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Determination of cadmium in tobacco by solid surface fluorescence using nylon membranes coated with carbon nanotubes ☆

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ABSTRACT

A new methodology based on fluorescent signal enhancement of o-cresolphthalein (o-CPT) for traces of cadmium determination is proposed. The dye was retained on membrane filters in the presence of a micellar surfactant solution of carbon nanotubes (CNTs). All the experimental variables that influence both the preconcentration procedure and the fluorimetric sensitivity were carefully optimized. The calibration graph using zeroth order regression was linear from 6.5 ng L^{-1} to 5.65×10^5 ng L^{-1}, with a correlation coefficient higher than 0.999. Under optimal conditions, the limits of detection and quantification were of 2 ng L^{-1} and 6.5 ng L^{-1}. respectively. The proposed method showed good sensitivity and selectivity, with good tolerance to foreign ions, and it was applied to the determination of trace amounts of cadmium in leachate from cigarettes' tobacco samples with satisfactory results. The trueness of the recommended procedure was assessed through parallel analysis of the samples with electrothermal atomization atomic absorption spectrometry. This methodology represents an innovative and attractive application of membrane filters that enables metal traces determination by solid surface fluorescence.

1. Introduction

Cadmium is a well known human carcinogen and it is one of the components of tobacco [1]. It is commonly found in air, soil and water and, due to its long biological half-life, it accumulates in plants and animals. The main sources of cadmium exposure are industrial workplaces, cigarettes and foods. Cadmium toxicity is associated with several clinical complications: cancer, liver and kidney dysfunction, increased risk of bone fracture, hypertension, atherosclerosis and severe anemia [2–7]. Current evidence suggests that exposure to cadmium induces genomic instability through complex and multifactorial mechanisms; there are no proven effective treatments for chronic cadmium intoxication [8].

Tobacco plants have a special ability to absorb cadmium from soil and to accumulate it in unusually high concentrations in the leaves (ranging from 0.77 to 7.02 $\mu g\ g^{-1}$) [9–11]. In cigarettes, cadmium concentrations range from 0.5 to 3.5 $\mu g\ g^{-1}$, with a mean level of 1.7 $\mu g\ g^{-1}$; these are very high levels compared to those in foods, which are normally below 0.05 $\mu g\ g^{-1}$ [12].

Smoking 40 cigarettes a day provides twice more cadmium than that present in foods. A large proportion of the metal contained in the cigarette is found in the smoke. Since the concentration of cadmium in the ash is practically constant (about 16% remains in the unsmoked cigarette and 15% is retained by the filter), the greater part passes through sidestream smoke [12].

The determination of cadmium traces constitutes a fundamental topic in environmental monitoring and toxicological-clinical areas. Metal traces are frequently determined by atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry associated to a previous preconcentration step [13–16]. Cadmium determination in biological and environmental samples at ultra-trace levels has been particularly supported by ETAAS with in-atomizer trapping [17].

Since their discovery in 1991, CNTs have aroused much attention from researchers in a number of fields. Thus, their adsorption properties have fostered their use as sorbent materials in many analytical processes—e.g., as sorbents in solid phase (micro) extraction, stationary phases in GC and LC, or pseudo-stationary phases in CE [18,19].

Carbon nanotubes (CNTs) have recently attracted great attention for the development of new membranes with advanced transport and selectivity features because of their unique

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☆ "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.

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properties, such as temperature stability, mechanical strengths, chemical inertness, conductivity and water transport properties [20–22]. Membranes with nanoscale pore diameters have been applied in molecular separation, adsorption, catalysis, energy storage, biosensing, cell culture, template synthesis and drug delivery [23–28].

The application of molecular fluorescence to cadmium traces determination has shown several analytical advantages, such as high sensitivity, proper selectivity and wide dynamic range when associated to the separation/preconcentration step [29,30].

Considering the need for development of simple, fast, sensitive and precise methodologies for cadmium traces determination without using expensive instruments, the aim of the present work is to develop a methodology alternative to traditional atomic spectrometries for cadmium monitoring in cigarette tobacco leachates, using an accessible instrument in control laboratories.

