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Determination of lead, copper, zinc, magnesium, calcium and iron in fresh eggs by atomic absorption spectrometry

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Abstract

In this study, lead, copper and zinc, calcium, magnesium and iron in fresh egg samples have been determined by electrothermal and flame atomic absorption spectrometry (ETAAS–FAAS) with Zeeman-effect background correction. $Y+Pd$ + citric acid (CA) has been found a powerful modifier mixture for the determination of Pb, Cu and Zn. Maximum pyrolysis and optimum atomization temperatures of analyte elements were determined in the presence or absence of modifiers. Atomization and background profiles of the analyte elements studied in the presence of $Y+Pd+CA$ have been compared with other modifiers such as $Mg+Pd$ and Mg + PO³⁻. The detection limits obtained were 1.88, 0.71, 0.03 ng/ml for Pb, Cu and Zn in ETAAS, 14.0, 32.3, 68.6 and 18.9 ng/ml for Mg, Ca, Fe and Zn in FAAS, respectively. The reliability of the measurements was confirmed by analysing a certified reference material, NIST, whole egg powder 8415. The percent recovery ranges of analytes were from 96.7 to 101% . \odot 2001 Elsevier Science Ltd. All rights reserved.

Keywords: ETAAS–FAAS–Zeeman background correction; Egg samples; Chemical modifiers

1. Introduction

Toxic and essential elements such as Pb, Cu, Ca, Mg, Fe and Zn in vegetables, meats and egg samples play an important role for human health. Lead is one of the toxic elements, dangerous to most human body organs if exposure exceeds tolerable levels (Baht & Moy, 1997). Accumulation of lead produces damaging effects in the hematopoetical, hematic, renal, gastrointestinal systems (Correia, Oliveria, & Oliveira, 2000). Accurate determination of lead in foodstuffs such as fresh eggs is important since intake of even low concentrations of lead can cause serious toxic effects. Analysis of these elements in foodstuffs such as fresh eggs is of great importance since they play a definite role in the intrinsic mechanism regulating vital biological processes (Shang & Wang, 1997). Fresh eggs are among the most important foodstuffs in the daily diet. FAO/WHO (1982, 1983) reported the contamination levels of some analytes studied. Provisional tolerable weekly intake of lead was 50 μ g/kg for

adults, $25 \mu g/kg$ of body weight for infants and children (Baht & Moy, 1997). Maximum tolerable daily intakes of Cu, Zn and Fe from all sources were 0.5, 1.0 and 0.8 mg/kg of body weight, respectively.

Electrothermal and flame atomic absorption spectrometric methods (ETAAS-FAAS) are widely used for the determination of trace and essential elements due to their inherent high sensitivities and good selectivities (Acar, Kı́lı́c & Türker, 2000; Meeravali & Kumar, 1998; Shang & Wang, 1997). The determination of volatile elements such as Pb and Zn in such samples by ETAAS is highly difficult because of chemical interferences and loss of analytes during the pre-treatment and atomization steps. To minimize most of the matrix interferences and to increase accuracy and precision in ETAAS, platform atomization, chemical modification, integrated absorbance and a powerful background correction technique are preferred (Cabrera & Lorenzo, 1995; Vinas, Martinez, & Cordoba, 2000). In recent years, many metal salts and some organic substances have been used as chemical modifiers in ETAAS for the stabilization of volatile elements during the pyrolysis stage (Acar et al., 2000; Falomir et al., 1999; Vinas et al., 2000). Mixed modifiers often exhibit better thermal

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stabilizing action and higher efficiency than single components for some analytes (Schlemmer & Welz, 1986).

