimized parameter was pH of aqueous solution used in pretreatment of Nylon membrane. The pH value of aqueous systems containing constant concentration of Ni(II) was adjusted between 4.5 and 9.5, by addition of Tris buffer solution. Subsequently, cigarette mainstream smoke was conducted through the Nylon membrane and the general procedure was applied for Ni(II) quantification. The maximum level of retention of Ni(II)-eo association was observed at pH values of 6.75 to 8.00 (Fig. 2). For following experiments, a pH value of 8.00 was chosen.

Subsequently, the buffer concentration was tested to obtain the maximum fluorescent signal. The concentration of Tris buffer was varied from 2.0 10^{-5} to 1.75 10^{-4} mol L^{-1}. A buffer concentration of 7.5 10^{-5} mol L^{-1} was chosen as optimal.

In order to study the influence of smoke exposition time on Nylon membrane previously conditioned with eo dye, assays were carried out varying this parameter and holding constant the others. The first experiment was performed using the smoke of whole cigarette. Membrane holes were saturated by abundant solid residues coming from the smoke particulate phase. Studies were done varying time of smoke exposition between 0.5 and 15 s. A time of exposition of 5 s was chosen as optimal for the following experiments being that under these conditions, the highest fluorescent signal was obtained and Ni (II) level in smoke was compatible with instrumental sensitivity.

Table 1
Characteristics of commercial studied cigarettes.

Sample	Tobacco type	Weight (g)	Length (cm)	Density (g cm^{-3})	Smoke pH
1	Blond	0.8785	8.360	0.232	5
2[a]	Blond	0.5323	9.720	0.230	6
3[b]	Blond	0.8828	8.305	0.247	5
4	Black	0.8571	8.380	0.219	6.5
5	Blond	0.8623	8.400	0.252	6
6[b]	Blond and mentholated	0.8854	8.300	0.245	5.5
7[c]	Blond	0.8529	8.300	0.239	6
8[b]	Black	0.8931	8.270	0.220	6
9	Blond	0.8853	8.300	0.258	5
10[d]	Black	0.8835	8.240	0.236	7
11[d]	Blond and mentholated	0.8829	8.355	0.195	5.5
12[d]	Blond	0.8998	8.270	0.216	6
13[d]	Blond and mentholated	0.8772	8.480	0.222	6
14[d]	Blond	1.032	9.76	0.217	6
15	Blond	0.9216	8.255	0.228	6
16	Blond	0.8914	8.330	0.245	5
17	Black	1.1482	9.855	0.264	5.5
18	Blond	0.9235	8.500	0.187	5.5
19	Blond	0.8009	8.500	0.226	5.5
20	Blond	0.9585	8.400	0.280	5.5

Tobaccolist: Samples 1–8: Nobleza Piccardo; 9–16: Massalin Particulares; 17: Sarandí S. A; 18–19: Coimexpor Argentina; 20: Espert S.A.
Filter ventilations: a – Four lines (25 holder each one); b – One line (6 holder); c – Two lines (11 holder each one); d- Two lines (25 holder each one).

4. Analytical parameters

Analytical figures of merit for univariate (i.e. zeroth-order) calibration have been employed. The concentrations of Ni(II) and the instrument response for each standard were fit to a straight line, using linear regression analysis. This yields a model described by the equation $y = mx + y_0$, where **y** is the instrument response, **m** represents the sensitivity, and $\mathbf{y_0}$ is a constant that describes the background. The analyte concentration (**x**) of unknown samples may be calculated from this equation.

The limit of detection (LOD) of new methodology was of 1.56 ng L^{-1}, calculated as 3 s/m, where s is the standard deviation of 10 successive means of the blank and m is the slope of the calibration curve (calibration sensitivity). The limit of quantification (LOQ) was 5.52 ng L^{-1}, calculated as 10s/m. Range of linearity (of 5.52 to 5.17 10^4 ng L^{-1} Ni(II)), particularly large due to the possibility of change of instrumental slits, was evaluated by checking the linear regression coefficient (r^2) of the calibration curve. The linearity of the calibration curve was considered acceptable when $r^2 > 0.999$.

