

Investigation of aging processes of graphite tubes modified with iridium and rhodium used for atomic spectrometry[☆]

Ewa Bulska^{a,*}, Marek Piaścik^a, Dmitri Katskov^b, Nicholas Darangwa^b, Marco Grotti^c

^a Faculty of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

^b Department of Chemistry and Physics, Tshwane University of Technology, Private Bag X680, Pretoria 0001, South Africa

^c Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso, 31-16146 Genova, Italy

Received 29 August 2006; accepted 24 August 2007

Available online 30 August 2007

Abstract

UV spectrometry (187–380 nm) with charge coupled device (CCD) detection was used to study the evolution of absorption spectra during the vaporization of various species in the pyrocoated graphite furnace, with electrodeposited Ir and Rh as modifiers. In order to mimic a typical matrix composition, various salts of aluminum, manganese, copper, magnesium, sodium, and lead were used in microgram amounts. Changes in spectra and vapor release rate, along with aging of the tubes in the repetitive temperature cycles, were observed.

Compared to the unmodified pyrocoated tubes, the presence of Ir or Rh causes a significant reduction in the vaporization efficiency, especially for microgram amounts of copper and aluminum introduced as nitrates, and manganese introduced as a sulfate. The vaporization efficiency, for magnesium and sodium as chlorides, and for lead as a sulfate, remained unchanged. Interestingly, the aging of the tubes was accompanied by partial restoration of the spectral characteristics for unmodified tubes. For example, with unmodified pyrocoated tubes, the vaporization spectrum, appearing as a consequence of the decomposition of aluminum nitrate, consisted of Al₂O bands overlapped by Al atomic lines. In the freshly modified tubes, intensities of those lines and bands were substantially reduced, and in this case, the dominance of AlO molecules was observed. The efficiency of vaporization of aluminum species increased in the aged modified tubes.

The scanning electron microscopy (SEM) images of the modified surfaces for the new and aged tubes indicated that aging of the tubes is accompanied by the destruction of the pyrocoating, formation of pyrographite shells around the areas where the modifier was electrodeposited, and finally, complete substitution of the metal on the graphite surface by pyrographite debris.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Atomic spectrometry; Chemical modifiers; Matrix compounds vaporization

1. Introduction

The influence of chemical modifiers on the release of various chemical species in a graphite furnace is of great interest. The graphite tube is not only used as an atomizer for atomic absorption measurements, but also serves as a vaporizer for atomic emission and mass spectrometry, when connected with inductively coupled plasma [1–3]. Identifying the species evolved during the vaporization is important for optimizing the experimental conditions of a graphite furnace time/temperature program, as

well as for evaluating the transport efficiency of the analyte and matrix compounds from the furnace into the plasma [4,5]. When electrothermal atomization is applied, special attention is always placed on the use of modifiers, especially noble metals that, since their introduction, are undoubtedly the most often employed [6]. In fact, much work has been done towards the application of noble metals modifiers for various analytes and matrices [7,8], and towards understanding the mechanisms of the analyte–modifier and substrate–analyte–modifier interactions [9–12]. An expected advantage of the modifier is improved long-term performance, and it was justified that noble metals modifiers could be used for this purpose [13–15]. It was found that electrodeposition of noble metals on the graphite surface offers significantly improved performance in the presence of a corrosive matrix [16,17]. According to the current understanding of the mechanism of the interaction between noble metals and graphite, they stabilize the

[☆] 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.

* Corresponding author.

E-mail address: ebulska@chem.uw.edu.pl (E. Bulska).

analyte and act as permanent modifiers via the formation of intercalation compounds in the subsurface layer of pyrographite [9,10,18,19]. Penetration of noble metals within the pyrographite domain is expected to occur immediately after injection of the modifier solution, at the sampling/drying stage, due to the porosity of the pyrographite and nanometer scale cracks on the virgin pyrographite surface. This is even more pronounced using electrodeposition to introduce the modifier, since this forces the transportation of noble metals into the subsurface domain of the graphite [10,17].

Noble metals were found to be very effective in stabilizing various analytes [6,7,14]. However, in each particular case, their effectiveness depends on both the nature of the analyte and also on the type of matrix. Therefore, it was of interest to investigate the influence of the modifier on the behavior of species present in microgram amounts, which is typical for the matrix components. For this reason, identifying the main species evolved during the heating of various inorganic substances and investigating the efficiency of their vaporization were considered crucial for atomic absorption measurements. This was also considered an efficient way to investigate the aging phenomena of the graphite tubes.

