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ATOMIC ABSORPTION SPECTROPHOTOMETRIC INVESTIGATION OF IRON

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ABSTRACT

Investigation of the interferences of some foreign ions on the absorption signal of iron are carried out. A new, more pertinent method of expressing flame conditions is presented. Ammonium chloride is used to overcome chemical interference on iron.

INTRODUCTION

The importance of iron as an alloying element focused the attention for its investigation by the flame atomic absorption method. The literature [1-3] provides little detail on the actual magnitudes of interference on iron. Platte [4] showed that silicon interferes in the determination of iron. Some authors [5-7] have postulated that a number of ions, including silicate, sulphate, phosphate, ammonium ions and citrate ions can affect the iron response. Phosphoric acid [8] has been shown to overcome the interference of citric acid on iron. Mostafa [9] used both 4-aminosalicylic acid and sulphosalicylic acid for removing the interference of some organic and inorganic compounds.

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The aim of the present work is to investigate the action of reducing and oxidizing substances on iron atom population in the flame. Also to show that the magnitude of interferences depend on the flame parameters. In this work the author postulated the releasing action of ammonium chloride in the determination of iron.

EXPERIMENTAL

SP 90A Series 2 atomic - absorption spectrophotometer with HTA photo-tube was used. Air was supplied from a compressor and acetylene was obtained from cylinders then passed through concentrated sulphuric acid and glass wool for purification.

The instrumental parameters were : Lamp current, 12 mA; wavelength, 248.3 nm; slit-width. 0.1 mm: observation height, 0.4 cm; air flow-rate, 5.0 $dm^3.min^{-1}$ and fuel flow rate 1.5 $dm^3.mim^{-}$

The preparation of standard stock solutions was described in an earlier paper [9].

RESULTS AND DISCUSSION

1- Effect of foreign ions:

The effect of various species on the atomic absorption of iron was examined. The inhibition release titration method [10] is used to show such investigation. The changes in the absorption signal of 20 ppm Fe as a function of the molar ratio of the [interferent]/ [Fe] are indicated in fig.1. Except for NH_4Cl which enhanced the iron signal, all the investigated compounds have depressive effect. The enhancement effect of NH_4Cl may be due to the increase in sample introduction efficiency in harmony with that mentioned in literature [11]. According to Sastri et al [12], the depressive effect of resorcinol and pyrogallol may be explained by increasing Fe-O species in solution due to complex formation [9], thus increases the amount of Fe-O species in the flame and decreases the number of free atoms of the analyte element. The depressive effect of sodium tungestate, ammonium molybdate, ammonium vanadate and potassium periodate may be due to enrichment of the flame with oxidizing entities such as OH, O and O_2 which preclude complete atomization of iron in the flame.

Moreover, the presence of the trimer $MO_3O_{10}^{-2}$, $W_3O_{10}^{-2}$ and $V_3O_9^{-3}$, as suggested by x-ray studies [13], in the condensed phase, led to the processes of dispersion of iron in these volumnous molecules and depopulation of iron atoms in the flame occurs.

2- <u>Effect of observation height and flame composition</u>

The investigation of various combinations at different observation heights and constant acetylene flow rate 1.5 $dm^3.min^{-1}$ is illustrated in table 1. Since the oxide formation in the flame which is represented by equation (1) causes the main problem in AAS study of iron.

$$Fe_g + O_g \rightleftharpoons FeO \quad \ldots\ldots \quad (i)$$

The following conclusion may be explained as follows:

(i) The oxidizing compounds enrich the flame by oxidizing entities such as OH, O, O_2 and NO, thus shift the equilibrium in equation (i) to the right.

As the oxidizing species increases, the magnitude of shifting increases and the relative interference percent is high and is of the following order, observation height 1.2 cm > 0.8 cm > 0.4 cm, mixtures [1-6].

