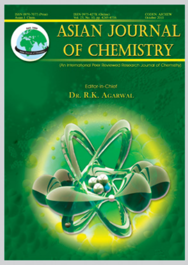
Asian Journal of Chemistry; Vol. 24, No. 6 (2012), 2613-2616

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Evaluation of the Platinum Group Metals as Modifiers for Determination of Cd, Pb and Ni in Syrian Cow Milk by Graphite Furnace Atomic Absorption Spectrometry

SAAD ANTAKLI[1,*], NAZIRA SARKIS[2] and AHMAD ABO HAJAR[1]

[1]Department of Chemistry, Faculty of Science, Aleppo University, Aleppo, Syria
[2]Department of Analytical and Food Chemistry, Faculty of Pharmacy, Aleppo University, Aleppo, Syria

*Corresponding author: E-mail: antakli@scs-net.org

(*Received*: 2 June 2011; *Accepted*: 17 January 2012) AJC-10956

Cadmium, lead and nickel contents in Syrian trade marks cow milk (goody, milk man, buon giorno, Rihana and Al-faiha) were determined, by using atomic absorption spectrometry with a transversely heated graphite atomizer (THGA) and a self-reversal (SR) background correction system, after microwave digestion. The electrothermal behaviour of aqueous solution containing 3 μg L^{-1} Cd, 50 μg L^{-1} Pb and 50 μg L^{-1} Ni in 0.2 % HNO_3 during pyrolysis and atomization steps was studied, without modifier and in modifier presence of 10 μg Pt, Ru, Ir, Rh and Pd. Palladium was selected as the optimum modifier with concentration range 1-5 μg for Cd and 1-10 μg for Pb and Ni. The pyrolysis and atomization temperatures in presence of Pd as modifier were fixed at 850 ºC and 1600 ºC for Cd, at 950 ºC and 2000 ºC for Pb and at 1550 ºC and 2300 ºC for Ni respectively. The characteristic masses (m_0) were 1.19 pg Cd, 27.75 pg Pb and 34.46 pg Ni. Limits of detection (LOD, 3s) were 0.037 μg L^{-1} Cd, 1.06 μg L^{-1} Pb and 2.04 μg L^{-1} Ni. Analytical linear ranges were 0.25-5 μg L^{-1} for Cd, 5-80 μg L^{-1} for Pb and 25-100 μg L^{-1} for Ni with the Pd modifier.

Key Words: Palladium, Modifier, Cd, Pb, Ni, Syrian cow milk.

INTRODUCTION

Milk as close as possible to be ideal food for children because of the combination food-rich and availability[1]. Milk contains a large number of metal elements, which are important and necessary to human body where it plays a key role in maintaining the metabolism of the human body. They are classified in biochemical processes such as ring carbs and installation of hormones[2]. Milk and its products contain a number of toxic metal elements as cadmium, lead and nickel, due to these elements presence in the biosphere in general[3], but often their concentrations are low and fall within the permissible limits, according to the world health organization. Among the available modern technologies, graphite furnace atomic absorption spectrometry (GFAAS) is still the most widely used technique, fastest, most accurate and sensitive determination of the metal elements in several samples such as blood[4], human teeth[5], diesel and gasoline[6], chewing gum[7], tea leaf[8], mineral water[9], wine[10], membranes of animal[11], honey[12], *etc*. There are many difficulties in determination of trace metals, especially in very low concentration and differences their contents[11]. In order to decreasing the effects of matrix sample and increasing the thermal stability of the considered elements, a large number of modifiers was suggested, first at all platinum group metals (PGMs), but the obtained results were variable[7,9,10,12,13]. These variable results led us to find the appropriate modifier kind and its concentration.

EXPERIMENTAL

The determinations were performed with a biotech (phoenix-986) atomic absorption spectrometer equipped with self-reversal (SR) background corrector, pyrolytically coated transverse heated graphite atomizer, argon 99.998 % was used as a purge gas. The instrumental conditions adopted for the spectrometer are presented in Table-1.

