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Arsenic Pollution at Obuasi Goldmine, Town, and Surrounding Countryside

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Human hair samples from mine workers and Obuasi citizens; various food items; drinking and washing water from Obuasi town; vegetation and soils from the countryside bordering on the goldmine; and geological materials from the mining process were collected and analyzed by volumetric, gravimetric, colorimetric, and neutron activation methods in order to assess the degree of arsenic pollution brought about as a result of the goldmining operations at Obuasi.

Introduction

As a result of the roasting operation in goldmining at the Obuasi Goldmine huge volumes of poisonous smoke of arsenous oxide and sulfur oxides incessantly pour out of the giant 186-ft. mine chimney onto the surrounding countryside and render it brown and barren.

This defoliation is not confined to the immediate periphery of the mine but extends about 5 miles to the north and about 2 miles to the northeast of the chimney. Some of the palm trees within about half a mile of the chimney look as if they have been burnt by fire.

While collecting samples from some of the surrounding villages such as Nainti (about 5 miles north of Obuasi) we were told that the whole area used to be a cocoa growing zone but that the cocoa trees no longer bear fruit. Some of the giant palm trees have now been converted into dwarf species of their original selves. Some of the villagers at Nainti (5 miles north) and Anyinabrem (7 miles north) claim to have developed chronic eye inflammation as a result of the mine smoke.

Studies (*1, 2*) were carried out previously at the Prestea Goldmine to assess the degree of arsenic pollution at the mine and the exposure of villagers at Apentu, about a mile away on the windward side of the Prestea mine chimney.

The present arsenic pollution survey is a more comprehensive and integrated venture aimed at covering all the five Ghanaian goldmines and their surrounding villages, i.e., Obusai, Prestea, Konogo, Bibiani, and Tarkwa. Samples from the above mines were accordingly collected and are currently being analyzed polarographically to ascertain the total spectrum of arsenic pollution around the above mines.

Experimental

Sample Collection and Preparation

Hair samples from Obuasi mine workers and townspeople were carefully collected, bottled, and labeled. Food items, water, vegetation, soils, and mining materials such as ore concentrate and chimney dust were also collected.

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The food items and vegetation materials were dried for about 3 weeks, ground, and stored in labeled bottles. The soil samples were collected about 1 ft below ground level.

Analysis

The hair samples were analyzed by the neutron activation method; ore dust, ore concentrate, soils, and chimney stack dust by volumetric and gravimetric methods, and water, food items, soil, and vegetation by colorimetric and volumetric methods.

Volumetric Analysis: About 0.05 g of the sample was first mixed with about 4 g of a fusion mixture of 1:1 Na_2CO_3 and KNO_3 in a porcelain crucible, covered, and heated for about 30 min. After cooling of the crucible, distilled water is added, left overnight (to extract the arsenate), and filtered. The filtrate was acidified with 1:4 nitric acid and boiled to expel CO_2. Sufficient NaOH was then added to make the solution alkaline to phenolphthalein and the red color just discharged with acetic acid. The arsenate formed was then precipitated with excess silver nitrate and filtered through a sintered crucible. After washing the precipitate with cold distilled water it was redissolved in 1:4 HNO_3 and titrated against 0.095*N* potassium thiocyanate, ferric alum being used as indicator.

The chemical reactions involved are given in eqs. (1)-(3).

$$AsO_4^{3-} + 3AgNO_3 \rightarrow Ag_3AsO_4 + 3NO_3^- \qquad (1)$$

$$Ag_3AsO_4 + 3HNO_3 \rightarrow 3Ag^+ + 3NO_3^- + 3H^+ + AsO_4 \qquad (2)$$

$$Ag^+ + KSCN \rightarrow AgSCN + K^+ \qquad (3)$$

From eqs. (1)–(3) the arsenic content of the sample was calculated by using the standard KSCN solutions.

Gravimetric Method: The sample was fused as in the volumetric method. After cooling of the crucible, 5 ml of concentrated HCl was added to extract the arsenate. After filtering, about 20 ml of ethyl acetate was added and the mixture poured into a separatory funnel and shaken to remove any traces of gold.

The aqueous layer was then warmed on a water bath for 10 min, after which excess ammonium hypophosphite was added to precipitate elemental arsenic. This was filtered through a sintered crucible, dried under an infrared lamp and weighed as elemental arsenic.

$$H_3AsO_4 + NH_4H_2PO_2 \rightarrow H_3PO_3 + AsO_2^- + NH_4OH + 2H^+ \qquad (4)$$

$$AsO_2^- + 3e + 4H^+ \rightarrow As^0 + 2H_2O \qquad (5)$$

Colorimetric (Guzeit—Molybdenum Blue) Method: Weighed amounts of biological samples were wet-ashed with 10 ml of 75% $HClO_4$ in Kjeldhal flasks till the solution became colorless. Soil samples (ca. 0.6 g) were first fused as in the above methods and the arsenate extract digested with 8 ml of 75% $HClO_4$.

