

Some problems connected with boron determination by atomic absorption spectroscopy and the sensitivity improvement

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Two atomizers were compared: an $N_2O-C_2H_2$ flame and a stabilized U-shaped DC arc with aerosol supply. Both the high plasma temperature and the reducing atmosphere obtained by acetylene addition to the argon stream substantially increase the sensitivity of boron determination by atomic absorption spectroscopy (AAS) when the arc atomizer is used. The results were compared with those for silicon as a control element. The experimental characteristic concentrations for both elements were compared with the computed values. The experimentally obtained characteristic concentration for boron when using the arc atomizer was in better agreement with the calculated value. It was estimated that the influence of stable monoxide formation on the sensitivity for both elements was about the same, but reduction of analyte and formation of non-volatile carbide particles was more important for boron, which is the main reason for the low sensitivity of boron determination using a flame atomizer. The use of an arc atomizer suppresses this interference and significantly improves the sensitivity of the determination.

Keywords: boron, atomic absorption spectroscopy, characteristic concentration, DC arc plasma.

INTRODUCTION

In our laboratory, a U-shaped DC arc, with argon as the supporting gas, has been used for a long time as the excitation source for spectrochemical analysis. The construction details of the arc device, designed for both emission and absorption analysis, have been described elsewhere.^{1–3} The data for the use of this source in emission spectrometric analysis for the determination of 33 elements are given in Refs. 4 and 5. In spite of its very convenient design and shape for absorption measurements, its use in atomic absorption analysis has been rather limited.^{2,3,6}

In this work, the plasma of the U-shaped arc was investigated as an atomizer for atomic absorption analysis of boron. Boron belongs to the small group of elements that exhibit low sensitivity of determination by atomic absorption spectroscopy (AAS). Its

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characteristic concentration, even in the case of the very effective $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame atomizer, is too high. When expressed in $\mu\text{mol}/\text{ml}$, it is two orders of magnitude greater than for most elements. This could be connected with the low efficiency of boron atomization. Because of its strong tendency to carbide formation, boron is also very difficult to determine in a graphite tube furnace.⁷ The use of an inductively coupled plasma (ICP) as a free atom reservoir could solve the problem of low efficiency of atomization, but the strong atomic emission compared to the emission of the primary source, hollow cathode lamp, deteriorates its performance. For the majority elements, the measurements of atomic absorption along the diameter of ICP yields about 10 times smaller sensitivities than flame AAS,⁸ but the very high emission intensity of the boron and silicon resonance lines hinder their absorption measurements.

In this paper, the measurements of the characteristic concentrations for boron using an arc and a flame as atomizers were performed on the same commercial atomic absorption spectrometer, and the results were compared with these obtained on a laboratory assembled spectrometer, which included a commercial Lock-in-amplifier and a mechanical chopper with a chopping frequency of 558 Hz. The results for silicon were also compared and used as control measurements.

EXPERIMENTAL

Arc device.

The arc column of the U-shaped DC arc was stabilized with combined gas and wall stabilization. A gas vortex formed the 50 mm long, cylindrically-shaped analytical part of the arc column which was convenient as a free atom reservoir for atomic absorption measurements. The arc with aerosol supply was operated at atmospheric pressure. A direct current of 6 A was used in all measurements. The arc device is a modified version of the model employed in earlier studies.³⁻⁶ The modified

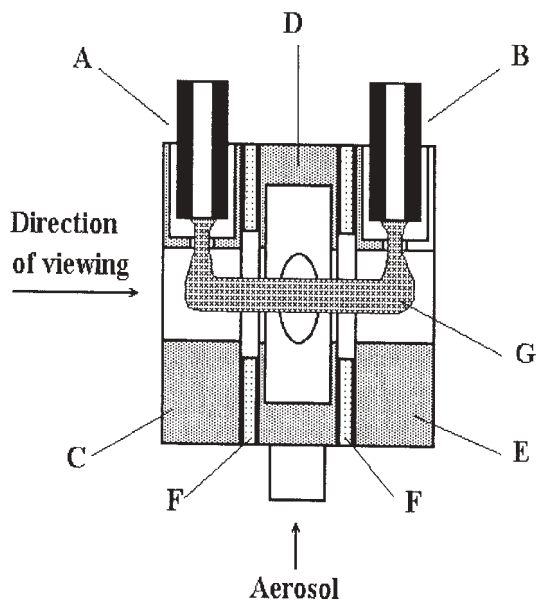


Fig. 1. Schematic representation of the U-shaped DC arc device. A and B – electrodes, C, D and E – metal segments, F – insulators and G – arc column.

central segment enables the easy replacement of the burner head of an atomic absorption spectrometer with the arc device. This new construction gives two possibilities: (i) the arc device can be mounted on any commercial spectrometer, and (ii) the construction allows rotation around the vertical axis which enables selection of the optimal zone of the analytical part of the plasma column to be projected on the entrance slit of the monochromator. The cross-section of the arc device and the central segment are shown in Fig. 1.

