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Determination of Lead, Copper, Iron and Zinc Levels in Fruit Jams, Nectars, Juices and Beverages by Electrothermal and Flame Atomic Absorption Spectrometry

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Abstract

Lead, copper, iron and zinc levels in fruit jams, nectars, juices and beverages were determined by electrothermal atomic absorption spectrometer (ETAAS) and flame atomic absorption spectrometer (FAAS) with a Zeeman-effect background corrector. Ni + Ir + NH_4NO_3 modifier mixture was used for the direct determinations of copper and lead in samples by ETAAS. Optimum mass and mass ratios of modifiers obtained were 30 µg Ni, 4 µg Ir, 8 µg NH_4NO_3. Pyrolysis and atomization temperatures, atomization and background profiles, characteristic masses and detection limits of Cu and Pb in samples were obtained. Detection limits and characteristic masses of Cu and Pb obtained by ETAAS in tomato leaves 1573a solution (0.8% m/v) were 21 µg kg^{-1} and 14 pg for Cu, and 1.8 µg kg^{-1} and 21 pg for Pb, respectively. Iron and Zn contents in samples were determined by FAAS. Detection limits of Zn and Fe obtained in tomato leaves 1573a solution (0.8% m/v) were 1.2 and 3.2 µg g^{-1} for Zn and Fe, respectively. Recovery tests for analytes in apple leaves 1515, tomato leaves 1573a standard reference materials and a peach nectar sample solution were studied and the results obtained were compared with certified and added values. The results of analytes obtained in samples were compared with previous literatures and works studied..

Keywords:

Lead; Iron; Beverage; ETAAS with Ni + Ir + NH_4NO_3 modifier mixture; FAAS

1. Introduction

Metal contents such as copper, lead, iron and zinc in fruit jams, nectars, juices and beverages consumed by people in large amounts are important due to their essential or toxic effects on human metabolism, human health and contamination [1-4]. The main sources of the elements in such samples may be water, fruit, soil, manufacturing process, containers and environmental contamination due to fertilizers, pesticides, raw materials, etc [3, 5, 6]. Iron, copper and zinc are essential elements because of their roles in biological samples, while lead is toxic even in trace amount [2, 3]. These elements can also be toxic when they are taken in excessively. Copper plays an important role as catalyst in the oxidation of organic compounds that are responsible for the stability and it is required in hemoglobin synthesis [5]. Zinc is essential for many enzymes involved in several physiological functions, such as protein synthesis and energy metabolism [2, 5, 6]. Lead is a highly toxic element that accumulates in biological systems and it leads to deficits in psychological functions such as intelligence and learning ability in humans [7]. Metal levels of various beverages and fruit jams and, etc. have been widely reported in the literatures [1, 2, 4, 6-14], but there is no study on the

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determination and evaluation of metal levels in such samples marketed from Turkey. Therefore, determinations of these metal levels are important for fruit and beverage samples consumed in Turkey.

Electrothermal atomic absorption spectrometric and flame atomic absorption spectrometric techniques are widely used for trace element determinations due to their inherent high sensitivities, selectivities, low detection limits and direct analysis of samples with minimal sample preparation [10, 15, 16]. The samples such as fruit jams, nectars, juices and beverages have organic substances and inorganic species, which may cause errors in the analytical measurements for element analysis [10]. Lead is a volatile element and common problem is the thermal stabilization of Pb in the graphite furnace up to the atomization stage. Platform atomization, chemical matrix modification, integrated absorbance and a powerful background correction technique have been used to overcome these problems. Different permanent modifiers (W-Rh, W-Ir and W-Ru) [17] and other suitable modifier solutions, such as Ni + Pd + TA [16], Pd-$Mg(NO_3)_2$ [18, 19] and ammonium nitrate (NH_4NO_3) [20-23] have been used for the determination of elements such as Cd and Pb in various sample matrices in order to stabilize the analytes to higher permissible pyrolysis temperatures and to reduce interference effects in the sample matrix before atomization steps. Yi-Ching and Shiuh-Jen [23] explained that NH_4NO_3 could delay the vaporization of Pb and could increase Pb signal when it was used as modifier. The use of NH_4NO_3 as a chemical modifier facilitates the removal of Na^+, K^+, Ca^{2+}, Cl^-, etc ions during pyrolysis and background absorption signals of analytes in samples are considerably reduced [20].

Aims of this study were to determine the concentration levels of Pb, Cu, Fe and Zn in fruit jams, nectars, juices, beverages, apple leaves 1515 and tomato leaves 1573a by ETAAS using Ni + Ir + NH_4NO_3 modifier mixture proposed and by FAAS, and to compare the results of analytes found in samples with the maximum permissible values given in Turkish standards and Turkish food regulations [24] and the other literatures in terms of human health and contamination [2, 3, 25, 26]. The thermal stabilization effects of Ni + Ir + NH_4NO_3 modifier mixture and its components on Cu and Pb in sample solutions were investigated to reduce such interferences. Effects of modifiers on analytes, such as pyrolysis and atomization temperatures, atomization / background profiles, limits of detection (LOD) and characteristic masses (m_o) were compared comprehensively. Ni + Ir + NH_4NO_3 modifier mixture was applied for the determination of the Cu and Pb in samples and SRMs by ETAAS. Iron and Zn in samples and SRMs were determined by FAAS.

