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Three-dimensional time-dependent computer modeling of the electrothermal atomizers for analytical spectrometry

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ABSTRACT

A full three-dimensional nonstationary numerical model of graphite electrothermal atomizers of various types is developed. The model is based on solution of a heat equation within solid walls of the atomizer with a radiative heat transfer and numerical solution of a full set of Navier–Stokes equations with an energy equation for a gas. Governing equations for the behavior of a discrete phase, i.e., atomic particles suspended in a gas (including gas-phase processes of evaporation and condensation), are derived from the formal equations molecular kinetics by numerical solution of the Hertz–Langmuir equation. The following atomizers test the model: a Varian standard heated electrothermal vaporizer (ETV), a Perkin Elmer standard THGA transversely heated graphite tube with integrated platform (THGA), and the original double-stage tube-helix atomizer (DSTHA). The experimental verification of computer calculations is carried out by a method of shadow spectral visualization of the spatial distributions of atomic and molecular vapors in an analytical space of an atomizer.

1. Introduction

In most of analytical spectrometry methods, to obtain information of an elemental composition of the substance, one has to be atomized, i.e., to put into a state of an atomic vapor. One of the most popular means of atomization is the electrothermal vaporization of a substance, which is based on resistance heating of the atomizer's body by electric current. Currently, there are many variations of the electrothermal atomization, such as a single-step and a double-step, which are widely used as an independent method (electrothermal atomization, ETA) and in tandem with other methods (chemical flames, inductively coupled plasmas).

Phase transitions from a solid state to an atomic vapor occur at high temperatures and is accompanied by gas flows and dozens of physicochemical surface reactions. Therefore, in modern analytical spectrometers the atomizer not only defines the key characteristics of a metrological analysis, but it is also the most "misunderstood" part of the whole spectrometer. Since a first time of use of the electrothermal atomization method [1] to a present time, numerous researchers have attempted to make this method more predictable and manageable. To achieve this goal, dynamics of a graphite temperature and gas phase, e.g., [2,3], evaporation/condensation on an inner surface of the atomizer, e.g., [4], were studied experimentally and dynamics of absorbing layers in a gas phase were also visualized, e.g., [5–7]. Kinds and ways of gas-phase and surface reactions were successfully predicted on a basis of thermodynamic calculations, e.g., [8–10]. There are also a number of attempts to create a numerical model of the atomizer, starting from simple static symmetric cases, e.g., [11,12], to complex multivariable models, e.g., [13,14]. Analyzing the results, it can be noted, that for the most accurate description of the process of the atomization, it is necessary to consider simultaneously a transient three-dimensional spatial distribution of all the key parameters of the system: real geometry of the atomizer's body, the electric current, gas dynamics within and outside a body of the atomizer, evaporation, and condensation processes occurring on the surface of the atomizer and in a gas phase. This model can already be used as a "virtual" atomizer for the numerical simulation of its behavior under different conditions, which can significantly reduce a time required to develop novel systems of electrothermal atomization and to optimize the existing ones.

The aim of the current work is to demonstrate possibilities of the numerical simulation of various types of a single-stage and a double-stage atomizer (ET vaporizer with longitudinally heating, transverse heating atomizer and double-stage tube-helix atomizer).

The following objects were modeled: a graphite tube electrothermal vaporizer by Varian ® (GFAA) widely used for a preparation of analytical samples prior to entering the torch of the emission spectrometer with inductively coupled plasma, a transversally heated graphite atomizer (THGA) for atomic absorption analysis, and a working prototype of a double-stage tube-helix atomizer [15]. The last one is designed as a vertically oriented graphite tube. A sample is vaporized from the heated

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