Use of voltammetric methods for the analysis of trace metals in engine oils

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The quality and characteristics of engine oil and other lubricating oil has been improved in recent years by addition of many additives\(^1,2\). These additives are organic/organometallic formulations. Among the additives, the trace metals are added in lubricating oils in small amount in the form of organometals. The concentration of certain metals is usually low and their analysis is very important in determining the quality of the product. Therefore, there is a need for the determination of metals at trace levels in lubricating oil to ensure the proper control of blending and quality of products.

Instrumental techniques are particularly well suited for such trace metal determination. In past years, both atomic emission and absorption spectrosopic methods have been utilized for routine monitoring of samples of petroleum products\(^3,6\). X-ray fluorescence and neutron activation analysis have also been applied in certain case\(^7-10\). Besides, some research workers have used electroanalytical methods, viz., DPP and DPASV, for the determination of trace metals in petroleum products including lubricating oils\(^11-13\). In fact, voltammetry and related techniques have emerged as powerful tools for the rapid and simultaneous determination of trace metals in different origin samples\(^14,17\).

The present paper deals with the use of voltammetric methods, viz., direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV), for the analysis of trace metals in unused engine oil samples.

Materials and Methods

Polarographic and voltammetric measurements were made on an Ellico(India). Pulse polarograph (Model CL-90) coupled with a recorder X-Y polarocardi (Model LR-108). The electrode system consisted of a dropping mercury electrode (DME) as working electrode, a coiled platinum wire as an auxiliary electrode and a saturated calomel electrode as reference electrode. The electrochemical cell had the provision for inserting a bubbler for deaerating the solution. A glassy carbon fibre electrode (NF 12 Sigittii Eletitogitit, UK) was used for the differential pulse anodic stripping voltammetric analysis.

The IEC lab furnace model IIC-5546/1 was used for ashing the samples and a Systronics digital pH meter model-335 was used for pH measurements.

All the chemicals used were of AR/(BDH) grade. Standard stock solutions of ammonium tartrate (1M), potassium chloride (1M), EDTA disodium salt (0.1M), Cu\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Fe\(^{3+}\) and Cr\(^{6+}\) (0.01M) were prepared by dissolving the required amount of their soluble salts in doubly distilled water. Gelatin solution (0.1%) was prepared in hot distilled water. The solutions were standardised by known methods and diluted as required.

Preparation of sample solution

Three engine oil samples (A, B & C) of three different companies were purchased from a local automobile shop of civil line area, Sagar (M.P.).

Each sample of engine oil (10 g) was taken in platinum crucible with 1 ml of conc. H\(_2\)SO\(_4\) and heated on hot plate to dryness. The crucible was then
placed in a muffle furnace at 500°C for one hour to ash the sample. After cooling, the ash was dissolved in 20 ml aqua-regia and heated for about 30 min. The residue so obtained, was treated with 5ml conc. HF for about 10 min. and then both the solutions were mixed. The final volume of each sample solution was made up to 100ml with doubly distilled water.

Procedure
To 10 ml of the aqueous solution of each sample, 10 ml of 1 M (NH₄)₂ tartrate/1 M KCl/0.1 M EDTA was added as a supporting electrolyte and 1 ml of 0.1% gelatin solution as a maximum suppressor. The final volume of the analyte was made up to 100 ml with doubly distilled water. The pH of each solution was adjusted to desired values using dil. HCl / NaOH solution. The analyte was then placed in the polarographic cell, equipped with the electrode assembly specified above. Pure nitrogen gas was passed through the test solution for about 15 min. at the beginning of the experiment. The polarograms and voltammograms were then recorded, with instrumental parameters as follows: Sensitivity 1 μA/V; Pulse amplitude, 50 mV; I.R. compensation, 4; C. C. compensation, 5; Drop time, 0.5 s; O/P Zero, 0 and Scan rate, 12 mVs⁻¹. For DPASV analysis, the deposition potential was fixed at -2.0 V, deposition time 60 s., and resting period 10 s.

All the experiments were carried out at room temperature 25±2°C.

Results and Discussion

Sample A
The direct current polarogram and differential pulse polarogram (Fig. 1) of the sample solution in 0.1 M (NH₄)₂ tartrate at pH=2.2±0.1 showed one well defined wave/peak with Eᵢ/Eₛ = -0.42 V/-0.44 V vs SCE, indicating the presence of Pb²⁺ in the sample. The differential pulse anodic stripping voltammogram of the sample also produced one well defined peak with Eₛ = -0.44 V vs SCE corresponding to the presence of Pb²⁺ in the sample. At pH=8.4 ± 0.1 in 0.1M (NH₄)₂ tartrate, two distinct waves/peaks were observed with Eₛ = -1.34 V/-1.38 V and -1.58 V/-1.58 V vs SCE, indicating the presence of Co²⁺ and Fe³⁺ in the sample. The DPAS voltammogram of the sample also produced two well defined peaks with Eₛ = 1.36 V and -1.56 V vs SCE, revealing the presence of Co²⁺ and Fe³⁺ in the sample.

