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Determination of lead and copper in chewing gum samples by electrothermal-flame atomic absorption spectrometry using various chemical modifiers and arsenic by hydride generation

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Abstract

Lead and copper in chewing gum samples were determined by electrothermal atomic absorption spectrometry (ETAAS) with Zeeman background correction using various chemical modifiers and by flame atomic absorption spectrometry (FAAS) using 2% m/v ammonium pyrrolidine dithiocarbamate (APDC) complexing reagent in methyl isobuthyl keton (MIBK). Arsenic in samples was determined by hydride generation atomic absorption spectrometry (HGAAS). In order to decrease the interferences in sample matrix by ETAAS, Pd, Pt, W, Mo, Mg, PO_4^{3-}, their mixtures and W + Pd + tartaric acid (TA) have been tested as matrix modifiers in sample solutions. Modifiers have been compared in terms of pyrolysis temperature, atomization and background profiles of analytes. W + Pd + TA modifier mixture found as preferable was used for the determination of analytes by ETAAS. The reliability of the procedures was verified by analyzing several certified reference materials (CRMs). Detection limits of Pb and Cu determined by ETAAS and As determined by HGAAS were 1.2, 0.8 and 3.0 μg l^{-1} for Pb, Cu and As, respectively. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Lead; Copper; Arsenic; Chewing gum; ETAAS

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1. Introduction

In recent years, the determination of arsenic, lead and copper in clinical and biological materials, foods and beverages have been considerable interest because of the well-documented toxicity of them. These elements in foodstuffs are of great importance since they play a toxic and a definitive role in the intrinsic mechanisms regulating vital biological process (Shang & Hong, 1997). Overall exposure to lead is of public health concern because of several hazardous effects that may occur to humans. Lead poisoning may provoke irritability, anorexia, malaise and headache. Intoxication progress may lead to attacks of abdominal pain until coma and death. Approximately 80% of total human lead intake is supplied by diet. Thus, there is a current interest in the determination of this element in foods and foodstuffs (Lima, Krug, & Arruda, 1998). In addition to the analyses of human diary diet, lead is analyzed in whole blood, urine, hair and teeth as the indicators of lead exposure in most country (Spevackova & Smid, 1999).

Since food is a potential source of lead and copper in the diet, there is an ever increasing interest in lowering the acceptable limits especially for regular consumed foods. Chewing gum is not a food, but, it is especially consumed by children and pregnant women with chewing by teeth in the mouth. It also contains an important level of As, Pb and Cu (Dietz, 1990; Kupchella & Syty, 1980). Childhood lead poisoning is a major public health problem in many countries (Zhou, Parsons, Aldous, Brockman, & Slavin, 2001). The Committee on Food Chemical Codex sets the limits for heavy metals and other chemicals. The current limits for lead, heavy metals (as Pb) and arsenic are not more than 3 mg kg^{-1}, 0.002% and 3 mg kg^{-1} (this specification was deleted, but new value not known), respectively. In Turkish

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standard (TS 8000, 1996), the permissible level of Pb, As and Cu are 1.0, 1.0 and 10.0 mg kg^{-1}, respectively.

