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Analysis of Metal Contents in Maraş Powder and Different Cigarette Brands in Turkey

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Abstract: The metal contents in hand made Maraş powder, mixed oak–ash Maraş powder and twelve different cigarette brands sold in Kahramanmaraş, Turkey were the aim of this study. The concentration of tin (Sn), cadmium (Cd), lead (Pb), aluminium (Al), iron (Fe), zinc (Zn), chromium (Cr), nickel (Ni), copper (Cu), manganase (Mn), arsenic (As) and mercury (Hg) in hand-made pure Maraş powder and mixed oak–ash Maraş powder were determined using inductively coupled plasma-optic emission spectrometry (ICP-OES) instrument. Before the analyses, all the samples were digested in closed teflon vessels under microwave power and diluted to appropriate volume with ultrapure water and then, analyzed with ICP-OES instrument. According to the results, Al, Mn, Cu, Zn and Pb contents in Maraş powder and oak–ash mixed Maraş powder were found as very high for human health, whereas, different cigarette brands were clean.

Keywords: Cigarette, tobacco, Maraş powder, metal analysis, ICP

Maraş Otu ve Türkiye'de Satılan Farklı Sigara Markalarının Metal İçerik Analizleri

Özet: Kahramanmaraş, Türkiye' den temin edilen, el yapımı saf Maraş otu, meşe kömürü karıştırılmış Maraş otu ve Türkiye' de satılan on farklı sigara markasında, kalay (Sn), kurşun (Pb), alüminyum (Al), demir (Fe), çinko (Zn), krom (Cr), nikel (Ni), bakır (Cu), mangan (Mn), arsenik (As) ve civa (Hg) içerikleri indüktif eşleşmiş plazma optik emisyon spektrometresi (ICP-OES) ile belirlendi. Bu analiz öncesinde tüm numuneler mikrodalga fırın kullanılarak, teflon kaplar içerisinde parçalandı ve ultrasaf su uygun hacimlere seyreltildi ve sonrasında ICP-OES ile analiz edildi. Elde edilen sonuçlara göre, sigara markaları temiz iken, saf Maraş otu, meşe kömürü karıştırılmış Maraş otu içerisindeki Al, Mn, Cu, Zn ve Pb konsantrasyonlarının insan sağlığı için çok tehlikeli olabilecek düzeyde yüksek olduğu bulunmuştur.

Anahtar kelimeler: Sigara, tütün, Maraş otu, metal analizi, ICP

1. Introduction

There are a lot of tobacco products manufactured in different countries and marketed under various names. Using tobacco products is one of the bad habits of people in the world. Tobacco smoking is a worldwide problem with 1.3 billion people currently smoking cigarettes and one person loosing life every 6s due to tobacco related illnesses. Tobacco smoking is one of the significant sources of toxic metals in both human body and environment. [1]. Worldwide tobacco causes nearly 5 million deaths annually (one in 10 deaths) with 2.41 million deaths in the developing and 2.43 million in

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the developed countries [2,3]. Element containing in tobacco is a function of many factors like soil characteristics, climatic conditions and plant variety [4]. In general, tobacco plants accumulate heavy metals like Pb, Cd, and Zn preferentially [5]. Presence or concentration of one element in the soil also affects the uptake of other element by plant, for example, absorption or uptake of cadmium is stimulated in the presence of lead [6]. Trace elements in living organisms, even in minute concentration, play a significant biological role in life process. Cigarette smoking is a source of radiation exposure due to the concentrations of natural radionuclides in the tobacco leaves. From the health point of view, measurement of ^{210}Pb and ^{210}Po contents in cigarette tobacco is important to assess the radiological effects associated with the tobacco smoking for the smokers. A plant powder called Maraş powder has been used widely instead of cigarette in the city of Kahramanmaraş¸ in Turkey and its surroundings [7-10]. It was confirmed that this powder has been made of tobacco Nicotiana Rustica Linn. The leaves of Nicotiana Rustica Linn are powdered, mixed, crushed with the ash obtained from the oak, walnut tree, or vine stick in the proportion of 1/2 or 1/3, and humidified a little before it is used. It is known that the ash blended during the preparation stage of Maraş powder eases the absorption of nicotine from the mouth mucous membrane by making the medium alkaline. Maraş powder is a kind of smokeless tobacco that is used by the addicts through buccal mucosa instead of cigarette or in order to give up smoking [11]. There is different work related Maraş powder in the literature [12-15]. Moreover, radioactivity of tobacco leaves and radiation dose induced from smoking has been measured by Papastefanou [16]. The aim of this study is to determine trace elements in Maraş powder by using ICP-OES method. The determination of trace elements in the samples can be done by different methods. Undoubtedly, one of the most popular methods for this purpose at present are inductively coupled plasma atomic emission spectrometry (ICP-OES). Because, ICP-OES method is very fast and reliable.

