Determination of Respirable Dust for Heavy Metals in Some Nigerian Coals.

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ABSTRACT

X-ray diffraction technique was used to analyze coal processing dusts of four samples from Lafia-Obi, Lamja, Doho and Okaba. The diffractograms show a number of inorganic substances and some heavy metals such as lead, cadmium, arsenic and titanium at very high concentrations. Uranium and gold were among the compounds that appeared in Doho coal dusts. Apart from the health hazards, gold and uranium represent high potentials for prospecting and mining in a growing economy.

INTRODUCTION

There is a growing global concern on the rate of depletion of petroleum as wells dry up in whole oil fields. If oil reserves dry up the energy crises would be ugly. Coal is the world's most abundant energy source, being the fossil fuel of the industrial revolution, and contributed 4.3 x 10^3 million joules of energy to the total world energy demand of about 7.0 x 10^3 million joules. The world proven reserve is about 698 billion tons[1]. This represents about 80% of the world's non-renewable energy reserves. Others, including crude oil, constitute only 20%[2].

However, growing and sustained interest in the development of an effective, economically and environmentally-friendly coal conversion technology has generated a large scale research on coal in Nigeria. Coal processing techniques, whether on industrial or laboratory scale, are always accompanied by the release of particulate matter into the atmosphere, which may be harmful upon prolonged inhalation and accumulation in the human body. Black-lung disease is a chronic occupational lung disease contracted by the prolonged breathing of coal processing dust. Black-lung disease is also called coal workers' pneumoconiosis, miners' asthma and silicosis. The risk of having black-lung disease is directly related to the amount of coal dust inhaled over years. Black-lung disease usually affects workers over age 50[3].

X-ray diffraction analysis is primarily used for the study of crystalline materials. X-rays are diffracted off the surfaces of crystalline materials and by studying the diffraction as the material is rotated in the path of x-rays, much information about the structure of the material can be obtained.

The theory of x-ray diffraction is hinged on the fact that when x-ray beams are incident on minerals, all exhibit their characteristic diffraction patterns. There will be obvious overlaps when there are many minerals in the sample being analyzed. But when mono, bi or tri-mineralic materials are analyzed, individual patterns are easily disentangled and minerals are easily identified in the diffractogram. The diffraction equipment can cross-match the peaks with peaks of an inbuilt standard and come up with identification of the mineral constituents.

The deciphering of the peaks and the mineral content of the powdered sample under analysis follows the Bragg's law, which is given mathematically as:

$$n\lambda = 2d \sin \theta$$

where

n = integer 1

λ = wavelength of incident beam

d = distance between adjacent atomic planes

θ = angle between incident beam and reflecting crystal plane

2θ = angle between diffracted beam and transmitted beam

This paper reports the application of x-ray diffraction to determine the elements or other substances that could be indicated in the incidence of coal workers' diseases.

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EXPERIMENTAL

Materials

The coal samples, Lafia-obi, Okaba, Doho and Lamja were obtained from the National Steel Raw Materials Exploration Agency, Kaduna, Nigeria. binders such as sodium borax and organic liquid binders of Analar grade were purchased from Galson Laboratories, U.K.

Dust Collection

Pre-weighed PVC filters were used for the collection of the coal dust. The PVC filter was fitted to the extractor fan in the room where the coal crusher is mounted. The four different coal samples were pulverized and screened separately. For each coal sample a fresh filter was used to trap the dust coming out as a result of the crushing and screening. The dust was then scraped carefully off the filter into a sample container, closed air-tight and stored for analysis.

X-ray Diffraction (XRD)

This analysis was carried out at National Steel Raw Materials Exploration Agency, Kaduna. The x-ray diffractometer used was Philips PW 1800, with inbuilt standard peaks/widths.

The coal samples were further pulverized into very find powder. The powder for each sample measuring about 2.5g was fed into the x-ray diffraction equipment.

The diffractometer now prints the first fourty available compounds in the sample with their percentage intensities. The diffractometer then cross-matches the peaks with the inbuilt standard peaks/widths and then comes up with the final diffractogram with peaks/widths of the most intense minerals in the sample under analysis.

