A Review of Sequential Extraction Method for Lead in Samples: A Case Study of Artisanal Mines of Sokoto Basin (Zamfara State)

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ABSTRACT

This paper reviews the speciation of Lead which is a stable trace metal with alpha and beta particle emitting radioactive isotopes known to have drawn global attention in Zamfara state and recently in Niger state all in Nigeria for poisoning thousands of villagers and leading to numerous death tolls. It is termed as a pollutant environmentally, as it could be subsequently absorbed into food chain of organisms and thereby posing a health concern to the public. Acceptable threshold of lead is also a global concern due to its potency even at lower concentration in ppm. This calls for frequent environmental assessment and consumables for a precise reference to its occurrence. This paper hence, reviews the occurrence of lead and sequential extraction method to ascertaining environmental vulnerability free of lead.

Keywords: Radioisotope, Sequential-Extraction, Environment, Zamfara and Lead-Poisoning

I. INTRODUCTION

Lead is one of the known trace metal which has caused an epidemic of poisoning in some parts of Zamfara state, Nigeria [1]. During a childhood lead poisoning outbreak related to gold ore processing that was confirmed [2]. High toxicity have been attributed to environmental pollution by lead from the activities of miners in search for alluvial minerals [3]. Similar epidemics of lead poisoning was also reported to have claimed 23 children lives in a village in Niger state, Nigeria [4]. Exposure to radiation emitting elements like lead has been linked to mortality rate due to various ailments in recent times [5]. Hence, the study of their concentration and speciation method becomes imperative in empirical terms. Exposures to radiation emitting trace metals like lead have been thought to emanate from the search of natural sources [6]. Nigeria is a country endowed with numerous mineral resources [7,8]. There are proven reserves of both alluvial and primary deposit of the world's major demanded minerals which during mining and extraction, various metal and their relative

radioactive emitting isotopes are exposed to the public health detriments. At present, exploitation of alluvial deposits is being undertaking mostly by illegal and artisanal miners in different location in Zamfara and other parts of the country [9,10,11,12].

II. LEAD CONCENTRATION

The concentration of lead in living systems can result in a number of structural and behavioural abnormalities, neurophysiological disturbances, genetic alteration of cell (mutation), tetratogenesis and carcinogenesis [3,13]. There is common mode of accumulation of metals like lead in both natural and anthropogenic samples. Thus posing herculean task to isolate and determine the origin of various metals present in a given samples [14]. Although their concentration my point o their overall presence in a given sample, but it is difficult to ascertain information regarding the chemical nature or potential mobility and availability in biological systems [15,16,17,18].



In a deemed desperate situation, single extractions is used generally to provide a rapid evaluation of the exchangeable metal function in sample [19,20]. Sequential extraction method is a frequent approach to evaluate metal distribution base on reactive form present in a solid phase [18]. In principle, to determine lead concentration using normal extraction method possess high level of uncertainties than to do the procedures in which the total content Is determined in a direct mode [21]. This is due to the following reasons:

- 1. The task in separating the compounds to be studied from their substrates
- 2. The probability of upsetting the equilibrium between the different chemical species embedded in the system;
- 3. The analytical inadequacy in sensitivity of the adopted techniques especially when trace elements are found at very low concentrations
- 4. The unavailability of certified reference materials [22,21].

III. OVERVIEW OF SEQUENTIAL METHOD

However, different demanding task of sequential extraction method have been used to report more detailed information associated with metal phase [23,24,25]. Although often discard due to problem of specificity of extraction [26].

In essence, several studies have been conducted in this direction, this paper aims to review sequential extraction method for solid phase lead in soil sample as it affects remediation and analytical methods used as well as to compare results of other experiments of metal speciation.