To investigate for the presence of other trace metals in the sample the polarograms and voltammograms were recorded in 0.01 M EDTA as supporting electrolyte. The dc polarogram and dp polarogram of the sample solution in 0.01 M EDTA at pH=9.6 ± 0.1 produced a well defined wave/peak with Eᵢ/Eₛ = -0.48 V/-0.50 V vs SCE indicating the presence of Cu²⁺ in the sample. The DPAS voltammogram of the sample also showed a well defined peak with Eₛ = -0.50 V vs SCE, revealing the presence of Cu²⁺ in the sample.

Sample B
The direct current polarogram and differential pulse polarogram (Fig. 2) of the sample solution in 0.1 M (NH₄)₂ tartrate at pH=9.9 ± 0.1 gave three distinct waves/peaks with Eᵢ/Eₛ = -0.38 V/-0.40 V, -0.56 V/-0.60 V, and -0.80 V/-0.84 V vs SCE, indicating the presence of Cr⁶⁺, Pb²⁺ and Cd²⁺ in the sample. The differential pulse anodic stripping voltammogram of the sample also showed three well defined peaks with Eₛ = -0.36 V, -0.62 V and -0.86 V vs SCE indicating the presence of Cr⁶⁺, Pb²⁺ and Cd²⁺ in the sample.

To investigate for the presence of other trace metals in the sample B, the polarograms and voltammograms were recorded in 0.1 M KCl as supporting electrolyte. The dc polarogram and differential pulse polarogram of the sample in 0.1 M KCl at pH = 10.0±0.1, produced a well defined wave/peak with Eᵢ/Eₛ = -1.30

Fig. 1—Voltammetric analysis of engine oil (sample A) in 0.1M ammonium tartrate + 0.001% gelatin at pH=2.2 ± 0.1. [curve A, direct current polarogram; curve B, differential pulse polarogram; curve C, differential pulse anodic stripping voltammogram].
The dc polarogram and dp polarogram (Fig. 3) of the sample C in 0.1 M (NH₄)₂ tartrate at pH= 9.6 ± 0.1 showed three well defined waves/peaks with E₁/₂= -0.36V/-0.38V, indicating the presence of Cu²⁺, Pb²⁺ and Zn²⁺ in the sample. The DPASV voltammogram of the sample also produced three distinct peaks with E₀ = -0.38 V, -0.50 V and -1.28 V vs SCE corresponding to the presence of Cu²⁺, Pb²⁺ and Zn²⁺ in the sample.

To ascertain the presence of the said metal ions in the samples, a known quantity of standard solution of each metal ion was added to the analyte and polarograms and voltammograms were recorded under identical experimental conditions. An increase in wave and peak height of each metal ion signal was observed without any change in half wave potential (E₁/₂) and peak potential (EP) values, thus, confirming the possibility of an accurate simultaneous multielement qualitative and quantitative analysis of the reported metal ions in the lubricating oil samples.

Table 1—Analysis of engine oil samples for trace metals content

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Amount found by AAS (in mg g⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>Zn²⁺</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>0.735(0.730)</td>
</tr>
<tr>
<td></td>
<td>0.356(0.355)</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.103(0.103)</td>
</tr>
<tr>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0.795(0.790)</td>
</tr>
<tr>
<td></td>
<td>0.453(0.453)</td>
</tr>
<tr>
<td></td>
<td>0.566(0.560)</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>0.098(0.102)</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>0.098(0.098)</td>
</tr>
<tr>
<td></td>
<td>0.735(0.730)</td>
</tr>
<tr>
<td>Co³⁺</td>
<td>0.654(0.657)</td>
</tr>
<tr>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.200(0.198)</td>
</tr>
<tr>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>0.2540(0.2528)</td>
</tr>
</tbody>
</table>

# Amount found by AAS (in mg g⁻¹) given in parantheses

Quantitative analysis of metal ions

After ascertaining the presence of the said metal ions in the samples the method of standard addition was used for their quantitative presence in the samples. The percentage recovery is over 99% for most of the metal ions with great accuracy and precision. The standard deviation and coefficient of variance shows reliability of the observed data.

The results of analysis on engine oil samples are reported in Table 1. These results have been compared with those obtained using atomic absorption spectrometric method, which are found in good agreement. The electroanalytical techniques are versatile, specific and selective for the qualitative and quantitative oligo analysis of trace metals in engine oil samples. These techniques are less time consuming and more economical.
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References