The following programme was used:

Diffractometer type:	PW 1800
Tube anode:	Cu
Generator tension (kV):	40
Generator current (mA):	55
Wavelength alpha 1 (λ):	1.54056
Wavelength alpha 2 (λ):	1.54439
Intensity ratio (alpha 2/alpha 1):	0.500
Divergence slit:	FINE
Irradiated length (mm):	2
Receiving slit:	FINE
Spinner ON:	1
Monochromator used:	Yes
Start angle (020):	0.010
End angle (020):	70.000
Step angle (020):	0.030
Maximum intensity	23932.09
Time per step (s):	0.200
Type of scan:	CONTINUOUS
Intensities converted to:	FIXED
Peak positions defined by:	Minimum of 2nd derivatives of peak
Minimum peak tip width:	0.05
Maximum peak tip width:	5.00
Peak base width:	2.00
Minimum significance:	0.75
Number of peaks:	

RESULTS AND DISCUSSION

The x-ray diffraction results for Lagia-Obi, Okaba, Lamja and Doho coal dusts are presented in Figures 1A, 1B, 2A, 2B, 3A, 3B, 4A, 4B and Tables 1, 2, 3 and 4 respectively.

Analyses of the four dust samples show the presence of numerous amount of inorganic and some traces of heavy metals. Some of these heavy metals include Lead (Pb), Telurium (Te), Cesium (Cs), Chromium (Cr), Scandium (Sc), Vanadium (V), Hafnium (Hf), Titanium (Ti), Nickel (Ni), Gadolinium (Gd), Cadmium (Cd), Strontium (Sr) and Barium (Ba) for Lafia-Obi sample.

In the case of Lamja coal sample, compounds of Zinc, Erbium, Plutonium, Copper, Aluminium, Silver, Yitrium, Ytterbium and Rubidium were present. Doho sample showed the presence of Uranium, Gold, Nickel, Bismuth, Cobalt and Manganese, among others.

On the other hand, Okaba coal dust revealed the presence of Antimony, Tin, Iron, Silicon, Niobium, Gallium, Titanium, Lithium, Vanadium and others.

The most prominent peaks in the diffractogram with relatively high percentage intensity in the coal dust include those of graphite, gadolinium selenide hydride, ytterbium sulphide and potassium chromium oxalate for Lafia-Obi, yttrium germanium oxide ($Y_2Ge_2O_7$) and titanium ammine sulphide (TiS_2NH_3) for Lamja sample; barium, copper, strontium and iron oxide for Doho coal, and quartz, rubidium, boronhydride, potassium and zinc methyl phosphonate for Okaba sample. The effects of these elements and heavy metal compounds have been well studied and documented[4-5]. For instance, copper, selenium and zinc are essential for the maintenance of body metabolism but at higher concentrations may lead to poisoning.

Most heavy metals bioaccumulate, cadmium in particular is biopersistent. Long-term exposure to it leads to renal dysfunction and obstructive lung disease linked to cancer, bone defects (osteomalacia) and high blood pressure[6].

Lead can cause, in humans (mainly infants), toxic biochemical effects that cause problems in the synthesis of haemoglobin, effects on kidneys, gastro-intestinal tract and acute or chronic damage to the nervous system. At intermediate concentrations lead can have subclinical effects particularly on neuropsychological development in children[7].

Long-term exposure to chromium causes kidney and liver damage. Although the polymorphs of quartz, tridymite, crystobalite and amorphous free silica are present in many minerals, the only form found in coal is λ-quartz. The diffractogram of Okaba coal reveals the presence of quartz. Quartz has been linked, possibly synergistically, to coal workers' pneumoconiosis (CWP)[8]. The presence of trace elements and the chemical nature of organic constituents could affect the incidence of CWP[9].

