

SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

Dr Magdalena Luty-Błoch, Master of Engineering
AGH University of Science and Technology in Cracow
Faculty of Non-Ferrous Metals

1. Name and surname:

Magdalena Luty-Błocho

2. Obtained diplomas, scientific degrees – providing name, place and date they were obtained, title of doctoral thesis, and names of the supervisor and reviewers:

Doctor of Science in Technology

Subject: Metallurgy

Work title: Synthesis of gold and platinum nanoparticles in microsystems

Date of defence: 3rd July 2012

Place: AGH University of Science and Technology in Cracow
Faculty of Non-Ferrous Metals

Supervisor: Prof. Ph.D. Krzysztof Fitzner, Master of Engineering

Reviewers: Ph.D. Leszek Blacha, Master of Engineering, Associate Professor at Silesian University of Technology

Prof. Ph.D. Konrad Szaciłowski, AGH University of Science and Technology in Cracow

Master of Engineering

Subject: Metallurgy

Work title: Kinetics of Pt(IV) complex *cis*-[PtCl₄(NH₃)₂] reduction with ascorbic acid

Date of defence: 28th June 2007

Place: AGH University of Science and Technology in Cracow
Faculty of Non-Ferrous Metals

Supervisor: Prof. Ph.D. Krzysztof Fitzner, Master of Engineering

Reviewer: Dr hab. Krzysztof Paclawski, Master of Engineering

3. Information of employment history in scientific institutions

Assistant Professor:

University of Science and Technology in Cracow, Faculty of Non-Ferrous Metals,
Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals

06.2014 – present

Assistant lecturer:

University of Science and Technology in Cracow, Faculty of Non-Ferrous Metals,
Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals

10.2011 – 05.2014

4. Indication of an academic achievement obtained after receiving the PhD degree, contributing significantly to development of Metallurgy, pursuant to *Art.* 16 sec. 2 of the Act of 14th March 2003 on academic degrees and titles and on degrees and titles within art.

a. title of academic achievement

**INFLUENCE OF ELECTROSTATIC, STERIC AND MIXED STABILIZATIONS ON
MORPHOLOGY OF NOBLE METALS PRODUCED WITH THE
HYDROMETALLURGICAL METHOD**

**WPLYW STABILIZACJI ELEKTROSTATYCZNEJ, STERYCZNEJ ORAZ
MIESZANEJ NA MORFOLOGIĘ NANOCZĄSTEK METALI SZLACHETNYCH
WYTWARZANYCH METODĄ HYDROMETALURGICZNĄ**

b. list of academic works documenting academic achievement (achievements), being the base to apply for the degree of doctor habilitated

The list of academic works

A1. M. Luty-Błoch, M. Wojnicki, K. Fitzner, Gold nanoparticles formation via Au(III) complex ions reduction with L-ascorbic acid, *International Journal of Chemical Kinetics*, 49 (2017) 11, 789–797.

(Impact Factor: 1.416)

(Rank list of MNiSW (Ministry of Science and Higher Education): 20)

My contribution to this work was to plan the experimental part, to do all the experiments related to the kinetics of the formation of gold nanoparticles. I described and interpreted obtained results. I estimate my contribution to 85%.

A2. M. Luty-Błocho, M. Wojnicki, J. Grzonka, K.J. Kurzydłowski, K. Fitzner, *Linking the gold nanoparticles formation kinetics with their morphology*, International Journal of Chemical Kinetics 50 (2018) 3, 204–214.

(Impact Factor: 1.416)

(Rank list of MNiSW: 20)

My contribution to this work was to plan and carried out all the experiments. I described and interpreted the obtained results. I estimate my contribution to 75%.

A3. M. Luty-Błocho “*The influence of steric stabilization on process of Au, Pt nanoparticles formation*”, Archive of Metallurgy and Materials 64 (2019), 1, 55-63.

(Impact Factor: 0.652)

(Rank list of MNiSW: 30)

My contribution to this work was to plan and carried out all the experiments, writing the manuscript. I described and interpreted the obtained results. My contribution was 100%.

A4. M. Wojnicki, M. Luty-Błocho, Marek Bednarski, Magdalena Dudek, Joanna Knutelska, Jacek Sapa, Małgorzata Zygmunt, Gabriel Nowak, Krzysztof Fitzner, *Tissue distribution of gold nanoparticles after single intravenous administration in mice*, Pharmacological Reports 65 (2013) 4, 1033–1038.

(Impact Factor: 2.165)

(Rank list of MNiSW: 25)

My contribution to this work consisted of editing a part of the manuscript, performing the synthesis of gold nanoparticles and preparing samples for an analysis on ICP-MS. I estimate my contribution to 35%.

A5. M. Bednarski, M. Dudek, J. Knutelska, L. Nowiński, J. Sapa, M. Zygmunt, G. Nowak, M. Luty-Błocho, M. Wojnicki, K.Fitzner, M. Teşiorowski, *The influence of the route of administration of gold nanoparticles on their tissue distribution and basic biochemical parameters*, Pharmacological Reports 67 (2015) 3, 405–409.

(Impact Factor: 2.251)

(Rank list of MNiSW: 25)

My contribution to this work consisted of editing a part of the manuscript, performing the synthesis of gold nanoparticles and preparing samples for an analysis on ICP-MS. I estimate my contribution to 30%.

A6. M. Wojnicki, M. Luty-Błocho, M. Kotańska, M. Wytrwal, T. Tokarski, A. Krupa, M. Kołaczkowski, A. Bucki and M. Kobielski, *Novel and effective synthesis protocol of AgNPs functionalized using L-cysteine as a potential drug carrier* Naunyn Schmiedebergs Arch Pharmacol. 391 (2018) 2, 123–130.

(Impact Factor: 2.558)

(Rank list of MNiSW: 25)

My contribution to the creation of this work consisted in developing a method of synthesis of silver nanoparticles with high concentration and analyzed them. I described and interpreted the obtained results. I have written part of the manuscript (materials and methods, results, conclusions). I estimate my contribution to 64%.

A7. M. Wojnicki, K. Fitzner, M. Luty-Błocho, *Kinetic studies of nucleation and growth of palladium nanoparticles*, Journal of Colloid and Interface Science 465 (2016) 190–199.

(Impact Factor: 4.233)

(Rank list of MNiSW: 30)

I planned and conducted all the experiments, described the mechanism of palladium nanoparticles formation, determined kinetic parameters and interpreted the obtained results as well as edited the manuscript. I estimate my contribution to 90%.

