Determination of Lead, Copper and Selenium in Turkish and American Cigarette Tobaccos by Anodic Stripping Voltammetry

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A method for the determination of Pb, Cu and Se in tobacco samples by anodic stripping voltammetry has been developed. Pb, Cu and Se were determined in Turkish and American cigarettes using a mercury film graphite electrode, by digesting the tobacco sample in acid or acid mixtures following extraction with 1-butanol. The appropriate results for Pb, Cu and Se were obtained from the digestion mixtures of HNO_3–$HClO_4$ (1/1) for Pb, HNO_3–$HClO_4$–H_2SO_4 (2/2/1) for Cu and Se. Interference due to the large amount of Cu was reduced to the proper level by 1-butanol extraction, that made the determination of Se possible. The effects of deposition potentials, deposition times and pH of the medium have been discussed. The applied deposition potentials for Pb, Cu and Se were −850, −600 and −400 mV (*vs.* Ag/AgCl) respectively. The peak potentials in $HClO_4$ solution (pH≅2) were −350 mV for Pb, −20 mV for Cu and +60 mV for Se. The relative standard deviations are 4.5% at the concentrations of 2.2 ppm Pb (n=5) and 4.4 ppm Cu (n=6), and 8.3% at 0.12 ppm Se(IV) (n=8).

Keywords Tobacco, lead, copper and selenium, anodic stripping voltammetry

Tobacco has been one of the most studied plants for well over 300 years. Schoesing[1] in 1860 related the inorganic composition of tobacco leaf to its burning qualities. Several carcinogens have been identified in tobacco as well as in gaseous and particulate phases of tobacco. Some metals are known to be carcinogenic and these are toxic and harmful to the human body. Thus, trace elements are important in the physiological development of man. Smoking is one way in which trace elements can enter the human body. Studies have indicated that there is a definite correlation between trace element level in the body and that of certain diseases.[2] Several investigations have shown that Co, As, Se, Br, Cd, Hg, and Sb are toxic for a human biosystem even at the very low levels on intake.[3,4] The chemical composition of wrapping paper generally reflects the non-fibrous material used in papermaking, such as kaolin, titanium oxide, calcium carbonate or zinc sulfide, that were added to the paper to achieve the desired optical and burning properties. Twenty seven elements in cigarette tobacco, wrapping paper and cigarette ash was determined by instrumental neutron activation analysis (INAA).[5]

The use of INAA in determining selected elements in cigarette tobacco has been reported by numerous authors.[5–7] Data on some toxic elements like Pb and Cu that were not measured in INAA are present in our study. Several investigations were done for the determination of trace elements in tobacco and tobacco smoke by X-ray fluorescence (XRF) method.[8,9] Adeloju reported the determinations of inorganic elements in biological and environmental materials at trace and ultra-trace levels by differential pulse cathodic stripping voltammetry.[10] Removal of matrices by extraction with organic solvents has never been mentioned. Al-Saleh and Saleh have used combined nuclear techniques and obtained X-ray spectrum of cigarette tobacco with Cd-109 isotope.[9] Here, Cu concentration in tobacco was between 7 – 24 ppm and in wrapping paper 2 – 6 ppm, but determination of Pb was not included. Mishra and coworkers have analyzed the trace elements in tobacco and tobacco smoke by X-ray fluorescence method.[8] Here, concentration of some toxic elements like Pb, Cu, and Ni could be measured. Copper and lead in chewing tobacco were determined between 10 – 17 ppm Cu and 1.9 – 7.0 ppm Pb, in snuff tobacco 4.4 – 63 ppm Cu and 1.5 – 29 ppm Pb. Cülovali and Gündüz have reported 20 elements in nine different brands of Turkish cigarette tobacco by INAA.[6] Results in nine different Turkish cigarette tobacco indicated that Se concentration is 0.14±0.01 ppm (minimum) and 0.29±0.05 ppm (maximum).

Aydin and Somer detected Se in the presence of Cu ion by ASV.[11] They determined 2×10^{-9} M of Se with a relative standard deviation (n=6) of 3.7%, in solutions containing Cu (up to 10% of concentration of Se). Aydin and Tan studied differential pulse polarographic method for determination of Se in the presence of Cu, Cd and Pb. Suitable buffer medium, effect of scan rate, peak potentials and drop-times were tired in differential pulse polarographic methods.[12] Aydin and Yahaya de-

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scribed a method for specific and accurate determination of Se in a synthetic sample by ASV following seperation of the Se with pentyl alcohol.[13] Here, Cu ions were removed by single extraction and acidic solution was used for the determination of Cu. Selenium was in NaOH solution and it was shown that the minimum recovery of Se was 76%.

