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The Effect of Source/Absorber Width in Continuous Source Atomic Absorption Spectroscopy†

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The effect of source/absorber width in Continuous Source Atomic Absorption Spectroscopy (CSAAS) profiles is studied to increase the intensity of atomic absorption lines. The effect of slit width in source/absorber profiles is studied too, to obtain some sharp absorption lines. Some good results are obtained when $\sigma_s << \sigma_a$. Some good results are achieved for lanthanide elements. The absorbances obey Beer's law and the calibration curves are linear in a good range of concentration.

INTRODUCTION

Since Fassel et al.[1] were the first to apply continuous sources to direct atomic absorption measurements, numerous works have been done to evaluate the method[2–4]. Recently several authors have used high-resolution power spectrophotometer combined with array diodes for multielement analysis with Continuous Source Atomic Absorption Spectroscopy (CSAAS)[5–7], but no commercial apparatus was used for this purpose.

The signal to noise ratio expression of absorption spectrophotometry developed by previous investigators has ordinarily been based on the assumption that the spectral distribution of the light source is much narrower than the spectral distribution of the absorption signal $\sigma_s << \sigma_a$. This is the common case of analytical absorption measurements and adherence to Beer's law[5].

The half width (σ_s) of spectral lines emitted from hollow cathode lamps (HL) is about 0.002 nm, when the half width (σ_a) of spectral absorption profiles of different elements is about 0.004 nm, the half width (σ_s) of spectral lines emitted from hollow cathode lamps (HCL) considered being constant, because the parameters of the lamp (current, frequency, temperature, pressure, etc.) are considered to remain constant too. The half width (σ_a) of absorption lines of the elements depends on the concentration of the element, temperature and pressure, so it varies in the interval 0.004 to 0.05 nm. In all cases σ_a is much smaller than σ_s and fulfils the condition $\sigma_s \ll \sigma_a$.

The increment of the slit width of the instrument provides additional signal on

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the detector, the intensity of the radiation increases, but results in poor resolution power[6]. The increment of the slit width of the instrument could change the peak height and the peak position. A wide slit width can change two neighbouring peaks into a single one with different height and different position[8]. It decreases the selectivity and sensitivity of the analysis.

Theory

It has been common in curve fitting practice to assume that all the peaks in atomic absorption measurements are of equal width[9]. It is not true in continuous source atomic absorption measurements (CSAAS). The width of the radiation signals which fall on the monochromator is directly dependent on the parameters of the entrance slit. It means that this radiation signal is not pure. There are many other radiation lines, equal to or more intensive than the signal (σ_0) of the element, which fall on the monochromator simultaneously. It results in a poor resolution power and makes the calibration curves to be crooked[10]. It is necessary in practice to ensure an optimal slit width, which should ensure the maximal intensity of the radiation signal, minimal noise level and maximal sensitivity of the element. The half width of radiation lines of hollow cathode lamps (σ_s) is smaller than the half width of the absorption profiles ($\sigma_s << \sigma_a$), but the situation should be different in CSAAS measurements for both cases: source and absorption profiles. It is due to the limitation of half width of σ_s by the amount of mechanical slit of the apparatus, in CSAAS measurements. It is well known that

$$I = I_0 \exp(-K_\sigma \cdot l) \tag{1}$$

Let us have

$$I/I_0 = \exp(-K_\sigma \cdot l) \tag{2}$$

or

$$A = -\log(I/I_0) = K_\sigma \cdot l = K_\sigma \cdot a \cdot C \tag{3}$$

When $\sigma_s << \sigma_a$, as in line AAS occurs, K_σ, which depended on the frequency σ, should be considered as a constant parameter; so the absorbance is only the function of the concentration of the element the measurements obey Beer's law and formula (3) can be written:

$$A = K \cdot C \tag{4}$$

In polychromatic or wide-bond radiation, where spectral width of the radiation signal is bigger than the half width of absorption profiles, K_σ is the function of the frequency σ. It has been expected to have a poor detection limit and a very short range of linear calibration in this case. May be the situation should improve, if we decrease the spectral width of radiation profile and make it to fulfill the condition $\sigma_s << \sigma_a$. In this case K_σ soluld be considered constant, too. Fairies[11] recommends using Fourier transformation technique to decrease the source width σ_s and to obtain more pure emitted signal from the lamp. The signal of the lamp can be sharper and more intensive after Fourier transformation. Each frequency should be modulated independently and σ_s should be smaller than without Fourier transformation. O'Haver[7] mentioned that the high resolution power of FT makes continuous-source multi-element AAS an attractive method.

EXPERIMENTAL

Instrumentation: Hitachi-180-80 is used. Some modifications are done in it. Fig. 1 is a schematic diagram of the optical system used in this work. We employed a 250 W halogen lamp as a radiation source. These kinds of lamps are widely used in UV-VIS spectrophotometry and was for the first time used in AAS measurements. Some mirrors and lenses are used (Fig. 1) to collimate the radiation signal of the lamp. A mechanical chopper is used for pulsing the optical signal of the lamp. The measurements are done under 0.1 and 0.2 nm slit width.

