Technical Overview

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Characteristic Mass in Graphite Furnace Atomic Absorption Spectrometry

Introduction

In flame atomic absorption spectroscopy (AAS), the sensitivity is defined as the concentration of analyte that produces 1% absorption signal (0.0044 Abs). This proved to be a very valuable diagnostic concept. When instrumental conditions were set correctly, this value for sensitivity was very predictable. As graphite furnace AAS deals with an absolute amount of analyte, it seems preferable that mass be substituted for concentration. By analogy with flame AAS, it is defined as the amount in mass units that produces 0.0044 integrated absorbance (1% absorption).

Characteristic Mass

In 1955, Alan Walsh (*1*) noted that graphite furnace AAS could be an absolute method. In 1984, Walter Slavin (*2*) proposed the concept of characteristic mass in graphite furnace, defined as the absolute mass of analyte giving a peak area of 0.0044 absorbance. In 1986, Boris L'Vov (*3*) published a comparison of the theoretical and calculated characteristic mass for 40 elements using integrated absorbance signals. If the results showed some limitations of the absolute method, the experimental characteristic mass became a tool to control/check the day to day operation of a given GFAAS instrument and the applied methodology.

The Stabilized Temperature Platform Furnace (STPF) concept (*6*), developed by Slavin in 1981, demonstrated that the characteristic mass can be relatively independent of the sample matrix.

Theoretical characteristic masses were calculated with the model developed by L'Vov in 1986 (*3*). This correlation can be used to optimize operating conditions and steps of the temperature program to give an experimental mass close to theoretical characteristic mass.

The theoretical characteristic mass, m_0 (pg) is calculated from the parameters which describe the absorption process, the mean residence time of atoms in the atomizer, and is directly dependent of the tube length and radius:

$$m_0(pg) = 0.508 \frac{A_r \Delta\nu_D D}{\mathrm{H}(\acute{\alpha},\omega)\gamma\delta_\mathrm{f}} \, x \, \frac{Z(T)}{g_1 \exp\left(-{E_1}/{kT}\right)} \, x \, \frac{r^2}{l^2}$$

The calculation of characteristic mass assumes:

- Atomization occurs from one point in the tube center
- Temporal and spatial isothermality
- Homogeneous cross-sectional atom cloud distribution
- 100% atomization efficiency
- No ionization of analyte atoms
- Diffusion of atoms from the center to the tube ends

Knowing the graphite tube geometry (length and radius) as well as the element of interest and wavelength, it is possible to calculate the characteristic mass (theoretical response of the atoms in the tube).

Experimental characteristic masses can be calculated by using the equation below. The absorbance in the equation is the measured integrated absorbance for a volume of a known concentration of analyte injected in the atomizer. Table 1 gives the experimental characteristic masses for principal elements analyzed in graphite furnace. Data was generated by using an Agilent 240 Zeeman graphite furnace AAS.

$$m_0\,(pg) = \frac{Vol(\mu l) \times [Conc.\ (pg.\mu l^{-1})\,] \times 0.0044}{Abs.}$$

Table 1. Typical experimental values of the Characteristic Masses of elements and for a Zeeman background correction instrument.

Element	Wavelength	Atomization*	240Z Characteristic mass m_0 (pg)
Ag	328.1	Platform	3.0
Al	309.3	Platform	7.5
Al	396.2	Platform	11
As	193.7	Platform	13
Au	242.8	Tube or Platform	9.0
B	249.8	Tube	700
Ba	553.6	Tube	10
Be	234.9	Tube or Platform	0.8
Bi	306.8	Platform	18
Ca	422.7	Tube	1.2
Cd	228.8	Platform	0.4
Co	242.5	Tube or Platform	9.0
Co	240.7	Tube or Platform	6.0
Cr	357.9	Tube	2.5
Cs	852.1	Tube	6.0
Cu	324.8	Tube or Platform	5.0
Cu	327.4	Tube or Platform	10
Fe	248.3	Tube or Platform	4.0
Ga	287.4	Platform	12
Ge	265.1	Platform	17
Hg	253.7	Platform	75
In	303.9	Platform	20
K	766.5	Tube	1.0
Li	670.8	Tube	0.8
Mg	285.2	Tube or Platform	0.35
Mn	279.5	Tube or Platform	1.6
Mo	313.3	Tube	5.5
Na	589.9	Tube	0.7
Ni	232.0	Tube or Platform	9.0
P	213.6	Tube	5600
Pb	283.3	Platform	13
Pb	217.0	Platform	6.5
Pd	244.8	Tube	12
Pd	247.6	Tube	17
Pt	265.9	Tube	120
Rb	780.0	Tube	3.5
Rh	343.5	Tube	13
Sb	217.6	Platform	15
Sc	391.2	Tube	30
Se	196.0	Platform	20
Si	251.6	Platform	38
Sr	460.7	Tube	1.3
Sn	286.3	Platform	21
Te	214.3	Platform	16
Ti	364.3	Tube	45
Tl	276.8	Platform	16

** The proposed atomisation mode will assist to achieve best performance.*

Element	Wavelength	Atomization*	240Z Characteristic mass m_0 (pg)
Tm	371.8	Platform	3.5
V	318.5	Tube	20
Yb	398.8	Tube	1.5
Zn	213.9	Platform	0.3

To obtain the best characteristic masses, it is crucial to have optimum values for ash and atomization temperatures (*4*) but also the optimum amount of a specific modifier. As reported in literature, if a certain quantity of modifier can enhance the sensitivity, a higher amount of modifier can cause an increase in the background and decrease the sensitivity (*5*).

Characteristic mass is also a very powerful tool to predict the absorbance of a solution injected in the graphite tube. It was demonstrated by L'Vov (*3*) that the Stabilized Temperature Platform Furnace (STPF) concept provides the highest sensitivity that can be reached in graphite furnace AAS. Using the STPF concept and knowing the characteristic mass for the element of interest in these conditions it is possible to estimate the concentration of an unknow sample.

Characteristic mass and surface response methodology can be routinely used during the optimization of the furnace temperature program for GFAAS analysis in order to obtain the best sensitivity.

References

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