Sequential determination of nickel and cadmium in tobacco, molasses and refill solutions for e-cigarettes samples by molecular fluorescence

María Carolina Talio[b], Magdalena Alesso[a], Mariano Acosta[b], Verónica S. Wills[c], Liliana P. Fernández[a,b,*]

[a] Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina
[b] Instituto de Química de San Luis (INQUISAL-CONICET), Chacabuco y Pedernera, 5700 San Luis, Argentina
[c] UWorld, 545 E John W Carpenter Fwy, Irving, TX 75062, USA

ABSTRACT

In this work, a new procedure was developed for separation and preconcentration of nickel(II) and cadmium(II) in several and varied tobacco samples. Tobacco samples were selected considering the main products consumed by segments of the population, in particular the age (youth) and lifestyle of the consumer. To guarantee representative samples, a randomized strategy of sampling was used. In the first step, a chemofiltration on nylon membrane is carried out employing eosin (Eo) and carbon nanotubes dispersed in sodium dodecylsulfate (SDS) solution (phosphate buffer pH 7). In this condition, Ni(II) was selectively retained on the solid support. After that, the filtrate liquid with Cd(II) was re-conditioned with acetic acid /acetate buffer solution (pH 5) and followed by detection. A spectrofluorimetric determination of both metals was carried out, on the solid support and the filtered aqueous solution, for Ni(II) and Cd(II), respectively. The solid surface fluorescence (SSF) determination was performed at λ_{em} = 545 nm (λ_{ex} = 515 nm) for Ni(II)-Eo complex and the fluorescence of Cd(II)-Eo was quantified in aqueous solution using λ_{em} = 565 nm (λ_{ex} = 540 nm). The calibration graphs resulted linear in a range of 0.058–29.35 µg L^{-1} for Ni(II) and 0.124–56.20 µg L^{-1} for Cd(II), with detection limits of 0.019 and 0.041 µg L^{-1} (S/N = 3). The developed methodology shows good sensitivity and adequate selectivity, and it was successfully applied to the determination of trace amounts of nickel and cadmium present in tobacco samples (refill solutions for e-cigarettes, snuff used in narguille (molasses) and traditional tobacco) with satisfactory results. The new methodology was validated by ICP-MS with adequate agreement. The proposed methodology represents a novel fluorescence application to Ni(II) and Cd(II) quantification with sensitivity and accuracy similar to atomic spectroscopies, introducing for the first time the quenching effect on SSF.

1. Introduction

Smoking is a major cause of adverse health effects in most countries. In Argentina alone, an estimated 40,000 people die prematurely from smoking or from exposure to secondhand smoke each year, and another 18,000 have a serious illness caused by smoking [1]. Tobacco smoke is an aerosol consisting of solid/liquid droplets (particulate phase) in a gaseous phase generated by the combustion of its components at a high temperature [2]. More than 4000 compounds have been identified in environmental tobacco smoke [3,4].

Tobacco is considered one of the main risk factors associated with chronic disease [5], in conjunction with malnutrition and physical inactivity, excessive alcohol consumption, uncontrolled high blood pressure and hyperlipidemia [6]. In recent years, alternatives like electronic cigarettes (e-cigs) and narguile water pipes (WP) have appeared with the cover as a "*healthy option*".

Since the market launch of e-cigs in 2004, an ample range of devices operated by batteries that vaporize nicotine for inhalation has been purchased by millions of people [7]. Numerous studies have been carried out to probe cigarette's toxicity and its association with many diseases [8–10]. Currently, there is considerable controversy about effects on health from e-cigs, especially compared to conventional cigarettes [11]. Researchers have concluded that the use of e-cigs has encouraged the consumption of traditional cigarettes among US adolescents [12].

Water pipes (WP) or narguile, is a traditional way of smoking and an alternative to e-cigs originally from the East, and has spread worldwide among young adults. This custom plays a clearly defined

social role, accentuated by the perception of reduced harm and greater social acceptance in comparison with cigarettes. Its regular use has been associated with several respiratory problems [13,14].

While WP smoking has become a global phenomenon, knowledge about toxic content, addictive properties, and health consequences are absent. Previous research studies have determined the presence of carbon monoxide, nicotine, tar, polycyclic aromatic hydrocarbons (PAHs) and volatile aldehydes in the mainstream smoke aerosol of WP [15–18]. Nevertheless, the research to determine the presence of heavy metals in these new products is scarce.

At trace concentration, nickel (Ni) is an essential mineral for human nutrition. However, in chronic exposure it causes health problems [19]. Conclusive evidence implicates Ni in the development of pulmonary and nasal cancers, involving cellular changes at the genetic level [20,21]. The average Ni content in tobacco and cigarettes is about 10.74 mg kg^{-1}, with a maximum of 27.8 mg kg^{-1} and minimum of 2.2 mg kg^{-1}. However, evidence shows that the Ni content in samples was found to be below the maximum permissible limits of 100 mg/day [22].

Cadmium (Cd) is another heavy metal present in tobacco. Kidney damage has been described to be the main problem for patients chronically exposed to Cd. Glomerular and tubular damages are irreversible [23,24]. Cd is efficiently absorbed when inhaled, and cigarette smoke is the major source of inhaled Cd. Shortness of breath, lung edema and destruction of mucous membranes have been described as part of Cd-induced pneumonitis [25].

Determination of trace concentrations of both metals is an interesting issue in fields of clinical toxicology, environmental analysis and control processes. Furthermore, the development of analytical methodologies with high sensitivity and accuracy is necessary for the quantification. Methodologies such as Electrothermal atomic absorption spectroscopy (ETTAS), Inductively coupled plasma optical emission spectroscopy (ICP OES) or Inductively coupled plasma mass spectrometry (ICP-MS) are demonstrated to be suitable for determination of metals [26,27]. Application of molecular fluorescence in trace determination of Ni and Cd has shown several analytical advantages, including high sensitivity, appropriated selectivity and wide dynamic range [28,29].

