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Development indirect spectrophotometric method for measurement Lead in Al-Zn-Pb ingot by using eriochrome black t

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Abstract

Lead element 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 Al-Zn-Pb ingot by using UV-Visible spectrophotometer instrument. The accuracy of the method was 99.83 ± 0.13 and the limits of detection (LOD) and qualification (LOQ) were 0.0050 and 0.0153 µg ml^{-1} respectively. The developed method can be applied to water, biological, environmental and fuel sample.

Keywords. Aluminum alloy, Lead, Zinc, Eriochrome Black T, Spectrophotometer

الخلاصة

يستخدم عنصر الرصاص في العديد من المنتجات الصناعية ، بما في ذلك السبائك ، لأهميته في تحسين الخواص الفيزيائية والكيميائية. وفي هذه الدراسة ، تم تطوير طريقة تحليلية طيفية حساسة وبسيطة واقتصادية وسريعة ودقيقة باستخدام Eriochrome Black T كليكاند مخلبي لتكوين معقد مع ايونات الرصاص وتقدير كميتها في سبيكة Al-Zn-Pb باسلوب غير مباشر دون الحاجة الى استخدام عمليات الفصل والعزل باستخدام مطيافية الأشعة فوق البنفسجية - المرئية. وقد كانت دقة الطريقة 99.83 ± 0.13 وبحدود الكشف (LOD) والتقدير الكمي (LOQ)) 0.0050 و0.0153 ميكروغرام/ مل على التوالي. ويمكن تطبيق الطريقة المطورة على عينات حياتية وبيئية ومن المياه والوقود. وتعد الطريقة الجديدة من الطرائق التي تحد من انتشار الملوثات في البيئة.

1. Introduction

Leaded aluminum alloys which are one types of bearing alloys used in many applications owing to exceptional machinability and corrosion resistance and other specifications(1). The addition of Pb to the ZA-8 alloy increased wear resistance of the alloy for all of the sliding speeds at different forces and the friction coefficients(2,3). Trace element determination plays a significant role in the preparation of alloys since many elements can be added as microcomponents to bring particular characteristics to the alloys. For instance, lead and bismuth added to aluminium alloys improve their machine ability. However, lead is also one of the elements that affects significantly the machinery properties of high temperature alloys. Chelating resin catcher for capture, preconcentration and determination of toxic trace metals (Zn, Cd, Hg, Pb) in

waters(4). Some toxic heavy metal ions, including lead, in the treated waste water were determined by Polarographic and voltammetric methods(5,6).

The simultaneous multi elements determination of Pb, Sn, Ni and Cu in aluminium alloys by electrothermal atomic absorption spectrometry (ETAAS) was performed by a quick method using slurry sampling(7–9). An automatic flow-injection method was developed for the determination of lead m the range 50-2000 ng l^{-1}. The method is based on the extraction of lead with the crown ether dicyclohexyl-18-crown-6 into chloroform from an acidic medium, subsequent addition of dithizone as chromogenic reagent to the extract and measurement of absorbance (10). A study serves to focus attention on the modification of multiwalled carbon nanotube with 2-(5- bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and its application for the development of a new, simple, and selective modified electrode in order to determine Pb (II) in standard alloys and water samples(11). A spectral method was developed for the determination of trace amounts of lead in different matrixes (12). The lead and others heavy metals emitted from the combustion ofgasoline were determined by ICP-OES(13). In our study has been developed an indirect spectral method which has high sensitivity and great accuracy to estimate the lead in Al-Zn-Pb alloy.

2. Experimental

2.1. Preparation solutions of sample, working, standards and reagent

All solutions were prepared with analytical grade reagents and freshly deionized DI water. The leaded alloy sample (55% (w/w) Al, 45% (w/w) Zn, 5% (w/w) Pb) was drilled, and about 0.5 grams of the fine drilling was accurately weighed and transferred to 250 ml Erlenmeyer flask containing 9 ml of a 6 mol./l HNO_3 solution and sited the flask onto hot plate with moderate boiling for 35 minutes or assimilate the sample by microwave digester. After dissolution the solution was evaporated to a minor volume, chilled to room temperature, conveyed to a 100-ml volumetric flask and marked up with DI water.

