A novel spectral method indirectly to estimate the lead in Cu-Zn-Pb bronze alloy

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Abstract. Lead is used in many industrial products, including alloys, because of its importance in improving physical and chemical properties. In this study, a sensitive, simple, economical, fast and accurate, an indirect spectral analytical method was developed using Eriochrome Black T as chelating agent without use of separation and isolation to estimate the amount of lead in the Cu-Zn-Pb bronze alloy by using UV-Visible spectrophotometer instrument. The accuracy of the method was 99.97 ± 0.35 and the limits of detection (LOD) and qualification (LOQ) were 0.034 and 0.104 μg ml⁻¹ respectively. The developed method can be applied to water, biological, environmental and fuel samples.

Keywords. Bronze alloy, Lead, Copper, Zinc, Eriochrome Black T, Spectrophotometer

1. Introduction
Leaded brass alloys which are one types of bronze alloys used in many applications owing to exceptional machinability and corrosion resistance and other specifications [1]. The most significant element in this setting is lead, bettering the machinability with regard to chip break-age, tool wear, cutting forces, and applicable cutting parameters. However, in recent years, the lawmaking on protecting health and environment has been tightened in Europe, USA, Japan, and China. The use of lead in copper alloys is restricted more and more as lead is a hazardous heavy metal[2]. Analytical methods are one of the most important methods used in the follow-up to the production and control of lead ingots in terms of quality and quantity. M. Roxburgh et al conducted a typical and structural analysis of leded brass alloys [3]. M. C. Fernández-Feal el al [4] have proposed an analysis method that makes possible the simultaneous determination of Pb(II), Cu(II) and Ni(II) using MEDTA as a reagent and ultraviolet-visible and derived spectrophotometry. B.Saritha el al [5] determined the lead in a spectral manner in alloys and other sample. M. Y. Hayal [6] developed a new method for estimating lead using an organic reagent. T. Takahashi et al [7] had reached to results which indicate that calibration-free analysis of brass alloys using long-ns-duration pulse laser-induced breakdown spectroscopy is suitable for the estimation of lead in brass alloys at high concentrations greater than 5%.

H. Bagheri et al [8] estimated the lead in different samples in an electrochemical manner using a developed electrode. E. Sakar et al [9] found that the leaded brasses have greater protecting properties against gammas and fast neutrons when compared with protecting concretes. E. D’Andrea and B. Lazzerini have proposed an ensemble of learning machine for determining the elemental composition
of bronze alloys represented through Leaser-Induced Breakdown Spectroscopy spectra [10]. M. R. Jan et al [11] al have determined the Pb(II) in aqueous sample using functionalized dowex 1X8. N. H. Gale [12] had reached to a new low blank separation scheme for lead is presented for the preparation of ultrapure lead samples for isotopic analysis by thermal ionization mass spectrometry. Sensitive non-flame atomic absorption spectrometry with simultaneous background correction was utilized in a new method for the determination of trace elements without prior separation [13]. A new indirect spectral method has been developed to estimate lead in bronze alloy using Eriochrome Black T at a concentration above its quantification limit to eliminate signal interference with noise and to detect a decrease in the concentration of the reagent due to its reaction with lead ions easily by using UV-VIS spectrophotometer instrument.

2. Experimental

2.1. Solutions of sample, standards and reagent

All solutions were prepared with analytical grade reagents and freshly deionized distilled DI water. The hard bronze alloy sample (89% (w/w) Cu, 9% (w/w) Zn, 2% (w/w) Pb) was drilled, and about 0.5 g of the filling was accurately weighed and transferred to 150 ml Erlenmeyer flask containing 10.0 ml of a 7.0 mol l^{-1} HNO_{3} solution and placed on the flask onto hot plate with gentle boiling for not less than 30 minutes or digest the sample by microwave digester. After dissolution the solution was evaporated to a small volume, cooled to room temperature, transferred to a 100-ml volumetric flask and marked up with DI water. Then 1 ml of this solution was withdrawn to a 100-ml volumetric flask and diluted with DI water.