Due to low concentrations of metals present in samples, the analyte determination is usually associated with a pre-concentration step before detection [30,31]. A variety of procedures for pre-concentration, including solid phase extraction (SPE), liquid–liquid extraction (LLE), co-precipitation and cloud point extraction (CPE) have been developed [32–34]. Compared to other techniques, SPE offers several advantages such as flexibility, higher enrichment factors, simplicity and safety with respect to hazardous samples [35,36].

In analysis of complex matrices, improving selectivity of sorbents is important. Several solid materials, such as silica gel, exchange resins, aluminum oxide, poly(vinylalcohol), C18 membranes, cyclodextrins, filter papers, Nylon membranes, among others have been successfully employed as supports for SPE [37–39].

Here we propose an alternative methodology to traditional atomic spectroscopies for monitoring Ni and Cd at trace levels in e-cigs essences and narguille samples using instruments accessible in control laboratories coupled to SPE strategies.

2. Experimental

2.1. Reagents

Stock solutions of Ni (II) and Cd (II) (3.7×10^{-4} mol L^{-1}) were prepared by dilution of 100 µg mL^{-1} standard solution plasma-pure (Leeman Labs, Inc.) in ultrapure water.

Buffers solutions (1×10^{-2} mol L^{-1}) of Tris (Mallinckrodt Chemical Works, NY, USA), potassium dihydrophosphate (Biopack, Buenos Aires, Argentina), sodium biphthalate and sodium tetraborate

(Mallinckrodt Chemical Works, NY, USA) were used and brought to the desired pH by addition of dilute HCl (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works) using a pH meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940.

Stock solution of eosin (Eo, H.E – Daniel Ltd., England) (1×10^{-6} mol L^{-1}) was prepared by dissolving the appropriate amount of reagent in ultrapure water. The stability of solutions was checked by spectrophotometric measurements.

Sodium dodecylsulfate (SDS), Triton® X-100 and hexadecyl trimethylammonium bromide (HTAB) were purchased from Tokyo Kasei Industries (Chuo-Ku, Tokyo, Japan). Multi-walled carbon nanotubes (MWNTs, diameter = 110–170 nm; length = 5–9 µm) were purchased from Merck (Darmstadt, Germany).

All glassware used material was washed with a 10% v/v HNO$_3$ solution and Milli-Q ultrapure water. All used reagents were of analytical grade.

Nylon membranes (Millipore, Sao Paulo, Brazil) with 0.45 µm pore size and 47 mm diameter, cellulose acetate (Whatman, England) with 0.45 µm pore size and 47 mm diameter, mixed esters (Schleicher & Schuell, Germany) with 0.45 µm pore size and 47 mm, Immobilon (+) (Millipore, Sao Paulo, Brazil), filter papers Blue Ribbon (FP, Whatman, England) with 2–5 µm pore size and 12.5 cm diameter were used in SPE studies.

2.2. Apparatus

Spectrofluorimetric measurements were made using a Shimadzu RF-5301 PC spectrofluorometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. For solid surface fluorescence measurements, a solid sample holder was used.

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.

An inductively coupled plasma mass spectrometer (ICP-MS), PerkinElmer SCIEX, ELAN DRC-e (Thornhill, Canada) was used for validation measurements. An argon gas with minimum purity of 99.996% was supplied by Air Liquide (Córdoba, Argentina). An HF-resistant and high performance Teflon Nebulizer model PFA-ST, was coupled to a quartz cyclonic spray chamber with internal baffle and drain line cooled with the PC^3 system from ESI (Omaha, NE, USA) (Table 1). Tygon black/black 0.76 mm i.d. and 40 cm length peristaltic pump tubing was employed. The instrument conditions were: auto lens mode on, peak hopping measure mode, dwell time of 50 ms, 15 sweeps/reading, 1 reading/replicate, and 3 replicates.

2.3. Sampling procedure

The samples, which are popular with consumers and typically sold throughout Argentina were purchased (October - November 2016) from supermarkets (Traditional tobacco), drugstores (molasses) and via the internet (refill solutions for e-cigarettes). Samples were selected considering the main products consumed by segments of the population, in particular the age (youth) and lifestyle. In order to guarantee

Table 1
Instrument settings and data acquisition parameters for ICP-MS [40].

Sample uptake rate (µL min^{-1})	400
Sample introduction	Nebulizer model PFA-ST.
RF power (W)	1150
Nebulizer Gas flow rates (mL min^{-1})	0.87
Interface	Ni cones (sampler and skimmer)
Isotope	^{60}Ni and ^{111}Cd
Scanning mode	Peak hopping
Dwell time (ms)	50 in standard mode
Number of replicate	3

representative samples, a randomized sampling was used; a total of three examples of the same brand of each product was acquired. Entire products were homogenized and reserved for sample preparation.

2.3.1. Refill solutions for e-cigarettes

A wide variety of liquids are available in the market, mainly differing in flavor and content of propylene glycol (PG) and glycerol. All types of studied refill liquids were purchased via the internet with different levels of nicotine as follow: no nicotine, 11, 12 and 18 mg mL^{-1} nicotine. Samples were produced no more than three months before tests took place and were stored in a cool, dark place throughout the test duration.

The refill liquids examined were:

- Tobacco USA Mix (18 mg Nicotine).
- Cappuccino (12 mg Nicotine).
- Ice Mint (0 mg Nicotine).
- Tobacco Whinston (11 mg Nicotine).