2. Experimental

2.1. Reagents

Nylon membranes (Millipore, Sao Paulo, Brazil) of 0.45 μm pore size and 47 mm diameter were used in sorption studies.

Stock solutions of Cd(II) 1×10^{-5} mol L^{-1} were prepared by dilution of 100 μg mL^{-1} standard solution plasma-pure (Leeman Labs, Inc.).

Buffer Tris-(Hydroxymethyl)-aminomethane (Mallinckrodt Chemical Works, New York, Los Angeles, St. Louis, USA) 1×10^{-2} mol L^{-1} solution was prepared. This solution was adjusted to the desired pH, with aqueous $HClO_4$ (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 of o-CPT solution 1×10^{-7} mol L^{-1} (Fluka AG, Chemische Fabrik, Buchs SG, Switzerland) was prepared by dissolution of the appropriate amount in Millie-Q ultrapure water on a weekly basis. The stability of solutions was spectrophotometrically checked.

Sodium dodecylsulfate (SDS), Triton® X-100 and hexadecyl trimethylammonium bromide (HTAB) were purchased from Tokyo Kasei Industries. (Chuo-Ku, Tokyo, Japan). SWNTs were purchased from Merck (Darmstadt, Germany).

A HTAB (Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) solution 1 × 10–3 mol L–1 was prepared by dissolution of the appropriate amount in Millie-Q ultrapure water.

All solutions were prepared with ultrapure water (18 MΩ cm^{-1}) obtained from a Milli-Q EASY pure RF (Barnsted, IA, USA). All the reagents were analytical grade.

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. 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 glass materials were previously washed with a 10% v/v HNO3 water solution, and then, with ultrapure water.

Measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, an EX7-GFA electrothermal atomizer and an ASC-6100 autosampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. Cadmium hollow-cathode lamp (Hamamatsu, Photonics K., Japan) was employed as the radiation sources. The wavelength used was 228.80 nm using a pyrolysis time of 13 s at 500 C and atomization time of 4 s at 2200 C.

2.3. Sampling procedure and sample treatment

Commercial cigarettes were acquired in drugstores of San Luis city (Argentine). Once in the laboratory, cigarette samples were observed and characterized in terms of physical appearance and chemical–physical parameters [33].

The cigarettes were weighed and tobacco was extracted from cigarettes in recently opened packages. The tobacco extracted was weighed independently. Afterward, the whole of tobacco in each cigarette was put in individual leaching solutions of HCl 9×10^{-3} mM. Leachate treatment for each sample was carried

