Determining the Concentrations of Elements in Tobacco Selected in Iraqi Markets Using X-Ray Fluorescence Technique

Jamal K. Alsaide
Nada M. Hasan
Fadi H. Khudhur

Ministry of Science and Technology/ Baghdad

Received in : 8/May/2017,Accepted in :6/Septemper/2017

Abstract

X-rays fluorescence technology was used to measure the concentrations of trace and toxic elements in tobacco smoke. One sample local and eight samples were imported selected from Iraqi markets. The results proved that tobaccos contain few concentrations of element (calcium, potassium, sodium, manganese, magnesium, chlorine, and sulfur), trace concentrations of element (aluminum, vanadium, iron, cobalt, nickel, copper and zinc), and toxic concentrations of element (arsenic, selenium, bromine, antimony, cadmium, mercury and lead). Results are proved the concentrations of elements of samples are lower levels with the other countries in few element like (calcium, potassium, sodium and manganese), while the other elements were highest than the other countries.

Key words: X-rays fluorescence, toxic elements, tobacco

Introduction

Tobacco is herbaceous plant that contains nicotine ,carbon monoxide, tar, irritants and other noxious gases emitted in tobacco smoke. Also it contains heavy metals, toxic elements . These element affects on biochemical processes in the human body[1]. Cigarette smoke is a complex mixture of chemical compounds. Researchers had estimated that cigarette smoke contain 7,357 chemical compounds from many different classes [2]. In assessing the nature of tobacco, scientists must consider chemical composition, concentrations of components, particle size, and particle charge. These characteristics vary with the cigarette design and the chemical nature of the product. More than 3040 chemical compounds have been isolated from processed tobacco leaf. They are considered the risk for cancer, cardiovascular disease, and heart disease [3]. According to WHO, at least one person dies per 10 second as a result of cigarette smoking . These deaths can ultimately be traced to repeated toxicant exposures overtime [4].

Increasing the concentration of toxic elements is attributable to the atmosphere pollution, fertilizer, agriculture pesticides, packaging storage and other operations , as well as other chemicals to improve the taste and burn better [5] .Variety of analytical techniques are used to measure the heavy metals and other elements in tobacco cigarette. These techniques are comprised : inductively coupled plasma- mass spectrometry (ICP-MS) [6-7], inductively coupled plasma-atomic emission spectroscopy (ICP AES) [8-9], optical emission spectroscopy (ICP-OES) [10], atomic absorption spectrometry (AAS) [11-12] .

These techniques are destructive to the original sample. Several methods are applied to determination of trace metals in tobacco. Instrumental Neutron Activation Analysis (INAA) [13], and X-Ray Fluorescence (XRF) [14]. These techniques are non-destructive.

Identifying the chemical components in tobacco with the greatest potential for toxic effects in samples . This study done is to explore the toxic heavy metal concentrations in the tobacco from a selected cigarettes sample used XRF.

Materials and methods

Procedure for sample analysis:

In this study material consisted of selected-brands cigarettes (local and foreign) grouped according to most widely used in Iraqi market and more purchased at the same time. Eight imported samples were selected namely (PINE Light, GITANES, ROYAL, MARLBORO GOLD, MARLBORO EXTRA, KINT SILVER, GAULUISES, PINE SLIMS), and one local sample (SUMER) . The cigarettes sample paper -wrap was removed. Tobacco was mixed with a binder (PVC) added to the samples. They were crushed to dimeter range of less than 125 µm and greater than 63 µm, then drying in at 100-120 ^{0}C for 24 h. After cooling samples were pressed in hydraulic press into 15 Ton/cm^2 in dimeter 32 mm. The pellets were loaded in the sample chamber for measurement.

X-Ray Fluorescence (XRF):

XRF is one of the most important techniques for the analysis of metals and trace elements which is independent to the chemical form of the elements [15].

In this work X-ray tube manufactured by Spectro Xepos company is used, with detector silicone – lithium, with energy resolution 45ev in 5.9Kev of iron (Fe-55) isotope. The detector is cooled using Peltier phenomenon. The analysis work out using the comparative method with standard sources. There are advantages of connecting to the computer via Ethernet technology and XLab- pro program. The thickness of beryllium window is 0.076mm. Several targets were used to generate different X – ray energy. The targets are highly oriented pyrolytic graphite (HOPG), alumina (Al_20_3) and Molybdenum. Figures 1, 2 and 3 depicted the ROYAL sample spectrum. Precision and accuracy were tested by normal standard reference analysis in XRF unit. Table 1 shows the results which are proof that the unit XRF is credible for use in such measurements.