4.1. Sample characterization

Commercial cigarettes were acquired in drugstores of San Luis city (Argentine). Once in the laboratory, cigarette samples were observed and characterized for physical appearance and chemical-physical parameters.

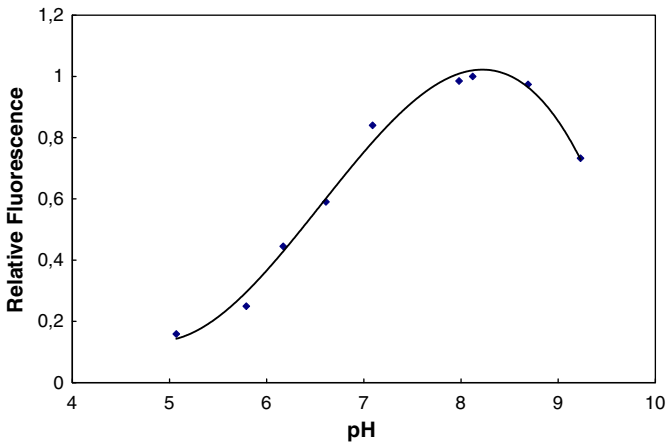

Fig. 2. Influence of retention pH on Ni(II)-eo fluorescence.

Author's personal copy

Special emphasis was put in determination of smoke pH, because of its correlation with the nitrate content of tobacco. Additionally, a major reason for the range of pH determination in the smoke is the concentration of ammonia in the smoke, which is directly tied to the concentration of nitrate in the tobacco. Protonated nicotine is only slowly absorbed in the oral cavity; yet, unprotonated nicotine, which is partially present in the vapor phase of the smoke, is quickly absorbed through the mucosal membranes of the mouth [36].

The pH of each sample was determined (Table 1) in order to verify the adequate value of this parameter for Ni(II) determination. In all samples, pH was close to neutrality (between 5 and 7), permitting the correct application of the developed methodology.

4.2. Tolerance studies

The effect of foreign ions on the recovery of Ni(II) was tested. An ion was considered as interfering when it caused a variation in the fluorescent signal of the sample greater than ± 5%. Fig. 3 shows the obtained results for the assayed cations. Good tolerance was obtained at interferent/Ni(II) 1000/1 ratio for Na(I) and K(I), and at interferent/Ni(II) 100/1 ratio for the other assayed cations. For the anions studied (CO_3^{2-}; SO_4^{2-}; CH_3COO^-; NO_3^-; F^- and Cl^-), at optimal working conditions, a good tolerance was obtained for interferent/Ni(II) 1000/1 ratio.

4.3. Applications

Taking into account that for Ni(II) determination in cigarettes smoke certified reference materials aren't suitable, the accuracy of the methodology was assessed by using the standard addition method. The reproducibility of the method was evaluated repeating 4 times the proposed approach for each addition in a total of three level of spiked Ni(II) for each cigarette brand. The recoveries of Ni(II) in twenty cigarettes brands studied, based on the average of four replicate measurements, are illustrated in Table 2.

The obtained results showed that the proposed methodology is suitable for determination of Ni(II) in smoke of cigarettes, in all the range of studied concentrations. Also, Table 2 shows Ni(II) contents/cigarette, for each studied sample. The highest nickel level corresponds to sample number 17, Argentine-manufactured black tobacco cigarettes of the cheapest brand available in the country.

Cigarettes manufacturers have indicated that filter ventilations represent a beneficial effect to smokers due to the fact that they reduce the portion of the puff volume coming from the lighted end. As a consequence, less tobacco is burnt and the generated smoke is diluted with the incoming air as it passes through the filter [37].