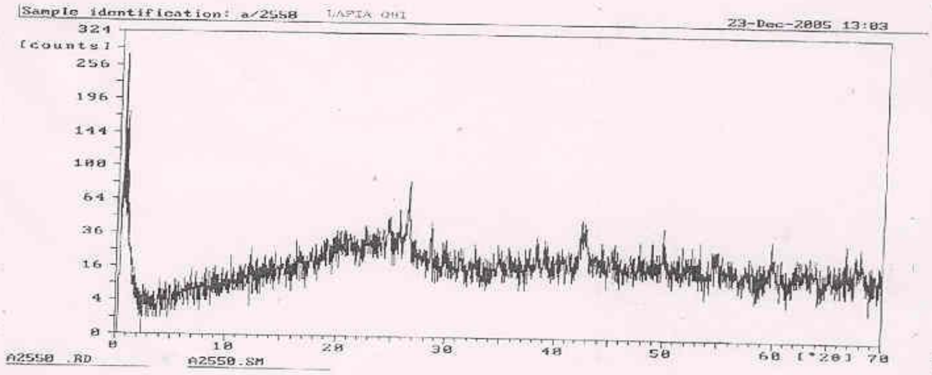

Fig. 1a: X-Ray diffraction of Lafia-Obi Coal Dust.

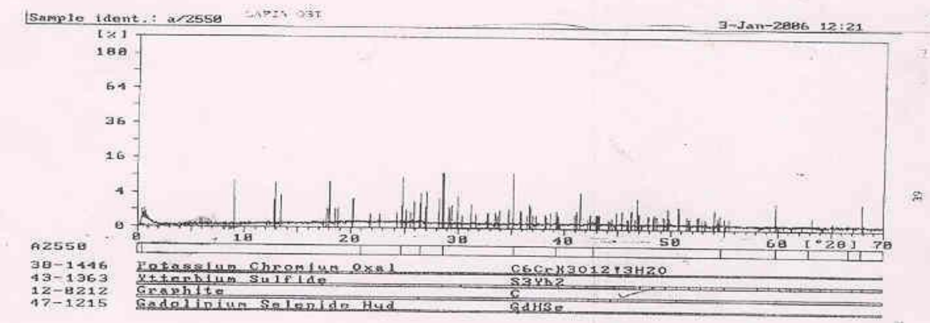

Fig. 1b: Element Identification of Lafia-Obi Coal Dust.

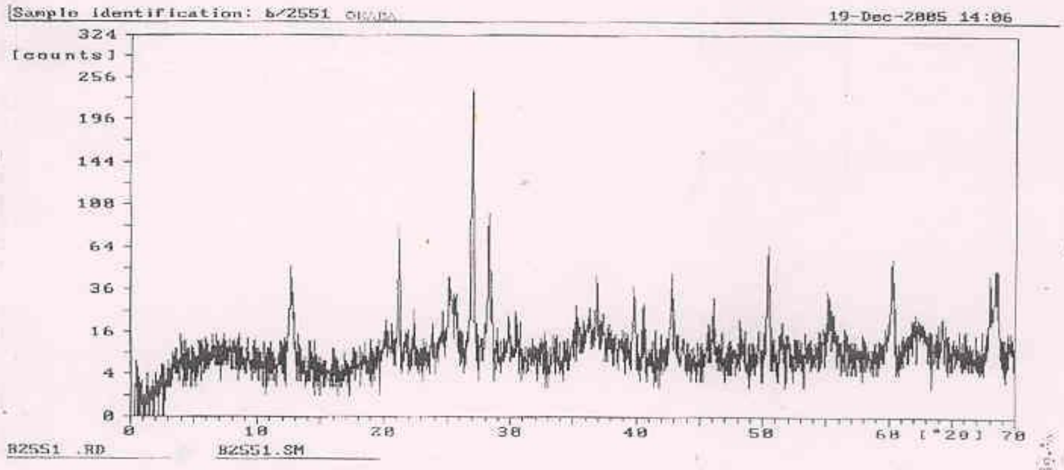

Fig. 2a: X-Ray Diffraction of Okaba Coal Dust.