A8. M. Luty-Błocho, M. Wojnicki, G. Włoch, K. Fitzner, *Green method for efficient PdNPs deposition on carbon carrier in the microreactor system*, Journal of Nanoparticles research, 20 (2018) 239.

(Impact Factor: 2.127)

(Rank list of MNiSW: 30)

My contribution to this work was to plan and carry out all experiments on the synthesis of palladium nanoparticles in the microreactor. I described and interpreted the obtained results. I wrote the manuscript. I estimate my contribution to 85%.

A9. M. Luty-Błocho, M. Wojnicki, J. Grzonka, K.J. Kurzydłowski, *The synthesis of stable platinum nanoparticles in the microreactor*, Archives of Metallurgy and Materials 59 (2014) 2, 509–512

(Impact Factor: 1.09)

(Rank list of MNiSW: 25)

My contribution to this work was to plan and carry out all experiments on the synthesis of platinum nanoparticles in the microreactor and in the batch reactor. I described and interpreted the obtained results. I wrote the manuscript. I estimate my contribution to 75%.

A10. M. Luty-Blocho, M. Wojnicki, *Single-step synthesis of onion-like Au-Pd-PtNPs nanoparticles using microflow system*, Journal of Flow Chemistry, 5(2015) 4, 197–200

(Impact Factor: 1.942)

(Rank list of MNIŠW: 30)

My contribution to the creation of this work consisted in planning and carrying out experiments involving the synthesis of a nanomaterial in a microreactor. I described and interpreted the obtained results. I have written part of the manuscript (paragraphs 1, 2 and 3). I estimate my contribution to 50%.

Applied research techniques

The presented achievement (A1-A10) was realised with the use of the following measurement methods.

- UV-Vis spectroscopy

In order to analyse morphology and kinetics of individual stages (reduction, nucleation, growth of particles in process of metal nanoparticles formation, the UV-Vis spectrometry was applied. The method is commonly used for analysis of coloured solutions and for observation of metallic phase formation in a solution. In my studies I have applied two types of spectrophotometers. The first one is the UV-Vis spectrophotometer (Shimadzu, Japan) which was mainly used to register spectra of characteristic reagents (ions of metal, reducer) and plasmons. The second one is the ‘stopped-flow’ spectrophotometer (SX 20, Applied Photophysics, UK) that was used for both tracking and registering courses of fast reactions (of the order of ms) related to formation of particles and their plasmons. Both devices worked within the UV-Vis range, namely, from 190 to 900 nm and were equipped with a measurement cell with a possibility of changing the length of optical path. Measurement in the devices relied on placing the sample (containing the examined solution) and the reference one (containing solvent) and shine a monochromatic light beam of different length through them. The measurement in the ‘stopped-flow’ spectrophotometer included placing reagents in reservoirs, whereas they were mixed automatically in the measurement cell. The measurement showed that part of the emitted light I_0 passing through the examined sample was absorbed while the remaining amount I goes to the detector where it is calculated. As a result of the analysis a spectrum is obtained

(dependence of absorbance in the function of wavelength) and correlation between density of the monochromatic radiation beam passing through homogeneous solution of the examined substance is, in accordance with Lambert-Beer law, directly proportional to the density of solution C and to the thickness of the absorbing layer (the length of optical path of the measurement tray) l .

The Lambert-Beer law:

$$A = \log \frac{I_0}{I} = \varepsilon \cdot C \cdot l$$

where: I_0 – intensity of radiation falling on the sample, I – intensity of radiation after passing through the sample, ε - absorption coefficient [$\text{dm}^3/(\text{mol} \cdot \text{cm})$], C – concentration of the examined sample [mol/dm^3], l – length of the optical path [cm].

I analysed the obtained spectra with the use of programs such as UV-Probe and PRO-DATA SX. Whereas, the obtained characteristic spectra, plasmons, and kinetic curves were worked out with the use of the Origin Pro 8.5 program.

- STEM and HRTEM microscopy

Morphology of the obtained materials (nanoparticles, functional materials) was analysed applying scanning transmission electron microscopy (STEM, Hitachi Su70, Japan) or high-resolution transmission electron microscopy (HRTEM). STEM and HRTEM belong to the basic techniques used in studies of solid bodies in the nanoscale. They allow, among others, to determine size, shape and elemental composition of the examined sample. Moreover, high-resolution microscopy enables imaging individual atoms in an elementary cell.

On the basis of the obtained microscope photographs I analysed distribution of the particles size with the use of the ImageJ program.

- The Method of Dynamic Light Scattering (DLS)

Morphology (size, polydispersity) of the particles was analysed with the DLS method (Nano Zeta S, Malvern, UK.). As a result, I obtained a value of the hydrodynamic radius for which the relation between the particles size and their motion velocity (Brownian motion) is described by the Stokes-Einstein equation:

$$R_h = \frac{kT}{6\pi\eta D}$$

where: R_h – value of the particles hydrodynamic radius, k – Boltzmann constant, T – temperature (Kelvin scale), η – viscosity of the solvent, D – diffusion coefficient.

- The Laser Doppler Electrophoresis method (LDE)

The measurement of electrokinetic potential of zeta (ζ) was conducted with Nano Zeta S (Malvern, UK.). The potential is defined at, so-called, sliding boundary i.e. the contact of motionless ions layer on the particle and its surroundings. The measurement relied on passing a laser beam through a measurement tray containing the examined solution during electrophoresis. The value of (ζ) potential was used to assess stability of the created particles.

- X-ray Diffraction (XRD)

In order to determine crystallography of the obtained material and thus to obtain the information on the grain size, I applied X-ray diffraction (XRD).

- Analysis XPS X-ray photoelectron spectroscopy, X-ray photoelectron spectroscopy (PHI 5000 Versa Probe II, ULVAC-PHI, Chigasaki, Japan)

This method allows qualitative and quantitative analysis of all elements except hydrogen. It also allows the determination of the type of chemical bonds in which elements present on the surface participate, makes it possible to identify the chemical states of the elements.