Spectrometers.

Absorption was measured with a Perkin-Elmer atomic absorption spectrometer, Model 360 with a digital read-out unit UDR-3. An argon filled hollow cathode lamp of boron (Perkin-Elmer Intensitron HCL) was used as the primary source.

For the plasma temperature and the line profiles measurements a 2-meter plane grating spectrograph PGS-2 (Carl Zeiss) with a laboratory made attachment for photoelectric detection was used as the monochromator. Two interchangeable gratings were used: a Zeiss standard grating, 651 grooves/mm, blazed at 330 nm and Bausch and Lomb echelle grating, 316 grooves/mm, blaze angle $63^{\circ}26'$.

Operating conditions.

Argon, with a flow rate of 3.96 l/min, was used as the carrier gas for the arc atomizer. A small acetylene stream of 0.08 l/min was admixed to the carrier gas to obtain a reducing environment. The aerosol density was assessed to be 0.030 g of solution per liter of carrier gas-argon. The volume flow rates for the flame were: 13.1 l/min for N_2O and 9.6 l/min for acetylene.

The rate of liquid aspiration for the flame and the arc (6.52 ml/min and 4.88 ml/min, respectively) were determined by aspiration of 100 ml of water.

The details of the instrumental set-up and the operating conditions are shown in Table I.

RESULTS AND DISCUSSION

The numerical estimation of the characteristic concentration (the concentration required to produce 1 % absorption) can be evaluated, for given experimental conditions, from the basic equation relating the integrated absorption coefficient to the number density of free atom in the ground state, n_p , and the absorption oscillator strength, f_{pq} :⁹

$$\int k_{\nu} d\nu \frac{\pi e^2}{m_e c} n_p f_{pq} = 2.65 \times 10^{-6} n_p f_{pq} \quad (1)$$

In analytical atomic absorption spectroscopy, instead of the integrated absorption, the absorption at the peak of the absorption line is measured. Inserting numerical values for the constants in the SI system (introducing decadic absorbance and assuming a Gaussian profile) the basic relation becomes:

$$A_{\nu_0} = 3.60 \times 10^{-15} \frac{\lambda_0^2}{\delta\lambda_D} \ln p f_{pq} \quad (2)$$

where A_{ν_0} is the peak absorbance, $\delta\lambda_D$ (m) the Doppler width of the absorption line, λ_0 (m) the wavelength in the center of the analytical line, l (m) the absorption path length, f_{pq} the absorption oscillator strength, and n_p is the number density of a free atom in its ground state (in m^{-3}). If one considers the molar concentration in the absorption cell (in mol/m^3), which is more frequently used in chemistry, instead of the number density, Eq. (2). becomes:

$$A_{v_0} = 2.17 \times 10^9 \frac{\lambda_0^2}{\delta\lambda_D} I(c_M)_{gas} f_{pq} \quad (3)$$

Relating the molar concentration in the absorption cell, $(c_M)_{gas}$, to the molar concentration of a sample in solution including the dilution factor, f_d , and considering the correction factors from the literature data for sensitivity,^{8,10} one finally obtains for the sensitivity S (in m^3/mol) the following relation:

$$S = \frac{dA}{dc} = (2.17 \times 10^9) \frac{g_p f_{pq}}{Z(T)} \frac{l}{f_d} \frac{\lambda_0^2}{\delta\lambda} \beta_s \beta_v f_c (1 - \beta_i) \quad (4)$$

where g_p is the statistical weight of the lower level and $Z(T)$ the partition function. $\delta\lambda_D$ is replaced by $\delta\lambda$ [Eq. 5] which takes into account the HCL line width. The dilution factor, f_d , is the ratio of the total number densities of analyte atoms in the solution and in the free atom reservoir. β_s is the desolvated fraction, β_v the volatilized fraction, β_i the degree of ionization, and f_c the total degree of chemical dissociation.