Matrix modification is usually necessary in electrothermal atomic absorption spectrometry (ETAAS) to remove matrix effects. The chemical modifier stabilizes the analyte to higher pyrolysis temperatures and makes possible the removal of interferents before analyte atomization. The chemical modifiers should be available in high purity, not contain the analyte elements and the analyte elements should be stabilized to as high a pyrolysis temperature as possible, to allow volatilization of bulk of contaminants for an acceptable chemical modification. In addition, the modifier should not be markedly deposited in a graphite tube since it may change the conductivity of the tube and also reduce the lifetime (Bermejo-Barrera, Barcielo-Alonso, Moredo-Pineiro, Gonzalez-Sixto, & Bermejo-Barrera, 1996). The choice of the best chemical modifier for a specific sample is one of the most difficult problems in ETAAS if it includes complex matrix and trace level of volatile elements. In recent years, a great number of substances have been investigated as chemical modifier for lead and copper. The most common substances are $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, Pd + Mg, Pd, Mo, Mo + Pd, W, W + Pd and etc. (Acar, Turker, & Kılıç, 1997, 1998; Bruhn, Piwonka, Jeradino, Navarrete, & Maturana, 1987; Correia, Oliveira, & Oliviera, 2000; Manning & Slavin, 1983; Slaveykova & Tsalev, 1990; Tsalev & Slaveykova, 1992a; Welz, Schlemmer, & Mudakavi, 1992) for lead. Platinum group metal modifiers are more effective and universal compared with other modifiers (Tsalev & Slaveykova, 1992b; ; Tsalev, Slaveykova, & Mandjuckov, 1990; Volynsky & Wennrich, 2001). Organic analytical reagents have been shown to be effective (due to the change in the composition of the gas phase in the atom reservoir) in reducing the matrix effects and improving the sensitivity in ETAAS. Besides offering the thermal stability of the analyte element, the control of the chemical environment is also an important function of a chemical modifier. The proposed model of the modifier action was complexing the analyte by ascorbic acid (Tsai, Shiue, & Chang, 1997). The addition of ascorbic acid and tartaric acid caused the enhancement of copper signals because of the increasing the population of copper atoms. ETAAS is commonly used for the determination of these elements. But, the problem of the method is that severe interferences attributed to the matrix effect are usually encountered. Today, many matrix effects have been successfully eliminated from graphite furnace when samples are atomized on the L'vov platform and chemical modifiers, such as Pd, are used (Delafuente, Guerro, & Juárez, 1995).

The aim of this study was to develop an interference-free method for the determination of low concentrations of lead and copper, and also arsenic in chewing gum by electrothermal, flame and hydride generation atomic absorption spectrometry. There are a few studies about the determination of trace elements in chewing gum, but any of them does not include the matrix modification studies as mixed modifiers (Vinas, Campillo, Garcia, & Cordoba, 1994; Zaidi, Arif, Fatima, Ahmad, & Qureshi, 2000).

2. Materials and methods

2.1. Apparatus

All measurements were carried out using a Hitachi Model 180/080 flame and graphite furnace (Hitachi Model 180/078) atomic absorption spectrometer equipped with a Zeeman-effected background corrector, an automatic data processor (Hitachi 180/0205) and hydride generation system (Hitachi HFS-2). The radiation sources were hollow cathode lamps for Pb, Cu and As (Super lamp, Photron, P/N-3529). The instrumental parameters were set as recomended by the manufacturer. Hitachi pyrolytic graphite coated tubes (P/N 180/7444) were employed in tube-wall atomization to measure absorbance values by using integrated mode throughout the works. A 20 ml volume of sample solution was injected into the atomizer by an auto sampler (Hitachi 170/0126). Argon was used as the purge gas and interrupted during atomization. A Varian Model 9176 recorder was used to obtain atomization and background profiles in 20 mV/FS span. The optimized graphite furnace temperature programme for Cu and Pb is given in Table 1.

2.2. Reagents

Stock standard solutions of As, Cu, Pb and Mg (1.0 g l^{-1} each) were obtained from BDH. Each test solution and reagents were prepared with deionized water obtained by using ultra pure water system (Barnstead, P/N-1161, $\geqslant 18$ MΩ Cm) and diluted with 0.2% (v/v) HNO_3 (Merck) solution as required immediately before use. All reagents were of analytical grade. Stock standard solutions of Pd and Pt (2.0 g l^{-1} each) in 15% HCl were prepared from palladium chloride (Merck) and ammonium hexachloroplatinate (VI) (Aldrich), respec-

Table 1
Optimized furnace temperature programme for the determination of Pb and Cu in samples

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (ml min^{-1})
Drying	50–120	30	20	270
Pyrolysis	120–Var[a]	40	40	270
Atomization	2000/2700	–	7	0
Cleaning	Var[b]	–	5	270

[a] Varied according to modifier.