Each of the above mixtures was then diluted to 100 ml, and 10 ml of it was transferred to a beaker and reduced to As(III) with 0.03 g $NaHSO_3$.

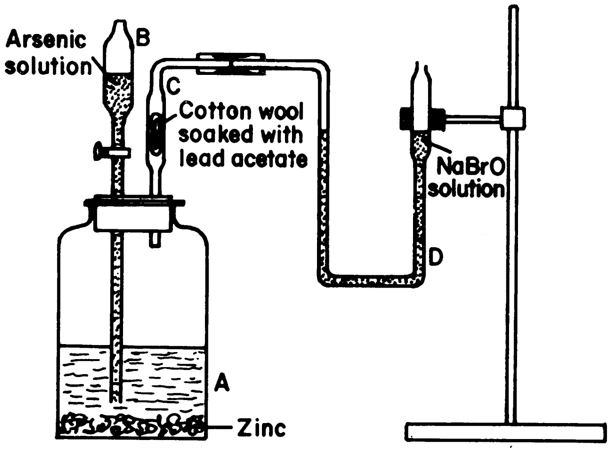

FIGURE 1. Gutzeit generator used in generation of arsine from arsenic solutions.

The As(III) solution was then transferred into the dropping funnel of the Gutzeit generator (Fig. 1) containing 2 g of powdered zinc. The As(III) solution was then added dropwise to generate arsine. The AsH_3, after passing over cotton wool containing lead acetate (to absorb any H_2S), was trapped in tube D containing 3 ml of NaBrO solution. Here the arsine was oxidized to arsenate. Tube D was disconnected and the contents added to 1 ml of ammonium molybdate solution to form a complex.

The complex solution was then reduced with 1 ml of half saturated hydrazine sulfate. The solution was then transferred into a 25 ml volumetric flask and made up to the mark. A 10-ml aliquot of this blue solution was then taken and the absorbance recorded at 840 nm of the SP 600 spectrophotometer. The absorbance was compared to that of a standardized curve prepared from standard solutions. A stock solution was prepared by dissolving 0.132 g of As_2O_3 in 3 ml of 0.5*N* NaOH and making it up to 100 ml with HCl. A 10 ml portion of this solution was made up to 100 ml to give a solution containing 100,000 μg/l. From this solution, standards containing 20, 18, 16, ..., 2 ppm were prepared. Each standard was poured into the Gutzeit generator as above and the arsine generated treated as above and the corresponding absorbance found at 840 nm. From this an absorbance/concentration curve was plotted as shown in Figure 2.

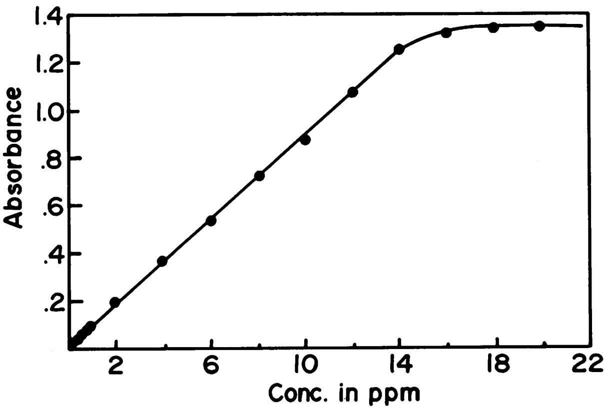

FIGURE 2. Graph of absorbance against As concentration.

The chemical reactions involved in the colorimetric method are shown in eqs. (6)—(9).

$$\mathrm{As(III)} + 3e \rightarrow \mathrm{As^0} + 3\mathrm{H} \rightarrow \mathrm{AsH_3} \qquad (6)$$

$$\mathrm{AsH_3} + 4\mathrm{NaBrO} \rightarrow \mathrm{H_3AsO_4} + 4\mathrm{NaBr} \qquad (7)$$

$$2\mathrm{H_3AsO_4} + 7\mathrm{H_2MoO_4} + 4\mathrm{H_2O} \rightarrow \mathrm{H_6As_2Mo_7O_{29}} \cdot 11\mathrm{H_2O} \qquad (8)$$

$$\mathrm{H_6As_2Mo_7O_{29}} \cdot 11\mathrm{H_2O} \xrightarrow[\text{Reduction}]{\mathrm{H_2N_4} \,\cdot\, \mathrm{H_2SO_4}} \underset{\text{(Blue Complex)}}{\mathrm{H_7As[As(Mo_2O_7)_5OMo_2]O_5}} \qquad (9)$$

Neutron Activation Analysis: Neutron activation analysis was as described in a previous report

Table 1. Arsenic content of Obuasi hair samples analysed by neutron activation analysis method.

