Concentration curves in atomic absorption spectrometry*

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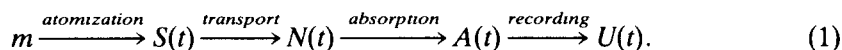
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Abstract—A detailed analysis of the correlation between the number of absorbing atoms, *N*, and the absorbance, *A*, produced by them, i.e. $A = f(N)$, is given. This analysis is valid for any optical thickness of the absorbing layer and accounts for Doppler broadening and pressure broadening of the emission and absorption lines, hyperfine structure and collisional shift as well as spatial temperature distribution and analyte distribution non-uniformities of the absorbing layer. It is shown that all the spectral features lead to curvature and a decreasing of the slope of the initial portion of the concentration curves. However, these effects are considerable only for analysis lines that consist of widely spaced hyperfine components. High stability of the concentration curves to variations of parameters defining the profile of the analysis line is shown. Parameters of the concentration curves, sensitivity, characteristic concentrations, curvature coefficient, and linearity range are introduced and calculated. Spatial non-uniformities of the absorbing layer affect the concentration curves much more strongly than the above spectral features of the analysis line. It is shown that the spatial non-uniformities act in two different ways: longitudinal temperature and concentration gradients result in a decrease in the slope of the concentration curves while cross-sectional non-uniformities lead to curvature of the concentration curves. It is suggested that the lateral non-homogeneity of the analyte distribution is a main cause of the curvature of analytical working curves in GFAAS.

1. INTRODUCTION

IN ATOMIC absorption spectrometry (AAS) the correlation between an analytical signal, $U(t)$, recorded at the spectrophotometer output and the amount of analyte, *m*, in a sample includes a few intermediate stages [1]:

$$m \xrightarrow{\text{atomization}} S(t) \xrightarrow{\text{transport}} N(t) \xrightarrow{\text{absorption}} A(t) \xrightarrow{\text{recording}} U(t). \tag{1}$$

During thermal atomization the analyte is converted into the gaseous phase at a rate of $S(t)$ atoms/s and is then transported into and out of the atomizer volume. These processes combine to form a transient absorbing layer with $N(t)$ number of atoms. The exposure of the atomic cloud to line radiation from a primary source provides an absorbance, $A(t)$, at the atomizer output which is then transformed into an electrical output signal, $U(t)$, in the spectrometer read-out system. Therefore, the shape of the resulting analytical calibration curve, $U = f(m)$, will be dependent on particular features of all these processes.

The effects of all the steps of this sequence are not equally understood at this time. Modern spectrometers provide a record of the transient absorbance, $A(t)$, that is practically undistorted. Therefore, the last link of the sequence is no longer a problem. On the other hand, some basic features of the formation of the absorbing layer (atomization and subsequent transfer of the analyte vapour into the analysis volume) are not understood as well as they should be. This lack of understanding makes it difficult to provide a comprehensive description of the steps of atomization and transport. The situation is intermediate for the third link of the sequence of steps, that is establishing the relationship between the number, *N*, of analyte atoms in the gaseous phase and the absorbance, *A*, produced by these atoms at a given wavelength.

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