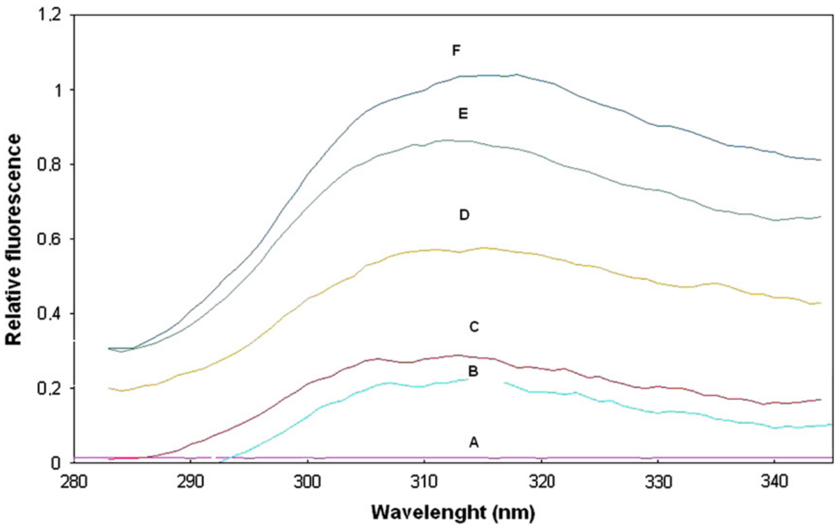

Fig. 1. Solid phase fluorescent emission of o-CPT/ SWNTs/Cd(II) system (λ_{em}=305 nm and λ_{exc}=282 nm). (A) Membrane of nylon. (B) Membrane of nylon with o-CPT. (C) Membrane of nylon with o-CPT/SWNTs. (D) Idem B with Cd(II) 56.5 μg L^{-1}. (E) Idem B with Cd(II) 85 μg L^{-1}. (F) Idem B with Cd(II) 113 ng L^{-1}. Conditions: 5×10^{-8} mol L^{-1} o-CPT, 50 μL sub-micellar solution de SWNTs, pH 8.0 buffer Tris. Other experimental conditions are described under procedures.

out in parallel with continuous shake during 1 min. The general procedure was applied to an aliquot of each leachate solution.

All glass materials were previously washed with a 10% v/v HNO_3 solution and then with Milli-Q ultrapure water.

2.4. SWNTs activation

Several small portions of SWNTs were put into an Erlenmeyer's, and each one was washed with a different solutions: H2SO4, HCl, HNO3 and NaOH, in all cases 2 meq mL − 1. Moreover, a mix of H2SO4:HNO3 (50:50) was also assayed in the activation step. Then, SWNTs were raised with ultrapure water for removing the excess of used reagent, filtered through filter paper (S&S blue ribbon) and dried at room temperature.

Table 1
Study of retention of o-CPT/SWNTs and o-CPT/SWNTs/Cd(II) systems on different types of membranes.

Type of membrane	Observations	Relative fluorescence
Cellulose acetate		
(Whatman)	o-CPT/SWNTs retention:(+)	0.35
Pore size: 0.45 mm	Cd(II) retention; (−)	0.18
Immobilon (+) (Millipore)		
Pore size: 0.45 mm	o-CPT/SWNTs retention: (+)	0.39
	Cd(II) retention; (−)	0.10
Mixed Esters		
(Schleicher & Schuell)	o-CPT/SWNTs retention: (−)	–
Pore size: 0.45 mm	Cd(II) retention; (−)	–
Filter paper		
(S&S)	o-CPT/SWNTs retention: (+)	0.32
Black ribbon	Cd(II) retention; (−)	0.09
Filter paper		
(S&S)	o-CPT/SWNTs retention: (+)	0.30
Blue ribbon	Cd(II) retention; (−)	0.01
Nylon		
(Millipore)	o-CPT/SWNTs retention: (+)	0.41
Pore size: 0.45 mm	Cd(II) retention; (+)	1.00

o-CPT concentration = 5 × 10–8 mol L^{-1}. HTAB-SWNTs volume = 50 μL; Filtration flow rate = 0.05 mL min^{-1}; pH = 8.0 (Tris buffer solution); Cd(II) concentration = 56.5 μg L^{-1}. Methodology is detailed in text.

2.5. Preparation SWNTs solution

A total of 5 mg of SWNTs were weighed and suspended in a HTAB solution 1 × 10–3 mol L–1. Subsequently, they were allowed to stand for 24 h at room temperature, and the supernatant of the micellar solution was employed in the General procedure.

2.6. General procedure

An aliquot of cigarette tobacco leachate solutions (25 μL–75 μL), Cd(II) aliquot (0.11 μg L^{-1}–5.65 × 10^2 μg L^{-1}), 100 μL buffer Tris 1 × 10^{-2} mol L^{-1} (pH = 8.0), 500 μL o-CPT (1 × 10^{-7} mol L^{-1}) and 50 μL micellar solution of SWNTs were placed in a 10 mL glass volumetric flask. The whole mixture was diluted to 10 mL with Millie-Q ultrapure water. Systems were filtered across Nylon membranes using a peristaltic pump at 0.05 mL min − 1 and dried at room temperature. Cadmium concentration was determined through o-CPT signal enhancement on the membranes by fluorescent emission at λem = 305 nm using λexc = 282 nm (Fig. 1), using a solid sample holder. For quantification purposes, the blank signal (Fig. 1B) has been subtracted to emissions of systems with Cd(II).