2.3.2. Snuff used in WP or narguile (molasses)

Snuff used in narguile or hookah (molasses) was acquired in drugstores located in San Luis city (Argentina). Once in the laboratory, samples were observed and characterized in terms of physical appearance and chemical-physical parameters.

From recently opened packages, 0.6 g of molasses was weighed and extracted. Each aliquot was put in an individual leaching solution of acetic acid (1 × 10^{-3} mol L^{-1}) and shaken for 5 min. The supernatant was separated and a general procedure was applied to an aliquot of each leachate solution.

2.3.3. Traditional tobacco

Commercial cigarettes from different brands were acquired in drugstores located in San Luis city (Argentina). Once in the laboratory, cigarette samples were observed and characterized in terms of physical appearance and chemical-physical parameters.

The cigarettes from recently opened packages were individually weighed and tobacco was extracted. Afterwards, tobacco was homogenized, and an aliquot of 0.6 g of each cigarette was put in an individual leaching solution of acetic acid (1 × 10^{-3} mol L^{-1}) and shaken for 5 min. The general procedure was applied to an aliquot of each leachate solution.

2.4. MWNTs activation

Portions of MWNTs were place in erlenmeyers, and each one was washed with different solution 2 meq mL^{-1}: H$_2$SO$_4$, HCl, HNO$_3$, and NaOH. A mix of H$_2$SO$_4$: HNO$_3$ (50:50) was also assayed in the activation step. Then, MWNTs were rinsed with ultrapure water to remove any excess reagent used, filtered through S & S blue ribbon filter paper and dried at room temperature.

2.5. Preparation MWNTs micellar solution

A total of 5 mg of MWNTs were activated with HNO$_3$ and were weighed and suspended in an SDS solution (1 × 10^{-3} mol L^{-1}). After 24 h of repose at room temperature, a supernatant of the MWNTs micellar solution was employed in the General procedure.

2.6. General procedure

Adequate volumes of sample/standard solutions containing Ni(II) and Cd(II) (0.058 – 29.35 µg L^{-1} and 0.124 – 56.20 µg L^{-1}, respectively), 250 µL Eo (1 × 10^{-6} mol L^{-1}), 100 µL buffer phosphate solution (1 × 10^{-3} mol L^{-1}, pH = 7.0) and 100 µL MWCNTs/SDS
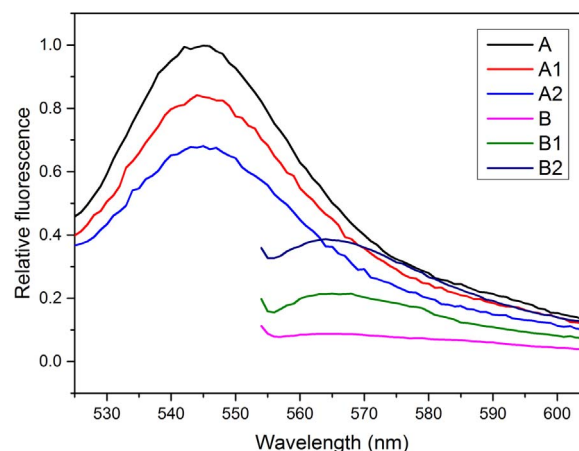

Fig. 1. Emission spectra for Ni(II) and Cd(II)-Eo complexes. A: Nylon membrane with Eo (C$_{Eo}$ = 2.5 × 10^{-8} mol L^{-1}) and MWNTs/SDS (V = 0.1 mL); A1: Idem A with Ni(II) 2.94 µg L^{-1}; A2: Idem A with Ni(II) 5.88 µg L^{-1}. B: Blank filtrated solution. B1: Idem B with Cd(II) 2.81 µg L^{-1}. B2: Idem B with Cd(II) 5.62 µg L^{-1}. Conditions: SSF (λ$_{em}$ = 545 nm; λ$_{exc}$ = 515 nm) C$_{Eo}$ = 2.5 × 10^{-8} mol L^{-1}; Volume $_{MWNTs/SDS}$ =0.1 mL; C$_{buffer}$ $_{phosphate}$ =1 × 10^{-4} mol L^{-1}, pH 7.0; Filtrated solution: λ$_{em}$ = 565 nm; λ$_{exc}$ = 540 nm; C$_{Eo}$ = 2.5 × 10^{-8} mol L^{-1}; C$_{buffer\ Acetic/acetate}$ =1 × 10^{-3} mol L^{-1}, pH 5.0; Other experimental conditions are described under procedure.

solution were placed into a volumetric flask. The whole mixture was made to 10 mL with ultrapure water. Systems were filtered across Nylon membranes, using a vacuum pump and dried at room temperature. The filtered solution containing the Cd(II)-Eo complex was collected and pH was reconditioned by adding 1 mL acetic acid/acetate buffer (1 × 10^{-2} mol L^{-1}, pH = 5.0). The Ni (II) concentration was determined on the Nylon membrane by SSF at λ$_{em}$ = 554 nm (λ$_{exc}$ = 515 nm), using a solid sample holder; the Cd (II) concentration was quantified in the filtered solution by fluorescent emission at λ$_{em}$ = 565 nm (λ$_{exc}$ = 540 nm) using a conventional quartz cell (see Fig. 1).

2.7. Interferences study

Different amounts of ions which could be present in refill solutions for e-cigs, snuff used in narguile (molasses) and traditional tobacco samples (1/1, 1/10, 1/100 and 1/1000 Ni (II) or Cd (II)/interferent ratio) were added to the test solution containing 2.94 µg L^{-1} of Ni (II) and 5.62 µg L^{-1} of Cd (II), respectively, and the general procedure was applied.

2.8. Precision study

The repeatability (same-day precision) of the methodology was tested for replicate samples (n = 4) spiked with 2.94 µg L^{-1} Ni (II) and 5.62 µg L^{-1} Cd (II), respectively, and concentrations were determined by the developed methodology.

