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## Determination of Lead in Soil Sample and Validation on Multiwall Carbon Nanotube Modified Electrode

J. Rathidevi<sup>1</sup>, H. Mary Helen<sup>2,\*</sup><sup>1</sup>Research Scholar (Reg. No. 12197), Department of Chemistry, S.T. Hindu College, Nagercoil, Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli – 627 012, Tamilnadu, India.<sup>2</sup>Department of Chemistry, S.T. Hindu College, Nagercoil, Kanyakumari District – 629 002, Tamilnadu, India.

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### ABSTRACT

In this investigation, lead in roadside soil at Thirparappu falls (S<sub>1</sub>), Muttom Beach (S<sub>2</sub>), Mandaikadu Beach (S<sub>3</sub>), Chothavilai Beach (S<sub>4</sub>) and Kanyakumari Beach (S<sub>5</sub>) were examined. Soil samples were obtained at different saturation. The concentrations of lead were determined using atomic absorption spectroscopy. Lead values in soil samples ranged from 13.81 to 35.2 ppm. Lead studies revealed that there was significant contamination in soil affected by traffic intensity. Cyclic voltammetry was used to explore the electrochemical behaviour of Pb at these electrodes in different supporting electrolytes. Soil extract is pH adjusted and examined with a modified carbon electrode using stripping voltammetry. The amount of detection for the electrochemical analysis was calculated as range between 10 and 35 ppm.

### 1. Introduction

Lead (Pb) is widely recognized as a hazardous and toxic pollutant that harms both the environment and human health around the world. Pb exposure is linked to a variety of health issues [1-3]. The World Health Organization estimates that over one million deaths worldwide in 2017 could be attributable to Pb exposure. Ingestion of soil and/or dust is the primary source of Pb exposure, and urban soils can contain high amounts of a variety of dangerous metals such as arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and others [4].

Many sensitive analysis methods for ambient Pb are available, including inductively coupled plasma-optical emission spectroscopy/mass spectrometry and atomic absorption spectroscopy; however, these approaches are usually expensive and cannot be conducted in situ [5,6]. Another impediment to using laboratory methods for environmental investigation is the need to convert the solid matrix into a solution [7-9]. There are several types of acid digestions that use mineral acids such as nitric and hydrochloric, as well as appropriate digestion apparatus, for this goal. Unfortunately, these processes necessitate rigorous safety precautions and, due to their dangerous nature, cannot be used in the field [10,11].

Alternatively, electrochemical methods such as potentiometry and stripping voltammetry can be employed to quickly determine Pb on-site. Stripping voltammetry has also become more accessible in the field in recent years, thanks to portable, downsized instrumentation. For these reasons, as well as short analysis durations and minimum training requirements, electrochemistry is an appealing option for point-of-use analyses [12-15]. This work discusses mainly the use of voltammetry in the detection of the presence of lead metals using modified electrodes and presents a comprehensive overview of modifiers electrodes.

### 2. Experimental Methods

The soil samples, after removing the overlying wastes were called from the five different stations throughout the year continuously from June 2016 to May 2017. Thirparappu falls (S<sub>1</sub>), Muttom Beach (S<sub>2</sub>), Mandaikadu Beach (S<sub>3</sub>), Chothavilai Beach (S<sub>4</sub>) and Kanyakumari Beach (S<sub>5</sub>) were the

sample collection station. Samples were collected in pre-cleaned polythene containers from each station every month. The soil samples collected were shade-dried, ground and sieved through 2 mm sieve. The heavy metal lead was estimated using Perkin Elmer A Analyst 200 Atomic absorption spectroscopy.

All the electrochemical measurements were carried out by CHI 650C electrochemical work station (CH Instruments, Inc., U.S.A.). Electrochemical studies were carried out in a conventional undivided three electrode cell using modified glassy carbon electrode (GCE) as a working electrode (area 0.0341 cm<sup>2</sup>), Ag|AgCl as a reference electrode and Pt wire as a counter electrode. Prior to each electrochemical experiment, the electrolyte solutions were deoxygenated with pre-purified nitrogen for 10 min unless otherwise specified. Were prepared and used for different pH solution as supporting electrolyte for throughout the electrochemical studies. All the experiments are carried out three times and the average value is used to plot figures and calibration plots.