(2) The reducing compounds enriched the flame with reducing fragments such as NH, CH_4, CN thus reacting with FeO as the following:

$$FeO + NH \longrightarrow Fe + N + OH$$

$$FeO + CN \longrightarrow Fe + N + CO$$

Accordingly, shifting equilibrium in equation (i) to the left and the relative interference percent is low.
As the amount of reducing fragments increases, the shifting in equilibrium is increased and a lower degree in relative interference percent occurs. The amount of decrease is of the following order, observation height 0.4 cm > 0.8 cm > 1.2 cm, mixture [7-12].
(3) Mixtures of oxidized and reduced compounds are used and show no effect on iron at observation height 0.8 cm. But on oxidizing flame (1.2 cm) and reducing flame (0.4 cm), some oxidizing and reducing fragments are predominant and a shift in equilibrium (1), recognized in both directions, is attained, mixture [13 - 20].
(4) Mixtures of oxidizing compounds have a pronounced relative interference percent in the following order, observation height 1.2 cm > 0.8 cm > 0.4 cm, mixtures [22-25]
(5) Mixtures of reducing compounds have a small relative interference percent in the same order as in case (4), mixture [26-30].

It was found that the change of acetylene flow rate could have an effect on the magnitude of interferences. Table 2 shows the effect of change of this rate on the interference of some reducing substances on iron at constant observation height 0.4 cm.

The absorbance was measured at maximum sensitivity for the analyte alone for each of the four different fuel conditions. Since the reduced fragments produced from the decomposition of these compounds in the flame are excess in fuel-rich flame, than stoichiometric flame, than lean flame. Thus with a lean flame (1.0 dm^3 min^{-1}) the magnitude of interference is high.

3- <u>Elimination of interferences</u>

Data in Fig. 2 and table 3, support the use of ammonium chloride as flame buffer for iron. The addition of 0.25 M NH_4Cl to both samples and standards, restores the iron recovery percentage. The releasing action of NH_4Cl in the flame, may be due to its role in converting FeO which is easily formed in the flame (D_o = 4.3 ev) into FeH (D_o = 2.7 ev) [14]. The latter easily dissociates with an increase in the production of Fe atom population in the flame.

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Table 1- Effect of height of observation on Interferences on 20 $\mu g/ml$ Fe, at constant acetylene flow rate 1.5 $dm^3 min^{-1}$

No.	Added species (200ppm)	Relative interferences, % 0.4 cm	0.8 cm	1.2 cm observation height
1	KIO_3	-8	-14	-29
2	$K_2Cr_2O_7$	-6	-12	-30
3	$K_2S_2O_8$	-4	-10	-36
4	$(NH_4)_2MoO_4$	-6	-12	-30
5	NH_4VO_5	-9	-16	-40
6	KIO_4	-5.	-14	-48
7	* CAH	-4	-10	-16
8	** INH	-3	-10	-24
9	n-butylamine	-2	-8	-21
10	KI	-8	-16	-25
11	** NTA	-7	-14	-26
12	EDTA	-6	-12	-25
13	KIO_3 + CAH	-10	0	-14
14	KIO_3 + INH	-13	0	-18
15	KIO_3 + n-butylamine	-11	0	-16
16	$K_2Cr_2O_7$ + KI	-14	0	-19
17	$K_2Cr_2O_7$ + NTA	-14	0	-18
18	$K_2Cr_2O_7$ + EDTA	-13	-2	-19
19	$K_2Cr_2O_7$ + CAH	-9	0	-13
20	$K_2S_2O_8$ + KI	-12	0	-16
21	$K_2S_2O_8$ + n-butylamine	-10	0	-14
22	$K_2S_2O_8$ + $K_2Cr_2O_7$	-51	-66	-70
23	$K_2S_2O_8$ + KIO_3	-51	-65	-68
24	$K_2S_2O_8$ + KIO_4	-75	-84	-87
25	$K_2S_2O_8$ + NH_4VO_3	-59	-76	-80
26	CAH + INH	-10	-14	-21
27	CAH + KI	-12	-17	-20
28	CAH + n-butylamine	-11	-15	-18
29	n-butylamine + KI	-12	-18	-22
30	n-butylamine + INH	-16	-20	-22