2. Experimental

2.1. Apparatus

A Hitachi (Japan) Model 180/80 flame and graphite furnace (Hitachi 180/78) atomic absorption spectrometer equipped with a Zeeman-effect background corrector and an automatic data processing unit (180/205) was used for all absorption measurements of analytes. Hitachi pyrolytic graphite coated graphite tubes (P/N-190/6007) inserted with graphite platforms (P/N-190/6008) were employed throughout the experiment and integrated absorbance (peak area) mode was used for signal evaluation. Single element hollow cathode lamps of Cu (324.8 nm, 7.5 mA), Pb (283.3 nm, 10 mA), Fe (248.3 nm, 12.5 mA) and Zn (213.9 nm, 10 mA) were used as radiation sources. Spectral band pass used for all lamps was 1.3 nm. Instrumental parameters and operating conditions recommended by the manufacturer for the analytes and air-acetylene flame were used, unless otherwise stated. Argon (99.995%, w/w) was used as a carrier gas during all stages except for atomization in ETAAS. A 20 µL volume of calibration or sample solution together with modifier solutions was injected into the platform by an autosampler (P/N-170/126). A Varian Model 9176 recorder was used in a 20 mV/FS span in order to obtain atomization and background signal profiles. Milestone microwave oven (MLS Ethos 1600, Italy) was used for decomposition of samples in a short time and to avoid analyte loss and contamination.

2.2. Reagents and materials

All aqueous solutions were prepared by dissolving analytical grade reagents in ultra pure water (resistivity 18 MΩ cm) taken from an ultra pure water system (Nanopure infinity, Barnstead, P/N-1161, Dubuque, USA). HNO_3 (65% m/m) and H_2O_2 (30% m/m) (Merck, Darmstadt, Germany) were used. All solutions prepared were stored in high density polypropylene bottles. Plastic bottles, autosampler cups, pipettes, Teflon digestion vessels and glassware materials were cleaned by soaking in HNO_3 (20% v/v) for two days, rinsing four times with ultra pure water and dried. Autosampler washing solution containing HNO_3 (0.1% v/v) plus triton X-100 (0.1% v/v) was used to avoid clogging of the autosampler pipette and to improve dispersion of sample solution onto the platform [7, 17]. Triton X-100 was also added to modify the physical properties of sample and aqueous solutions, such as viscosity.

Standard solutions of Ni (II) (6 g L^{-1}) and Ir (IV) (2.0 g L^{-1}) were prepared from 2.97 g $Ni(NO_3)_2$. $6H_2O$ (Merck) dissolved in HNO_3 (1% v/v) and 235 mg IrO_2 (Merck) dissolved in HNO_3 (10% v/v) solution and diluted to each 100 mL with ultra pure water after evaporation of acids. 320 mg NH_4NO_3 (Merck, 99.99% pure) solution dissolved in ultra pure water and diluted to 100 mL was prepared daily before use. All modifier solutions were diluted as required.

Stock standard solutions of Cu, Pb, Fe and Zn (1.0 g L^{-1}) obtained from BDH chemicals (Poole, UK) were used. Calibration solutions of analytes were freshly prepared by successive dilution of the stock standard solutions to the desired concentrations in nitric acid (0.2% v/v) solution immediately before use.

2.3. Sampling

Some of the samples were taken from Turkish Standard Institution for element analysis and the other samples were purchased from different supermarkets in Ankara at different dates. Apple leaves 1515 and tomato leaves 1573a standard reference materials (SRMs) taken from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used.

2.4. Decomposition of samples

The jam and nectar jelly samples, apple leaves 1515 and tomato leaves 1573a were dissolved according to the methods described in previous studies [9, 14]. A portion of a sample and apple leaves 1515 (3.0-4.0 g each sample) or a portion (0.2-0.4 g) of tomato leaves 1573a was accurately weighed into a Teflon digestion vessel with a cover, 6 mL mixture of HNO_3 (65% m/m) plus H_2O_2 (30% m/m) (2:1) and 2 mL H_2O were added to each sample and left overnight at laboratory temperature in order to dissolve the samples without heating. 1.0 mg L^{-1} of Pb aqueous standard solution was added to the tomato leaves 1573a before decomposition because there was no Pb certified value. The vessel was placed on a hot-plate and heated at 100°C for 40 min to decompose some organic contents of the matrix, such as oils [9, 11, 12, 14]. After cooling and adding 2 mL H_2O_2, samples were decomposed by using the Milestone Ethos microwave oven according to the procedures described in previous works [17, 27, 28]. Steps of the microwave program were the heating from laboratory temperature to 140°C for 20 min and waiting at this temperature for 20 min (up to

800 W) and turning off the microwave and waiting for 20 min. After cooling, the vessel was opened and gently heated on a hot plate at about 100°C to evaporate the sample nearly to 4 mL. When the residue was left, a further 3 mL of HNO_3 and H_2O_2 mixture was added and the procedure given above was repeated. After cooling, the resulting solution was transferred into a 25-mL calibrated flask by washing interior surface of the vessel with a sufficient volume of 0.05 mol L^{-1} HNO_3 for three times. The final solution was diluted to the mark with ultra pure water. A portion (5 mL or 5.0- 5.5 g) of each juice or beverage sample was poured into a Teflon vessel, 6 mL of HNO_3 and H_2O_2 mixture was added to the vessel and the procedure given above was used. The resulting solution was transferred into a 25-mL calibrated flask. Blank solutions were also prepared to check the possible analyte contaminations in the reagents used during the preparation of sample solutions and to obtain detection limits and characteristic masses of analytes.