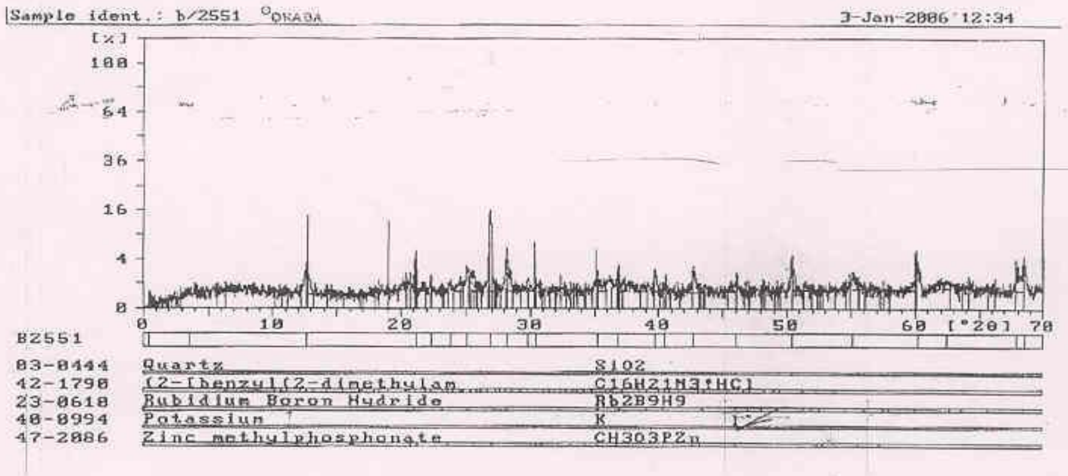

Fig. 2b: Element Identification of Okaba Coal Dust.

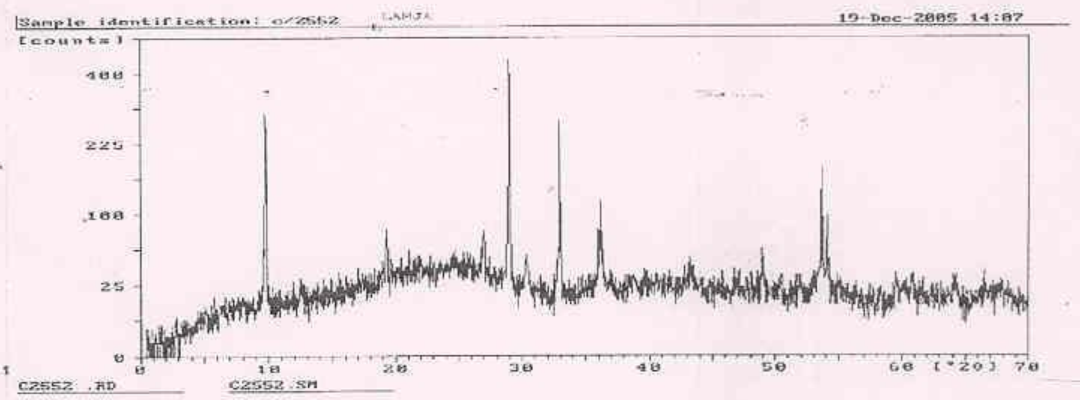

Fig. 3a: X-Ray Diffraction of Lamja Coal Dust.