TABLE-1
INSTRUMENTAL CONDITIONS FOR THE GFAAS

Parameters	Cd	Pb	Ni
Wavelength (nm),	228.8	283.3	232.0
Lamp current (mA)	2.0	2.0	4.0
Slit (mm)	0.2	0.4	0.2
Background corrector	SR	SR	SR
Negative high voltage (V)	377.7	433.5	448.5
Broad pulse current (mA)	1.3	1.1	1.5
Narrow pulse current (mA)	3.0	2.5	3.5

Sample digestion was carried out by using a closed-vessel microwave system, model Ethos D (Milestone, Sorisole, Italy), equipped with 10 TFM® vessels of 100 mL and a ceramic vessel jacket.

High purity deionized water obtained from a Milli-Q water purification system was used. Analytical reagent grade HNO_3 65 % (ww^{-1}) and H_2O_2 30 % (w w^{-1}) (Merck, Germany) were used for sample digestion. The analytical reference solutions were prepared by successive dilution of 1000 mg L^{-1} of Cd, Pb and Ni standard solutions (Merck, Germany) in 0.2 % HNO_3 and were stored at 4 ºC in dark glass bottles.

Palladium modifier was obtained by dilution of 10 g L^{-1} of high purity $Pd(NO_3)_2$ solutions, platinum modifier was obtained from platinum(IV) chloride (57.5 % Pt), ruthenium modifier was obtained from high purity ruthenium red, iridium modifier was obtained from iridium(III) chloride hydrate and rhodium modifier was obtained from rhodium(II) acetate dimer (46.5 % Rh) all of them from (Merck, Germany). All solutions were stored at 4 ºC in dark glass bottles.

RESULTS AND DISCUSSION

Pyrolysis and atomization temperature curves: Pyrolysis and atomization temperature curves for Cd, Pb and Ni in aqueous standard solutions were established to determine the optimum temperature program. Since chemical modifiers can alter the thermal behaviour of the matrix, they can be used for thermal stabilization of the analytes and for the removal of matrix constituents that may cause interference during measurements. In this study, we evaluated Pt, Ru, Ir, Rh and Pd as chemical modifiers for Cd, Pb and Ni. Solutions containing 3 µg L^{-1} Cd, 50 µg L^{-1} Pb and 50 µg L^{-1} Ni in 0.2 % HNO_3 were used to optimize the heating programs for GFAAS determination in the absence and presence of each 10 µg of Pt, Ru, Ir, Rh and Pd as modifiers. Pd is found to be the best modifier, depending on the pyrolysis and atomization temperature curves as illustrated in Figs. 1-3.

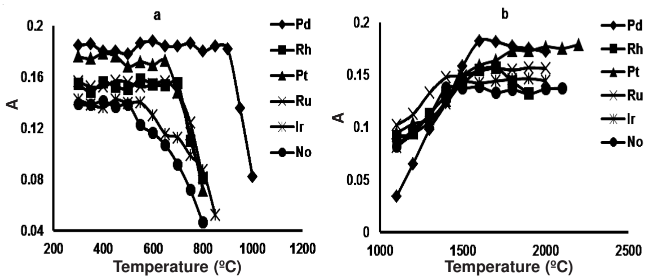


Fig. 1. Modifiers effect on the pyrolysis temperature (a) and atomization temperature (b) of 3 µg L^{-1} cadmium in aqueous standard solutions; Pd (◆), Rh (■), Pt (▲), Ru (×), Ir (*), no modifier (●).

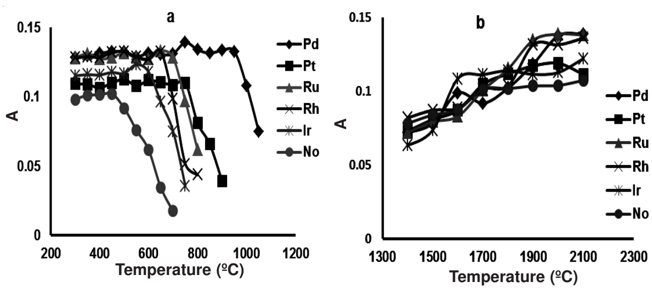


Fig. 2. Modifiers effect on the pyrolysis temperature (a) and atomization temperature (b) of 50 µg L^{-1} lead in aqueous standard solutions; Pd (◆), Pt (■), Ru (▲), Rh (×), Ir (*), no modifier (●)