With the purpose of evaluate the effectiveness of filter microperforations in decreasing Ni(II) levels in mainstream smoke, cigarettes were burned with previous 100% blocking of the filter ventilations (see Table 1). The proposed methodology was not satisfactory for Ni(II) determination under these burning conditions due to excessive particulate material generated and deposited on the membrane with eo, preventing the arrival of excitation radiation and avoiding the production of fluorescence signal due to eo-Ni(II) association. This technical obstacle prevented from arriving at a conclusive opinion respect to the incidence of filter microperforations on Ni(II) contents in mainstream cigarette smoke.

Fig. 4 shows the graphical dispersion of nickel contents obtained and density data. This representation, chosen among others possible, allows a classification of the obtained results into four groups:

- Group 1 (5–10 μg/cigarette) represents the lowest nickel content levels obtained; with only one brand of blonde cigarettes with filter ventilation in this group.
- Group 2 (10–15 μg/cigarette) includes six brands of blonde cigarettes, four of them with filter ventilation.
- Group 3 (15–20 μg/cigarette) includes six brands of cigarettes; four are blonde cigarettes without filter ventilation and two are black cigarettes, only one with filter ventilation.
- Group 4 (20–25 μg/cigarette) represents the highest nickel content levels obtained. In this group, there are three brands of

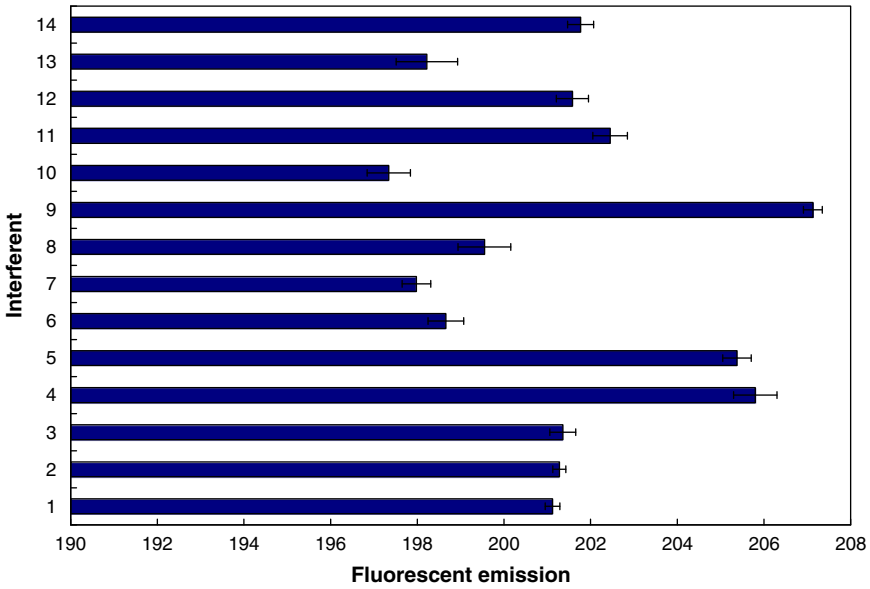

Fig. 3. Tolerances of cations of Ni(II) quantification. %SDs (l-l) have been included for each interferent.

Author's personal copy

Table 2
Nickel determination in cigarettes smoke. Recovery study.

