Neutron Activation Analysis of Trace Metals in Cigarette

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ABSTRACT

The amount of Mn, La, Th, Eu, and Hf in fourteen brands of cigarettes randomly collected at a retail outlet in Samaru market, Zaria-Nigeria have been determined by neutron activation analysis (NAA) techniques based on thermal neutron from a nuclear reactor in combination with high resolution gamma-ray spectrometry at Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria. The cigarette brands are: CRM1, CBH2, CEX3, CLF4, CDC5, CAS6, CSM7, CCT8, CLD9, CLK10, CLM11l, CPM12, CFM13 and CBK14. The average levels of the determined metals in each of the brands are Mn: 173.0 ppm, 198.75 ppm, 227.90 ppm, 198.55 ppm, 214.10 ppm, 168.60 ppm, 150.70 ppm, 123.65 ppm, 267.10 ppm, 123.60 ppm, 183.10 ppm, 167.35 ppm, 118.50 ppm, 160.20 ppm respectively; and La: 1.39 ppm, 16.93 ppm, 1.30 ppm, 1.25 ppm, 1.37 ppm, 12.81 ppm, 11.12 ppm, 0.72 ppm, 1.02 ppm, 31.09 ppm, 1.98 ppm, 1.01 ppm, 0.86 ppm, 3.23 ppm respectively. The elements Th, Eu, Hf, which are known to have radioactive isotopes, were also detected in some brands of the cigarette. Thorium was found in L & D at 0.16 ppm. Eu was detected in London filter, Aspen and Link at 0.01 ppm, 0.01 ppm and 0.02 ppm respectively. Hafnium was detected in Excel and London filter at 0.47 ppm and 1.10 ppm respectively. Lichens (IAEA – 366) and Cabbage (IAEA – 359) as the certified reference material (standard) were applied for calibration and validation of analytical procedure. The techniques have proved sensitive, and therefore suitable for routine determination of these metals in tobacco cigarettes.

INTRODUCTION

Tobacco leaf and cigarette smoke is known to contain complex mixture of several hundreds chemical components, some of which have been identified as tars, nicotine, carbon monoxide, hydrogen cyanide, oxides of nitrogen and metals. Many of these chemicals are pharmacologically active, highly toxic, carcinogenic, mutagenic, and antigenic. Tobacco is known to easily absorb heavy metals and radioactive element from the soil and concentrate them in leaves, some of these metals is transferred by the smoke into the human body where they accumulate, damage the organs and act as promoters in conjunction with carcinogens[1]. The continuous analysis of trace element in processed tobacco is relevant for the protection of our health and environment. Environmental tobacco smoke (ETS) has been identified as good source of trace metals in our environment.

Several methods exist for the determination of trace metals in tobacco cigarettes but the need for multi-element analysis is receiving greater

attention as the toxicity might be greatly influenced by synergistic effects of several metals. Some of the multi-element techniques successfully applied includes: Energy Dispersive X-ray Flourescence Spectrometry (EDXRF)[2,3,4]. Reversed-Phase High-Performance Liquid Chromatography (RP-HPLC)[5], Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[6,7,8]; Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[9,10] Graphite Furnace Atomic Absorption Spectrometry (GF-AAS).

ICP-AES, ICP-MS show good sensitivity but are limited because of expensive instrumentation and high cost for routine analysis while AAS and X-ray Fluorescence Spectroscopy often suffer the problem of low sensitivity. RP-HPLC method shows the advantage of low cost, excellent selectivity and sensitivity[5]. The most widely used of the multi-element techniques is the Neutron Activation Analysis (NAA) which have found wider application in trace metal analysis in tobacco samples and cigarettes smoke.

In the present work, Neutron Activation Analysis (NAA) techniques based on thermal neutrons from a nuclear reactor in combination with high resolution gamma-ray spectrometry was used to determine the levels of trace metals in sampled cigarette brands commonly available in Nigeria. Attention was also directed towards the synergistic effects of these metals and the kind of threat they could pose to the survival of cigarettes users.

EXPERIMENTALS

Different brands of cigarettes cheaply used in Zaria, North central- Nigeria were collected and transported to Nuclear Reactor (NIRR-1) sample preparation laboratory at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria - Nigeria. To obtained laboratory samples, cigarette were removed from their wrappers, dried to a constant weight at 90°C in a laboratory oven and allowed to cool in a desiccators. The dried sample of each brand was in turn fined powdered and homogenized properly by using agate mortal. Analytical samples both for short and long-lived irradiations were weighed and wrapped in a well prepared contaminant free polyethylene films. The bags were cleansed by soaking in 1:1 HNO_3 for 3 days, washed twice with deionized water, dried in laboratory oven and cooled in a desiccators. The prepared samples were packaged to avoid contamination on transportation to the reactor room and during radiation.