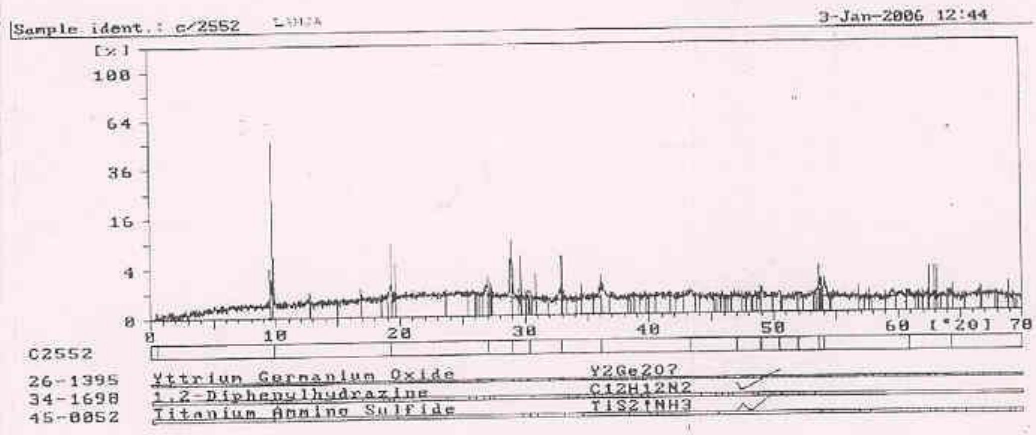

Fig. 3b: Element Identification of Lamja Coal Dust.

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Sample identification: c/2552
First database used : C:\IDENTDB
Second database used : C:\USERDB

Results:

	Card Id	Match score	Rel m score	I [%]	Displ [μm]	Formula
1	37-0801	31.20	0.29	4	-109	RbHSO4
2	38-0290	25.93	0.32	2	12	Er2Ge2O7
3	44-0455	27.33	0.29	4	45	CoSrV2O7
4	37-1359	20.80	0.32	1	45	Er2Ge2O7
5	47-0296	19.69	0.33	1	-97	Tm2Ge2O7
6	22-0818	18.26	0.30	1	-97	K3Fe(CN)6
7	32-0304	13.92	0.39	2	93	CoNb2O6
8	35-0739	14.99	0.34	3	-122	PbZrO3
9	26-0995	14.99	0.33	1	50	CaHf4O9
10	21-1445	14.74	0.33	1	45	Y2Ge2O7
11	26-1395	14.74	0.33	1	45	Y2Ge2O7
12	25-0898	14.19	0.34	1	-3	SrPbO3
13	03-1105	14.76	0.32	1	17	Ca3Si2O7
14	22-1010	12.02	0.38	1	-92	Zn2.54In2.31S6
15	43-1086	12.98	0.34	2	86	PuWC2
16	42-1497	13.84	0.31	1	-84	BaEu2O4
17	35-0048	10.64	0.38	1	50	Rb10Nd2(CrO4)5(MoO4)3
18	22-1433	10.19	0.39	2	70	SrPbO3
19	23-1021	11.26	0.35	4	-4	Ba3Ga2O6
20	45-1457	10.71	0.37	1	116	Pb(F,Cl,OH)2
21	18-1847	11.47	0.33	7	-92	C4H4KN
22	32-1668	10.84	0.34	8	-92	C12H12N2
23	45-0024	13.64	0.27	3	12	Cu2(OH)3NO2
24	34-1698	10.74	0.34	8	-92	C12H12N2
25	15-0904	10.69	0.33	4	12	CH3KO4S
26	39-1498	10.39	0.34	2	25	La1.67Sr0.33Cu2O5
27	28-0300	9.07	0.38	2	-129	CsGaSiO4
28	07-0285	9.07	0.38	2	50	AlTh2
29	27-0461	10.09	0.34	2	45	KYb3F10
30	44-1310	8.83	0.38	4	-125	Yb7.24Se8
31	21-0991	9.73	0.35	1	-117	K4PbO3
32	43-1478	9.00	0.37	2	30	(Cu,Fe)12As4S13
33	25-0023	8.60	0.39	2	-22	AlTh2
34	05-0610	8.18	0.41	1	-109	NaClO3
35	15-0685	9.13	0.37	1	50	ZnTa2O6
36	37-0158	10.68	0.31	1	-99	Ca5Si2O8F2
37	29-1217	10.28	0.29	1	93	NaFeRuO4
38	09-0126	8.33	0.35	1	-36	Ag3Pb2Sb3S8
39	32-1323	8.46	0.34	1	-122	TlSm(WO4)2
40	15-0536	8.35	0.33	1	50	Li2Al2Ti4O12