[b] 2650 °C for Pb, 2800 °C for Cu.

tively. A tungsten acidic solution containing 0.4% (m/v) W (V) was prepared from W powder (Eimer and Amed) by dissolving in hydrogen peroxide (35% m/m, Merck). A molybdenum solution containing 0.4% (m/v) of Mo (VI) was prepared from molybdic acid (H_2MoO_4, Merck) by dissolving in 1% (v/v) ammonia (Merck) solution. A tartaric acid (TA; 4% m/v) solution was prepared daily. A diammonium hydrogen phosphate (Merck) solution containing 2.0% (m/v) was prepared with deionized water. Ten grams of sodium tetrahydroborate (III) ($NaBH_4$, Fluka) and 1 g of sodium hydroxide (NaOH, Merck) were dissolved in deionized water and diluted to 100 ml. Potassium iodide (20% m/v; KI, Merck) was prepared by dissolving and mixing strongly in deionized water. Methyl isobutyl keton (MIBK, Merck) and 2% m/v ammonium pyrrolidine dithiocarbamate (APDC, Merck) complexing reagent purified by MIBK were used.

2.3. Preparation of sample solution

New glasswares and crucibles, which are suitable for Pb and Cu were used throughout this work to reduce the risk of contamination. They were initially cleaned with detergent, followed by rinsing with deionized water three times and dried in an oven. Also new disposable plastic pipet tips were used after soaking in acidic solution, rinsing and followed by drying as similar above mentioned.

Chewing gum samples obtained from the manufacturer were dissolved according to Fetterolf and Syty (1979). A portion (4.0–5.0 g) of a sample was accurately weighed into a crucible and heated gently in a flame until dry. The sample was placed into a cold muffel furnace, gradually heated up to 450 °C and waited approximately 4 h at this temperature for pyrolysis. Upon cooling, 1.5 ml of concentrated nitric acid was added drop by drop and sample was heated slowly on a sandy bath until dry. The residue was then ashed again at 450 °C for 2 h. After cooling, 1 ml of concentrated nitric acid was added and heated in a water bath until the sample was dissolved completely. After decomposition, the final solution was transferred into a 25 ml volumetric flask by washing the interior surface of crucible with 0.01 mol l^{-1} HNO_3 three times and diluting to the mark with deionized water. To check the concentrations of analytes in the samples and to control the analyte loss during the dissolution, different concentrations of aqueous analyte standard solutions were added into other chewing gum samples after finishing to get doughy in a flame. These samples of the same brand were separated into two parts whether they contained sugar or not. They were dissolved according to the method described earlier.

An appropriate amount of a biological CRM was accurately weighed into a 50 ml acid-cleaned PTFE beaker and dissolved in concentrated nitric acid and hydrogen peroxide according to the methods described in previous studies (Miller-Ihli, 1996; Prohaska, Pomazal, & Steffan, 2000).

In all instances, blanks were prepared with the same reagents used under the same conditions in order to check for possible contamination during the preparation of the sample solution.

3. Results and discussion

3.1. Sample dissolution

Neither wet ashing alone nor dry ashing alone were found to oxidize the samples adequately to permit complete dissolution. A combination of the wet and the dry ashing procedures yielded a suitable sample preparation technique. Perchloric acid is known to be incompatible with the analysis of the sample digest by atomic absorption with electrothermal atomization. Sulfuric acid is undesirable because of its high boiling temperature and the possibility of adsorption of lead on some insoluble particles, which form in the presence of H_2SO_4 (Fetterolf & Syty, 1979). Therefore, these acids were not used in dissolving the samples and a combination of wet and dry ashing procedures with nitric acid was applied to dissolve the chewing gum samples.