In addition, in order to determine the metal content in the tested samples, I used the following analyzers:

- ICP-MS, Inductively Coupled Plasma – Mass Spectrometry, ELAN 6100, Perkin Elmer
- MP-AES, Microwave Plasma Atomic Emission Spectroscopy, 4200MP-AES Agilent

Realisation of the scientific achievement

Nanoparticles of noble metals such as silver, gold, palladium and platinum are commonly used in many branches of industry, chemical and process engineering and in medicine. Their high applicability, despite high price per 1kg, results from unique physicochemical properties of nanoparticles, e.g. plasmon resonance effect and ability to adsorb different compounds. Applying the size of the matter in nanoscale made the price a secondary issue in comparison to the used amounts and benefits connected with their use. The process of formation noble metals nanoparticles has been known for a few decades and there are still new publication in the field. Therefore, it is possible to find many procedures both physical and chemical in the literature that allow synthesis of materials of different morphology (size, shape) and properties. The most popular method among them (due to simplicity and cost) is the hydrometallurgical method (chemical reduction) that comprises reduction of metal ions with a suitable reducer in aqueous environment. The particles can still grow until the substrates are finished. As a consequence, stable particles or deposit can be formed. The form of the obtained particles depends on the presence of stabiliser or its lack. Three types of stabilisation can be distinguished. These are electrostatic, steric and mixed stabilisations. The first of them bases on surrounding the nanoparticles with ions of the charge opposite to its surface charge. It creates a double layer consisting of opposite charges that stabilises the particle. The second method includes application of steric stabiliser. This type of stabilisation is most frequently realised by addition of polymer which, following the physical or chemical adsorption, gets attached to the particle blocking its surface and thus isolating it from the medium it is in. The last type of stabilisation, the mixed one, combines the two former ones.

A review of literature shows that for at least 10 years scientists have been searching for formation procedures that are directed at particular application e.g. in catalysis or medicine. Taking into account that application of noble metals nanoparticles in medicine or catalysis can be affected by the particles properties, I started my work defining factors that determine them. Literature overview indicates clearly that nanoparticles properties are tightly connected with their morphology and stability in time. It is also known that the features depend on the kinetics of the process of particles formation determined by the type of the metal ions precursor, type of reducer (weak, strong), their initial concentration, surrounding conditions (temperature, pH, ions force) and the presence of stabilising factor. Whereas, literature does not present any data that would enable linking the kinetics of particles formation with their shape, size, monodisperse and stability, and they influence the final morphology of the particles and their properties. Therefore, I suggested the following ***research hypothesis***: juggling kinetics

parameters and a proper selection of stabilisation, can make it possible to influence morphology, and subsequently determine particles properties and finally their usefulness for particular applications.

In order to confirm the validity of the research hypothesis, the main goal of the research was to find the relationship between kinetic parameters, the type of stabilization applied to the final morphology of materials obtained by hydrometallurgical method.

In connection to such a research goal, at first, I focused on kinetic study.

In the work, appendix (A1):

M. Luty-Błocho, M. Wojnicki, K. Fitzner, Gold nanoparticles formation via Au(III) complex ions reduction with L-ascorbic acid, *International Journal of Chemical Kinetics*, 49 (2017) 11, 789–797

I presented detailed kinetic study concerning the process of gold nanoparticles formation obtained with the hydrometallurgical method, i.e. chemical reduction of Au(III) ions with the use of L-ascorbic acid as a reducer and also electrostatic stabiliser. The main parameter that influences efficiency of electrostatic stabilisation action is maintaining low concentration of ions in the solution, i.e. the value of ionic strength below 0.01M. As in the work of Luty-Błocho et al. [A1, item 45] I had already described in detail the first step kinetics while examining reduction of ions Au(III) to Au(I) with the spectrophotometric method, in the work (A1) I focused on testing the kinetics of nucleation process and autocatalytic growth of gold particles. In the publication, I showed that initial concentration of reagents (precursor of metal ions and reducer), addition of chloride ions as well as temperature influence kinetics of nucleation and growth. In order to define rate constants of the stages, the process of gold particles formation in time was registered spectrophotometrically. The obtained spectra (dependence of absorbance in the function of wavelength) with characteristic maximum within the range of visible light (so-called plasmon) result from the particles plasmon resonance. Depending on the shape, size and monodisperse of the particles, the position of the plasmon peak, its width and intensity differ. On the basis of the obtained plasmons, I obtained kinetic curves (dependence of absorbance in time at defined wavelength which is corresponded by a maximal value of absorbance) describing formation of nanometric particles. Each time I received sigmoidal character of the curves which proves that the particles formation process consists of two stages: slow nucleation and fast autocatalytic growth. Therefore, the phenomena was described with the use of the Finke-Watzky model that enabled determining values of the observed rate constants of individual stages i.e. nucleation and autocatalytic growth of particles. Moreover, applying the Arrhenius and Eyring equation with the graphic method (A1, Fig. 4) I determined

values of activation energy ($22.5 \text{ kJ}\cdot\text{mol}^{-1}$ for nucleation stage and $30.3 \text{ kJ}\cdot\text{mol}^{-1}$ growth stage), entropy (about $-228 \text{ JK}^{-1}\cdot\text{mol}^{-1}$ for nucleation stage and $-128 \text{ JK}^{-1}\cdot\text{mol}^{-1}$ for growth stage) and enthalpy ($19,8 \text{ kJ}\cdot\text{mol}^{-1}$ for nucleation and $27,8 \text{ kJ mol}^{-1}$ for particles growth). I also showed that disproportionation reaction (A1, equation 12) affected rate of nanoparticles formation and can have an influence on their final morphology. The values of the observed rate constants allowed comparison of the nucleation process and growth as well as indicating which parameter influences rate of the process, and consequently, morphology. I demonstrated that an increase of the reducer initial concentration inhibits the nucleation process, namely reactions (A1, equations 6a, b) whereas accelerates the autocatalytic growth (A1, equations 7a, b), and thus the values of observed rate constants grow ($k_{3,\text{obs}}$) (A1, Table 1).