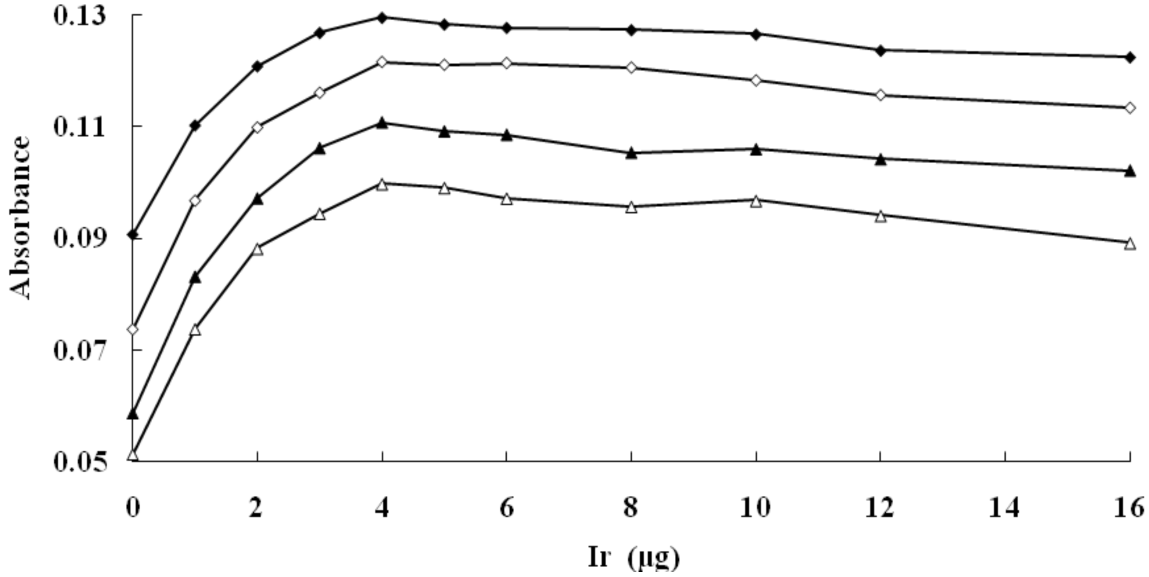
2.5. Optimization procedures

Samples and standard reference materials were diluted with nitric acid (0.1% v/v) plus triton X-100 (0.1% v/v) in order to get suitable absorbance signals of analytes (below 0.20 absorbance units). They were used to obtain optimum pyrolysis and atomization temperatures, mass and mass ratio of modifiers used and atomization / background profiles for Cu and Pb. One mL of analyte in sample solution diluted to appropriate concentration was mixed with 1 mL of modifier solution (3.0 g L^{-1} Ni or 0.4 g L^{-1} Ir or 0.8 g L^{-1} NH_4NO_3 or 3.0 g L^{-1} Ni + 0.4 g L^{-1} Ir or 3.0 g L^{-1} Ni + 0.4 g L^{-1} Ir + 0.8 g L^{-1} NH_4NO_3) and injected into the platform. The maximum absorbance values of Cu and Pb in a sample solution were obtained by changing the heating temperatures, ramp and hold times in preliminary studies. Graphite furnace heating temperature program optimized for the determinations of Cu and Pb was given in Table 1. Effects of mass and mass ratios of modifiers on analytes were studied by injecting a suitable concentration of analyte in a sample or a standard reference material solution mixed together with an appropriate concentration or concentration ratio of single and mixed modifiers and they were shown in Fig.1. Pyrolysis and atomization temperature curves for Cu and Pb in a sample solution randomly chosen were studied in the presence or absence of the modifiers and they were shown in Fig.2. Obtained maximum pyrolysis and atomization temperatures of analytes in the presence or absence of modifiers are given in Tables 1 and 2. Mean of three absorbance measurements of Cu and Pb versus pyrolysis and atomization temperatures, and mass and mass ratios of modifiers were obtained. Atomization and background profiles of analytes obtained in samples with and without of modifiers were given in Fig.3 as an example. Cu, Pb, Fe and Zn in blanks, apple leaves 1515, tomato leaves 1573a and samples were analyzed by ETAAS using Ni + Ir + NH_4NO_3 modifier mixture and heating conditions described in Table 1 and by FAAS using air-acetylene flame.

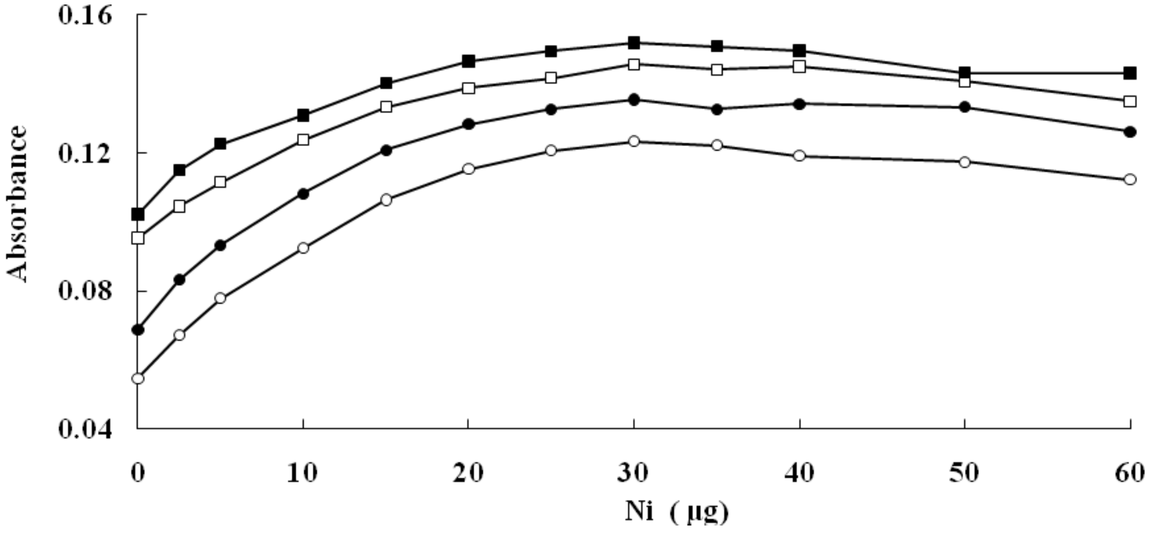
Table 1. Heating program for the determinations of Cu and Pb in samples with various modifiers