The main aim of this work was to experimentally evaluate a new chemical modifier mixture, $Y + Pd + ci$ tric acid (CA) and to compare with other modifiers such as $Mg + Pd$ and $Mg + PO₄³⁻$ (Shan & Wen, 1995; Welz, Schlemmer, & Mudakavi, 1992) in terms pyrolysis temperatures, atomization and background profiles. Effect of mass and mass ratio of Y and Pd on thermal stabilization of Pb, Cu and Zn was investigated. Additionally, citric acid was added as chemical reductant to the sample solutions together with the $Y+Pd$ mixed modifier to provide higher thermal pyrolysis temperatures of analytes and help to reduce chemical interferences (Acar, Kiliç & Türker, 1999; Zhuang, Yang, Luo, Wang, & Huang, 1991). The accuracy of the method by using $Y + Pd + CA$ modifier mixture was tested by analyzing the Whole Egg Powder CRM 8415. Therefore, proposed $Y + Pd + CA$ modifier mixture that provided the higher pyrolysis temperatures for analytes and higher atomization/background absorption ratio was applied to the determination of lead, copper and zinc in fresh egg samples. Iron, Mg, Ca and Zn contents in reference material and samples were determined by using FAAS. The aim was to find out the differences in skin-colour and sources of feed in village and farm egg samples.

2. Materials and methods

2.1. Apparatus

All atomic absorption measurements were carried out with a Hitachi Model 180-80 flame and graphite furnace (Hitachi 180/078) atomic absorption spectrometer equipped with a Zeeman effect background corrector, and an automatic data processor. A 20-µl volume sample solution was injected by an auto sampler (P/N-170/0126). Single element hollow cathode lamps of analytes were used as radiation source. Operating parameters of analytes were set as recommended by the manufacturer. Hitachi graphite platforms (P/N-190/6008) inserted into pyrolytically coated graphite tubes (P/N-190/6007) were used to measure all absorbance values by using integrated mode throughout. Argon was used as a carrier gas during all the stages except for atomization. Optimized graphite furnace temperature programme for the determination of Pb, Cu and Zn by ETAAS with testing $Y + Pd + CA$ modifier mixture or its components was given in Table 1. An acetylene-air or acetylene-nitrous oxide flame was used for the determination of analytes by FAAS.

2.2. Reagents

All reagents were of analytical-reagent grade or better. All aqueous solutions were prepared with deionized water obtained using Ultra pure water system (Barnstead, P/N-1161, \geq 18 M Ω Cm). HNO₃ (65%), HClO₄ (70–72%) and H_2O_2 (35%) Merck suprapur grade acids were used to dissolve the samples and in dilution.

One mg/ml of Pb, Cu, Zn, Ca, Mg and Fe stock standard solutions (BDH chemicals) were used. Working standard solutions were freshly prepared by successive dilution of the stock standard solution to the desired concentrations in 0.2% HNO₃ as diluent.

Pd (2 mg/ml) was prepared from 0.25 g of $Pd(NO_3)_{2}$. $2H₂O$ (Merck) dissolved in 1 ml of $HNO₃$ and diluted to 50 ml with deionized water. $NH_4H_2PO_4$ (2.5 mg/ml; Merck) was prepared by dissolving 0.15 g of $NH_4H_2PO_4$ in 7 M HNO₃ and diluting to 50 ml with deionized water. Four per cent (m/v) of citric acid (Hydrous, granular) solution was prepared daily before use. A 10 mg/ml of Y was prepared from 1.28 g of Y_2O_3 (BDH reagent) dissolved in 10 ml of 4.2 M $HNO₃$ by heating until the volume was nearly 3 ml and diluted to 100 ml with deionized water. Mg (2.5 mg/ml) was prepared from 1.33 g of $Mg(NO_3)_2$. 6H₂O (Merck) dissolved in 3 ml of 7 M HNO_3 and diluted to 50 ml with deionized water.

2.3. Collection and preparation of samples

Village and farm egg samples were collected from different villages and farms of three districts of the Ankara. Seventeen village and 17 farm eggs are from district 1 (East), 13 village and 13 farm eggs from district 2 (North) and 11 village and 11 farm eggs from district 3 (West).