In another work, appendix (A2):

M. Luty-Błoch, M. Wojnicki, J. Grzonka, K.J. Kurzydłowski, K. Fitzner, *Linking the gold nanoparticles formation kinetics with their morphology*, International Journal of Chemical Kinetics 50 (2018) 3, 204–214

I confronted the obtained results from kinetic tests describing the process of formation of electrostatically stabilised particles (app. A1) with their morphology. In the work, I applied only two reagents (metal precursor and reducer) for synthesis of gold nanoparticles of different shapes to minimize the number of factors that could affect morphology. I showed that with the use of different concentrations of reagents, formation of gold nanoparticles of different morphology (size, shape) is possible with the hydrometallurgical method. The colour of the obtained colloidal gold changed from pink (A2, Fig. 1a, b Fig. 8b), purple (A2, Fig. 1c, Fig. 8c) to blue (A2, Fig. 8a) which corresponded with the change of the particles shape. The obtained colloids were analysed spectrophotometrically (plasmons registration, A2, Fig. 2, 9) and with the use of HRTEM microscopy (verification of shape and size). Valuable information was delivered by high-resolution microscopy which finally confirmed that spherical shape of nanoparticles (A2, Fig. 3) is responsible for pink colour of the colloidal gold, whereas blue one contains particles in the shape of 'stars' (A2, Fig. 10). A mixture of particles different shapes (polydispersity) (A2, Fig. 12b) is responsible for purple colour of the colloid. I also showed that the kinetics of nucleation process and growth is controlled by a reaction occurring on the surface of the old particle, i.e. comproportionation of Au(III) and Au(0) to Au(I) which can be inhibited by different concentration of metal ions precursor and reducer.

Summarising, a detailed analysis of kinetics data and the results of morphology analysis showed that very slow nucleation and fast autocatalytic growth provide monodisperse particles. High

excess of reducer and consequent excess of electrostatic stabiliser in the examined system (Au-L-ascorbic acid) allowed to obtain colloidal gold of blue colour and a star-like shape.

In another work, appendix (A3):

Magdalena Luty-Błocho “*The influence of steric stabilization on process of Au, Pt nanoparticles formation*”, *Archive of Metallurgy and Materials* 64 (2019), 1, 55-63

I examined the influence of steric stabilisation action and a lack of stabilisation factor on kinetics of particular stages, i.e. ion reduction Au(III) to Au(I), nucleation i.e. ions reduction Au(I) to Au(0) and particles growth. For this purpose I registered spectrophotometrically kinetic curves for each step of kinetics, determined values of the observed rate constants and presented them in tables (A3, Table 2-4) and defined with the DLS method the size of the obtained particles (A3, Table 9). The first examined system was Au(III)-L-ascorbic acid, and the stabilising activity of the reducer was neutralised by an increase of ionic strength to 0.1M. Whereas steric stabilisation of the particles was achieved by addition of polymers such as polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) to metal ions solution. As a result of mixing the reagents i.e. ions of Au(III) with or without addition of polymer and with L-ascorbic acid, I obtained colloidal gold. The forming process was tracked spectrophotometrically. On the basis of the registered kinetic curves (A3, Fig. 2a), I determined values of the observed rate constants ($k_{1,obs}$) for the first stage (ions reduction Au(III) to Au(I)), presented in a table (A3, Table 2). The obtained results show a slight difference between individual values of the observed rate constants (A3, Tab. 2). It indicates that the rate of ions reduction reaction Au(III) to Au(I) does not depend significantly on addition of steric stabiliser. Whereas comparing the obtained kinetic curves illustrating ions reduction Au(I) to Au(0) and autocatalytic growth, I noticed divergences in their course (A3, Fig. 2b, A3). They were the base to determine that the values of the observed rate constants ($k_{n,obs}$, $k_{g,obs}$) also differ (A3, Table 3). In case of polymers addition, the process of nucleation and autocatalytic growth were inhibited which was connected with action of steric stabiliser (its adsorption on the particles surface). The formed particles were analysed with the DLS method and the results are presented in a table (A3, Table 9). The size of the obtained particles differed significantly. In case of lack of stabilisation, I obtained polydisperse particles, which was connected with their progressing aggregation. Whereas, application of polymer allowed to stop further growth of particles and the value of their hydrodynamic radius ranged from about 15nm (PVA) to 40nm (PVP). Taking into account the fact that L-ascorbic acid is known as a ‘weak’ reducer, an analogous synthesis of particles

was performed in the same work with the use of a 'strong' reducer i.e. sodium borohydride. Similarly, I analysed kinetics of gold particles formation process. Kinetic curves of individual stages (ions reduction Au(III) to Au(I), nucleation and autocatalytic growth) were registered spectrophotometrically (A3, Fig. 4) and they were the base to define values of the observed rate constants, presented in a table (A3, Table 4). During the tests I noticed that the course of the kinetic curves for the first stage i.e. ions reduction Au(III) to Au(I) is very fast (of the order of ms). This made it impossible to determine experimental values of the observed rate constants on the basis of the obtained curves containing only few points (A3, Fig. 4a). Moreover, unexpectedly it turned out that addition of polymers to the solution containing metal ions affects the mechanism of the first reaction step. The registered kinetic curves take form of sigmoid (A3, Fig. 4a) which can prove that the process consists of at least two other ones. On the basis of the registered kinetic curves of the nucleation and autocatalytic growth process, I determined the values of the observed rate constants ($k_{n,obs}$, $k_{g,obs}$) presented in a table (A3, Table 4). The obtained results confirm that addition of a stabilising factor inhibits the nucleation and autocatalytic growth process. Absence of addition of stabilising agent caused particles formation size of about 2nm, and for the following few hours their further aggregation was observed. Therefore, precise data are needed to help systemize and organize the existing knowledge. On the basis of the obtained results, the influence of steric factor on the formation process of gold nanoparticles with the hydrometallurgical method was clearly visible. Addition of polymer to metal ions precursor and reducer can affect both the kinetics of stages II and III and also stage I, which has not been discussed in literature so far.

The obtained results presented in works A1-A3 provided complete information concerning possibilities of gold nanoparticles synthesis of defined morphology and stability, thus enabled moving to the phase of practical application of the formed particles. It is known from literature that nanoparticles (including gold) can be applied in medicine, e.g. as a factor strengthening contrast in computed tomography of soft tissues as they feature high coefficients of absorbing x-ray radiation and surface plasmon resonance effect. Moreover, nanoparticles of gold can significantly strengthen fluorescence in therapeutic window thus allowing detection of tumour with fluorescence imaging and x-ray computed tomography as imaging in two modes (A4, items 14, 18, 24). Gold nanoparticles in connection with different ligands can be used as drug or gene carriers to cells in different diagnostic and therapeutic tests (A4, item 20). Therefore, I conducted literature review and it was the base to present requirements needed to apply the particles in medicine. These are: nontoxicity of both particles and their surroundings