Sample	Description	Sex	Age	As content, ppm (by weight)
1	Mine worker (shaft)	M	25	69.6±2.8
2	“	M	41	17.4±1.4
3	“	M	26	26.2±1.5
4	“	M	26	50.0±2.0
5	“	M	45	78.0±3.2
6	“	M	46	38.7±1.9
7	“	M	22	7.7±0.9
8	“	M	25	63.0±2.6
9	Mine worker (PTP)	M	60	1513 ±47
10	“	M	35	1940 ±62
11	“	M	33	1794 ±47
12	“	M	28	196 ± 7
13	“	M	50	431 ±14
14	“	M	40	340 ±12
15	“	M	25	880 ±27
16	Citizen (not employed at mine)	F	13	15.3±1.2
17	“	M	33	26.4±1.5
18	“	F	23	96.0±4.0
19	“	M	11	39.1±2.0
20	“	M	17	13.9±0.9
21	“	M	20	8.8±0.9
22	“	F	30	123 ±0.9
23	“	F	30	57.9±2.5
24	“	F	17	61.9±3.3
25	“	F	28	165 ±6
26	“	F	26	268 ±10
27	“	F	13	23 ±1.4
28	“	M	17	21.5±1.3
29	“	M	14	22.2±1.4
30	“	F	11	30.6±1.7

(*1*). The equation for the activation is given by eq. (10).

$$\mathrm{As}^{75} + n \rightarrow \mathrm{As}^{76} + \gamma \tag{10}$$

A 0.56 MeV photopeak was used in the counting.

Results and Discussion

Hair is a useful source of investigation in arsenic poisoning. Table 1 gives the results of Obuasi hair samples analyzed by the neuton activation method. The hair samples were taken from both mine workers and townspeople of Obuasi not employed at the mine. Two types of mine workers are involved: namely those working in the shaft, and those working in the roaster and chemical processing sections (PTP workers).

The hair arsenic content of PTP workers are the highest, the maximum being 1940 ± 62 ppm and the minimum being 196 ± 7 ppm. The highest level for the shaft workers is 78.0 ± 3.2 ppm and the lowest is 7.7 ± 0.9 ppm.

Surprisingly, two women not employed by the mine also have hair arsenic contents as high as 165 and 268 ppm.

Leniham and Smith reported previously (*3*) a maximum arsenic content of 606 normal male hair samples was 2.5 ppm and a minimum of 0; the maximum arsenic content found in normal 386 female hair samples was 2.5 ppm. and the minimum found was 0.

Another study by Smith (*4*) reported the average arsenic content of normal hair found from the analyses of 1250 normal persons to be 0.650 ppm.

It is very obvious that the arsenic contents of all the 30 samples analyzed in the present work are far above the normal levels of hair arsenic content. All the three categories of individuals show high arsenic levels, the PTP workers showing the highest values. In the report of Smith (*5*) giving the distribution of arsenic concentration in 39 samples of known industrial exposure, the highest value recorded was

Table 2. Food items, water, vegetation, soil, and mine materials.

Sample	Sample description	Method	As content (by weight)	
			%	ppm
31	Cocoyam leaves (Obuasi)	Colorimetric		4.80±0.22
32	Cassava, 500 yd from chimney	"		0.605±0.035
33	Sugar cane (Obuasi)	"		14.75±0.21
34	Orange (Obuasi)	"		2.29±11
35	Cassava (Obuasi market)	"		2.65±0.09
36	Cassava (Obuasi farm, 4 mi from mine)	"		1.83±0.06
37	Cocoyam, 150 yd from mine	"		1.89±0.07
38	Plantain (Obuasi market)	"		0.615±0.015
39	Obuasi-Kwabrafoso dam water	"		2.25±0.083
40	Obuasi-Kwabrafoso drinking water	"		1.40±0.051
41	Fern (*Pteris vitatae*), 100 yd from chimney	Volumetric	0.47±0.1	4700±110
42	Fern (*Pteris vitatae*), 150 yd from chimney	"	0.125	1252±113
43	Fern (*Pteris vitatae*), 220 yd from chimney	"	0.110	1100±100
44	Grass, 200 yd from chimney	Colorimetric		14.15±15
45	Bahama grass, 150 yd from chimney	"		20.9 ±0.5
46	Bahama grass, 250 yd from chimney	"		11.6 ±0.25
47	Palm tree, 150 yd from chimney	Volumetric		2875 ±25
48	Soil, 300 yd from chimney			147 ±2.5
49	Soil 2.5 mi from chimney			67.2 ±1.8
50	Soil 1.5 mi from chimney			96.5 ±1.7
51	Soil 9 mi from chimney			11.15±0.35
52	Soil 5 mi from chimney			
53	Chimney dust (Obuasi)	Volumetric	21.1±0.87	
		Gravimetric	21.8±0.25	
54	Ore concentrate (Obuasi)	Volumetric	17.6+1.12	
		Gravimetric	17.5+0.59	
55	Ore dust (Obuasi)	Volumetric	15.5+0.41	
		Gravimetric	14.4+0.35	

