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The Role of Lanthanum Chloride as a Releasing Agent for Iron in its Determination by Flame Atomic Absorption Spectrophotometer in Nitrate and Sulphate Media

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دور كلوريد اللانثانيوم كمحرر لتحديد الحديد باستخدام لهب طيف الامتصاص الذري في وسطى النترات والكبريتات

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لقد تم دراسة تأثير إضافة كلوريد اللانثانيوم لتحديد عنصر الحديد في عينات من النفط الخام تم تحضيرها في حمض النيتريك (15% بالحجم) وحمض الكبريتيك (5% بالحجم)، وتُشير النتائج أن كلوريد اللانثانيوم (0.5–1.0% كتلة/حجم) يعمل كمحرر لإمتصاص عنصر الحديد في وسط النترات بينما هبط تأثيره كخافض للإمتصاص في وسط حمض الكبريتيك في مدى تركيز للحديد يتراوح بين 3.0–0.5 جزء في المليون.

Abstract: *The effect of lanthanum chloride addition for iron content determination in crude oil samples prepared in 15% v/v HNO_3 and 5% v/v H_2SO_4, respectively, was studied. The results indicated that the addition of lanthanum chloride (0.5–1.0% m/v) serves as releasing agent for iron determination in nitrate medium, whereas the absorption is depressed in sulphate medium and this depression is proportionally increased by increasing iron concentration in the range of 0.5–3.0 ppm.*

INTRODUCTION

Flame Atomic Absorption is commonly used for trace metals determination (Sychra *et al*, 1981). Because of the fact that the absorption of radiation by individual atoms is a characteristic of the element, atoms of any other element do not normally absorb this radiation, which results in almost complete freedom from spectral interference in the method. However, other types of interference, for example, vaporization, ionization, or background, may be present (Willard *et al*, 1988). Different approaches are normally employed to overcome such interference. These include the addition of specific chemicals to minimize interference (Price, 1974). In this respect, some metal chlorides are commonly added to overcome various kind of interference, such as the addition of calcium and lanthanum chlorides to eliminate the phosphate and silicon interferences on strontium (Amos and Willis 1966). Similarly, excess sulphuric and hydrochloric acids were found to enhance the absorption of iron. On the other hand, Silicon was reported to suppress the absorption by iron, calcium and magnesium and the addition of lanthanum salt overcomes silicon interference of the aforementioned elements (Roos and Price, 1969, and Thompson and Reynolds, 1978). Although lanthanum chloride is widely used as a

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releasing agent during iron determination, in order to enhance the absorption signal produced by iron (Platte, and Marcy 1965), the effect of lanthanum chloride was found to depend on the digestion media. This paper describes the effects of adding variable concentrations of Lanthanum (as $LaCl_3$) for iron determination, in different acidic media.

EXPERIMENTAL

Analytical Procedure

A known amount (10 grams) of two crude oil samples A and B were dry ashed, and digested with 15% v/v HNO_3 and 5% v/v H_2SO_4, respectively. They were then subjected to Atomic Absorption Spectrometry using Pye Unicam, model SP9, equipped with a PU 9090 data graphic system and Pu 998 video graphic programmer. The instrument also has facilities of graphite furnace automatic sampling. Measurements were made with air acetylene flame in the absorbance mode; hollow cathode lamp and gases of high purity were used. The experimental parameters including spectral wavelength, hollow cathode lamp current, burner height, flame gases and spectral slit are listed in Table 1. The data were obtained by using calibration graph least mean square method with regression coefficient (r = 0.99969. Calibration graph of iron in aqueous media is represented (Fig.1).

Reagents

Chemicals of analytical reagents grade were used without further purification. The standard solutions of the element of interest were prepared by appropriate dilution from stock standard solution supplied by BDH chemicals Ltd, Poole, England. High purity doubly distilled water was used throughout this study.