IV. METALS (Lead) and POLLUTION

The biological potentially pollutions that are released into the environments have tracing pathways and, ultimately, the bioavailability of both radioactive and non-radioactive pollutants is of paramount consideration [27]. If individual or organisms are not exposed to pollutant or contaminants, or the level of exposure is slight, then the impact of these pollutants is likely to be insignificant or non-existent [28,29,30]. Availability of information about the degree of exposure of one to a source or sources of pollution of all type is central to the success measured of their environmental impact [31]. Common pollution pathways are generally air, water, food or soil through the environment and consequently to living organisms [32]. The degree of concentration of lead depends on the type of activity taken place in a particular area. In Nigeria, several pathways have been identified through which specific heavy metal can be of pollution to living species [33].

Lead is a toxic metal which exists in trace amount in some part of the globe but very significant in polluting environment. It can cause a grave damage to the brain, kidney, bone marrow, and other body systems in humans, especially among young children [34]. Lead exposure among children is associated with developmental problems including impaired cognitive function, reduced intelligence, impaired hearing, and reduced statue; with no safe level of toxicity known in blood lead level (BLL) [35,36]. As leaded gasoline is still popularly patronized, the consequence is that a great contribution to the number of cases of childhood lead poisoning will be anticipated. However, numerous studies have been reported that efforts to reduce leaded gasoline remain a mere theory and not in practice in most developing world [37]. Organic lead contents when undergoes contribution, the leaded gasoline is oxidized to lead oxide as shown in the equation (1) below

 $2Pb(C_2H_5)_4+270_2 \longrightarrow 2PbO+1bCO_2+2OH_2O$ (1) [33]

The subsequent oxide from the above reaction reacts with halogen carrier to form lead halides Viz: PbCl₂, PbBr₂, PbBr, which are given off through vehicles exhaust pipes. Lead contamination form automobile have well long been documented [33]. Developing countries like Nigeria are faced with major sources of exposure to lead through lead mining smelting, paints, battery recycling and traditional medicine [38,39].

V. GROUND VALUE/ QUALITY FACTOR

This is a value usually determined by miners in a particular field. As there are no miners without an outlined procedure. This procedure was adopted from Carthcat and McGreary (1959). They looked into the weight of $1M^3$ of mineralized units (e.g shale/siltstone, phosphate rock e.t.c) they also adopted a valid calculation for one hectare as shown in the equation (2) below.

$$\frac{10,000 \times 1m^3 \times Qtonnes}{1000}$$
(2)

VI. ANALYTICAL METHOD

The amount of pollutant exposed to the environment and it include relative metal (Lead). The soil, water (stream, river, well) and the atmospheric air are the receivers of every pollution because of their abundance which is capable of diffusion, dilution and reduction of the toxic substances introduced with time [40.41.42]. Nevertheless, the dissolution and selective destruction of collected sample components is unavoidable in any sequential extraction technique, due to non-specificity of addition and possibility of the redistribution of metals during the extraction [43]. Since the early 1980s and 1990s sequential extraction method has been adopted to determine speciation of metals in samples [24,44]. This is because of the fact that the total concentration of metals often does not accurately represent their characteristics and toxicity. In order to overcome the said obstacles it is helpful to evaluate the individual fraction of the metals to fully understand their actual and potential environmental effects [24]. However, to cub the problem of mobility of heavy metals in sediments, various sequential extraction procedures have been developed [45,46,47]. Interestingly, this analysis could not be impressive without a mention of noble methods of investigating the distribution of heavy metals in sample by the 5 steps Tessier et al., [24] and the 6-step extraction method, laerstin and Frontier [48]. Which were widely used to harness these two noble schemes, some modified procedures with different sequences of reagents or experimental conditions have been developed [49,50].

Wang et al., [51], adopted the modified Tessuer procedure of sequential extraction method to investigate the distribution and speciation of Cd, Cu, Pb, Fe and Mn in the shallow sediments of Jinzhou Bay, Northeast of China [51].