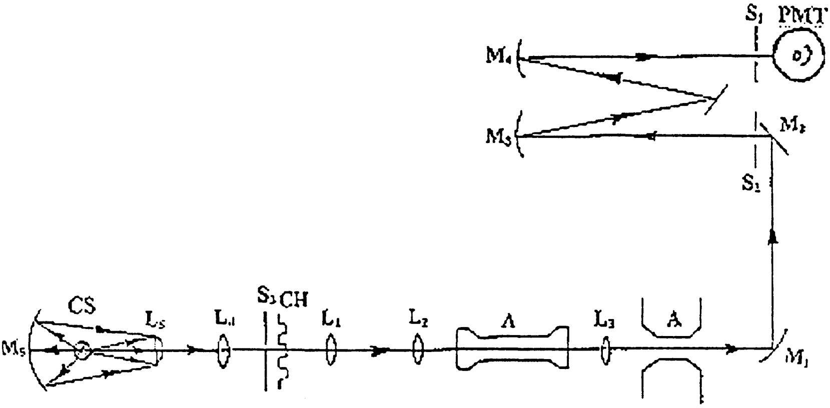

Fig. 1. The schematic diagram of optical system used in Hitachi-180-80 Spectrophotometer CS—Continuous lamp; M_1–M_5—Mirrors; L_1–L_5—Lenses; S_1–S_3—Mechanical slots; CH—Chopper; A—Atomizer; G—Grating; PMT—Photomultiplier tube.

RESULTS AND DISCUSSION

(a) *The influence of the slit width on* σ_s/σ_a *ratio*: As we mentioned before, the amount of σ_s and σ_a depended deeply on the amount of slit width in CSAAS measurements. As it has been expected the amount of σ_s increased more quickly than σ_a, because for a certain resolution power of the instrument, σ_s of continuous sources depended only on the amount of slit width. We have investigated the absorption profiles of nine different elements (Li, Na, K, Ca, Ba, Sr, Nd, Ho, Eu) in different slit widths. There are no absorption signals of these elements for a big slit width (1.3 and 0.4 nm). As the amount of slit width decreased, the absorption intensity is increased (Table-1).

The data listed in Table 1 show that σ_a of lanthanides is smaller than σ_a of other elements and the influence of slit width is not so significant as in other elements. Maybe it is due to their 4f electronic level, which moves in a very short interval of energy. For this reason the difference of their transition energy is very low and makes their absorption profiles to be sharper, with a smaller half width σ_a. If we suppose that there is no scattering process of light in our optic system of the apparatus, it is expected that the half width of the radiated signal (σ_s) is equal the amount of slit width so the data listed on Table-1 give us a wrong impression that $\sigma_s >> \sigma_a$. As we mentioned before, some mirrors and lenses are used to collimate the radiation of the lamp (Fig. 1); so the band of the radiation signal (σ_s) is much smaller than the amount of slit width. For a small slit width it is near the condition $\sigma_s << \sigma_a$.

TABLE-1
THE VARIATION OF ABSORBANCE OF THE ELEMENTS VIA SILT WIDTH IN CSAAS

Element	Slit width (nm)	Conc. of element (ppm)	Half width (σ_a) (nm)
Na	0.2	25.0	0.118
	0.1	4.0	0.050
Ca	0.2	150.0	0.190
	0.1	10.0	0.052
Eu	0.2	500.0	0.080
	0.1	20.0	0.045

When the amount of slit width is decreased from 0.2 to 0.1 nm, the half width σ_a is at least two times smaller. We did not continue the experiments for a smaller slit width, because we have met with difficulty in the preparation of slit width from 0.5 nm to 1 nm.

(b) *The influence of the concentration of the element on* σ_a: We have investigated the absorption profiles of Ca (50 and 500 ppm) and Nd (250 and 1000 ppm) under 0.1 and 0.2 nm slit width. The results are listed in Table-2.

TABLE-2
THE VARIATION OF σ_a VIA THE CONCENTRATION OF THE ELEMENT

Element	Slit width (nm)	Conc. of the element (ppm)	Half width (σ_a) (nm)
Ca	0.2	500	0.218
	0.2	50	0.153
	0.1	500	0.068
	0.1	50	0.054
Nd	0.2	1000	0.082
	0.2	250	0.065
	0.1	1000	0.046
	0.1	250	0.043

The data listed in Table-2 show that for a big slit width, σ_a depends on the concentration of the element. As the concentration of the element increases, the half width σ_a increases too. The result is better for lanthanide elements. Their half width is smaller than other elements and is not a significant variation of σ_a via the concentration of the element (see Table-2, Nd). Maybe it is due to the 4f electronic level of lanthanides. The energy of 4f electronic level twisted in a very short range of energy; so the difference of the energy during transition of the electrons is small and some sharp absorber lines are obtained. The half width

σ_a decreases as slit width decreases, and it depends very little on the concentration of the element (Table-2).