3.2. Thermal stabilizing effects of modifiers on Pb and Cu

The stabilizing effects of chemical modifier mixtures such as Mo + Pd, Pd + Pt and Pd + W and their single components on Pb and Cu in samples and aqueous standard were investigated systematically. In this study, mass and mass ratio of these modifier components found in previous works (Acar et al., 1997, 1998) were used. By this purpose, optimum graphite furnace temperature programme for the determination of Pb and Cu in chewing gum samples was determined by changing temperatures, ramp and hold times in the presence of chemical modifiers or their mixtures and given in Table 1. Thermal pretreatment curves for Pb and Cu in aqueous standards and in samples with the presence or absence of modifiers were plotted as absorbance versus pyrolysis temperature. Pyrolysis curves for Pb are shown in Figs. 1 and 2 as an example. As can be seen in Fig. 1, the pyrolysis curves for 50 μg l^{-1} Pb in aqueous standard and in 20 μg l^{-1} standard Pb plus a chewing gum sample solution, which contain a different matrix, were obtained in the absence of a modifier. The absorbance values of Pb in sample matrix were constant up to 900 °C while absorbance values of Pb in aqueous standard was decreasing above 700 °C. As shown in Fig. 2b, when the pyrolysis temperature of Pb in sample was increased up to about 1250 °C in the presence of W + Pd modifier mixture, it was observed that mass of analyte was not lost. Atomization temperatures of analytes were kept constant at 2000 °C for Pb and 2700 °C for Cu as given in Table 1. It was observed that stabilizing effects of single and mixed modifiers on analytes in aqueous standards and samples studied were similar with the literature (Acar et al., 1997, 1998; Havezov, Detcheva, & Rendi, 1995; Slaveykova & Tsalev, 1990; Tsalev & Slaveykova, 1992b). By using the same amount of analyte in samples with various modifier mixtures, different absorbance values were found and they may be based on the reactivities of the modifiers (Ni & Shan, 1987). In this study, the effect of Ti + Citric acid modifier mixture on aqueous Pb standard has been examined since the chewing gum sample may be contain titanium and citric acid and they can be affected as matrix modifiers but, pyrolysis temperature of standard Pb was found as 750 °C and this modifier mixture was not used.

The effects of organic acids such as ascorbic acid, oxalic acid, tartaric acid and citric acid on Pb in aqueous standard and samples have been studied as described in previous literatures (Acar et al., 1997; Byrne, Chakrabarti, Gilchrist, Lamourex, & Bertels, 1993; Havezov et al., 1995). The pyrolysis temperature of Pb in sample was found as 1300C in the presence of W + Pd + TA modifier mixture and similar stabilizing effect of TA on standard Pb as described in previous work (Acar et al., 1997) was observed. The chewing gum samples contain some organic acids such as citric acid and maleic acid. The aim of addition of TA together with mixed modifiers to working standard solutions and to the sample solutions was also to provide the similarity between them in the determination of analytes. By the addition of TA as a reducing agent together with mixed modifiers, radicals produced from hydrogen, organic acids and other substances at the surface of the tube might react with chloride or nitrate in the aqueous sample matrices to form $HCl_{(g)}$ or $HNO_{3\,(g)}$, which is removed from the tube at low temperatures (Russeva, Haverov, & Detcheva, 1993).

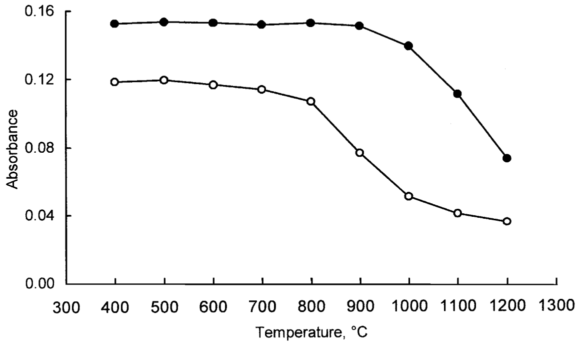

Fig. 1. Pyrolysis curves for Pb in aqueous solution (50 μg l^{-1}) (○); in chewing gum sample plus aqueous solution (20 μg l^{-1} Pb) (●).