Stock solutions 10 µg/µl of Al(III), Zn(II), and Pb(II) were prepared by dissolving (13.9050, 4.5480 and 2.9520 g) of aluminum nitrate nonahydrate, zinc nitrate hexahydrate and lead nitrate respectively in DI water and made up to 100-ml volumetric flasks. Working solution (reference solution) was prepared by diluting a 27.5, 10 and 5 ml of stock solutions of the Al(III), Zn(II) and Pb(II) respectively, in a 100 ml volumetric flask. The reference solution has been used to create optimal conditions for maximum reliability and accuracy of the new method. Buffer solution pH 9 was prepared by mixing 0.2M ammonia and 0.2M NH_4NO_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 (0.2 g) of (EBT) to a 200 ml volumetric flask by means of small portions of water. The total volume of water used was about 10 ml. Four milliliters of pH 9 buffer solution were added and the solution was diluted to 100 ml with absolute ethanol.

3. Procedure

To each flask in a set 100 ml volumetric flasks, 1 ml of reference solution was added except the first flask, a variable volume of solution 50 µg/ml Pb(II) was added except the first flask and second flask, 2 ml of solution (20% w/v) NaCN, 15ml of triethanol amine, 3ml hydroxyl amine, 5 ml of the buffer solution pH 9 and 10 ml of solution µg/µl (EBT) were added. Then all of the volumetric flasks were supplemented by deionized water to the marks. The blank solution was prepared at the same procedure without addition solutions of EBT and lead. The absorbance of these solutions was measured at 531 nm. A straight line is obtained which corresponded to the equation (A_{531}= 0.0169 C + 0.169. C is the amount of lead in µg ml^{-1}). The developed method was applied to a live sample of aluminum bearing alloy by using sample solution in place of reference solution to estimate lead in the alloy.

4. Results and Discussion

Eriochrome black T (EBT) is amongst the most significant azo indicators used in complexation titration of numerous metals: Ca, Mg, Mn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni, and the Pt metals. Therefore, the formation constants of complexes for those ions with EBT were studied(14). Studies referred to the high sensitivity of the EBT reagent to react with lead ions in a 1:1 molar ratio, which helped us to find the new indirect method of estimating lead in a leaded aluminum alloy (15,16).

The maximum wavelength of the absorption of the EBT reagent changes according to the change in the acidity of the medium that is chosen to form the complex with an ion to be studied and to estimate its quantity(17). In this study the spectra of the EBTand Pb(II)-EBT showed a maximum absorption peak at 531and 407 nm in an acidity solution equals to 9 as in Figure 1and 2 respectively.

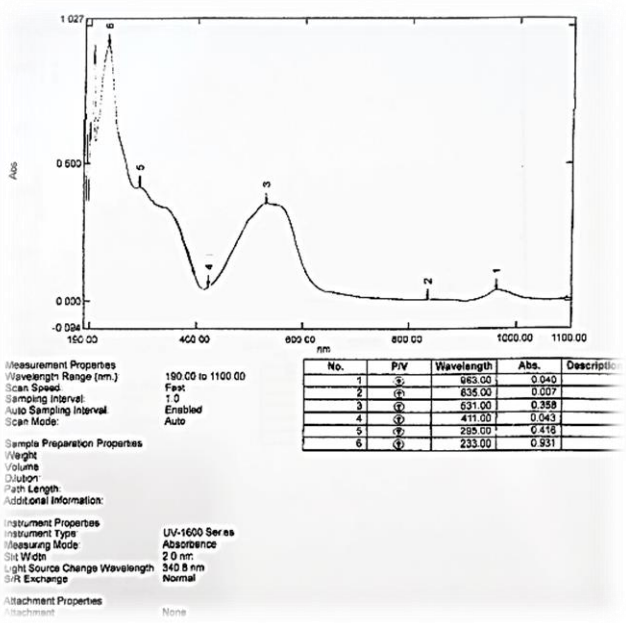


Figure 1. Spectrum of EBT at pH 9.