The reactor in CERT is of low power and comprises of the following: enriched uranium as the fuel, light water as a moderator and beryllium as reflector. Other facility indispensible of the reactor is the gamma-ray data acquisition system responsible for the measurement of radioactivity. Complete description of the reactor, irradiation facility, standardization of irradiation and counting facilities for instrumental neutron activation analysis, the determination of efficiency curves for the detector system at near and far source detector, geometry and extension of energy range fro 59.5 – 2254 KeV to 4000 KeV by semi emperical method were as reported previously[11,12,13].

Samples and standards were in turn irradiated in the radiation channels of the miniature neutron source reactor (MNSR) at centre for Energy Research and Training, Ahmadu Bello University, Zaria - Nigeria. Based on the half-life of product radionuclides, two irradiation

regimes were adopted. For elements leading to short lived activation, the samples were sent for irradiation in turn in an outer irradiation channel B4. This region is suitable as the neutron flux is ideal to bring about distortion in the nucleus of elements with shorter half-life. For elements leading to long-lived activation, the samples and standards were subjected to irradiation for 6 hours in two smaller inner irradiation channels designated B1 and B2. In these regions, the value for thermal neutron flux is sufficient to activate elements with longer half-lives. At the completion of each irradiation, measurement of the activity for the induced radio-nuclides were performed by a personal computer based gamma-ray spectrometry. For short lived irradiation regimes, conditions that necessitate effective counting after 5 minutes irradiation with 2.5 x 10" n/cm^2 s thermal neutron flux includes: 5 minutes cooling time-enough to remove the prompt gamma-ray leaving only the delay gamma-ray which is the most important and 10 minutes counting period for first round of counting and second round after time lapses of 3-4 hours. For long-lived activation regime, conditions necessary for counting after irradiation with a thermal neutron flux of 5.0 x 10" n/cm^2 s for 6 hours includes: cooling time of 4-5 hours and 10-15 day, counting time of 30 minutes on H1 geometry as oppose to H2 geometry for short-lived for both first and second round of counting for long-lived radionuclide. Each spectrum was analyzed using analysis software, WINSPAN 2004. This calculated average background by integrating areas indicated by the analysis on each side of the desired peak then subtracted from the peak. The result from above were corrected for dead time, tobacco weights and half-life and then compared to the mean value of all standards for the same peak. The computer then process this information by a programme called SPAN USERS and calculates the concentration in part per millions for each sample.

RESULTS AND DISCUSSION

The elements analyzed under the study are those leading to short lived activation and long-lived activation products. The conditions necessitating the use of the above mentioned regimes have been highlighted in this work.

Table1 gives the half-life of the radioisotopes, energy of the radio-nuclides, radioisotopes produced, and the % rate. Difference between half-life of radio-nuclides as well its energy can be exploited in identification or qualitative analysis of peaks. Each radioisotope has half-life or decay pattern and energy of its own characteristics. Those element with more than one radioisotope appears at different energy/channel, this provide an easiest way of identification of peak.

Table 2 shows the result of the analysis of cabbage (IAEA-359) reference standard. There is a good agreement between the tested value and the true value obtained from the literature. Therefore the method to a greater extent is efficient.

Table1: The half-life and energy of radio-nuclides

Element	Radioisotopes produce	Half-life t QUOTE	Her Energy (kev)	Rate (%)
Na	$^{24}N_a$	15hr	2754.0	2.22
K	^{42}K	12.4hr	1524.6	97.32
C_a	^{49}Ca	8.72M	3084.5	80.79
Rb	^{86}Rb	18.7d	1076.6	
Mg	^{27}Mg	9.46m	1014.4	17.96
AI	^{28}AI	2.24m	1779.0	1.26
Mn	^{56}Mn	2.58hr	2113.1	0.46
La	^{140}La	40hr	1596.2	0.28
Sm	^{153}Sm	46.3hr	103.2	0.00
Br	^{82}Br	35.3hr	776.5	0.00
Sb	^{122}Sb	64.8hr	564.2	0.00
Sc	^{46}Sc	83.8d	889.3	0.00
Fe	^{59}Fe	44.5d	1099.3	0.00
Ba	^{131}Ba	11.8d	496.3	0.301
Zn	^{65}Zn	344d	1115.6	1.10
Co	^{60}Co	5327yr	1332.5	0.009
Hf	^{181}Hf	42.4d	4808.0	
Cr	^{51}Cr	27.7d	320.1	0.36
Eu	^{152}Eu	13.3yr	1408.0	0.00
Yb	^{175}Yb	4.19d	396.3	0.003
Th	Th^{233}	27d	312.0	0.05

Table 2: IAEA-359 cabbage certified reference standard compared to true value obtained from literature