Stock solutions μg/μl of Pb(II), Zn(II) and Cu(II) were prepared by dissolving (0.1599, 0.2896 and 0.2952 g) of lead, zinc and Cupper nitrate respectively in water and made up to 100-ml volumetric flasks. Standard solution (reference solution) was prepared by diluting a 1, 4.5 and 44.5 ml of stock solutions μg/μl of the Pb(II), Zn(II) and Cu(II) respectively, in a 100-ml volumetric flask. This solution was used to establish optimum conditions for maximum dependability and accuracy of the method. Buffer solution pH 8.0 was prepared by mixing 0.2M ammonia and 0.2M NH_{4}NO_{3} solutions in suitable proportion and the pH was adjusted by a pH meter. Stock standard solution μg/μl of Eriochrome BlackT (EBT) was prepared by transferring a (0.1 g) of (EBT) to a 100-ml volumetric flask by means of small portions of water. One milliliter of pH 8.0 buffer solution was added and the solution was diluted to 100 ml with absolute ethanol.

3. Procedure

A 5 ml of reference solution was added to each flask in a set of 30-ml volumetric flasks except the first flask and a variable volume of solution 20 μg/ml of Pb(II) was added to the set except the first and second flask. Then a 2 ml of solution (20% w/v) of NaCN, 5 ml of buffer solution pH 8.0 and a 5 ml of solution μg/μl of the (EBT) were added to all the flasks in the set and the volumes of flasks were completed to the marks with deionized water. The blank solution was prepared at the same procedure without addition solutions of EBT and lead. The absorbance of these solutions was measured at 556 nm. A straight line is obtained which corresponded to the equation (A_{556}= 0.2464C + 0.5985. C is the amount of lead in μg ml^{-1}). The method was applied to a sample of hard bronze alloy by using sample solution instead of reference solution to determine the lead in the alloy.

4. Results and Discussion

The interference effect of the Cu and Zn matrix on the determination of Pb was eliminated by using the sodium cyanide as masking agent. To ensure that there is no interference between the reagent EBT spectrum, the spectra of Cu(II) and Zn(II) cyanide complexes and Pb(II)-EBT complex, absorption spectrum was recorded using a UV-1600 Series by Shimadzu Scientific Instruments Inc. and a solution containing a 5 ml of reference solution, 2 ml of solution (20% w/v) of NaCN, 5 ml of buffer solution pH 8.0, 5 ml of solution μg/μl of the (EBT) and diluted to 30 ml with deionized distilled water. The blank
solution was prepared at the same procedure without addition solutions of EBT and lead. The maximum wavelengths of EBT, complexes of Cu(II) and Zn(II) cyanide and Pb(II)-EBT complex were 558, 341, 300 and 647 nm respectively (Figure 1).

**Figure 1.** Absorption spectrum of EBT, Cu(II) and Zn(II) cyanide complexes and Pb(II)-EBT complex.

Quantitative analysis of Lead in hard bronze alloy is performed by measuring the decrease in the absorbance of the EBT using the new indirect method based on the calculation of the difference between the absorbance of EBT at its initial concentration ($A_0$) and its absorbance at residual concentration ($A_R$) as a result of its reaction with lead ions in the sample solution by using standard addition method and application of the following equation:

$$\text{Absorbance of lead (A)} = A_0 - A_R \quad \text{(Eq.1)}$$

Where $A_0 = K C_0$

$A_R = K C_R$

$C_R = C_0 - C_Y$

$C_0$, $C_Y$ and $C_R$ represent the initial, reactant and residual concentrations of EBT respectively.

The absorbance of EBT at $\lambda_{max}$ (558 nm) with a concentration (166.67 ppm) is equal 1.834 in present of Cu(II) and Zn(II) cyanide complexes (Figure 2).