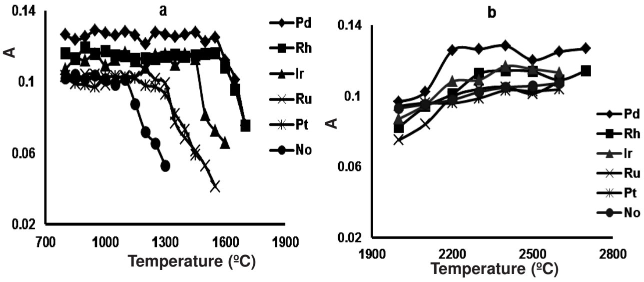


Fig. 3. Modifiers effect on the pyrolysis temperature (a) and atomization temperature (b) of 50 µg L^{-1} Nickel in aqueous standard solutions; Pd (◆), Rh (■), Ir (▲), Ru (×), Pt (*), no modifier (●).

The optimized conditions for the pyrolysis and atomization temperatures of Cd, Pb and Ni in the absence and presence of Pt, Ru, Ir, Rh and Pd as modifiers were presented in Table-2. The optimized heating program of the employed graphite tube for determining Cd, Pb and Ni with Pd modifier is presented in Table-3.

TABLE-2
OPTIMIZED PYROLYSIS AND ATOMIZATION TEMPERATURES OF Cd, Pb AND Ni IN THE ABSENCE AND PRESENCE OF Pt, Ru, Ir, Rh AND Pd AS MODIFIERS

Element	Modifier	Pyrolysis temperature (ºC)	Atomization temperature (ºC)
Cd	No modifier	500	1400
	Pt	650	1800
	Ru	650	1600
	Ir	550	1500
	Rh	700	1600
	Pd	850	1600
Pb	No modifier	450	1700
	Pt	750	1800
	Ru	700	1900
	Ir	600	1700
	Rh	650	1900
	Pd	950	2000
Ni	No modifier	1100	2300
	Pt	1250	2400
	Ru	1300	2300
	Ir	1450	2300
	Rh	1550	2400
	Pd	1550	2300

TABLE-3
OPTIMAL GRAPHITE FURNACE TEMPERATURE PROGRAM

Step	Temperature (ºC)	Ramp time (ºC s^{-1})	Hold time (s)	Argon flow rate (mL min^{-1})
Drying 1	75	4	5	250
Drying 2	85	3	5	250
Drying 3	95	3	3	250
Drying 4	120	3	8	250
Pyrolysis	850^a 950^b 1550^c	10	10	250
Atomization	1600^a 2000^b 2300^c	0	5	0
Cleaning	1800^a 2200^b 2500^c	0	1	250

^{a}according to cadmium; ^{b}according to lead; ^{c}according to nickel

Concentration of Pd modifier: There are variable concentrations for Pd as chemical modifier in different studies, for that we decided to determine of the best concentration of Pd modifier on depending on absorption and pyrolysis temperatures. Different concentrations range from 2 ng to 100 μg of Pd modifier were studied in aqueous standard solutions, containing for each element a constant concentration as follow: 3 μg L^{-1} Cd, 50 μg L^{-1} Pb and 50 μg L^{-1} Ni. The results showed that the best Pd concentration was in the range 1 to 5 μg for Cd, 1 to 10 μg for Pb and Ni (Fig. 4).

