

## STUDY OF SURFACE EFFECTS ON AG-CU NANOPARTICLES BY KNUDSEN EFFUSION MASS SPECTROMETRY

František ZELENKA<sup>1</sup>, Pavel BROŽ<sup>1,2\*</sup>, Aleš STÝSKALÍK<sup>1,2</sup>, David ŠKODA<sup>1,2</sup>, Ondřej ZOBAČ<sup>1</sup>

<sup>1</sup>Masaryk University, Faculty of Science, Department of Chemistry, Kotlářská 2, 611 37, Brno, Czech Republic, [broz@chemi.muni.cz](mailto:broz@chemi.muni.cz)

<sup>2</sup>Masaryk University, Central European Institute of Technology, CEITEC, Kamenice 753/5, 625 00, Brno, Czech Republic

### Abstract

Surface effects on AgCu nanoparticles synthesized in aqueous solution of 1,10-phenanthroline were investigated by Knudsen effusion mass spectrometry during slow heating in order to understand their thermal stability and behaviour. Selection of a mass range for mass spectra monitoring was performed on the basis of data acquired by direct inlet probe mass spectrometry during rapid heating realized prior the Knudsen effusion method. As follows from the measurements, the organic substance which protects the nanoparticles against coagulation suddenly and quantitatively evaporates at elevated temperatures during the heating process. The data were subsequently used for specification of surface effects on the nanoalloys. Results are summarized and discussed in view of previous studies.

**Keywords:** nanoalloy, evaporation, surface analysis, Knudsen effusion mass spectrometry, direct inlet probe mass spectrometry

### 1 THEORETICAL PART

Under a term nanoparticle, a small particle of 0-100 nm sized dimension is meant. Such small object has a large surface to volume ratio and, therefore, it is very sensitive to surface reactions such as oxidation, desorption of various substances from surroundings, mutual coagulation etc.

#### 1.1 Nanoparticles and organic substances as a core-shell system

Organic compounds as a part of metalloorganic precursors in synthesis of nanoparticles or as additives in organic solvents or organic solvents themselves are important from the point of view of nanoparticles stabilisation and preventing from their mutual coagulation. Organic compounds and metal nanoparticles create so called (metal/organic) core-shell system M@O (M - metal, O - organics).

#### 1.2 System AgCu@1,10-phenanthroline

It is known that metallic nanoparticles play an important role as antibacterial and even cytotoxic agents in medicine and that presence of some organic compounds on the nanoparticle surface deepens these capabilities. Within our testing of influence of AgCu bimetallic nanoparticles modified by 1,10-phenanthroline on cell viability [1] a requirement for a study of surface behaviour of this organic compound on the AgCu nanoparticle surface during heating arose in order to better understand a stability of this system and surface effects.

#### 1.3 Mass spectrometry as a tool for surface analysis

Mass spectrometry is an analytical method based on ionization of atoms and molecules from an evaporated sample and a subsequent ion separation and detection. A mass spectrometer consists of three main parts, ion source, mass analyser and mass detector. Electron impact ionization yielding positively charged ions (EI<sup>+</sup>), i.e. interaction of electrons originated from a filament (a heated metal wire) with the atom or molecule is

commonly used. Low pressure conditions are required for this technique to insure a sufficiently long mean free path without collisions between the ion source and the detector. As an output a relative abundance of ions in dependence on their mass to charge ratio ( $m/z$ ), so called mass spectrum, is obtained. Mass spectra of organic compounds are usually composed of a number of peaks owing to fragmentation processes taking place after ionization which clearly shows this method to be convenient for qualitative as well as for quantitative purposes.

### 1.3.1 Direct inlet probe mass spectrometry

Direct inlet probe mass spectrometry (DIP/MS) is method for a fast analysis of little volatile or nonvolatile compounds. Sample is placed in a small silica ampoule or applied onto a surface of a wire from resistant material like W, Re etc. which create the end part of a metal rod, a specially designed interface for solid sample introduction. The probe is then pushed through the open valve into the ion source and mass spectra are collected from evaporating sample during heating. The heating rate and the heating process are typically fast.