**Figure 2.** Absorption spectrum of EBT and cyanide complexes Cu(II) and Zn(II) in absent of Pb(II) ions.

L. Szabo et al [14] referred to the mole ratio of the Pb(EBT) complex in a study they conducted. The study by T. Wang et al [15] indicates the high sensitivity of the EBT reagent to react with lead ions in a 1:1 molar ratio, which helped to find the new indirect method of estimating lead in a solid bronze alloy as in the table 1 and figure 3.
Table 1. Data were used to obtain absorbance of Pb(II) as $A = A_0 - A_R$.

| No. | Volume of standard-ml | Volume of sample-ml | Volume of EBT-ml | $A_0$  | $A_R$  | $A$  |
|-----|-----------------------|---------------------|------------------|--------|--------|------|
| 1   | 0                     | 0                   | 5                | 1.834  | 1.834  | 0    |
| 2   | 0                     | 5                   | 5                | 1.698  | 0.136  | 1.562|
| 3   | 1                     | 5                   | 5                | 1.642  | 0.192  | 1.45  |
| 4   | 2                     | 5                   | 5                | 1.586  | 0.248  | 1.338 |
| 5   | 3                     | 5                   | 5                | 1.53   | 0.304  | 1.226 |
| 6   | 4                     | 5                   | 5                | 1.474  | 0.36   | 1.108 |
| 7   | 5                     | 5                   | 5                | 1.418  | 0.416  | 1.002 |
| 8   | 6                     | 5                   | 5                | 1.362  | 0.472  | 0.89  |
| 9   | 7                     | 5                   | 5                | 1.306  | 0.528  | 0.778 |
| 10  | 8                     | 5                   | 5                | 1.25   | 0.584  | 0.665 |
| 11  | 9                     | 5                   | 5                | 1.194  | 0.64   | 0.55  |
| 12  | 10                    | 5                   | 5                | 1.138  | 0.696  | 0.442 |

Figure 3. Standard additions curve to determine the lead in the preparative bronze alloy solution using new indirect spectral method.

From the linear regression: $S = mV_S + b$  
(Eq. 2)

Where:  
$S$ = instrument response (signal)  
$V_S$ = volume of standard

Theoretically, if the curve started where the device response is zero, the volume of standard $(V_S)^0$ from that point to the point of the first solution on the curve $(X = 0)$ contains the same amount of analyte as the sample. So:

$V_X \cdot C_X = (V_S)^0 \cdot C_S$  
(Eq.3)

Where : $V_x$ = volume of the sample aliquot  
$C_X$ = concentration of the sample  
$C_S$ = concentration of the standard

Linking Eq. 2 and Eq. 3 and solving for $C_X$ results in:

$C_X = \frac{b \cdot C_S}{m \cdot V_X}$

Where $b$ = intercept and $m$ = slope

And one can then calculate the concentration of analyte in the sample from the slope and intercept of the standard addition calibration curve.

$\text{Pb}\% = \frac{C_X \times V \times D \times F \times 100}{W}$

Where $C_X$ = Concentration of Lead ($\mu g/ml$)
V = Markup volume (ml)  
D.F = dilution factor  
W = weight of sample

In order to validate the indirect spectral analytical method, a series of standard solutions were prepared and their absorption measured according to the above procedure and the accuracy of the method was estimated from the calculation of percentage recovery and its standard deviation. The standards error and deviation of intercept and the limits of detection (LOD) and quantification (LOQ) were also calculated from Fig. 4 as shown in Table 2.

![Graph](image.png)

**Table 2.** Results of calibration curve analysis.

| Parameter           | Value          |
|---------------------|----------------|
| Accuracy            | 99.9654 ± 0.3469 |
| Slope               | 0.352          |
| Intercept           | 0.0001         |
| Linearity range     | 0.1- 40 μg ml⁻¹ |
| Correlation Coefficient (r) | 0.99995 |
| SE of intercept     | 0.001103       |
| SD of intercept     | 0.003657       |
| LOD                 | 0.034283 ppm   |
| LOQ                 | 0.103888 ppm   |

**Figure 4.** Calibration curve of validation of the indirect spectral analytical method.

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