2.9. Validation

Ni(II) and Cd(II) contents in refill solutions for e-cigarettes, molasses and tobacco traditional samples were determined by ICP-MS, using operational conditions stated in the apparatus section.

3. Results and discussion

Eosin is a well-known dye molecule that reacts with metal ions forming neutral chelates. In order to study luminescent spectral behaviors, systems containing Ni (II) and Cd (II) were separately prepared adding Eo, phosphate buffer and MWCNs/SDS aqueous

solutions. Also, a reagent blank solution was prepared. Optimal excitation and emission wavelengths were selected and respective spectral emission of Ni (II) and Cd (II) chelates were scanned. The fluorescent emission of organic dye was increased by the presence of Cd (II). However, in the case of the Ni (II)-Eo complex, a decrease of the signal was evident. Under these experimental conditions, an important overlap in maximum emission wavelength (545 nm) was produced among both metallic chelates, hindering the correct single quantification. Due to the similar spectral responses of both analytes in aqueous solution, a separation strategy based on the selective retention on solid supports was explored.

The above prepared systems were both filtered through Nylon membrane (solid support) using a vacuum pump. The filtered solutions were received in clean separated vessels and Nylon membranes were dried at room temperature. Nylon membranes were put in solid sample holders and SSF was registered for Ni (II) and Cd (II) chelates. Likewise, filtered solutions were explored by molecular fluorescence. The results showed that the Ni (II)-Eo complex was selectively retained in the solid support, allowing for its determination by SSF (quenching effect), while Cd (II)-Eo remained in the filtered solution (Fig. 1).

The main variables that affect the separation and determination processes for Ni (II) and Cd (II) trace quantification were studied and optimized, including pH, buffer nature and concentration, nature of solid support, and concentration of chelating agent.

To assure the quantitative formation of both metallic chelates, the effect of Eo concentrations on analytical responses was evaluated in range from 1×10^{-9} to 1×10^{-6} mol L^{-1}. The emission of Eo was remarkably modified in the presence of the analytes. The signal reached a maximum when the concentration of Eo was 1×10^{-8} mol L^{-1}. When the concentration was increased to 1×10^{-6} mol L^{-1}, the emission slightly decreased. An Eo concentration of 2.5×10^{-8} mol L^{-1} was chosen as the optimal concentration for the following assays.

The effect of pH $5.0 - 12.0$ was studied to achieve the selective retention of Ni (II) and a sensitive detection of Cd (II). An optimum Ni (II) recovery was found at pH 7.0. Of the assayed buffers, potassium dihydrophosphate (1×10^{-4} mol L^{-1}) was the optimal buffer to obtain the maximum SSF for Ni (II)-Eo. Furthermore, the emission for Cd(II)-Eo was poor at pH 7.0. Therefore, the filtered solution was re-conditioned by the addition of acetic acid (1×10^{-2} mol L^{-1}), obtaining the best emission signal at pH 5.0 (Fig. 2).

The nature of the solid support for Ni (II)-Eo retention is another experimental condition to be optimized. Different types of membranes (cellulose acetate, Nylon, Teflon, Filter Papers) without previous
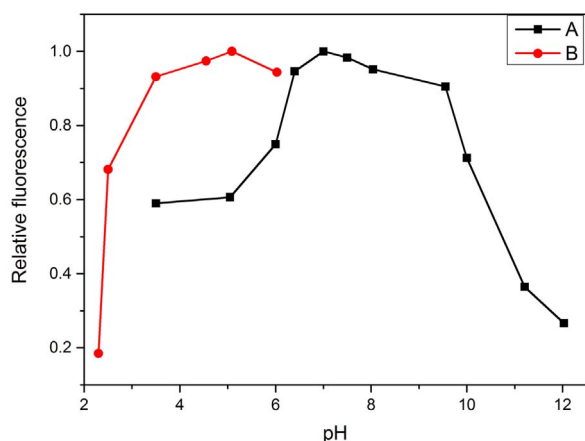
Table 2
Experimental conditions and analytical parameters for nickel and cadmium determination.

Parameters	Ni (II) SSF determination Studied Range	Optimal conditions
Support	Cellulose acetate, Nylon, Teflon, Filter Paper	Nylon membrane
pH	5.0–12.0	7.0
Buffer Potassium dihydrophosphate	1×10^{-5} - 0.5 mol L^{-1}	1×10^{-4} mol L^{-1}
MWNTs/SDS volume	0.025–1 mL	0.1 mL
Eosin concentration	1×10^{-9} - 1 10^{-5} mol L^{-1}	2.5×10^{-8} mol L^{-1}
LOD	–	0.019 µg L^{-1}
LOQ	–	0.058 µg L^{-1}
Linearity range	–	0.058 – 29.35 µg L^{-1}
r^2	–	0.999
Cd(II) fluorescent determination		
Parameters	Studied Range	Optimal conditions
pH	2.0–10.5	5.0
Buffer Acetic/acetate	1 10^{-5} – 0.1 mol L^{-1}	2 10^{-4} mol L^{-1}
Eo concentration	1 10^{-9} – 1 10^{-5} mol L^{-1}	2.5×10^{-8} mol L^{-1}
LOD	–	0.041 µg L^{-1}
LOQ	–	0.124 µg L^{-1}
Linearity range	–	0.124 – 56.20 µg L^{-1}
r^2	–	0.999

treatment were assayed in the filtration step. The Nylon membrane is the most suitable for selective and quantitative retention of the Ni (II) complex.

