American Journal of Applied Sciences 2 (2): 573-578, 2005
ISSN 1546-9239

ED-XRF Analysis of Total Suspended Particulates from Enamelware Manufacturing Industry

[1]J.A. Sonibare, [1]F.A. Akeredolu, [2]O. Osibanjo and [3]I. Latinwo
[1]Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife. Nigeria
[2]Department of Chemistry, University of Ibadan, Ibadan, Nigeria
[3]Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Abstract: Concentration and elemental composition of the total suspended particulates (TSP) emitted due to manufacturing activities of an enamelware industry in Lagos, Nigeria were investigated. Gravimetric method was used in mass concentration determination and an energy dispersive x-ray fluorescence (ED-XRF) analyzer was employed in the multi-elemental analysis. The Federal Ministry of Environment (FMENV, Nigeria's environment regulating body) set limit of 250 $\mu g/m^3$ for ambient TSP was exceeded in five of the seven sampling locations within the company premise. The maximum concentration (about 8 fold of the limit) was recorded in the Decorating section and the minimum in Front of the Administrative Block (about 3 times less than set limit) that is an outdoor location. Elements detected from all the samples were Al, Si, P, K, Ca, Ti, Mn, Fe, Cu, Zn, Cd and Na. The work showed that installation of dust extractors, provision of spraying boot and proper training of factory workers in the handling of spraying guns are part of measures required for the control of total suspended particulates (TSP) emission in the enamelware manufacturing industry.

Key words: ED-XRF Analysis, TSP, Enamelware, Manufacturing Industry

INTRODUCTION

Lagos is the economic and commercial nerve center of Nigeria. It is located on latitude 6° 25' N and longitude 3° 27' E [1] and with a present population of 13 million with a growth rate of 5.8 % annually [2]. This large population makes it important to attract attention in environmental protection.

As indicated by Botkin and Keller [3] particulates in the atmosphere over a city is more abundant than in surrounding areas. Manufacturing industries are some of the sources of particulates in these cities [4,5]. One of the identified industries with air particulates in the cities is the enamelware manufacturing industry. Enamelling is the coating of cast irons or sheet steel that has previously been stamped into proper shape. Industrial enamel is applied by either wet or dry. The wet process involves grinding frit with water, clay and pigments and then applied to the cleaned metal surface by dipping or spraying. The enamel is then fused to the metal in a furnace. In dry enameling, the wet process is used in applying first coating but this is not cooled. Frit is prepared by grinding and the dry frit powder is applied by sieve to the soft, hot surface of the first enamel coating. This enameled object is then returned to the furnace and the dry coating is fused; more than one dry coating is usually necessary.

In the enamelware manufacturing industry where this study was carried out, both approaches are being employed depending on the materials to be produced. For bathroom washbowls, the dry method is usually employed while for articles such as kitchen utensil, the wet process is the adopted method. Its product range includes curry dish and cover, finger bowl and cover, mixing pot, deep pot, footed basin and cooking pot and cover. All these are useful materials which make existence of such industries of utmost importance in Nigeria.

Manufacturing industry is one of the anthropogenic sources of total suspended particulates (TSP) because it involves several stages (e.g. cutting, frit milling, pickling, paint spraying, heating, etc) that could lead to the generation of total suspended particulates (TSP) into the immediate and distant environment [6].

Shop floors which are the main center of activities and where total suspended particulates (TSP) is being generated are made up of: (1) Decorating Section with about 22 spray guns in use during sampling exercise,(2) Frit mills with 33 mills in use during sampling, (3) Pickling Section and (4) Enamelling Ovens section with 7 ovens in operation during sampling. The processes employed in the production of steel that is a key material in the manufacturing of enamelware makes the particulates generated during operation to be suspected of contain some elements like Pb, Zn, Cd, Ni, Hg, Cr, Cu, Sn, Fe, among others [7].

