



Determination of Cd(II) by FAAS in Turkish Cigarette Tobacco: A Pre-Concentration Procedure with Diethyldithiocarbamate Immobilized Amberlite XAD-2 Resin

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A simple and rapid procedure for the pre-concentration of Cd(II) in Turkish cigarette tobacco was developed. Present Cd(II) in the tobacco samples was pre-concentrated by sodium diethyldithiocarbamate immobilized Amberlite XAD-2 resin and determinations were carried out by using flame atomic absorption spectrometry. Parameters such as the effects of pH, nitric acid concentration and flow rate on the pre-concentration procedure were investigated. A pre-concentration factor of 100 was achieved by employing optimum conditions. The calibration plot for Cd(II) was linear in 0.1-2.0 mg mL⁻¹ concentration range with the detection limit of 0.03 mg mL⁻¹ and the relative standard deviation (RSD) was 2.3 % for the overall procedure (n = 6). The accuracy of the proposed procedure was evaluated by means of cadmium determination in certified reference oriental tobacco leaves (CTA-OTL-1). The result obtained was in good agreement (1.07 ± 0.14 mg kg⁻¹) with certified value (1.12 ± 0.12 mg kg⁻¹). The procedure was applied to the determination of Cd(II) in cigarette tobacco samples. The concentration of Cd(II) in the two cigarettes tobacco samples was determined as 2.5 and 2.8 mg kg⁻¹, respectively.

Key Words: Cadmium, Tobacco cigarette, Amberlite XAD-2, Flame atomic absorption spectrometry.

INTRODUCTION

Three distinct categories may be recognized with respect to cadmium-in-air *e.g.*, (i) cadmium in ambient air, (ii) cadmium air levels in occupational exposure situations and (iii) cadmium in air from the smoking of tobacco. Whereas cadmium from occupational environments and cadmium from cigarette smoke are transferred directly to humans, cadmium in ambient air is generally deposited onto waters or soils, then eventually transferred to plants and animals and finally enter the human body through the food chain¹. Tobacco leaves naturally accumulate and concentrate relatively high levels of cadmium and therefore smoking of tobacco is an important source of air cadmium exposure for smokers.

A comprehensive search carried out by the international agency for research on cancer (IARC) revealed that nine of the 44 chemical agents in the mainstream of cigarette smoke were classified as group I carcinogens. These agents are benzene, cadmium, arsenic, nickel, chromium, 2-naphthylamine, vinyl chloride, 4-aminobiphenyl and beryllium². The cumulative and summative effects of metal ions are believed to play a significant role in the toxicity and carcinogenicity of tobacco smoke³. The most common way of the cadmium analysis is employing graphite furnace atomic absorption spectrometry and this technique was used in several studies in the literature such as Cd in cigarette tobacco, cigarette smoke and cigarette

filters^{1,4-7}. Other employed techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES) and flame atomic absorption spectrometry are either difficult to apply or having low sensitivity to determine low level cadmium. Due to lack of the sensitivity of flame atomic absorption spectrometry, a separation and pre-concentration step is necessarily required for the determination of low level cadmium in various samples. In general, Amberlite XAD resins, activated carbon, naphthalene, silica gel, chromosorb resins are used as adsorbents for the pre-concentration of trace elements from sample matrixes⁸⁻¹⁵. Amberlite XAD-2 (polystyrene-divinylbenzene polymer) seems a suitable resin to use in the pre-concentration procedure due to its eligible physical and chemical properties such as porosity, high surface area, durability and purity¹⁶. In this study, a simple and rapid procedure for the pre-concentration of Cd(II) in Turkish cigarette tobacco was developed. Present Cd(II) in the samples was pre-concentrated on sodium diethyldithiocarbamate immobilized Amberlite XAD-2 resin and determinations were carried out by using flame atomic absorption spectrometry.

EXPERIMENTAL

A Unicam 929 atomic absorption spectrometer (AAS) operating with an air-acetylene flame and equipped with a Cathodeon Cd-Hollow cathode lamp (228.8 nm) at 6 mA

current setting and 0.5 nm band-pass was employed in the determination of Cd(II) in samples. The pH measurements were performed by employing a Jenway Model 3040 pH meter combined with a glass electrode (standardized by pH: 4.00 and 8.00 buffers). A Clifton model thermostat water bath shaker set to 250 cpm was used in the experiments.

