

## NEUTRON ACTIVATION AND FLAME ATOMIC ABSORPTION ELEMENTAL ANALYSES OF SELECTED HAIR DYES

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**Abstract.** Two hair dye types, one liquid and the other solid, were analyzed to determine their elemental compositions and possible radioactivity. The liquid dye sample was analyzed using Flame Atomic Absorption Spectroscopy and based on the American Standard Test Method (ASTM), five ions namely:  $Fe^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $S^{2-}$ , and  $SO_4^{2-}$  were detected with concentrations of 0.702, 0.002, 0.003, 0.044, and 0.059  $mg.l^{-1}$  respectively. The solid hair dye sample was analyzed using the Neutron Activation Analysis technique. Eighteen elements (Al, Ti, K, Fe, Na, V, Mn, Sb, La, Sm, Sc, Cs, Eu, Br, Ce, and Th) were measured. Six of the elements (Al, Na, Eu, Br, Ce, and Th) were found in trace concentrations of  $31.9 \pm 5.4$ ,  $40.6 \pm 5.9$ ,  $0.16 \pm 0.05$ ,  $0.18 \pm 0.04$ ,  $0.37 \pm 0.08$ , and  $0.13 \pm 0.02$  ppm respectively. Ce and Eu presently have no known negative effects on humans, while Pb, Cd, and Fe cannot easily get into the body through skin absorption. Hence the application of dyes containing these elements may not bring about effects associated with the intake of these elements, unless the dye mistakenly finds its way into food. The presence of Al, Na, Br, Th, S, and  $SO_4$  could result in those adverse effects associated with each element. In addition, the major active ingredient, Paraphelylene diamine (1, 4-diaminobenzene) has cancerous effects usually directed at the bladder.

**Key Words:** Hair dye, elemental composition, Flame Atomic Absorption Spectroscopy, Neutron Activation, trace concentrations, cancerous effects

### 1. INTRODUCTION

Due to adverse environmental conditions in recent times, which include the enhanced green house effect, excessive air and water pollution, noise (vibration), and thermal pollution, man is faced with untimely ageing, including such symptoms as the wrinkling of

the skin and the emergence of grey hair (Lind et al, 2005). As a result, there is need for man to devise means of improving his looks. One of these means is the application of hair dye by some individuals, especially the middle-aged group.

Hair dyes are chemicals used to darken or change the colour of human or animal hair to a desired colour. The change is due to the ability of the dye to emit only light whose wavelength is that of the desired colour, while all other wavelengths are absorbed (Sadaji et al., 1982). Based on their duration or persistence, hair dyes can be grouped into three main types: permanent, semi-permanent, and temporary dyes. Temporary dyes can be removed in just one washing. They are mainly used for festive purposes and then washed off after the activity. Temporary dyes do not change the natural underlying colour of the hair. The risk associated with the use of temporary dyes is negligible. Semi-permanent dyes are mostly organic and do not involve developers like hydrogen peroxide, to fix the colour in the hair fiber. They can survive several washings before they completely disappear. How long the dye lasts depends on the active ingredients, the frequency of hair washing, and also the frequency of exposure to environmental modifiers like sunlight, and chemicals in the air (Vann, 2000). The permanent dye gives the most dramatic colour change. Users of this dye usually have visible roots as their hair grows. These dye types have very high affinity for hair fibers, hence cannot be removed by washing (Lind et al., 2005).

Hair dye analysis is essential as many of the available formulations are known to be unsuitable for human use [Allan, 2005; Hans and Tlaytmas, 2000; Lind et al., 2005, Sphoted et al., 2004; Vann, 2000]. Some constituents have been found to be carcinogenic and there have been suspected cases of breast and duodenal cancer after prolonged use of certain hair dyes [Andrew, 2000]. Furthermore, there is now a growing risk of occupational skin diseases among hair dressers from exposure to skin irritants and sensitizers [Lind et al., 2005]. Severe allergic contact dermatitis has been observed in hairdressers, their clients and home users of permanent hair dyes [Sphoted et al., 2004; Lind et al., 2005].