Experimental

Apparatus

A home hand-made anodic-stripping analyzer was used for both plating and stripping procedure. The analyzer was connected to "Goerz ABB Metrawatt SE 790" X–Y recorder. The cell was designed with an Ag/AgCl reference electrode, a Pt counter electrode and a wax-impregnated graphite working electrode. A platinum wire is located in a section of Pyrex tube which is contained 2/3 of 1 M NaCl. The reference and counter electrodes are isolated from the sample solution by means of leached glassy (Vycor) plug. The end of working electrode was polished with a fine abrasive and plated with mercury film of 4.51 cm^2. Deaeration and stirring of the solution was done by passing through nitrogen gas at a uniform flow rate.

Reagents

All reagents used were of analytical reagent grade (Merck). Triply distilled deionized water was used for preparation of all solutions and at all other stages of analysis. The stock solution of Hg(II) (0.102 M) was prepared by dissolving $HgCl_2$ in 10 ml hot water which contained 1 ml concentrated HNO_3 and 1 ml concentrated HCl. The stock solution of Pb(II) (0.0367 M) was prepared by dissolving $Pb(NO_3)_2$ in water. Copper nitrate was dried in an oven at 120° C for 1 h to maintain constant hydration, and the stock solution of copper(II) (0.0842 M) was prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ in water. A 0.0209 M stock solution of Se(IV) was prepared by dissolving SeO_2 in hot water. Working solutions were daily prepared by diluting stock solutions with water.

Plating of the wax-impregnated graphite working electrode with mercury

A 0.5 ml of 1.02×10^{-3} M mercury(II) chloride solution was added to 20 ml of Pyrex cell, which contained 5 ml of triply distilled water, then nitrogen gas passed through for several minutes. The electrode was plated for 15 min at −500 mV without passing nitrogen and then plated for a further 15 min while passing nitrogen. During the plating, the cell system was shaken with small hand-shocks to prevent any gas bubbles on the electrode surface. The electrode was plated with mercury for a short period after every five or six strippings. For short plating, 0.25 ml of 1.02×10^{-3} M mercury(II) chloride was added to 5 ml triply distilled water, followed by plating for 5 min.

Procedure

Preparation of samples. Tobacco was removed from the same cigarette brand, dried for 2 h in oven at 110° C to remove any humidity and to obtain a constant weight. The samples were carefully weighed as 2.00 g.

Digestion of samples. Nitric acid and mixtures of $HNO_3 : HClO_4 : H_2SO_4$ (2/2/1), $HNO_3 : HClO_4$ (3/1), $HNO_3 : HClO_4$ (1/1), $HNO_3 : HClO_4 : H_2SO_4 : HCl$ (4/2/2/1) were tried to completely digest samples. Two grams of samples and 10 ml acid or mixture of acids were transferred into a volumetric glassware. It was heated on a hot plate at approximately 300° C until nitrogen oxide fumes are just given off for about 1 h. After the evaporation of nearly all the acid, three separate additions of 2 ml acid or of a mixture of acids were carried out to obtain complete digestion (clear colorless solution). When this was evaporated until nearly dryness, the glassware was cooled for about 2 min and diluted up to 10 ml with water.

Extraction of sample with 1-butanol. Ten milliliters of digested sample solution, 10 ml of 1-butanol and 100 µl of HNO_3 were transferred into a separatory funnel. It was shaken for 1 h and kept overnight. Acidic phase was separated and heated on a hot plate nearly to dryness. After 2 min of cooling time, 10 ml of water was added and this solution was kept as a working sample solution for the determination of Pb and Cu by ASV.

Ten milliliters of 1 M NaOH solution was added into 10 ml alcohol phase. This mixture was shaken for 1 h and kept overnight in separatory funnel. Alkaline phase was taken and heated on hot plate until nearly dryness. After 2 min of cooling time, 10 ml of water was added. This solution was kept for the determination of Se by ASV.

Voltammetric determination. The blank solution was prepared with the addition of 6 µl of $HClO_4$ into 4.5 ml of the blank sample solution in the cell and the pH was approximately 2. After the addition of 0.5 ml sample solution, −850, −600 and −400 mV deposition potentials (*vs.* Ag/AgCl) were applied during the flowing of nitrogen gas through the solution at a uniform flow rate. Five minutes of deposition time was used for Pb, Cu and Se. After the rest period of 30 s, a potential scan of 50 mV/s was applied on a positive direction. The above procedure was repeated after standard additions of Pb(II), Cu(II) and SeO_3^{2-} solutions.