2.7. Accuracy study

A volume of cigarette tobacco leachates were spiked with increasing amounts of Cd(II) (0.11 μg L^{-1}–5.65 × 10^2 μg L^{-1}). Cadmium concentrations were determined by the proposed methodology.

2.8. Precision study

The repeatability (within-day precision) of the method was tested for replication of samples (n = 3) spiked with 56.5 μg $^{-1}$ of Cd(II), and the contents were determined by the proposed methodology.

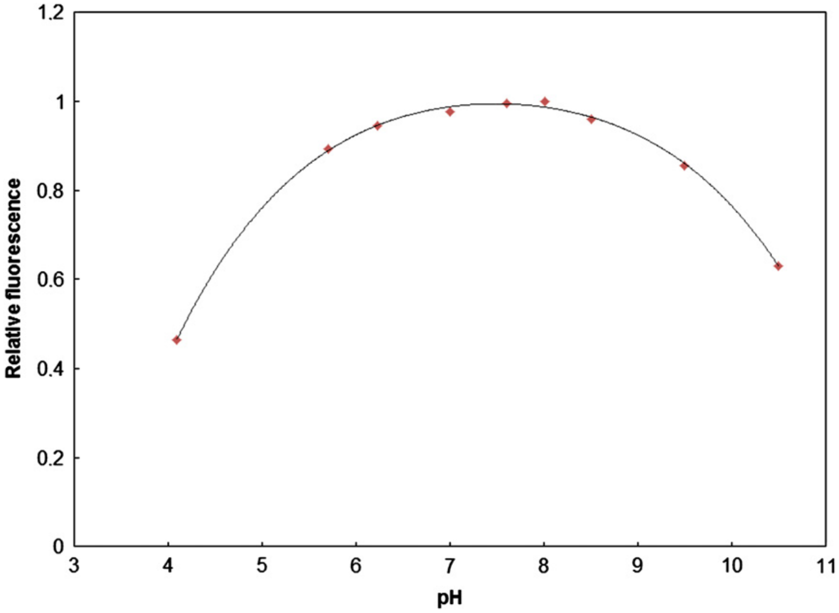

Fig. 2. Influence of pH on cadmium retention. Conditions: 5 × 10^{-8} mol L^{-1} o-CPT, 50 μL sub-micellar solution of SWNTs, Cd(II) 56.5 μg L^{-1}, buffer Tris. Other experimental conditions are described under procedures.

2.9. Validation

The validity of the proposed methodology was checked for cadmium content in tobacco samples by electrothermal atomic absorption spectroscopy (ETAAS).

3. Results and discussion

o-Cresolphthalein [1(3H)-Isobenzofuranone, 3,3-bis(4-hydroxy-3-methylphenyl)] is a common metal chelator with strong absorption in the visible region. Previous research works have shown that o-CPT presents the feasibility reaction with metallic ions [31,32].

The fluorescence of the o-CPT–Cd(II) system was explored in aqueous medium without satisfactory results of enhancement or decrement of fluorescent signal of dye due to the presence of Cd(II). Then, the effect of a micellar solution of SWNTs on the fluorescent signal of the system under study was examined. In this medium, the o-CPT fluorescent signal was affected by metal presence; this fact supports the formation of an association between Cd(II), o-CPT and SWNTs (Fig. 1).

Previous research works have shown the versatility of membranes in the solid phase of extraction which eliminate interferences of complex matrices, and permit metal traces determination [33–35]. Subsequently the possibility of using SPE to determine the fluorescent signal of the formed association on a solid support was studied.

.66In order to assure quantitative metal retention, assays were carried out at different o-CPT concentrations from $1\times 10-9$ to $1\times 10-6$ mol $\mathrm{L}^{-}1$. The outcome indicated that $5\times 10-8$ mol $\mathrm{L}^{-}1$ was the optimal concentration, which is high enough to warrant an o-CPT excess with respect to expected cadmium contents in samples.

Systems were filtered through different solid supports (Table 1). The retention levels for each material were checked measuring solid surface fluorescence signals at λem=305 nm using λexc=282 nm. The best results were obtained using Nylon membrane.