Step	Temperature (°C)	Time (s)		Ar flow rate (mL min^{-1})
		Ramp	Hold	
Dry-1	50-130	30	-	250
Dry-2	130-300	15	15	250
Pyrolysis	300-Var[a]	30	20	250
Atomization	Var[b]	0	5	0
Cleaning	Var[c]	-	3	250

[a] See Table 2; [b] Optimized atomization temperatures of Cu and Pb are 2700 and 2000°C, respectively; [c] Cleaning temperatures of Cu and Pb are 2800 and 2650°C, respectively.



(a)



(b)

Fig. 1. Effect of mass of modifiers on (a) Cu in tomato leaves 1573a (37.6 ± 2.2 µg L^{-1} Cu) with Ir (Δ); Ir with fixed 8 µg NH_4NO_3 (▲), Ir with fixed 30 µg Ni (◊) and Ir with fixed 30 µg Ni + 8 µg NH_4NO_3 (♦), and (b) Pb in apple leaves 1515 (37.6 ± 3.2 µg L^{-1} Pb) with Ni (○); Ni with fixed 8 µg NH_4NO_3 (●),Ni with fixed 4 µg Ir (□) and Ni with fixed 4 µg Ir + 8 µg NH_4NO_3 (■).

Table 2. Pyrolysis temperatures (Tpyrolysis), detection limits (LOD) and characteristic masses (m_o) of Cu and Pb in samples with various chemical modifiers (dilution factor of 125 mL g^{-1})

	Tpyrolysis (°C)		LOD, µg kg^{-1}		m_o, pg	
Modifier	Cu	Pb	Cu	Pb	Cu	Pb
No	950	800	51	7.3	46	54
NH_4NO_3	1000	900	46	6.5	41	44
Ir	1100	1000	41	5.4	37	38
Ni	1100	1100	36	5.1	34	35
Ir + NH_4NO_3	1150	1100	32	4.2	28	32
Ni + NH_4NO_3	1200	1150	28	3.7	25	28
Ni + Ir	1250	1200	25	2.4	21	25
Ni+ Ir + NH_4NO_3	1300	1250	21	1.8	14	21