Most of these dyes change to the required colour on exposure to ultra-violet radiation from the sun, which is also a carcinogen. When the skin is exposed to UV radiation, it acts directly on the skin cells, causing changes in the cell DNA. This effect may result in skin cancer if the body repair mechanism is slow. Some active ingredients in hair dyes exert their effect about twenty years or more after initial use [Allan, 2005] while continuous use produces more effects in later years. Hair dye studies often focus on analyzing the organic compound constituents of the dye. Sadaji et al. (1982) used high performance liquid chromatography (HPLC) to determine the organic compounds present in commercial oxidative hair dyes. Using the same HPLC approach Vincent et al. (1999) studied the effect of matrix compounds on the analysis of the organic compounds in hair dyes. The work of Shih et al. (2004) relied on the use of a screen-printed electrode to evaluate the toxic lead level in hair dyes.

In this present study, we seek to determine the elements that are present in hair dyes. To do this we use two techniques, viz flame atomic absorption spectroscopy (FAAS) and neutron activation analysis (NAA). We further investigate the possible presence of radioactivity in hair dyes as a result of the presence of radioactive elements in the dyes.

Atomic Absorption is based on the measurement of light irradiation absorbed by the unexcited ground state of an analyte atom. If the atoms are produced by a flame, it is called Flame Atomic Absorption Spectroscopy (FAAS). If the atoms are produced by other means, for example electrical, it is called non-flame or flameless atomic absorption. The flame is known as the atom cell or the atomizer. The outlay consists of a light source, usually a hollow cathode lamp. This light source is usually made up of the material of the

analyte, that is, the material to be determined, for example a nickel or lead lamp. The lamp is followed by the monochromator (usually made of a filter, prism or grating) and a detecting device (usually a micro-processor or a moving coil galvanometer, or stripe chart recorder). The absorption technique is used for the determination of several elements in several environmental samples like soil, rock, water, plant, clinical samples, cosmetics, and food (Schrenk, 1975). They are not used for potassium, sodium, calcium, because they are soft metals (that is alkali and alkaline earth metals).

Neutron activation analysis is a sensitive analytical technique used for both qualitative and quantitative multi-element analysis of major, minor and trace elements. To determine the concentration of elements in a given sample, both the sample and a comparator standard containing a known amount of the element of interest are irradiated within the reactor. The mass of an element in the sample relative to the comparator standard is then given by:

$$\frac{A_{sam}}{A_{std}} = \frac{M_{sam}}{M_{std}} \frac{(e^{-\lambda T_d})_{sam}}{(e^{-\lambda T_d})_{std}} \quad (1)$$

where  $A_{sam}$ , and  $A_{std}$  are the activity of the sample and the activity of the standard respectively;  $M$  mass of the element;  $\lambda$  decay constant of the isotope and  $T_d$  decay time (Akaho and Nyarko, 2002).

For short irradiations, the irradiation, decay and counting times have the same fixed value for both sample and standard so that the time-dependent factor cancels and eq (1) then becomes:

$$C_{sam} = C_{std} \frac{W_{std} A_{sam}}{W_{sam} A_{std}} \quad (2)$$

where  $C$  is the concentration of the element and  $W$  is the weight of the sample and the standard.

The sensitivity for NAA depends on the irradiation parameters (neutron flux, irradiation and decay times); measurement conditions (measurement time, detector efficiency) and nuclear parameters of the element being measured (isotope abundance, neutron cross-section and half-life).

Health effects associated with elements identified in the two analyses (NAA and FAAS) include: damage to the central nervous system; dementia; loss of memory; restlessness and severe trembling; disturbances in genetic materials; cancer; damage to the lungs and kidneys (David and Norman, 2005); diarrhea; stomach pains and severe vomiting; anemia; loss of appetite; abdominal pain; constipation; fatigue, headache and kidney problems; skin, eyes, nose and throat irritation causing sneezing and coughing; difficulty in breathing and chemical bronchitis; disturbance of blood circulation; heart damage; reproductive failure; damage to liver and kidney functions. Apart from serving as a medium for further sensitizing hair dye users, this work will also serve as a reminder to hair dye manufacturers of the need to use human friendly elements in their products and formulas.

## 2. MATERIAL AND METHODS

Three methods were used to carry out the analysis. The first was the use of questionnaires to get the responses of hair dye users on the kind of dyes they use as well as any unexplained medical condition they encountered. The Flame Atomic Absorption Spec-

troscopy (FAAS) was used to analyze the liquid dye sample selected through the information obtained from the questionnaire, while the Neutron Activation Analysis (NAA) was used to analyze the solid dye sample.

