# Simultaneous Trace Metal Analysis in Wine Samples

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A highly sensitive, convenient and accurate analytical procedure has been proposed for the simultaneous determination of metal ions like Cu(II), Pb(II), Zn(II) and Mn(II) in wine using direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV) by standard addition method in ammonia/ ammonium chloride medium.

Wine is used as intoxicant all over the world. Some toxic metal ions present as impurity in it are harmful to human health [1-3]. Some country liquors contain a higher level of toxic metals [4-6]. It is therefore necessary to monitor the toxic metal ion content in the liquor sample. Some physicochemical methods are in use for the purpose of analysis of toxic metals in such samples [7-8]. Looking at the sensitivity and minimum detection limits, polarographic / voltammetric methods have been used for this purpose here. The present paper deals with such analysis for toxic metal content using four samples of wine.

## EXPERIMENTAL

Polarographic and voltammetric measurements were made on an Elico (India) pulse polarograph model CL-90 coupled with x-y polarocard model LR-108 using a three electrode (dme, Pt,, sce) system. A glassy carbon fibre electrode was used as working electrode in DPASV mode. pH measurements were made on an Elico digital pH meter model LI-120.

AnalaR BDH grade chemicals were used. Stock solutions (0.001 M) of Cu, Pb, Zn and Mn and (1 M) solutions of ammonium chloride and ammonia were prepared by dissolving requisite quantities of the respective chemicals in deionised water. The solutions were standardised by standard methods [9] and diluted as required.

Three local wine samples were purchased from authorised wine shops and the old monk (English) wine from English wine shop. 10 ml of wine sample along with 10 ml each of 1 M ammonia and 1 M ammonium chloride (both as buffer and supporting electrolyte) were mixed and made up to 100 ml with distilled water; its pH was checked. The sample was taken in a polarographic cell, deaerated and measurement was carried out.

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## RESULTS AND DISCUSSION

Typical DC polarogram, DP polarogram and DPAS voltammogram of the local wine (red) in 0.1 M ammonia and 0.1 M ammonium chloride at pH = 8.36±0.02 are shown in Fig 1A,B & C. Other wine samples gave similar polarograms.

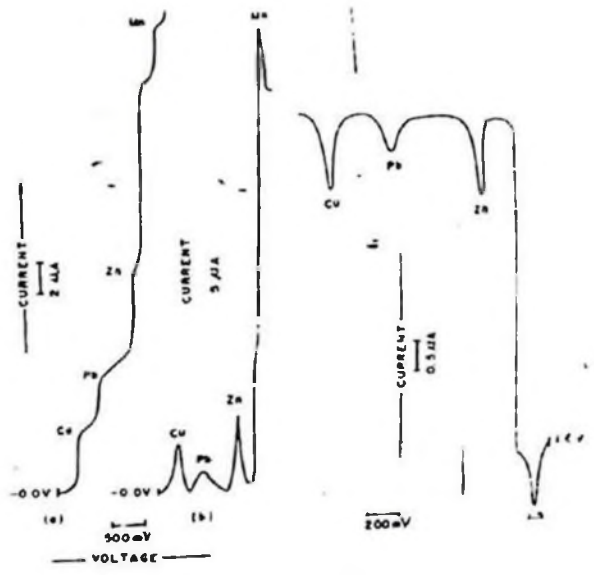



Fig.1 a. Direct Current Polarogram
b. Differential Pluse Polarogram
c. Differential Pluse Anodic Stripping voltammogram
local wine (Red) Sample
0.1M $NH_4Cl$+0.1M $NH_4OH$; pH 8.36 ± 0.02

All the samples showed four well-defined waves with $E_{1/2}$ /$E_p$ of -0.25/-0.25, -0.55/-0.61, -1.4/-1.5 and -1.7/-1.7 volts in DC and DP polarograms and peaks with $E_p$ values -0.20, -0.66, -1.2 and -1.5 volts in DPASV mode indicating the presence of Cu(II), Pb(II), Zn(II) and Mn(II) in the samples [10]. Synthetic samples with varying concentrations of the above metal ions were prepared and subjected to polarographic analysis under the same experimental conditions. The agreement of $E_{1/2}$ / $E_p$ of synthetic samples with those of wine samples confirmed the qualitative identification of the metals. The quantitative results in the synthetic samples have been reported in Table 1. This confirmed suitability of conditions selected by the authors for ascertaining a quantitative estimation of the above metals.