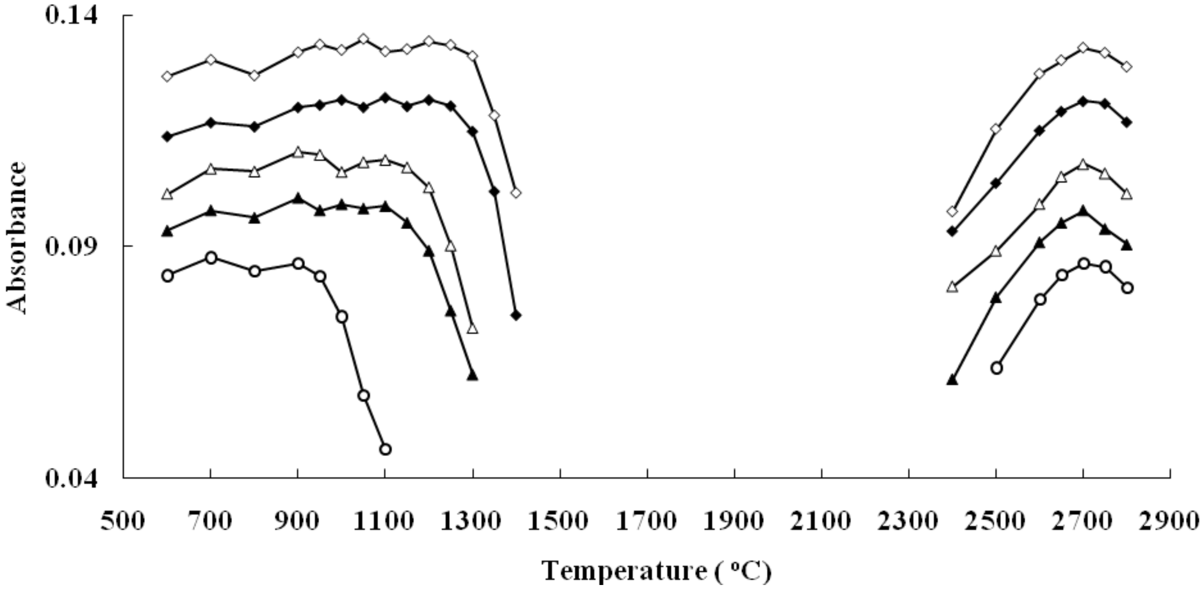
3. Results and discussion

3.1. Thermal stabilization and optimization studies of modifiers on analytes

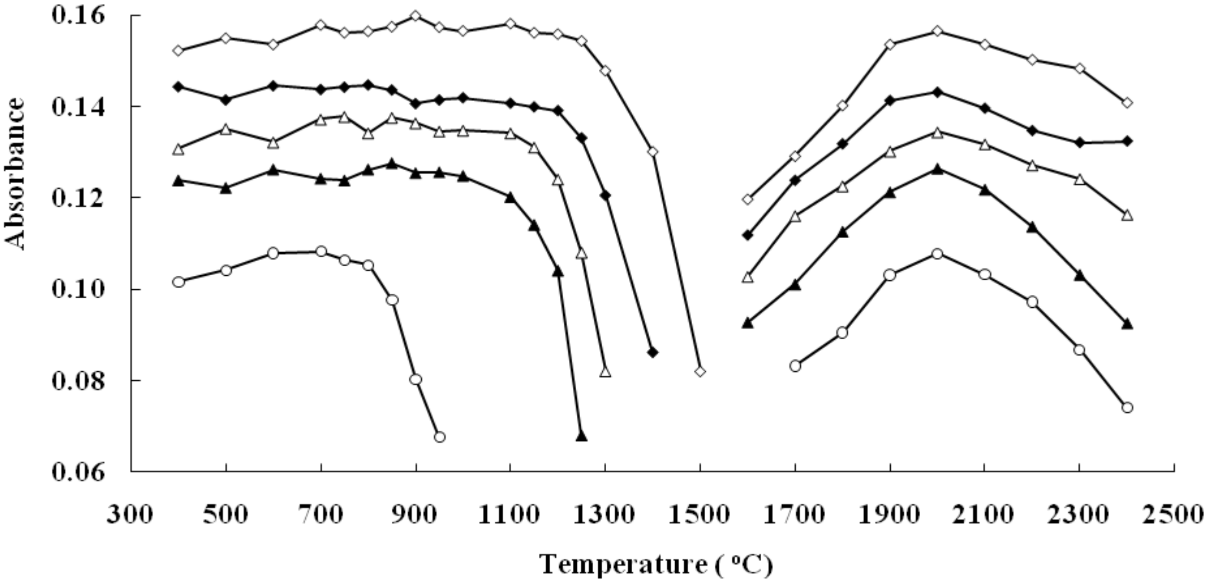
The thermal stabilization studies of chemical modifiers and their mixtures such as Ni, Ni + Ir, Ni + Ir + NH_4NO_3 on Pb and Cu in samples were investigated systematically. The main purposes of using chemical modifiers in ETAAS are to stabilize the analyte elements up to pyrolysis temperatures as high as possible by forming chemical compounds or intermetallic phases [29] and to remove most of the sample matrix efficiently without loss of analyte mass. In this study, thermal stabilization and optimization conditions of ETAAS such as effect of mass and mass ratio of modifiers on analytes, pyrolysis and atomization temperatures, atomization and background profiles were systematically investigated in sample solutions. The effects of mass and mass ratio of Ni, Ir, Ni + NH_4NO_3, Ir + NH_4NO_3, Ni + Ir and Ni + Ir + NH_4NO_3 modifier mixture on the pyrolysis and atomization temperatures of analytes in sample solutions were studied by preliminary experiments. Absorbance values of Cu in tomato leaves 1573a and Pb in apple leaves 1515 found versus mass and mass ratios of modifiers were plotted and shown in Fig.1 as examples. As can be seen in Fig.1, optimum mass and mass ratios of the modifier components were found to be 30 µg Ni, 4 µg Ir and 30 µg / 4 µg for Ni/Ir ratio. 8 µg NH_4NO_3 taken from previous work [30] was used in this work to decrease such interferences and background. These values were compared with previous works [16, 21, 29-31] and similar results were observed.

Pyrolysis and atomization temperature curves for Pb and Cu in a sour cherry jam sample solution obtained in the presence or absence of modifiers were shown in Fig. 2. Pyrolysis temperatures of analytes in solutions with and without of modifiers were changed by setting the atomization temperatures according to the specifications of the manufacturer of the instrument. Atomization curves were also obtained by measuring the absorbance values at various atomization temperatures, while the pyrolysis temperatures of analytes were kept constant in the presence or absence of modifiers. As can be seen in Fig.2a, in the case of Cu, a constant signal was obtained in the interval 1000-1300°C with the Ni + Ir + NH_4NO_3 modifier mixture. At higher temperatures, the analytical signal began to decrease. The pyrolysis temperature of Cu (1300°C) found in sample with the Ni + Ir + NH_4NO_3 modifier mixture was good for the mineralization of the samples. As can be seen in Fig.2b, pyrolysis temperature of Pb obtained without a chemical modifier was 800°C. When Ni + Ir + NH_4NO_3

modifier mixture was used, the analytical signal of Pb began to decrease above 1250°C and 1250°C was selected as pyrolysis temperature of Pb to avoid possible losses of Pb. Maximum pyrolysis and atomization temperatures of analytes in the presence or absence of modifiers obtained from these curves were given in Tables 1 and 2. As can be seen in Table 1, in drying step, the temperature was set at 50°C in the first step and finished at 300°C in the last in order to evaporate water and some volatile species in this temperature interval. As can be seen in Table 2 and Figure 2, in the presence of Ni + Ir + NH_4NO_3 modifier mixture, pyrolysis temperatures of analytes are 50°C higher than in the presence of Ni + Ir modifier mixture due to the effect of NH_4NO_3 on the thermal stabilization of analytes. Maximum pyrolysis temperatures of Pb and Cu obtained in samples with Ni + Ir + NH_4NO_3 were compared with the previous studies [16, 17, 31, 32] and small differences observed with Ni + Ir + NH_4NO_3 may be due to the differences of set and the actual temperatures, instrumental parameters, tubes and platforms used. Pyrolysis temperatures of analytes obtained with Ni + Ir + NH_4NO_3 are suitable to remove the most of interferences and matrix components efficiently without loss of analyte mass prior to atomization step and a temperature at least 1100°C should be aimed for the analytes in food and biological samples. Clean temperatures of analytes given in Table 1 are also the same with the recommended values of manufacturer. Mean of blank signals obtained with Ni + Ir + NH_4NO_3 are 0.0156 for Pb and 0.0098 for Cu, respectively.



