Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3971-3978

Elemental Analysis of Some Important Tobacco Varieties (*Nicotiana tabacum* L.) by WDXRF Spectroscopy

NECDET ÇAMAS*, BÜNYAMIN KARABULUT† and ABDULHALIK KARABULUT‡
Vocational School of Bafra, Ondokuz Mayis University, Samsun, Turkey
Tel.: (90)(362)5426763; Fax: (90)(362)5426761
E-mail: necdetc@omu.edu.tr; cnecdetc@gmail.com

Wavelength dispersive X-ray fluorescence (WDXRF) analysis, a rapid and non-destructive technique, is used for determining trace and heavy elements in tobacco selected from different districts of Turkey. By this technique, 22 non-organic elements are determined. The concentrations of substance are given both as per cent type of dry weight and as part per million (ppm). The variations of heavy metal and trace element concentrations in tobacco leave show small change depending on the region where the leaves are harvested. The accuracy of the measurements is evaluated to 4th order of magnitude and the results are compared with the standards CTA-OTL-1 (Oriental) and CTA-OTL-2 (Virginia) tobacco leaves.

Key Words: *Nicotiana tabacum*, Tobacco leaf, WDXRF, Trace elements, Heavy metals.

INTRODUCTION

Tobacco though unhealthy is an important industrial crop in the world. The leaves of this crop are widely used for manufacturing smoking materials. The trace element concentrations in tobacco leaves have been determined in cited papers by several techniques[1-6]. Some trace elements in tobacco are hazardous for human metabolisms even at a very low level of intake[1]. As this product provides routes of entry into the body system it is particularly important to characterize the composition of elements that may have toxic properties[5]. Large number of toxic elements is present in tobacco leaves. This is an important issue as many trace elements, in particular the heavy metals, are accumulating in soils where intensive fertilizer application is practiced[7]. Nitrate in the form of manure and sewage sludge and rock-derived phosphate fertilizers are implicated in the accumulation of heavy metals[8] and unlike many organic contaminants, most

†Department of Physics, Faculty of Science and Art, Ondokuz Mayis University, Samsun, Turkey.
‡Department of Physics, Faculty of Science and Art, Atatürk University, Erzurum, Turkey.

inorganic contaminants are not removed by chemical or microbial degradation. There is need to determine the levels of trace elements of especially heavy metals that can become bioavailability in soils and which concentrate in plant materials that are consumed as cigarettes[5]. We have seen that the mortality rate of diseases caused by smoking is more than 350 000 per year in the USA and so it can be seen that it is a worrying public health problem[9]. Besides the heavy metals, more than 4000 individual chemical constituents of cigarette smoke have been identified and most of the constituents are responsible for various concerns in the body and especially 90 % of lung cancers[4]. Because of a large consumption of tobacco and tobacco products in the world, studies on heavy metals and rare earth elements in tobacco leaves are necessary.

Toxic elements and other substances are partly or completely vitalized in the smoke of tobacco and these elements are inhaled and absorbed through lungs during smoking by both active or passive smokers. The metabolism is altered by these toxic substances[4]. Cu and Zn concentrations in the tissues of smokers are found to be significantly higher. The effects of other biologically important elements, Al, As, Cd, Cr, Pb, Mn, Hg, Ni, Po-210 and Se are also altered in the tissues of smokers.

The altered mechanisms related with trace elements in the body of smokers have been proposed to be a factor for in cardiovascular disease (CDV). The concentrations of heavy elements are known to be effecting the functions of liver, kidney, lung and heart[10]. Similarly, the adverse health effects of toxic elements on the fetus through maternal smoking and on infants through parental smoking are of special concern[11]. High concentrations of Al, Cu, Cr and Ni in bodily tissues are known to be hazardous especially for respiratory and urinary systems[12].

Turkey is known for producing high quality oriental tobacco and therefore it seems to be necessary to analyze the tobacco varieties (broad-leaf) produced in various districts in Turkey. The tobacco types that have been analyzed in this study are those of primary importance not just in Turkey, but also in the rest of the world. For example, 85 % of total 6 million tons of total tobacco produced per year in the world consist of the same types[13,14]. In addition, these types are used in tobacco blends of the highest international quality.