Results and Discussion

Effect of deposition time

Peak currents increase with increments of deposition time but reach a constant level after a certain time for 10^{-8} M of Pb, Cu and SeO_3^{2-}. Deposition potentials of −850, −600 and −400 mV, were applied to Pb, Cu and Se, respectively. A deposition time of 4 – 6 min was needed to reach a maximum peak current for each element. Therefore, the deposition time of 5 min was suited for each element at a pH of approximately 2.

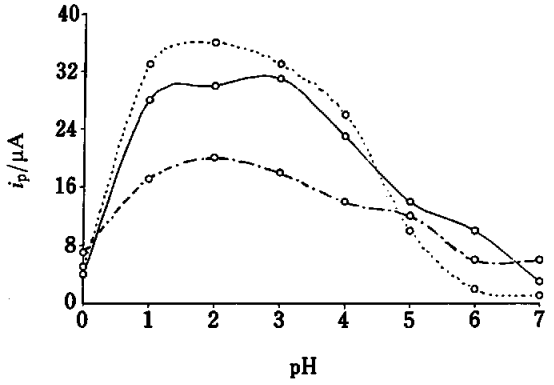


Fig. 1 Effect of pH on peak height for 10^{-8} M Pb, Cu and SeO_3^{2-}. Deposition potentials: −850 mV, −600 mV, −400 mV (*vs.* Ag/AgCl), respectively. Scan rate=50 mV/s. Deposition time=5 min. ·····O····· Pb; -·-O-·- Se; —O— Cu.

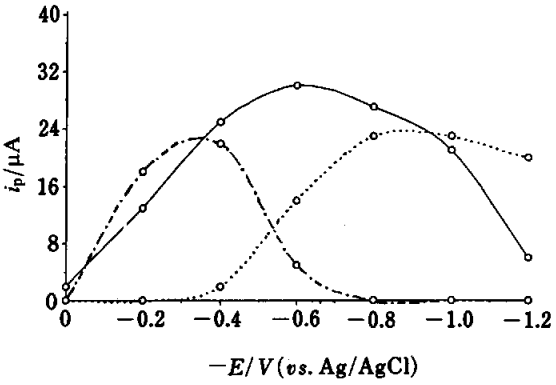


Fig. 2 Effect of deposition potentials on peak height for 10^{-8} M Pb, Cu and SeO_3^{2-}. pH≅2. Scan rate=50 mV/s. Deposition time=5 min. ·····O····· Pb; -·-O-·- Se; —O— Cu.

Effect of pH

The pH of the medium has to be investigated to provide highest sensitivity for the determination of trace quantities of Pb, Cu and Se. Acidic eletrolytes gave much better sensitivity for Pb, Cu and SeO_3^{2-} than neutral or basic electrolytes. Figure 1 shows the dependence of peak currents (i_P) of Pb, Cu and SeO_3^{2-} on pH. Each point represents the average of five determinations. A pH of about 2 was chosen for the determination of each element. For the optimization of pH dependence 10^{-8} M Pb, Cu and SeO_3^{2-} were tired.

Effect of deposition potential

The effect of deposition potentials on peak currents was examined over the range of 0.0 to −1.2 V (Fig. 2). Dependence of deposition potentials on peak current at concentrations of 10^{-8} M Pb, Cu and SeO_3^{2-} was studied in a solution of pH≅2. Peak currents showed appropriate relative increments with standard additions.

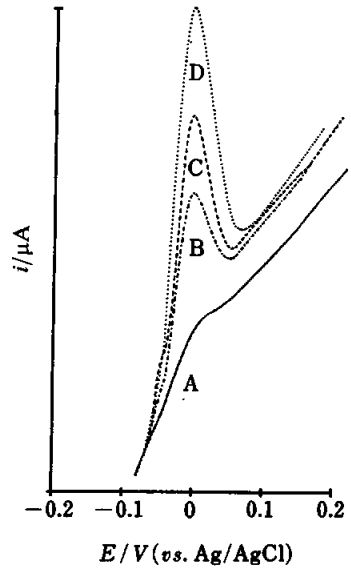


Fig. 3 ASV peak of Cu in A brand tobacco after extraction with 1-butanol. A) 4.5 ml of water+0.5 ml of blank solution+6 μl of $HClO_4$; B) A+0.5 ml of sample solution; C) B+100 μl of 8.42×10^{-6} M Cu^{2+} solution; D) C+100 μl of 8.42×10^{-6} M Cu^{2+} solution. Deposition potential= −600 mV, Deposition time=5 min, Scan rate=50 mV/s, pH≅2 in $HClO_4$.