2. Experimental

2.1. General

Cigarette samples were completely digested using Berghof MWS3+ (Germany) instrument having 2.45 GHz magnetron provides 1450 watt microwave power. Perkin Elmer Optima 2100 DV coupled with AS93 plus auto sampler were used for ICP-OES analyses. $NaBH_4$ was used in order to obtain As and Hg hydrides with continuous hydride system attached to ICP-OES for As and Hg analyses. External calibration curves were drawn for each element. Mixed calibration standard solutions were prepared with appropriate dilutions of Inorganic Ventures (USA) calibration stocks (about 1000 mg l^{-1}). Calibration points and emission wavelengths of the elements were determined according to the elements. Ultrapure water obtained from a Milli-Q purifier system (Millipore Corp., Bedford, MA) was used throughout the work. All solutions were prepared using a Milli-Q ultrapure water. Concentrated nitric acid (Merck, Darmstadt, Germany) and hydrogen peroxide 35 % (m/m) (Merck) were used in the microwave vessels.

2.2. Microwave Digestion of Cigarette Samples

The modified digestion method of the instrument was applied for the samples. Approximately 0.35-1.00 g sample was placed into teflon DAP 60 vessels. Then, 3 mL HNO_3 (65 %) and 2 mL H_2O_2 (35 %) were added slowly into each vessel and stirred for 20 min., then, the vessels were closed and applied the heating program shown in Table 1.

Table 1. Optimized microwave digestion method.

Temperature (^{o}C)	150	180	100	100	100
Rise Time (min.)	5	5	1	1	1
Hold Time (min.)	5	10	10	1	1

Power: 60 % of 1450 watt.

Digested samples were diluted appropriate amount of ultrapure water. The appropriate amount of the samples were digested in order to analyse in LOQ limits for each element. Polypropylene autsampler vials were used in autosampler.

2.1. Measurement of trace elements in the samples by ICP-OES

Calibration standards of the elements were prepared by diluting stock standards with %2 (v/v) HNO_3. Optimum ICP-OES parameters have been determined and applied all calibration standards and samples (Fig.1, Table 2). Calibration was checked with Merck CertiPUR ICP Multi Element Standarts.