(a)



(b)

Fig. 2. Pyrolysis and atomization curves for (a) Cu and (b) Pb in a sour cherry jam sample solution (Dilution ratio is 2 for Pb and Cu) with and without of the modifiers: without (○); 4 µg Ir (▲); 30 µg Ni (Δ); 30 µg Ni + 4 µg Ir (♦); 30 µg Ni + 4 µg Ir + 8 µg NH_4NO_3 (◊).

Atomization and background profiles of Cu and Pb in sample solutions with and without of modifiers plotted were comparatively investigated to demonstrate how the modifier affects the signals of analytes [19, 33, 34]. Fig.3 shows atomization /background profiles of Pb in the sour cherry jam sample solution obtained with Ni + Ir + NH_4NO_3 modifier mixture or without a modifier as an example. As can be seen, higher absorbance values and lower background signals of Pb were obtained in the presence of Ni + Ir + NH_4NO_3 than those obtained in the absence of a modifier. Signal/noise ratios of Pb obtained with Ni + Ir + NH_4NO_3 are higher than those obtained without a modifier. It was observed that the peak of Pb absorbance in the presence of Ni + Ir + NH_4NO_3 shifted to the later appearance time than in the absence of a modifier [33, 34]. With the addition of NH_4NO_3, a narrower, more symmetric atomic absorption profile was obtained. NH_4NO_3 can convert Na^+, K^+, Ca^{2+}, etc ions into nitrates such as $NaNO_3$ and they vaporize nearly 600°C [21] and interferences in sample matrix can be reduced [23].

3.2. Analytical characteristics

The determination of Pb, Cu, Fe and Zn in sample solutions was performed by using calibration graph methods on the base of single element solutions with the instrumental parameters recommended by manufacturer and optimum conditions given in Tables 1 and 2. Calibration graphs obtained against working standard solutions of analytes were in analytical ranges of 5-80 µg L^{-1} for Pb and Cu by ETAAS using Ni + Ir + NH_4NO_3, 0.05-1.0 mg L^{-1} for Zn and 0.2-4.0 mg L^{-1} for Fe by FAAS, respectively. Optimum concentrations of modifier components were added to the aqueous standard and sample solutions for ETAAS determinations. All calibration graphs for analytes were linear and correlation coefficients (r) were higher than 0.996 for Pb and Cu, 0.998 for Zn and Fe.

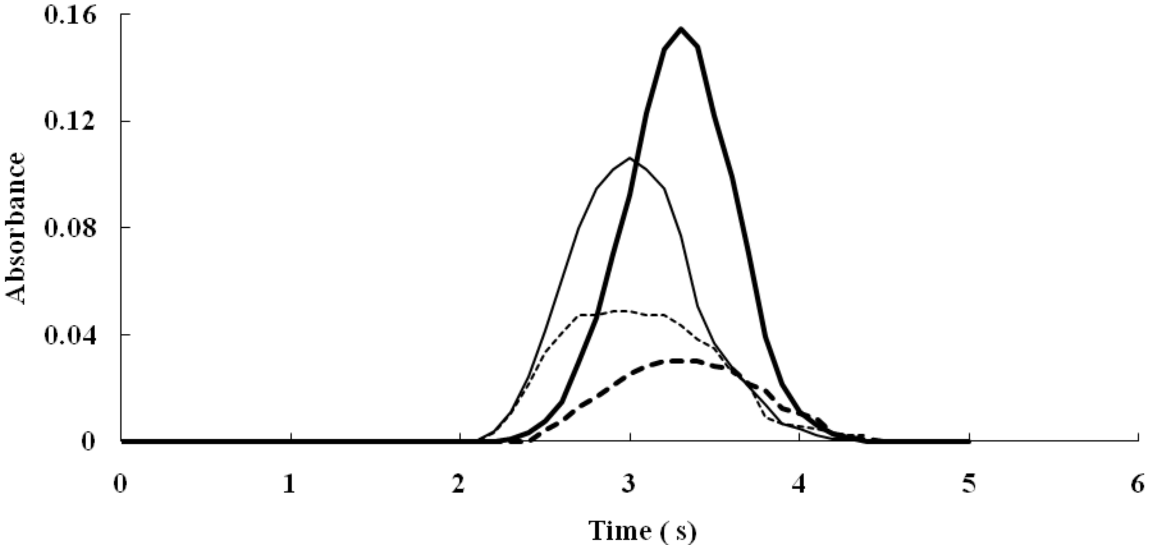


Fig. 3. Atomization and background profiles of Pb in the sour cherry jam sample solution obtained without (—,----) and with 30 μg Ni + 4 μg Ir + 8 μg NH_4NO_3 (▬▬, ▪ ▪ ▪ ▪) modifier mixture.

Limits of detection (LOD, $3\sigma_{blank}$-criterion) and characteristic mass (m_o, mass of the analyte corresponding to 0.0044 absorbance unit) are important parameters for the sensitivity of the method and they might be influenced by instrumental parameters [15, 35, 36]. Detection limits and characteristic mass of Cu and Pb calculated from 20 consecutive measurements of blank solutions (nitric acid (0.1% v/v) plus triton X-100 (0.1% v/v)) for tomato leaves 1573a (0.8% m/v) with and without of modifier, based on integrated absorbance [15, 37] are summarized in Table 2. As can be seen, the lowest m_o values and detection limits were obtained with Ni + Ir + NH_4NO_3 in triton X-100 (0.1% v/v) plus HNO_3 (0.1% v/v) mixture. Detection limits of Fe and Zn by FAAS were also determined by 20 consecutive measurements of blank solutions. The LOD and m_o results obtained for Pb, Cu, Fe and Zn were compared with previous works [7, 16, 17] and small differences observed in results are due to instrumental parameters and modifiers used. As a consequence, Ni + Ir + NH_4NO_3 modifier mixture in triton X-100 (0.1% v/v) plus HNO_3 (0.1% v/v) mixture used as diluent was recommended for the determination of Pb, Cu by ETAAS in samples.

