

A Comparison of Methods of Analysis for Lead in Environmental Samples

¹J.K. Tubonimi Ideriah, ¹A. Solomon Braide, ²O. Herbert Stanley and ³B. Collins Osaisai

¹Institute of Pollution Studies, University of Science and Technology, Port Harcourt, Nigeria

²Department of Microbiology, University of Port Harcourt, Port Harcourt, Nigeria

³Institute of Geosciences and Space Technology, University of Science and Technology,
Port Harcourt, Nigeria

Abstract: Lead concentrations in soil, leaves and crop samples were determined with Atomic Absorption spectrophotometric and Diphenylthiocarbazone colorimetric methods. Results for lead concentrations as determined by the 2 methods were linear, yielding the regression equation: $Y = 2.2096 + 1.0345x$, where Y was the concentration of lead determined by the AAS method and x was that determined with the Dithizone colorimetric method. Both methods proved to be good as the correlation ($r = 0.9939$) and squared correlation coefficient ($R^2 = 0.9879$) between lead levels obtained by the two methods were high. The instrumental method has proven to be fast and simple. However, the Dithizone colorimetric method produces satisfactory result and is sensitive, less expensive and recommended for the analysis of heavy metals in environmental samples.

Key words: Lead, colorimetric, dithizone, spectrophotometer, environmental sample, Nigeria

INTRODUCTION

Lead is a natural constituent of the environment and most of the naturally occurring lead is found in the soil. Since soils are strong accumulators of lead, the analysis of lead in soil is an excellent indicator of accumulated deposition in the vicinity of source of the metal.

The chemistry of lead in soils is an extremely complex subject not yet fully understood. Lead added to soil may react with available soil anions such as SO_4^{2-} , PO_4^{3-} or CO_3^{2-} to form sparingly soluble salts (Khalid *et al.*, 1981). X-ray powder diffraction studies by Olsen and Skogerboe (1975) have shown $PbSO_4$ to be the major crystalline lead compound in contaminated soils.

Lead is released to the atmosphere from both natural and man-made sources. Natural sources mostly from windblown dusts and volcanoes are relatively small compared to man-made sources (UNEP and WHO, 1988). However, the same study reported that the present concern is on lead emitted to the environment by the use of lead alkyl anti-knock compound in gasoline. Also petrol combustion globally contributes an estimated 60% of the total lead emissions from human activities. Lead is a non-essential element for man and has toxic potential for all biological systems. The major source of lead in man is the food chain. Plants, animals and ultimately man receive most of their lead from that naturally present in soil. Studies on man's daily food intake have shown lead

in quantities of 200-300 $\mu\text{g}/24\text{ h}$, fairly equally distributed on all foods (WHO, 1972).

The methods for the determination of lead include Diphenylthiocarbazone (Dithizone) colorimetric, Atomic Absorption Spectroscopic (AAS) and polarographic methods. The instrumental methods are preferable because they are rapid and do not require extensive separations. Many of the colorimetric methods or determination of individual metals must include procedures for the elimination of interference (APHA, 1995). The selectivity of the Dithizone extraction process can be improved by choice of suitable pH and use of masking agents such as EDTA, Cyanides, etc (Minczewski, 1982). The atomic absorption method does not have serious interference problems. However, it is reported (APHA, 1995) that the AAS method is subject to interference in the flame mode and required an extraction procedure for low concentrations; the dithizone method is more sensitive and is preferred by some analysts for low concentrations. The polarographic determination of lead requires an effective base electrolyte (e.g. 5% $\text{v}\cdot\text{v}^{-1}$ HCl solution). To eliminate interference, it is necessary to buffer the electrolyte to approximately pH 4 using ammonium or sodium acetate. Polarographic techniques are preferable to colorimetric methods because of the rapidity of analysis and because the method may be applied simultaneously to a variety of metals (APHA, 1995).