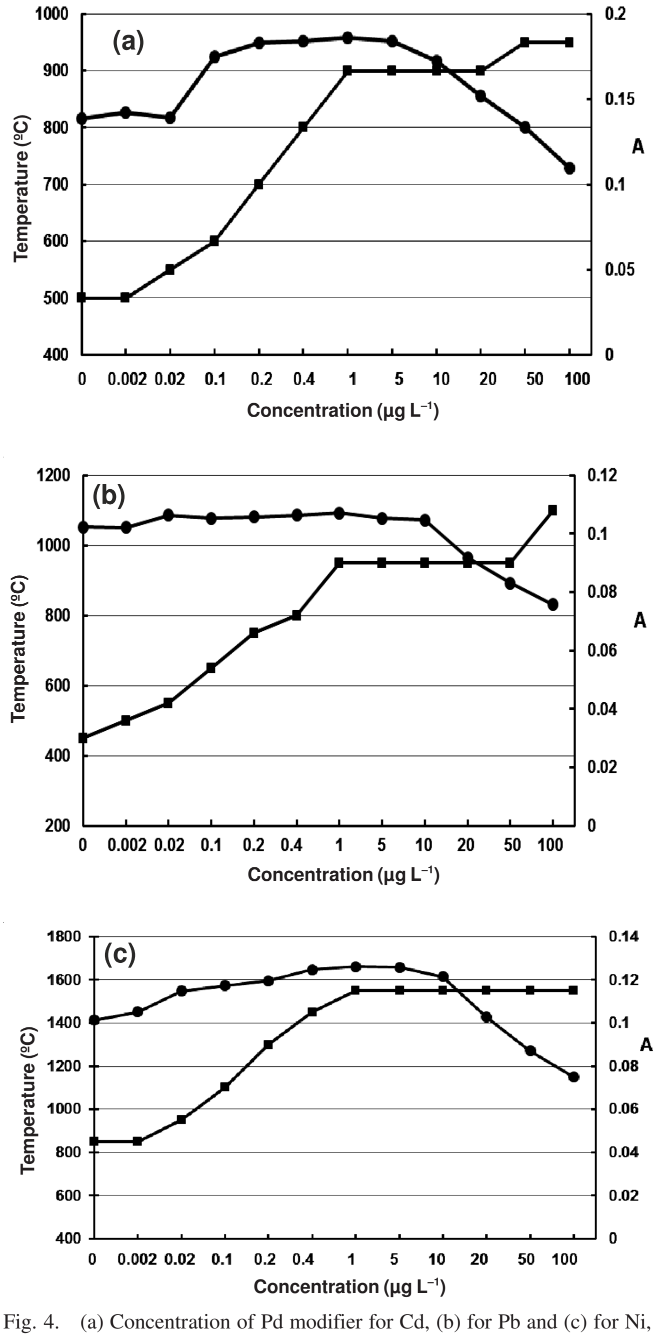


Fig. 4. (a) Concentration of Pd modifier for Cd, (b) for Pb and (c) for Ni, in aqueous standard solutions

Analytical characteristics and results: After establishing the optimal heating program, Pd as the best modifier among platinum group metals and its best concentration for determining Cd, Pb and Ni. Linear range in the absence of Pd modifier was 1 to 5 μgL^{-1} for Cd, 10 to 80 μgL^{-1} for Pb and 25 to 100 μgL^{-1} for Ni. And linear range in the presence of Pd modifier was 0.25 to 5 μgL^{-1} for Cd, 5 to 80 μgL^{-1} for Pb and 25 to 100 μgL^{-1} for Ni (Fig. 5).

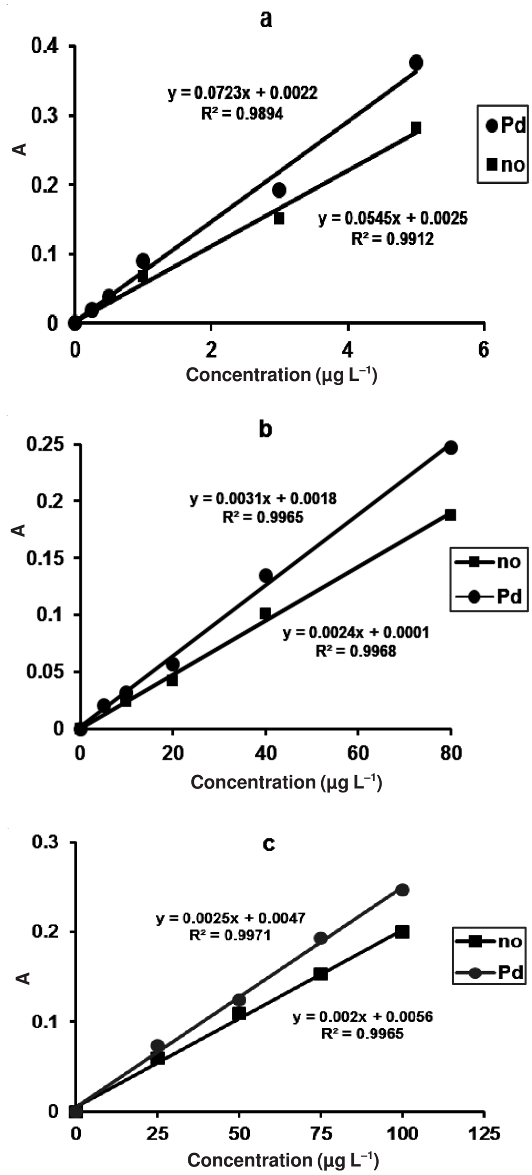


Fig. 5. Analytical calibration curve (a) Cd, (b) Pb and (c) Ni, in aqueous standard solutions; no modifier (■), with Pd modifier (●)