### 3. Results and Discussion

#### 3.1 Atomic Absorption Spectroscopy

Lead occurs naturally in soil. Most of lead concentrations that are found in the environment are due to the human activities. Due to the use of lead in gasoline an unnatural lead-cycle has generated. Lead used in storage batteries, solders, bearings, cable covers plumbing, pigments, and sound and vibration absorbers [16]. Seasonal variations of lead from selected tourist spot during the study period was shown in Table 1 and Fig. 1. The lead concentration was maximum (43.4 ppm) in the month of May at station V during pre-monsoon season and minimum lead concentration (7.5 ppm) was observed in the month of October at station II during post-monsoon season.

The highest mean concentration of lead (35.20 ppm) was recorded at station V during pre-monsoon season and lowest mean concentration of lead (10.55 ppm) was recorded at station II during post-monsoon season. The ANOVA tests carried out for lead in soil samples between stations and seasons were shown in Table 2. The variations between stations are significant because  $p < 0.05$  and variations between seasons are significant because  $p > 0.05$ . (F- Value = 17.62173 and 0.974951; P-value = 0.000496 and 0.417912).

Lead is a well-known metal toxicant and it is gradually being phased out of the materials that human being regularly use. Lead concentrations in aquatic and terrestrial vertebrates tend to increase with increasing age of

\*Corresponding Author: [helencolumbus@gmail.com](mailto:helencolumbus@gmail.com) (H. Mary Helen)

organism, and to localize in hard tissues such as bone and teeth. Health advisories warning anglers against eating Pb contaminated fish have been posted in Missouri [17]. Lead toxicity results in several ill effects such as anaemia, a rise in blood pressure, kidney damage, disruption of nervous system and brain damage etc. [18].

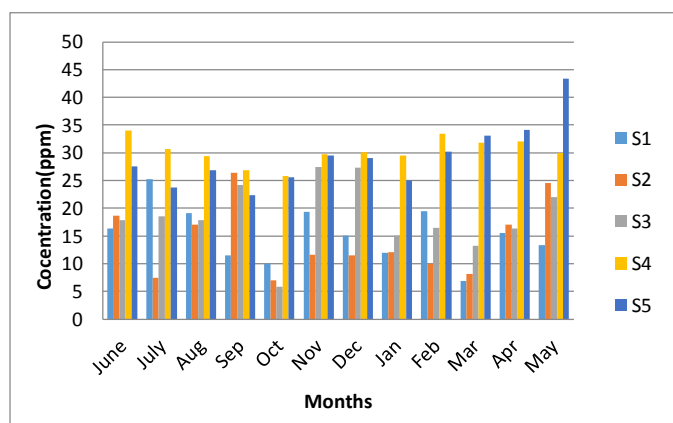
In the present study, the lead concentrations was high during pre-monsoon season at station V. This may be due to tourist vehicles came to the tourism beach resorts and then transported to the sea water. The same was studied by Davenport and Davenport [19].

**Table 1** Seasonal variation of lead (ppm)

Stations	Monsoon	Post-monsoon	Pre-monsoon
S1	18.07	14.1	13.81
S2	17.4	10.55	14.92
S3	19.63	18.92	17.03
S4	30.23	28.82	31.8
S5	25.13	27.28	35.2

**Table 2** ANOVA for data on Lead

Source of Variation	SS	df	MS	F	P-value	F crit
Stations	706.259	4	176.564	17.6217	0.00049	3.83785
Seasons	19.5374	2	9.76874	0.9749	0.4179	4.45897
Error	80.1577	8	10.0197			
Total	805.954	14				



**Fig. 1** Monthly variations of lead concentration (ppm) at five stations

### 3.2 Electrochemical Studies

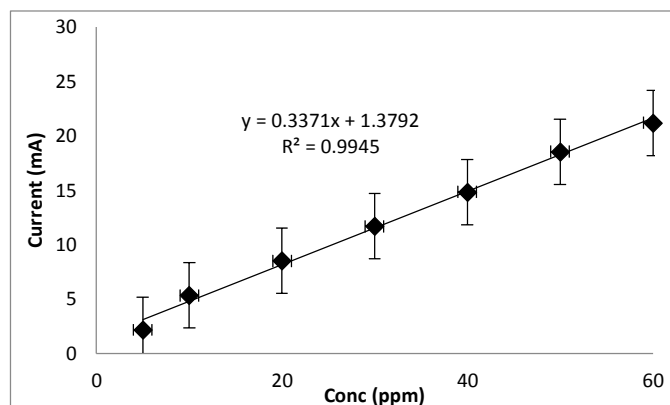
During cyclic voltammetry experiments, a current is produced by sweeping the potential applied between two electrodes over a range that is associated with the redox reaction of the analyte. This redox reaction generates a change in peak current that can be correlated to the concentration of the analyte, thus leading to specific quantitative analytical information. This method has the advantage of providing both qualitative information deduced from the potential location of the current peak and quantitative information deduced from the intensity of the peak current.