TABLE I. Instrumentation and operating conditions

<i>U-shaped DC arc</i>	
Carrier gas, argon	3.69 l/min
Reducing gas, acetylene	0.08 l/min
Aspiration rate	4.88 ml/min
Operating current	6 A
Monochromator	PGS-2 (Carl Zeiss, Jena)
Diffraction gratings	316 grooves/mm (Bausch & Lomb)
Reciprocal linear dispersion at 250 nm	0.033 nm/mm (XXII order)
	650 grooves/mm (Carl Zeiss)
Reciprocal linear dispersion at 250 nm	0.365 nm/mm (II order)
Lock-in-amplifier	Princeton Applied Research, Model 5101
Mechanical chopper	Princeton Applied Research, Model 125 A
Photomultiplier tube	Hamamatsu, R212
Recorder	B1G1 (Carl Zeiss)
<i>Flame</i>	
Oxidant gas, N_2O	13.1 l/min
Fuel gas, acetylene	9.6 l/min
Aspiration rate	6.52 ml/min
<i>Atomic absorption spectrometer</i>	
Reciprocal linear dispersion at 250 nm	1.6 nm/mm (I order)

When the half-intensity width of the source emission line is taken into account, as defined in Refs. 8 and 10, the following relation gives the effective width of the absorption line:

$$\delta\lambda = (\delta\lambda_a^2 + \delta\lambda_{\text{HCL}}^2)^{1/2} \quad (5)$$

where $\delta\lambda_a$ is the half-width of the absorption line in the arc (or $\delta\lambda_f$ for the absorption line in the flame) and $\delta\lambda_{\text{HCL}}$ is the half-width of the emission line from the HCL.

The characteristic concentrations were evaluated from:

$$c_{\text{char.}} = \frac{0.0044}{S} \quad (6)$$

In the calculation of the characteristic concentration it was assumed that $\beta_s\beta_v f_c(1 - \beta_i) = 1$. The characteristic concentrations calculated in this way should be considered as ideal because they are calculated assuming that the atomization of the analyte (that reaches the atomizer) is complete and that ionization is absent.

The half-intensity widths of the investigated analytical lines emitted in the DC arc and the boron hollow cathode lamp were evaluated from the measured profiles obtained with a high resolution echelle grating. Correction for instrumental broadening was estimated by measurements of the iron emission lines from the HCL. The half-width of the boron emission line was rather large (15 pm) because the argon filled HCL emits abnormally broad boron lines.¹¹ The consequence of this is that the sensitivity of boron determination is about three times lower than when a neon filled lamp is used. However, the radiation from an argon filled HCL is more intense than from a neon filled HCL. Because of the necessity of a high emission intensity of the arc used as a free atom reservoir, the use of an argon filled HCL was indispensable. The half-width of the silicon emission line was calculated in terms of the Doppler half-width corresponding to an average HCL temperature of 500 K. Data concerning the half-width of the analytical lines, measured and calculated, are shown in Table II.

TABLE II. Relevant data for the calculation of the characteristic concentrations

	Boron	Silicon
Wavelength, λ	B I 2.497×10^{-7} m	Si I 2.5161×10^{-7} m
gf^{15}	0.45	0.58
$Z(5600)^{14}$	5.99	9.67
$Z(2860)^{14}$	5.97	8.56
$\delta\lambda_{\text{HCL}}$ (experimental)*	15×10^{-12} m	-
$\delta\lambda_{\text{HCL}}$ (calculated)	-	1.22×10^{-12} m
$\delta\lambda_a$ (5600)	4.07×10^{-12} m	2.54×10^{-12} m
$\delta\lambda_f$ (2860)	2.91×10^{-12} m	1.81×10^{-12} m
Arc temperature		5600 K
Flame temperature ¹³		2860 K
Absorption path length	0.05 m for both atomizers	
f_d (arc)		6.26×10^5
f_d (flame)		3.20×10^5

*Boron HCL filled with argon

The temperature of the arc plasma was measured by the method of the relative intensities of iron lines.¹² For the observed horizontal part of the arc column, a value of 5600 K was obtained. The flame temperature was taken from Ref. 13. The electronic partition functions were evaluated from the data in Ref. 14, and the gf values were taken from Ref. 15.

