

# Measurement of transient signals in flame atomic absorption spectrometry

## A theoretical approach

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The measurement of peak height and peak area of transient signals in flame atomic absorption spectrometry was compared from the point of view of calibration, dynamic response range and versatility. Theoretical considerations imply that the measurement of peak area enables a simple and universal quantitation due to the direct proportionality of peak area to the absolute amount of analyte entering the nebulizer. At instrumental parameters kept constant peak area does not depend on the concentration profile of the sample solution entering the nebulizer.

Flame atomic absorption spectrometry (FAAS) belongs to the commonly used techniques in analytical laboratories. Its main advantage is simplicity, reproducibility, and high selectivity. Though sensitive enough, for the purposes of ultra trace analysis it demands special sample preparation procedures, *e.g.* a preconcentration step. Due to the relative high sample consumption, FAAS is less suitable for the analysis of microsamples. Another disadvantage of the method is the narrow linear concentration response range arising from the principle of the absorbance measurement.

All these items were tried to be overcome using special techniques and adjusting properly the FAAS instrument. To improve the detection power of the method preconcentration or enrichment techniques are in common use [1]. Microsamples (biological fluids, concentrates) have been analyzed by the injection sampling technique [2–7]. For the analysis of concentrated sample solutions the decrease of the instrument sensitivity and/or the dilution of the sample are usually used. The last procedure can be performed either manually (off-line) or by using a flow system coupled on-line to the FAAS nebulizer [8].

When transient signals are measured (*e.g.* in injection sampling, on-line preconcentration, flow injection analysis — FIA) the signal peak height is mostly registered and evaluated. Modern instruments equipped with an on-line microcomputer enable an easy evaluation of the peak area, too, which can be an additional or even a primary information about the analyte content in the sample.

This paper presents a critical comparison between peak height and peak area measurement of transient signals from the point of view of calibration, dynamic concentration range, and universality.

### Theoretical

In FAAS the instrument response can satisfactorily be described by the well stirred simple tank model [9, 10]. According to this theory the nebulizer of the

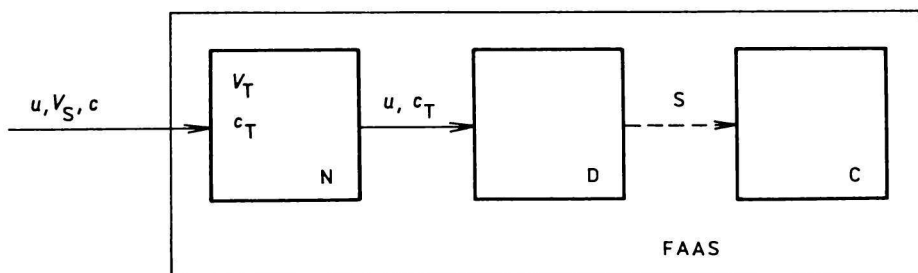


Fig. 1. Block diagram of the FAAS instrument. N — nebulizer, D — detector, S — signal from the detector, C — microcomputer.

instrument is described mathematically as a hypothetical well stirred mixer chamber of the volume  $V_T$  and actual analyte concentration  $c_T$  (Fig. 1). The actual instrument response (absorbance  $A$ ) in the linear response range is directly proportional to the concentration  $c_T$  entering the detector

$$A = kc_T \quad (1)$$

Considering the above well stirred tank model, the following differential equation is valid for the change of the analyte amount in the tank

$$dm_T = m_{in} - m_{out} = c dV - c_T dV \quad (2)$$

Rearranging eqn (2) and using eqn (1) we obtain

$$dA/dt = u(kc - A) V_T \quad (3)$$

where  $u$  is the aspiration rate of the sample solution.

We consider a sample solution with an analyte concentration  $c$  entering the nebulizer while the concentration is constant ( $c = \text{const.}$ ). On integrating eqn (3) the following relation can be derived for the actual absorbance

$$A = kc(1 - e^{-ut/V_T}) \quad (4)$$

According to eqn (4) the absorbance is limited to its steady-state value ( $\lim_{t \rightarrow \infty} A = kc$ ).

When a discrete volume  $V_s$  of the sample is injected at the same conditions, the maximum absorbance  $A_s$  (peak height) is given as follows

$$A_s = kc(1 - e^{-V_s/V_T}) \quad (5)$$

For the falling part of the signal ( $t \geq t_s = V_s/u$ ) the actual absorbance is given by the following equation

$$A = kc(e^{V_s/V_T} - 1)e^{-u/V_T} \quad (6)$$

When the analyte concentration of the sample solution entering the nebulizer is time-dependent ( $c = f(t)$ ), the analytical solution of eqn (3) is difficult or even impossible. In general, the signal height  $A_s$  is significantly dependent on the concentration profile of the sample entering the nebulizer.