The detection limits was calculated, by considering the variability of 10 consecutive measurements of blank solution, according to 3 S_b/a (S_b = standard deviation of the blank and a = calibration curve slope), in the absence and presence 1 μg Pd as modifier, were 0.06 and 0.037 μg L^{-1} respectively for Cd, 1.62 and 1.06 μg L^{-1} respectively for Pb, 2.70 and 2.04 μg L^{-1} respectively for Ni. The characteristic masses (m_0) calculated from the calibration curves and were based on the integrated absorbance in the absence and presence 1 μg Pd as modifier, were 1.58 and 1.19 pg respectively for Cd, 37.12 and 27.75 pg respectively for Pb, 42.18 and 34.46 pg respectively for Ni.

Cadmium, lead and nickel determinations in some syrian cow milk trade-marks: A microwave-assisted wet decomposition of cow milk samples purchased from local supermarket in Aleppo city was performed according to a slightly modified procedure[5]. Sample masses of around 1 g were digested using an oxidant mixture (8 mL HNO_3 + 2 mL H_2O_2). The microwave oven heating program was performed in six steps as depicted in Table-4. After digestion, samples and blank solutions were transferred to beaker capacity 50 mL and then vapourized on electric heater, at relatively low temperature, to near drought, then transferred to the 10 mL flask and add 1000 µL of Pd modifier (1 mg L^{-1}) then completed up to 10 mL with deionized water.

TABLE-4
MICROWAVE HEATING PROGRAM FOR SAMPLE DIGESTION

Step	Time (min)	Power (W)	T (ºC)
1	1	250	180
2	1	0	180
3	6	250	200
4	5	400	210
5	5	650	220
6	Vent : 5 min		

After samples digestion, we applied the optimized conditions. The measurements were made by injection of 20 µL from the sample inside the graphite furnace. The results obtained are presented in Table-5.

TABLE-5
ELEMENTS CONCENTRATIONS IN COW'S MILK IN SOME SYRIAN TRADE MARKS

Milk trade marks	Type	Cd (µg kg^{-1} ± SD)	Pb (µg kg^{-1} ± SD)	Ni (mg kg^{-1} ± SD)
Goody	Flavourless	1.2 ± 0.1	24.6 ± 2.5	0.20 ± 0.01
	Strawberry milk	0.9 ± 0.1	18.2 ± 1.9	0.38 ± 0.01
	Banana milk	2.6 ± 0.1	10.8 ± 1.0	0.26 ± 0.01
	Chocolate milk	3.1 ± 0.2	36.0 ± 3.6	0.30 ± 0.02
Milk man	Flavourless	1.5 ± 0.2	19.7 ± 2.3	0.32 ± 0.02
	Strawberry milk	1.2 ± 0.1	28.3 ± 1.5	0.48 ± 0.01
	Banana milk	1.8 ± 0.2	16.1 ± 1.7	0.51 ± 0.01
	Chocolate milk	2.8 ± 0.4	20.9 ± 1.7	0.57 ± 0.01
Buon giorno	Flavourless	2.0 ± 0.2	26.3 ± 2.0	0.46 ± 0.01
	Strawberry milk	1.7 ± 0.2	17.7 ± 1.2	0.53 ± 0.02
	Banana milk	1.9 ± 0.2	11.1 ± 1.4	0.36 ± 0.02
	Chocolate milk	2.2 ± 0.3	32.5 ± 3.2	0.40 ± 0.02
Rihana	Flavourless	2.4 ± 0.3	23.6 ± 2.0	0.37 ± 0.02
Al-faiha	Flavourless	1.1 ± 0.1	15.1 ± 1.7	0.29 ± 0.02
Mean		2.2	25.0	0.38