Particulate emissions contained several toxic metals that accumulate in the tissues of animals [8]. Their metallic constituents were identified as a potential health hazard to human beings [9]. They may consist of

Pb, Cr, Zn, Al, Cd, Mn, Cu, Ba, Ni, etc [10-12], depending on their sources. If they contain mercury and this find its way into aqueous system, natural biological processes convert mercury into the potent neurotoxin dimethylmercury ($(CH_3)_2Hg$) which when accumulated in flesh of fish in ionic, form monomethyl mercury (CH_3Hg^+). When man consumes this, it leads to mercury poisoning [13]. In a work carried out by Ibald-Mulli [14], continuous concentrations of total suspended particulates was found to be influencing systolic blood pressure of 1.79 mm Hg per 90 $\mu g/m^3$ total suspended particulates while Heinrich [15] and Klemm [16] reported higher respiratory symptoms for areas with high concentrations of total suspended particulates. USEPA 1990 defined them as statutory nuisance [17].

Techniques for control of particle emission have one common principle – application of a force to cause the deposition of particles to a receiving surface. These techniques can be classified into sedimentation, filtration, centrifugation, washing and electrostatic precipitation [18].

For particles of diameter, D_p, all particle collectors have a collection efficiency given by:

$$E\left(D_p\right) = \frac{\text{concentration of particlkes of diameter } D_p \text{ in the exhaust gas}}{\text{concentration of particlkes of diameter } D_p \text{ in the inlet gas}}$$

Usually, this efficiency decreases as diameter decreases. Range of techniques need to be combined to form an effective emissions control strategy for particulate air pollution [19]. Thus, industries need to self monitor their discharges and report same to appropriate authority for advise on effective controls [20].

The aim of this study was to determine the mass concentration of this kind of emission in order to provide information for both control strategy and the study of emission from enamelware industries into the immediate and distant environment. The multi-elemental analysis of such emissions is important, both because of the health hazard constituted by these particles and the damage they provoke on materials [21].

MATERIALS AND METHODS

Various activities existing in the different sections of the industry's shopfloor were used to identify potential sources of total suspended particulates (TSP) and ambient air sampling was carried out in those places. These included enameling section, decorating section, pickling section, between milling and oven sections, oven section, machine shop and the front of administrative block.

The total suspended particulates (TSP) measurements were made by gravimetric air sampling method using Negretti air samplers. In this method, a metered volume of air is sampled through pre-weighed whatmann cellulose filter paper of size 2.5 cm diameter. Thereafter the loaded filter is re-weighed and the concentration of the particulates sampled determined as:

$$TSP_{concentration} = \frac{w_f - w_i}{Fr * t}$$

where, w_f = final weight of filter paper (µg)
w_i = initial weight of filter paper (µg)
Fr = air flow rate (m^3/s)
t = sampling period (sec.)

The concentration is obtained in microgram per cubic meter ($\mu g/m^3$).

The total suspended particulate (TSP) samples collected on filter papers were analyzed in an energy dispersive x-ray fluorescence (ED-XRF) analyzer.

The system used was the Links Analytical XR300 energy dispersive x-ray fluorescence system. This is one of the most versatile techniques being employed in environmental pollution controls studies all over the world. It is based on the principle that each element/atom has its own characteristic x-ray tube, which has a rhodium anode element, operates at a voltage of 20 kV. The generated x-rays excited the atoms of various elements in the sample. These excited atoms emit characteristic x-rays during the excitation. The characteristic x-rays were detected using a Si(Li) solid state detector whose resolution was less than 110 eV. A combination of amplifiers analogue to digital converter, multi-channel analyzer and computer was used to sort the signals into a spectrum. Elements to which the peaks in the spectrum belong were identified from the measured x-ray energies.

Intensity of each peak was used to determine the apparent concentration of each element in the sample. Corrections were made for absorption and enhancement effects. Standards with known composition were used to determine the concentration to within 5% accuracy.

RESULTS AND DISCUSSION

Treatment of Analytical Results: Elemental composition of the samples were used for computing the following ratios that serve to interpret the data in terms of possible source contributions:

K/Fe Ratio: This ratio is often calculated to establish the importance of bush burning/wood burning contributions to the aerosol composition obtained. Where bush burning contribution is high, K/Fe > 3.56.