In developing countries like Nigeria, the huge cost of instrumental analysis makes it difficult for researchers and students to carry out work involving heavy metal analysis. Consequently, a less expensive but sensitive and accurate method is needed for the determination of heavy metals concentrations, in particular lead in environmental samples.

In the present report, lead concentrations in soil and leaves samples determined by the colorimetric method are compared and correlated with the concentrations determined by the atomic absorption spectroscopic method.

MATERIALS AND METHODS

The study area, Port Harcourt lies within latitudes 4° 43' 07" and 4° 54' N and longitudes 6° 56' 04" and 7° 03' 20" E with a mean annual rainfall of over 2000mm and mean annual temperature of about 29°C. A map of the study area showing sampling stations is presented in Fig. 1.

Soil and leaves samples collected along selected roadsides (Fig. 1) were used for this study. Soil samples were collected with auger to a depth of 15 cm, at 0, 5, 10 and 30 m distances along the transect (away from the road). Available vegetation was sampled by collecting the leaves of plants and grasses at each distance along the transect. The samples were collected into polyethylene bags and transported to the laboratory.

Soil samples were put in Petri dishes and dried at 110°C for 3 h in an oven. The dried samples were ground to a fine dust with a mortar and pestle and sieved with a 2 mm (10 mesh) sieve. One gram of sieved soil sample was weighed into a conical flask and digested with 10 cm³ of 50% hydrochloric acid on a hot plate until 2-3 cm³ of acid was left. The content was then filtered into 50 cm³ cylinder and made up to the mark with deionized water. Leaf samples were oven-dried at 110°C, pulverized to uniform size with a laboratory mill and ashed in a muffle furnace at 500°C for 3 h. The ash was cooled and 1g of it digested

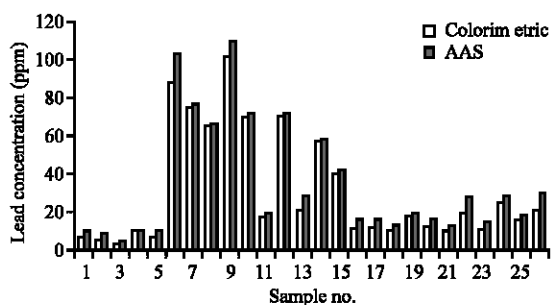


Fig. 1: Concentration of lead (ppm) measured by AAS and Colorimetric methods

with 10 cm³ of 50% hydrochloric acid, filtered and made up to 50 cm³ with deionized water. All digested samples were replicated and stored in washed, dried polyethylene bottles.

Lead in one set of the replicated samples was directly analyzed with Shimadzu AA-670 Atomic Absorption/Flame Emission spectrophotometer at a wavelength of 217nm. Lead in the other set of digested and replicated samples was analyzed using the Dithizone colorimetric method (Bassett, 1978; Christian, 1977) with a Bausch and Lomb spectronic 20 at a wavelength of 540 nm.

RESULTS AND DISCUSSION

The detailed results of lead concentrations in the samples obtained from the two methods of analysis are presented in Table 1 and graphically shown in Fig. 1.

Table 1: Lead concentrations (ppm) determined by dithizone colorimetric and atomic absorption spectroscopic (aas) methods