The dilution factors, f_d , were calculated from the aerosol density¹⁶ (0.030 g of solution per 1 l of argon at room temperature) and corrected for gas expansion due to the temperature of the corresponding atomizer.

From the spectroscopic data given in Table II, the sensitivities S were evaluated using Eq. (4). From these values, the characteristic concentrations for both the investigated elements and for both the atomizers, arc and flame, were calculated. The experimental values of the characteristic concentrations were evaluated from the slope of the analytical curves. Since the results for boron obtained on the two spectrometers were somewhat different, those obtained on the laboratory assembled set-up operating at a higher chopper frequency were preferred. The obtained values are summarized in Table III.

TABLE III. Calculated and experimental values of the characteristic concentrations for boron and silicon obtained with different atomizers

λ_0/nm	N ₂ O–C ₂ H ₂ flame $c_{\text{char}}/(\mu\text{g/ml})$		U-shaped DC arc $c_{\text{char}}/(\mu\text{g/ml})$	
	Calculated	Experimental	Calculated	Experimental
B 249.77	0.46	32	0.91	2.9
Si 251.61	0.17	1.1	0.50	1.0

For the flame atomizer, a comparison of the calculated and experimental characteristic concentrations shows that the sensitivity of the boron determination is about 70 fold smaller than that predicted by the calculation. The corresponding value for silicon is only about 6 fold smaller than the predicted value. For the arc atomizer, the experimental sensitivities are in better accordance with the calculated values for both elements.

Silicon was chosen as the control element since, under the given experimental conditions, it behaves in the same way as boron in the gaseous phase of both atomizers. Boron and silicon have very similar ionization energies (8.296 eV and 8.149 eV, respectively), and also the excitation energies of the investigated analytical lines are about the same (4.96 eV and 4.95 eV). The thermodynamic quantities for monoxides and monocarbides are about the same for both elements. The fact that the intensities of the lines for both elements are enhanced by about 30 % on acetylene addition to the carrier gas suggest that the formation of monoxides contributes less to the atomization efficiency than the formation and vaporization of non-volatile compounds. It is supposed that the main reason of the low atomization efficiency of boron and of its low determination sensitivity in the flame atomizer is the formation of non-volatile metal and carbide particles. When the DC arc atomizer is used, the temperature is sufficiently high to compensate this effect. The difference between boron and silicon could be explained by the formation of a refractory compound, probably B₄C. The carbides of silicon are less stable and could be dissociated in the fuel rich flame.

CONCLUSION

The high plasma temperature of the U-shaped DC arc close to the axis zone enables the complete dissociation of stable boron molecules. However, due to the high plasma temperature, the gas expansion decreases the concentration of free atoms and greatly increases the spectral emission intensity in the absorption cell which hinders the absorption measurements. The addition of hydrocarbons to the plasma supporting gas (argon) creates a reducing atmosphere which prevents the formation of stable monoxide at lower temperatures making the cooler, peripheral plasma zone, the temperature of which are close to the optimal one, suitable for absorption measurements.

For the DC arc, the experimentally obtained characteristic concentrations are comparable to the calculated values, which indicates almost complete atomization.

ИЗВОД

ПРОБЛЕМИ ВЕЗАНИ ЗА ОДРЕЂИВАЊЕ БОРА АТОМСКОМ АПСОРПЦИОНОМ СПЕКТРОСКОПИЈОМ И ПОБОЉШАЊЕ ОСЕТЉИВОСТИ

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Упоредена су два атомизатора: $N_2O-C_2H_2$ пламен и стабилизовани једносмерни лук U-облика. Када се као атомизатор користи лук висока температура плазме и редукциона атмосфера, добијена додавањем ацетилена струји аргона, битно повећавају осетљивост одређивања бора атомском апсорпционом спектроскопијом (AAS). Резултати су упоређени са резултатима добијеним за силицијум као контролни елемент. Експерименталне карактеристичне концентрације за оба елемента су упоређене са израчунатим вредностима. Карактеристична концентрација за бор, експериментално одређена са луком као атомизатором, показивала је боље слагање са израчунатом вредношћу. Процењено је да је утицај формирања стабилних монооксида на осетљивост приближно иста за оба елемента, али да су редукција и формирање неиспарљивих честица карбида значајнији код бора, што представља главни разлог мале осетљивости одређивања бора пламеним атомизатором. Употреба лука као атомизатора сузбија ове интерференције и значајно побољшава осетљивост.

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