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1	30-0799	16.06	0.35	2	-109	MgWO4!H2O
2	39-0462	18.51	0.30	1	98	Sr3Si2As4
3	29-1107	15.21	0.35	1	111	Rb2U4O13
4	32-0642	11.96	0.41	1	131	MnIn2Te4
5	43-0222	15.39	0.31	1	-104	Bi2Sr2Eu1.3Ce0.7Cu2O10.17
6	36-0803	14.03	0.33	1	-46	NH4Ag(NO3)2
7	30-0630	10.77	0.43	1	131	In2MnTe4
8	46-0574	11.19	0.40	1	-4	BaSrEuCu3O6+x
9	43-1162	14.39	0.29	1	-71	CsSnI3
10	39-0241	13.57	0.31	1	-46	CaEuGaAl2O7
11	13-0194	12.67	0.32	1	12	Sr2P2O7
12	18-1060	10.07	0.40	1	37	K2SO4
13	32-0738	10.87	0.36	1	-31	KSb4F13
14	39-1498	10.86	0.35	1	-129	La1.67Sr0.33Cu2O5
15	46-0578	8.91	0.42	2	-4	BaSrSmCu3O6+x
16	03-0788	7.23	0.52	1	50	MgCO3
17	39-1415	10.20	0.36	1	25	BaCu5La4O13
18	33-1488	9.83	0.36	1	-51	In2Te3
19	25-0744	8.00	0.42	1	-42	RuZrSi
20	46-0575	8.84	0.37	1	-4	BaSrGdCu3O6+x
21	30-1664	8.65	0.38	2	103	C9H5N3
22	44-1027	9.61	0.33	1	-26	Cs3ErF6
23	29-0944	9.46	0.33	1	70	Ni2(UO2)6(SO4)3(OH)10!16H
24	42-1235	4.82	0.60	1	111	AuGaLi2
25	15-0904	9.59	0.30	1	-46	CH3KO4S
26	06-0605	6.97	0.41	1	-117	CuInTe2
27	11-0692	6.73	0.42	1	91	CoCO3
28	47-1061	5.80	0.48	1	-122	Pd5Ti3
29	33-0410	9.75	0.29	1	12	CrWO4
30	03-0893	4.89	0.54	1	-150	CaCO3
31	20-0167	6.24	0.42	1	98	BeSiN2
32	27-0002	4.49	0.56	1	45	Al0.2C6Br1.6
33	42-1236	4.46	0.56	1	-3	AuGeLi2
34	16-0609	7.74	0.31	1	-132	NaAl8V10O38!30H2O
35	43-1285	5.30	0.44	1	40	CdCe2S4
36	14-0086	7.14	0.32	1	-99	CoMoO6!0.9H2O
37	42-0400	5.01	0.46	1	-99	Sr0.09Ca0.91CuO2
38	47-0102	6.59	0.35	1	-59	Ba3Cu6Eu3O14.1
39	32-0643	5.17	0.43	1	70	Mn12Ni4.04Si2.84
40	36-1305	5.56	0.40	2	-117	Mn0.87Ga2.09S4