VII. STATISTICAL ANALYSIS

Fanasidez et al.,[21], aimed at to test the European Community Berean of Reference usually called BCR technique for the determination of the concentration of 11 elements including lead from fine soil samples. Labeled 3Ah, 3Bwk 6Ap 6Be and 6Bw. So as to calculate the BCR total concentration, C^{α} , of each element in each sample according to the following expression.

$$C^{\alpha} = \sum_{i=1}^{3} C_i + r^{\alpha}$$
(3)

Where { $C_i i = 1, 2, 3$ } represents the concentrations determined in each of the three BCR steps and r^{α} signifies that of the residue. The super-index α reforms to the time residues (A and B) describe earlier. The corresponding uncertainties, $\sigma(C^{\alpha})$. Were calculated as the quadratic sun of the respective errors of the concentrations resulting from each of the BCR steps and the residue

$$\sigma(C^{\alpha}) = \sqrt{\sum_{c=1}^{3} \left[\sigma(C_{i})\right]^{2} + \left[\sigma(r^{\alpha})\right]^{2}}$$
(4)

Fernandez et al.,[21].

The resulting value were compared to the reference values provided by the total analysis, which gives us the total concentrations, T, as well as the corresponding uncertainties, σ (T), for each element in each soil sample [21].

In addition to the direct comparison of the values found, they have calculated, for each element and each soil, the quality

$$r = \frac{C^{\alpha} + T}{\sqrt{\left[\sigma\left(C^{\alpha}\right)\right]^{2}} + \left[\sigma\left(T\right)\right]^{2}}$$
(5)

From Frodesen et al., [51] it could be shown that if the total concentrations determined with two methods derived from the same parental distribution, the variable r should be a Gaussian distribution centred at O with variation 1. [21]. Finally, for each step of the BCR method, they calculated the correlation between the concentrations of each element and the soil characteristics listed in the table (1) below, by means of the Pearson's linear correlation coefficient [52].

Table 1

Comp. Hor.	Clay	CaCO ₃	pН	Fine Silt and Clay	Organic Matter
Error %	5.0	2.0	0.2	5.0	0.2
3Ah	47.4	11.4	8.0	76.4	2.71
3Bwk	57.6	21.7	8.0	87.3	1.43
6Ap	51.5	9.6	8.2	73.8	2.57
6Bw	51.7	7.6	8.1	85.3	1.07
6Bx	65.9	7.5	8.1	71.4	1.71

*Table 1. Was adapted from Ferna'ndeza et al., (2004) for the Purpose of review with slight modifications not intended to alter the prior work for claim of ownership

$$r_{i} = \frac{\Sigma \left(C_{i} - \overline{C}\right) \left(r - \overline{v}\right)}{\sqrt{\Sigma \left(C_{i} - \overline{C}\right)^{2} \sqrt{\left(v - \overline{v}\right)^{2}}}}$$
(6)

Where the sum for the fine soils analysed, C is the mean of the values C_i for those soils, refers to the soil characteristics and v is the corresponding mean value. Also, the uncertainty for those correlation coefficients was determined following a Monte Carlo technique. For each C_i value, Fernandez et al., [21] generated a random value according to the Gaussian distribution centred on it, with variance. The some procedure was performed for each r value. Which gave new sets of values $C_i^{(k)}$ and $v^{(k)}$ for the five soils considered by Fernandez et al., [21]. By repeatedly using equation (5), they obtained a set of values. While the uncertainly of the original linear coefficient r_i is given by the standard derivation of these N values. They verified that N=1000 was adequate for convergence in the results [52,53].

VIII. CONCLUSION

This paper has reviewed the analytical and statistical methods for sequential extraction method of lead in a given sample. The review has highlighted various effects, occurrence and a number of speciation methods to determine concentration of lead among other metals and their mobility in different fractions. It could also be concluded based on the bounden of pollutant and environmental vulnerability at may part of the globe if not most locations that inhabitants of such localities are also vulnerable to radioactivity of varying sources.

Although leads as a metal has been identified as a health potent trace metal in the environment, but very limited literatures are available on the systemic effect that sound as nearing to artisanal mines and illegal mines in developing world.

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