### Minimum Detection Limits Tried

After ascertaining the suitability of the method, the mimimum detection limits observed in different techniques for individual and oligo analysis of the metal ions are examined. Results given in Table

**Table 1**
**Analysis of Synthetic Samples** Composition is given as mg / 100 ml sample

| Sample No | Cu | | Pb | | Zn | | Mn | |
|---|---|---|---|---|---|---|---|---|
| | Taken | Found | Taken | Found | Taken | Found | Taken | Found |
| 1 | 0.063 | 0.061 | 0.01 | 0.01 | 0.05 | 0.05 | 0.022 | 0.022 |
| 2 | 0.106 | 0.107 | 0.02 | 0.02 | 0.09 | 0.09 | 0.086 | 0.087 |
| 3 | 0.126 | 0.126 | 0.03 | 0.03 | 0.12 | 0.12 | 0.128 | 0.127 |
| 4 | 0.335 | 0.334 | 0.04 | 0.04 | 0.16 | 0.15 | 0.224 | 0.223 |
| 5 | 0.672 | 0.671 | 0.05 | 0.05 | 0.24 | 0.23 | 0.326 | 0.326 |
| 6 | 0.778 | 0.777 | 0.06 | 0.06 | 0.32 | 0.32 | 0.483 | 0.484 |

Table 2

**Minimum Limits Observed**

(Both in Synthetic samples and Diluted Wine Samples)

| Metal ion | DCP µg/l | DPP µg/l | DPASV ng/l |
|---|---|---|---|
| Cu(II) | 6.0 | 0.06 | 6.0 |
| Pb(II) | 2.6 | 0.06 | 2.6 |
| Zn(II) | 6.4 | 0.64 | 12.8 |
| Mn(II) | 2.4 | 0.24 | 2.4 |

Average of four determinations

2 show that DPASV method using glassy carbon fibre electrode is highly sensitive for such analysis.

**Quantitative Analysis of Wine Samples Using DPASV**

The method of standard addition was applied for the quatitative analysis of the samples. Spiked samples were prepared and the percentage recovery in the spiked samples were determined. The results indicated a

Table 3

**Voltammetric (DPASV) Analysis of Different Wine Samples for Their Metal Ion Content**
(Values given in mg / 100 ml)

| Metal ion | Found in Sample | Spiked with | Found in Spk.Samp. | Average Recovery % | S.D ± | CV % |
|---|---|---|---|---|---|---|
| **Sample Red wine** | | | | | | |
| Cu | 0.670 | 0.635 | 1.201 | 99.6 | 0.008 | 0.61 |
| Pb | 0.049 | 0.041 | 0.009 | 100 | 0.0004 | 0.44 |
| Zn | 0.326 | 0.326 | 0.650 | 99.6 | 0.001 | 0.15 |
| Mn | 0.316 | 0.274 | 0.586 | 99.3 | 0.002 | 0.34 |
| **Sample White Wine (A)** | | | | | | |
| Cu | 0.550 | 0.635 | 1.180 | 99.5 | 0.004 | 0.33 |
| Pb | 0.041 | 0.041 | 0.082 | 100 | 0.0006 | 0.73 |
| Zn | 0.570 | 0.326 | 0.893 | 99.6 | 0.006 | 0.72 |
| Mn | 0.211 | 0.274 | 0.483 | 99.5 | 0.002 | 0.47 |
| **Sample White Wine (B)** | | | | | | |
| Cu | 0.254 | 0.635 | 0.887 | 99.7 | 0.002 | 0.22 |
| Pb | 0.033 | 0.041 | 0.074 | 100 | 0.002 | 0.27 |
| Zn | 0.489 | 0.326 | 0.812 | 99.6 | 0.002 | 0.24 |
| Mn | 0.211 | 0.274 | 0.483 | 99.5 | 0.001 | 0.20 |
| **Sample Old Monk** | | | | | | |
| Cu | 0.067 | 0.063 | 0.129 | 99.2 | 0.001 | 0.77 |
| Pb | 0.004 | 0.004 | 0.008 | 100 | 0.0001 | 1.25 |
| Zn | 0.065 | 0.032 | 0.096 | 99.8 | 0.0001 | 1.04 |
| Mn | 0.032 | 0.027 | 0.058 | 99.6 | 0.0004 | 0.68 |

recovery of over 99.5 % for nearly all the metal ions in all the wine samples (Table 3).

Table 4

**Metal Content (mg/l) in Different Wine Samples**

| Metal | Red Wine | A wine | B Wine | Old Mink |
|---|---|---|---|---|
| Cu(II) | 6.71 | 5.51 | 2.55 | 0.67 |
| Pb(II) | 0.49 | 0.41 | 0.33 | 0.04 |
| Zn(II) | 3.26 | 5.70 | 4.89 | 0.65 |
| Mn(II) | 3.16 | 2.12 | 2.11 | 0.33 |

The final finding is presented in Table 4. A perusal of the data clearly reveals that Red wine sample has high concentration of Cu & Pb and is the most toxic among the samples studied.

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