Co/Zn and Ni/Fe Ratios: These ratios relate some of the marker elements for enamelware production to those of metal forming processes and the outdoor air constituents.

Enrichment Factors (E.F): This ratio is defined as:

$$EF = \left(\frac{\left((\text{wt \% of element } i \text{ in sample}) / (\text{wt \% of element Ti in the sample}) \right)}{\left((\text{wt \% of element } i \text{ in soil}) / (\text{wt \% of element Ti in soil}) \right)} \right)$$

It indicates the association of heavy metals to the earth's crust and anthropogenic sources.
EF > 4 signifies that soil contribution alone does not explain the concentration of the element under consideration in the aerosol sample.

Toxicity Potential (TP): Because of the proximity of residential houses to the plume path, the probability of human health effects exists. Thus, toxicity potentials are calculated vis:

$$TP = \frac{\text{observed gross dust concentration}}{\text{statutory limit set for ambient dust concentration}}$$

By definition, TP exceeding unity gives cause for concern.

TSP Concentrations: The TSP concentrations were generally higher than the FMENV standard for ambient particulate matter (250 $\mu g/m^3$) during the period of sampling at all locations except the front of the Administration Block and the Machine Shop (Table 1). It should be noted that most of the locations sampled were shop floors at which the work force spend 8 hours daily. The TSP concentrations measured at metal forming shopfloor were lower than those measured at the enamelware oven shopfloor. The former process involves particulate generation while the later does not.
But for these Machine Shop and the front of the Administration Block, the toxicity potential of the measured TSP concentrations within the company's premises exceeded unity (Table 2). Decorating Section concentration been the highest could be attributed to spraying activity going on there. The type of spray-guns (22 of these were seen to be in use during the air sampling) being employed and the non-provision of spray booth allowed emission of particulates directly into the environment. These two factors stand out as contributing factors in emission release in industries with spraying activity [22]. Pickling process is required in preparation of sized steel for enamelling. Usually, it leads to emission of liquor mists from the pickling baths. Milling Section is where frit milling takes place (33 frit mills were in use during measurements). During operation, there is usually associated emission of dusts through mill loading. Fugitive dust emissions are common here. In the Oven Section, 11 ovens were in operation during measurements. They are made of two types that include both manual and automatic. The manual ovens comprised an enamel drying section (where the wares are led in and out of the chamber by means of a rotary tray) and the baking ovens. In the baking ovens, the wares are raised to red heat conditions (enemelling) in oil-fired box ovens. The automatic ovens had an elaborate system of conveyor chain loop that takes the decorated wares through the drying zone and the enamelling zone. The drying process resulting in these oven allows some of the materials used in enamelling to become dried and thus some are removed in the process of being moved in and out of the ovens. The movement of these wares in both the rotary tray and conveyor chain also account for particulates generation in the section. Enamelling process generates particulates and all these might account for higher concentration measured in the factory.

Table 1: TSP Concentrations Measured at the Company's Locations

Sample	Concentration ($\mu g/m^3$)
In front of admin Block	84
Enamelling Section	905
Decorating Section	1929
Pickling Section	812
Between Milling Section and Oven #11	1429
Oven #10	606
Machine Shop	83
FMENV Standard	250

Table 2: Toxicity Potential (TP) of TSP Concentrations Measured at the Company's Locations

Sampling Location	Toxicity Potential (TP)
In front of admin Block	0.34
Enamelling Section	3.6
Decorating Section	7.72
Pickling Section	3.25
Between Milling Section and Oven #11	5.72
Oven #10	2.42
Machine Shop	0.33

Elemental Analysis: Considering the TSP elemental analysis, the following elements were detected in all the samples: Al, Si, P, K, Ca, Ti, Mn, Fe, Cu, Zn, Cd and Na (Table 3). Other elements including V, Co, Ni, Rb and Zr were detected in 71 % of the sampling locations, S, Cr, As, Se and Pb in 57 % of the sampling locations and Br and Sr detected in 73 % of the sampling locations. Ti, Br and Sr are not among the elements commonly associated with core enamelling manufacturing process [23]. Their detection in some of these samples is an indication that many other sources can be attributed to the presence of some of these elements. Power generation is one of these.

