

# Potentiometric Stripping Analysis of Heavy Metals in Gasoline and Dust Particulate

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**Summary:** Determination of heavy metals such as Cd, Pb and Cu by potentiometric stripping analysis (PSA) in gasoline and dust particulate, was made. Initially optimum pH of the analyte, plating voltage and electrolysis time of the technique was established. The test samples were taken from service station and different locations at Peshawar. High octane blend, regular and super gasoline contained range mean levels of Pb 0.275-0.614 gm L<sup>-1</sup> and Cu 0.0042-0.008 gm L<sup>-1</sup> while Cd was not detectable. High speed diesel had mean values of Cd 0.003, Pb 0.0038 and Cu 0.023 gm L<sup>-1</sup>. The dust particulate matter contained maximum levels of 3.92, 84.23 and 49.67 gm Kg<sup>-1</sup> of Cd, Pb and Cu respectively depending upon the position on the road-side.

## Introduction

Monitoring of heavy metals in environmental samples is important because of the high toxicity of some of them. Increasing industrialization and motorization have greatly polluted the environment with several toxic trace elements. Although, it is difficult to classify trace metals into essential and toxic groups, yet it is well known that an essential metal becomes toxic at sufficiently high intake [1]. Important pathways for ingestion of toxic metals from the environment are food, gasoline and dust particulate and reliable trace analysis for heavy metals has become an urgent task [2,3]. Toxic metals constitute a significant health hazard as they accumulate in the vital organs [4]. Particular risk arise from the highly toxic metals such as Hg, Cd and Pb which are rather ubiquitous in the environment [5,6]. Although levels of heavy metal concentration in biological materials and waters have been determined [7-9], gasoline and dust particulate have not been studied. Heavy metals can be determined by

several techniques [10-3], however, potentiometric stripping analysis (PSA) is an electrochemical approach for the assay of trace metals [14]. It appears to be widely applicable as stripping voltammetry and differential pulse stripping voltammetry [15,16]. High correlation between atomic absorption spectrophotometry (AAS) and PSA techniques for the analysis of heavy metals in biological materials has already been described [8,17]. The objective of this study was to determine the concentration of cadmium, copper and lead in gasoline and dust particulate materials.

## Experimental

### Sample Collection

Various brands of gasoline samples were obtained from the Hydrocarbon Development Centre (Petroleum Testing Laboratory), University Town,

Peshawar. Roadside dust particulate samples were collected by petrie dish method from various sites in the Peshawar area. Ten labelled petrie dishes were placed at about 5 and 20 meters away in each case from the roadside and left exposed for 15 days. The weather condition was dry during the sampling period. After 15 days of exposure, these dishes were collected and the content of each dish were weighed and stored in a safe place in the laboratory for further treatment.

#### Acid Digestion

For trace metal analysis of various samples the following digestion procedure primarily based on the one reported by Sattar *et al* [18] was employed.

In the case of gasoline, 50 ml were taken into a volumetric flask and concentrated HCl (50 ml) was added. The flask was then connected with a reflux condenser and heated rapidly to boiling for 30 minutes under refluxed condition. Boiling was continued until HCl fumes were lost through the condenser. Then the volumetric flask was cooled and gasoline was separated from the aqueous layer with the help of separating funnel. The aqueous layer was collected in a china dish while gasoline was again refluxed with 50 ml of deionized water. Again the extracted aqueous layer was added to the china dish and evaporated on a water bath to dry residue. Then 30 ml of concentrated HNO<sub>3</sub> was added to this dry residue and evaporated to dryness in order to oxidise the organic material. This process was repeated three times and finally the dry residue was dissolved in 10 ml of 1:10 HNO<sub>3</sub>. The solution obtained was filtered and made up to a known volume for further analysis.

Dust particulate samples were digested on a hot plate with a mixture of nitric and perchloric acids in order to destroy the organic material. After digestion the residue obtained was dissolved in concentrated HCl and evaporated to almost dryness. Again the dry residue was dissolved in 10 ml of 1:10 HNO<sub>3</sub>. The solution obtained was filtered and made up to a known volume.

#### Analytical Procedure

Simultaneous determination of cadmium, lead and copper was carried out in the acid digest (pH 2-3) by the potentiometric stripping technique [2]

using a Tecator Striptec system comprising glassy carbon electrode, saturated calomel electrode (SCE) and platinum wires as counter electrode. To 50 ml of the acidified sample, mercury (II) ions were added to give a total concentration of 2-4 mg L<sup>-1</sup>. The sample was placed in the analyser, the stirrer started and a stress of N<sub>2</sub> passed through the sample at a rate of about 200 ml min<sup>-1</sup>. The analytical signal for each element is taken as the interval of time between two consecutive equivalence points on the time-potential curve. The stripping curves were measured at potential -1.1 volt vs SCE and 180 second plating time for Cd, and Pb while - 0.95 volt vs SCE and 180- seconds plating times for Cu. The concentration of the metals in the samples was evaluated by means of the standard addition techniques; the 1-min pre-electrolysis/stripping cycle being repeated after each addition. In comparison to calibration curves, the standard addition method is considered to be appropriate especially when the samples are of varying type and origin. In most experiments, two standard additions were used and the concentration of the standard addition solution was chosen so that the first addition almost doubled the concentration of the analyte. The stripping time for the element considered was prolonged in proportion to the added amount. Then the unknown content in the acid digest and finally the sample was determined by simple calculations. Detail of the methodology are available elsewhere [17].