An egg sample was broken and separated to egg yolk and egg white by polypropylene spoon into two glass beakers. All samples were dried in a Hetosicc freeze dryer (Type CD 2.5, 0.02 mbar, -40 °C) four days. Humidity losses obtained were approximately 51–53% for egg yolk and 71–75% for egg white. All samples were homogenized in a homogenizer for a few seconds.

2.4. Decomposition

The egg yolk and egg white samples and the whole egg powder CRM 8415 were dissolved according to the

Table 1 Optimum graphite furnace temperature programme

Step	Temperature $(^{\circ}C)$			Time(s)		Ar flow	
	Pb	Cи	Zn	Ramp	Hold	(ml/min)	
Drying-I		50-120		30		250	
Drying-II		120-300		15	15	250	
Pyrolysis		30 -var ^a		30	30	250	
Atomization	2000	2700	2000		7	0	
Cleaning	2650	2800	2650		5	250	

^a See Table 2

method described in previous work (Shang & Wang, 1997) and given as follows.

For egg yolk: a portion $(0.5-1.5 \text{ g})$ of sample was accurately weighed into a 50-ml teflon beaker and 3 ml concentrated $HNO₃$, 1 ml $HClO₄$ and 0.5 ml $H₂O₂$ were added and covered with a teflon cover. After waiting at laboratory temperature for 30 min, the beaker was placed on a hot-plate and heated at $60 °C$ for 30 min. A half millilitre of H_2O_2 was added, the temperature raised to 80 °C for 30 min. After adding 0.5 ml H_2O_2 , temperature was increased to 110 °C for 30 min. Then, temperature was gradually increased to 140 °C until complete decomposition of sample was achieved and total volume was nearly 2 ml. When the residue was left, a further 1 ml concentrated nitric acid and 1 ml H_2O_2 were added and the earlier procedure was repeated. After cooling, the resulting solution was transferred into a 25-ml calibrated flask. The interior surface of the beaker was washed with a minimal volume of 0.05 mol/l $HNO₃$ for three times and the final solution was diluted to the mark with deionized water.

For egg white: a portion (1.46–1.61 g) of sample was accurately weighed into a 50 ml Teflon beaker and 3 ml concentrated $HNO₃$ and 2 ml $H₂O₂$ were added and covered with a Teflon cover. The procedure described for egg yolk was followed and the final temperature was gradually raised to 130 °C to dissolve the sample completely. The resulting solution was transferred into a 25 ml calibrated flask.

A portion (1.0–5.0 g) of the CRM 8415 was accurately weighed into a 50-ml Teflon beaker and 5 ml of concentrated nitric acid, 1 ml HClO₄ and 1.5 ml H_2O_2 were added and covered with a Teflon cover. The procedure for egg yolk was run with the same reagents to dissolve the sample completely and resulting solution was transferred into 10-ml calibrated flask.

In all instances, blank solutions were run with the same reagents used under the same conditions to control possible contamination from digestion procedures.

2.5. General procedure

One millilitre of analyte standard solution (0.5–100 ng/ml) or 1 ml of sample solution was added to 1 ml of modifier solution (0.4 mg/ml of Pd, 2.0 mg/ml of Y or

Table 2 Maximum pyrolysis temperatures of analytes studied

Modifiers	Maximum pyrolysis temperatures $(^{\circ}C)$			
	Pb	Cu	Zn	
No modifier	800	950	450	
Y	1000	1200	900	
Pd	1100	1100	950	
$Y + Pd$	1200	1250	1000	
$Y + Pd + CA$	1250	1300	1000	

2.0 mg/ml of $Y + 0.4$ mg/ml of Pd) were injected into the graphite platform in order to obtain a sufficient absorbance signal (Acar et al., 2000). It was observed that 50 ng/ml of Pb, 50 ng/ml of Cu and 0.25 ng/ml of Zn were suitable. Thermal pyrolysis curves were then plotted, i.e. absorbance versus pyrolysis temperature by initiating the temperature programme as shown in Table 1. Pyrolysis temperatures varied between 300 and 1700 °C for analyte elements.