Table 1. FAAS experimental conditions for iron determination

Wave length (nm)	Lamp current (mA)	Burner height (cm)	Fuel/oxida-nt (ratio)	Slit (nm)
248.3	14	7	20/35	0.2

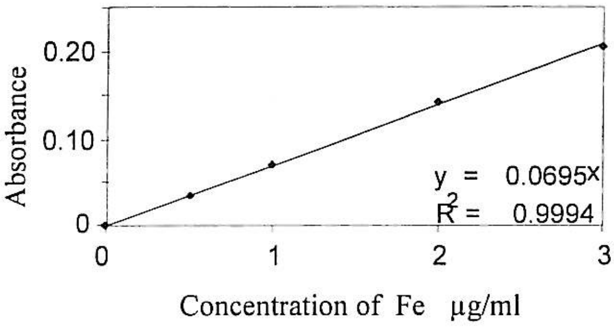

Fig. 1. Calibration curve of iron.

RESULTS AND DISCUSSION

The effect of interference which is generally accompanied by the addition of lanthanum chloride, on the iron determination, was studied. In the present study two sets of experiments were performed to assess the efficiency of the addition of $LaCl_3$ in nitric acid and sulfuric acid media. Also, four standard solutions of iron were used to assess the effect of lanthanum addition on iron absorption in sulphate medium. Table 2 summarizes the addition of $LaCl_3$ in nitric acid medium.

The results from Table 2 suggest that the addition of $LaCl_3$ liberate some iron from an interfering matrix so that sample A increased by 0.22 μgg^{-1} and sample B, by 1.00 μgg^{-1}. The addition of 1.0% m/v La^{3+} showed no significant increase which probably indicates that 0.5% m/v La^{3+} (as $LaCl_3$) is enough to overcome the problem of interference with iron. However results from Table 3 indicate that there is an obvious decrease in the results for the two samples through the addition of $LaCl_3$ in H_2SO_4 medium (A, –0.32; B, –1.03 for 0.5 m/v% La^{3+} addition and: A, –0.79; B, –1.64 for 1.0 m/v% La^{3+} addition respectively; all values are in μgg^{-1}. The reduction in the results

Table 2. Effects of $LaCl_3$ addition in nitric acid medium

Addition of La^{3+} (m/v%)	Concentration of iron in (μgg^{-1})*	
	Sample A	Sample B
0.0	20.87	25.07
0.5	25.07	26.07
1.0	21.10	26.09

*Average of triplicate results

Table 3. Effects of $LaCl_3$ addition in H_2SO_4 medium

Addition of La^{3+} (m/v%)	Concentration of iron in (μgg^{-1})* Sample A	Sample B
0.0	21.19	25.64
0.5	20.87	24.61
1.0	20.40	24.00

*Average of triplicate results

remains roughly proportional to the increasing $LaCl_3$ concentration. This indicates that the addition of $LaCl_3$ in H_2SO_4 medium depresses the iron absorbance.

Table 4 gives the iron absorbances in different media, and these results are illustrated (Fig. 2).

Table 4. Iron absorbance values (by FAAS) in different media

Fe(Conc.) μgml^{-1}	H_2O	5%v/v H_2SO_4	Enhance-ment (%)	0.5%m/v La^{3+} 5% H_2SO_4	Depression (%)
0.5	0.035	0.057	62.8	0.030	14.2
1.0	0.071	0.093	31.0	0.045	36.6
2.0	0.142	0.166	16.9	0.057	59.8
3.0	0.206	0.229	11.1	0.077	62.6

The percentage depression and the percentage enhancement were compared to the aqueous medium. From Table 4 it is clear that a general enhancement is caused by the addition of 5% v/v H_2SO_4 and this enhancement decreased with increasing iron concentration. The results indicate that the percentage enhancement, made by 5% v/v H_2SO_4 addition, is found to assume optimum value (62.8%) at low concentration. On other hand, the addition of 0.5% m/v La^{3+} to these acidified solutions caused a noticeable depression in iron absorption values. The percentage depression, contrary to the acidified only solutions was found to increase with iron concentration. It might be conjectured that the addition of $LaCl_3$ may react with H2SO4 to form a stable compound according to the following reaction.