Each point represents the average of five determinations. The maximum sensitivity was achieved at the deposition potentials of −850, −600 and −400 mV (*vs.* Ag/AgCl) for Pb, Cu and SeO_3^{2-}, respectively.

The cigarette tobacco samples were labeled as A, B, C and D to avoid commercial identification. ASV voltammograms of Cu in A brand Turkish cigarette tobacco before extraction procedure showed very broad and irregular peaks because of interference of Se in the sample solution. Selenium could not be detected without extraction with 1-butanol. Specific and accurate determination of Se in various samples by ASV requires the separation of this element from interferences.[14,15]

After extraction of 10 ml of digested sample solution (as given in procedure) with 1-butanol, acidic phase was studied for the determination of Cu and Pb. Removal of Se into alcohol phase made the determination of Cu in the tobacco sample more proper, so that peaks were sharper, as shown in Fig. 3. Voltammograms of Pb also showed irregular and broad peaks in non-extracted samples. After extraction procedure, those undesired effects were overcome and standard additions of Cu or Pb gave definite peak currents, which made quantitative determination of those elements possible.

Figure 4 shows Se determination in A brand Turkish cigarette tobacco sample. As given in the general procedure Se which had been taken into 10 ml of alcohol phase was back extracted into 10 ml of 1 M NaOH solution. It was evaporated until nearly dry and neutralized with HNO_3, followed by dilution with water

Table 1 Determination of Pb and Cu in A brand of Turkish cigarette tabacco digested with several acid and acid mixtures by ASV

Solvent	Pb, ppm		Cu, ppm	
	$\bar{x}\pm s(n)$	$\bar{x}\pm ts/\sqrt{n}$	$\bar{x}\pm s(n)$	$\bar{x}\pm ts/\sqrt{n}$
HNO_3–$HClO_4$ (3/1)	1.9±0.2 (7)	1.9±0.16	3.0±0.3 (8)	3.0±0.21
HNO_3–$HClO_4$ (1/1)	2.2±0.1 (5)	2.2±0.11	2.7±0.2 (7)	2.7±0.16
HNO_3	0.6±0.2 (7)	0.6±0.16	0.6±0.1 (5)	0.6±0.11
HNO_3–$HClO_4$–H_2SO_4 (2/2/1)	N.D.	N.D.	4.4±0.2 (6)	4.4±0.18
HNO_3–$HClO_4$–H_2SO_4–HCl (4/2/2/1)	N.D.	N.D.	3.7±0.1 (6)	3.7±0.09

t: confidence interval (90%). n: number of experiments. N.D.: not determined.

to 10 ml. ASV voltammograms of this sample showed that two new peaks appeared at about −20 mV and +60 mV. The former corresponds to Cu which was partially taken into alcohol phase during extraction procedure, but falls in to the range of $1.8\leq r\leq 11$, where r is Cu/Se concentration ratio.[11] The peak at +60 mV shows Cu-Se intermetallic compound peak which increased proportionally with standard addition of SeO_3^{2-}, while the Cu peak at −20 mV decreased. The interference of Cu ion may occur through the formation of an intermetallic compound with Se:

$$H_2SeO_3 + 4H^+ + Hg + 6e^- + Cu^{2+} \rightleftharpoons Se(Hg)Cu + 3H_2O \quad (1)$$

The formation of such a compound resulted in a positive shift of the peak on the anodic stripping voltammogram. The peak at about +60 mV corresponds to the oxidation of Se(Hg)Cu intermetallic compound (Fig. 4). Selenium in the cigarette tobacco was determined in this range where Cu/Se concentration range was $1.8\leq$Cu/Se≤ 11. Copper distributed in both phases was the total amount and is given as total Cu content of tobacco samples. The extraction reaction occurring in acidic media is:

$$SeO_2 \text{ or } H_2SeO_3 + 2ROH \rightleftharpoons (RO)_2SeO + H_2O \quad (R = \text{alkyl}) \quad (2)$$