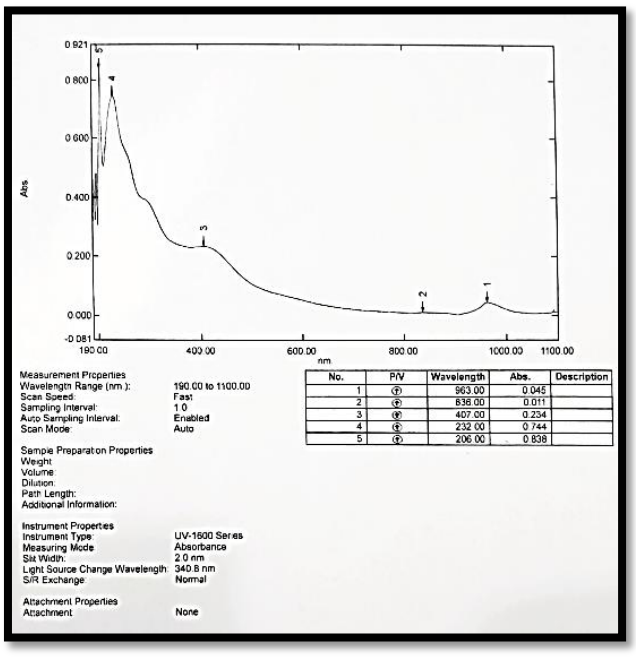


Figure 1. Spectrum of Pb(II)-EBTcomplex at PH equals 9.

4.1. Interferences study

The interference effect of the Al, Zn, and other ions on the determination of Pb was eliminated by using sodium cyanide, triethanol amine and hydroxyl amine as masking agents and wavelengths of the maximum absorbance for Al and Zn ions complexes were near from the wavelength of maximum absorbance for EBT as shown in table 1.

Table 1. wavelengths of the maximum absorbance for EBT and other compounds

Compound	λ_{max} nm
EBT	531
Al(III)-ethanolamine complex	412
Pb(II)-EBT complex	407
Zn(II)-cyanide complex	320

To ensure that there is no interference between the signal of reagent EBT and signals of Al(III) and Zn(II) cyanide complexes and Pb(II)-EBT complex, the absorption spectrum was recorded for a solution containing a 1 ml of reference solution, 2 ml solution (20% w/v) of NaCN, 15ml of triethanol amine, 3ml solution (10% v/v) hydroxyl amine, 5 ml of buffer solution pH 9, 10 ml of solution µg/µl of the (EBT) and diluted to 50 ml with deionized distilled water by using a UV-1600 Series by Shimadzu Scientific Instruments Inc. The blank solution was prepared at the same procedure without addition solutions of EBT and lead. Where the wavelengths of greatest absorption of EBT and Pd(II)-EBT complex are 531 and 407 nm respectively as shown in fig.1and fig.2 in this study. And the wavelengths of greatest absorption of complexes Al(III) ethanolamine and Zn(II) cyanide are 412 and 300 nm respectively(18).

4.2. Quantitative study

Quantitative analysis of lead in leaded aluminum alloy is performed by measuring the decrease in the absorbance of the EBT by the new developed method based on the calculation of the difference between the absorbance of EBT at its initial concentration (A_{L_o}) and its absorbance at residual concentration (A_{Lr}) as a result of its reaction with lead ions in the sample solution by using standard addition method and application of the following equation:

Absorbance of lead $A_{ML} = A_{L_o} - A_{Lr}$

Where $A_{L_o} = K\, C_{L_o}$

$A_{Lr} = K\, C_{Lr}$

C_{L_o} and C_{Lr} represent the initial and residual concentrations of EBT respectively.

The absorbance of 0.1 µg/µl EBT at λ_{max} (531 nm) is (0.358) as shown in fig.1. And the decrease in EBT concentrationis illustrated in fig.3.