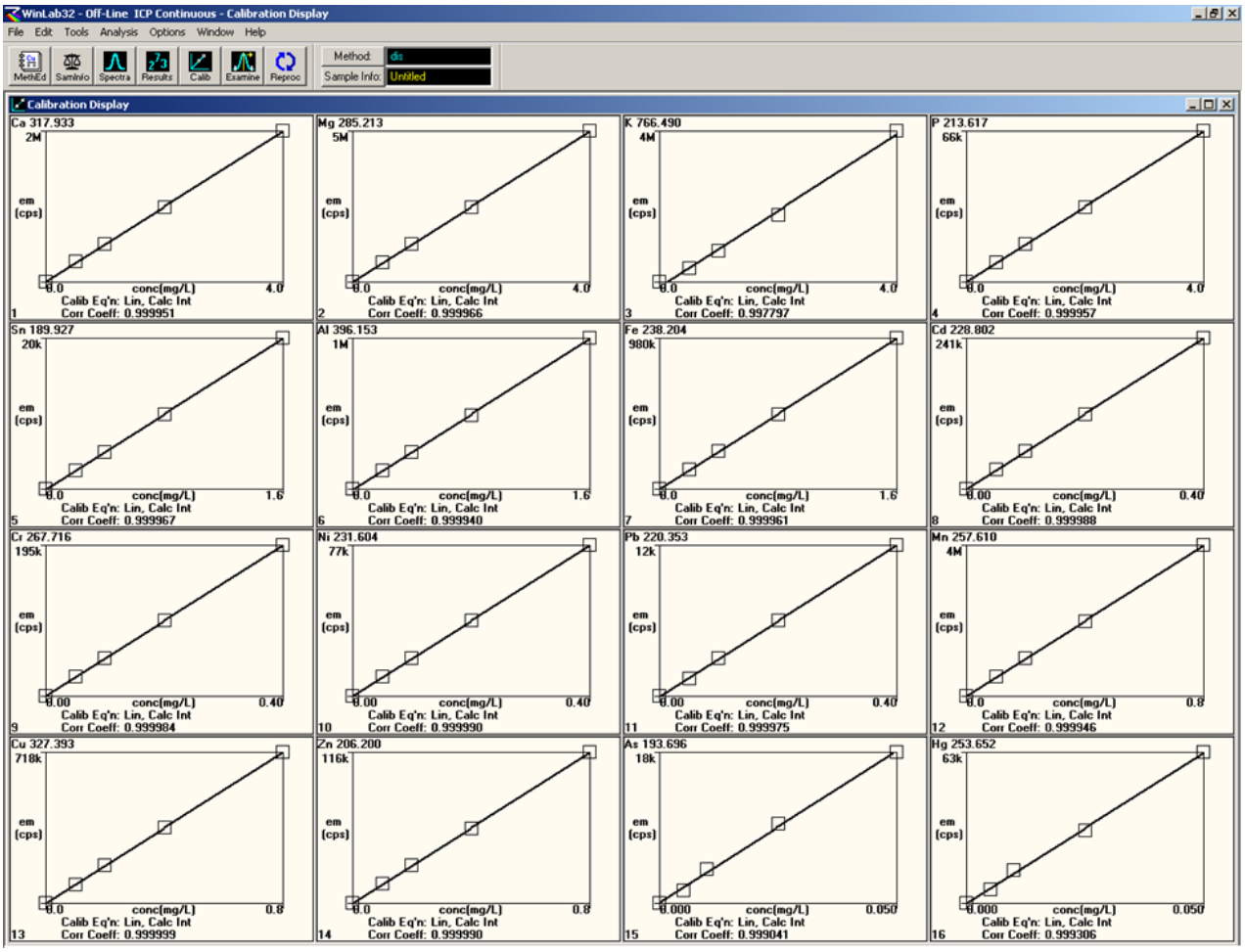

Figure 1. Calibration curves.

Table 2. Operational parameters used for ICP-OES analyses.

Operational Parameters	
RF power (W)	1450
Generator frequency (MHz)	40.68
Plasma gas-flow rate (L min^{-1})	17
Nebulizer gas-flow rate (L min^{-1})*	0.8
Auxiliary gas-flow rate (L min^{-1})	0.2
Sample flow-rate (mL min^{-1})	1.5
Spray Chamber*	Rayton Scott
Nebulizer	GemTip Crossflow
Injector	2 mm inner diameter (i.d.) Alumina

Elements	Emission Wavelengths (nm)
Sn	189.927
Al	396.153
Fe	238.204
Cd	228.802
Cr	267.716
Ni	231.604
Pb	220.353
Mn	257.610
Cu	327.393
Zn	206.200
As*	193.696
Hg*	253.652

*Spray chamber was not used and 0.45 L min^{-1} nebulizer flow was applied for continuous hydride system.

3. Results and Discussion

Sample digestion with minimum interference and contaminant under microwave power is the basis of quantitative analysis. The digestion procedure must dissolve the analytes of interest in a matrix suitable for the type of analysis with minimal sample loss and contamination. Optimum digestion method was determined after doing some pre-tests. HNO_3 and H_2O_2 were suitable mixture for digestion under microwave power.