329 ppm as compared to our present case showing a level of 1940 ppm.

The highest recorded arsenic content in the plants is in a fern, *Pteris vitatae*, in which a level of 4700 ppm at 100 yd from the chimney was recorded; the level decreased gradually with distance from the chimney to a value of 1100 ppm at 220 yd away from the chimney (Table 2). Values recorded previously (*1*) for the normal plant are less than 1 ppm.

The arsenic content recorded for other plants such as the Bahama grass and the palm trees are 20 and 2875 ppm, respectively, at distances of 150 yd from the chimney. These levels are also far far higher than values for the corresponding normal plants (< 1 ppm).

Food items such as oranges and sugar cane have values of 2.29 and 14.75 ppm, respectively, while Kwabrafoso dam water and drinking water have values of 2.25 and 1.40 ppm, respectively. These values are all above the normal values.

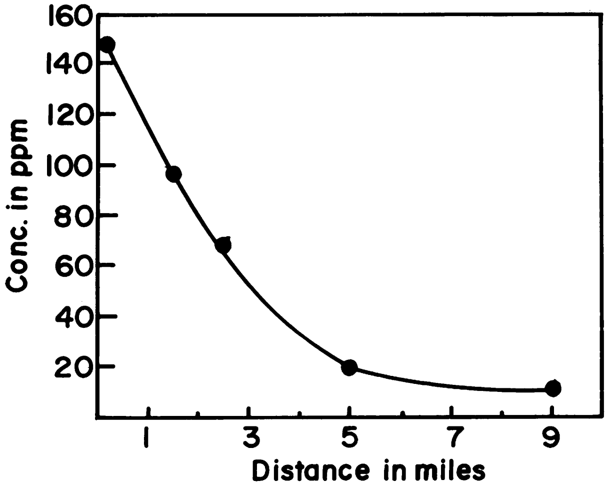

FIGURE 3. Variation of arsenic content with distance from Obuasi chimney.

A plot of the arsenic content of the soil as one moves north from the chimney to Akrokerri is shown in Figure 3. The highest at 300 yd is 147.5 ppm and the lowest at 9 miles away (Akrokerri) is 11.15 ppm. Between these we have values of 96.5, and 67.2, and 19.45 ppm at distances of 1.5, 2.5, 4 miles, respectively, from the chimney. Although there are some soils which have naturally high arsenic content and are used as indications of the presence of the previous minerals, the present value of 147 ppm at 1 ft level is far too high and obviously comes from contamination from the mines. It has been proved (*6*) that an As level of value of more than 69.5 ppm results in plant injury and inhibition of growth.

Conclusion

The mine workers examined have shown abnormal arsenic levels in the hair, as do most of the townspeople.

The vegetation in the immediate periphery of the mine, i.e., about 1 mile to the north of the chimney is also polluted with arsenic. Some food items and water have been contaminated with arsenic and the soil between the chimney and Akrokerri have unusually high arsenic contents. Arsenic levels as much as 2.5 miles away from the chimney are sufficiently high to cause plant injury and plant growth inhibition (*6*).

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REFERENCES

1. Amasa, S. K. Arsenic pollution around the Prestea Goldmine, Ghana. U.S.T. Journal (December 1973).
2. Farmilo, G. C, Sandi, E., and Mempel, S. Arsenic poisoning of Prestea people. Report to the National Institute of Health and Medical Research (Ghana), 1966.
3. Leninham, J. M. A., and Smith, H., Proc. 2nd U.N. Intern. Conf. Peaceful Uses Atomic Energy, Geneva 26: 238 (1958).
4. Smith, H. The distribution of antimony, arsenic, copper, and zinc in human tissue. Forensic Sci. Soc. J. 7: (April 1967). 1967).
5. Smith, H. Interpretation of the arsenic content of human hair. Forensic Sci. Soc. J. 4: 192 (1964).
6. Anastasia, F. B., and Kender, W. J. The influence of soil arsenic on the growth of lowbush blueberry. J. Environ. Quality 2: 335 (1973).