3. Results and discussion

3.1. Thermal stabilization studies

The main purpose of using a chemical modifier is to stabilize the analyte element by forming a chemical compound or an intermetallic phase, etc (Acar et al., 1999; Shan & Wen, 1995; Welz et al., 1992) to a pyrolysis temperature as high as possible. More of the sample matrix is efficiently removed during the thermal pre-treatment stage and less interferences are encountered in the atomisation step.

Thermal stabilizing effects of $Y + Pd + CA$ modifier mixture and its components on Pb, Cu and Zn in graphite furnace were investigated. The effect of mass and mass ratio of Y and Pd on the pyrolysis temperatures and absorbance values of analytes were studied and shown in Fig. 1. The optimum mass and mass ratio of the components were found to be 20 μ g for Y, 4 μ g for Pd and 20 μ g /4 μ g for Y/Pd. The mass effect of citric acid in the presence of optimum mass ratio of $Y+Pd$ modifier mixture on the absorbance values of analytes was also studied and found to be 200 µg for CA as shown in Fig. 1c. These values obtained were compared with the previous works (Acar et al., 1999; Byrne, Chakrabarti, Gilchrist, Lamoureux, & Bertels, 1993; Tsalev & Slaveykova, 1992) and they are approximately the same.

Thermal pretreatment curves for analytes studied in aqueous standards and samples in the presence or absence of modifiers were shown in Fig. 2. Atomization temperatures of analytes in standards (Std) and in a sample (S) were also studied in absence or presence $Y + Pd + CA$ modifier mixture as shown in Fig. 3 and optimized atomization temperatures were given in Table 1. Obtained maximum pyrolysis temperatures (T_{max}) of Pb, Cu and Zn in the presence or absence of modifiers were given in Table 2. The maximum pyrolysis temperatures for analytes were compared with the literature (Acar et al., 1999; Havezov, Detcheva, & Rendl, 1995; Shan & Wen, 1995; Slaveykova & Tsalev, 1990; Tsalev & Slaveykova, 1992; Welz et al., 1992). The maximum pyrolysis temperatures for Pb, Cu and Zn that could be used with $Y+Pd+CA$ mixed modifier was the same or higher than previously recommended

Fig. 1. Effect of the mass of (a) Y[Y(5 to 40 µg)+ Pd(4 µg)], (b) Pd [Y(20 µg)+ Pd(0.5 to 15 µg)], and (c) CA [(20 µg Y + 4 µg Pd)+CA (50 to 400 μ g)] in a Y + Pd + CA mixed modifier on the absorbance values of 50 ng/ml Pb, 50 ng/ml Cu, and 0.25 ng/ml Zn in aqueous solutions.

Fig. 2. Matrix modification studies for: (a) Pb, (b) Cu, and (c) Zn in aqueous solutions (Std) and samples (S) with the modifiers; 20 µg of Y; 4 µg of Pd; 20 μ g of Y + 4 μ g of Pd; 20 μ g of Y + 4 μ g of Pd + 200 μ g of CA.

mixed modifiers for the elements investigated. Some inconsistencies in the maximum pyrolysis temperatures may be dependant on the instrumental parameters and mass of a modifier. Significantly differing absorbance values by using the same amount of analyte may be based on the reactivities of modifiers (Ni & Shan, 1987). It is suitable to use a pyrolysis temperature as high as possible to remove the matrix efficiently and a temperature at least 900 °C should be aimed for analytes in food and biological samples (Lynch & Littlejohn, 1989; Zong et al., 1996). It was observed that the addition of CA together with $Y+Pd$ has an additional effect on pyrolysis temperatures of analytes (Acar et al., 1999; Byrne et al., 1993).