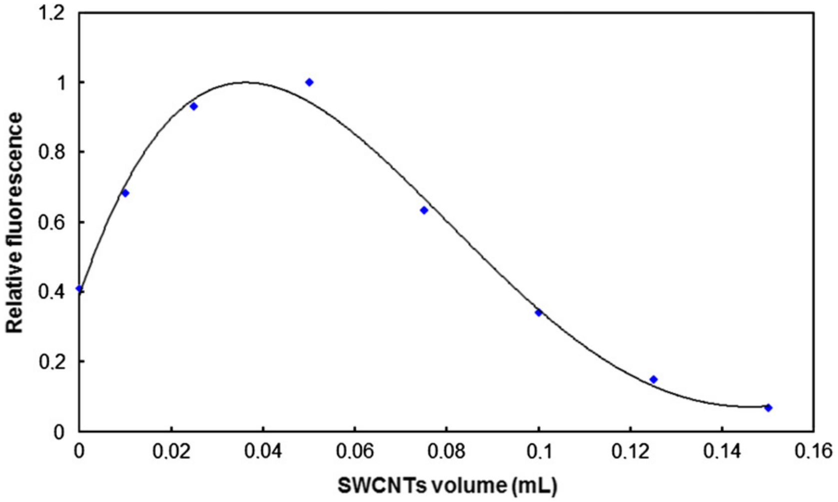

Fig. 3. Influence of volume solution SWNTs on cadmium retention. Conditions: 5×10^{-8} mol L^{-1} o-CPT, Cd(II) 56.5 μg L^{-1}, buffer Tris (pH 8.0). Other experimental conditions are described under procedures.

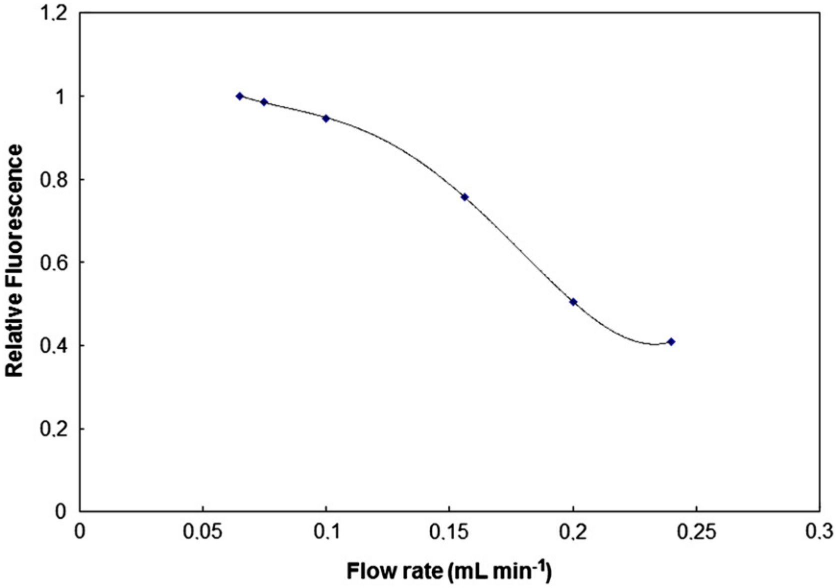

Fig. 4. Influence of filtration flow rate on cadmium retention. Conditions: 5×10^{-8} mol L^{-1} o-CPT, Cd(II) 56.5 μg L^{-1}, buffer Tris (pH 8.0). Other experimental conditions are described under procedures.

The pH value of aqueous systems containing a constant concentration of cadmium was adjusted between 4.0 and 10.5 by the addition of different buffer solutions: sodium tetraborate, Tris, phthalate acid, acetic acid/acetate. The obtained results showed that the best level retention of cadmium was achieved at pH 8.0 using Tris buffer (Fig. 2). For all subsequent experiments, this pH value was chosen. After that, the buffer concentration was tested in order to obtain the maximum fluorescent signal. The concentration of Tris buffer was varied from 1×10^{-5} to 0.5 mol $L^{-}1$. Buffer concentration of 1×10^{-3} mol $L^{-}1$ was chosen as optimal.