### 1.3.2 Knudsen effusion mass spectrometry

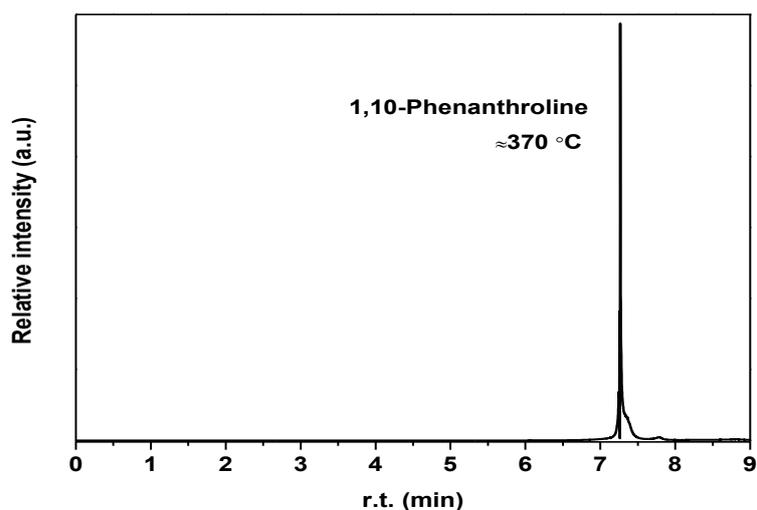
Knudsen effusion mass spectrometry (KEMS) is method based on thermodynamic equilibrium formation between a given phase of a sample in condensed state (solid or liquid) and its vapour above the sample and the measurement of the equilibrium vapour pressure of gaseous species. In order to ensure the equilibrium state, the sample is placed in a small so called Knudsen cell (KC), usually from alumina, and closed by a lid from the same material having an effusion orifice of approximately 1mm in diameter in the centre. During the experiment, the originated vapour including volatile components of the sample leaves the cell through the orifice and the collimated molecular beam, in which the flux of each vapour species can be related to the partial pressure of that atom or molecule, enters the ion source of a mass spectrometer. The heating rate and the heating process are typically slow.

## 2 EXPERIMENTAL PART

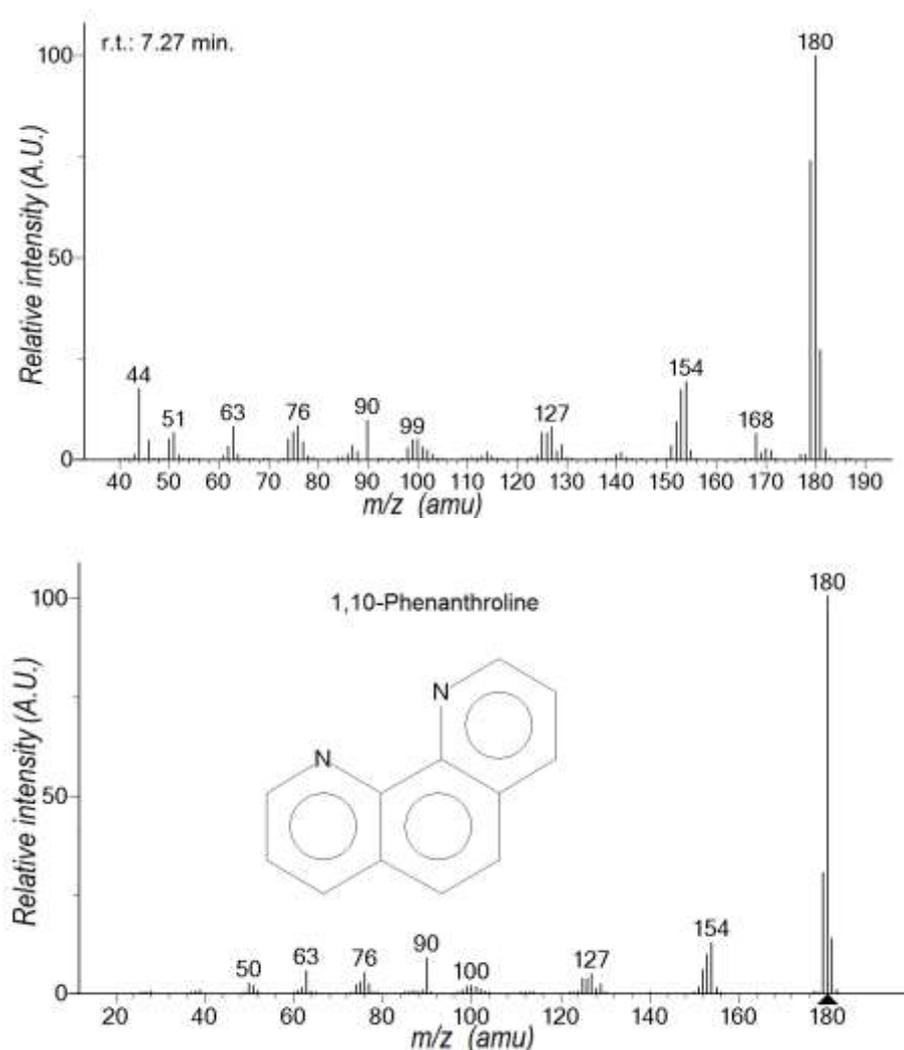
AgCu nanoparticles of eutectic composition Ag<sub>59.7</sub>Cu<sub>40.3</sub> (at.%) having 35 nm in diameter were prepared by synthesis in aqueous solution of 1,10-phenanthroline as described in [2] and investigated by Knudsen effusion mass spectrometry (KEMS) on a Netzsch STA 409 CD/3/403/5/G apparatus, a specially-adapted type of the commercial STA 409 CD - QMS 403/5 Skimmer Coupling Instrument [3]. Selection of a mass range for mass spectra monitoring was performed on the basis of data acquired by direct inlet probe mass spectrometry (DIP/MS) performed on TSQ Quantum XLS (Thermo Scientific) instrument equipped by NIST 11 spectral library.

