J. ENVIRONMENTAL SYSTEMS, Vol. 25(3) 303-308, 1996-97

CONTRIBUTION OF HEAVY METALS TO THE AIR (BIOSPHERE) POLLUTION IN THE WORKING ENVIRONMENT OF GOLDSMITHS IN NIGERIA*

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ABSTRACT

Energy Dispersive X-ray Fluorescence (EDXRF) using isotopic sources was employed to determine the concentrations of selected heavy metals (Ti, Zn, Pb) in aerosols produced in the working environment of goldsmiths in Nigeria. Sampling was done using micropore filters and analysis carried out using a microcomputer-based S100 multi-channel analyzer and a beryllium windowed Si(Li) detector. Concentrations obtained ranged between 11.9 ± 1.0 μgm^{-3} and 42.7 ± 0.3 μgm^{-3} for Ti, 47.5 ± 1.3 ngm^{-3} and 140.5 ± 1.7 ngm^{-3} for Zn, and 0.5 ± 0.1 ngm^{-3} and 5.1 ± 0.4 ngm^{-3} for Pb. The detection limits determined for the system are 0.3 μgm^{-3} for Ti, 1.3 ngm^{-3} for Zn, and 0.1 ngm^{-3} for Pb.

INTRODUCTION

Nuclear detection methods have become accepted worldwide owing to their obvious advantages over the other orthodox techniques. The most common methods are neutron activation analysis (NAA), proton induced X-ray emission (PIXE),

*Our sincere thanks go to the Federal Government of Nigeria, particularly the Presidency, that funds the Centre for Energy Research and Development and the IAEA for supplying the EDXRF facilities through a Technical Co-operation Assisted Programme.

doi: 10.2190/XQL8-A8TP-9EFT-AVLV
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and X-ray fluorescence (XRF). In particular, XRF is rapid, non-destructive, and good for both qualitative and quantitative elemental analyses. It can compete favorably with other more sophisticated analytical methods in accuracy and precision. The theory of interaction of X-rays with matter, applications, and models for quantitative analysis are documented in Jenkins et al. [1]. The versatility of the method in environmental studies is the main impetus that motivated our group to conduct research in this area when a radioisotope-excited X-ray fluorescence facility was installed at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria. The present study focuses on problems especially relevant to the provision and control of a safe working environment for the Nigerian workers. This presentation is part of a broader research program in environmental pollution studies emphasizing the contribution of heavy metals to the biosphere in the working environment of goldsmiths.

The presence of heavy metals is a major problem in the field of biosphere pollution. Gaseous compounds and aerosols in concentrations significantly higher than their normal natural level in the air are constantly being introduced to the biosphere. These pollutants are potentially harmful to man and his environment if their concentrations are greater than the threshold limit values [2].

Reliable dispersive modeling of pollutants in the biosphere requires complete source identification. Since small scale cottage industries are expected to contribute significantly to the total heavy metal load of the biosphere, this project sets out to determine the contribution from the average goldsmith. Air samples were collected in aerosol filter papers and analyzed using energy dispersive X-ray fluorescence (EDXRF).

FACILITY

The X-ray fluorescence facility at the CERD uses Fe-55, Cd-109, and Am-241 sources that fit onto the cap of thin beryllium window Si(Li) detector. Other components are a power supply, a preamplifier located at the base of the detector to minimize electronic noise, spectroscopic amplifier, an analog to digital converter (ADC), and a personal computer-based S100 multi-channel analyzer, all from Canberra.

The low atomic number and thinness of the beryllium window of the Si(Li) detector makes it suitable for the detection of low energy X-rays associated with EDXRF. Measurements showed that at energies of 5.898 KeV of Fe-55 and 22.706 KeV of Cd-109 the energy resolution of our detector are 100 eV and 500 eV, respectively. This low energy resolution of the Si(Li) detector enhances the multi-elemental nature of this technique. The stability of the spectrometer was routinely checked using the prominent L X-rays of lead and zinc. No peak drift was recorded.

TECHNIQUE

Micropore filter papers of 25 mm diameter were weighed before sampling with a "PRECISA 80 A-200 AIR QUALITY" air sampler and marked with corresponding filter identification number. Each filter paper was kept in a clean and well-labeled polyethylene bag. An aluminum filter holder was used in each sampling line. Pumping rate was 10 liters per minute. Each sample was collected over a period of six hours of continuous pumping. Twelve locations were sampled four or five times. Each sample was kept in a desiccator for at least twenty-four hours prior to analysis to eliminate the effect of moisture. Each sample was then re-weighed to determine the dry-weight of the air particulate so collected. Thin-film standards were prepared with specpure chemicals, purified reagents. APDC precipitation technique was employed with the AXIL and QXAS X-ray spectrum analyzer programs to quantitatively analyze the samples.

RESULTS AND DISCUSSION

Cl, Ti, Zn, Au, and Pb were detected in all samples. However, concentrations of only three heavy metals were accurately determined in all the twelve locations. The average findings for the four or five samples taken at each location are presented in Table 1. The detection limits for our system were estimated at 0.3 μgm^{-3} for Ti, 1.3 ngm^{-3} for Zn, and 0.1 ngm^{-3} for Pb.