In the following stage, different surfactant solutions were tested as dispersant of CNTs. Anionic (SDS) and cationic (HTAB) surfactants were assayed, and the cationic one was determined to be the best dispersant in terms of homogeneous distribution in solid support and quantitative analyte retention. The volume of SWNTs solution varied from 0 to 0.250 mL. The best results were obtained by employing 0.05 mL (Fig.3).

In order to optimize the number of processed samples/time units, the filtration flow rate was made to vary between 0.05 and 0.25 mL min^{-1}, maintaining other experimental conditions constant. A filtration flow rate of 0.05 mL min^{-1} turned out to be the most appropriate for quantitative analyte retention (Fig. 4).

4. Analytical parameters

4.1. Calibration curve and analytical figures of merit

Calibration plot for concentration levels of Cd(II) from 6.5 ng L^{-1} to 5.65×10^5 ng $L^{-}1$ was assayed applying the developed methodology. Table 2 summarizes the main characteristics of the calibration plot and optimized experimental conditions, which sustain the proposed procedure for quantification of Cd(II) traces.

The limits of detection (LOD) and quantification (LOQ) were calculated in accordance to the formulas given by the official compendia methods [36], using the relation $k(SD)/m$ where $k=3.3$ for LOD and 10 for LOQ. SD represents the standard deviation from 15 replicate blank responses and m is the slope of the calibration curve.

Table 2
Experimental conditions and analytical parameters for cadmium determination.

Parameters	Studied Range	Optimal conditions
pH	4.0–10.5	8.0
Buffer Tris	1×10^{-5}–1×10^{-2} mol $L^{-}1$	1×10^{-3} mol L^{-1}
o-CPT concentration	1×10^{-9}–1×10^{-6} mol $L^{-}1$	5×10^{-8} mol L^{-1}
SWNTs volume	0–0.25 mL	0.050 mL
Filtration flow rate	0.05–0.25 mL min^{-1}	0.05 mL min^{-1}
LOQ	–	6.5 ng $L^{-}1$
LOL	–	6.5–5.65×10^5 ng L^{-1}
Calibration sensitivity	–	2.25×10^3 L ng^{-1}
r^2	–	0.999

Since no standard or reference material was available, the trueness of the proposed methodology was assessed through spike-recovery tests and by comparison with another independent technique, such as ETAAS.

The replicability of the method was evaluated by repeating the proposed approach 3 times for each addition in a total of three levels of spiked Cd(II) for each cigarette brand. The recoveries of Cd(II) in the ten cigarette brands studied and the validation with ETAAS based on the average of three replicate measurements are illustrated in Table 4. The results obtained showed a satisfactory agreement with good precision.

4.2. Interferences studies

The effects of foreign ions on the recovery of Cd(II) were tested. Different amounts of common ions in tobacco samples were added to the test solution containing 56.5 μg L^{-1} of Cd(II) and the developed procedure was applied. An ion was considered to be an interference when it caused a variation greater than ± 5% in the fluorescent signal of the test solution. The tolerance limits of

Table 4
Recuperation and validation studies.