$$2LaCl_3 + 3H_2SO_4 \rightarrow La_2(SO_4)_3 + 6HCl \quad (1)$$

Somehow, the formation of $La_2(SO_4)_3$ retards the nebulization process, resulting in a depressive effect on the iron absorption value. Another tentative explanation that sulfuric acid causes the precipitation of a relatively insoluble lanthanum sulphate (as given in equation 1 above) containing some of the iron occluded within the precipitate. Otherwise, iron absorption in nitric acid media has no noticeable effect compared to aqueous media. A final, concluding remark is supporting evidence from literature, where Curtis (1969), reported that for iron determination using air acetylene flame, interference is more pronounced in sulphate medium than in nitrate or chloride media. Therefore, for satisfactory iron determination in H_2SO_4 medium, the standard should contain the

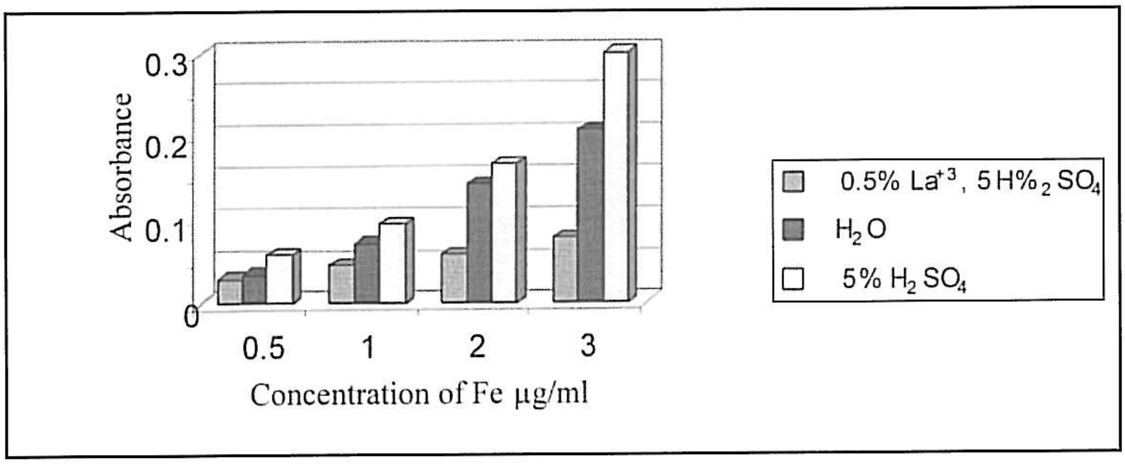

Fig. 2. Iron absorbance values (By FAAS) in different media.

same concentration of acid as that present in the analyte sample.

CONCLUSIONS

1. The addition of $LaCl_3$ serves as a releasing agent for iron in its determination by FAAS in nitric acid medium.
2. The addition of 1.0 – %m/v La^{+3} as ($LaCl_3$) showed no significant increase than that of 0.5% m/v La^{+3}.
3. In sulfuric acid medium $LaCl_3$ is considered as a severe depressant.

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REFERENCES

Amos, M. D. and Willis, J.B.,1966. *Spectrochim. Acta*, **22**, 1325.

Curtis, K. E., 1969. *Analyst*, **94**, 1068.

Platte, J. A. and Marcy, V. M.,1965. *At. Absorption Atom. Spect.*, 4,341–426.

Price, J. W.,1974. *Analytical Atomic Absorption* Spectrometry, Heyden & Son. Ltd.

Roos, J. T. H, and Price, W.J.,1969. *Analyst*, **94**,89.

Sychra, V., Lang, I. and Sebor, G., 1981. *Progr. Anal. Newsletter*, **4**, 289,

Thompson, K. C. and Reynolds, R.J.,1978. *Atomic Absorption, Fluorescence and Flame Emission Spectroscopy: Practical Approach*, 2nd ed., Charles

Griffin & Co, Ltd.

Willard, H, H., Merritt, L, L, Jr., Dean, J. A., and Settle, F, A., Jr., 1988. *Instrumental Method of Analysis*, Seventh, Edition, Wadsworth, Inc.P.250.