Sample	Ni(II) added (ng L^{-1})	Ni(II) found ± CV (ng L^{-1})	Recovery (%, n = 4)	Ni (II) (μg)/ cigarette
1	–	45.58 ± 0.03	–	11.78
	20	65.63 ± 0.05	100.1	
	30	74.97 ± 0.01	98.66	
2	–	48.63 ± 0.05	–	8.77
	30	79.00 ± 0.04	100.76	
	45	93.52 ± 0.07	99.77	
3	–	50.77 ± 0.07	–	13.27
	20	70.22 ± 0.08	98.91	
	30	81.01 ± 0.05	100.47	
4	–	61.89 ± 0.04	–	17.31
	30	92.04 ± 0.08	100.24	
	45	106.91 ± 0.04	100.03	
5	–	73.94 ± 0.01	–	18.99
	30	104.22 ± 0.03	100.38	
	45	119.07 ± 0.03	100.17	
6	–	86.02 ± 0.04	–	21.19
	30	115.94 ± 0.04	99.91	
	45	131.07 ± 0.08	100.06	
7	–	58.86 ± 0.07	–	13.03
	30	88.23 ± 0.08	99.44	
	45	104.09 ± 0.05	100.39	
8	–	79.48 ± 0.05	–	20.47
	20	99.50 ± 0.09	100.02	
	45	124.36 ± 0.07	99.84	
9	–	60.06 ± 0.02	–	12.41
	30	90.77 ± 0.04	101.18	
	45	104.33 ± 0.01	98.80	
10	–	74.59 ± 0.01	–	18.46
	30	104.60 ± 0.03	100.01	
	45	119.61 ± 0.03	100.02	
11	–	78.53 ± 0.04	–	21.06
	30	108.44 ± 0.04	99.88	
	45	123.68 ± 0.08	100.19	
12	–	49.68 ± 0.02	–	11.36
	30	80.01 ± 0.03	100.66	
	45	94.75 ± 0.03	100.14	
13	–	79.66 ± 0.03	–	20.57
	20	99.51 ± 0.05	99.81	
	30	110.12 ± 0.01	100.57	
14	–	51.23 ± 0.02	–	14.36
	30	81.35 ± 0.04	100.23	
	45	95.88 ± 0.01	99.31	
15	–	67.41 ± 0.02	–	15.83
	20	87.45 ± 0.03	100.06	
	45	112.96 ± 0.03	100.81	
16	–	71.06 ± 0.05	–	17.94
	30	101.05 ± 0.09	99.98	
	45	115.89 ± 0.07	99.76	
17	–	88.62 ± 0.06	–	24.87
	30	118.68 ± 0.06	100.06	
	45	133.45 ± 0.07	99.81	
18	–	81.23 ± 0.05	–	19.97
	30	111.85 ± 0.04	100.76	
	45	126.09 ± 0.07	99.83	
19	–	87.15 ± 0.04	–	22.73
	30	117.33 ± 0.08	100.20	
	45	132.12 ± 0.04	99.96	
20	–	89.55 ± 0.06	–	23.07
	30	120.01 ± 0.06	100.51	
	45	135.49 ± 0.07	101.04	

blonde mentholated cigarettes with filter ventilation, two brands of blonde cigarettes and two brands of black cigarettes.

As a general conclusion of the present work, it can be stated that the blonde cigarettes studied have nickel contents <15 μg/cigarette and they are included in the lower half of the graphical representation. On the other hand, the black cigarettes and blonde cigarettes of second-rate quality are in the upper half of the graphical representation, with nickel contents >15 μg/cigarette. A remarkable data is the high nickel content of blonde mentholated cigarettes with filter ventilation (>20 μg/cigarette), occupying the upper zone of the

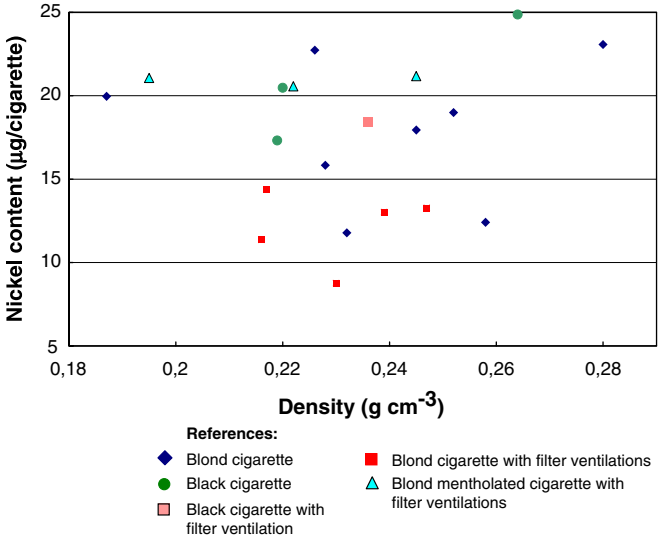

Fig. 4. Representation of dispersion of smoke nickel and density data for studied cigarettes.