(c) *Calibration and performance parameters*: We have plotted the calibration curves of nine elements, Li, Na, K, Ca, Ba, Sr, Nd, Ho and Eu.

The parameters of calibration curves, such as the slope, intercept and correlation coefficient of the fitted values obtained by using method of linear regression are shown in Table-3. Table-3 shows that there is good linearity of all calibration curves fitted. Correlation coefficients of the fitted values are higher than 0.999, and the intercept is smaller than 0.008, which present good relationship between concentration and absorption signals.

TABLE-3
SLOPE, INTERCEPT AND CORRELATION COEFFICIENT OF CALIBRATION CURVES

Element	Opt. conc. (ppm)	Slope	Intercept	Corr. coeff.
Li*	0.2–10	0.025	0.00796	0.9995
Na*	0.1–5	0.056	–0.001	0.9996
K*	0.2–10	0.03	0.0039	0.9998
Ca†	0.2–10	0.02	0.0022	0.9996
Ba†	5.0–100	0.011	0.0022	0.9992
Sr†	2.5–50	0.014	0.0057	0.9993
Nd†	120–1200	$8.1 \cdot 10^{-4}$	0.002	0.9996
Eu†	5.0–50	$1.5 \cdot 10^{-2}$	0.0011	0.9994
Ho‡	5.0–50	$9.8 \cdot 10^{-3}$	0.0053	0.9998

*C_2H_2/air flame, 2% CsCl as ionization buffer, 5% HCl solution
†C_2H_2/air flame, 2% NaCl as ionization buffer, 5% HCl solution
‡C_2H_2/N_2O very reductive flame, 5% $LaCl_3$ as ionization buffer[12], 5% HCl solution

To evaluate the precision of the apparatus, we measured the absorption signal of the same standard sample five times, keeping all conditions constant. The results are presented in Table-4.

TABLE–4
THE PRECISION, LIMIT OF DETECTION AND THE SENSIBILITY OF THE METHOD

Element	λ (nm)	Prec. of the apparatus		Sensitivity (μg/mL)	
		conc. (ppm)	RSD, %	CSAAS	HCLAAS
Li	670.8	2	6.8	0.16	0.005
Na	589.0	2	7.2	0.065	0.001
K	766.5	2	9.3	0.15	0.005
Ca	422.6	2	6.3	0.17	0.003
Ba	553.6	30	12.7	4.0	0.09
Sr	460.7	30	8.2	2.4	0.06
Nd	492.5	250	15.6	5.4	20
Eu	459.4	20	5.8	2.9	0.6
Ho	405.4	20	9.3	4.5	1.1

Data of Table-4 show that the sensibility obtained from the method used compared to those of AAS method using a hollow cathode lamp[7] as radiation source is more than 20 times lower, except Ln elements. The sensitivity of Ln elements is about 2 to 3 times lower than the line AAS. The sensitivity of all elements can be improved if we decrease the amount of slit width to about 0.6 nm and increase the resolution power of the apparatus. We think it is very interesting to use this method for Ln elements, because their hollow cathode lamps are very expensive. Table-4 shows too that good precision is achieved, comparable with other methods reported[13]. The RSD within samples (n = 5, P = 95%) is less than 16%, when the reported one between samples[13]. is less than 24%. Data in Table-5 show that the reproducibility of the apparatus is the main source of the error this method. It is related the parameters of the apparatus, mainly its resolution power.

Conclusion

1. The σ_s/σ_a ratio is an important parameter of CSAAS measurements, which is the main factor which determines the sensitivity and the accuracy of the method. To ensure a good sensitivity of the method, the condition of $\sigma_s << \sigma_a$ should be achieved.
2. The amount of σ_s/σ_a ratio depend much on the amount of slit width of the spectrophotometer. It is a main factor, which determines the band of the absorption and radiation signal (σ_a and σ_s). For a small slit width (smaller than 1 nm), the half width of absorption profiles decreases quickly, so the sensitivity of the elements increases.
3. The half width of Ln elements is smaller than for other elements and there does not exist a significant variation of σ_a via concentration of these elements (Table-2, Nd). Maybe it is due to the 4f electronic level of lanthanides. The energy of 4f electronic level twisted in a very short range of energy, so the difference of the energy during transition of the electrons is small and some sharp absorber lines are obtained.
4. The sensitivity achieved for Li, Na, K, Ca, Ba, Sr is about 20 times lower than line AAS. It is better (2 to 3 times lower) for Nd, Eu, Ho. It is due to this fact that the parameters achieved for Ln elements are better than for other elements.
5. We think that the results should be improved, if we decrease the amount of slit width to 0.6 nm and improve the resolution power of the apparatus. We think that this method is of more interest for Ln elements, because their hollow cathode lamps are very expensive.

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