Results and discussions

Concentration of essential elements detected in the selected brands of cigarettes analyzed were presented in Table (2) . The trace and toxic elements is presented in table (3) and (4) .The result of this work was compared with other reports in Table (5) . The range of elements are (0.11-0.15)% , (2.27-3.84)% , (1.94-2.6)% , (0.01-0.023)%, (0.017-0.022)% , for Na, K , Ca, Mn , Mg respectively. We found K is higher than Ca level. The averaged levels are obtained for K , Ca and Mn in this work agree with the other in most reported value [16,17] . The value obtained for magnesium was observed to be ten times lower than magnesium level in cigarette reported in the other countries [17] . Heavy metals in tobacco include Aluminum (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Iron (Fe),Copper (Cu), Lead (Pb), Mercury (Hg), Selenium (Se), Nickel (Ni), and Cobalt (Co) are designated by the International Agency for Research on Cancer (IARC) as Group 1 carcinogens [18]. Table (3) shows the trace elements can quickly become toxic when in higher concentrations. The range is obtained for Fe (393-790.7)ppm which is lower than the other reported[1,18]. Aluminum concentration are less than the other reported [19].The range for Al are (39-371)ppm, Cu (12.7-22.0)ppm, and Zn(33.1-40.4)ppm were observed higher than the other reported level in cigarette [20]. The toxic elements, in this work has high toxicity even at a very low concentration in Table (4).

Arsenic was found in all samples convergent concentrations. The chemical is contains arsenic compound either to boost yield or as insecticide. In this work was observed to be higher level than arsenic in cigarette reported in the literature for countries[21,22]. The range of Pb is (3.5-6.0)ppm . The value was obtained in this work was observed to be five times higher than lead level in cigarette reported in the literature for countries [21,23]. Maximum permitted levels (MPL) are (3 mg/kg) and (10 mg/kg) for As and Pb respectively in tobacco cigarettes [21]. The similarity in the antimony to arsenic chemically in some biological effect leads. Pterions work conclude that tobacco smoke and antimony could interact in similar way to arsenic in producing toxicity[24] and the range for Sb are (5.0-23.0)ppm .This study confirms that tobacco is a notable source of many heavy metal pollutants particularly Cd. Smoking of 20 cigarettes per day has been estimated to result in the inhalation of 2–4 µg Cd and 1–5 µg Pb, or even more [25] . The range of Cadmium is (3.0-6.3) ppm was observed higher than the other reported level in cigarette [21,23]. Another high toxicity element found mercury with low concentration range of (1.0-2.1) ppm. This work applied to the American Environmental Protection Agency for medium weight adult human organism. Daily dose of mercury that does not invoke apparent health disturbances may reach up to 21 µg[26].

Conclusion

This study confirms that tobacco is a notable source of many ‘‘toxic’’ heavy metal pollutants particularly (Cd, Pb, As, Hg, Cu), and evaluate the contents of ‘‘essential’’ (Ca,Mg,K,Na,P)

The value obtained for some elements like Iron and magnesium lower than the other reported . The other elements like Copper ,Zinc, Arsenic , Cadmium , Mercury , Lead were observed higher than the other reported level in cigarette.

According to the World Health Organization Study Group on Tobacco Product Regulation (TobReg), further studies are required on the concentrations of metals in cigarette tobacco [27], as well as concentrations of metals in tobacco smoke obtained with the ISO.