Typical cyclic voltammograms obtained in a range of supporting electrolytes for 100 ppm Pb solution at MWCNT electrode. Generally, the obtained voltammograms displayed one anodic peak on the return positive scan, which occurred from stripping of Pb metal deposited on the electrode surface. Little evidence of cathodic processes was found, but it was assumed to be concealed by the simultaneous lowering of the background supporting electrolyte. The production of a metal film at the electrode surface was required for the accumulation stage in anodic stripping voltammetry, which suggested that these CREs may be used to determine Pb using anodic stripping voltammetry.

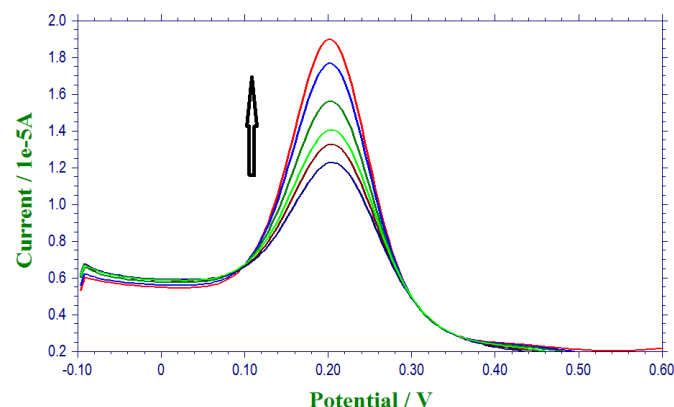
Differential pulse voltammetry is a derivative of the linear sweep voltammetry technique with a series of regular voltage pulses superimposed on the potential linear sweep. In DPV, a base potential value is chosen at which there is no faradaic reaction, and this potential is applied to the electrode. The base potential is increased between pulses with equal increments. The current is measured just before each potential change, and the current difference is plotted against the potential. Sampling the current immediately before the potential is modified reduces the effect of the charging current. In the linear sweep technique, an oxidation process leads to the formation of a wave in the voltammogram, but in the DPV technique, an oxidation process originates a peak. This

sharper shape facilitates the interpretation of the voltammogram and renders DPV more accurate than linear voltammetry.

Optimised study conditions were used to study the effect of concentration. A calibration plot was made and it resulted in linear dependency of peak current with concentration of substrate (Fig. 2). The ranges of concentration limit 20 to 100 ppb. The precision of the method was ascertained by measuring the peak current of the Pb responses in five standard samples. Ten replicates were analysed and standard deviations were calculated for a concentration 50 ppb. The low value of standard deviation, 2.5% indicates good reproducibility and feasibility of this method for the determination of Pb. As the concentration of Pb increased, the current increased. A typical DPV response obtained under the optimum experimental conditions for a Pb concentration is given in Fig. 3.



**Fig. 2** Calibration plot of different concentration lead



**Fig. 3** DPV behaviour of various concentration lead

### 4. Conclusion

Multiwalled carbon nanotube was fabricated, and their lead detection ability was examined. According to the DPV results, MWCNT with a diameter of 10 nm and a deposition time of 150s showed the best performance for Pb detection. The linear range of the platform was found to be 10–60 ppm lead with an LOD of 10 ppb, which was suitable for the sensitive detection of lead. However, the concentration of such a heavy metal in these sampling sites was lower than the World Health Organization's permissible limit. A soil sample taken from a roadside sampling site exposed to gasoline and vehicular emissions shows a significant difference in lead concentrations compared to the soil in atomic absorption spectroscopy and electrochemical studies. This demonstrates that the levels of lead in these sites were predominantly caused by automobile emissions. The low value of standard deviation, 2.5% indicates good reproducibility and feasibility of this method for the determination of Pb by DPV.

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