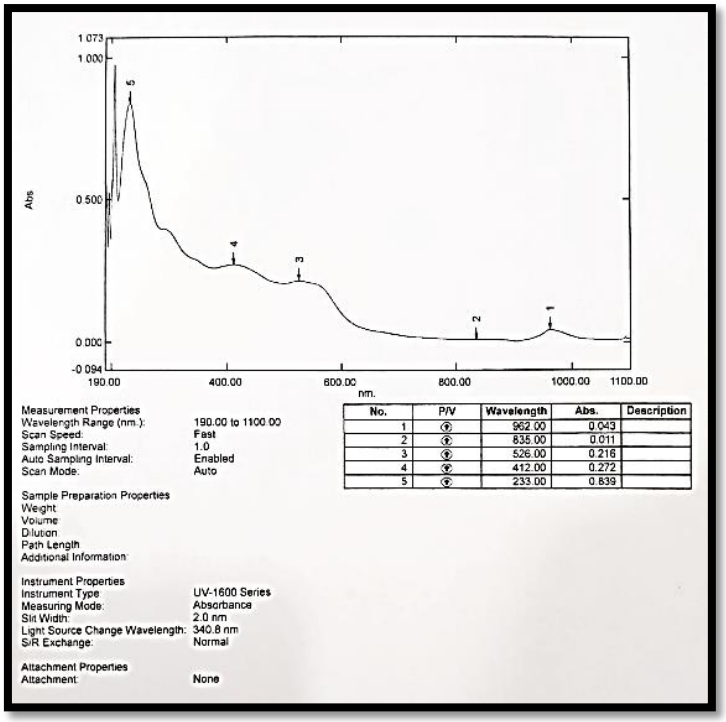


Figure 3. Absorption spectrum of the decrease in EBT concentration and increase in lead ions concentration.

Studies indicated that (15, 16) the molar ratio of Pb(II):EBT is 1:1. They contributed to the development of our new method for determining lead in the leaded aluminum alloy as shown in table 2.

Table 2. Data were used to obtain absorbance of Pb (II) as $A_{ML} = A_{L_o} - A_{Lr}$

No.	Volume of sample ml	Volume of standard ml	Volume of EBT ml	A_{L_o}	A_{Lr}	A_{ML}
1.	0	0	10	0.716	0.716	0
2.	1	0	10		0.5470	0.1690
3.	1	5	10		0.4625	0.2535
4.	1	10	10		0.3780	0.3380
5.	1	15	10		0.2935	0.4225
6.	1	20	10		0.2090	0.5070
7.	1	25	10		0.1245	0.5915
8.	1	30	10		0.040	0.6760

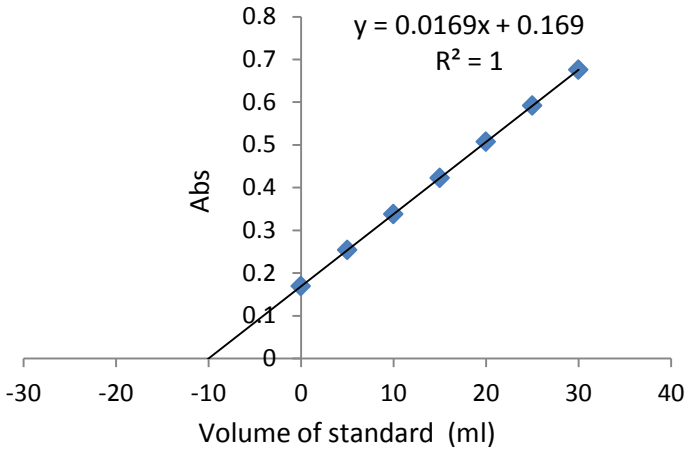


Figure 4. Standard additions curve to determine the lead in the preparative leaded aluminum alloy solution using the new developed spectral method

In general(18): $S=K*C_a$

Where: C_a = concentration of analyte = $(C_x . V_x + C_s . V_s) / V_t$

K = constant

S = instrument response (signal) = $K . (C_x . V_x + C_s . V_s) / V_t$

V_x = volume of the sample aliquot

C_x = concentration of the sample

V_s = volume of standard

C_s = concentration of the standard

$$S = K . C_s . V_s / V_t + K . C_x . V_x / V_t$$

From the linear regression: $y = m . x + b$

$y = S$

m = slope = $K . C_s / V_t$

$V_s = x$

b = intercept = $K . C_x . V_x / V_t$

The concentration of analyte can be calculated by applying one of the two equation :

$$C_x = b . C_s / m . V_x \text{ or } C = (V_s)_0 . C_s / V_x$$

Where $(V_s)_0$ is the volume of standard when the device response is zero.