* CAH cyanoacetylhydrazine
* TNH isonicotinic acid hydrazide
* NTA nitrilotriacetic acid

Table 2- Effect of oxidant/fuel ratio on interferences on 20 μg/ml Fe at constant observation height 0.4 cm

No	Added species (200 ppm)	Relative interference %			
		1.8	1.5	1.2	1.0 cm^3 min^{-1} Fuel flow rate
	None	0.28	0.32	0.22	0.18
1	KI	-8	-12	-25	-28
2	n-butylamine	-6	-10	-21	-26
3	INH	-5	-8	-24	-27
4	CAH	-3	-5	-16	-23
5	glycine	-1	-3	-20	-25

Table 3- Interference of various compounds (3.6×10^{-3} M) on 20 μg/ml (3.6×10^{-4} M Fe) without and with masking by 0.25 M ammonium chloride.

No	Added substance	Recoverd percentage	
		without masking	with masking *
	Catechol violet	72	98
	bromophenol blue	78	100
	4-aminosalicylic acid	82	102
	pyrogallol	75	100
	Resorcinol	70	98
	Hydroxylamine HCl	82	100
	triethylamine	115	98
	Hexamine	110	100
	Sodium tungestate	68	100
	n-butylamine	79	98
	Maleic acid	64	98
	Gallic acid	65	102
	Formamide	114	100
	Semicarbazide HCl	80	102
	glycine	68	102

* The absorbance of 20 μg/ml Fe plus 0.25 M NH_4Cl was taken as 100 recovery percentage . All other absorbance were normalized against this value .

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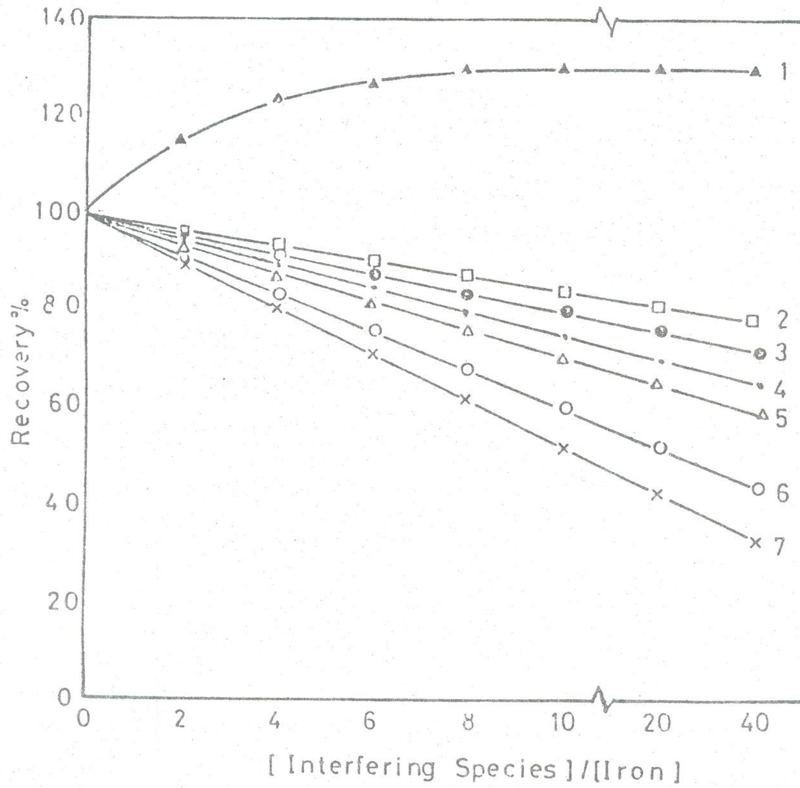

Fig . 1- Change in the absorption signal of 20 $\mu g/ml$ iron[3.6×10^{-4}M] as a function of interfering species: iron ratio: [1] ammonium chloride,[2] resorcinol ; [3] pyrogallol ; [4] sodium tungestate ; [5] ammonium molybdate ; [6] ammonium vanadate and [7] potassium periodate .