Scott spray chamber was used for Sn, Al, Mn, Cr, Fe, Ni, Cu, Zn, Cd, Pb analyses in ICP-OES analyses. Optimum instrument parameters have also been determined after some pre-tests shown in Table 2. Continuous hydride system was used for As and Hg analyses by using basic solution of $NaBH_4$ as a hydride generation[17,18].

Some metal ions such as lead, copper or cadmium causes many specific diseases. Tobacco leaves naturally accumulate and concentrate relatively high levels of cadmium and lead, and therefore smoking of tobacco is an important source of cadmium and lead exposure for smokers. It has been reported that one cigarette contains about 0.5 - 2 μg of cadmium and that about 10% of the cadmium content is inhaled when the cigarette is smoked. Smokers generally exhibit significantly higher cadmium body burdens than non-smokers. Other hazards were reported in the literature [11-15, 17]. The Maraş powders have high amounts of Al, Mn, Cu, Zn and Pb metals possibly because of the grinding process of tobacco and oak-ash in the old metallic materials.

The quantitative ICP-OES results, standart deviations and RSD (relative standart deviation) % of samples have been shown in table 3 and 4. A reagent blank was run with sample digestion experiment. The reagent blanks were treated and analyzed in exactly the sameway as the real samples. The limit of quantification (LOQ) is the lowest concentration of an element that can be determined to be statistically different from an analytical blank. Concentrations of toxic elements such as Pb, Cd, Cu, As and Hg etc. in tobacco samples of ten different brands are not high as shown

in Table 3, if compared with pure Maraş powder and oak-ash mixed Maraş Powder and the literature [2,5,19-23].

Table 3. ICP-OES results of the cigarettes after microwave digestion.

		Samples											
Elements	LOQ	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	Pure Maraş powder	Mixed oak-ash Maraş powder
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Al	0.020	0.448±0.005	0.417±0.006	0.503±0.004	0.422±0.003	0.362±0.006	0.386±0.007	0.424±0.005	0.384±0.006	0.411±0.002	0.435±0.012	1844.00±5.00	2978.00±4.93
Mn	0.010	0.175±0.002	0.218±0.001	0.117±0.005	0.190±0.001	0.141±0.004	0.142±0.001	0.196±0.005	0.149±0.006	0.243±0.006	0.176±0.003	135.70±1.10	233.90±1.30
Cr	0.015	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	4.46±0.05	4.35±0.06
Fe	0.010	0.688±0.020	0.652±0.004	0.788±0.008	0.643±0.005	0.557±0.008	0.595±0.004	0.638±0.010	0.559±0.011	0.642±0.007	0.556±0.009	2211.00±2.29	1348.00±2.14
Ni	0.025	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	8.18±0.07	6.833±0.08
Cu	0.010	UD	0.012±0.002	0.014±0.002	0.013±0.001	0.012±0.001	0.012±0.001	0.011±0.002	0.012±0.002	0.011±0.002	0.010±0.001	5.14±0.06	19.36±1.10
Zn	0.015	0.0520±0.006	0.058±0.005	0.048±0.002	0.058±0.004	0.060±0.005	0.051±0.001	0.059±0.002	0.047±0.006	0.064±0.004	0.051±0.001	34.10±0.4	45.108±0.4
Sn	0.030	0.045±0.012	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD
Pb	0.015	0.016±0.004	UD	UD	UD	UD	UD	UD	UD	0.017±0.003	UD	2.56±0.02	8.062±0.2
As*	0.0025	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD
Cd	0.015	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	0.84±0.001	0.624±0.001
Hg*	0.0025	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD	UD

Results are mean ± SD of three replicate analyses.
UD: < LOQ: Limit of quantification (mg/kg).
*Continuous hydride system was used for As and Hg analyses.

Table 4. RSD % values of ICP-OES analyses for three replicates.