Table 3: Measured TSP Elemental Composition (wt.% Except Where Otherwise Stated)

Element	Typical soil	Pickling section	B/W Mill section	Machine shop	Oven # 10	Outdoor adminblock	Decorating section	Enamelling section
Al	7.13	4.2262	3.3780	3.6404	3.6525	3.6845	3.5568	3.7760
Si	30.54	3.4725	12.1472	7.5912	4.9807	10.6383	22.7251	17.2811
P	0.065	12.1408	9.2498	10.5552	12.4468	9.1296	3.0319	5.9944
S	0.031	-	<1.1084	-	-	1.6540	1.8440	1.3543
K	2.59	1.0479	1.9972	1.4517	1.1769	1.3350	4.5105	3.5627
Ca	1.37	11.4981	9.8470	10.4539	11.8692	8.7943	7.1121	7.6179
Ti	0.46	<0.4942	1.8978	0.8176	0.6421	0.5840	2.0580	1.8966
V	100 ppm	-	<0.2619	-	<0.3772	<0.2115	<635 ppm	<0.1407
Cr	2 ppm	-	-	<0.2144	-	<0.1582	0.4130	0.2795
Mn	0.085	<0.2555	0.2032	<0.1817	<0.2373	<0.1373	0.1190	<917 ppm
Fe	3.80	0.2767	1.4442	1.1363	0.5487	1.3103	1.5861	1.0804
Co	23 ppm	-	-	<0.1460	<0.1889	<0.1100	0.2418	0.1786
Ni	4 ppm	<0.1827	<0.1254	<0.1322	-	-	317 ppm	<667 ppm
Cu	20 ppm	<0.1707	<0.1184	<0.1239	<0.1589	<930 ppm	0.1086	0.1042
Zn	0.005	<0.1506	<0.1077	<0.1111	<0.1432	<849 ppm	0.1152	0.1125
As	2 ppm	<0.2945	-	-	<0.2757	<0.1601	<490 ppm	-
Se	0.09 ppm	-	-	<781 ppm	<987 ppm	-	222 ppm	<400 ppm
Br	3 ppm	-	<0.1432	<0.1510	-	<0.1105	-	-
Pb	10 ppm	-	<0.6407	0.6763	-	-	<0.1521	<0.3298
Cd	0.20 ppm	9.3522	6.5164	6.9444	8.9021	5.6586	4.1762	6.0435
Rb		<541 ppm	-	394 ppm	<499 ppm	<288 ppm	<88 ppm	-
Sr		-	-	<0.3680	<0.4448 -	<0.2632	-	-
Zr		<2.5887	<1.7526	-	-	<1.2813	<0.4006	<0.9069
Na	0.01	19.0991	9.6993	18.0548	17.1662	15.7749	4.0317	7.5355

Table 4: TSP Enrichment Factors Computed from the Elemental Compositions Detected

Element	Pickling section	B/W Mill section	Machine shop	Oven # 10	Outdoor adminblock	Decorating section	Enamelling section
Al	0.55	0.11	0.29	0.37	0.4170	0.11	0.13
Si	0.11	0.10	0.14	0.12	0.27	0.17	0.14
P	174	34	91	137	111	10	22
S	-	9	-	-	42	13	11
K	0.38	0.19	0.32	0.33	0.41	0.39	0.33
Ca	7.8	2	4	6	5	1	1
Ti	1	1	1	1	1	1	1
V	-	6	-	27	17	1	3
Cr	-	-	655	-	677	500	370
Mn	2.8	0.58	1	2	1	0.30	0.26
Fe	0.07	0.09	0.17	0.10	0.27	0.09	0.07
Co	-	-	35	59	38	24	19
Ni	410	73	179	-	-	17	39
Cu	80	14	35	57	37	12	13
Zn	28	5	12	20	13	5	5
As	1490	-	-	1073	685	60	-
Se	-	-	4900	7800	-	551	1080
Br	-	108	264	-	270	-	-
Pb	-	153	376	-	-	34	79