(reducer and its oxidised form, biocompatible stabiliser), insensitivity to changes of pH, temperature, ion force, plasmon resonance effect (shape, particles size) and their stability in time. Particularly unfavourable effect is connected with disturbing particles stability in Ringer's solution, blood etc. It is known that electrostatic stabilisation is not sufficient and will not be effective in so differentiated environment. Therefore, to prevent particles aggregation it was necessary to use steric stabiliser, additionally featuring neutrality towards surrounding environment. Taking the conditions into account I chose particles formed with the hydrometallurgical method for further examination. L-ascorbic acid was used as ions reducer Au(III) and gold particles were modified with polyvinyl alcohol as a steric stabiliser. Medical tests were possible with cooperation of the Pharmaceutical Department at Jagiellonian University where a course of tests was performed on mice and rats. The tests results are described in app. (A4-A5). In both works, I used gold nanoparticles which are characterised by plasmon with maximal absorbance at wavelength about 530 nm and spherical shape. The particles were additionally stabilised sterically with polyvinyl alcohol (PVA, MW. = 6700 Da) which is permitted for pharmaceutical industry use. The size of colloidal gold particles (diameter is 25 ± 8 nm) was defined using techniques HR SEM and DLS; ζ particles potential ($-5,2 \pm 5,4$ mV) was determined with Malvern Zetasizer Nano ZS.

In another work, app. **A4**:

Marek Wojnicki, Magdalena Luty-Błoch, Marek Bednarski, Magdalena Dudek, Joanna Knutelska, Jacek Sapa, Małgorzata Zygmunt, Gabriel Nowak, Krzysztof Fitzner, *Tissue distribution of gold nanoparticles after single intravenous administration in mice*, Pharmacological Reports 65 (2013) 4, 1033–1038

I presented procedures of particles formation and their concentration for medical purposes. Colloidal gold of intense red colour (concentration 29.55mg/l) of a clear plasmon and symmetrical distribution of peak with maximum at 531nm (A4, Fig. 1a), size about 25 nm (hydrodynamic diameter) of spherical shape (A4, Fig. 1b) in a dose of 10 ml of concentrated colloid per kg of an animal was administered intravenously in mice of Albinos breed. After 24 hours after administration, an analysis was performed to detect presence of metal in organs (liver, brain, heart, kidneys, stomach, blood) and the results are presented in a table (A4, Table 2). The analysis of gold content in particular organs was performed with the use of inductively coupled plasma – mass spectrophotometry. The tests showed that after single intravenous administration, nanoparticles preferentially gathered in liver (12.7% of the applied

dose) while in other organs the accumulated amount was 0.1% or less. However, it can be seen that the process of delivering particles to organs is slow.

That is why in another work, app. **A5**:

Marek Bednarski, Magdalena Dudek, Joanna Knutelska, Leszek Nowiński, Jacek Sapa, Małgorzata Zygmunt, Gabriel Nowak, Magdalena Luty-Błocho, Marek Wojnicki, Krzysztof Fitzner, Maciej Tešiorowski, *The influence of the route of administration of gold nanoparticles on their tissue distribution and basic biochemical parameters*, *Pharmacological Reports* 67 (2015) 3, 405–409

I examined the influence of the particles administration method on metal distribution in tissues. The experiments were performed on two groups of rats of Wistar breed. Gold particles in a dose of 0.36 mg/ml per kg of animal were administered orally to one group and intravenously to the other one. For 10 days excreta got collected to investigate how organism gets rid of the metal and obtained results are presented in a table (A5, Table 2). All the examined animals were tested on the third day after intravenous administration to check the influence of particles on biochemical parameters i.e. levels of alanine aminotransferase (ALT), aspartate aminotransferase (AST), total cholesterol, triglyceride (TG), glucose (GLc) and a decrease of plasma content in blood (FRAP) and the obtained results are presented in a table (A5, Table 3). Whereas, after 10 days the content of metal in particular organs was analysed with the ICP-MS method and the obtained results are presented in a table (A5, Table 2). I demonstrated that gold nanoparticles are mainly accumulated in liver, lungs and spleen after intravenous administration and only slightly are removed from the body with urine and faeces. The accumulation increases FRAP and the glucose level, respectively to 27% and 73%. Subsequently, it suggests that intravenous administration of the particles can induce serious medical complications. On the other hand, accumulation of about 50% of the particles introduced to the bodies of rats in the liver is promising for phototherapy and ‘opens’ the door for transportation of drugs to the organ.

The results of the works (A4-A5) allow the statement that gold nanoparticles reduced and stabilised with L-ascorbic acid and additionally with a polymer can be applied in live organisms. During the tests no inflammatory conditions were found in mice/rats that could indicate gold ‘intolerance’ of the body. Location of spherical particles of 25 nm diameter in the liver can be a potential weapon in fighting tumours of the organ. Besides, gold nanoparticles can be used as a carrier of drugs to the liver increasing efficiency of a conducted therapy.

In another work, app. **A6**:

M. Wojnicki, M. Luty-Błocho, M. Kotańska, M. Wytrwal, T. Tokarski, A. Krupa, M. Kołaczkowski, A. Bucki and M. Kobiela, *Novel and effective synthesis protocol of AgNPs functionalized using L-cysteine as a potential drug carrier* Naunyn Schmiedebergs Arch Pharmacol. 391 (2018) 2, 123–130

I presented a procedure of a one-step synthesis of silver nanoparticles functionalised with L-cysteine as a steric stabiliser. I determined distribution of particles size (A6, Figs. 3, 4). Crystallography and chemical properties were examined with XRD, HR-TEM and XPS methods. Moreover, I tested toxicity and irritating properties of the obtained nanoparticles using mice and rats as an animal model. The results showed that the applied procedure enabled synthesis of silver nanoparticles of narrow distribution of their size. Moreover, concentration of the final product was exceptionally high in comparison to other known methods of synthesis. The obtained nanoparticles did not demonstrate irritating properties or acute toxicity.

Another analysed aspect was a possibility to apply particles of metals like palladium and platinum in catalysis. It turns out that the catalysis process uses 73.5% of the world production of palladium (<https://www.advantagefutures.com/outlook-2016/>) and 50% of platinum. It seems that the demand for the metals will grow due to fast development of the automotive industry. According to literature reports, the best catalytic properties are connected with the size of nanoparticles, which results from a high proportion of their surface to the volume. However, in case of many catalytic systems, creation of the catalyst only is not sufficient. An equally important aspect of catalysers is both easiness of their removal from gas reaction mixture or liquid phase, and their ability to be used again. In order to do so, a catalyst carrier is used, such as active carbon Al_2O_3 , TiO_2 , SiO_2 . The selection of the materials results from their neutral activity in different environments.