4. Analytical figures of merit

The limit of detection (LOD) is set based on 3.3 times the standard deviation of the blank. Under optimal experimental conditions, the LOD of each investigated element was studied by applying the proposed procedure to blank solutions (N = 15). This value for Ni (II) was 0.019 µg L^{-1} and 0.041 µg L^{-1} for Cd (II).

The calibration plots were linear in the range of 0.058 – 29.35 µg L^{-1} for Ni (II) and 0.124 – 56.20 µg L^{-1} for Cd (II). Table 2 summarizes the main characteristics of the calibration graphs and optimized experimental conditions for Ni (II) and Cd (II) trace quantification.

4.1. Interferences study

The effect of foreign ions on Ni (II) and Cd (II) recoveries was tested. Different amounts of ions commonly present in refill solutions for e-cigs, molasses and traditional tobacco samples were added to the test solution containing 2.94 µg L^{-1} of Ni (II) and 5.62 µg L^{-1} of Cd (II). The developed procedure was applied. An ion was considered as interferential when variation in fluorescent signal greater than ± 5% was observed. The tolerance limits of various foreign ions are shown in Table 3. These results demonstrate that considerable amounts of some common cations and anions do not interfere with the determinations of both analytes, making it evident that the developed methodology has an adequate selectivity.

5. Applications and validation

The proposed methodology's versatility was evaluated for analyte determination in refill solutions for e-cigs, molasses and traditional tobacco samples. The methodology was performed using the standard addition method and validated by ICP-MS [40]. Sample aliquots of 25 µL were spiked with increasing amounts of Ni (II) (2.94 and 5.88 µg L^{-1}) and Cd (II) (5.62 and 11.25 µg L^{-1}). The results obtained

Fig. 2. Influence of pH on Ni(II) and Cd(II)-Eo complexes emission. Conditions: (**A**) SSF (λ_{em} = 545 nm; λ_{exc} = 515 nm); $C_{Ni(II)}$ = 2.94 µg L^{-1}; C_{Eo} = 2.5×10^{-8} mol L^{-1}; Volume $_{MWNTs/SDS}$ =0.1 mL; $C_{buffer\ phosphate}$ =1×10^{-4} mol L^{-1}, pH 7.0. (**B**) Filtrated solution: λ_{em} = 565 nm; λ_{exc} = 540 nm; $C_{Cd(II)}$ = 5.62 µg L^{-1}; C_{Eo} = 2.5×10^{-8} mol L^{-1}; $C_{buffer\ Acetic/acetate}$ =1×10^{-3} mol L^{-1}, pH 5.0; Other experimental conditions are described under procedure.

Table 3

Tolerance limits of interfering species in Ni(II) and Cd(II) determination.

Interferent/Ni (II) mole ratio	Interferent specie
1000:1	Na^+, K^+, Cl^-, NO_3^-
100:1	Fe^{3+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}
	As^{3+}, CO_3^{2-}, SO_4^{2-}
Interferent/Cd(II) mole ratio	**Interferent specie**
1000:1	Na^+, K^+, Cl^-
100:1	Ca^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}
	Pb^{2+}, Zn^{2+}, Fe^{3+}, As^{3+}, Cr^{3+}, CO_3^{2-}, SO_4^{2-}, NO_3^-

Conditions:

SSF Ni(II) determination (λ_{em} = 545 nm; λ_{exc} = 515 nm) C_{Eo} = 2.5× 10^{-8} mol L^{-1}; Volume $_{MWNTs/SDS}$ =0.1 mL; $C_{buffer\ phosphate}$ =1×10^{-4} mol L^{-1}, pH 7.0; $C_{Ni(II)}$ = 2.94 µg L^{-1}. Other experimental conditions are described under procedure.

Cd(II) fluorescence determination λ_{em} = 565 nm; λ_{exc} = 540 nm; C_{Eo} = 2.5× 10^{-8} mol L^{-1}; $C_{buffer\ Acetic/acetate}$ =1×10^{-3} mol L^{-1}, pH 5.0; $C_{Cd(II)}$ = 5.62 µg L^{-1}. Other experimental conditions are described under procedure.

Table 4

Recovery and validation studies by nickel determination in tobacco, molasses and refill solutions (e-cigarettes) samples.

Sample	Ni (II) added (µg L^{-1})	Proposed methodology Ni (II) found ± CV (µg L^{-1})	Recovery (%, n=4)	ICP-MS Ni (II) found ± SD (µg L^{-1})
1	–	28.9 ± 0.01	–	28.9 ± 0.01
	2.94	31.83 ± 0.03	99.96	
	5.88	34.80 ± 0.06	100.70	
2	–	9.30 ± 0.02	–	–
	2.94	12.25 ± 0.05	100.10	
	5.88	15.16 ± 0.07	99.78	
3	–	18.90 ± 0.04	–	24.9 ± 0.13
	2.94	21.85 ± 0.08	100.53	
	5.88	24.80 ± 0.04	100.11	
4	–	10.20 ± 0.02	–	9.9 ± 0.04
	2.94	13.15 ± 0.04	100.10	
	5.88	16.05 ± 0.07	99.70	
5	–	29.30 ± 0.04	–	–
	2.94	32.24 ± 0.03	100.00	
	5.88	35.20 ± 0.02	100.70	
6	–	26.60 ± 0.01	–	–
	2.94	29.75 ± 0.03	100.79	
	5.88	32.46 ± 0.07	99.92	
7	–	18.80 ± 0.07	–	–
	2.94	21.77 ± 0.05	100.16	
	5.88	24.73 ± 0.07	100.26	
8	–	39.90 ± 0.03	–	40.5 ± 0.01
	2.94	43.27 ± 0.02	101.07	
	5.88	45.32 ± 0.06	98.85	
9	–	51.6 ± 0.04	–	51.7 ± 0.02
	2.94	54.43 ± 0.05	99.79	
	5.88	57.45 ± 0.07	99.95	
10	–	44.70 ± 0.01	–	44.1 ± 0.03
	2.94	47.78 ± 0.07	100.31	
	5.88	50.62 ± 0.05	100.90	