Element	Tested value	True value
K	3597	3250
Na	5722.3	580

Table 3: Concentration of trace element in cigarettes

Samples	CRM 1	CBH 2	CEX 3	CLF4	CDC 5	CAS6	CSM 7	CCT8	CLD 9	CLK 10	CLM 11	CPM 12	CFM 13	CBK 14
La (ppm)	1.39	16.9	1.30	1.25	1.37	12.8	11.1	0.72	1.02	31.1	1.98	1.01	0.86	3.23
Mn (ppm)	173.01	98.82	27.11	89.62	14.11	68.61	50.71	23.72	67.11	23.61	83.11	67.41	18.51	60.2
Hf (ppm)	ND	ND	0.47	1.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Eu (ppm)	ND	ND	ND	0.01	ND	0.01	ND	ND	ND	0.02	ND	ND	ND	ND
Yb (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.16	ND	ND	ND	ND
Th (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	0.16	ND	ND	ND	ND	ND

Table 3 shows the average concentration of trace metals analyzed for each brand under this study. High concentration of 31.09ppm La was observed in CLK10 and minimum value of 0.72ppm La in castle. For manganese, maximum and minimum value of 267.10ppm Mn and 118.50ppm Mn was seen in CL.D9 and CFM13 respectively. CLK10, CCT8, CLD9 and CFM13 are known to be among the low price cigarette brand sold in Nigeria. The observed trend suggest that the concentration or level is not attributed to manufacturing processes but to some extent, to other possible route of these metals as highlighted somewhere in this work. Barium (Ba) minimum and maximum level were recorded in CCT8 and CBK14 at 5.05ppm and 18.14ppm respectively. From our observation

with respect to this work, low levels of the identified trace metals are found in CCT8. In this work concentration range of 118.10ppm - 267.10ppmMn;5.05-18.14ppm Ba and 0.72-31.09ppm La was obtained compared to 113-144ppm Mn; 81.3-144ppm Ba and 1.61-28.3ppm La reported[6]. It is also suggested that the observed trend may likely result from Agricultural practices such as use of herbicides, pesticides and chemical fertilizers.

The elements Th, Eu, Hf, Yb which is known to have radioactive isotopes where also detected in some brand of the cigarettes. Thorium (Th) was found in CLD9 at 0.01ppm. Europium (Eu) was detected in CLF4, CAS6, and CLK10 at 0.01ppm, 0.01ppm, and 0.02ppm respectively. Hafnium (Hf) was detected in CEX3 and CLF4 at 0.47ppm and 1.10ppm respectively. Thabium was found in CLK10 at 0.16ppm.

One can link cases of serious cancer of the mouth, lungs, pharynx etc to the interaction of radioactive elements, metals and other chemical compounds found in cigarette smoke. It has been reported somewhere else that radioactive compounds in cigarette smoke are deposited in "hot spot" where bronchial tubes branch. Since the tar from cigarette smoke is resistant to dissolving in lung fluid, radioactive compound have a greater deal of time to undergo radioactive decay before been cleared by natural processes[14]. Also it has been suggested that the radioactive elements and chemical carcinogens in tobacco smoke act synergistically to cause higher incidence of cancer than each alone. A bladder incidence was observed to be proportional to amount of tobacco smoke[15]. This supports the link of cancerous and other related diseases to chemicals in tobaccos. Radioactive polonium-210, though not detected in the presented work is known to cause damage to protective epithelia tissues. Smoking prolonged retention of insoluble polonium- 210 compound produce from burning cigarettes[14].

Metals have the tendency to interact not only with itself but act synergistically with other chemicals as in the case of radioactive elements. This phenomenon may be responsible for some health risk of active smokers. Barium in chemical respect is similar to calcium[16], when absorbed into the blood stream under 24hrs it get deposited in delicate organs (Liver, spleen, brain, heart, hair and bones) in similar way to calcium. Beliles[17] linked paralysis of central nervous system to the displacement of calcium from the cell membrane by barium thereby increase permeability and stimulation of the muscles which eventually resulted to the above stated condition. Antimony at concentration 0.01 μgm^{-3} is recognized as urban air pollutants. It interacts with arsenic which are both present in the analyzed cigarettes. In conjunction with other metals (Co, Zn, Pb) multi-factorial risk of lung cancer resulted[18]. The most identifiable route of these metals into human system once inhaled is by absorption because of their relative solubility which may be aided by alcoholic drinks. Metals and other ingredients of cigarettes lead to narrowing of blood vessels, increasing the likelihood of blockage and thus heart attack or stroke. Research revealed that people under the Age of 40 are five times more likely to have heart attack as they smoke[19].

CONCLUSION

In this study the concentration of trace metal in part per million have been measured. These substances can act synergistically with one another and inflict health hazard than each alone. Radioactive elements are also found to be present in cigarettes. The presence of radioactive elements is cause for concern.

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