### 2.1 Direct inlet probe mass spectrometry

This technique was used for mass spectra monitoring as a basis for sub-sequent KEMS measurements. Samples were placed into a small silica ampoule and quickly heated from temperature 30°C to 450°C with the heating rate of 50°Cmin<sup>-1</sup> until 1,10-phenanthroline was completely evaporated. Dwell time for 30s at the lower temperature and for 60s at the final one was used at the beginning and at the end of the analysis. During the heating, spectra were measured every 1 s after EI<sup>+</sup> ionization at electron energy of 70 eV. Results in the form of total ion current vs. retention time (r.t.) and hence the temperature, so called thermogram, together with information on the respective organic compounds is shown in Fig. 1. Acquired mass spectra as well as the tabulated one from the NIST 11 spectral database are shown in Fig. 2.



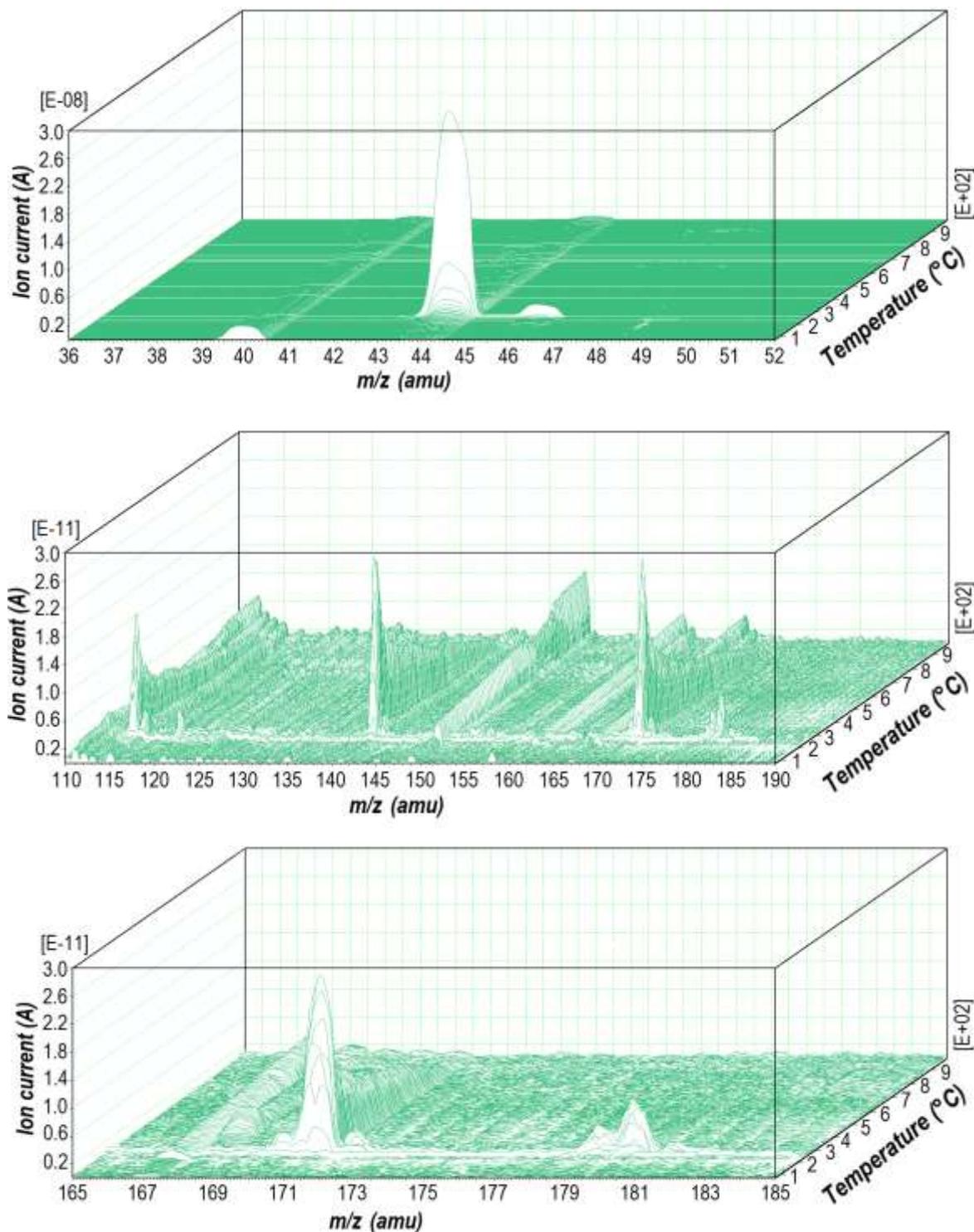
**Fig. 1** DIP/MS thermogram of the AgCu nanoparticles, heating from 30°C up to 450°C with heating rate 50°C min<sup>-1</sup> and dwell time of 30s at the beginning and of 60s at the end of the analysis.