graphical representation. This fact leads to believe that, through the cigarette burning, additives as menthol can enhance the liberation of nickel compounds, increasing metal levels in mainstream smoke and therefore, the smoker exposition.

In a previous work [35], urinary nickel was determined in fifty subjects with different levels of tobacco addiction. Fig. 5 shows hemi-logarithmic graphic, presenting a good lineal correlation between urinary nickel contents associated to type of cigarettes smoked by each subject.

5. Conclusions

Nickel chemisorption has been employed for its separation using Nylon membranes containing eo dye and its subsequent quantification by molecular fluorescence. The developed methodology is simple, environmentally friendly and inexpensive. Adequate selectivity was evidenced by good tolerance at elevated levels of regular foreign constituents. Precision and accuracy were tested with good results. The proposed methodology was applied to nickel determination in mainstream cigarette smoke, representing an alternative to metal analysis routine methods, with the advantage of using simple and low cost instrumental. Based on the obtained results, it can be concluded that the exposure of smokers to tobacco smoke nickel is high, regardless of the kind of tobacco. No conclusive information regarding the incidence of filter holder microperforations on smoke nickel content can be offered. Cigarettes nickel contents showed good

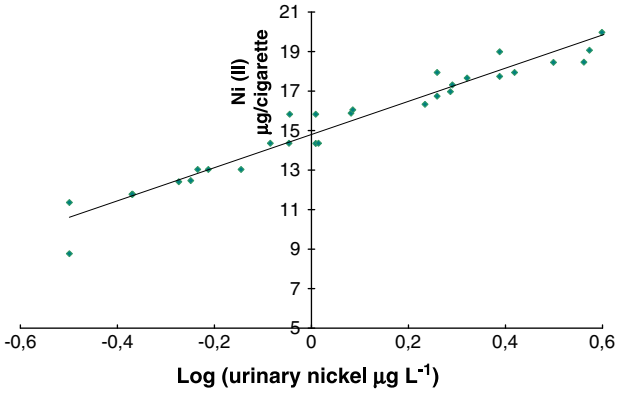

Fig. 5. Representation of hemi-logarithmic ratio between cigarettes nickel contents and urinary nickel of fifty subjects with different level of tobacco addiction.

Author's personal copy

correlation with urinary nickel levels determined in a previous work. Efforts should be made by the control agencies and health agents to discourage the consumption of cigarettes. It is thanks to these activities than our childhoods teach the devastator consequences of this habit and they are good prepared for a free and consciousness choice in front of tabaquism.

Acknowledgements

Authors wish to thank Instituto de Química de San Luis - Consejo Nacional de Investigaciones Científicas y Tecnológicas (INQUISAL-CONICET), FONCYT (Fondo Nacional de Ciencia y Tecnología) and Universidad Nacional de San Luis (Project 22/Q828) for financial support.