All the reagents used were analytical reagent grade. Deionized water was used in the preparation of all solutions. The stock solution (1000 mg L^{-1}) of Cd(II) was prepared by dissolving the appropriate amount of analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized water with 2.5 M HNO_3 . The pH was adjusted with 0.1 M HCl or 0.1 M ammonia-acetate buffer was used to adjust pH values to 5.5. Sodium salt of diethyldithiocarbamic acid trihydrate (NaDDTC) and Amberlite XAD-2 resin (polystyrene divinyl benzene type, surface area $330 \text{ m}^2/\text{g}$, pore diameter 90 \AA) was purchased from Merck and Supelco respectively. Nitric acid (Merck) was used without additional purification. Cigarettes (any brand) have been obtained from local supermarkets. Certified reference material (CTA-OTL-1) was provided by Institute of Nuclear Chemistry and Technology.

Preparation of sodium diethyldithiocarbamate immobilized Amberlite XAD-2 resin: The Amberlite XAD-2 resin (10 g) was soaked in nitric acid solution of 4 M overnight¹⁷. Then resin was rinsed thoroughly with deionized water until supernatant water pH becomes neutral. Afterwards, it was dried at $60 \text{ }^\circ\text{C}$ for 24 h in an oven. The XAD-2 resin was added in to 50 mL of aqueous solution of NaDDTC of 0.05 M. Then the mixture was shaken at room temperature for 2 h and filtered off, dried at $30 \text{ }^\circ\text{C}$ for 24 h in an oven.

Column preparation: A glass column (25 cm length \times 1 cm *i.d.*) was filled with 2 g Amberlite XAD-2 resin coated with NaDDTC. The stop cork of the column was covered with a glass-wool plug and another plug of glass-wool was covered on top of the resin. A 10 mL 4 M nitric acid and a 10 mL of deionized water were passed through the column in order to condition and clean it.

Procedure for the adsorption of cadmium ion on the Amberlite XAD-2: A 100 mL of the sample solution containing $50 \text{ } \mu\text{g L}^{-1}$ of Cd(II) was taken in a 250 mL flask¹⁷. The solution pH was adjusted to 5.5 by using acetate buffer solution. The solution was passed through the column at the desired flow rate of 2 mL min^{-1} . After that, the adsorbed Cd(II) on the NaDDTC immobilized Amberlite XAD-2 resin was eluted with a 10 mL of 4 M HNO_3 . Cd(II) in the eluate was determined by flame atomic absorption spectrometry. A blank solution was run under the same conditions without adding Cd(II).

Recovery of Cd(II) spikes from tobacco cigarette with NaDDTC immobilized Amberlite XAD-2 resin: Ten cigarettes were taken out of the package, the papers and filters were removed and the pooled sample was placed in a glass vial. An aliquot of 4 g was taken from the pooled sample and lyophilized for 72 h and the moisture content was estimated from the weight loss¹. A 4 g of tobacco sample was digested in 10 mL of HNO_3 of 4 M at $60 \text{ }^\circ\text{C}$ for 18 h. The digestate was filtered and made to 100 mL by deionized water, then spiked with a 0.1 mL of 50 mg L^{-1} standard Cd(II) solution. The pH value of the solution was adjusted to 5.5 by using acetate buffer and passed through the column containing 2 g of the NaDDTC immobilized Amberlite XAD-2 resin, at a flow rate of 2 mL

min^{-1} . The adsorbed Cd(II) on the NaDDTC immobilized Amberlite XAD-2 resin was eluted 10 mL of 4 M HNO_3 . Then, Cd(II) in the eluate was determined by flame atomic absorption spectrometry.

Pre-concentration of Cd(II) in cigarette tobacco samples:

An aliquot of 4 g was taken from the pooled sample and lyophilized for 72 h and the moisture content was estimated from the weight loss¹. Sample was digested in 10 mL of HNO_3 of 4 M at $60 \text{ }^\circ\text{C}$ for 18 h in a 100 mL flask. The digestate was filtered and made to 100 mL by deionized water and pH value of the solution was adjusted to 5.5 with acetate buffer. The sample solution was passed through the column containing 2 g of the NaDDTC immobilized Amberlite XAD-2 resin, at a flow rate of 2 mL min^{-1} . The adsorbed Cd(II) on the NaDDTC immobilized Amberlite XAD-2 resin was eluted with a 10 mL of 4 M HNO_3 . Then, the eluate solution was evaporated to 1 mL volume and Cd(II) were determined by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Effect of pH on the Cd(II) adsorption: The effect of pH on the adsorption of Cd(II) ions showed that the recovery of Cd(II) ion is maximum and quantitative ($> 90 \%$) within the pH range of 5 to 6 (Fig. 1). The graph includes standard deviation on each point, but most of them were smaller than the marks used. Therefore, the optimum working pH was chosen as 5.5 for the rest of the experiments.