This questionnaire was designed in such a way so as to have three parts. The first part revealed the name and form of the dyes used. The second part was on the frequency and number of years of usage. The third part dealt with unexplained medical history: the respondents had to select from a list of illnesses (stomach upset, vomiting, diarrhea, headache, nausea, and weakness, loss of appetite, body pains, urinary problems, and indigestion) or specify any not on the list.

For the FAAS (carried out at the Central Research Laboratory, University of Uyo, Akwa Ibom State, Nigeria), a standard solution of the analyte (the liquid dye) using distilled water was prepared. A stock solution was prepared, followed by a serial dilution of the stock solution. The instrument was switched on and allowed to run for about 30 minutes to warm up. The gas was turned on and the flow rate adjusted until a blue flame (2-layer, distinct) was observed. A premixed gas with a laminar flow was used. The instrument was zeroed with the zero adjustable knobs. The clamp which unlocks the read out device was removed. The instrument was checked for full scale deflection. The blank solution (de-ionized water) was aspirated and the instrument zeroed. The maximum standard was aspirated and the instrument adjusted to give full scale reading at 100. Blank and maximum standard were rechecked three times. Each standard solution was aspirated and the instrument scale reading obtained. A calibration graph was plotted. In addition to all the steps already presented, it is necessary to add that a concentration step was required generally for water sample. A known volume of about 500 ml of the water sample was taken, and extracted into the extraction flask. Two important extracts are usually used like Ammonium Pyroline Dithio-Carbamate (APDC) and Methyl Isobutyl Ketone (MIBK). They are called chelating agents. During the extraction process, two layers were observed in the extraction flask because water and the APDC do not mix. The water layer is drained off through a tap. All the metals were concentrated in the APDC layer but MIBK was added to the APDC to concentrate the metals before aspiration to the Atomic absorption instrument. All the elements analyzed for are suspected chemical carcinogens. Part of the sample used to analyze for trace metals was treated with nitric acid to remove organic matter and to dissolve the metals.

Nigerian Research Reactor 1 (NIRR-1) was used for the NAA. The analysis was done at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria. It is a miniature neutron source reactor (MNSR) and has a tank-in-pool structural configuration with a nominal thermal power rating of 31KW. The NIRR-1 is specifically designed for neutron activation analysis and it has enhanced the capability for the analyses of traces of minor and major elements in different sample matrices. The neutron flux parameters of the MNS reactors are known to be very stable, thus permitting the use of the semi-absolute NAA method [Akaho and Nyarko, 2002; Jonah et al., 2006]. The procedures involved include minimum sample preparation, two irradiation regimes and four counting strategies, which have been adopted on the basis of the half-life of product radionuclide and the neutron spectrum parameters in the inner and outer irradiation channels. The NIRR-1 has highly enriched uranium as fuel, light water as a moderator and Beryllium as a reflector. The associated facility for radioactive measurement is a gamma-ray data acquisition system. It consists of a horizontal, deep-stick high purity germanium (HPGe) detector with a relative efficiency of 10% at 1332.5KeV gamma ray line, the MAESTRO emulation software compatible with the ADCAM<sup>R</sup> multi-channel analyzer

(MCA) card. There are also associated electronic modules, all made by EG&G ORTEC and a personal computer. The efficiency curves of the detector system at near and far source detector geometrics were determined by standard gamma ray sources in the energy range of 59.5-2254KeV and were extended to 4000KeV by a semi-empirical method. For data processing, the gamma-ray spectrum analysis software, WINSPAN2004 [Liyu, 2004] was used. It is software developed at CIAE, Beijing, China. On the basis of a well known activation equation, the software requires that a calibration factor be pre-determined by a multi-element standard reference material for the elements of interest, using adopted irradiation and counting regimes. In addition to the NAA calculations, the WINSPAN2004 performs peak analysis, remote-control of the MCA and other auxiliary functions such as efficiency calibration and nuclear data generation.

### 3. RESULTS AND DISCUSSION

Seventy-eight percent of the questionnaires given out were substantially filled. The responses showed that the most commonly used solid dye was Paraphenylene Diamine (PPD) and the liquid dye was the "Youth Hair" dye. A theoretical survey of the constituents of these dyes showed that all the dye brands consisted of azonium compounds. The results obtained from the questionnaire showed that the longer the usage time, the more the unexplained medical conditions. The medical conditions are shown in Fig. 1. Those with significant percentage occurrence were headache (16%), body pains and stomach upset (15.5%), and weakness (15%). Next to these were urinary problems (9.5%), indigestion (8.5%) and loss of appetite (6%). It should however be noted that, some interfering habits like smoking, snuff intake and drinking of alcohol may present symptoms similar to those suspected to be caused by hair dye usage.