References

[1] Encuesta Nacional de Factores de Riesgo, Sección TABACO, Ministerio de Salud de la Nación, Argentina, 2006. www.msal.gov.ar/tabaco.
[2] J. Fowles, E. Dybing, Application of toxicological risk assessment principles to the chemical constituents of cigarette smoke, Tob. Control. 12 (2003) 424–430.
[3] S. Hecht, Tobacco carcinogens, their biomarkers and tobacco-induced cancer, Nat. Rev. Cancer 3 (2003) 733–744.
[4] V. López García-Aranda, J.C. García Rubira, Tabaco y enfermedad cardiovascular, Adicciones 16 (2004) 101–113.
[5] H. Afridi, T. Kazi, N. Kazi, M. Jamali, M. Sirajuddin, J. Baig, G. Kandhro, S. Wadhwa, A. Shah, Evaluation of cadmium, lead, nickel and zinc status in biological samples of smokers and nonsmokers hypertensive patients, J. Hum. Hypertens. 24 (2010) 34–43.
[6] R. Pappas, G. Polzin, C. Watson, D. Ashley, Cadmium, lead, and thallium in smoke particulate from counterfeit cigarettes compared to authentic US brands, Food Chem. Toxicol. 45 (2007) 202–209.
[7] A. Sasco, M. Secretan, K. Straif, Tobacco smoking and cancer: a brief review of recent epidemiological evidence, Lung Cancer 45 (2004) S3–S9.
[8] T. Yoshida, R.M. Tuder, Pathobiology of Cigarette Smoke-Induced Chronic Obstructive Pulmonary Disease, Physiol. Rev. 87 (2007) 1047–1082.
[9] T. Adam, J. McAughey, C. Mocker, C. McGrath, R. Zimmermann, Influence of filter ventilation on the chemical composition of cigarette mainstream smoke, Anal. Chim. Acta 657 (2010) 36–44.
[10] D. Stojanović, D. Nikić, K. Lazarević, The level of nickel in smoker's blood and urine, Cent. Eur. J. Public Health 12 (2004) 187–189.
[11] World Health Organization (WHO), Air Quality Guidelines for Europe, WHO Regional Publications, European Series, No. 91, 2nd edition, WHO Regional Office for Europe, Copenhagen, 2000.
[12] Department for Environment Food and Rural Affairs (DEFRA) and Environment Agency (EA), Contaminants in soil: Collation of toxicological data and intake values for humans, Nickel, Environment Agency, Bristol, 2002.
[13] http://faculty.virginia.edu/metals/cases/ramdeen2.html visited on August 27, 2010.
[14] T. Kazi, M. Arain, J. Baig, M. Jamali, H. Afridi, The correlation of arsenic levels in drinking water with the biological samples of skin disorders, Sci. Total. Environ. 407 (2009) 1019–1026.
[15] W. Torjussen, H. Zachariasen, I. Andersen, Cigarette smoking and nickel exposure, J. Environ. Monit. 5 (2003) 198–201.
[16] D. Stojanović, D. Nikić, K. Lazarević, The level of nickel in smoker's blood and urine, Cent. Eur. J. Public Health 12 (2004) 187–189.
[17] Y. Liu, X. Chang, S. Wang, Y. Guo, B. Din, S. Meng, Solid-Phase Extraction and Preconcentration of Cadmium(II) in Aqueous Solution with Cd(II)-imprinted Resin (poly-Cd(II)-DAAB-VP) Packed Columns, Anal. Chim. Acta 519 (2004) 173–179.
[18] V. Camel, Solid phase extraction of trace elements (review), Spectrochim. Acta Part B 58 (2003) 1177–1233.
[19] M. Saraji, H. Yousefi, Selective solid-phase extraction of Ni(II) by an ion-imprinted polymer from water simples, J. Hazard. Mater. 167 (2009) 1152–1157.
[20] C. Poole, New trends in solid-phase extraction, Trends Anal. Chem. 22 (2003) 362–373.
[21] T. Prasada Rao, S. Daniel, J. Gladis, Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIP-SPE), Trends Anal. Chem. 23 (2004) 28–35.