The presence of chlorine in air is not unexpected since common salt (NaCl) is an ingredient used routinely by goldsmiths in their work. Excessive Cl levels can be an irritant to mucous membranes of the respiratory tract, and, when dissolved

Table 1. Elemental Concentration in Working Environment of Some Goldsmiths

Sample Code	Ti (μgm^{-3})	Zn (ngm^{-3})	Pb (ngm^{-3})
FPG01	33.1 ± 0.4	101.2 ± 1.5	4.1 ± 0.3
FPG02	42.7 ± 0.3	140.5 ± 1.7	5.1 ± 0.4
FPG03	31.6 ± 0.4	117.3 ± 1.6	2.3 ± 0.3
FPG04	29.3 ± 0.4	96.1 ± 1.5	3.5 ± 0.3
FPG05	21.5 ± 0.3	93.4 ± 1.6	4.1 ± 0.3
FPG06	18.8 ± 0.3	56.8 ± 1.9	2.6 ± 0.5
FPG07	35.5 ± 0.4	100.2 ± 1.5	2.0 ± 0.2
FPG08	37.7 ± 0.4	79.1 ± 1.4	4.5 ± 0.3
FPG09	11.9 ± 1.0	49.0 ± 1.1	3.6 ± 0.3
FPG10	31.9 ± 0.4	79.7 ± 1.4	0.5 ± 0.1
FPG11	31.3 ± 0.5	75.6 ± 1.3	4.4 ± 0.4
FPG12	21.1 ± 0.6	47.5 ± 1.3	3.8 ± 0.3

in water, to the skin. The recommended allowable concentration in air is about 1 ppm for prolonged exposure [3]. Chlorine exposures exceeded this limit in our samples.

Titanium is a metal with a silvery luster, low density, and high melting point. At ordinary and moderately high temperatures, titanium shows great resistance to corrosion because of the formation of a thin protective film of oxide. It is stable in air at ordinary temperatures and it is not attacked by water or sea-water. These properties make it attractive for use in making jewelry. However, its great affinity for oxygen and nitrogen may not be in the best interest of the goldsmiths or any other person breathing these suspended particles. Another possible source of airborne Ti is the coal used by most goldsmiths to fire their furnaces. Concentrations ranging between 810 and 1499 ppm had been recorded for this metal in various coals of Nigerian origin [4]. The concentrations of Ti in the areas sampled are very high and their values are directly related to the volume of work carried out in each workshop. For example, the samples from location FPG02, which has the largest volume of work, had the highest average values of Ti, Zn, and Pb.

Zinc is a white lustrous metal readily oxidized in air. It burns with a vivid blue-green flame forming a white residue of zinc oxide. In fact, its relatively low melting point and ease of vaporization are striking features of this metal. Goldsmiths usually use zinc salt among others to reduce the melting point of the compound formed. The ease of vaporization makes zinc a ready candidate for air pollution. Though zinc is an essential element for human metabolic processes, an excess of it in the air can be toxic. The lowest average values of Zn and Ti occurred in the samples at location FPG09. However, the Pb concentration was relatively high there, suggesting a possible supplementary use of Pb, Zn, and Ti in gold smelting.

Toxic effects of lead are well known: absorption in the blood reduces blood plasma albumin content; reduces clotting; and can lead to anemia, high blood pressure, and heart attack. High Pb concentrations in blood also are correlated with mental instability in adults and impaired mental ability in children. Known symptoms of lead poisoning include headaches, constipation, loss of appetite, fatigue, anemia, and paralysis [5]. Although the concentration of lead in our samples ranging between 0.5 and 5.1 ngm^{-3} is not considered high, its presence should give some concern. The minimum value accepted by WHO is 1.5 μgm^{-3} and it is taken as the threshold limit value (TLV) below which no observable health effect is expected. Apart from the goldsmith as a source of the detected Pb, traffic could also contribute significant to this pollution since most of the sampled areas are located near main roads. Furthermore, the porcelain crucibles used by the goldsmiths contain Pb as a binder. At working temperatures, lead could easily vaporize and contribute to air pollution.

Gold was detected in all samples, as expected. But the software used found it difficult to fit a Gaussian function on each of the photopeaks, making it impossible to determine accurately the peak areas and hence the concentrations. Both the detection of gold and its very small amount in the air are not unexpected. Large quantities of gold undergo many processes every day in the goldsmith's shop. Gold's high density, its high melting and boiling points, and its non-reactivity in air or with most reagents, do not support its easy suspension in air as a pollutant. Moreover, gold is the most malleable and ductile metal, requiring alloying with other metals like Ti and Zn to give it strength.

Air particulates inhaled are retained by the lungs causing a variety of respiratory disorders. These include pneumozomoses of various kinds, asthma, and influenza [6]. Particles of respiratory sizes (~3 nm) can reach the lungs via the respiratory tract and may even travel to the alveoli sacks depending on size [7]. In this way air particulates increase the mechanical load on the lungs thus aggravating the toxic effects of Pb [8].

CONCLUSION

This study has shown that the present method of goldsmithing in the country constitutes a significant source of Ti, Zn, and Pb pollutants in the working environment.

As a result of the economic turndown in Nigeria, the establishment of cottage industries is being encouraged to revitalize the ailing economy. As these cottage industries spring up, it is important to continue to monitor their working environment. Further study is needed to ascertain the contribution of these cottage industries to the biosphere's total heavy metal load. These measures will help Nigeria's Federal Environmental Protection Agency establish an effective control program to minimize health hazards to the workers and to the general populace.

ACKNOWLEDGMENTS

We acknowledge the contributions of Prof. A. F. Oluwole and Mr. I. B. Obioh to the success of this project.

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