A rapid and accurate means of analyzing such plant material with adequate sensitivity was required involving minimal sample preparation and relatively short analysis time[5]. WDXRF is a non-destructive, fast, multi-element technique for all sizes and forms. It can be used to measure virtually every element from B to U in the Periodic Table. It can measure elemental concentrations ranging from a few ppm to nearly 100 per cent. Certain trace elements are located within relatively insoluble mineral phases acquired by tobacco leaves from the atmosphere or soil, or grow as biominerals within cell vacuoles or by fungal decay on leaf surfaces[15-17]. In recent years, the EDXRF and WDXRF methods have been used for elemental analysis by several authors[18-23].

EXPERIMENTAL

A wavelength-dispersive X-ray fluorescence spectrophotometer (WDXRF, Rigaku ZSX-100e with Rhodium target) was used. This instrument was controlled by a computer running ZSX software. The ZSX 100e wavelength-dispersive spectrometer characteristics are given in its[24].

SQX advanced semi-quantitative software

Rigaku has improved their semi-quantitative software package further with the introduction of SQX. It is capable of automatically correcting for all matrix effects, including line overlaps. SQX can also correct for secondary excitation effect by photoelectrons, varying atmospheres, impurities and different sample sizes. Increased accuracy is achieved using Matching Library and Perfect Scan Analysis Programs[6,24].

Experimental Procedures

Samples investigated in this research were prepared from leaves of different tobacco varieties to WDXRF analysis. 2 g from each sample is pressed under 15 tons to make pellets with the diameter of 35 mm. The samples were dried in a Heraeus furnace at a temperature of 110°C for 0.5 h.

The measurements were obtained from $K\alpha$ X-ray intensity of elements. It was used the ZSX software programme for the sample analysis. The ZSX software is build around the most advanced Fundamental Parameter (FP) methods. This method guarantees the most accurate semi-quantitative analysis possible by combining the certainty of full qualitative scans with precise peak and background measurements for selected or trace elements[24].

The WDXRF analyzer uses X-rays that have wavelengths, characteristic to the elements within the sample are emitted and they, along with scattered source X-rays, disperse in all directions. The sample is placed in the way of the X-rays coming off the sample. An X-ray detector is positioned where it can detect the X-rays that are diffracted and scattered off the sample. Depending on the spacing between the sample and orientation where the detector is placed, specific wavelengths directed at the detector can be detected. The angle can be changed in order to measure elements sequentially, or multiple crystals and detectors may be arrayed around a sample for simultaneous analysis[25].

RESULTS AND DISCUSSION

Turkey is known for producing the high quality oriental and semi-oriental tobacco. Therefore, it seems to be necessary to analyze the trace elements in the cultivars from various cites. Tobacco leaves from 14 different cites are gathered from 2005 harvest long-period average of climatic data of each region. The cites where the samples are collected Düzce (39° 55´ N 27° 19´ E), Sakarya (40° 47´ N 30° 24´ E), Akhisar (38° 58´ N 27° 58´ E), Gümüshaciköy (40° 55´ N 35° 11´ E), Bafra (41° 30´ N 35° 54´ E), Çarsamba (41° 15´ N 36° 42´ E), Samsun (41° 14´ N 36° 14´ E), Yenice (39° 55´ N 27° 19´ E), Akçaabat (40° 57´ N 39° 32´ E), Yayladag (35° 58´ N 36° 6´ E), Bitlis (38° 19´ N 42° 8´ E), Adiyaman (37° 44´ N 38° 18´ E) and Mus (38° 51´ N 41° 33´ E).

High quality tobacco leaf samples-between 12 to 27- from each site are collected into three groups; broad-leaf (Virginia and Burley), oriental (Izmir, Bafra, Basma, Canik, Maden, Evkaf, Agonya) and semi-oriental (Trabzon, Yayladag, Bitlis, Adiyaman and Mus). The measurements of only one sample of each group are reported in this work, because of that each sample represents mostly the characterizes of its own group. The discrepancies are given in the following paragraph.

