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Views and criticisms

A discussion about the significance of Absorbance and sample optical thickness in conventional absorption spectrometry and wavelength-modulated laser absorption spectrometry

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Abstract

One of the most frequently used concepts in atomic absorption spectrometry (AAS) is that of Absorbance, an easily measurable quantity that is linear with the concentration of the analyte over a large range of concentrations whenever Beer's law is valid. Laser-based modulation techniques, however, in particular wavelength modulated diode laser absorption spectrometry (WMAS), do not measure exactly the same physical quantities as conventional AAS techniques do, since they do not rely upon separate measurements of the intensities in the presence and in the absence of the sample, but rather (a certain fraction of) the difference between the signals 'on' and 'off' resonance. Hence, Absorbance is not as natural for the modulated laser-based absorption techniques as it is for the conventional AAS techniques. The entity called sample optical thickness (SOT) appears to be a natural entity as well as a natural unit (denoted SOT units) for the quantification of signals in WMAS. The present paper discusses the concept of measurable quantities and their units in WMAS in some detail and compares them (theoretical and practical considerations) with those of conventional AAS. In particular, it makes a distinction between the 'observed' sample optical thickness and the 'true' sample optical thickness and shows how these two entities are related to the Absorbance entity. Finally, this work also introduces a dimensionless sensitivity of the WMAS technique, and shows this quantity to be equal to the *n*th Fourier coefficient of the wavelength modulated, peak-normalized line shape function.

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1. Introduction

One of the most frequently used concepts in atomic absorption spectrometry (AAS) is that of Absorbance, A [1,2]. The reason for the usefulness and the popularity of Absorbance is that it expresses an easily measurable quantity that is linear with the concentration of the analyte over a large range of concentrations whenever Beer's law is valid. It is also fairly straightforward to work with since A consists of the (decadic, i.e. base 10) logarithm of the ratio of two quantities that are easily measurable in conventional AAS: the intensities in the absence and in the presence of the analyte, I_0 and I , respectively.

Wavelength-modulation techniques and the associated name 'derivative spectrometry' are well known in spectrochemical applications and have been extensively used in the past in emission and absorption spectrometry, mainly for improving the selectivity of the techniques in the presence of spectral interferences (see, for example, the discussion given in the book by Alkemade et al. [2] and an old instrumental paper by O'Haver [3]). The advent of diode lasers and the possibility of high frequency modulation of the light source have revitalized the field of modulation spectroscopy in the recent years by also improving the signal-to-noise ratios of the spectrometric techniques in general. The introduction of a rapid modulation of the wavelength or the frequency of the light is motivated by the fact that the detection can be shifted to higher frequencies where the flicker noise (or the so-called $1/f$ -noise) is substantially reduced [4–9]. As a consequence, the new laser-based wavelength- and/or frequency-modulated absorption techniques, commonly referred to as wavelength-modulation diode laser absorption spectrometry (WMAS)² [6–12] and frequency-modulated absorption spectrometry (FMS) [4–9,13–15], are capable of detecting significantly lower concentrations of atoms and molecules than conventional (unmodulated) AAS techniques.³

² Often also abbreviated as WMS, WM-DLAS or WM-DLAAS, or sometimes also referred to as tunable diode laser absorption spectrometry (TDLAS).

³ Although many of the general conclusions in the introduction are valid also for the FMS technique, we will in this paper focus on the WMAS technique because of its wider use.

Typical limits of detection (LODs) for the modulated laser-based absorption techniques are in the 10^{-5} – 10^{-6} range, although a few demonstrations of detection in the 10^{-7} range also have appeared [16–27]. These numbers refer to the minimum fractional absorption (also called 'absorption units' [24]) obtained for a given atomic or molecular absorption transition (see below) and can be translated into more familiar LODs, expressed either as absolute amounts (e.g. in g), relative concentrations (e.g. pg/ml) or number densities of atoms and molecules in the gas phase (e.g. $1/\text{cm}^3$) by the simple relation, which holds at low concentrations, between the fractional absorption and the product of the absorption cross-section, the number density and the absorption length (Eqs. (2)–(5)). For example, the LOD for ammonia corresponding to a fractional absorption of 10^{-6} was reported as 2.4×10^8 molecules/ cm^3 , corresponding to a concentration of $0.007 \mu\text{g}/\text{m}^3$ or 9 pptv [22]. Atomic number densities down to approximately 1000 atoms/ cm^3 can correspond to fractional absorption of 10^{-7} [20]. In electrothermal AAS, a value of 6.5×10^{-6} for rubidium translates into a characteristic mass of 6.5 pg and an absolute LOD of approximately 10 fg [18]. It is important to note, however, that *fractional absorption* is expressed as the minimum detectable relative intensity difference, $\Delta I/I_0$, where ΔI is given by the difference between the signals 'on' and 'off' resonance, i.e. $I_0 - I$, and is therefore *not the Absorbance*. The reason stems from the fact that the laser-based modulation techniques in fact do not measure exactly the same physical quantities as conventional AAS techniques do. They do not rely upon separate measurements of the intensities in the presence and in the absence of the sample, I_0 and I (which are needed for determination of Absorbance), but rather (a certain fraction of) the *difference* between the signals 'on' and 'off' resonance, i.e. ΔI , as clearly has been pointed out in Refs. [7,8,11,12,28–30], often referred to as the *absorption* of the sample. It should be clear that it is neither straightforward nor extremely convenient to compare a technique that measures the *difference* between the signals 'on' and 'off' resonance to an entity that is defined in terms of the *logarithm of the ratio* of the two intensities, as is the

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