References

1. NNOROM, INNOCENT CHIDI, (2015), Copper, Iron and Zinc concentrations of tobacco leaves and ready-to-use snuff products on sale in Imo State Southeastern Nigeria., J. Appl. Sci. Environ. Manage. Sept, 19 (3): 459 – 467.
2. U.S. Department of Health and Human Services. How tobacco smoke causes disease: the biology and behavioral basis for smoking-attributable disease: a report of the surgeon general. Atlanta, GA: US Department of Health and Human Services, Centers for Disease Control and Prevention, National Center for Chronic Disease Prevention and Health Promotion, Office on Smoking and Health, 2010. (accessed 27 Jan 2014).
3. Kleenman, M.J., Schauer, J.J., and Cass, G.R., (1999).J. Environ. Science. Technol.V0l. 33: 3516-3523.
4. WHO 1999 Environmental Health Criteria 211 – Health Effects of Interactions between Tobacco Use and Exposure to Other Agents (WHO), 1999. Geneva.
5. Cobb GP, Sands K, Waters M, et al. (2000), Accumulation of heavy metals by vegetables grown in mine wastes,J. Environ Toxicol Chem.19,.:600–607
6. Mark R. Fresquez, Steven R. Pappas, and Clifford H. Watson , (2013),Establishment of Toxic Metal Reference Range in Tobacco from US Cigarettes , journal of Analytical Toxicology , 37 (5) June .
7. Steven R. Pappas, Naudia Martone, Nathalie Gonzalez-Jimenez, Mark R. Fresquez and Clifford H. Watson, (2015), Determination of Toxic Metals in Little Cigar Tobacco with 'Triple Quad' ICP-MS, Journal of Analytical Toxicology Advance Access published, 27,:1-6.
8. Joshua Ryan and Michael Clark, (2010), Trace metal determination in tobacco and cigarette ash by inductively coupled plasma, Journal of Analytical Chemistry, 1, : 34-41.
9. Perez-Bernaa J.L., Amigo J.M., Fernandez-Torresa R., Belloa M.A., Callejon-Mochon M., (2011), Trace metal determination in tobacco and cigarette ash by inductively coupled plasma-atomic emission spectroscopy, J. Forensic Science International, 204, : 119–125.
10. Moerman J. W., Potts G. E., (2011), Analysis of metals leached from smoked cigarette litter, J.Tobacco Control , 20,: 30-35.
11. Wang N.X., Cui X.G., Han L., Zhaxi Y.and Dawa Z., (2007), Change of the trace elements content from cigarettes (tobacco) to its ash and to look at harm of stuck cigarette, NCBI, Sep;27(9):1845-7.
12. Asneem Gul Kazi, Nusrat Jalbani, Muhammad Balal , Muhammad Khan Jamali, Hassan Imran Afridi and Abdul Qadir Shah, (2009), Determination of toxic elements in different brands of cigarette by atomic absorption spectrometry using ultrasonic assisted acid digestion,J. Environmental Monitoring and Assessment, 154 :155-167 .
13. Hosseini A.A., Amirabadi A., Afarideh H., Hadji-Saeid S.M., Behrozi A.H.,(1996), Determination of toxic and non-toxic hair trace elements in tobacco smokers using PIXE and NAA techniques , j.Nuclear Interactions with Materials and Atoms,.109,.: 239-242
14. Rosalie V. Caruso, Richard Connor J. O., Edryd Stephens W., Michael Cummings K. and Geoffrey T. Fong, (2014), Toxic Metal Concentrations in Cigarettes Obtained from U.S. Smokers in 2009: Results from the International Tobacco Control (ITC) United States Survey Cohort, Int. J. Environ. Res. Public Health,.11.:202-217