Therefore, I overviewed literature to be able to indicate parameters important for catalysis. These are: slight size (high proportion of surface to the occupied volume), particular shape, stability in time, adsorption ability on a catalytic carrier. Whereas, toxicity is an insignificant parameter. Taking into account the determinants, I started works over synthesis of palladium nanoparticles which can present catalytic properties.

The tests began with a proper selection of the reducer and stabilisation type. It is known that addition of steric stabiliser blocks catalytically active surface of a particle. Such reaction is typical and results from the action method of steric stabilisation based on adsorption (physical

or chemical) occurring between the polymer and stabilised particle. Therefore, I used L-ascorbic acid as a reducer of Pd(II) ions and, at the same time, stabiliser of the particles formed with the hydrometallurgical method.

Firstly, I examined kinetics of the process of palladium nanoparticles formation following the mechanism described by the Finke-Watzky model with results presented in the publication **A7**:

Marek Wojnicki, Krzysztof Fitzner, Magdalena Luty-Błocho, *Kinetic studies of nucleation and growth of palladium nanoparticles*, Journal of Colloid and Interface Science 465 (2016) 190–199.

The process of palladium nanoparticles formation was conducted in different conditions: initial concentration of reagents, chlorides, temperature and ionic strength (A7, Table 1). For the obtained colloids I registered the level of turbidity (lack of plasmon for palladium particles, A7, Fig. 3b, 5b, 7b, 9b, 12b) and kinetic curves (A7, Fig. 3a, 5a, 7a, 9a, 12a). Subsequently, they were the base to determine values of rate constants and, respectively, for the process of nucleation and autocatalytic growth, presented in figures (A7, Fig. 4, 6, 8, 13) and in a table (A7, Table 5). The particles size was defined with the method of dynamic light scattering and the results are in tables (A7, Tables 2-4, 7, 8). On the basis of the obtained results, I suggested a mechanism of palladium nanoparticles formation which are electrostatically stabilised. Applying the logarithmic form of the Eyring-Polanyi equation (A7, equation 8), I determined values of activation enthalpy and entropy for the process of nucleation and growth of palladium nanoparticles (A7, Table 6).

On the basis of the obtained results (A7), I selected optimal conditions for palladium nanoparticles synthesis in a flow reactor. The idea of applying the microreactor was formed on the basis of results obtained in my former publications (App. 4, II A, p. 1,4,6). They indicated that conducting the process in a microreactor allows a precise control of process parameters like temperature due to low dimensions of the microreactor channels. Moreover, the particles obtained in such a synthesis present higher monodisperse. Therefore, the process of palladium nanoparticles formation was ‘moved’ from a batch reactor (synthesis in a beaker) to a flow reactor and the obtained results are presented in a publication, app. **A8**.

In another work, app. **A8**:

Magdalena Luty-Błocho, Marek Wojnicki, Grzegorz Włoch, Krzysztof Fitzner, *Green method for efficient PdNPs deposition on carbon carrier in the microreactor system*, Journal of Nanoparticles Research, 20 (2018) 239

I presented a possibility of conducting the process of palladium nanoparticles formation and deposition in one cycle of a flow microreactor. Such concept is an improvement of a currently applied technique in which catalytic particles are formed with the method of chemical reduction, and the metal precursor is reduced with the reducer. The size and shape of the formed particles can be additionally controlled by application of stabilisers and ligands. Next, the formed particles are deposited, typically on a carrier through impregnation (A8, Munnik et al. 2015). It is a multistage process, takes a lot of time and requires further purification of the product. Therefore, it is essential to work out a relatively inexpensive and simple technique of particles formation that will eliminate the drawbacks and makes the catalyser preparation time shorter. One of the methods to improve the process is its transfer from macro to micro scale that can be realised in microsystems (A8, Ehrfeld et al. 2000). The term 'microsystem' should be understood as a system consisting of microreactors, mixers, micropillars and pumps. Most of benefits connected with using a microreactor results from its low dimensions of a channel (high proportion of surface to volume) that allows fast mixing of reagents, very fast transportation of heat and mass, and controlled time of keeping reagents in microchannels is realised by e.g. flow intensity and channels dimensions, which subsequently ensures low usage of reagents and generates low amount of waste after the reaction. Besides, the system is flexible because it enables joining many reactors together. In case the process requires combining many reagents at the same or different time. It can also be used for multiphase processes that require different conditions. The microsystem allows intensification of the process (A8, Yao et al. 2015) and can be applied in fields like biofuels production (A8, Madhawan et al. 2018), catalysis (A8, Tanimu et al. 2017), green and sustainable synthesis, synthesis of nanoparticles (A8, Wojnicki et al. 2015, Zhao et al. 2011) and their deposition on active carbon (A8, Luty-Błocho et al. 2013) and synthesis of metallic particles in aqueous solution, even in temperatures above 100°C (A8, Luty-Błocho et al. 2014).

In the work A8, I examined conditions necessary to obtain composite consisting of palladium nanoparticles deposited on carbon fibre as a catalytic carrier and the process was conducted in a flow system. All steps connected with metal ions reduction, nucleation and autocatalytic growth of particles and their deposition were conducted in a microreactor in one cycle only. Rate of the reagents flow i.e. metal ions and reducer, was selected based on results of kinetic tests (app. A7). The process was conducted in conditions of different densities of both metal precursor and reducer (A8, Table 1). As a result of conducted syntheses I obtained colloidal palladium of the colour from light brown to grey (A8, Fig. 2). Solutions containing particles were analysed spectrophotometrically and with the methods of dynamic light

scattering and scanning microscopy. The results are presented in figures (A8, Figs. 2-11) and tables (A8, Tables 2-4). Depending on the provided conditions, nanoparticles of different size were obtained (hydrodynamic radius varied from 12 to 37 nm) and different shape (spherical, cube, pyramid) (A8, Fig. 7). Next, a filter with carbon active fibres as a catalyser carrier was attached to the flow microreactor system (A8, Fig. 1) at selected conditions (A8, Table 1). In such a system and conditions of conducted synthesis i.e. different densities of reagents, in temperature of 40°C, palladium particles were formed with the hydrometallurgical method and then deposited on carbon fibres. It was observed that depending on parameters of the conducted process, a different degree of covering the carbon fibres by metal particles was obtained (A8, Fig. 10). The most favourable deposits (even distribution of particles on fibres) were obtained for ions Pd(II) concentrations higher than 0.2 mM (A8, Figs. 10e-h). An analogous synthesis was conducted in a batch reactor to compare efficiency of the deposition process. The obtained colloid was analysed spectrophotometrically, and the appearance of fibres with deposited particles was additionally analysed with the use of a microscope. The level of covering the fibres was significantly lower in comparison to deposition conducted in a microreactor, which is presented in a figure (A8, Fig. 11b).