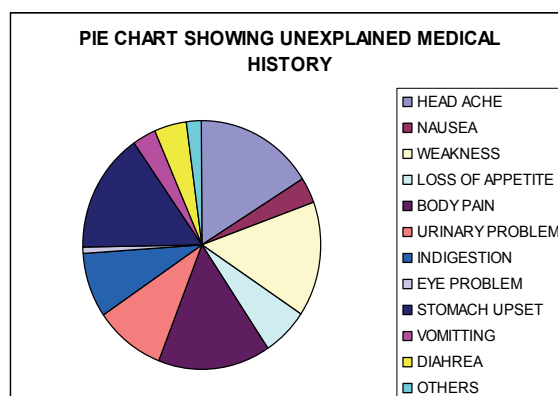


Fig. 1. Pie chart showing unexplained medical conditions

The results of the analysis from the Flame Atomic Absorption Spectroscopy (FAAS) are tabulated in Table 1. The results are based on the American Standard Test Method (ASTM). Five ions namely:  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{S}^{2-}$ , and  $\text{SO}_4^{2-}$  were detected with concentrations of 0.702, 0.002, 0.003, 0.044, and 0.059  $\text{mg.l}^{-1}$  respectively. No permissible limits have been quoted specifically in hair by any regulatory authority for any of the ions.

However, permitted Dietary Reference Intake level for  $\text{Fe}^{2+}$  in the human body is 45mg/kg. Permissible levels for Pb are  $1.5\mu\text{g}/\text{m}^3$  (United States Environmental Protection Agency) and  $50\mu\text{g}/\text{m}^3$  (United States Occupational Safety and Health Administration). In air the permissible levels for Cd are 5ppb (United States Environmental Protection Agency). Though the metals observed in the sample are in traces, there is a high tendency for accumulation due to regular use of these dyes which may lead to the hazardous effects associated with each of the identified elements.

Table 1. Sample Parameters in mg/l for the liquid hair dye using FAAS

S/N	SAMPLE ID	ASTM D3539 $\text{Fe}^{2+}$	ASTM D3557 $\text{Pb}^{2+}$	ASTM D516 $\text{Cd}^{2+}$	ASTM D4658 $\text{S}^{2-}$	ASTM D4658 $\text{SO}_4^{2-}$
1	A	0.702	0.002	0.003	0.044	0.059

Results from Neutron Activation Analysis (NAA) are shown in Table 2. The six elements found to be present are Al, Na, Eu, Br, Ce, and Th, in trace concentrations of  $31.9 \pm 5.4$ ,  $40.6 \pm 5.9$ ,  $0.16 \pm 0.05$ ,  $0.18 \pm 0.04$ ,  $0.37 \pm 0.08$ , and  $0.13 \pm 0.02$  ppm respectively. Here also no permissible limits have been quoted specifically in hair by any Regulatory Authority for Na, Eu, Ce or Th. However, permitted level in the human body for Al is  $10\text{mg}/\text{m}^3$  (United States National Institute for Occupational Safety and Health) and for Br is 1ppm (United States Occupational Safety and Health Administration). Since the solid dye sample is the main constituent used in the manufacture of most other permanent hair dyes, this result is valid for all the dye brands used in this work, unless there were processes aimed at extracting these elements from the parent substance.

Table 2. Result for the solid hair dye from NAA

Elements	Symbol	Concentration (ppm)
Aluminum	Al	$31.9 \pm 5.4$
Titanium	Ti	BDL
Calcium	Ca	BDL
Magnesium	Mg	BDL
Potassium	K	BDL
Iron	Fe	BDL
Sodium	Na	$40.6 \pm 5.9$
Vanadium	V	BDL
Manganese	Mn	BDL
Antimony	Sb	BDL
Lanthanum	La	BDL
Samarium	Sm	BDL
Scandium	Sc	BDL
Cesium	Cs	BDL
Europium	Eu	$0.16 \pm 0.05$
Bromine	Br	$0.18 \pm 0.04$
Cerium	Ce	$0.37 \pm 0.08$
Thorium	Th	$0.13 \pm 0.02$

BDL = below detection limit

The presence of the radioactive isotope, thorium (Th), even though in trace amounts and bromine (Br) serve as potential carcinogens. Whether the effects associated with all the elements detected are synergistic or antagonistic is yet to be proven with information available at present. In addition to elements present in the dyes analyzed, the major active ingredient; Paraphenylene diamine (PPD; IUPAC name- 1, 4-diaminobenzene) has its own cancerous effects. PPD is also the most widely used primary intermediate in hair dye formulation. Most of its cancerous effects are directed towards the bladder. The Aryl group present in PPD has high affinity for DNA.