15. Erick K. Towett , Keith D.Sheoherd and Geory Cadisch ,(2013), Quantification of total element concentration in soil using X-Ray fluoresce spectroscopy ,J. Science of the Total Environment, 463: 374-388.
16. ABDULKADIR LEVENT, YAVUZ YARDIM AND CENGIZ DEMIR , (2013),Determination of Trace Metal and Mineral Levels in the Tobacco and Cigarette samples using by FASS, J.Chem.Soc.Pak, 35(2).:257-261.
17. Chiba M. and Masiron R.,(1992),Toxic and trace elements in tobacco and tobacco smoke, J.Bull World Health Organ., 70(2) : 269–275
18. Adams, S.V., Passarelli, M.N.and Newcomb, P.A. (2012), Cadmium exposure and cancer mortality in the Third National Health and Nutrition Examination Survey cohort. Occup. Environ. Med., 69:153–156.
19. Yebpella G. G., Oladipo M. O. A., Magomya A. M.,. Abechi S. E, Udiba U. U.and Kamba E. A., (2013),Multi-element analysis of selected brands of cigarettes in Nigerian market , Archives of Applied Science Research, 5 (6):61-67 .
20. Akpoveta O.vincent , Osakwe A. Steven , Aqharevba Felix , Osaro K. Ize-Lyamn , Akpoveta A. Veronica and Osazuwa E.Jato ,(2011),A Comparative Evaluation and Toxicity Assessment of Heavy Metals in Commonly Smoked Cigarette Brands and Local Tobacco Snuff Purchased and Consumed in Nigeria, Research journal of Environmental Toxicology , 5, (6) :359-368.
21. Konstansa Lazarevic, Dejan Nikolic, Ljiljana Stosic, Suzana Milutinovic, Jelena Videnovic and Dragan Bogdanovic, (2012), DETERMINATION OF LEAD AND ARSENIC IN TOBACCO AND CIGARETTES: AN IMPORTANT ISSUE OF PUBLIC HEALTH, Cent Eur J Public Health 20 (1): 62–66 .
22. Oyewele A.O., Funtua I.I. and Ekwmengbo P., (2002), A Comparative Evaluation and Toxicity Assessment of Heavy Metals in Commonly Smoked Cigarette Brands and Local Tobacco Snuff Purchased and Consumed in Nigeria , Journal of scientific & Induvial Reserch , 61:45-52 .
23. Muhammad A.and ,Waqar Ashraf ,(2012),Levels of Heavy Metals in Popular Cigarette Brands and Exposure to These Metals via Smoking, The Scientific World Journal, 2012: 1-5 .
24. SMODIS B., DERMEU M., JAIMOVI R., (1995) , DETEMINATION OF TRACE ELEMENTS IN TOBACCO USING DIFFERENT TECHNIQUES OF NEUTRON ACTIVATION ANALYSIS , Jourrral of Radoaralytical and Nuclear Chenristty, Articles, 190(1) :3-11 .
25. Massadeh A. M., Alali F. Q., and Jaradat Q. M., (2005), Determination of cadmium and lead in different cigarette brands in Jordon, Environmental Monitoring and Assessment, 104 : 163–170.
26. ZAWARTOSC RTECI W, DYMIE I ,WYPEŁNIENIU WYBRANYCH and MAREK PAPIEROSÓW, (2009), MERCURY CONTENT IN SMOKE AND TOBACCO FROM SELECTED CIGARETTE BRANDS , J.ECOLOGICAL CHEMISTRY AND ENGINEERING S,16(52).
27. WHO Study Group on Tobacco Product Regulation. Report on the Scientific Basis of Tobacco Product Regulation; (2012), WHO Technical Report Series; World Health Organization: Geneva, Switzerland: 25–28.

Table(1) : Shows the comparison of results between experimental data and the results published in [certificate data]

Ele.	Measured Concentration	Certified value	Error%	E.S.	Measured Concentration	Certified value	Error%
Na	0.44	0.46	4.34	Mn	0.617	0.6	2.83
Mg	10.80	11.19	3.48	Fe	1.511	1.35	11.92
Al	0.32	0.35	8.57	Co	0.0054	0.0056	3.57
Si	9.69	9.48	2.21	Ni	0.44	0.37	18.91
p	2.38	2.40	0.83	Cu	0.0003	0.0003	0.0
Cl	0.75	0.87	13.79	Se	0.003	0.004	25
K	6.012	7.00	14.11	Mo	0.01	0.0092	8.69
Ca	2.21	2.23	0.89	Hg	0.001	0.0011	0.91
Cr	0.021	0.031	32.25	Pb	0.0001	0.0001	0.0

Table(2):Major concentration elements % ± S.D. using XRF

Name	Na	Mg	S	Cl	K	Ca	Mn
PINE Light	0.12±0.0	0.018±0.0	0.12±0.0005	0.29±0.0005	2.39±0.007	2.38±0.006	0.02±0.0006
GITANES	0.12±0.0	0.018±0.0	0.11±0.0004	0.27±0.0005	2.58±0.007	2.32±0.006	0.017±0.0005
ROYAL	0.11±0.0	0.017±0.0	0.1±0.0004	0.21±0.0004	2.38±0.007	2.15±0.008	0.017±0.0005
MARLBORO GOLD	0.11±0.0	0.018±0.0	0.11±0.0004	0.19±0.0004	2.52±0.007	2.01±0.006	0.016±0.0005
MARLBORO EXTRA	0.12±0.0	0.017±0.0	0.12±0.0005	0.23±0.0004	2.58±0.007	2.44±0.007	0.022±0.0006
KINT SILVER	0.15±0.0	0.022±0.0	0.13±0.0005	0.35±0.0006	3.84±0.01	2.6±0.004	0.017±0.0006
SUMER	0.12±0.0	0.019±0.0	0.10±0.0004	0.30±0.0005	3.04±0.008	1.94±0.006	0.023±0.0006
GAULUISES	0.12±0.0	0.018±0.0	0.11±0.0004	0.23±0.0004	2.99±0.008	2.0±0.006	0.01±0.0005
PINE SLIMS	0.11±0.0	0.017±0.0	0.11±0.0004	0.25±0.0005	2.27±0.007	2.08±0.006	0.02±0.0006

