Pakistan Journal of Applied Sciences 2(3): 405-407, 2002

Study of Interference in the Flame Atomic Absorption Spectrometric Determination of Aluminum by Using Factorial Design

M.Mazloum
Department of Chemistry, Kashan University, Kashan, Iran

Abstract: Acid rain (rain with a pH of less than 5.6) is able to leach several metals from sediments and soils, among the metals that pass into ground water and, some times surface water is aluminum, which is believed to be toxic to fish, other aquatic organisms and several plant species. Difficulties is measurement of aluminium by AAS arises from the effect of interferences generally results in relatively high detection limits. This paper deals with the mathematical evaluation of important experimentel parameters including concentration, burner height, lamp current and fuel/oxidant ratio influencing the AAS response of aluminium. Factorial design was used to obtain reliable information for the effects of each parameter or their combined influence. The statistical models obtained make it possible to evaluate the weight to any experimental value and obtain an idea for possible analytical application of the systems studied. Results indicates that the most significant input factors affecting absorbtion signal are the instrumental parameters. The effects of lamp current and burner height are positive, but the effect of concentration of anions is negative.

Keywords: Atomic Absorption, Spectrometric Determination and Factorial Design

Introduction

The effectiveness of flame atomic spectroscopic procedures for analysis of elements depend not only on the external variables such as the fuel and oxidant flow rates, flame height, sample uptake rate, dimensions of the burner head, nebulizer efficiency and etc., but also on the internal variables such as the nature of the solvent and kinds of concomitant species present in solution. The presence of some cations and anions can severely effect the absorption or emission signal of the analyte. Unfortunately in many cases the effect of concomitant species is not linear, so that the standard addition method is not applicable. Detailed information for particular elements can be found in references(Herrmann and Alkkemade, 1963; Elwell and Gidley, 1966; Robinson, 1966; Slavin, 1968; Schrenk, 1975; Price, 1979 and Cantle, 1982).

Parczewski and Rokosz have explained the application of experimental design to study the effect of interfering species(Parczewski and Rokosz, 1978 and Simenov *et al.*, 1992. In this paper the application of factorial design on the atomic absorption signal of aluminum is described. Acid rain (rain with pH of less than 5.6) is able to leach several metals from sediments and soils, among the metals that pass into grand water and, some times surface water is aluminum which is believed to be toxic to fish, other aquatic organisms, and several plant species (Baraj *et al.*, 1999). The forms of aluminum in water included the hydrated ion, Al $(H_2O)_6^{3+}$, relatively weak inorganic complexes and strong organic complexes and there is evidence that the toxicity decreases in this sequence. The aluminum levels of concern are µg/L(ppb). Any study of the aluminum toxicity of water would be aided if one could determine the ionic aluminum rather than simply the total aluminum. The approach of Campbell *et al.* (Massart *et al.*, 1988) was to equilibrate with a chelating ion exchange resin and determine the non-exchanged aluminum remaining in solution: the exchanged or ionic aluminum amounted to the difference between the first value and the total. Most of their actual aluminum determinations were made by atomic absorption spectroscopy(AAS) although the Lumogal spectrofluorometric method was also found to be satisfactory. The paper deals with the mathematical evaluation of important experimental parameters(concentration, current lamp, fuel/oxidant ratio and height burner) influencing the AAS response. Factorial design was used to obtain reliable information for the effects of each parameter or their combined influence. The statistical mode obtained makes it possible not only to evaluate the weight of any experiment value but- also to have an idea for possible analytical application of the systems studied.

Material and Methods

Reagents and Apparatus: The aluminum stock solution was prepared from $Al(NO_3)_3.9H_2O$ (Merck).
Merck analytical grade metallic chloride and nitrates were used in the preparation of the solutions of other metals. Flasks were polypropylene and were acid -water washed prior to use. The atomic absorption analysis was performed using AAS Perkin-Elmer model 2380 in the absorption mode. Nitrous oxide /acetylene flame was used.Gas flows and sample up-take volume were optimized for obtaining the maximum sensitivity. The instrumental parameters were wavelength 309.3 nm, band pass 0.7nm and burner height 5 cm.