Acid and acid mixtures for the determination of Pb, Cu and Se were tried in A brand of Turkish cigarette tobacco (Table 1) and the selected mixtures are used in further analysis of B, C and D brand of tobaccos. All the results in Tables were obtained by the extraction procedure which was given above. Table 1 shows the concentration of Pb and Cu in A brand of Turkish cigarette tobacco which has been digested in acid and acid mixtures. The results summarized here indicated that the different acid mixtures showed different powers to decompose tobacco samples. The tobacco sample digested with HNO_3 showed relatively low concentration of Pb and Cu, but HNO_3–$HClO_4$ (1/1) was more effective to decompose tobacco samples. This was due to the incomplete decomposition of tobacco samples and the low boiling point of HNO_3. Effect of extraction with 1-butanol resulted in clear and colorless solution and gave well-defined peaks. When H_2SO_4 was used in acid mixtures, it was impossible to obtain Pb peak just because of precipitation of lead sulfate. A well-defined ASV peak for Cu was obtained with the digestive mixture of HNO_3–$HClO_4$–H_2SO_4 (2/2/1).

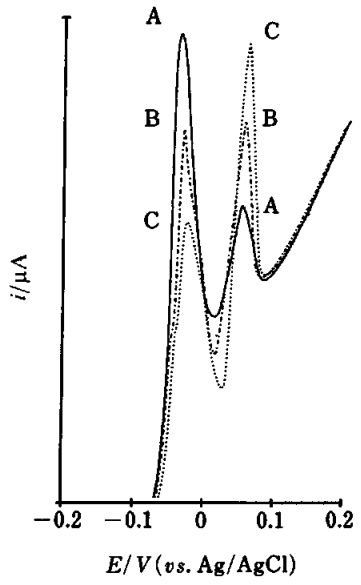


Fig. 4 ASV peak of Se in A brand tobacco after extraction with 1-butanol: A), ——, 4.5 ml of water +0.5 ml of sample solution+6 μl of $HClO_4$; B), —·—, A+100 μl of 2.09×10^{-6} M SeO_3^{2-}; C), ·····, B+100 μl of 2.09×10^{-6} M SeO_3^{2-}. Deposition potential=−400 mV, Deposition time=5 min, Scan rate=50 mV/s, pH≅2 in $HClO_4$.

Selenium could only be determined in A brand of Turkish cigarette tobacco digested in HNO_3–$HClO_4$–H_2SO_4 (2/2/1) followed by extraction with 1-butanol. Because of the relatively high concentration of Cu in tobacco, it was impossible to determine selenium without reducing the amount of Cu from the sample solution by using 1-butanol extraction. This made it possible to determine Se in the presence of Cu in the range of $1.8\leq r\leq 11$, where r is Cu/Se concentration ratio.[11]

Nitric acid–perchloric acid (1/1) digestive acidic mixture is preferable for the voltammetric analysis of

Table 2 Determination of Pb, Cu and Se in Turkish and American cigarette tobacco by ASV

Tobacco sample	$\bar{x} \pm s(n)$, ppm			$\bar{x} \pm ts/\sqrt{n}$, ppm		
	Pb	Cu	Se	Pb	Cu	Se
A brand Turkish cigarette tobacco	2.2±0.1 (5)	4.4±0.2 (6)	0.12±0.01 (8)	2.2±0.11	4.4±0.18	0.12±0.007
B brand Turkish cigarette tobacco	1.5±0.1 (8)	0.9±0.1 (8)	N.D.	1.5±0.07	4.4±0.07	N.D.
C brand USA cigarette tobacco	2.8±0.2 (7)	3.0±0.1 (5)	N.D.	2.8±0.16	3.0±0.11	N.D.
D brand USA cigarette tobacco	1.5±0.1 (6)	6.5±0.3 (6)	N.D.	1.5±0.09	6.5±0.27	N.D.

t: confidence interval (90%). n: number of experiments. N.D.: not determined. Acid mixtures used to digest: Pb, HNO_3–$HClO_4$ (1/1); Cu, Se, HNO_3–$HClO_4$–H_2SO_4 (2/2/1).

Pb in tobacco, while HNO_3–$HClO_4$–H_2SO_4 (2/2/1) is better for Cu and Se. Analytical results were shown in Table 2. Selenium could not be dedected in American cigarette tobacco. This method can be used to determine Pb, Cu and Se in cigarette tobacco after reducing interfering substances by 1-butanol extraction. The relative standard deviations are 4.5% at the concentration of 2.2 ppm Pb (n=5) and 4.4 ppm Cu (n=6), and 8.3% at 0.12 ppm Se(IV) (n=8).

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