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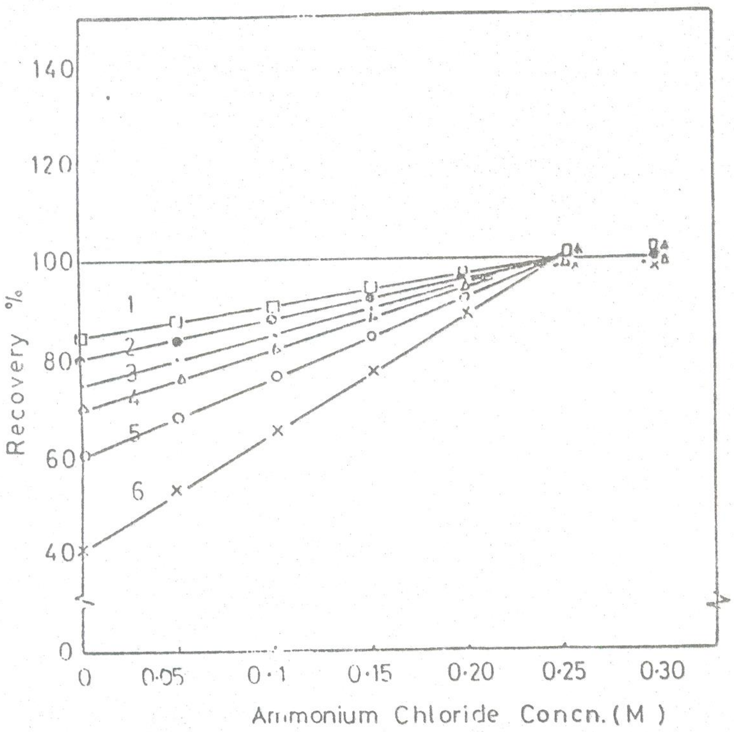

Fig .2- Effect of ammonium chloride on the absorbance of 20 $\mu g/ml$ iron in presence of $3.6\times10^{-3}M$: [1] resorcinol ; [2] pyrogallol ; [3] sodium tungestate ; [4] ammonium molybdate; [5] ammonium vanadate and [6] potassium periodate .

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بحـــث على عنصر الحديد بطريقـــة الامتصاص الذرى

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تم دراسة تأثير بعض المركبات العضوية وغير العضوية على اشارة الامتصاص الذرى لعنصر الحديد باستخدام جهاز معايرة حديث نسبيا متصلا بجهاز الامتصاص الذرى حيث امكن تحديد نوع المركبات المحتمل تكوينها فى اللهب.

وجـد ان جميع المواد المستخدمة لها تأثيرا مهبطا على خط الامتصاص لعنصر الحديد باستثناء كلوريد الامونيـــوم.

فســرت تدخلات بعض المركبات الفينولية على اساس تكوين متراكب مع الحديد وبالتالـى زيادة Fe-O فى الهب وبالتالى نقصان فى عدد ذرات الحديد المتعادلة وكذلك امكن تفسير بعض المركبات غير العضوية على اساس انها عوامل موءكسدة وتزيد من الكفاءات الموءكسدة فى اللهب مثل O_2، O, OH وبالتالى تعوق عملية تكوين الذرات المتعادلة الكامل فى اللهب لعنصر التحليل.

كذلك تم دراسة تأثيرات بعض المركبات الموءكسدة والمختزلة عند ارتفاعات رصد متغيرة وايضاح دورها على خط امتصاص عنصـــر الحديد.

اتضح أن كلوريد الامونيوم يزيل جميع هذه التداخلات وبكفاءة عالية واستغل هذا المحرر لايجاد طريقة تحليلية بسيطة تعتمد على اضافة ٢٥ر٠ مولار منه الى عينات الحديد التى تحتوى على عناصر متداخـلة.