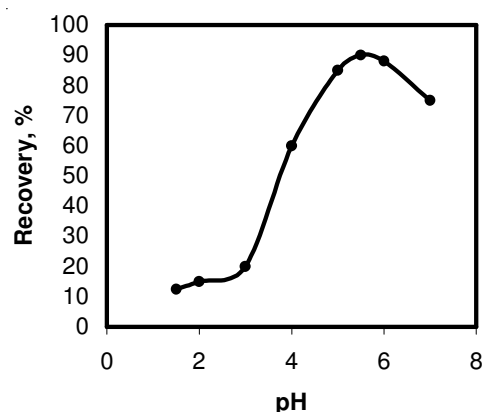


Fig. 1. Effect of pH on the complexation of cadmium with DDTC coated Amberlite XAD-2 resin

Effect of nitric acid concentration on recovery: The effect of nitric acid concentration on the recovery of Cd(II) ion from XAD-2 resin was also studied. As shown in Fig. 2 the recovery was increased as the nitric acid concentration increased up to 4 M, then the recovery was dramatically decreased. Therefore, a 10 mL volume of 4 M nitric acid was selected as the best volume for the elution of adsorbed Cd(II) ions.

Adsorption capacity of resin and preconcentration factor: In order to determine the optimum amount of XAD-2 resin, a 4 g of tobacco cigarette sample containing $50 \text{ } \mu\text{g}$ of Cd(II) ions and 1.13 g of NaDDTC were added in to 100 mL flask and proposed pre-concentration procedure was applied. The amount of XAD-2 resin was tested in the range of 0.5 to 2.5 g resin. Eventually, a 2 g XAD-2 resin was chosen as the optimum adsorbent amount for an efficient extraction.

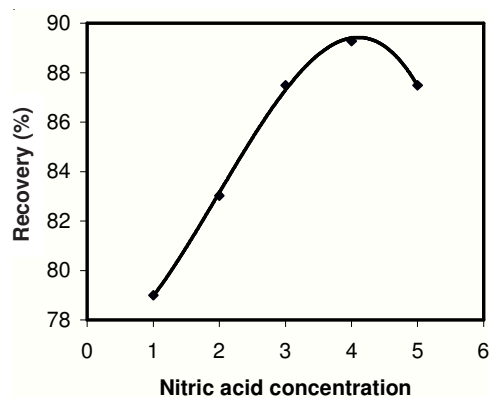


Fig. 2. Variation of the recoveries (%) with the concentration of nitric acid

The adsorption capacity of the NaDDTC immobilized Amberlite XAD-2 resin for Cd(II) ions was also evaluated. The calculated adsorption capacity of XAD-2 resin was 10 mg L⁻¹ of Cd(II) for per gram of resin. The pre-concentration factor for 100 mL tobacco sample was found as 100.

Effect of flow rate: The retention of the Cd(II) complex on the adsorbent depends upon the flow rate of the sample solution. Thus effect of the flow rate was examined by the optimum conditions. The sample solution was passed through the column with the flow rate adjusted in the range of 0.5-5 mL min⁻¹. The flow rate of 2 mL min⁻¹ was found to be suitable for optimum loading of Cd(II) ions on to the adsorbent. At flow rates higher than 2 mL min⁻¹, the Cd(II) complex does not equilibrate adequately with the XAD-2 resin column and poor recoveries are obtained. The flow rates slower than 2 mL min⁻¹ causes longer time of analysis.

Analytical parameters: The calibration graph, was linear in the range of 0.1- 2 mg L⁻¹ Cd(II) under the optimum recommended conditions for the procedure ($r^2 = 0.998$). The regression equation is $y = 0.160x - 0.001$. The statistical limit of detection was calculated from the calibration equation by using three times of the standard deviation of the intercept as described elsewhere¹⁸. The detection limit was calculated as 0.03 mg mL⁻¹. The relative standard deviation for six replicate measurement of 50 µg L⁻¹ Cd(II) solution was 2.3 %.

Accuracy and recovery: The accuracy of the overall procedure was evaluated by determining Cd(II) ions in certified reference material oriental tobacco leaves (CTA-OTL-1). The result described in Table-1 was in good agreement with the certified value. The recovery value was given for the cigarette tobacco samples in Table-2.

Cadmium determination in cigarette tobacco sample:

The proposed procedure was applied to the determination of Cd(II) in cigarette tobacco samples. To evaluate the applicability of the proposed procedure, known mass (50 µg) of cadmium was added into the sample volumes of 100 mL. The cigarette

TABLE-1
ACHIEVED RESULT FOR THE ANALYZED CERTIFIED
ORIENTAL TOBACCO LEAVES (n = 4)*

Sample	Found Cd(II) (mg kg ⁻¹)	Certified Cd(II) (mg kg ⁻¹)
Oriental tobacco leaves (CTA-OTL-1)	1.07 ± 0.14	1.12 ± 0.12

*At 95 % confidence level

TABLE-2
RECOVERY OF Cd(II) IN SPIKED CIGARETTE TOBACCO (n = 6)

Spiked Sample	Added Cd(II) (µg L ⁻¹ ± RSD %)	Found Cd(II) (µg L ⁻¹ ± RSD %)	Recovery (%) ± RSD
Cigarette tobacco	50	41	82 ± 2.3

tobacco samples were subjected to the recommended procedure for the pre-concentration and determination of Cd(II) before and after the standard addition. The results are presented in Table-3. In the present study, the Cd(II) content of the cigarette tobaccos was determined as 2.5 and 2.8 mg kg⁻¹, respectively.