S/no	Station no.	Location	Type of sample	Lead concentrations	
				Dithizone colorimetric	AAS
1	1	U.S.T. Farm	Soil	6.8	10.1
2			Soil	5.1	8.3
3			Soil	3.2	4.6
4			Soil	10.4	10.6
5			Soil	7.1	9.9
6			Pawpaw leaf	10.2	10.5
7			Pawpaw leaf	5.7	8.5
8			Pawpaw leaf	18.9	22.6
9	2	Ikwerre Road	Soil	52.9	54.4
10		East-West Road			
11	3	Junctio	Lemon grass	48.6	50.0
12		Aba Road/	Soil	88.0	103.1
13		Kaduna Street			
14		Junction	Soil	74.9	76.3
15			Soil	65.6	66.3
16			Soil	101.3	109.6
17			Soil	69.9	71.3
18			Lemon grass	65.4	70.3
19			Bitter leaf	51.3	56.3
20	4	Aba Road	Soil	17.5	19.8
21			Soil	70.7	71.5
22			Soil	20.8	28.6
23			Soil	56.8	57.4
24			Soil	40.0	41.9
25			Bitter leaf	50.3	55.1
26	5	Ikwerre Street	Soil	11.0	15.8
27			Soil	12.3	15.8
28			Soil	10.8	13.0
29			Bitter leaf	20.5	25.3
30			Bitter leaf	24.7	29.5
31			Pumpkin	11.8	16.0
32	6	Dick Tiger Street	Soil	18.2	19.6
33			Soil	12.1	16.4
34			Soil	9.5	12.9
35			Sugar cane leaf	12.2	18.2
36			Sugar cane leaf	15.4	18.2
37			Cassava tuber	5.0	5.6
38			Cassava peel	7.5	8.5
39	7		Soil	19.8	27.8
40			Soil	10.5	14.5

Continue Table 1

S/no	Station no.	Location	Type of sample	Lead concentrations	
				Dithizone colorimetric	AAS
39			Soil	25.1	28.4
40			Soil	16.0	18.1
41			Pumpkin	14.5	14.8
42			Pumpkin	17.8	13.9
43	8		Soil	20.9	30.0
44			Izora leaf	14.8	18.3
45	9		Lemon grass	32.1	34.4
46	10		Lemon	21.7	24.1
47	11		Mango leaf	55.2	62.9
48	12		Hibiscus leaf	63.4	65.3
49	13		Lemons	15.8	17.2

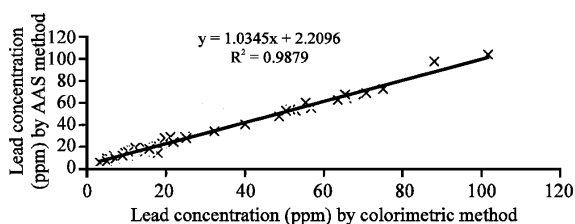


Fig. 2: Variation of lead concentration (ppm) measured by AAS and Dithizone colorimetric methods

The results showed that lead concentrations measured by AAS method varied between 4.6 and 109.6ppm while those by colorimetric method varied between 3.2 and 101.3ppm with concentrations soils higher than the concentrations in leaves. This is attributed to the fact that soil serves as a sink for air borne lead. Although lead concentrations from the Atomic Absorption spectroscopic method were slightly higher than the concentrations from the Dithizone colorimetric method and t-test showed significant difference ($p < 0.05$) between them, the correlation between the AAS and Dithizone colorimetric lead concentrations was positive and highly significant ($r = 0.9939$). The lead concentrations determined by the two methods were found to be related by the linear regression equation:

$$Y = 2.2096 + 1.0345x$$

Where x is the lead concentration determined by the Dithizone colorimetric method and Y is that determined by the AAS. This relationship is shown in Fig. 2.

These observations indicate that the AAS method may find application in the rapid determination of lead and therefore saves time. However, the Dithizone colorimetric method also produces satisfactory results when handled by skilled personnel and is sensitive in addition to being

less expensive. The observations from this study agree with the report (APHA, 1980) that the AAS method is subject to interference in the flame mode and required an extraction procedure for low concentrations; the dithizone method is more sensitive and is preferred by some analysts for low concentrations. Since the Dithizone colorimetric method produced satisfactory results researches involving heavy metal analyses could be carried out with minimum costs in public and private laboratories which cannot afford the cost of atomic absorption spectrophotometer and its maintenance. This can be of immense economic benefit to developing countries.

CONCLUSION

This study has shown that colorimetric methods are sensitive, selective, less expensive and very useful for measurement of low metal concentrations. It is therefore economically recommended for analysts especially students who cannot afford the instrumental method for the analysis of heavy metals in environmental samples.

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