Table 5: Elemental Ratios of the TSP Analyzed Samples

	Elemental Ratios					
Locations	K/Fe	Co/Zn	Ni/Fe	Ni/V	V/Fe	Pb/Br
Pickling Section	3.79	-	0.66	-	-	-
B/W Mill Section and Oven	1.38	-	0.09	0.48	0.18	4.47
Machine Shop	1.28	1.31	0.12	-	-	4.48
Oven	2.14	1.32	-	-	0.69	-
Admin Block	1.02	1.30	-	-	0.16	-
Decorating Section	2.84	2.10	0.02	0.50	0.04	-
Enamelling Section	3.30	1.59	0.06	0.47	0.13	-

Highly enriched (EF>100) were : P and As (at the Pickling, Oven and Admin Sections), Cr (Machine Shop, Admin, Decorating and Enamel Sections), Ni (Pickling Section), Se (Machine Shop, Oven, Decorating and Enamelling Sections), Br (Milling, Machine Shop and Admin Block) and Pb (Mills and Machine Shop) while moderately enriched (4.0 < EF < 100) were: Co, Pb (at the oven and decorating section), Zn, Cu and V (Table 4). The following were non-enriched: Al, Si, K, Fe, Mn and Ca especially in Machine, Oven and Admin Block sections. V and Co that are considered marker elements for enamelware production processes were significantly enriched (EF > 10.0). The air pollution control implication is that a mechanical induced draft ventilation system fitted with appropriate dedusters may be required.

Mn, Fe, K and Si were only marginally enriched (EF =4-10) or non-enriched (EF <4). This suggests their presence to be from crustal contributions.

The Ni/V, Ni/Fe and V/Fe ratios computed were compared with world averages (Ni/V = 0.40, Ni/Fe = 0.0011 and V/Fe = 0.0026 indicated that there is a relative enrichment of both Ni and V in the factory area. The Pb/Br ratio was found to be 4.47 and 4.48 in both the Mill/Oven and Machine Shop, respectively in the measured samples. Comparison of these ratios with that reported for Nigerian gasoline (i.e. 2.57) shows that there are other sources of Pb in that environment apart from automobile. During sampling, it was observed that a sandblasting operation was going on in the company. This sandblasting (paint stripping) activity ought to have been carried out in a manner to minimize the fugitive emission of lead bearing dusts. The air quality implication is that mechanical ventilation of the sort that will not increase fugitive dust emissions should be considered. The Co/Zn ratio shows that enameling contributes more to the air pollution problems encountered in the factory more than the metal forming activity taking place in the machine shop. But for the measured concentration in this enameling section, K/Fe ratio showed that the measured TSP concentrations were mostly generated within the factory and not from the soil (Table 5). One of the problem areas identified were the decorating section and the enameling ovens attached to the decorating section.

CONCLUSION

The study on the concentration levels of total suspended particulates (TSP) in the enamelware manufacturing industry in Lagos, Nigeria has revealed that the contribution of the industry to the measured concentration in the environment is significant and that effective control measure needs to be taken to control this.

Many metals were identified to be present in the emitted total suspended particulates. The danger poses by the presence of some of these metals in ambient air and shopfloors equally calls for concern. The enrichment factor analysis ruled out soil as major contributor of these measured particulates.

Spray booths need to be provided for the spraying activity. Also, operators should be continuously trained in the proper handling of these spray guns to improve efficiency and to reduce emissions from them. Finally, with the present situation being found during sampling activity, dust masks should be provided to workers working at the shopfloor. This would help reduce the level of exposure to dust.

REFERENCES

1. NIMR, 2001. Gloss Station Information Sheet. Nigerian Institute for Oceanography and Marine Research, Lagos.
2. WHO., 2002. Poverty Alleviation Programmes of the Government of Lagos State. World Health Organization Regional Office for Africa, Harare, Zimbabwe.
3. Botkin, D.B and E.A. Keller, 1998. Environmental Science–Earth as a Living Planet. John Willey and Sons, New York.
4. Sponza, D. and M. Karaoglu, 2002. Environmental Geochemistry and Pollution Studies of Aliaga Metal Industry District. Environ. Intl., 27: 541-553.
5. Fang, G., Chang, C., Chu, C., Wu, Y., Fu, P., Yang, I. and Chen, M., 2003. Characterization of Particulate, Metallic elements of TSP, $PM_{2.5}$ and $PM_{2.5-10}$ Aerosols at a Farm Sampling Site in Taiwan, Taichung.