3.3. Effects of modifiers on the atomization profiles of analytes

One of the advantages of chemical modification is that the atomization signals become symmetrical and shifted to higher pretreatment temperatures and appearance times for volatile elements (Acar, Kılıç, & Tüker, 1999; Shan & Wen, 1995). In order to demonstrate how the modifiers studied affect the atomization and background absorption profiles of Pb and Cu in samples, a comparative study was conducted. Atomization and background profiles of Pb in samples obtained with and without modifiers are shown in Fig. 3 as an example. As can be seen in Fig. 3, higher background and lower atomization signals were observed in the absence of a modifier or in the presence of Mo or $Mg + PO_4^{3-}$ modifier mixture in chewing gum samples. Therefore, Mo and $Mg + PO_4^{3-}$ were not preferred as chemical modifiers to determine Pb and Cu in samples. When Pd + W + TA was used, it was observed that atomization signal of analyte increased as the background absorption decreased. By using this modifier mixture, signal/background ratio increased when compared with other modifiers (Fig. 3). Therefore, Pd + W + TA mixture was found to be suitable for the determination of Pb and Cu in chewing gum samples by direct calibration method or standard addition method.

3.4. Analytical conditions and calibration

The determination of Pb and Cu in chewing gum sample solutions was performed by ETAAS using W + Pd + TA modifier mixture and flame atomic absorption spectrometry (FAAS) using APDC complexing reagent in MIBK extraction solvent. Arsenic determination was also performed by using hydride generation FAAS. The calibration graph method based on the single element solution and standard addition technique was used for the determination of analytes. Calibration against to standard solutions in the presence of W + Pd + TA or APDC in MIBK was performed for Pb and Cu by using instrumental and optimum parameters such as furnace temperature programme (Table 1) and pyrolysis temperatures. All calibration graphs were linear and correlation coefficients (r) were about >0.999. Analytical ranges of analytes were 10–100 μg l^{-1} for Pb and 10–160 μg l^{-1} for Cu with the W + Pd + TA modifier mixture or with the solvent extraction technique and 5–50 μg l^{-1} for As in HGAAS.

Detection limits (LOD, 3σ-criterion) and characteristic mass (m_0) of analytes in blank solutions were determined by ETAAS and HGASS. Detection limits were 1.2, 0.8 and 3.0 μg l^{-1} for Pb, Cu and As, respectively. Characteristic masses of analytes were 16.4, 7.2 and 16.4 pg for Pb, Cu and As, respectively.

3.5. Determination of Cu, Pb and As in chewing gum samples and CRMs

The recovery tests for analytes in samples by FAAS using APDC complexing reagent in MIBK and by ETAAS using W+Pd+TA modifier mixture were studied. In the determination of Pb and Cu in samples by FAAS and ETAAS, direct calibration graph and standard addition techniques were used separately. In the determination of analytes by FAAS, APDC in MIBK was also added to the Pb and Cu working standard solutions to resemble samples and standards to each other in calibration graph and standard addition techniques. In the determination of analytes by ETAAS, Pd+W+TA was added to the working standard solutions and samples in both the direct calibration graph and standard addition techniques. The concentration results of analytes in samples found by these two methods and recovery test results obtained are given in Tables 2 and 3. As can be seen in Tables 2 and 3, results obtained by FAAS using APDC in MIBK and by ETAAS using Pd+W+TA are approximately the same. It was observed that extraction of Pb and Cu from sample solutions to APDC in MIBK phase was about 100%. Concentrations of Pb and Cu in samples spiked with aqueous standards were determined by ETAAS using Pd+W+TA modifier mixture. The recoveries were calculated from the concentrations