1- E-cig refill solutions: Tobacco USA Mix (18 mg Nicotine).
2- E-cig refill solutions: Cappuccino (12 mg Nicotine).
3- E-cig refill solutions Ice Mint (0 mg Nicotine).
4- E-cig refill solutions Tobacco Whinston (11 mg Nicotine).
5-Tobacco of traditional cigarettes: popular brand.
6- Tobacco of traditional cigarettes: Ice Mint convertible.
7- Tobacco of traditional cigarettes: economic brand.
8- WP Molasses: Mint.
9-WP Molasses: Chocolate.
10-WP Molasses: Coca- Cola.

showed satisfactory accuracy with adequate precision. Reproducibility of the method was evaluated with 4 repetitions of the proposed methodology for each sample. Tables 4 and 5 show the recovery results

Table 5

Recovery and validation studies by cadmium determination in tobacco, molasses and refill solutions (e-cigarettes) samples.

Sample	Cd (II) added (µg L^{-1})	Proposed methodology Cd (II) found ± CV (µg L^{-1})	Recovery (%, n=4)	ICP-MS Cd (II) found ± SD (µg L^{-1})
1	–	8.20 ± 0.09	–	–
	2.81	11.05 ± 0.03	100.49	
	5.62	13.84 ± 0.08	100.25	
2	–	12.50 ± 0.05	–	12.4 ± 0.01
	2.81	15.30 ± 0.09	99.92	
	5.62	18.15 ± 0.07	100.24	
3	–	18.60 ± 0.07	–	18.2 ± 0.02
	2.81	21.51 ± 0.02	100.53	
	5.62	24.20 ± 0.01	99.89	
4	–	19.50 ± 0.03	–	–
	2.81	22.33 ± 0.04	100.10	
	5.62	25.19 ± 0.06	100.36	
5	–	10.20 ± 0.04	–	10.9 ± 0.01
	2.81	13.13 ± 0.02	101.18	
	5.62	15.91 ± 0.09	100.88	
6	–	13.82 ± 0.05	–	–
	2.81	16.52 ± 0.09	99.20	
	5.62	19.51 ± 0.08	100.50	
7	–	19.51 ± 0.06	–	19.25 ± 0.03
	2.81	22.34 ± 0.09	100.10	
	5.62	25.19 ± 0.08	100.31	
8	–	28.73 ± 0.01	–	28.8 ± 0.012
	2.81	31.52 ± 0.09	99.93	
	5.62	34.30 ± 0.08	99.82	
9	–	31.52 ± 0.06	–	–
	2.81	34.39 ± 0.09	100.20	
	5.62	37.15 ± 0.08	100.03	
10	–	33.60 ± 0.04	–	–
	2.81	36.32 ± 0.09	99.73	
	5.62	39.32 ± 0.08	100.30	

1- E-cig refill solutions: Tobacco USA Mix (18 mg Nicotine).
2- E-cig refill solutions: Cappuccino (12 mg Nicotine).
3- E-cig refill solutions Ice Mint (0 mg Nicotine).
4- E-cig refill solutions Tobacco Whinston (11 mg Nicotine).
5- Tobacco of traditional cigarettes: popular brand
6- Tobacco of traditional cigarettes: Ice Mint convertible
7- Tobacco of traditional cigarettes: economic brand
8- WP Molasses: Mint.
9- WP Molasses: Chocolate.
10- WP Molasses: Coca- Cola.

for each sample. The analytical quality parameters of the developed methodology make the accurate quantification of both analytes in selected samples possible with similar sensitivity to previously reported data (Table 6).

6. Conclusion

This novel procedure provides a simple, economical, rapid and precise methodology for the sequential determination of Ni(II) and Cd(II) in refill solutions for e-cigarettes, molasses and traditional tobacco samples using eosin as a chelating agent. A solid phase extraction strategy was used for selective retention/ preconcentration of Ni (II) on a Nylon membrane, which is an interesting tool for its sensitive determination in the studied samples. The quenching effect associated with SSF is determined for the first time in this work, representing an innovative contribution. Furthermore, Cd (II) was analyzed in a filtered solution with adequate selectivity and sensitivity. A suitable tolerance at high levels of regular foreign constituents was evident. Precision and accuracy were tested and validated by ICP-MS. The sensitivity obtained was comparable with those determined by atomic spectroscopies. This methodology employs a simple and inexpensive instrument and was successfully applied to quantification of

Table 6

Metals contents reported in e-cigarettes, traditional cigarette and molasses samples.

Reference	Units	Cadmium	Nickel
Aerosols and cartridges of e-cigarettes			
Goniewicz et al. [41]	μg/150 puff	N.D. to 0.22 ± 0.16	0.11 ± 0.05 to 0.29 ± 0.08
Williams et al. [42]	μg/10 puffs	N.T.	0.005
Laugesen [43]	μg/cartridge	N.D.	N.D.
This work	e-cig refill solutions (μg L^{-1})	14.7 (*)	16.82 (*)
Argileh smoke condensate			
Shihadeh [44]	100-puff smoking session (ng)		990
Apsley et al. [45]	mg kg^{-1}	0.32 (*)	0.25 (*)
This work	WP molasses (μg L^{-1})	31.27 (*)	45.4 (*)
Traditional cigarette			
Shihadeh [45]		–	ND–600
O'Connor et al. [46]	mg g^{-1} tobacco	3.6	0.79
Pourkhabbaz and Pourkhabbaz [47]	μg g^{-1} tobacco	2.71	10.03
Omari et al. [48]	μg g^{-1} tobacco	0.073	–
This work	(μg L^{-1}) by a cigarette	14.51 (*)	24.9 (*)

N.D., not detected; N.T., not tested by the study.

