

Spectrochimica Acta Part B 51 (1996) 1121-1132

SPECTROCHIMICA ACTA PART B

Effects of atomization surfaces and modifiers on the kinetics of copper atomization in electrothermal atomic absorption spectrometry<sup>1</sup>

María A. Alvarez\*,2, Nereida Carrión, Héctor Gutiérrez

Centro de Química Analítica, Facultad de Ciencias, Universidad Central de Venezuela, P.O. Box 47102, Caracas 1041-A, Venezuela Received 4 October 1995; accepted 20 February 1996

## Abstract

Atomization of copper from different atomization surfaces and in the presence of chemical modifiers has been investigated. The atomization surfaces are molybdenum and tungsten carbide-coated platforms obtained by physical vapour deposition and pyrolytic graphite coated platforms. Molybdenum, tungsten and palladium have been used as chemical modifiers. The kinetic parameters of copper atomization in electrothermal atomic absorption spectrometry have been determined by three different methods. Although in all cases, differences in the atomization profiles are observed, the appearance temperatures when the carbide-coated platform and chemical modifiers are used, are not significantly different from those observed with conventional pyrolytic graphite platforms. Nevertheless, a longer tailing of the atomization profile and a slight thermal stabilization of the copper atomic vapour are found when tungsten and palladium modifiers are employed. In these later cases, two different activation energies are determined for each absorbance profile by the different models employed, indicating the presence of two possible precursors in the atomization mechanism. The activation energy  $(E_a)$  values calculated in these cases are 75–104 kJ mol<sup>-1</sup> when the atomic vapour starts to appear and 170–300 kJ mol<sup>-1</sup> at high temperatures. The lower  $E_a$  values are comparable to the single  $E_a$  value obtained with pyrolytic graphite platform and the other cases studied, in which a single precursor mechanism is proposed. In these cases, the copper atomic vapour seems to desorb from the surface as highly dispersed atoms. When the palladium modifier is employed, the high  $E_a$  and changes in the reaction order found at high temperatures, would indicate that the atomic vapour is additionally originating from the evaporation of aggregates. These aggregates could be formed by redistribution and agglomeration at higher temperatures and possibly trapping by the modifier. In the case of the tungsten modifier, dispersed atoms present in the cooler places of the platform could be responsible for the apparent increase of the  $E_a$  value found. This second release could provide the longer tailing observed in the absorbance profiles when palladium and tungsten modifiers are used. A first-order kinetic release found in some of the cases studied could suggest a strong interaction with the surface; however, the low frequency factor value found gives no evidence for any substrate-analyte interaction in any of the cases studied.

Keywords: Atomization surfaces; Cu; ETAAS; Kinetics

0584-8547/96/\$15.00 © 1996 Elsevier Science B.V. All rights reserved *PII* S0584-8547(96)01509-1

Cedex, France A 0R6. Canada

Belaium

alia

Poland D DC H OR

MD ia nany MD

ntered on a calendar year alia, Brazil, Canada. Hong Korea, Taiwan, Thailand,

1000 AE Amsterdam, The

er Science B.V. (P.O. Box ir speed delivery. Second

mont, NY 11003.

, The Boulevard, Langford an Lipner, P.O. Box 1110, , 20-12 Yushima, 3-chome,

<sup>\*</sup> Corresponding author at: Centro de Química Analítica, Facultad de Ciencias, Universidad Central de Venezuela, P.O. Box 47102, Caracas 1041-A, Venezuela.

<sup>&</sup>lt;sup>1</sup> This paper was presented (in part) at the CSI XXIX Post Symposium 'Electrothermal Atomization in Analytical Atomic Spectroscopy', University of Ulm, Germany, September 1995, and published in the Special Issue of *Spectrochimica Acta, Part B*, dedicated to that Symposium.

<sup>&</sup>lt;sup>2</sup> Temporary address: Interface Analysis Centre, University of Bristol, 121 St. Michael's Hill, Bristol BS2 8BS, UK.