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Establishment of a method for the improvement of the sensitivity of Atomic Absorption Spectrometer (AAS) for zirconium

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ABSTRACT

Due to refractory nature of zirconium oxide, the sensitivity of Zirconium in Flame Atomic Absorption Spectrometer (FAAS) is low even with nitrous oxide-acetylene flame as the maximum temperature reached is insufficient to break down the compound of Zr and other refractory elements and hence the sensitivity of FAAS for Zr is too low to be measured. Several compounds of fluorides and ammonium ions reported in the literature have been tried for the enhancement of absorption signal of Zr by FAAS and determined the optimum concentrations of NH_4F and HF+Al for enhanced absorption signal. A mixture of HF and Aluminium Salt has been found to be most effective in the enhancement of absorption signal. Results and optimum concentration of the added species for the enhancement of sensitivity of FAAS for Zr have also been reported in this paper.

KEYWORDS

Zirconium Sensitivity;
Flame Atomic Absorption Spectrometry (FAAS);
Hydrofluoric acid;
Aluminium Salt.

INTRODUCTION

Increasing use of Zirconium in High Energy Materials such as Pyrotechnics (as metal fuel), Ramjet Propellants, Solid Propellant Thruster (Zirconium Perchlorate Potassium, ZPP and Glycidyle Azide Polymer mixed with Ammonium Perchlorate and Zirconium, GAP/AP/Zr), and Incendiary Compositions[1-3], etc has drawn attention for the analysis of Zirconium and Zirconium Compounds for quality assurance. The Zirconium is analysed by Flame Atomic Absorption Spectrometer (FAAS). But, due to the refractory nature of its oxide, maximum temperature of flame even with nitrous oxide-acetylene flame is inadequate to break down the compounds because of the interelemental and chemical interferences in the nitrous oxide-acetylene flame[4]. As a result, the sensitivity response of FAAS for Zr and other refractory metals such as Ti is not good as other elemental analysis techniques. In an unpredictable fashion, certain elements or compounds can cause either suppression or enhancement of the absorbance of the element being measured. The aim of this study was to identify such elements or compounds which can enhance the sensitivity of Zr analysis in FAAS.

The extensive survey of literature revealed that the use of fluoride compounds enhances the absorbance of Zr not only in the FAAS but also in the Graphite Furnace Atomic Absorption Spectrometer (GFAAS)[5]. It has also been observed that the ammonium ion and a considerable number of other nitrogen containing compounds cause enhancement of the Zr absorption in the Nitrous oxide-acetylene flame[6]. Therefore, the present study deals with the improvement of atomic absorption of FAAS by the possible use of several fluoride compounds (NaF, NH_4F & HF), ammonium compounds (NH_4Cl, NH_4F) and HF + Aluminium salt mixture and the subsequent determination of their optimum concentration for the enhancement of absorption signal. Of the several compounds tried for sensitivity enhancement, a mixture of HF and Aluminium Salt has been found to be most effective in the enhancement of absorption signal.

EXPERIMENTAL

Chemicals and Reagents

All chemicals and reagents used were of analytical grade. Zirconium solutions were prepared by diluting Merck Standard of 1000 ppm (or mg/L). All the solutions contained 0.1 M KCl to suppress the ionization interference for Zr in nitrous oxide-acetylene flame. Calculated amount of added species dissolved in the Zr standards to get the desired concentrations.

Instrumental Procedure

All atomic absorption measurements were carried out by using AA800 Atomic Absorption Spectrometer (Perkin Elmer, USA) fitted with 5cm burner head, 0.7 nm slit width and with nitrous oxide-acetylene flame having 7.8 l/min C_2H_2 flow. Absorptions were measured in fuel rich flame and with Hollow Cathode Lamp (HCL) of Zr made by Perkin Elmer. All atomic absorption measurements for Zirconium were made at the wavelength of 360.1 nm.