**Fig. 2** Mass spectra of 1,10-phenanthroline in EI<sup>+</sup> mode (a) acquired during DIP/MS measurement on the AgCu nanoparticles and (b) tabulated in the NIST 11 mass spectral database.

## 2.2 Knudsen effusion mass spectrometry

Knudsen effusion mass spectrometric (KEMS) measurement was performed for detailed surface analysis of AgCu nanoparticles. Samples were put into a small alumina crucible and placed into a Knudsen cell which was covered by a lid with central effusion orifice of 1mm in diameter. Samples then underwent slow heating process from 60 to 980°C with the heating rate of 5°Cmin<sup>-1</sup> and the mass spectra were collected every 40s. Records from the KEMS measurements are shown in Fig. 3.

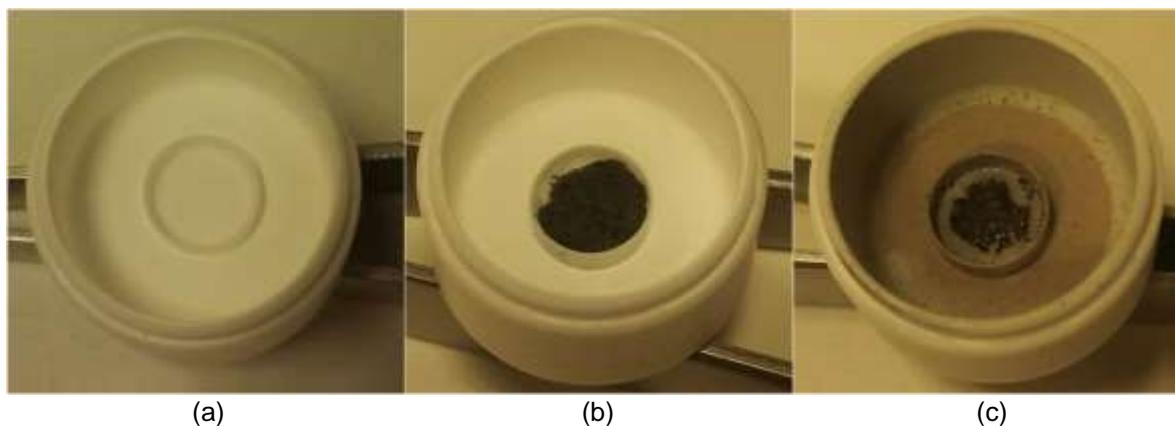


**Fig. 3** Selected parts of mass spectra acquired during KEMS measurement of Ag-Cu nanoparticles, heating from 60 to 980°C with the heating rate of 5°C min<sup>-1</sup>, showing masses typical for 1,10-phenanthroline.

### 3 RESULTS AND DISCUSSION

A preliminary fast surface analysis using DIP/MS technique clearly shows a quantitative evaporation of 1,10-phenanthroline around the temperature 370°C and hence a possible existence of surface effects on the metal/organic core-shell interface during the heating.