	Samples											
Elements	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	Pure Maraş powder	Mixed oak-ash Maraş powder
Al	0.14	2.35	0.80	0.61	0.01	1.87	1.17	1.48	0.46	0.44	2.42	0.59
Mn	0.08	0.40	0.20	0.12	1.07	0.46	0.18	0.31	0.23	0.15	0.70	0.59
Cr	--	--	--	--	--	--	--	--	--	--	0.51	0.41
Fe	0.27	0.68	0.64	0.79	1.03	0.62	0.11	0.21	1.03	0.43	1.20	1.44
Ni	--	--	--	--	--	--	--	--	--	--	0.38	1.06
Cu	--	15.56	10.93	2.47	0.85	2.57	18.07	15.27	14.24	5.38	1.07	1.14
Zn	6.98	8.67	2.25	6.83	8.13	3.88	3.57	12.99	6.27	0.44	1.18	0.98
Sn	26.24	--	--	--	--	--	--	--	--	--	--	--
Pb	22.54	--	--	--	--	--	--	--	21.10	--	6.47	0.18
As*	--	--	--	--	--	--	--	--	--	--	--	--
Cd	--	--	--	--	--	--	--	--	--	--	1.95	1.62
Hg*	--	--	--	--	--	--	--	--	--	--	--	--

Especially, concentrations of cadmium (Cd), lead (Pb), aluminium (Al), iron (Fe), zinc (Zn), chromium (Cr), nickel (Ni), copper (Cu) and manganase (Mn) have been found very high in hand made pure Maraş powder and oak-ash mixed Maraş Powder. Probably, the metal contamination happens due to grinding, drying and packaging processes. Because, it is used old metal equipments

especially including aluminium metal having impurities such as cadmium, lead, iron, zinc, chromium, nickel, copper and manganese. There is an important difference between pure Maraş powder and oak-ash mixed Maraş powder shown in Table 3. Maraş Powder mixed oak-ash has heavy metals higher than pure Maraş powder. Burned oak-ash containing some inorganic metal oxides pollute Maraş powder addition to the grinding process. Maraş Powder is consumed a lot in the Southern-East and east side of Turkey. The Maraş Powder addicts should be warned towards the serious health problems such as alzheimer, lung, kidney and pancreas cancer [6,8-13].

4. Conclusions

Maraş powder is commonly consumed in the southern part of Turkey. This study shows that Maraş powder is very harmful for the health in short and long period of time. A microwave digestion method in a closed vessel was developed and optimized for the determination of trace amounts of Sn, Cd, Pb, Al, Fe, Zn, Cr, Ni, Cu, Mn, As and Hg in cigarette tobacco samples and Maraş Powder. It has been found that Maraş powders have had heavy metals after ICP-OES analyses. The found amounts are over the hazardous levels if compared with the studies [1, 4, 6, 12, 13, 19-23].

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References

[1] Asma S., Mackay J.,, Song S.Y., Zhao L., Morton J.,, Palipudi K.M., Bettcher D., Bhatti L., Caixeta R., Chandora R., Dias R.C., Silva V.L.C., Fouad H., Hsia J., Husain M.J., McAfee T., Ramanandraibe N., Rarick J., Sinha D., Talley B., d'Espaignet E.T., "The GATS Atlas, Global Adult Tobacco Survey", CDC Foundation, World Health Organisation, Word Lung Foundation, Department of Health & Human Services, Centers for Disease Control and Preventation, UK, "2015".

[2] Schneider G., Krivan V., "Multi-elemental analysis of tobacco and smoke condensate by instrumental neutron activation analysis and atomic absorption spectrometry", Int. J. Environ. Anal. Chem. 1993, 53: 87–100.

[3] Ezzati M., Loprz A.D., "Estimates of global mortality attributed to smoking in 2000", Lancet, 2003, 362: 847–852.

[4] Lugon-Moulin N., Martin F., Krauss M.R., Ramey P.B., Rossi L., "Cadmium concentration in tobacco (Nicotiana tabacum L.) from different countries and its relationship with other elements", Chemosphere, 2006, 63: 1074–1086.

[5] Angelova V., Ivanov K., Ivanova R., "Effect of chemical forms of lead, cadmium and zinc in polluted soils on their uptake by tobacco", J. Environ. Prot. Ecol., 2003, 4: 316–327.