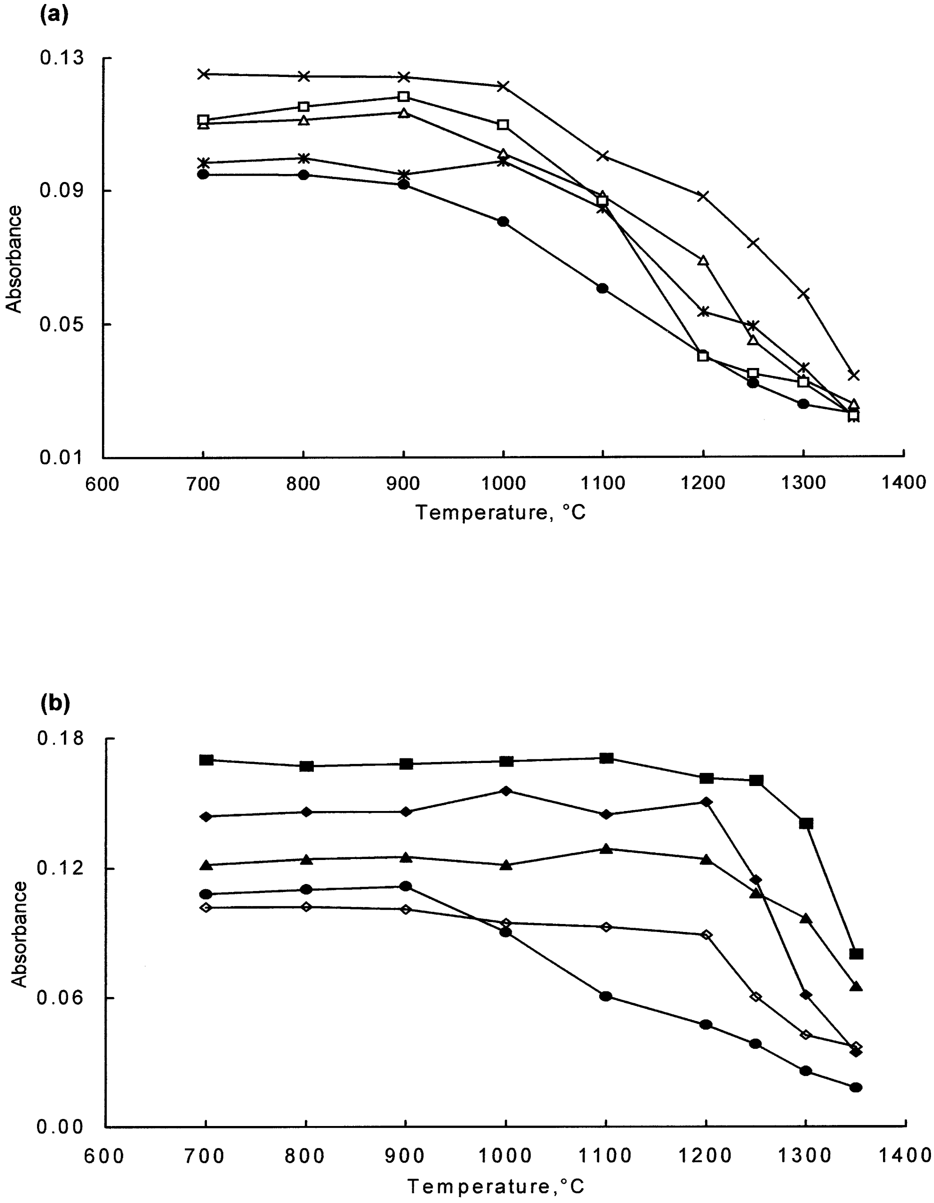

Fig. 2. (a) Effect of single modifiers on the pyrolysis temperature of lead in sample S; no modifier (•), Mo (△), Pd (x), Pt (*), W (□). (b) Effect of mixed modifiers on the pyrolysis temperature of lead in aqueous standard (Std); Std+Mo+Pd (▲); in sample S without modifier (•); with modifier S+Pd+Pt (◇); S+Mo+Pd (◆); S+W+Pd (■).

obtained by APDC in MIBK and the concentrations found by ETAAS. The ranges of analyte recoveries are from 98.8 to 101.0%. As a result of this, lead and copper in chewing gum samples were analyzed by using these two methods in order to check the concentrations of elements. Duplicate dissolution was made for each chewing gum sample. Ammonium pyrrolidine dithiocarbamate (APDC) in MIBK was added to a first series of chewing gum sample solutions to extract the Cu and Pb from samples into MIBK phase and they were analyzed by flame atomic absorption spectrometer (FAAS). Cu and Pb in the second series of sample solutions were determined with ETAAS by using Pd + W + TA modifier mixture. The results were given in Table 4.

Arsenic was determined by using hydride generation FAAS because its concentration level in chewing gum samples was too low and it was not determined directly with ETAAS. The operating parameters of the hydride generation FAAS system for As were set as recommended by manufacturer. The chemicals such as hydrochloric acid and sodium hydroborate, etc., required for hydride generation were prepared and As was analyzed in samples by direct calibration graph method as shown in Table 4.