[22] N. Jiang, X. Chang, H. Zheng, Q. He, Z. Hu, Selective solid-phase extraction of nickel (II) using a surface-imprinted silica gel sorbent, Anal. Chim. Acta 577 (2006) 225–231.
[23] M. Karbasia, B. Jahanparast, M. Shamsipur, J. Hassan, Simultaneous trace multielement determination by ICP-OES after solid phase extraction with modified octadecyl silica gel, J. Hazard. Mater. 170 (2009) 151–155.
[24] A. Khorrami, T. Hashempur, A. Mahmoudi, A. Karimi, Determination of ultra trace amounts of cobalt and nickel in water samples by inductively coupled plasma-optical emission spectrometry after preconcentration on modified C18-silica extraction disks, Microchem. J. 84 (2006) 75–79.
[25] J. Otero Romaní, A. Moreda Piñeiro, P. Bermejo Barrera, A. Martin-Esteban, Synthesis, characterization and evaluation of ionic-imprinted polymers for solid-phase extraction of nickel from seawater, Anal. Chim. Acta 630 (2008) 1–9.
[26] G. Yang, W. Fen, C. Lei, W. Xiao, H. Sun, Study on solid phase extraction and graphite furnace atomic absorption spectrometry for the determination of nickel, silver, cobalt, copper, cadmium and lead with MCI GEL CHP 20Y as sorbent, J. Hazard. Mater. 162 (2009) 44–49.
[27] J. Suleiman, B. Hu, C. Huang, N. Zhang, Determination of Cd, Co, Ni and Pb in biological samples by microcolumn packed with black stone (Pierre noire) online coupled with ICP-OES, J. Hazard. Mater. 157 (2008) 410–417.
[28] A. Ersoz, R. Say, A. Denizli, Nickel(II) ion-imprinted solid-phase extraction and preconcentration in aqueous solutions by packed-bed columns, Anal. Chim. Acta 502 (2004) 91–97.
[29] M. Bidabadi, S. Dadfarnia, A. Shabani, Solidified floating organic drop microextraction (SFODME) for simultaneous separation/preconcentration and determination of cobalt and nickel by graphite furnace atomic absorption spectrometry (GFAAS), J. Hazard. Mater. 166 (2009) 291–296.
[30] R. Hurtubise, Solid-matrix luminescence analysis: photophysics, physicochemical interactions and applications, Anal. Chim. Acta 351 (1997) 1–20.
[31] R. Correa, G. Escandar, A new analytical application of nylon-induced room-temperature phosphorescence: Determination of thiabendazole in water samples, Anal. Chim. Acta 571 (2006) 58–65.
[32] G. Escandar, D. González Gómez, A. Espinosa Mansilla, A. Muñoz de la Peña, H. Goicoechea, Determination of carbamazepine in serum and pharmaceutical preparations using immobilization on a nylon support and fluorescence detection, Anal. Chim. Acta 506 (2004) 161–170.
[33] G. Escandar, Phosphorescence properties of *p*-aminobenzoic acid immobilized on a Nylon membrane, Appl. Spectrosc. 58 (2004) 836–842.
[34] G. Ibañez, G. Escandar, A. Espinosa Mansilla, A. Muñoz de la Peña, Determination of triamterene in pharmaceutical formulations and of triamterene and its main metabolite hydroxytriamterene sulfate in urine using solid-phase and aqueous solution luminescence, Anal. Chim. Acta 538 (2005) 77–84.
[35] M. Talio, M. Luconi, A. Masi, L. Fernández, Solid surface spectroscopic methodology for ultra-trace urinary nickel monitoring in smokers and non-smokers' subjects, J. Pharm. Biomed. Anal. 52 (2010) 694–700.
[36] A.K. Armitage, D.H. Turner, Absorption of nicotine in cigarette and cigar smoke through the oral mucosa, Nature 226 (1970) 1231–1232.
[37] T. Adama, J. McAughey, C. Mockerb, C. McGrath, R. Zimmermann, Influence of filter ventilation on the chemical composition of cigarette mainstream smoke, Anal. Chim. Acta 657 (2010) 36–44.