(*) Average value.

both analytes in tobacco cigarette samples and new smoking alternatives, highlighting snuff toxicity in any of its forms of consumption.

Acknowledgements

References

[1] A. Pichon-Riviere, A. Alcaraz, A. Bardach, F. Augustovski, J. Caporale, F. Caccavo, Carga de enfermedad atribuible al tabaquismo en Argentina. Documento Técnico IECSNº 7, Instituto de Efectividad Clínica y Sanitaria, Buenos Aires, Argentina, 2013.

[2] M. Borgerding, H. Klus, Analysis of complex mixtures cigarette smoke, Exp. Toxicol. Pathol. 57 (2005) 43–73.

[3] M. Kleeman, J. Schauer, G. Cass, Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes, Environ. Sci. Technol. 33 (1999) 3516–3523.

[4] D. Hoffmann, I. Hoffmann, The changing cigarette, 1950–1995, J. Toxicol. Environ. Health 50 (1997) 307–364.

[5] M. Eriksen, J. Mackay, N. Schluger, F. Islami Gomeshtapeh, J. Drope, The tobacco atlas. Fifth edition. Published by the American Cancer Society, Inc., 250 Williams Street Atlanta, Georgia 30303 USA, 2015.

[6] U.E. Bauer, P.A. Briss, R.A. Goodman, B.A. Bowman, Prevention of chronic disease in the 21st century: elimination of the leading preventable causes of premature death and disability in the USA, Lancet 384 (2014) 45–52.

[7] D. Purkayastha, BAT Ramps-up E-cigarette Expansion as Sales Go up in Smoke International Business Times. 〈http://www.thefreelibrary.com/BAT Ramps-up E-cigarette Expansion as Sales Go Up in Smoke.-a0338323170〉 , July 31 2013 (accessed 27 September 2016).

[8] L.E. Crotty Alexander, S. Shin, J.H. Hwang, Inflammatory Diseases of the Lung Induced by Conventional Cigarette Smoke: a Review, Chest 148 (5) (2015) 1307–1322.

[9] L.F. Li, R.L.Y. Chan, L. Lu, J. Shen, L. Zhang, Cigarette smoking and gastro-intestinal diseases: the causal relationship and underlying molecular mechanism, Int. J. Mol. Med. (2014) 372–380.

[10] Y. Nagasawa, R. Yamamoto, H. Rakugi, Y. Isaka, Cigarette smoking and chronic

[11] M.C. Talio, K. Zambrano, M. Kaplan, M. Acosta, R.A. Gil, M.O. Luconi, L.P. Fernández, New solid surface fluorescence methodology for lead traces determination using rhodamine B as fluorophore and coacervation scheme: application to lead quantification in e-cigarette refill liquids, Talanta 143 (2015) 315–319.

[12] L.M. Dutra, S.A. Glant, Electronic cigarettes and conventional cigarette use among US adolescents: a cross-sectional study, JAMA Pediatr. 168 (2014) 610–617.

[13] S. Rastam, F.M. Li, F.M. Fouad, H.M. Kamal, N. Akil, A.E. Moustafa, Water pipe smoking and human oral cancers, Med. Hypothes. 74 (2010) 457–459.

[14] M. Jawad, S. Jawad, A. Mehdi, A. Sardar, A.M. Jawad, F.L. Hamilton, A qualitative analysis among regular waterpipe tobacco smokers in London universities, Int. J. Tuberc. Lung Disc 17 (2013) 1364–1369.

[15] M. Katurji, N. Daher, H. Sheheitli, R. Saleh, A. Shihadeh, Direct measurement of toxicants inhaled by water pipe users in the natural environment using a real-time in situ sampling technique, Inhal. Toxicol. 22 (2010) 1101–1109.

[16] M. Katurji, A. Shihadeh, In situ carbon monoxide, 'tar', and topography measurements for 20 narghile waterpipe smokers in natural settings using a novel smoke sampling device, in: 13th Annual Meeting of the SRNT, Austin, Texas, 2007.

[17] A. Shihadeh, R. Saleh, Polycyclic aromatic hydrocarbons, carbon monoxide,"tar", and nicotine in the mainstream smoke aerosol of the narghile water pipe, Food Chem. Toxicol. 43 (2005) 655–661.

[18] M.A. Rashidi, A. Shihadeh, N.A. Saliba, Volatile aldehydes in the mainstream smoke of the narghile waterpipe, Food Chem. Toxicol. 46 (2008) 3546–3549.

[19] F.B. Howard-White, Nickel, an Historical Review, Methuen & Co, Van Nostrand, 1963.

[20] R.P. Hausinger, Biochemistry of Nickel, Springer Science Business Media, New York, 1993, pp. 3–4.

[21] Y.F. Wang, H.W. Shyu, Y.C. Chang, Nickel (II)-induced cytotoxicity and apoptosis in human proximal tubule cells through a ROS- and mitochondria-mediated pathway, Toxicol. Appl. Pharmacol. 259 (2012) 177–186.

[22] G.E. Sebiawu, N.J. Mensah, F. Ayiah-Mensah, Analysis of heavy metals content of tobacco and cigarettes sold in Wa municipality of upper west region, Ghana Chem. Proceedings Eng., 25, 2014, pp. 24–33.

[23] O. Barbier, G. Jacquillet, M. Tauc, M. Cougnon, P. Poujeol, Effect of heavy metals on, and handling by, the kidney, Nephron. Physiol. 99 (2005) 105–110.

[24] M. Piasek, J.W. Laskey, Effects of in vitro cadmium exposure on ovarian steroidogenesis in rats, J. Appl. Toxicol. 19 (1999) 211–217.