Method used for the study of interference: The methodology utilized in factorial design requires the formulation of a mathematical model approximating the relationship between the measured signal(aluminum absorbance is the response to be monitored) and the concentrations of the reagents investigated. The compositions of the samples are selected on the basis of experimental design involving 2^n factorial (Massart *et al.*, 1979).

It is important to note that a series of experiments were carried out according to the two levels of variation design (each input parameter was varied only two levels of its possible values). Inputs were chosen for evaluation: concentration of the active substance, flow rates of fuel and oxidants, burner height and current lamp. As output function the value of the absorption was used. The traditional experimental design applied to all measurement systems is shown in Table 1, where both levels of variation are presented by "-" and "+" signs.

Table 1: Factorial Design of 2^n Type

Signal	ABC	BC	AC	AB	C	B	A	Factors Z	No. of Experimet
0.158	-	+	+	+	-	-	-	+	1
0.180	+	+	-	-	-	-	+	+	2
0.097	+	-	+	-	-	+	-	+	3
0.119	-	-	-	+	-	+	+	+	4
0.090	+	-	-	+	+	-	-	+	5
0.100	-	-	+	-	+	-	+	+	6
0.094	-	+	-	-	+	+	-	+	7
0.116	+	+	+	+	+	+	+	+	8

Results and Discussion

In the first experiment, the effect of SO_4^{2-} and PO_4^{3-} was considered. The levels of SO_4^{2-} and PO_4^{3-} were 0 , 20 ppm and 0 , 20 ppm respectively. The absorption signal of the solutions was measured and results of the full factorial design are given in Table 1. From Table 1 the values of the regression coefficients are as follows:

$b_0 = 0.12$, $b_1 = 0.0096$, $b_2 = -0.013$, $b_3 = -0.019$

From replicate measurements of solution the standard deviation of the coefficients can be calculated.The regression equation is:

$$Y=1.2\times10^{-1}+95.8\times10^{-4}A-12.8\times10^{-3}B-19.2\times10^{-3}C+14.2\times10^{-4}AB-14.2\times10^{-4}AC+17.7\times10^{-3}BC+15.8\times10^{-4}ABC \quad (1)$$

Where coefficients of A, B, C, AB, AC, BC and ABC represent the effects of sulfate, phosphate and the interaction of aluminum - sulfate - phosphate respectively. From the regression equation (equation 1), it may be concluded that sulfate and phosphate has depressing effect on aluminum signal. The interactive effect of aluminum – sulfate - phosphate on aluminum signal is enhancing.

In the second experiment the effect of flow rate of fuel (40 – 45 ml/min), flow rate of oxidant (30 – 35ml/min) and burner height (7 – 8 mm) were considered.

The experiments and calculations were carried out the same as in the previous experiment. The results are given in Table 2.

Table 2: Factorial Design for The Effect of Flow Rate Fuel, Oxidant and Burner Height on Aluminum Absorption Signal

No of experiment	signal
8	0.459
7	0.416
6	0.874
5	0.675
4	0.973
3	0.818
2	0.929
1	0.855

Calculations are the same as before, and the regression equation is:

$$Y=6.9\times10^{-1}+80.7\times10^{-3}A-22.9\times10^{-2}B-13\times10^{-3}C+21.2\times10^{-3}AB-44.1\times10^{-3}AC-15\times10^{-3}BC-36.3\times10^{-3}ABC \quad (2)$$

From equation 2, it can be concluded that only flow rate of fuel show enhance effect on aluminum signal, but flow rate of oxidant shows depress effect on aluminum signal. The interactive effect of flow rate fuel, oxidant and burner height on aluminum signal is also significant.

In the third experiment for the effect of current lamp and burner height on aluminum signal, the concentration of aluminum was also considered as a factor in the factorial design (i.e. the concentration of aluminum was varied). The results of the experiment are given in Table 3.

Table 3: Factorial Design for Current Lamp and Burner Height on Aluminum Signal With Variation of Aluminum Concentration

No. of experiment	Signal
8	0.261
7	0.211
6	0.229
5	0.206
4	0.223
3	0.196
2	0.216
1	0.190

Calculations were carried out the same as in the previous experiment and the regression equation is:

$$Y=2.2\times10^{-1}+15.7\times10^{-3}A+62.5\times10^{-4}B+10.3\times10^{-3}C+37.5\times10^{-4}AB+25\times10^{-4}AC+30.8\times10^{-4}BC+32.5\times10^{-4}ABC \quad (3)$$

From equation 3, also can be concluded that both current lamp and burner height on aluminum signal show enhancing effect. The interactive effect of current lamp, burner height and concentration of aluminum on signal is significant.