The lowest contents of Cd were found as 0.9 µg kg^{-1} for goody (strawberry milk) and the highest 3.1 µg kg^{-1} for milk man (chocolate milk), with average 2.2 µg kg^{-1} and relative standard deviations less than 16.4 %. The lowest contents of Pb were found as 10.8 µg kg^{-1} for goody (banana milk) and the highest 36.0 µg $kg^{-1}$for goody (chocolate milk), with average 25 µg kg^{-1} and relative standard deviations less than 12.9 %. The lowest contents of Ni were found as 0.20 mg kg^{-1} for goody (flavourless) and the highest 0.57 mg $kg^{-1}$for milk man (chocolate milk), with average 0.38 mg kg^{-1} and relative standard deviations less than 8.3 %. There are wide variations in the published data for the elemental concentrations of cow's milk of different countries. Table-6 presents the Cd, Pb and Ni metals concentrations, recorded in several countries, to be compared with our results.

TABLE-6
COMPARISON OF THE ELEMENTAL CONCENTRATIONS OF COW'S MILK IN SYRIA WITH THE PUBLISHED VALUES

Country	Concentration (µg kg^{-1})		
	Cd	Pb	Ni
Japan	1.0	50.0	-
Germany	0.1	5.5	-
India	0.1	1.6	-
Spain	-	49.3	-
Poland	15.0	20.0	-
USA	9.7	34.0	-
Saudi Arabia	4.7	3.5	-
Turkey	20.0	25.0	300.0
Syria	2.2	25.0	380.0

Cd, Pb and Ni metals levels in analyzed samples were found to be under permissible limits compared with World Health Organization[14].

Conclusion

In the present work, platinum group metals as modifiers with three elements cadmium, lead and nickel were studied. Pyrolysis and atomization temperatures were found to be the best with palladium modifier. The optimal Pd concentration as modifier was from 1 to 5 µg for cadmium, 1 to 10 µg for lead and nickel. Optimum temperature program and analytical conditions were determined at 1 µg Pd as modifier and determining cadmium, lead and nickel concentrations in Syrian cow's milk and evaluation the contamination risk with these three toxic heavy metals, as well as comparison the results with world published data and World Health Organization.

REFERENCES

1. P.C. Aleixo and J.A. Nobrega, *Food Chem.*, **83**, 457 (2003).
2. R.S. Kumar, M. Aqrawal and F. Marshall, **66**, 258 (2008).
3. P. Licata, D. Trombetta, M. Cristani, F. Giofre, D. Martino, M. Calo and F. Naccari, *Environ. Int.*, **30**, 1 (2004).
4. C.D. Palmer, M.E. Lewis Jr., C.M. Geraghty, F. Barbosa Jr. and P. Parsons, *Spectrochim. Acta B*, **61**, 980 (2006).
5. D.S Junior, F.B. Junior, S.S. de Souza and F.J. Krug, *J. Anal. Atom. Spectrom.*, **18**, 939 (2003).
6. M.N. Matos Reyes and R.C. Campos, *Spectrochim. Acta B*, **60**, 615 (2005).
7. Z. Kilic, E. Kenduzlerb and O. Acarc, *Food Chem.*, **77**, 85 (2002).
8. S.P. Han, W.E. Gan and Q.D. Su, *Talanta*, **72**, 1481 (2007).
9. V.R.A. Filho, K.G. Fernandes, M. de Moraes and J.A.G. Neto, *J. Braz. Chem. Soc.*, **15**, 28 (2004).
10. Z. Ajtonya, N. Szoboszlai, E.K. Susko, P. Mezei, K. Gyorgy and L. Bencs, *Talanta*, **76**, 627 (2008).
11. M.G.A. Korn, G.L. dos Santos, S.M. Rosa, L.S.G. Teixeira and P.V. de Oliveira, *Microchem. J.*, **96**, 12 (2010).
12. Z. Ajtony, L. Bencs, R. Haraszi, J. Szigeti and N. Szoboszlai, *Talanta*, **71**, 683 (2007).
13. W. Penninckx, D.L. Massart and J.S. Verbeke, *Fresenius J. Anal. Chem.*, **343**, 526 (1992).
14. FAO/WHO, Codex General Standard for Contaminants and Toxins in Food and Feed. Codex Standard 193-1995, Amended 2009, 2010.