Referring the Table-1 values, the concentrations of Ca, Na, Zn and Mn, P and S seen to be in the same order with CTA-OTL-1 standard in all varieties, but Mg contents in Akçaabat variety is far above the standards and in Mus, Yayladag, Maden and Canik varieties are slightly above the standards. The Fe contents in Izmir and Adiyaman varieties, Cu contents in Maden and Agonya and Zn contents in Maden and Evkaf varieties are found to be higher than standards. Surprisingly that the Ni contents in all varieties, except Bitlis variety, are found to be above the standards. The Rb, Sr and Ba contents in Akçaabat, Agonya and Maden varieties and the Al, Si and Ti contents in Izmir, Mus and Adiyaman varieties are above the standards.

Broad-leaf Virginia and Burley varieties, which are also cultivated in some districts of Turkey, exhibit no anomalies. The oriental and semi-oriental types, however, contains unexpectedly high Cl, even they are neither fertilised nor irrigated.

The reasoning of variations of the contents of the elements mentioned above, are thought to be genetic characteristics, fertilizers, irrigations, climate, soil characteristics and the storage conditions. This is a subject for another study.

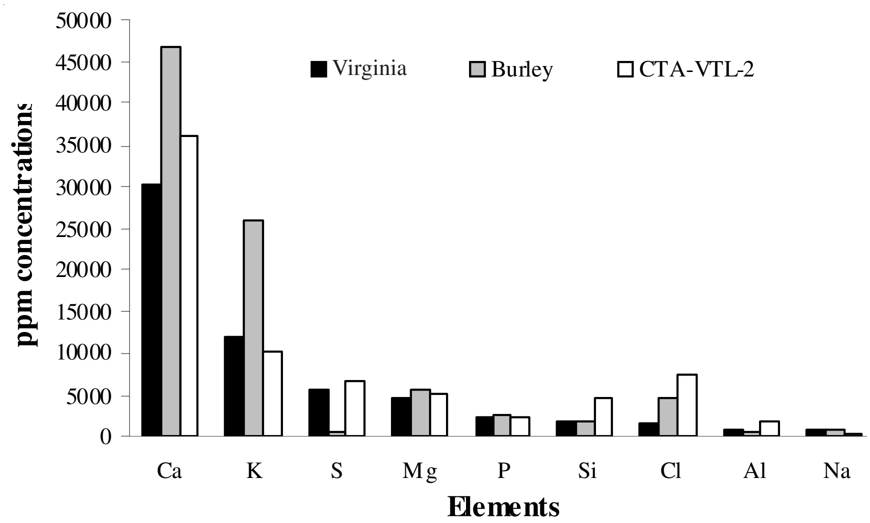
The concentrations of the elements and heavy elements, mostly metals, in trace amounts measured in Virginia and Burley tobacco leaves are plotted and shown in Fig. 1a and 1b together with the values of Institute of Nuclear Chemistry and Technology (ICHTJ)[5] for CTA-VTL-2 type tobacco. The concentrations of all elements, except K and Ca, are found to be smaller than these given by ICHTJ.