TABLE-3
Cd(II) FOUND IN VARIOUS TURKISH CIGARETTE
TOBACCO SAMPLES (n=6)

Type	Found Cd(II) (mg kg ⁻¹ ± RSD %)
I	2.5 ± 2
II	2.8 ± 3

Conclusion

The proposed procedure is simple and rapid for the determination of low level Cd(II) in cigarette tobacco samples. The average of two sorts was 2.7. This result is higher than Cd concentration reported for cigarettes available in Indian markets¹⁹ as an average 0.45 mg kg⁻¹. However, the Cd(II) concentrations in our study were found to be lower than some branded cigarette of Nigeria²⁰. The result found was in good agreement with other reported data from literature²¹. The pre-concentration factor was found 100 for the cigarette tobacco. This may show that a reasonable pre-concentration factor could be achieved by applying the proposed procedure. The accuracy of the proposed procedure was evaluated by means of cadmium determination in certified reference oriental tobacco leaves (CTA-OTL-1). The result obtained was in good agreement (1.07 ± 0.14 mg kg⁻¹) with certified value (1.12 ± 0.12 mg kg⁻¹).

REFERENCES

- W.S. Rickert and M.J. Kaiserman, *Environ. Sci. Technol.*, **28**, 924 (1994).
- C.J. Smith, S.D. Livingston and D. Doolittle, *J. Food Chem. Toxicol.*, **35**, 1107 (1997).
- S.J. Stohs and M. Bagchi, *Inhal. Toxicol.*, **9**, 867 (1997).
- M.V. Smith and J. Sneddon, *Spectrosc. Lett.*, **32**, 615 (1999).
- K. Rustemeier, R. Stabbert, H.J. Haussmann, E. Roemer and E.L. Carmine, *Food Chem. Toxicol.*, **40**, 93 (2002).
- M. Galazyn-Sidorczuk, M.M. Brzóska and J. Moniuszko-Jakoniuk, *Environ. Monit. Assess.*, **137**, 481 (2008).
- S.J. Fatemi, A. Sheikh, E. Noroozian and D. Afzali, *Asian J. Chem.*, **18**, 1285 (2006).
- A. Adachi, K. Asai, Y. Koyama, Y. Matsumoto and T. Okano, *Anal. Lett.*, **31**, 1769 (1998).
- P.K. Tewari and A.K. Singh, *Talanta*, **53**, 823 (2001).
- O. Abollino, M. Aceto, M.C. Bruzzoniti, E. Mentasti and C. Sarzanini, *Anal. Chim. Acta*, **375**, 293 (1998).
- P. Bermejo-Barrera, N.C. Martinez Alfonso and A. Bermejo-Barrera, *Atom Spectrosc.*, **22**, 379 (2001).
- H.C. dos Santos, M.G.A. Korn and S.L.C. Ferreira, *Anal. Chim. Acta*, **426**, 79 (2001).
- T. Okutani, Y. Tsuruta and A. Sakuragawa, *Anal. Chem.*, **65**, 1273 (1993).
- N. Pourreza and H.Z. Mousav, *Anal. Chim. Acta*, **503**, 279 (2004).
- A. Uzun, M. Soylak and L. Elçi, *Talanta*, **54**, 197 (2003).
- S.L.C. Ferreira, J.R. Ferreira, A.F. Dantas, V.A. Lemos, N.M.L. Araújo, and A.C. Spinola Costa, *Talanta*, **50**, 1253 (2000).
- A. Ramesh, K.R. Mohan and K. Seshiah, *Talanta*, **57**, 243 (2002).
- J.N. Miller and J.C. Miller, *Statistics and Chemometrics for Analytical Chemistry* Pearson Ltd., England, edn. 4, p. 107 (2000).
- S. Verma, S. Yadav and I. Singh, *Food Chem. Toxicol.*, **48**, 2291 (2010).
- I.C. Nnorm, O. Osibanjo and C.G. Oji-Nnorom, *African J. Biotechnol.*, **14**, 1128 (2005).
- T.G. Kazi, N. Jalbani, M.B. Arain, M.K. Jamali, H.I. Afridi, R.A. Safraz and A.Q. Shah, *J. Hazard. Mater.*, **163**, 302 (2009).