[25] K. Seidal, N. Jorgensen, C.G. Elinder, B. Sjogren, M. Vahter, Fatal cadmium-induced pneumonitis, Scand. J. Work Environ. Health 19 (1993) 429–431.

[26] 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.

[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] N. Aksuner, E. Henden, I. Yilmaz, A. Cukurovali, A novel optical chemical sensor for the determination of nickel(II) based on fluorescence quenching of newly synthesized thiazolo-triazol derivative and application to real samples, Sens. Actuators B 166 (2012) 269–274.

[29] H.N. Kim, W.X. Ren, J.S. Kim, J. Yoon, Fluorescent and colorimetric sensors for detection of lead, cadmium, and mercury ions, Chem. Soc. Rev. 41 (2012) 3210–3244.

[30] V.A. Lemos, G.T. David, An on-line cloud point extraction system for flame atomic absorption spectrometric determination of trace manganese in food samples, Microchem. J. 94 (2010) 42–47.

[31] M.G. Pereira, M.A.Z. Arruda, Trends in preconcentration procedures for metal determination using atomic spectrometry techniques, Microchim. Acta 141 (2003) 115–131.

[32] C. Duran, A. Gundogdu, V.N. Bulut, M. Soylak, M. Elci, H.B. Sentürk, M. Tüfekci, Solid-phase extraction of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions from environmental samples by Flame atomic absorption spectrometry, J. Hazard. Mater. 146 (2007) 347–355.

[33] S. Jafarvand, A. Bidari, P. Hemmatkhah, M.R.M. Hosseini, Y. Assadi, Dispersive liquid–liquid microextraction of silver prior to determination by microsample introduction-flame atomic absorption spectrometry, Anal. Lett. 42 (2009) 2214–2231.

[34] J.A. Baig, T.G. Kazi, A.Q. Shah, M.B. Arain, H.I. Afridi, G.A. Kandhro, S. Khan, Optimization of cloud point extraction and solid phase extraction methods for speciation of arsenic in natural water using multivariate technique, Anal. Chim. Acta 651 (2009) 57–63.

[35] A.J. Bucheit, M. Witzenbacher, Pesticide monitoring of drinking water with the help of solid-phase extraction and high-performance liquid chromatography, J. Chromatogr. A 737 (1996) 67–74.

[36] H. Ciftci, Solid phase extraction method for the determination of cobalt in water samples on duolite XAD-761 resin using 4-(2-Pyridylazo) resorcinol by FAAS, Curr. Anal. Chem. 6 (2010) 154–160.

[37] T. Prasada Rao, S. Daniel, J.M. Gladis, Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIPSPE), Trends Anal. Chem. 23 (2004) 28–35.

[38] R.A. Correa, G.M. Escandar, A new analytical application of nylon induced room temperature phosphorescence: determination of thiabendazole in water samples, Anal. Chim. Acta 571 (2006) 8–65.

[39] C. Peralta, L. Fernández, A. Masi, A novel application of immobilization on membranes for the separation and spectrofluorimetric quantification of amiloride and furosemide in pharmaceutical samples, Anal. Chim. Acta 661 (2010) 85–90.

[40] F. Moyano, E. Verni, H. Tamashiro, S. Digenaro, L.D. Martinez, R.A. Gil, Single-step procedure for trace element determination in synovial fluid by dynamic reaction cell-inductively coupled plasma mass spectrometry, Microchem. J. 112 (2014) 17–24.

[41] M.L. Goniewicz, J. Knysak, M. Gawron, L. Kosmider, A. Sobczak, J. Kurek, A. Prokopowicz, M. Jablonska-Czapla, C. Rosik-Dulewska, C. Havel, P. Jacob, N. Benowit, Levels of selected carcinogens and toxicants in vapour from electronic cigarettes, Tob. Control 23 (2014) 133–139.

[42] M. Williams, A. Villarreal, K. Bozhilov, S. Lin, P. Talbot, Metal and silicate particles including nanoparticles are present in electronic cigarette cartomizer fluid and aerosol, PLoS One 8 (2013) 57987.

[43] M. Laugesen, Safety Report on the Ruyan E-cigarette Cartridge and Inhaled Aerosol. Health New Zealand Ltd., Christchurch, 2008. ⟨http://www.healthnz.co.nz/RuyanCartridgeReport30-Oct-08.pdf⟩ (Accessed 10.25.16).

[44] A. Shihadeh, Investigation of mainstream smoke aerosol of the argileh water pipe, Food Chem. Toxicol. 41 (2003) 143–152.

[45] A. Apsley, K.S. Galea, A. Sánchez-Jiménez, S. Semple, H. Wareing, M. van Tongeren, Assessment of polycyclic aromatic hydrocarbons, carbon monoxide, nicotine, metal contents and particle size distribution of mainstream Shisha smoke, J. Environ. Health Res. 11 (2) (2015) 93–104.

[46] R.J. O'Connor, L.M. Schneller, R.V. Caruso, W.E. Stephens, Q. Li, J. Yuan, G.T. Fong, Toxic metal and nicotine content of cigarettes sold in China, 2009 and 2012, Tob. Control 24 (2015) 55–59.

[47] A. Pourkhabbaz, H. Pourkhabbaz, Investigation of toxic metals in the tobacco of different Iranian cigarette brands and related health issues, Iran. J. Basic Med. Sci. 15 (2012) 636–644.

[48] M.O. Omari, J.K. Kibet, J.K. Cherutoi, J.O. Bosire, N.K. Rono, Heavy metal content in mainstream cigarette smoke of common cigarettes sold in Kenya, and their toxicological consequences, Int. Res. J. Environ. 4 (2015) 75–79.