TABLE-1

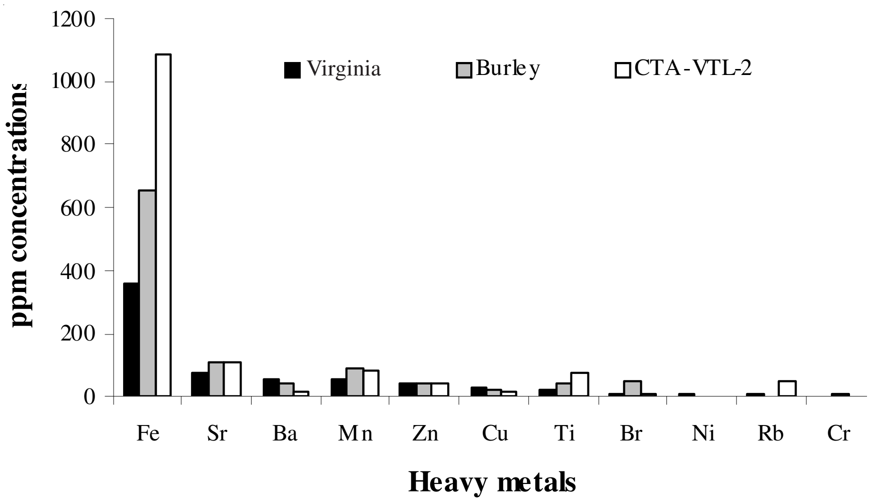
CONCENTRATIONS OF ELEMENTS (ppm) IN DIFFERENT TOBACCO VARIETIES DETERMINED BY WDXRF

Cites	Varieties	K	Ca	Mg	Na	Fe	Cu	Zn	Mn	Al	Si	P	S	Cl	Ti	Cr	Ni	Br	Rb	Sr	Ba
Düzce	Virginia	12090	30129	4363	662	360	28	41	58	716	1854	2304	5459	1538	21	ND	7	12	6	78	61
Sakarya	Burley	25906	45628	5633	662	652	24	25	87	542	1694	2376	468	4552	40	4	9	45	10	114	43
Akhisar	İzmir	15084	22516	6094	1511	2539	16	26	66	3637	19852	1616	3784	5375	352	12	9	26	16	53	12
Ghaciköy	Basma	19428	49202	8206	559	834	12	31	92	2136	4897	1657	3934	6243	96	14	8	12	4	182	44
Bafra	Bafra	21275	27143	6857	937	1278	16	53	106	2036	4409	2335	3883	9976	103	ND	8	35	13	82	52
Çarşamba	Canik	17828	36492	9790	596	848	29	52	75	1011	2741	2128	4255	9218	57	13	10	12	8	15	ND
Samsun	Maden	26815	34077	9959	471	1344	55	104	106	1226	2910	1968	4217	3747	64	7	15	27	13	136	111
Samsun	Evkaf	25440	28613	5305	543	734	22	44	73	1399	3462	2412	5112	3711	61	4	8	22	10	68	54
Yenice	Agonya	20654	21907	7902	543	611	30	87	152	1196	3219	1633	4037	2777	63	ND	11	13	15	115	101
Akçaabat	Trabzon	15847	38850	27227	915	626	24	42	224	560	1992	2460	5356	2495	44	ND	14	ND	22	284	61
Yayladağ	Yayladağ	15896	33180	10336	1741	876	20	59	73	1379	4185	1506	4285	8775	92	ND	19	34	15	166	87
Bitlis	Bitlis	10736	22537	5642	733	774	7	28	51	1649	3842	1143	2303	1231	70	ND	6	7	7	48	ND
Adiyaman	Adiyaman	10942	51113	8575	441	2412	14	8	151	2267	5133	1055	2447	3177	185	15	14	5	3	50	66
Muş	Muş	10985	39780	11569	568	1288	12	15	98	2470	5974	1885	3396	1159	144	ND	12	15	8	80	51
Cert/Info	CTA-VTL-2	10300	36000	5100	312	1083	18	43	80	1682	4590	2204	6690	7430	76	1.9	2	14	49	110	43
Cert/Info	CTA-OTL-1	15600	31700	4470	345	989	14	50	412	1740	4715	2892	7320	298	86	2.6	6	9	9.8	201	84

ND: not detected



(a)



(b)

Fig. 1. a) Concentrations of elements in Virginia and Burley
b) Concentrations of heavy elements in Virginia and Burley

The concentrations of elements and heavy elements, mostly metals, are plotted in Fig. 2a and 2b for Bafra (oriental) and Bitlis (semi-oriental) varieties together with the oriental standard CTA-OTL-1 concentrations. The concentrations of Ca, K, S, Sr, Ba and Mn are found to be higher than the oriental standard while the other elements are higher. Similarly the concentrations of Ti, Si, Cl, Al, Na and Mg in Bitlis tobacco are higher than those of the CTA-OTL-1 standards and the concentrations of other elements are smaller.