Sample	Cd(II) added (μg L^{-1})	Proposed methodology			ETAAS
		Cd(II) found ± CV (μg L^{-1})	Recovery (%, $n=3$)	Cd(II) (mg/g)	Cd(II) found ± CV (μg L^{-1})
1	–	8.140 ± 0.02	–		–
	15.0	23.21 ± 0.01	100.85	1.27	
	30.0	38.02 ± 0.05	98.53		
2	–	9.430 ± 0.08	–	1.30	–
	15.0	24.55 ± 0.06	101.27		
	30.0	39.62 ± 0.05	102.01		
3	–	10.34 ± 0.02	–	1.82	10.38 ± 0.002
	15.0	25.70 ± 0.02	103.48		
	30.0	40.29 ± 0.04	99.51		
4	–	10.62 ± 0.02	–	1.93	–
	20.0	30.56 ± 0.05	99.43		
	30.0	40.63 ± 0.04	100.09		
5	–	9.560 ± 0.02	–		
	15.0	24.51 ± 0.03	99.50		
	30.0	39.60 ± 0.08	100.42	1.63	–
6	–	10.46 ± 0.02	–	1.97	–
	15.0	25.78 ± 0.05	103.06		
	30.0	40.44 ± 0.06	99.80		
7	–	6.923 ± 0.01	–	1.42	6.926 ± 0.009
	15.0	21.92 ± 0.03	99.95		
	30.0	36.91 ± 0.05	99.81		
8	–	28.94 ± 0.03	–	3.45	–
	20.0	49.01 ± 0.07	100.24		
	30.0	58.91 ± 0.08	99.90		
9	–	24.15 ± 0.03	–	3.2	24.95 ± 0.008
	20.0	41.87 ± 0.09	98.74		
	30.0	52.16 ± 0.04	100.05		
10	–	17.26 ± 0.08	–	2.6	17.50 ± 0.003
	15.0	32.28 ± 0.09	100.11		
	30.0	47.31 ± 0.02	100.29		

Tobaccolist: Samples; 1–4: Massalin Particulares; 5–7: Nobleza Piccardo 8: Sarandí S.A; 9: Coimexpor Argentina; 10: Espert S.A.

Table 3
Study of tolerance of common ions in tobacco samples.

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

o-CPT concentration$=5 \times 10^{-8}$ mol L^{-1}. HTAB-SWNTs volume=50 μL; Filtration flow rate=0.05 mL min^{-1}; pH=8.0 (Tris buffer solution); Cd(II) concentration=56.5 μg L^{-1}. Methodology is detailed in text.

various foreign ions are given in Table 3. These results demonstrate that large excesses of some common cations and anions do not interfere with the determination of trace levels of Cd(II).

5. Applications

Cigarette tobacco was treated with different leaching solutions, as discussed above. An ideal leaching solution must satisfy two essential conditions:

- To leach the Cd(II) analyte selectively.
- To show maximum fluorescent emission of membrane Nylon/ o-CPT/ SWNTs/Cd(II) system.

To this end, different volumes of 3.5×10^{-4} mol L^{-1} HCl were assayed. A volume of 250 μL 3.5×10^{-4} mol L^{-1} HCl was selected as optimal, since it met the above mentioned requirements.

Other optimized variable was the contact time of cigarette tobacco with leaching solutions. Experiments where contact time was made to vary from 0.5 to 5 were carried. The best results in relation to sensitivity and selectivity were obtained for 1 min of contact time. For minor contact times, poor repeatability was obtained.

6. Conclusions

This work represents a novel application of SWNTs for cadmium retention and determination for enhancement of solid surface fluorescent signal of o-CPT. The proposed methodology represents an innovative application of luminescence to metal analysis comparable in sensitivity and accuracy to atomic spectrometries. The development of new simple and rapid analytical methods for Cd(II) trace determination continues to be a current topic due to the toxicological relevance of the metal. The proposed method symbolizes a promising approach for Cd(II) monitoring with low operation cost, simplicity of instrumentation and non-polluting solvents, and it represents a promising approach in the environmental area. The method was validated with real samples showing good tolerance to regular foreign constituents present in cigarette tobacco. Precision and accuracy were tested and validated by ETAAS with excellent results. In light of this and other studies in the field, efforts should be made by control and health agencies to discourage the habit of smoking and other forms of tobacco consumption due to the high concentrations of cadmium found in tobacco products and the subsequent risks for health.

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Glossary

o-CPT: o-cresolphthalein;
SPE: solid phase extraction;
CNTs: carbon nanotubes;
SWNTs: single-walled nanotubes;
ETAAS: electrothermal atomization atomic absorption spectrometry;
GC: gas chromatography;
LC: liquid chromatography;
CE: capillary electrophoresis;
SDS: sodium dodecylsulfate;
HTAB: hexadecyltrimethylammonium bromide;
LOD: limit of detection;
LOQ: limit of quantification;
LOL: limit of linearity;
CV: coefficient of variance.