#### Results and Discussion

Prior to analysis of the environmental samples the optimum experimental conditions for determination of cadmium, lead and copper were established and the resultant data are given in Table 1. Variation in pH of the analyte medium greatly affected the potentiometric stripping analysis measurements for heavy metal ions. Influence of pH value on the determination of cadmium, lead and copper ions in dilute nitric acid solution was determined. It became clear from the results that the most suitable/optimum pH conditions for potentiometric determination of cadmium, lead and copper ranged between 2-3 while zinc can best be determined in the pH range of 2-5.

Effect of plating voltage ( $E_{p1}$ ) on the signal response (stripping time) of cadmium, lead and copper in dilute nitric acid solution was studied. The optimum plating voltage determined for these

Table 1: Optimum experimental conditions for the stripping analysis of Cd, Pb, and Cu (IVs SCE)

Metal	Optimum pH	Optimum electrolysis time (second)	Optimum voltage (volts( E <sub>p1</sub> ))	Scanning voltage E <sub>1/2</sub> (volts)
Ca(II)	2-3	60	-0.9/ -1.20	-0.67
Pb(II)	2-3	60	-0.6/ -1.20	-0.45
Cu(II)	2-3	60	-0.5/ 0.95	-0.18

metals are given in Table 1. Cadmium, lead and copper were found to have an optimum plating voltage of -0.95 volts vs SCE for their determination while zinc had the optimum plating voltage as - 1.30 vs SCE and above this voltage (i.e. more negative value) there was no influence on the stripping time for the Zn measurements. The optimum plating voltage for biological materials was reported to - 1.1 for Cd, Cu and Pb while -1.3 for Zn [8,17].

It was observed that stripping time prolonged with increasing the electrolysis time for all the metal ions at a particular plating voltage and pH conditions. In this analysis, 60 seconds of electrolysis time was employed for determination of metal ions in gasoline and dust particulate samples. However, food samples are expected to have lowest concentration of metal ions and hence are analyzed at the electrolysis time of 120 seconds or 180 seconds depending on the concentration of metals [7,8].

In order to have an idea of the total heavy metal exhausted to the atmosphere of roadside by gasoline operated vehicles, cadmium, lead and copper level were determined in various brands of gasoline Table 2 shows the average lead and copper levels in high octane blended gasoline (HOBG), Gasoline Regular Super and high speed diesel (HSD). Cadmium was not detectable in either except HSD at the plating time of 60 seconds. HOBG contained high lead and copper concentrations ( $0.6144 \pm 0.108$  and  $0.008 \pm 0.002$  gm. L<sup>-1</sup>) than gasoline extra-super ( $0.367 \pm 0.135$  and  $0.0069 \pm 0.002$  gm. L<sup>-1</sup>) and regular ( $0.275 \pm 0.06$  and  $0.0042 \pm 0.003$  gm. L<sup>-1</sup>) respectively. The standard deviations were measured for triplicate determinations made under the same experimental conditions.

The results obtained for cadmium, lead and copper levels in High Speed Diesel (HSD) engine oils indicated that it contained very low concentration of cadmium ( $0.003 \pm 0.0014$  gm. L<sup>-1</sup>), lead ( $0.0038 \pm 0.004$  gm. L<sup>-1</sup>) and copper ( $0.023 \pm 0.012$  gm. L<sup>-1</sup>) as compared to gasolines. The limits of lead content in gasoline (in gm of Pb. L<sup>-1</sup>) have been established by the United States Environmental Protection Agency (USEPA) as followed [19]: January 1975, 0.45; and January 1976, 0.37; January 1977, 0.261; January 1978, 0.21; and January 1979, 0.13 mg of Pb.L<sup>-1</sup>. Comparison of these data

Table 2: Concentration of Cd, Pb and Cu in gasoline (gm L-1)