3.3. Analytical quality validation

In order to control the accuracy of the method for the determination of analytes in samples by ETAAS using Ni + Ir + NH_4NO_3 modifier mixture and FAAS determinations, apple leaves 1515, tomato leaves 1573a and a peach nectar solution added aqueous standard solutions were analyzed. There was no certified standard reference material available on the market related to fruit and beverage samples with such analytes. A peach nectar solution dissolved in 25-mL volumetric flask was divided into three equal volumes in three 25-mL acid cleaned PTFE volumetric flasks in order to perform a recovery test. A half mL of each 1.0 mg L^{-1} Pb and Cu, 25 mg L^{-1} Fe and 10 mg L^{-1} Zn aqueous standard solutions, respectively were added into the first 25-mL volumetric flask. One mL of each 1 mg L^{-1} Pb and Cu, 25 mg L^{-1} Fe and 10 mg L^{-1} Zn aqueous standard solutions, respectively were added into the second 25-mL volumetric flask. The aqueous standard solutions were not added into the third 25-mL volumetric flask. They were diluted to the mark again. The results of analytes found in apple leaves 1515, tomato leaves 1573a and the peach nectar sample solution were given in Table 3. As can be seen in Table 3, percent recoveries of analytes obtained are in a range of 96-103%. Relative error and the relative standard deviation were lower than 5%.

Table 3. Recovery tests of analytes in apple leaves 1515, tomato leaves 1573a and a peach nectar sample solution by ETAAS using Ni+ Ir + NH_4NO_3 mixture and FAAS

Element	Concentrations		Recovery, %
	Certified	Found[b]	
Apple leaves 1515, mg kg^{-1}			
Cu	5.64 ± 0.24	5.61 ± 0.17	99
Pb	0.47 ± 0.02	0.45 ± 0.01	96
Fe	83 ± 5	84 ± 5	99
Zn	12.5 ± 0.3	12.2 ± 0.24	98
Tomato leaves 1573a, mg kg^{-1}			
Cu	4.70 ± 0.14	4.56 ± 0.15	97
Pb, µg L^{-1}	40[a]	39 ± 1.5	98
Fe	368 ± 7	364 ± 11	99
Zn	30.9 ± 0.7	31.2 ± 1.0	101
Peach nectar sample solution, µg L^{-1}			
Cu	0.0	20.1 ± 0.7	-
	20[a]	38.8 ± 1.5	97
	40[a]	59.6 ± 2.2	99
Pb	0.0	16.3 ± 0.6	-
	20[a]	35.2 ± 1.4	97
	40[a]	57.4 ± 2.1	102
Fe	0	419 ± 17	-
	500[a]	912 ± 28	99
	1000[a]	1438 ± 50	101
Zn	0	210 ± 10	-
	200[a]	400 ± 18	98
	400[a]	628 ± 30	103

[a] Added values for tomato leaves 1573a and a Peach nectar sample solution; [b] Mean of six replicate measurements with 95% confidence level, $\bar{x} \pm ts/\sqrt{N}$

3.4. Sample analysis

Copper, Pb, Fe and Zn in sixty five fruit jam, nectar, juice and beverage samples were analyzed by ETAAS using Ni + Ir + NH_4NO_3 modifier mixture proposed and FAAS. The results of analytes found in samples are represented as average ± confidence interval (5 degrees of freedom (n-1) at 95% confidence level). Mean ± standard deviation (SD) (Min. value-Max. value) of analytes obtained in the same samples collected with sample numbers at different dates were given in Table 4. As can be seen in Table 4, minimum and maximum concentration values of analytes found in samples are 0.07 ± 0.02 in beverages and 0.28 ± 0.02 mg kg^{-1} in strawberry jam for Pb, 0.48 ± 0.12 in rose jam and 5.87 ± 0.49 mg kg^{-1} in peach juice for Cu, 0.87 ± 0.13 in orange nectar and 14.2 ± 1.40 mg kg^{-1} in quince jam for Fe, and 0.49 ± 0.09 in peach juice and 3.74 ± 0.57 mg kg^{-1} in strawberry jam for Zn. Maximum permissible values of Cu, Fe and Zn given in Turkish standards (Orange nectar, TS 11915, 2006; Orange Juice, TS 1535, 2003; Peach nectar, TS 1596, 2008; Sour Cherry Juice, TS 3631, 2003; Sour Cherry Jam, TS 3958, 1987; Strawberry Jam, TS 4186, 2005; Apricot Jam, TS 4187, 1989; Rose Jam, TS 5135, 1987; Figs Jam, TS 5136, 1987) and Turkish food codex regulations [24] for the related samples given in Table 4 are 5, 15 and 5 mg kg^{-1} for Cu, Fe and Zn, respectively.