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1	42-0905	43.84	0.29	1	-4	CsS2Sb
2	42-0225	35.19	0.29	1	-122	Fe2(SO4)3
3	46-1486	24.78	0.29	1	-51	Sn6O4(OH)4
4	03-0444	11.68	0.58	5	58	SiO2
5	09-0394	18.82	0.32	3	62	CsBF4
6	25-1337	19.57	0.29	2	-99	Rb2Zn(BeF4)2!6H2O
7	28-0339	18.56	0.30	1	-3	CsNa(ClO4)2
8	39-1266	18.16	0.29	2	-22	CuSr3Ge5O14
9	35-0299	15.80	0.33	2	111	EuSiO3
10	43-0488	16.74	0.31	2	-59	Zn2P2O7
11	42-1790	17.48	0.28	12	-56	C16H21N3!HCl
12	25-1772	11.79	0.41	5	-145	C4K2N2S2
13	35-1079	14.82	0.31	1	-79	SrI2O6
14	37-0635	14.03	0.32	1	-37	LiW3O9F
15	19-0675	13.84	0.32	1	-68	Pb2Cu(Pb,Bi)Bi2S7
16	30-1229	12.63	0.32	3	-26	Na2Nb8O21
17	34-1793	11.51	0.34	12	25	C15H15NO3
18	11-0345	8.76	0.44	4	116	Ca(Mn,Mg)(CO3)2
19	39-1460	9.58	0.37	2	-122	Ca0.5BaNbTe2O9
20	22-0694	9.88	0.34	3	-46	LiY5W8O32
21	15-0121	10.03	0.33	1	93	Ca2Zr5Ti2O16
22	24-1991	10.18	0.33	2	-68	C13H16N2O
23	02-1327	8.76	0.38	1	58	Mn2SiO4
24	42-0001	10.05	0.32	1	-4	Pb10(CrO4)3(SiO4)3Cl2
25	23-0610	9.35	0.35	2	-64	Rb2B9H9
26	11-0951	10.00	0.32	7	-109	C8H20BrN
27	38-0013	8.37	0.38	3	-4	KLi3TiO4
28	07-0165	8.92	0.36	2	-4	(Mg,Al,Fe)6(Si,Al)4O10(OH
29	28-0401	9.55	0.33	5	-24	Cu2SO4
30	40-0994	3.54	0.88	7	86	K
31	30-0270	6.29	0.48	2	-99	Ca3Nb2Ti3O14
32	40-1849	10.84	0.28	14	12	C2H6OS!Al2Si2O5(OH)4
33	04-0383	8.66	0.35	1	37	PbSBr2
34	47-2086	7.42	0.39	14	-122	CH3O3PZn
35	38-1026	3.37	0.84	14	119	Al86Cr14
36	18-0547	7.91	0.36	2	-26	V6Ga5
37	41-0400	6.08	0.47	3	-24	CuRhO2
38	19-0007	7.87	0.36	1	40	AlCoU
39	30-0857	6.27	0.45	6	73	Nd(IO3)3!5H2O
40	25-0190	7.60	0.36	4	16	CeSI

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Second database used : C:\USERDB

Results:

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1	47-2342	20.75	0.27	1	12	C13H9ClN2O4
2	38-1446	21.44	0.22	1	12	C6CrK3O12!3H2O
3	33-0774	17.03	0.25	1	-112	Tl4PbI6
4	38-0471	15.34	0.26	1	-24	Al2SiO5
5	42-1447	11.01	0.32	1	111	Bi2Te2S
6	31-0328	13.19	0.27	1	-3	CeDyS3
7	37-0674	8.90	0.37	1	-46	C2BaO4
8	08-0497	9.55	0.34	1	73	GaPO4
9	40-0225	7.37	0.43	1	-122	KCrO3F
10	18-1773	9.06	0.35	1	116	C21H18N3O10P
11	03-0543	6.01	0.50	1	45	Bi2(Te,S)3
12	42-1149	10.09	0.29	1	-79	NaCaAlF6
13	19-1193	10.44	0.26	1	-109	Na2SiF6
14	26-1080	4.92	0.49	1	-122	C
15	01-0649	5.33	0.44	1	-46	SiO2
16	40-0433	9.22	0.26	1	116	Na2Sc2V2O9
17	43-1363	7.96	0.27	1	-4	S3Yb2
18	29-0659	6.86	0.31	1	70	Hf4Zn2N
19	46-0695	3.52	0.59	1	-51	AlPO4
20	12-0212	3.48	0.58	2	73	C
21	08-0415	3.10	0.62	2	73	C
22	42-1178	4.76	0.40	1	-122	Ga2Gd
23	12-0377	5.86	0.31	1	-4	B
24	43-1291	6.37	0.28	1	12	Ge2.30Li2Pd2.70
25	18-0701	9.26	0.19	1	12	PbO!4H2O
26	43-0274	5.80	0.29	1	-122	H2CrP3O10!2H2O
27	06-0220	5.15	0.32	1	17	BaB2O4
28	44-0113	4.06	0.41	1	70	TiNi0.8Cu0.2
29	32-1375	5.40	0.30	1	-68	Ti(NaPO4)2!2H2O
30	36-1299	5.07	0.30	1	-46	ZrMoFeH2.6
31	13-0412	6.23	0.24	1	-122	CsTh6F25
32	25-0284	2.90	0.48	2	-122	C
33	47-1215	3.61	0.36	1	12	GdHSe
34	38-1024	5.19	0.25	1	-104	TlSbS3
35	45-0834	4.51	0.28	1	-36	Hf3Zn3O0.5
36	24-0699	4.54	0.27	1	-132	MgPt5P
37	25-1216	3.09	0.39	1	-122	CdCuIn
38	47-0232	4.64	0.26	1	12	Sr1.5Bi0.5O2.75
39	39-1207	2.68	0.45	1	-132	Gd(Al0.1Ga0.9)2
40	39-1206	2.67	0.45	1	98	Gd(Al0.2Ga0.8)2