Various approaches were used to evaluate the phenomena occurring during vaporization of chemical species from a graphite furnace, via inspection of vapor spectra inside the atomizer [20–22] and via inspection of the graphite surface [10,23,24]. The first approach, using UV vapor absorption spectrometry, gives information on the vaporization kinetics and transient vapor composition inside the graphite tube. The supporting information, including the changes in microstructure of the graphite substrate accompanying specific vaporization phenomena, could be obtained by scanning electron microscopy (SEM).

It is well known that the substrate material itself significantly affects the vaporization of inorganic compounds. The list of specific phenomena observed in the pyrocoated tube includes a non-uniform spatial distribution of absorption and emission continua during the vaporization of Mg and Be [25–27], or Cu, Ag, Au, Fe, Co, Ni, and Pd [28]; appearance of a non-resonance Mg emission from the area near the wall of the graphite tube during the vaporization of magnesium oxide [25]; and transformation of spectra of In, Ga and Tl oxides [22,29]. Detailed investigations of these phenomena support the hypothesis that the interaction of micrograms of a chemical species with the graphite substrate during the vaporization causes the evolution of chemical energy into the gas phase. The energy, being transferred back to the sample, facilitates sample vaporization and affects vapor composition. Accordingly, an alteration of spectral information can be expected from Ir and Rh modifiers that are intercalated into the graphite subsurface domain.

The investigations of aging phenomena of the graphite tubes presented in this work were designed to better understand the evolutions of various species present in real samples, not in ‘analyte’ amounts, but rather in ‘matrix’ amounts. We consider the importance of investigating how the vaporization of the matrix components of samples is influenced by the presence of modifiers, and thus how the evolution of matter to gaseous phase occurs. This work investigates the long-term performance of electrodeposited Ir and Rh on the vaporization of micrograms of various salts

introduced to graphite tubes, and their effect on structure of the graphite surfaces, and discusses it in connection with the spectral as well as surface phenomena observed.

2. Experimental

2.1. Instrumentation

Time resolved (0.2 s) molecular spectra (187–380 nm) were collected with the aid of JASCO spectrometer equipped with a charge coupled device (CCD) detector during a 10 s temperature ramp from 400 °C to 2400 °C. The experimental set-up for spectral measurements and methodology were similar to those described previously [30].

An HGA-500 atomizer (Perkin-Elmer) was used for vaporization of inorganic salts introduced into the graphite tube. Standard pyrocoated tubes were used with and without electrodeposited metal modifiers (Ir or Rh).

An infrared pyrometer MK (Model M90-H, Micron Instrument Co., Inc) was used to measure the temperature of the tubes during the heating of the atomizer.

A scanning electron microscope, LEO Stereoscan 440 (Cambridge, UK), equipped with secondary and backscattered electrons (SE and BE, respectively) was used to investigate the graphite tube surface. The accelerating voltage was 20 kV. SE were detected by a standard Everhart–Thornley scintillator detector, while BE were detected using the Centaurus detector by KE Developments (Cambridge, UK).

2.2. Reagents

Aqueous solutions of $\text{Al}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, MnSO_4 , MgCl_2 , NaCl , and PbSO_4 (all salts were from Merck, Germany), having element contents of 0.01–0.5% m/m, were used for preparing the solution of matrix components.

Solutions of rhodium and iridium of 1 g/L were obtained by dissolving the appropriate amounts of their salts (Merck, Germany).

2.3. Procedure

Modifiers (Rh or Ir) were electrodeposited according to the procedure described elsewhere [16,17]. Electrolysis was carried out from the solution of 500 μg of the respective metal (Rh or Ir) for about 45 minutes, up to the point when the amount of the modifier in the electrolytic bath was below a few micrograms.

Table 1
Heating time–temperature program applied to the Perkin-Elmer HGA 500 unit

Step	Temperature, °C	Ramp time, s	Hold time, s	Ar flow rate, ml/min
Drying	200	15	30	300
Pyrolysis	400	15	15	300
Vaporization ^a	2400	1	9	30
Cleaning	2500	1	3	300
Ageing	2200	1	30	300

^a Acquisition of spectra.

Download English Version:

<https://daneshyari.com/en/article/1240587>

Download Persian Version:

<https://daneshyari.com/article/1240587>

[Daneshyari.com](https://daneshyari.com)