3.2. Effects of modifiers on the atomization and background profiles of analytes

One advantage of chemical modification is that atomization signals of analytes rather symmetrical and are shifted to a later appearance time (higher temperatures) in the presence of a modifier (Acar et al., 2000; Shan & Wen, 1995). A later appearance time means that the analyte atoms were released into a hotter gas environment, which had already reached its final temperature (Welz et al., 1992). In order to demonstrate how Y, $Mg + PO₄³$, $Mg + Pd$, $Y + Pd$ and $Y + Pd + CA$ modifiers affect the atomization and background profiles of Pb and Cu, a comparative study was conducted by using the integrated absorbance mode. Optimum mass and mass ratio and pyrolysis temperatures of analytes in the presence of $Mg + PO₄³$ or $Mg + Pd$ modifier mixture described in references (Shan & Wen, 1995; Welz et al., 1992; Zong et al., 1996) were applied. The atomization and background profiles of Pb, Cu and Zn obtained for dissolved egg samples and for aqueous standards in the presence or absence of the modifier are shown in Fig. 4 as an example. In each instance, the atomization profiles of analytes in the sample were also compared with those of the elements in the aqueous standards. Similar

Fig. 3. Pyrolysis and atomization curves for analytes in aqueous solutions (Std) and samples (S) with and without Y+Pd+CA modifier mixture (20 μ g of Y + 4 μ g of Pd + 200 μ g of CA). (a) Pb and (b) Cu.

Fig. 4. Atomization profiles of Pb in standard solution and a sample after decomposition; Where Std, standard (50 ng/ml of Pb); S, sample; B1 and B2, background absorption profiles of Pb in standard and sample, respectively.

symmetrical atomization signal shapes were obtained for Pb, Cu and Zn in samples and standards. The appearance times of elements were identical when comparing the elements in the samples and in the aqueous standards, but the maximum peak times of Pb in the samples were slightly later than those in the aqueous standards in the absence of a modifier as seen in Fig. 4. When $Y + Pd + CA$ mixture was used, the appearance time of atomization signal for Pb and Cu in sample and in aqueous standard was shifted to a later time while increasing pyrolysis temperature and no reduction in atomic signal was observed up to a maximum pyrolysis temperature above 1200 °C.

In the presence of $Mg + PO₄³⁻$ or $Mg + Pd$, larger background absorption signals were observed in the atomization of analytes as shown in Fig. 4. The larger background absorption might be caused by $Mg + Pd$ and $Mg + PO_4^{3-}$ at the resonance line of Pb, probably due to atomic absorption by Mg atoms in the wings of the 285.2 nm resonance line. However, larger background absorption was also observed at the resonance lines of Cu and Zn, even though their resonance lines are far from the Mg resonance line at 285.2 nm. In this instance, the observed background absorption could at least in part, be ascribed to molecular absorption (Shan & Wen 1995). However, the background absorption of analytes in the presence of $Y+Pd$ and $Y+Pd+CA$ is much smaller than that of the $Mg + Pd$ and $Mg + PO_4^{3-}$ modifiers. From these reasons, $Y+Pd+CA$ was recommended for the determination of Pb, Cu and Zn in egg samples.

In the absence of a modifier, small analyte signal and higher background absorbance were obtained for analytes in samples even when the solution was diluted by a factor of $1+1$. When Y + Pd + CA was used, it was observed that atomic signals of analytes increased while the background absorption decreased. The background absorbance from the matrix is perfectly corrected using Zeeman corrector, which allows direct determination of analytes in egg samples. Citric acid (Zhuang et al., 1991) such as ascorbic acid (Shan & Wen, 1995) and tartaric acid (Acar et al., 1999) may reduce the modifiers and analytes to their free reactive metals at pyrolysis temperatures less than 800 °C and therefore the stabilizing effect of modifier is increased.