The thermal metal/organic core-shell stability and the potential surface effects were investigated in more detail by KEMS technique realized at slow heating rate. The measurement shows that 1,10-phenanthroline quantitatively leaves the AgCu nanoparticle surface around the temperature 295°C. The evaporation starts at about 240°C reaching a sharp maximum at 250°C. Furthermore, existence of a slight brown thin coating was observed in the Knudsen cell in vicinity of the inner small alumina crucible in which the sample was placed while the remaining sample in the alumina crucible was black with visible light microsized AgCu balls as documented in Fig.4 which shows empty alumina crucible and that after sample application before the KEMS measurement as well as the situation after the KEMS measurement. It means a surface reaction of the organic compound with the alloy nanoparticles may occur similarly as reported in our previous study [4] where more complicated system including more organic substances was investigated. Because the operating pressure in the instrument for the KEMS technique has a limiting value of  $1 \cdot 10^{-3}$  Pa and the partial pressure of Ag and Cu is far below this value in the measured temperature region it supports our assumption that a volatile organometallic compound may be formed during the heating process and chemical deposition may take place leading to creation of the thin coating. Furthermore, pronounced ion current intensity at 44 m/z which is of three order of magnitude higher than the others in the mass spectra of this organic compound implies this nanosystem produces a significant amount of carbon dioxide as a product of catalytic oxidation of the organic surface layer with oxygen traces in the apparatus which is in agreement with already studied catalytic decomposition of organic substances on nanoparticle surfaces of noble metals, published e.g. in [5], and with recent study of oxygen reduction reaction on bimetallic AgCu nanoparticles [6].



**Fig. 4** Knudsen cell with inner alumina crucible (a) before and (b) after application of AgCu nanoparticles before KEMS measurement and (c) after KEMS measurement.

### 4 CONCLUSION

Thermal stability and surface effects on AgCu/1,10-phenanthroline core-shell interface were investigated by means of direct inlet probe mass spectrometry (DIP/MS) and Knudsen effusion mass spectrometry (KEMS). The thermal stability of this system was found to be up to 250 -295°C. At these temperatures a fast and quantitative removal of the protective organic layer was observed, accompanied by simultaneous oxidation of the organic compound which follows from carbon dioxide production detectable as a strong signal at 44 m/z in the mass spectrum. During the heating, reactions between the nanoparticles and the organic compound may occur, leading to formation of volatile organometallic compound(s) which is attributed to existence of thin brown coating after the heating process.

The specified thermal stability of the nano AgCu@1,10-phenanthroline core-shell system is important information not only for characterization of stability of the synthesized AgCu nanoparticles but also for improvement of antibacterial and cytotoxic properties for which existence of the AgCu/1,10-phenanthroline core-shell interface is crucial.

Further studies are planned for a complete understanding of phenomena in this nanoparticle core-shell system.

## ACKNOWLEDGEMENT

***This work has been supported by the Ministry of Education, Youth and Sports of the Czech Republic under the project LD11046 (COST MP0903) and by the project "CEITEC – Central European Institute of Technology" (CZ.1.05/1.1.00/02.0068) from the European Regional Development Fund as well as by the Grant Agency of the Czech Republic under the project GA 14-12653S.***

## LITERATURE

- [1] BERNARD, V., ZOBAČ, O., SOPOUŠEK, J., MORNSTEIN, V., Ag-Cu bimetallic nanoparticles under effect of low intensity ultrasound - the cell viability study in vitro. *Journal of Cancer Research*, 2014, nr. 971769, submitted for publication.
- [2] ZOBAČ, O., SOPOUŠEK, J., VYKOUKAL, V., BURŠÍK, J., ROUPOVCOVÁ, P., Chemical wet synthesis and characterization of copper-silver nanoparticles. *NANOCON 2014, 6TH INTERNATIONAL CONFERENCE*, 2014, submitted.
- [3] BROZ, P., SOPOUSEK, J., VRESTAL, J., PINKAS, J. Combination of thermal analysis and Knudsen effusion mass spectrometry for study of metal materials on macro- and nano-scale. *ECS Transactions*, 2013, year 46, nr. 1, page 69.
- [4] SOPOUŠEK, J., PINKAS, J., BROŽ, P., BURŠÍK, J., VYKOUKAL, V., ŠKODA, D., STÝSKALÍK, A., ZOBAČ, O., VŘEŠŤÁL, J., HRDLIČKA, A., ŠIMBERA, J., Ag-Cu Colloid Synthesis: Bimetallic Nanoparticle Characterisation and Thermal Treatment. *Journal of Nanomaterials*, year 2014, nr. 638964.
- [5] HARUTA, M., Gold as a Novel Catalyst in the 21st Century: Preparation, Working Mechanism and Applications. *Gold Bulletin*, 2004, year 37, nr.1, page 27.
- [6] SHIN, K., KIM, D.H., LEE, H.M., Catalytic Characteristics of AgCu Bimetallic Nanoparticles in the Oxygen Reduction Reaction. *ChemSusChem*, 2013, year 6, nr. 6, page 1044.