The Zr standard solutions with and without added species were aspirated through the flame and absorbances were recorded (TABLE 1 and 2).

RESULTS AND DISCUSSION

TABLE 1 summarizes the influence of various added species on the absorbance of Zirconium and Figure 1 shows the absorbance vs. concentration curves for various zirconium solutions. From the graph it shows considerable increase in sensitivity of the instrument for Zr in the presence of 0.1 M of KCl, NaF, NH_4F, NH_4Cl and HF (along with Al) each. However, the extent of enhancement varies with the nature of the species added. The presence of 0.1 M KCl enhances the absorption approximately 1.5 times by suppressing the ionization interference. For the same concentration of Zr, the absorbance varies with the concentration of added species. It is also dependent on the concentration of Zr as given in TABLE 1. For example, for the same concentration of 50 ppm of Zr, the addition of 0.1 M NH_4Cl and 0.1 M NH_4F have enhanced the signal by 2.5 times and 2.7 times respectively where as 0.1 M of HF along with added 0.1M Al has led the absorption to 3.4 times. The same is also evident with higher concentration of Zr. However, the factor by which the absorption signal gets enhanced is somewhat lower but the trend remained the same. As expected from literature, NH_4F has shown marked enhancement on the absorption signal of Zr. These experimental facts are further supported by the observed effects of NH_4Cl and NaF separately on absorbance. However, it is the added species of HF+Al, which has shown the maximum enhancement of absorbance for a given concentration of Zr.

TABLE 1 : Influence of various added species on the absorbance of Zr

Chemicals Used	*Absorbance with 50 ppm*	*Absorbance with 100 ppm*	*Absorbance with 200 ppm*
Zr Standard w/o KCl	0.010	0.026	0.068
Zr Standard with 0.1 M KCl	0.016	0.029	0.072
Zr Standard with 0.1 M NaF	0.018	0.034	0.075
Zr Standard with 0.1 MNH_4Cl	0.024	0.047	0.103
Zr Standard with 0.1 M NH_4F	0.027	0.053	0.114
Zr Standard with 0.1M HF & 0.1M Aluminium	0.034	0.062	0.122

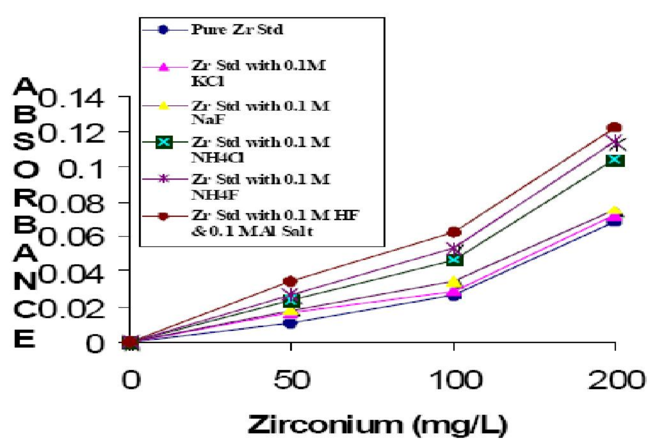

Figure 1 : Influence of various added species on the absorbance of Zr

The concentration dependence of added species have been studied for NH_4F and HF+Al as these two species have shown marked enhancement as compared to others. TABLE 2 summarises the influence of concentration of added species on Zr sensitivity for 100-ppm standard solution for different molar concentrations and graphically represented in Figure 2. The basic shape of both the curve is almost same but the HF+Al has much enhanced effect on Zr absorption. After reaching 2.5 times for NH_4F and 3.2 times for HF+Al, the absorbance becomes almost constant and the corresponding concentration of both the added species being 0.5M. This means that 0.5 M is the optimum concentration of both the added species for the enhancement of Zr absorption signal in AAS.