6. Ness, S.A., 1991. Air Monitoring for Toxic Exposures, an Integrated Approach. Van Nostrand Reinhold, N.Y.
7. Ohonba, E.A and S.O. Obaseki, 1988. Environmental Impact Assessment of Steel Production. in Sada, P.O and Odemerho, F.O (Eds.) Environmental Issues and Management in Nigerian Development. Evans Brothers (Nigeria Publishers) Ltd., pp: 182-195.
8. Kucera, E., 1988. Effect of Smelter Emissions on the Hemogram of the Deer Mouse (*Peromuyscus maniculatus*). Environ. Poll., 55: 173-177.
9. Sinha, S. and T.K, Bandhopadhyay, 1998. Review of Trace Elements in Air Environment and its Health Impact in some Indian Cities. Journal of IPHE, India, 1: 35-46.
10. Masters, G.M., 1997. Introduction to Environmental Engineering and Science. Pretence Hall Inc. Upper Saddle River, New Jersey.
11. Hibss, L.R., I.J. Beverland, M.R. Heal, R.M. Agius, R. Elton, D. Fowler and J.N. Cape, 2002. The Metal Content of Airborne Particles in Edinburgh: Application to Epidemiological Research. Ann. Occup. Hyg., 46: 450-451.
12. Kim, K., H.S. Lee, Y. Youn, S. Yun, C. Ro and J. Oh, 2002. Studies of Spatial Variabilities of Airborne Metals across Four Different Land-Use Types. Water, Air and Soil, 138: 7-24.
13. Heinsohn, R.J and R.L. Kabel, 1999. Sources and Control of Air pollution. Pretence Hall Inc. Upper Saddle River, New Jersey.
14. Ibald-Mulli, A., J. Stieber, H. Wichmann, W. Koeng and A. Peters, 2001. Effects of Air Pollution on Blood Pressure: A Population-Based Approach. Am. J. Public Health, 91: 571-577.
15. Heinch, J., 2000. Decline of Ambient Air Pollution and Respiratory Symptoms in Children. American J. Respiratory and Critical Care, 161: 1930-1936.
16. Klemm, R., 2000. Is Daily Mortality Associated Specifically with fine Particles? Data Reconstruction and Replication of Analyses. J. Air and Waste Manage. Assoc., 50: 1215-1222.
17. Garbutt, J., 1996. Environmental Law: A Practical Handbook. John Wiley and Sons. New York, pp: 84.
18. Colls, J., 1997. Air Pollution: An Introduction. E and FN Spon, London, pp: 34-42.
19. Simpson, R.W and G. Miles, 1990. Controlling emissions to Avoid Violations of Health Standards for Short term and Long term Exposures to TSP Concentrations. Atmosph. Environ., 24B: 75-86.
20. Mc-Addy, E., 2000. Overview of Air Pollutants in Nigeria. in Basuah, P.K.B., (Ed.) 2000. Monitoring of Air Pollution Due to Combustion Processes. Proceedings of Workshop on Monitoring of Air pollution Due to Combustion Processes, 30^{th} – 4^{th} Nov., pp: 67-72.
21. Sabbioni, C. and G. Zappia, 1992. Characterization of Particles Emitted by Domestic Heating Units Fuelled by Distilled Oil. Atmosph. Environ., 26A: 3297-3304.
22. USEPA., 1994. Alternative Control Techniques Document: Automobile Refinishing. EPA Report No. 453/R-94-031.
23. Ward, N.I., 2000. Trace Elements. in Fifield, F.W and Hainess, P.J (Eds.), 2000. Environmental and Analytical Chemistry. Blockwell Science Ltd., UK., pp: 360-392.