3.3. Analytical conditions and calibration

The determination of Pb, Cu, Zn, Ca, Mg and Fe in sample solutions were performed with the instrumental parameters recommended by manufacturer and optimum temperature programme (Table 1) by using calibration on the base of single element solutions. Calibration against working standard solutions of analytes was performed for all elements in analytical ranges of 5–80 ng/mI for Pb and Cu, and 0.05–2.00 ng/ml for Zn in ETAAS using $Y + Pd + CA$ and 0.05–1.5, 0.1–0.5, 1.0–8.0, 0.25–4.00 mg/l for Zn, Mg, Ca and Fe by FAAS, respectively. Modifier components at the optimum mass and mass ratio were added to the working standard and sample solutions. All calibration graphs were linear and correlation coefficients were about $>$ 0.999.

The sensitivity of the proposed method in ETAAS is expressed by means of the limit of detection (LOD) and characteristic mass (m_o) (Acar et al., 2000). Limit of detection can be expressed as the concentration of sample corresponding to three folds $(3\sigma$ criterion) of standard deviation of detectable ten absorbance measurements. Characteristic mass is defined as the mass of analyte, which yields a signal equal to 0.0044 absorbance. Limits of detection and characteristic masses of analytes were determined in the presence or absence of modifiers and results obtained are given in Table 3. As can be seen in Table 3, lowest detection limits and characteristic masses of analytes were obtained by using $Y+Pd+CA$ modifier mixture. The limits of detection of analytes determined in FAAS are 14.0, 18.9, 32.3 and 68.6 ng/mI for Mg, Zn, Ca and Fe, respectively.

3.4. Analytical quality validation

In order to validate the accuracy of the proposed method for the analytes in ETAAS by using Y+Pd+CA modifier mixture and FAAS determinations, the procedure was applied to the whole egg powder, CRM 8415 (NIST). The recovery of Pb was also

Table 3

Limits of detection (LOD, 3σ criterion) and characteristic masses (m_0) of analytes in egg samples

Modifier	LOD , ng/ml			$m_{\rm o}$, pg		
	Ph	Cи	Zn	Ph	Сu	Zn
No modifier	6.65	4.70	0.07	41.5	21.4	3.1
Y	4.48	3.24	0.06	29.9	15.6	2.2
$Y + Pd$	3.04	2.04	0.05	20.4	8.4	1.9
$Y + Pd + CA$	1.88	0.71	0.03	14.3	6.7	1.4

Table 4

Determination of analytes in whole egg powder (NIST, CRM 8415)

Element	Concentrations, μ g/g	Recovery	
determined	Certified value	Found ^a , \overline{X} ±ts/ \sqrt{n}	(%)
Ph	0.061 ± 0.012	0.059 ± 0.011	96.7
Cu	2.70 ± 0.35	2.73 ± 0.27	101.1
Z_{n}	67.5 ± 7.6	66.8 ± 6.9	99.0
Mg	305 ± 27	$303 + 21$	99.3
Ca	2480 ± 190	2464 ± 198	99.4
Fe	$112 + 16$	115 ± 18	102.7

^a The mean of 10 replicate measurements with 95% confidence level.

Table 5 Determination of Pb, Cu, Zn, Mg, Ca and Fe in village and farm egg samples