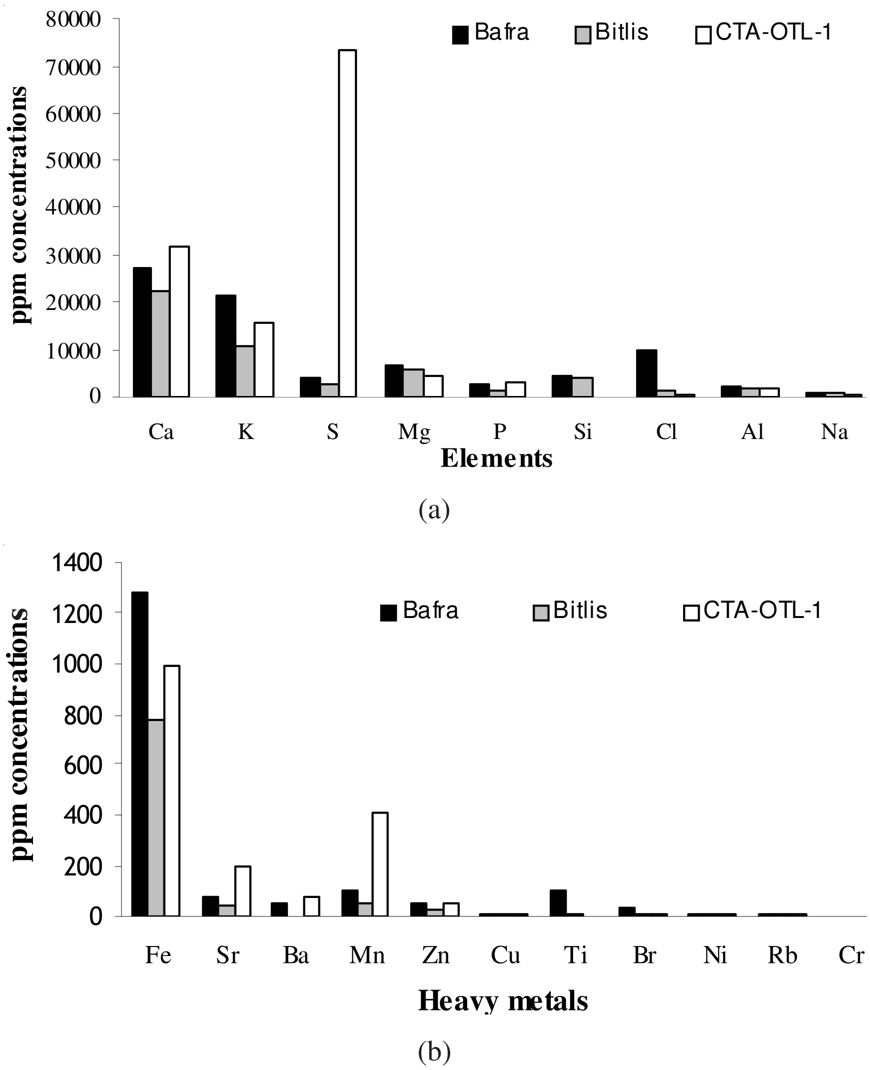


Fig. 2. (a) Concentrations of elements in Bafra (oriental) and Bitlis (semi-oriental) tobacco
(b) Concentrations of heavy elements in Bafra (oriental) and Bitlis (semi-oriental) tobacco

It must be noted that, most of the tobacco varieties grown in Turkey have potassium contents approximately equal to that of CTA-OTL-1 and CTA-OTL-2 standards except the potassium contents of Burley, Bafra, Evkaf and Agonya tobacco types which are slightly higher than standards.