Table(3):Trace elements PPM concentration ± S.D. using XRF

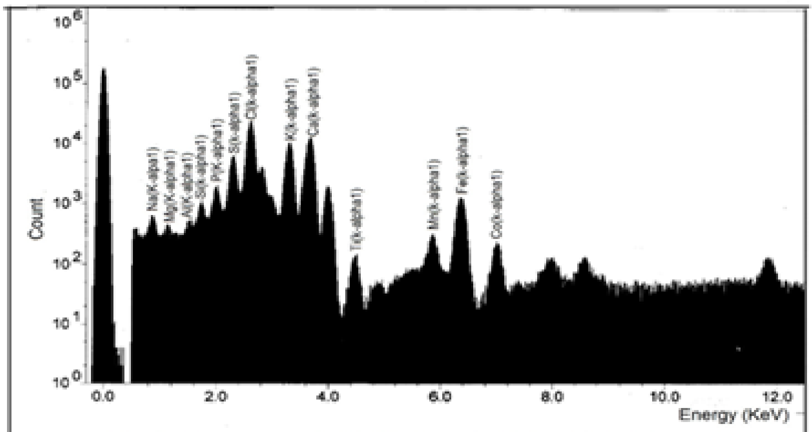
Name	Al	V	Fe	Co	Ni	Cu	Zn	Mo
PINE Light	44±0.0	5.3±0.4	532.5±7.6	12.7±1.5	5.2±0.9	18.7±0.9	33.6±0.8	17±0.0
GITANES	371±10	9.1±0.6	509±7.9	18.9±1.6	6.3±0.9	18.3±0.9	35.0±0.8	18.2±9.8
ROYAL	41.0±0.0	5.4±0.5	790.7±9.5	23.3±1.8	6.2±0.9	20.7±0.9	37.0±0.8	18.0±0.0
MARLBORO GOLD	39±0.0	4.5±0.4	566.4±7.7	17.7±1.5	6.5±0.9	16.8±0.8	36.6±0.8	16.0±0.0
MARLBORO EXTRA	43.0±0.0	4.3±0.4	732.4±9.1	20.3±1.7	5.7±0.9	17.6±0.8	36.0±0.8	24.0±5.2
KINT SILVER	55.0±0.0	6.1±0.5	639.2±9.8	20.5±1.9	5.4±1.0	22.0±1.0	40.4±1.0	26.0±0.0
SUMER	45.0±0.0	5.7±0.4	393.4±6.9	14.9±1.5	5.6±0.9	13.7±0.8	33.1±0.8	18.0±4.6
GAULUISES	52.2±12.0	4.3±0.4	608.9±8.2	13.5±1.6	4.8±0.9	15.8±0.9	36.3±0.8	21.0±4.8
PINE SLIMS	48.9±11.0	6.0±0.5	499.0±7.4	12.4±1.5	4.6±0.8	16.4±0.8	33.5±0.8	16.0±0.0
ASPEN EXPORT	40.0±0.0	3.9±0.3	400.4±6.4	8.7±1.4	5.8±0.8	12.7±0.8	30.1±0.7	16.0±0.0

