

An electrothermal vaporization unit with axially focusing convection upstream. Part II: Modeling of the condensation process[☆]

A. Trenin^{a,b}, G. Hermann^{a,*}

^a *I. Physikalisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany*

^b *Kazan State University, Kremlevskaja Str. 18, 420008 Kazan, Russia*

Received 19 September 2006; accepted 3 November 2006

Available online 18 December 2006

Abstract

A model is presented that describes quantitatively the condensation of analytes in pico- and nanogram masses sampled with electrothermal vaporization (ETV). It presumes that the analyte vapor condensation of such low amounts occurs mainly heterogeneously, predominantly on growing carbon particulates originating from the graphite furnace before the analyte vapor achieves saturation via cooling. The model regards the coagulation of carbon particles and the diffusion of analyte atoms. The criterion whether or not an analyte atom sticks to a colliding particle is chosen as a function depending on its temperature and on the common GFAAS pretreatment temperatures. Heterogeneous condensation of six analytes with different volatilities, Ag, Cu, Fe, Ni, Mn, and Pb, is calculated for the ETV unit with an axially focusing convection upstream described in Part I. Modifier effects are taken into account. The results are compared to measured data.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Electrothermal vaporization; Analyte vapor condensation; Transport efficiencies; Simultaneous multielement determination

1. Introduction

A first theoretical description of the condensation of an analyte vapor generated by electrothermal vaporization (ETV) has been given by Kántor [1]. The concept is based on the formation of thermodynamically stable droplet nuclei with sizes exceeding a critical diameter, upon which further particle growth takes place. For unsaturated vapors, no formation of stable nuclei takes place, i.e. the concentration of atoms in the gas phase is insufficient to promote homogeneous nucleation.

A rough estimate [2] shows that supersaturation for most analytes dosed in pico- and nanogram amounts into the ETV is achieved at temperatures below the melting point. At the same time, the carbon density released from the graphite furnace (GF) tube of the ETV unit during vaporization is highly supersaturated

even already within the furnace and probably forms polyatomic structures. Carbon masses of about 70–80 µg are released during one heating cycle which have been gravimetrically measured in our group [2] as well as by other authors [3,4]. Micrographs of particulates collected thermophoretically inside the GF tube and in the AFC upstream [2] show larger particles 2.5 mm above and particles forming chains already 22.5 mm above the GF outlet hole. Energy dispersive x-ray spectra [2] identify the high carbon content. Thus, we conclude [2] that heterogeneous condensation [5] at carbon particulates is predominant and occurs before the analyte vapor achieves supersaturation.

In this work, the heterogeneous condensation of six analytes with different volatilities Ag, Cu, Fe, Ni, Mn, and Pb is numerically simulated. Modifier effects are taken into account.

2. The model

2.1. Analyte atom — C particulate interaction

The kinetic model regards the measured temperature dependences on the axis of the AFC tube [2] and the diffusion of analyte atoms. Diffusion of the heavier carbon particles is

[☆] This paper was presented at the VII European Furnace Symposium on Atomic Absorption Spectrometry, Electrothermal Vaporization and Atomization (VII EFS) and XII Solid Sampling Colloquium with Atomic Spectrometry (XII SSC), held in St. Petersburg, Russia, July 2–7, 2006 and is published in the special issue of Spectrochimica Acta Part B, dedicated to that conference.

* Corresponding author. Tel.: +49 641 99 33120; fax: +49 641 99 33129.

E-mail address: gerd.hermann@expl.physik.uni-giessen.de (G. Hermann).