[6] Verma S., Yadav S., Singh I., "Trace metal concentration in different Indian tobacco products and related health implications", Food and Chemical Toxicology, 2010, 48: 2291–2297.

[7] Frank M., "Industrial X-Ray Fluorescence Analysis-New Applications and Challenges for Cryogenic Detectors Lawrence Livermore National Laboratory", 7. International Workshop on Low Temperature Detectors, Munich, Germany, 1-7, (1997).

[8] Erenmemisoglu A., Tekol Y., Kartal M., Kurucu S., "The use of a smokeless tobacco in our country Maraş powder", 2nd International Symposium of Pharmaceutical Sciences, Ankara, Turkey, 1-3, (1991).

[9] Ozkul Y., Donmez H., Erenmemisoglu A., Demirtas H., Imamoglu N., "Induction of micronuclei by smokeless tobacco on buccal mucosa cells of habitual users", Mutagenesis. 1997, 12 (4): 285–287.
[10] Buyukbese M.A., Koksal N., Guven A., Cetinkaya A., "Effects of smokeless tobacco "Maraş powder" use on respiratory functions", The Tohoku Journal of Experimental Medicine, 2004, 204 (3): 173–178.
[11] Aral M., Ekerbicer H.C., Celik M., Ciragil P., Gul M., "Comparison of Effects of Smoking and Smokeless Tobacco Maraş Powder Use on Humoral Immune System Parameters", Mediators of Inflammation, 2006, 1–4.
[12] Kılınç, M., Okur, E., Yıldırım, İ., Nanç, F., Kurutaş, E.B. "The investigation of the effect of Maraş powder (smokeless tobacco) on hematological parameters", Turk J. Haematol. 2004, 21(3): 131-136.
[13] Health Effects of Smokeless Tobacco Products, Scientific Committee on Emerging and Newly Identified Health Risks, European Commission, (2008).
[14] Sogut O., Sayhan M.B., Ustundag M., Orak M., "Paroxysmal Atrial Fibrillation After SmokelessTobacco (Maraş Powder) Use", J. Chin. Med. Assoc. 2009, 72 (5): 265-267.
[15] Papastefanou C., "Radioactivity of Tobacco Leaves and Radiation Dose Induced from Smoking", Int. J. Environ. Res. Public Health. 2009, 6:558-567.
[16] Hou X., Jones B.T., "Field instrumentation in atomic spectroscopy", Microchem. J. 2000, 66: 115-145.
[17] Martin T.D., "Determination of Trace Elements in Drinking Water By Axially Viewed Inductively Coupled Plasma-Atomic Emission Spectrometry", EPA Method 200.5-1, (2003).
[18] Bakircioglu D., Kurtulus Y.B., Ucar G, Determination of some traces metal levels in cheese samples packaged in plastic and tin containers by ICP-OES after dry, wet and microwave digestion. Food Chem. Toxicol. 2011, 49: 202-207.
[19] Queralt I., Ovejero M., Carvalho M.L., Marques A.F., Labres J.M., "Quantitative determination of essential and trace element content of medicinal plants and their infusions by XRF and ICP techniques", X-ray Spectrometry. 2005, 34: 213–217.
[20] Çiftçi H., Ölçücü A., "Determination of Iron, Copper, Cadmium and Zinc in Some Cigarette Brands in Turkey", International Journal of Science&Technology. 2007, 2(1): 29-32.
[21] Swami K., Judd C.D., Orsini J., "Trace metals Analysis of legal and counterfeit cigarette tobacco samples using inductively coupled plasma mass spectrometry and cold vapor atomic absorption spectrometry", Spectrosc Lett. 2009, 42: 472-490.
[22] Menden E.E., Elia V.J., Micheal L.W., Petering H.G., "Distribution of Cadmium and Nickel of Tobacco During Cigarette Smoking", Environ. Sci. Technol. 1972, 6(9): 830-832.
[23] Nrom I.C., Osibanjo, O., Oji-Nnorom, C. G. "Cadmium determination in cigarettes available in Nigeria", African Journal of Biotechnology. 2005, 4(10): 1128-1132.