As chewing gum samples with certified contents were not available, the methods were validated by using various biological certified reference materials (NIST CRM). Table 5 shows that lead, copper and arsenic were successfully determined in solutions prepared from three biological CRMs and that good agreement with the certified values was obtained.

4. Conclusions

Determination of lead and copper in chewing gum samples by ETAAS using W + Pd + TA and FAAS using APDC in MIBK solvent extraction technique was studied. Obtained results by ETAAS and FAAS were compared and similar results were observed. Arsenic was determined by HGAAS. The analytical problems arising from the sample matrix can be controlled by ETAAS with Zeeman effected background correction using W + Pd + TA modifier mixture. The characteristic

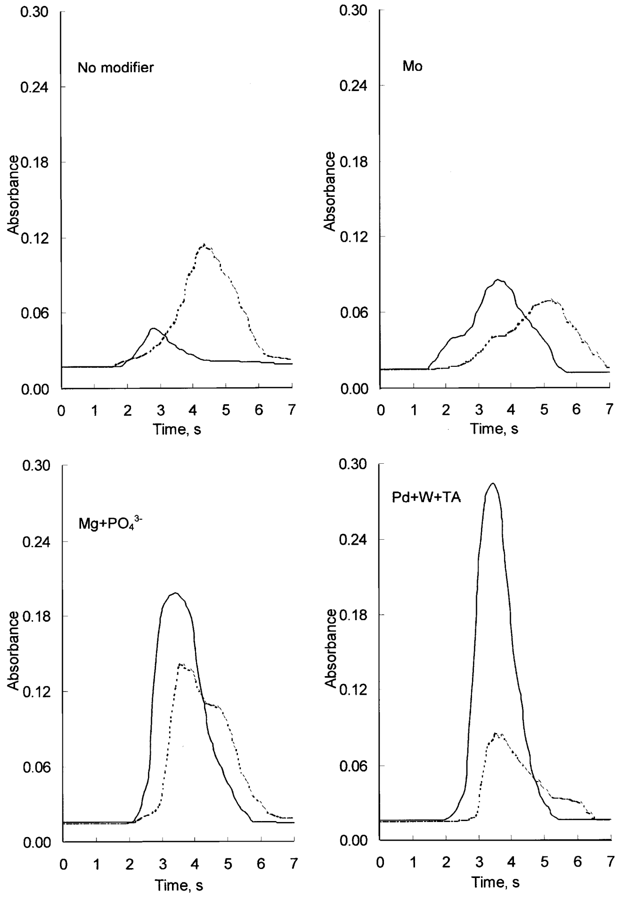

Fig. 3. Comparison of atomization and background profiles of Pb in sample with different matrix modifiers by using integrated mode (—, atomization; - - - -, background).

Table 2
Recovery tests of Pb in chewing gum samples

Concentration (µg g^{-1})					Recovery (%)
Sample[a]		Spiked	Total	Found[a]	
APDC + MIBK	ETAAS				
		0.39	1.24	1.23±0.13	99.19
0.85±0.08	0.83±0.09	0.43	1.28	1.29±0.14	100.78
(No sugar)		0.86	1.71	1.69±0.11	98.83
		0.38	0.97	0.98±0.06	101.03
0.59±0.04	0.60±0.07	0.55	1.14	1.15±0.09	100.88
(Contains sugar)		0.76	1.35	1.36±0.11	100.74

[a] Mean of 10 replicate measurements of one solution with 95% confidence level, $\overline{X} \pm ts/\sqrt{n}$.

Table 3
Recovery tests of Cu in chewing gum samples

Concentration (µg g^{-1})					Recovery (%)
Sample[a]		Spiked	Total	Found[a]	
APDC + MIBK	ETAAS				
		0.39	2.43	2.42±0.05	99.59
2.04±0.05	1.99±0.08	0.97	3.01	3.02±0.11	100.33
(No sugar)		1.94	3.98	3.96±0.15	99.50
		0.39	3.55	3.53±0.12	99.44
3.16±0.03	3.21±0.02	0.97	4.13	4.11±0.16	99.52
(Contains sugar)		1.94	5.10	5.04±0.21	98.82

[a] Mean of 10 replicate measurements of one solution with 95% confidence level, $\overline{X} \pm ts/\sqrt{n}$.