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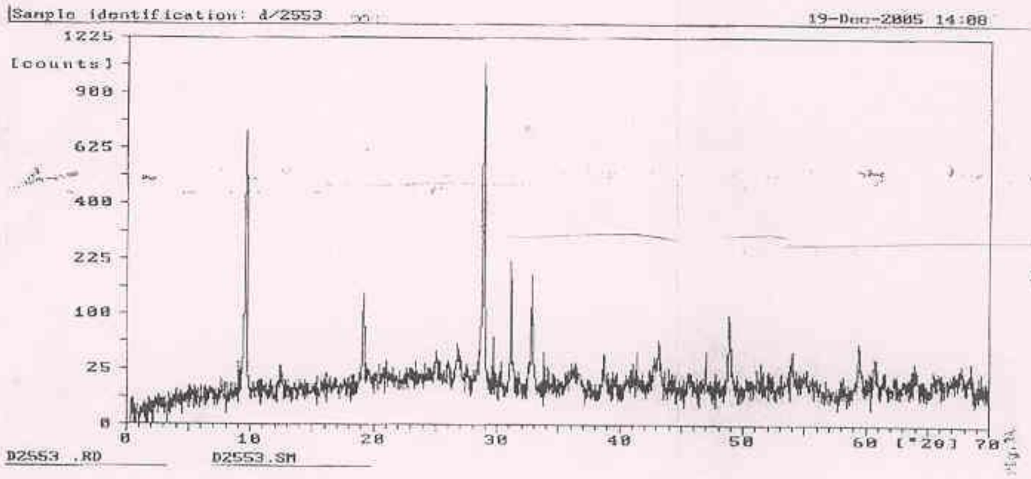

Fig. 4a: X-Ray Diffraction of Doho Coal Dust.

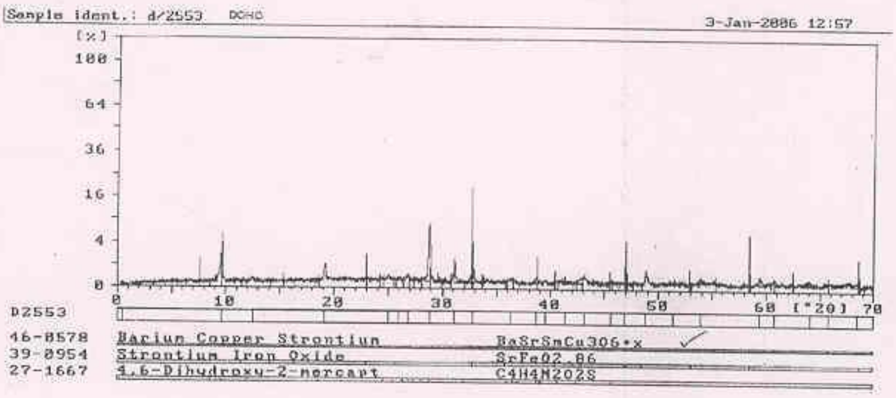

Fig. 4b: Element Identification of Doho Coal Dust

CONCLUSION

The results obtained from the x-ray diffraction of coal dusts from four locations in Nigeria reveal great amounts of organic and inorganic substances and heavy metals such as lead, cadmium, chromium, zinc, amongst others. Black-lung disease is not the only health hazard associated with prolonged exposure to coal dust.

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