Sample	Cd	Pb	Cu
1. High octane blended			
1	-	0.624	0.006
2	-	0.742	0.010
3	-	0.477	0.008
Mean & Standard deviation		$0.614 \pm 0.108$	$0.008 \pm 0.002$
2. Regular			
1	-	0.297	0.0045
2	-	0.193	0.0038
3	-	0.337	0.0042
Mean and Standard deviation		$0.275 \pm 0.060$	$0.0042 \pm 0.0003$
3. Super			
1	-	0.44	0.005
2	-	0.178	0.01
3	-	0.584	0.0057
Mean and Standard deviation		$0.367 \pm 0.135$	$0.0069 \pm 0.002$
4. High speed diesel			
1	0.005	0.0033	0.0175
2	0.0025	0.0043	0.04
Mean and Standard deviation	$0.003 \pm 0.0014$	$0.0038 \pm 0.004$	$0.023 \pm 0.012$
Overall Mean	$0.003 \pm 0.0014$	$0.3236 \pm 0.255$	$0.0105 \pm 0.010$
CV.	46.66	78.84	95.92
CV. coefficient of variation.			

revealed that the average level of lead in gasoline reported here ( $0.275 \pm 0.06$  --  $0.6144 \pm 0.108$  gm.  $L^{-1}$ ) was comparable to the level recommended by the USEPA for 1975-77. Copper was present in very low concentration and this may be due to refining of crude oils. HSD also contained detectable amount of cadmium. Similar levels have been reported elsewhere [5].

Since the auto-vehicles exhaust contributes significant amount of lead and other heavy metals to the roadside environment, therefore, the next step in the present investigation was to determine the concentration of toxic metals in the roadside atmosphere of Peshawar University and Cantt area. For this purpose sampling and analysis of roadside dust particulate was carried out in order to get a quantitative idea of the amount of these metals present in the roadside environment and to identify the most highly contaminated locations in this area.

The results of the analysis on roadside dust particulates are given in Table 3. Cadmium, lead and copper levels in dust particles collected at a distance of 5 meter from the roadside were found

to lie in the range of 3.22-3.92 mg.  $Kg^{-1}$ , 49.02-84.23 mg.  $Kg^{-1}$  and 10.23-49.67 mg.  $Kg^{-1}$  respectively. Those samples which were collected at a distance of 20 meter contained 0.84- 5.78 mg.  $Kg^{-1}$ , 19.02-62.76 mg  $Kg^{-1}$  and 8.51-39.48 mg.  $Kg^{-1}$  of cadmium, lead and copper respectively. The data showed that the concentration of lead at 5 meter was greater than that at 20 meter, which indicated that auto vehicles that burn gasoline with high lead content are the main cause of lead levels in roadside dust particulate matter. However, this relationship was not very strong in the case of cadmium and copper because apart from auto vehicular emissions, certain local anthropogenic source such as local burning, industrial emissions and other material originating might be responsible for trace element concentrations in the atmosphere dust particulate matter. Although, no literature value on this subject has been reported in Pakistan; Durando and Aragon [19] found that the lead levels in roadside dusts of Guatemala City varied in the ranges of 150-380 mg.  $Kg^{-1}$  with an average of  $247 \pm 97$  mg.  $Kg^{-1}$ . Hence the lead levels found in this report are much lower and this may be due to the fact that sample cups designed for collection of the dust particles

Table 3: Concentration of Cd, Pb and Cu in dust particulate (mg  $Kg^{-1}$ ).

Sample	Cd	Pb	Cu
1. Stadium Chowk, Cantt			
5 M. from Roadside	3.22	80.42	49.67
20 M. from Roadside	1.35	55.33	8.51
Mean + standard deviation.	2.29 + 1.32	67.87 + 17.74	29.09 + 29.10
2. Hayat Avenue, Cantt.			
5 M.	3.32	72.45	36.22
20 M	3.36	50.00	18.90
Mean + standard deviation.	3.34 + 0.028	61.22 + 15.87	27.56 + 12.25
3. University Town Chowk			
5 M.	84.23	10.23	
20 M	0.84	60.62	10.20
4. Khyber Hospital Stop			
5 M.	3.92	49.02	20.57
20 M.	2.36	19.02	39.48
Mean + standard deviation	3.14 + 1.10	34.02 + 21.21	30.03 + 13.37
5. Secondary Board Stop			
5 M.	3.42	70.30	43.64
20 M.	5.78	62.76	24.77
Mean + standard deviation	4.60 + 1.67	66.53 + 5.35	34.20 + 13.34
Overall - Mean 5 M.			
20 M.	2.78 + 1.575	71.28 + 134.68	32.07 + 16.356
CV.	2.74 + 1.956	49.55 + 17.767	20.37 + 12.558
5 M.	56.74	19.20	51.00
20 M	71.45	33.86	61.64

M = meter, CV. = coefficient of variation.

were placed at sufficient height above the ground level. The lead particles emitted do not fall generally on the earth surface and remain suspended for sometime in the air and slowly undergo setting and deposition processes. These studies indicated that the gasoline and dust particulate contained considerable quantities of heavy metals. Although the values were found to be within the reported permissible range, their high toxicity demands constant and careful monitoring of these products at various places and times of the year. Significantly higher concentrations of these metals in gasoline and dust particles will end up on the vegetation which indeed has been shown [7,11,20].

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