#### 4. CONCLUSIONS

The liquid dye sample, which was analyzed using Flame Atomic Absorption Spectroscopy, had five ions detected namely  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{S}^{2-}$ , and  $\text{SO}_4^{2-}$  with concentrations of 0.702, 0.002, 0.003, 0.044 and 0.059  $\text{mg.l}^{-1}$  respectively. The solid hair dye sample, which was analyzed using the Neutron Activation Analysis technique, had six elements (Al, Na, Eu, Br, Ce, and Th) in trace concentrations of  $31.9 \pm 5.4$ ,  $40.6 \pm 5.9$ ,  $0.16 \pm 0.05$ ,  $0.18 \pm 0.04$ ,  $0.37 \pm 0.08$ , and  $0.13 \pm 0.02$  ppm respectively. Twelve other elements (Ti, Ca, Mg, K, Fe, V, Mn, Sb, La, Sm, Sc and Cs) were below the detection limit. No permissible limits have been quoted specifically in hair by regulatory authorities for any of the ions or elements hence comparison with such values was not possible. Consequently, these results would be taken as baseline data for future work. The presence of radioactive isotopes could serve as a possible explanation for the observation that the negative health impact of certain hair dyes is felt many years after initial use [Allan, 2005].

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## NEUTRONSKA AKTIVACIJA I PLAMENA ATOMSKA APSORPCIJA: ANALIZA SASTAVA HEMIJSKIH ELEMENATA NA ODABRANOM UZORKU BOJA ZA KOSU

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*Dve vrste farbe za kosu, jedna u tečnom, druga u čvrstom stanju, analizirane su da bismo utvrdili njihovu strukturu elemenata i moguću radioaktivnost. Farba u tečnom stanju je analizirana uz pomoć procesa Spektroskopije atomske apsorpcije plamena i zasniva se na metodi nazvanoj Američka metoda standardnog tesitranja (ASTM), odnosno na pet jona:  $Fe^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $S^{2-}$ , i  $SO_4^{2-}$  su otkriveni u koncentracijama od 0.702, 0.002, 0.003, 0.044, i 0.059  $mg.l^{-1}$  tim redosledom. Uzorak farbe za kosu u čvrstom stanju smo analizirali uz pomoć tehnike Analize neutronske aktivacije. Osamnaest elemenata (Al, Ti, K, Fe, Na, V, Mn, Sb, La, Sm, Sc, Cs, Eu, Br, Ce, i Th) su mereni. Šest od tih elemenata (Al, Na, Eu, Br, Ce, i Th) pronađeni su samo u tragovima od  $31.9 \pm 5.4$ ,  $40.6 \pm 5.9$ ,  $0.16 \pm 0.05$ ,  $0.18 \pm 0.04$ ,  $0.37 \pm 0.08$ , i  $0.13 \pm 0.02$  ppm tim redosledom. Za Ce i Eu trenutno nije dokazano da su opasni po ljude, dok Pb, Cd, i Fe ne mogu lako prodrati u ljudsko telo putem apsorpcije preko kože. Iz toga razloga upotreba farbi koje sadrže ove elemente ne može izazvati efekte koji se obično javljaju nakon unošenja ovih elemenata, sem ako se farba slučajno ne nađe u nekom uzorku hrane. Prisustvo Al, Na, Br, Th, S, i  $SO_4$  moglo bi da dovede do negativnih uticaja koji se dovode u vezu sa svakim elementom. Pored toga, glavni aktivni sastojak: Paraphelylene diamine (1, 4-diaminobenzene) ima kancerogena svojstva koja se obično usmeravaju ka bešici.*

*Ključne reči: farba za kosu, sastav hemijskih elemenata, Spektroskopije atomske apsorpcije plamena, aktivacija neutrona, sadržaju tragovima, kancerogena svojstva*