Summarising, application of the flow microreactor enabled increasing efficiency of the conducted process on nanoparticles deposition in comparison to the impregnation process performed in a batch reactor (beaker). The presented method can be a technique of forming a catalyser with the hydrometallurgical method and its deposition on a catalytic carrier directly after synthesis. Application of electrostatic stabilisation only did not block the active surface of particles. Additional benefit of conducting the process in one microreactor cycle was shortening the catalyser formation time to about 10 minutes.

Another examined system comprised platinum nanoparticles stabilised electrostatically, sterically or in a mixed method that were obtained with the metallurgical method and the synthesis process was conducted in a batch reactor or a flow microreactor. In order to assess the influence of steric, electrostatic and mixed stabilisations as well as the flow conditions, kinetic tests were performed and their results are presented in the work **A3**

In the work (A3) I compared electrostatic, steric and mixed stabilisations and examined their influence on kinetics of platinum nanoparticles formation. The metal nanoparticles were synthesised with the hydrometallurgical method with the use of two types of reducers. The first was L-ascorbic acid, ranked as a 'weak' reducer, and the second was sodium borohydride that is a strong reducer of many metals but, unfortunately, it belongs to the group of toxic ones. The

stabiliser of platinum nanoparticles was steric one (by addition of polymer, i.e. PVA and PVP to the solution containing metal ions), electrostatic (L-ascorbic acid) and mixed (electrosteric) which combined the two previous components. The kinetics of the nanoparticles formation was tracked spectrophotometrically. In case of the mild reducer, the course of the kinetic curves for the first phase, i.e. ions reduction Pt(IV) to Pt(II) (A3, Fig. 5a) as well as sigmoidal character describing slow nucleation and fast autocatalytic growth (A3, Fig. 5b) allowed defining values of the observed rate constants (A3, Tables 5, 6). I noticed that addition of PVP to metal ions as a steric stabiliser of particles slightly inhibits stage I (A3, Table 5). Whereas, addition of PVA accelerates the process of ions reduction Pt(IV) to Pt(II). The values of the observed rate constants for nucleation process and autocatalytic growth determined based on obtained kinetic curves (A3, Fig. 5a) are comparable (A3, Table 6). The DLS method was used to determine the platinum particles size (A3, Table 9). In case of electrostatic stabilisation, the examined sample demonstrated polydisperse and the obtained particles underwent further aggregation. Whereas, addition of steric stabilisers allowed to ‘stop’ the particles size at the level of 3-4 nm (A3, Table 9). In another examined system for platinum ions reduction I used sodium borohydride. As a result of mixing the reagents, nanoparticles were obtained without addition of stabilising factor and with addition of polymers (PVP, PVA). Analogously to the previous system, I registered kinetic curves for each phase and the obtained results are presented in figures (A3, Fig. 6) and tables (A3, Table 7, 8). The defined values of the observed rate constants (A3, Table 7) indicate that addition of PVP to solutions of metal ions accelerates the stage I in the process of particles formation which is connected with ions reduction Pt(IV) to Pt(II). It suggests that the process is complex and an interaction between metal ions and polymer is possible. The defined values of the observed rate constants describing slow nucleation ($k_{2,obs}$) show that the process in the fastest in the system without polymer (A3, Table 8). Whereas, the values of the observed rate constants ($k_{3,obs}$) for autocatalytic growth confirm that the stage is the slowest in the system with addition of polyvinyl alcohol (A3, Table 8). The obtained particles were analysed with the method of dynamic light scattering and the results are in a table (A3, Table 9). Regardless of the fact whether polymers were used or not for stabilisation, the size of platinum particles varied from about 2.5 to 4.5 nm (A3, Table 9). Whereas, during experiments I observed that particles without any stabilising factor undergo further aggregation.

In another work, app **A9**:

M. Luty-Błocho, M. Wojnicki, J. Grzonka, K.J. Kurzydłowski, *The synthesis of stable platinum nanoparticles in the microreactor*, Archives of Metallurgy and Materials 59 (2014) 2, 509–512

I used a flow microreactor (A9, Fig. 1) for platinum nanoparticles formation with the hydrometallurgical method. In order to accelerate the process of particles formation the temperature was increased to 105°C and a back pressure regulator was applied which prevented boiling the solutions in the microreactor. It led to shortening the platinum nanoparticles formation from 40 mins (synthesis in a batch reactor in temp 40°C) to 6s (synthesis in a microreactor). Platinum particles were obtained through chemical ions reduction Pt(IV) with L-ascorbic acid as a reducer and a source of electrostatic stabilisation. Additionally, polymers (PVA or PVP) were introduced into the microreactor system which also stabilised the formed particles. Such addition of steric stabiliser was necessary as without it the platinum particles aggregated fast, and as a result after a few days coarse-grained deposit occurred on the vial bottom. The effect of the conducted synthesis of platinum nanoparticles in a flow microreactor was obtaining stable particles. An analysis of the particles size with the dynamic light scattering method and results of microscopic analysis (STEM, HRTEM) were similar. The particles size varied from about 3 to 4nm (A9, Table 1, Fig. 2) for an analysis performed after 10 mins. A proceeding aggregation of particles in time was observed and confirmed by another microscopic analysis and DLS. After 6 days since the synthesis of platinum nanoparticles, their size ranged from 43 to 59nm (A9, Figs. 4, 5, Table 1). It was, subsequently, connected with a proceeding process of 'flocculation' relying on particles gathering into larger centres by polymer chains (A9, Figs. 4, 5).