All experiments were studied by flame atomic absorption spectrometry at wavelength 309.3 nm. Also above experiments were considered by flame AAS at 396.2 nm. Results are given in Tables and equations of 4, 5and 6 respectively.

However, in this case, regression equations show which similar effects on aluminum signal as in the first experiments (at wavelength 309.3nm).

Table 4: Factorial Design for Sulfate and Phosphate Effects on Aluminum Signal with Variation of Aluminum Concentration (At Wâvelength, 396.2 nm)

No. of experiment	signal
8	0.027
7	0.022
6	0.030
5	0.023
4	0.029
3	0.032
2	0.031
1	0.037

In this case the regression equation is:

$$Y=2.6\times10^{-2}+66.7\times10^{-5}A-6.7\times10^{-4}B-83.3\times10^{-6}C+14.2\times10^{-4}AB-23.3\times10^{-11}AC+11.7\times10^{-4}BC-41.7\times10^{-5}ABC \quad (4)$$

Table 5: Factorial Design for The Effect of Flow Rate Fuel, Oxidant and Burner Height on Aluminum Absorption Signal (At Wavelength 396.2 nm)

No. of experiment	Absorbance
8	0.027
7	0.014
6	0.128
5	0.040
4	0.015
3	0.087
2	0.085
1	0.034

The regression equation is:

$$Y= 5.4x10^{-2}+10.1x10^{-3}A-18x10^{-3}B-14.2x10^{-4}C -24.8x10^{-3}AB + 15.1x10^{-3}AC - 13.8x10^{-3}BC + 58.3x10^{-4}ABC \quad (5)$$

Table 6: Factorial Design for Current Lamp and Burner Height on Aluminum Signal with Variation of Aluminum Concentration (At Wavelength 396.2 nm)

No. of experiment	Absorbance
8	0.011
7	0.019
6	0.021
5	0.014
4	0.013
3	0.001
2	0.018
1	0.012

Also, the regression equation is:

$$Y=1.6x10^{-2}+25.8x10^{-4}A+33.3x10^{-5}B+25.8x10^{-4}C -58.3x\ 10^{-5}AB-16.7x10^{-5}AC+12.5x10^{-4}BC- 33.3x10^{-5}ABC \quad (6)$$

From study equations (1-3) with (4-6), it is concluded that similar results have at two wavelengths.

The evaluation approach makes it possible to distinguish between linear effects of the inputs (by the values of the single regression coefficients a_i) and deviations from linearity (by the value of the mixed regression coefficients a_{ij} and a_{ijk}).The adequate statistical models for the systems in consideration are (adequacy was checked by F- test).

Where y is the output function (absorption), and A, B, C, AB, AC, BC and ABC indicates the coded value of the input parameters (the real value is transformed in such a way that A, B, C, ... for any parameter is between ±1).

Conclusion

The following conclusions can be made from the statistical analysis thus performed:

- The concentration of the anionic effect is relatively high but not so substantial as that of instrumental parameter. Equation of 1 shows concentration of aluminum has positive effect (increase of absorption with increasing concentration), but concentration of sulfate and phosphate have negative effect (decrease of absorption with increasing concentration).
- The most significant input factor to reach a substantial absorption effect is The instrumental parameters [flow rates of fuel (A), oxidant (B) and burner height (C)]. The direction of influence, however is the same (negative) and this holds true for all systems. Thus the best of flow rate fuel is 40 ml/min and flow rate oxidant is 30 ml/min.
- The most significant instrumental parameter was related to effect of current lamp and height burner. As equation (3) shows effect of current lamp and height burner are positive (increase of absorption with increasing current lamp and height burner).

As it is seen from the above results the effect of the matrix may be enhancing or depressing. These effects can not be eliminated by the conventional methods such as standard addition method, and internal standard. Chemical treatments are also not applicable in many situations. Therefore, the effects of such interferences must be considered for each sample and necessary corrections be made. For each system after finding the matrix parameters, the regression equations are obtained using appropriate factorial designs.

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