Table 4. Results of analytes obtained in jam, nectar, juice and beverage samples

Sample	Sample No	Concentrations, mg kg^{-1}, mean ± SD[a] (Min. Value- Max. Value)			
		Pb	Cu	Fe	Zn
Sour cherry Jam	5	0.24 ± 0.03 (0.20 - 0.29)	4.46 ± 0.38 (4.03 - 4.94)	10.0 ± 2.91 (7.81 - 14.4)	3.26 ± 0.21 (3.02 - 3.51)
Apricot jam	6	0.18 ± 0.03 (0.14 - 0.23)	0.76 ± 0.14 (0.57- 0.93)	12.8 ± 1.7 (10.6 - 15.3)	1.75 ± 0.14 (1.57 - 1.93)
Rose Jam	5	0.22 ± 0.01 (0.20 - 0.24)	0.48 ± 0.12 (0.35 - 0.64)	10.1 ± 1.18 (8.61 - 11.9)	1.23 ± 0.23 (0.96 - 1.51)
Quince Jam	5	0.22 ± 0.02 (0.18 - 0.25)	4.35 ± 0.22 (4.11- 4.66)	14.2 ± 1.40 (12.5 - 15.8)	3.22 ± 0.15 (3.04 - 3.42)
Figs jam	6	0.12 ± 0.03 (0.08 - 0.16)	2.22 ± 0.56 (1.61 - 2.98)	6.27 ± 2.62 (3.54 - 9.41)	2.80 ± 0.60 (2.14 - 3.64)
Strawberry Jam	5	0.28 ± 0.02 (0.25- 0.31)	4.33 ± 0.21 (4.10 - 4.59)	10.4 ± 2.14 (8.01 - 12.9)	3.74 ± 0.57 (3.12 - 4.38)
Orange nectar	5	0.19 ± 0.03 (0.15 - 0.23)	0.70 ± 0.12 (0.55 – 0.86)	0.87 ± 0.13 (0.71 - 1.04)	0.59 ± 0.11 (0.41 - 0.79)
Sour cherry nectar	5	0.22 ± 0.01 (0.19 - 0.24)	0.57 ± 0.11 (0.44 - 0.72)	2.24 ± 0.09 (2.12 - 2.36)	0.77 ± 0.14 (0.61 - 0.93)
Peach nectar	5	0.23 ± 0.02 (0.20 - 0.27)	5.62 ± 0.24 (5.35 - 5.90)	1.65 ± 0.12 (1.49 - 1.81)	0.56 ± 0.13 (0.41 - 0.72)
Peach Juice	4	0.24 ± 0.02 (0.21- 0.27)	5.87 ± 0.49 (5.21- 6.39)	2.41 ± 0.16 (2.21 - 2.61)	0.49 ± 0.09 (0.38 - 0.60)
Orange Juice	4	0.16 ± 0.01 (0.13 - 0.17)	0.56 ± 0.06 (0.48 - 0.64)	0.89 ± 0.09 (0.78 - 1.12)	0.53 ± 0.09 (0.38 – 0.63)
Sour cherry Juice	5	0.18 ± 0.01 (0.16 - 0.20)	0.75 ± 0.06 (0.67 - 0.84)	1.82 ± 0.09 (1.71 – 1.94)	0.88 ± 0.09 (0.78 - 0.99)
Beverages containing gas	5	0.07 ± 0.02 (0.03 - 0.10)	2.54 ± 0.49 (1.83 - 3.21)	4.45 ± 0.53 (3.84 - 5.06)	2.91 ± 0.32 (2.42 - 3.25)

[a] SD: standard deviation

The concentration levels of Cu, Fe and Zn found in samples are lower than these maximum permissible values. Maximum permissible value of Pb given in Turkish food codex regulations [24] and Turkish standards for orange nectar, orange juice, peach nectar and for sour cherry juice sample is 0.05 mg kg^{-1} and maximum permissible value of Pb for other jam samples given in Turkish standards (TS 3631, 2003; TS 4186, 2005; TS 4187, 1989; TS 5135, 1987; TS 5136, 1987) is 0.3 mg kg^{-1}. Pb contents found in samples are higher than 0.05 mg kg^{-1}, but smaller than 0.3 mg kg^{-1}. The sources of high values of Pb obtained may be due to water, fruit, manufacturing process, containers and etc [3, 5, 6]. The maximum contents of Pb, Cu, Fe and Zn obtained in samples were compared with the concentration levels of heavy metals interested in some beverages, fruit and food drinks in some parts of the world [2] and the results of analytes obtained from samples are similar or lower than the values reported in the literature, with a few minor exceptions. The FAO/WHO has limits for trace metals intake depending on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intake (PTDI) for lead, iron, copper and zinc are 214 µg, 48 mg, 3 mg, 60 mg, respectively [25]. The contents of these metals in fruit jam, nectar, juice and beverage samples may be variable due to factors such as possible contamination from equipment during the packaging process, characteristics of the manufacturing practices and differences between species. The maximum concentration levels of Fe, Cu and Zn obtained in the samples were also compared with the results of analytes for the related food samples reported in the literatures [3, 26] and contents of analytes found in this study were consistent with some values.

4. Conclusion

Lead and copper by ETAAS using Ni + Ir + NH_4NO_3 modifier mixture, iron and zinc by FAAS in fruit and beverage samples were determined and evaluated. Recovery tests for analytes in samples were performed for the accuracy of the method. Chemical interferences from the sample matrix are minimal by using the Ni + Ir + NH_4NO_3 modifier mixture and an acid mixture of HNO_3 plus H_2O_2 digestion. Modifier mixture can be applied for the determination of analytes in various matrixes, such as fruit and beverage samples and botanic materials. It can be concluded that metal levels found in samples are generally within safe limits and compare well with maximum levels of analytes in similar fruit and beverage samples given in Turkish standards, Turkish food codex and WHO/FAO. Metal levels obtained in samples are not sufficient to cause toxicological effects on human health problems when the samples are consumed by consumers. They can also be used to test the chemical quality of the fruit drinks, jams and beverage samples in order to evaluate the possible risk associated with their consumption by humans.

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