Table(4): Toxic elements ppm concentration ±S.D. using XRF

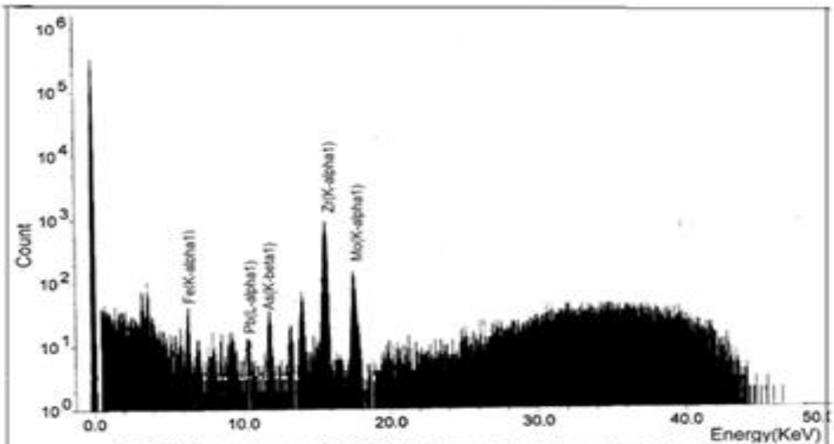
Name	As	Se	Br	Sb	Cd	Hg	Pb
PINE Light	0.6±0.0	0.7±0.3	46.4±0.5	23.0±2.9	3.7±0.0	1.2±0.4	4.2±0.7
GITANES	0.6±0.0	0.5±0.0	42.8±0.4	13.0±0.3	3.7±0.0	1.7±0.5	3.5±0.7
ROYAL	0.6±0.0	0.5±0.0	65.1±-.5	10.0±0.2	4.4±0.0	1.0±0.3	4.8±0.7
MARLBORO GOLD	0.5±0.0	0.4±0.0	36.2±0.4	5.0±2.4	3.7±0.0	1.6±0.5	4.1±0.6
MARLBORO EXTRA	0.6±0.0	0.5±0.0	42.2±0.5	11.0±3.4	5.4±0.0	1.1±0.4	4.2±0.7
KINT SILVER	0.6±0.0	1.3±0.3	82.5±0.7	9.1±0.0	6.3±0.0	2.1±0.5	4.3±0.8
SUMER	0.6±0.0	0.6±0.3	51.2±0.5	5.8±0.0	3.9±0.0	1.5±0.4	4.1±0.7
GAULUISES	0.6±0.0	0.5±0.0	43.1±0.5	6.3±2.9	4.7±0.0	1.7±0.5	6.0±0.7
PINE SLIMS	0.6±0.0	0.7±0.3	41.4±0.4	6.3±0.0	3.4±1.7	1.2±0.4	4.6±0.7
ASPEN EXPORT	0.5±0.0	0.9±0.3	66.8±0.5	13.0±2.5	3.0±1.2	1.8±0.4	3.9±0.6

Table(5):Comparison between the present result and another reported content of elements in cigarettes

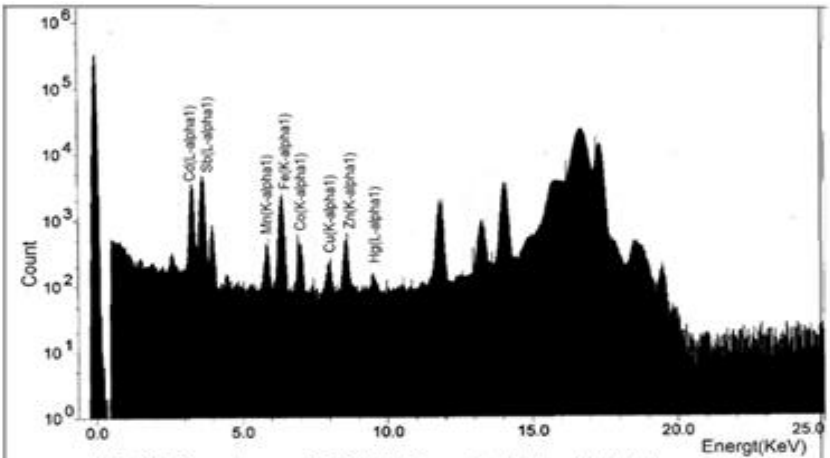
element	Concentration min	Concentration Max	Ref	Present work min	Present work max
Ca%	0.1389,2.1	1.0842,17.4	[16],[17]	1.94	2.6
K%	0.67, 2.39	2.116, 4.68	[16],[17]	2.27	3.84
Mg%	1.3, 0.4128	5.4,0.2358	[17],[16]	0.017	0.022
Mn%	0.016,0.0118	0.065,0.0267	[16],[17]	0.01	0.023
Fe/ ppm	678,168	919,393	[1],[16]	393	790.7
Al/ ppm	295	2302	[19]	39	371
Cu/ ppm	0.18	6.01	[2]	12.7	22.0
Zn/ ppm	6.97,7.3	25.25,24.02	[9], [20]	33.1	40.4
As/ppm	0.008,<0.02	0.02,2.04	[21],[22]	0.5	0.6
Pb/ppm	0.12,0.97	3.1,2.64	[21] ,[23]	3.5	6.0
Cd/ppm	0.02,0.18	3.55,0.78	[21],[23]	3.0	6.3
Hg/ppm	0.00648	0.01056	[25]	1.0	1.8



Fig(1):Spectrum of ROYAL Sample Using HOPG Target



Fig(2):Spectrum of ROYAL Sample Using Alumina Target



Fig(3):Spectrum of ROYAL Sample Using Molybdenum Target