TABLE 2 : Influence of concentration of added species on Zr sensitivity

Conc. of Added Species	*Absorbance of 100 ppm of Zr Standard with NH_4F**	*Absorbance of 100 ppm Zr Standard with HF+ Al Salt#*
0.0 M	0.028	0.028
0.1 M	0.052	0.061
0.3 M	0.059	0.075
0.5 M	0.064	0.082
0.7 M	0.066	0.083

Published Work [8] # Present Study

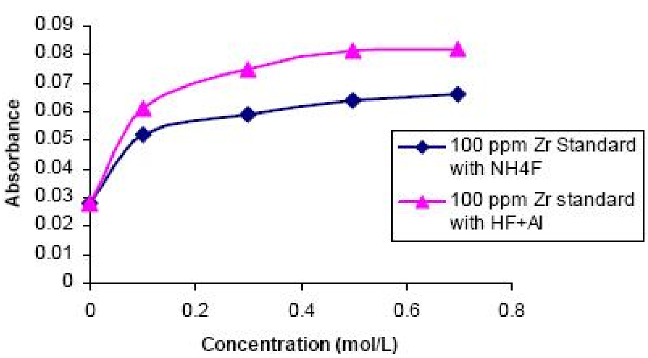

Figure 2 : Influence of Concentration of added species on Zr Sensitivity

In the absence of any activating species, Zr dries out in the flame as refractory oxides with high melting point and thereby making atomization inefficient. The melting point of its refractory oxide ZrO_2 is 2700C and therefore difficult to decompose even in nitrous oxide-acetylene flame with flame temperature 2500-2700°C. The same element form very strong fluoride complex in solution, and therefore in the presence of fluoride it dries out in the flame as volatile fluorides (m.p. of ZrF_4 being 912°C) which leads to greater efficiency of atomization than in the absence of fluorides, and gives rise to the observed enhancement of absorbance[4,6]. The effect of HF in presence of Al in the improvement of absorbance is probably due to the formation of a fluoride complex of Zirconium with Aluminium ($Al_2[ZrF_6]_3$ or $Al[ZrF_7]$ or both) and the flame temperature is sufficient for rapid decomposition of the complex resulting in efficient atomization. The effect of ammonium ion on the enhancement of Zr is similar to that caused by fluoride ions. The effect appears to involve the formation of Zirconium-nitrogen bond as literature shows that a number of nitrogen containing compounds also caused enhancement of zirconium absorbance in the nitrous oxide-acetylene flame[6,8]. The most probable reason being Zr-N bond is easier to be broken in comparison to Zr-O bond of ZrO_2 in the flame and this further leads to greater atomization efficiency.

CONCLUSION

It can be concluded that for the determination of Zirconium by the atomic absorption method, the addition of 0.5 M HF and Aluminium (in the form of Al salt) in all standard as well as unknown solutions will enhance the sensitivity of FAAS by approximately three to four times. Furthermore, many of the interferences are either removed or greatly suppressed in this method. The addition of HF and Al salt is also expected to be useful in the determination of other refractory elements having low sensitivity in FAAS.

REFERENCES

[1] B.Berger; Chimia, **58**, 363 **(2004).**
[2] S.Calsson, H.Schmid; US Patent 5339624 **(1994).**
[3] A.B.Chaalane, B.Larangôt, C.Rossi, H.Granier, D.Estève**;** CANEUS 2004—Conference on Micro-Nano-Technologies, AIAA-6706 **(2004).**
[4] A.M.Bond, T.A.O'Donnell; Analytical Chemistry; **40**, 560 **(1968).**
[5] A.A.Frishberg; Russ.J.Appl.Spectrosc., **5**, 8 **(1966).**
[6] A.M.Bond, J.B.Willis; Analytical Chemistry; **40**, 2087 **(1968).**
[7] F.A.Cotton, G.Wilkinson, C.A.Murillo, M.Bochmann; Advance Inorganic Chemistry, 6th edition; Wiley-India **(2004)**.
[8] A.M.Bond; Analytical Chemistry; **42**, 932 **(1970).**