Conclusion

WDXRF analysis of three tobacco types (broad-leaf, oriental and semi-oriental) produced in different distincts of Turkey for elements in trace amounts are given. Some unexpected results are found. Particularly, the aluminium content for the Izmir, Adiyaman and Mus varieties; chlorine content for all of the oriental tobacco varieties; nickel content for Virginia, Burley, Yayladag, Maden, Akçaabat and Adiyaman varieties; copper in Maden, Virginia and Agonya; iron in Izmir and zinc in Maden and Agonya are found to be above the certified CTA-OTL-1 and CTA-OTL-2 values. These elements are known to be harmful for human health when the natural concentrations are altered through smoking in active or passive way.

REFERENCES

1. M.C. Gulovali and G. Gunduz, *J. Radional. Nucl. Chem.*, **78**, 189 (1983).
2. H.R. Vega-Carrillo, F.Y. Iskander and E. Manzanares-Acuna, *J. Radional Nucl. Chem.*, **200**, 137 (1995).
3. A. Nada, M. Abdel-Wahab, A. Sroor, A.S. AbdeHaleem and M.F. Abdel-Sabour, *Appl. Radiat. Isot.*, **51**, 131 (1999).
4. U. Çevik, E. Ergen, G. Budak, A. Karabulut, E. Tirasoglu, G. Apaydin and A.I. Kopya, *J. Q. Spect. Rad. Trans.*, **78**, 409 (2003).
5. W.E. Stephens and A. Calder, *Anal. Chim. Acta*, **527**, 89 (2003).
6. F. Demir, G. Budak, E. Baydas and Y. Sahin, *Nucl. Instr. Meth. Phys. Res. B*, **243**, 423 (2006).
7. J.H. Duffus, *Pure Appl. Chem.*, **74**, 5, 793 (2002).
8. F.A. Nicholson, S.R. Smith, B.J. Alloway, C. Carlton-Smith and B.J. Chambers, *Sci. Total Environ.*, **311**, 205 (2003).
9. R.I. Stanley and I. Kumar, Basic Pathology, Philadelphia, PA: W.B. Saunders Company, p. 525 (1991).
10. M.A. Dubick and C.L. Keen, *Biol. Trace Elem. Res.*, **31**, 97 (1991).
11. M. Chiba and R. Masironi, *Bull. World Health Org.*, **70**, 269 (1992).
12. http://www.lenntech.com/periodic-chart.htm
13. Anonymous, U.S.D.A. FT (2004) 9-2004.
14. Anonymous, Tobacco: World Markets And Trade, United States Department of Agriculture Foreign Agricultural Service (2006).
15. E.A. Martell, *Nature*, **249**, 215 (1974).
16. N. Bouropoulos, S. Weiner and L. Addadi, *Chem. Eur. J.*, **7**, 1881 (2001).
17. K. Tait, J.A. Sayer, M.M. Gharieb and G.M. Gadd, *Soil Bio. Biochem.*, **31**, 1180 (1999).
18. J. Kystol and L.M. Larsen, *Geology of Greenland Survey Bull.*, **184**, 59 (1999).
19. R. Dumlupinar, T. Demir, T. Sisman, G. Budak, A. Karabulut, Ö.K. Erman and E. Baydas, *J. Q. Spect. Rad. Trans.*, **102**, 492 (2006).
20. A. Karabulut and G. Budak, *Spectrochim. Acta*, **55B**, 91 (2000).
21. A. Karabulut, G. Budak, R. Polat, A. Gurol, M. Levent, M and Y. Sahin, *J. Q. Spect. Rad. Trans.*, **72**, 741 (2002).
22. I. Aslan, G. Budak, A. Karabulut and E. Tirasoglu, *J. Q. Spect. Rad. Trans.*, **97**, 75 (2006).
23. R. Dumlupinar, F. Demir, G. Budak, A.N.K. Karabulut, N. Kadi, H. Karakurt and S. Erdal, *J. Q. Spect. Rad. Trans.*, **103**, 331 (2007).
24. http://www.rigakums.com
25. http://www.learnxrf.com/Principles_of_XRFedxvswdx.htm

(*Received*: 7 October 2006; *Accepted*: 9 March 2007) AJC-5506