Element	District	Concentrations ^a , $\overline{X} \pm S.D., \mu g/g$ (dry wt.)					
determined	No.	Village egg yolk	Village egg white	Farm egg yolk	Farm egg white		
P _b		0.59 ± 0.04	0.35 ± 0.03	0.49 ± 0.03	0.34 ± 0.02		
	$\overline{2}$	0.59 ± 0.02	0.37 ± 0.02	0.51 ± 0.02	0.35 ± 0.02		
		0.59 ± 0.02	0.38 ± 0.03	0.53 ± 0.02	0.34 ± 0.01		
Cu		1.38 ± 0.13	0.79 ± 0.14	0.93 ± 0.07	0.63 ± 0.09		
	2	1.21 ± 0.06	0.69 ± 0.04	0.89 ± 0.06	0.59 ± 0.04		
	3	1.37 ± 0.06	0.89 ± 0.04	0.95 ± 0.07	0.63 ± 0.03		
Zn		32.9 ± 2.6	0.38 ± 0.02	24.6 ± 1.2	0.27 ± 0.03		
		32.4 ± 1.4	0.38 ± 0.03	25.8 ± 1.6	0.28 ± 0.03		
		32.8 ± 1.1	0.33 ± 0.01	29.0 ± 0.7	0.25 ± 0.01		
Mg		175.4 ± 3.6	101.4 ± 7.6	154.6 ± 7.6	89.1 ± 6.1		
		169.9 ± 7.1	103.6 ± 4.3	148.9 ± 6.2	79.1 ± 7.2		
		176.5 ± 1.9	106.6 ± 6.9	145.8 ± 5.3	93.8 ± 4.4		
Ca		$794 + 27$	192 ± 22	$569 + 25$	122 ± 17		
		$737 + 21$	203 ± 20	560 ± 36	125 ± 11		
	3	$787 + 23$	162 ± 16	593 ± 15	108 ± 8		
Fe		62.1 ± 5.6	2.24 ± 0.21	47.8 ± 4.4	1.54 ± 0.13		
		53.7 ± 4.8	1.22 ± 0.11	40.2 ± 3.6	1.36 ± 0.06		
	3	64.9 ± 2.4	1.42 ± 0.12	47.1 ± 1.1	1.15 ± 0.04		

^a The mean and standard deviation of the sample solutions of each district obtained from the mean of 10 replicate measurements for a sample solution with 95% confidence level, $\overline{X} \pm ts/\sqrt{n}$.

tested with standard additions method by using the modifier mixture and nearly the same result was found with the direct determination method. The results are given in Table 4.

results of previous work (Shang & Wang, 1997). Small differences were observed for Zn and Fe in village egg yolks, but the other results were similar. It was also observed that concentrations of analytes studied in village eggs were higher than farm eggs.

3.5. Determination of analytes in egg samples

Determination of Zn (in egg white samples), Pb and Cu by ETAAS using $Y + Pd + CA$ modifier mixture and Zn (in egg yolk samples), Ca, Mg and Fe by FAAS was carried out in fresh egg samples. All results are based on the calibration graph method and seven replicate measurements of solutions. Maximum pyrolysis temperatures for analytes obtained with $Y + Pd + CA$ (Table 2) and optimized mass ratios of modifier components were used for the determination of Pb, Cu and Zn in sample solutions and for working standard solutions. The results are given in Table 5. As can be seen in Table 5, it was found that the Cu/Zn mean ratios were about 0.04 for village egg yolk, 0.04 for farm egg yolk, 2.17 for village egg white and 2.31 for farm egg white of the egg samples, respectively. Although Cu/Zn ratios for egg white of the samples were higher than egg yolk, no significant skin-colour difference was found. Concentrations of Ca in all parts are higher than Mg concentrations. Ca/ Mg ratios for village eggs obtained are higher than farm eggs and they showed obvious differences due to the different sources of feed. Concentrations of Zn in egg yolk are higher than the egg white. The obtained results of Cu, Zn Mg, Ca and Fe from Table 5 by converting to wet weight using humidity loss were compared with the

4. Conclusions

Determination of Zn (in egg white samples), Pb and Cu in egg samples by ETAAS using $Y+Pd+CA$ modifier mixture and Zn (in egg yolk samples), Mg, Ca and Fe by FAAS were studied. The analytical problems coming from a sample matrix can be lowered by using Y+Pd+CA modifier mixture and ETAAS with Zeeman background correction. Direct determination of low concentrations of Pb, Cu and Zn in food, biological samples, etc. may be carried out by using suitable modifiers such as $Y + Pd + CA$.

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