For a given aspirated sample volume  $V_s$  with the total amount  $m_s$  of the analyte in this volume, the peak area can easily be derived by integrating eqn (3)

$$a = \int_0^{\infty} A dt = km_s/u \quad (7)$$

The observed peak area at constant instrument parameters is a function of the total amount of the analyte in the aspirated sample volume and does not depend on the analyte concentration profile entering the nebulizer.

## Discussion

Though the steady-state signal is commonly measured in FAAS, there are situations when transient signals are to be handled. The theoretical description of the FAAS instrument response for such cases is rather complex. The instrument response is far from an ideal detector response [10] — the response is delayed and the response time profile is distorted with regard to the sample concentration—time profile.

A simple but satisfactory theoretical description of the FAAS response kinetics utilizes the well stirred tank model [9, 10]. The justification of this model for FAAS instruments with pneumatic concentric nebulizers was proved earlier [10, 11]. The volume of the hypothetical tank calculated from eqn (4) was found to be about 80—90 mm<sup>3</sup> [10, 11].

When a discrete sample volume  $V_s$  is injected to the nebulizer, either peak height (maximum absorbance) or peak area can be measured. If the analyte concentration is constant in this sample “plug”, the peak height  $A_s$  is directly

proportional to the analyte concentration  $c$  (eqn (5)). This is the case for injection (discrete volume) sampling and some FIA arrangements. By measuring the peak width at a constant height it is possible to use eqns (4) and (6) for calibration in an extremely broad concentration range [12].

Equations (4–6) are no more valid for samples with time-dependent (not constant) concentration profiles. This is the case, for example, of the preconcentrations coupled on-line with the FAAS instrument [13–21]. After or during the preconcentration step the collected trace elements are carried to the nebulizer, while the concentration–time dependence of the sample solution entering the nebulizer is peak-like. Since the analytical form of the dependence  $c = f(t)$  is usually unknown, moreover it may change during the experiments, the peak height is hardly related to the analyte concentration of the original sample. Thus the calibration and quantitation would be complicated.

As eqn (7) implies this problem can easily be overcome by peak area measurement. Keeping instrument parameters constant (aspiration rate, stoichiometry and geometry of flame, *etc.*), the analyte mass  $m_s$  in the aspirated sample volume  $V_s$  can easily be obtained on integrating the measured absorbance in the time interval from the beginning of the sample aspiration till the absorbance declines to the noise level. From the value of  $m_s$  the concentration in the original sample solution can be simply calculated. The observed peak area does not depend on the concentration profile of the aspirated sample, so the peak area measurement is in principle usable for any kind of discrete volume sampling (injection sampling, FIA, on-line preconcentration) while the proportionality constant  $k$  in eqn (7) remains valid for all these types of sampling.

The constant  $k$  can be obtained by calibration. The calibration consists of the measurement of standard solutions at steady-state conditions and calculation of  $k$  from eqn (1). Another possibility is to inject discrete volumes of standard solutions to the nebulizer and to calculate the ratio of  $k/u$  from the area of the response signal. The conditions for the successful calibration and quantitation are to measure solutions providing signal responses in the linear response range and to keep instrument parameters constant both at calibration and sample measurement.

Moreover, by measuring peak area it would be possible to enhance significantly the dynamic range of FAAS, particularly to higher analyte concentrations. Peak area, unlike peak height (absorbance) bears an additional information, *i.e.* a relation to the absolute analyte mass entering the nebulizer during the measurement period. By timing the sample solution uptake or by controlling the sample volume aspirated we can measure both diluted and concentrated sample solutions while making use of eqn (7) for quantitation. The condition of having sample solutions providing absorbance in the linear response range also for concentrated sample solutions can be fulfilled by using, for example, a mixer

chamber coupled on-line to the nebulizer [8] diluting continuously the injected sample.

## Conclusion

The above theoretical considerations imply that when discrete volume samples are to be analyzed by FAAS, peak area measurement is simpler from the point of view of calibration and is more universal as well than the peak height measurement. Peak area measurement may help to broaden the dynamic range of FAAS.

## Symbols

$a$	peak area
$A, A_S$	absorbance; maximum absorbance (peak height)
$c, c_T$	analyte concentration; analyte concentration in the hypothetical tank
FAAS	flame atomic absorption spectrometry
FIA	flow injection analysis
$k$	signal sensitivity
$m_T, m_S$	analyte mass in the tank; absolute analyte mass entering the nebulizer
$t, t_S$	time; time for aspirating a sample volume $V_S$
$u$	sample solution flow rate (aspiration rate)
$V, V_S, V_T$	volume; sample volume aspirated; hypothetical tank volume

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