Table 4
Results for the analysis of chewing gum samples

Sample no.	Concentration[a] (µg g^{-1})				
	Pb		Cu		As
	APDC +MIBK	ETAAS	APDC +MIBK	ETAAS	Hyride
1	0.78±0.01	0.77±0.01	4.60±0.04	4.50±0.01	0.08±0.02
2	0.83±0.02	0.83±0.02	4.93±0.11	4.94±0.11	<0.005
3	0.77±0.02	0.76±0.02	4.67±0.11	4.73±0.12	0.12±0.02
4	0.50±0.01	0.50±0.02	2.86±0.05	2.75±0.09	0.09±0.01
5	0.77±0.05	0.74±0.02	5.23±0.33	4.50±0.09	<0.005
6	0.36±0.02	0.36±0.02	2.08±0.12	2.13±0.07	0.14±0.01
7	0.77±0.03	0.78±0.01	4.41±0.21	4.32±0.20	<0.005
8	0.81±0.04	0.79±0.01	5.00±0.27	5.16±0.05	<0.005
9	0.58±0.03	0.60±0.02	3.72±0.22	3.69±0.13	0.17±0.03
10	0.70±0.03	0.67±0.03	4.23±0.33	4.25±0.30	0.09±0.03
11	0.39±0.03	0.38±0.01	2.35±0.20	2.19±0.01	<0.005
12	0.52±0.02	0.51±0.01	3.63±0.13	3.05±0.04	<0.005
13	0.87±0.04	0.85±0.01	5.36±0.21	5.38±0.01	<0.005
14	0.38±0.01	0.38±0.02	2.16±0.03	1.72±0.13	0.23±0.04
15	0.33±0.02	0.34±0.01	2.02±0.13	1.60±0.01	0.27±0.03
16	0.44±0.04	0.44±0.01	2.60±0.16	2.32±0.05	0.18±0.01
17	0.86±0.04	0.88±0.03	4.93±0.13	4.66±0.29	<0.005
18	0.72±0.03	0.72±0.02	4.69±0.20	4.64±0.12	0.09±0.02

[a] Mean of 10 replicate measurements of one solution with 95% confidence level, $\overline{X} \pm ts/\sqrt{n}$.

Table 5
Results for the analysis of certified reference materials

CRM[a]	Content	Concentration[b] (µg g^{-1})				
		PB		Cu		AS
		APDC+MIBK	ETAAS	APDC+MIBK	ETAAS	Hydride
NIST CRM 1573a	Certified	–		4.70±0.14		0.112±0.004
Tomato leaves	Found	–		4.51±0.18	4.68±0.16	0.110±0.03
NIST CRM 1515	Certified	0.470±0.024		5.64±0.24		0.038±0.007
Apple leaves	Found	0.453±0.017	0.472±0.019	5.53±0.19	5.65±0.21	0.040±0.006
NIST CRM 1570a	Certified	0.20[c]		12.2±0.6		0.068±0.012
Spinach leaves	Found	0.17±0.01	0.18±0.01	11.3±0.4	12.4±0.5	0.066±0.009

[a] Mean of ten replicate measurements of one solution with 95% confidence level, $\overline{X} \pm ts/\sqrt{n}$.

[b] NIST CRM, National Institute of Standards and technology, certified reference material.

[c] This value is not certified; it is information value only.

mass (m_0) of analytes obtained were 16.4, 7.2 and 16.4 pg for Pb, Cu and As, respectively. The results obtained for the analytes determined in CRMs are satisfactory for the reliability of the methods. Therefore, ETAAS using W+Pd+TA, FAAS using APDC in MIBK and HGAAS can be applied for the determination of lead, copper and arsenic at lower concentrations in such samples as chewing gum, food and biological, etc., samples.

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