Then the percentage of analyte in the sample is calculated by the following equation :

$Al\ \% = C_x . V . D.F . 100 / W$

Where C_x = Concentration of lead (µg/ml).

V = Markup volume (ml)

D.F = dilution factor

W = weight of sample

4.2. Calculation the accuracy and precision of developed method

In order to validate the developed 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. 5 as shown in Table 3.

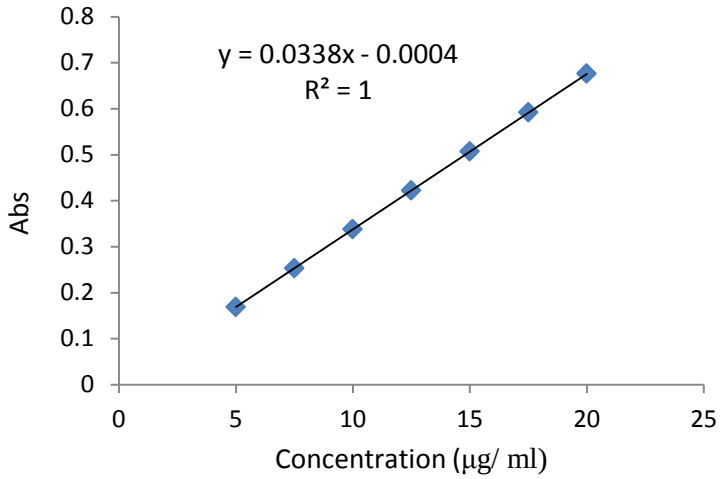


Figure 5. Calibration curve of the validation developed spectrophotometric analytical method

Table 3. Results of calibration curve analysis

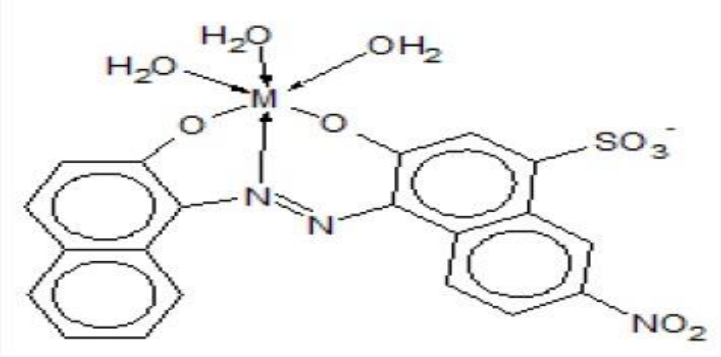
Parameters	Value
Accuracy	99.8321 ± 0.1321
Slope	0.0338
Intercept	0.0004
Linear range	0.1 – 40 µg ml^{-1}
Correlation coefficient	1.00
SE of intercept	1.95E-04
SD of intercept	5.17E-04
LOD	5.05E-02
LOQ	1.53E-01

5. Environmental study

One of several low cost adsorbents, PFAC displayed decent adsorptive features. PFAC material as an adsorbent is active for EBT elimination from dye solution. The adsorption of EBT was reliant on pH, original dye concentration, adsorbent amount as well as interaction time which were improved. The action of EBT is possible between pH of 4 and 6 whereas the maximum color removal was achieved at pH 6. The removal rate increased with the increase in adsorbent dosage and contact time while the rate decreased with the increase in EBT concentration and pH. The present study concluded that the Parthenium flowers activated carbon material as an adsorbent can be effectively utilized for the removal of EBT from aqueous environment(20).

6. Structure of complex

The structure of complex that was produced by reaction between Pb(II) and eriochrome black t as follows(14):



7. Conclusion

The our newly developed study is a spectrophotometric method for the quantitative determination of lead in alloys, which is a non-polluting method for the environment, so that the EBT reagent can be recovered from the solutions through the process of adsorption on activated carbon and reused again in the laboratory analyzes and the lead ions are precipitated by sodium carbonate and its separation and isolation without going to water.

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