In another work, app. **A10**

M. Luty-Blocho, M. Wojnicki, *Single-step synthesis of onion-like Au-Pd-PtNPs nanoparticles using microflow system*, Journal of Flow Chemistry, 5(2015) 4, 197–200

I described a method of synthesis of a complex, onion-like nanomaterial with using a microflow reactor. The core of the material was platinum nanoparticles stabilised with polymer (polyvinyl alcohol). Vitamin C itself was not a sufficient stabiliser. The data from the former work (app. A9) were used to select the optimal parameters of platinum nanoparticles formation (flow rate, concentrations, temperature). It enabled synthesis of stable nanoparticles of platinum in a very short time. Applying a system of microreactors allowed a very fast heating of aqueous solutions of reagents to temp. 105°C which accelerated the process of ions reduction Pt(IV) to metal, and then fast cooling of colloidal platinum to lab temperature (20°C). Synthesized and cooled down colloidal platinum was combined with palladium ions and L-ascorbic acid. As a result of conducted reduction reaction I defined the time of reagents stay in the reactor on the basis of the results obtained in a former work (app. A7). Due to so conducted process, reduced ions

Pd(II) were deposited on a platinum core creating the first layer. Another layer, consisting of gold was created as a result of combining a flux containing particles of Pd on Pt and a flux of gold ions precursor with a flux of L-ascorbic acid. The process resulted in obtaining a composite material consisting of platinum nanoparticles as a core, surrounded by two layers of different metals. Such a synthesis was possible in a flow system because only such a system grants wide possibilities within applying extreme process conditions, in this case – temperature. Moreover, the whole synthesis is a process optimised for one cycle containing integrated three flow microreactors. The created material characterised by a unique structure and a plasmon resonance can be potentially applied in medicine for signal strengthening.

I realized this scientific achievement using the following research methods: UV-Vis spectroscopy, STEM and HRTEM microscopy, dynamic light scattering, laser Doppler electrophoresis, X-ray diffraction, mass spectrometry coupled with inductively excited plasma, and microwave atomic emission spectrometry, X-ray photoelectron spectroscopy. As a result of my research I confirmed the hypothesis, which was put forward. The obtained results show that by controlling the kinetic parameters (concentration of reagents, temperature, ionic strength) and choosing the right way of stabilization (electrostatic, steric and mixed) I can influence the morphology of nanoparticles. Summing up the obtained results, I conclude that the introduction of electrostatic or mixed stabilization does not affect or slightly affects the rate constants of the first reaction step (i.e. Au (III) reduction to Au (I), Pt (IV) to Pt (II)). Kinetic studies have shown that the rate of nucleation and autocatalytic growth is influenced by the addition of a steric stabilizer that significantly slows down these steps. I also found, that the addition of an electrostatic stabilizer does not significantly affect the rate of the nucleation process of the particles, and slows the auto-catalytic acceleration in comparison with the system without stabilization. Consequently, slow nucleation and rapid auto-catalytic growth lead to monodispersity of the obtained particles (electrostatic stabilization) of spherical or "star" like shape (e.g. Au-L-ascorbic acid) with the size of about 20 nm. In turn, the use of steric stabilization allows generation of spherical particles with the size of 2-3 nm (e.g., sodium borohydride system). The lack of the addition of a particle stabilizing agent leads to their irreversible coagulation. As a result of my research, I received sterically stabilized gold and silver particles (biocompatible polymer, L-cysteine) or composite core-shell materials that can be used in medicine. Moreover, precious metal particles stabilized electrostatically can be used for catalytic purposes.

5. Review of the remaining scientific and research achievements.

5.1. General information

I have graduated from the Faculty of Non-Ferrous Metals (major: Metallurgy) at the AGH University of Science and Technology in Cracow. During my studies I was a member of a scientific association 'De Re Metalica' where I realised scientific research under supervision of Prof. Ph.D. Marian Kucharski, Master of Engineering (XLII Student Session of Scientific Associations, article: '*Napięcie powierzchniowe stopu Cu-In*', 05.2005(*Surface voltage of Cu-In alloy*)) and Prof. Ph.D. Krzysztof Fitzner, Master of Engineering (XLIV Student Session of Scientific Associations, article: '*Kinetyka redukcji kompleksu Pt(IV) cis-PtCl₄(NH₃)₂ za pomocą kwasu L-askorbinowego*', 05.2007 (*Kinetics of Pt(IV) complex cis-[PtCl₄(NH₃)₂] reduction with ascorbic acid*). Moreover, during my studies I completed a two-year-long pedagogical course in Pedagogical School at AGH, elevating my didactic qualifications. In 2006 within the IAESTE program I attended a two-month internship in the Max Planck Institute in Düsseldorf (Zał. 4, III L, p.1), Germany, where I realised tests connected with obtaining monocrystals. I graduated in 2007 receiving the degree of Master of Engineering. The diploma thesis '*Kinetyka redukcji kompleksu Pt(IV) cis-PtCl₄(NH₃)₂ za pomocą kwasu L-askorbinowego*' (*Kinetics of cis-PtCl₄(NH₃)₂ complex Pt(IV) reduction with L-ascorbic acid*) was supervised by Prof. Ph.D. Krzysztof Fitzner, Master of Engineering. The realised tests were connected with measurements of kinetics of complexes PtCl₄(NH₃)₂ reduction reactions of *cis* isomerism and description of the running processes mechanism. In 2008 at the 168th Kwartalna Konferencja Naukowo-Techniczna SITMN (Quarterly Conference of Science and Technology) in Szklarska Porębia I was awarded the first prize by the Association of Non-Ferrous Metals Engineers and Technicians for the best learning performance. Between 2007 and 2011 I attended Doctoral Studies at the Faculty of Non-Ferrous Metals at the AGH University of Science and Technology in Cracow. During the studies I participated in a 9-month internship at IMM Mainz (App. 4, III L, p.2), where supervised by Dr Michael Maskos, and then Prof. Volker Hessel I gained experience in the field of flow microreactors. The cooperation resulted in an article published in Chemical Engineering Journal (App. 4, II A, p.1). During the doctoral studies I received scholarship financed by European Union as a part of 'Małopolskie Stypendium Doktoranckie' and Max-Planck scholarship IMPRSM – (International Max-Planck Research School for Polymer Materials Science) which allowed me to attend the mentioned scientific internships in Germany. Since October 2011 I have worked at the Faculty of Non-

Ferrous Metals at the AGH University of Science and Technology in Cracow. In July 2012 I received the degree of a Doctor of Technical Science for the work: 'Synteza nanocząstek złota oraz platyny w mikrosystemach' (Synthesis of gold and platinum nanoparticles in microsystems).

In my doctoral thesis I presented results indicating new possibilities of nanoparticles synthesis of noble metals like gold and platinum conducted in a flow microreactor. The obtained results were compared with the analogous syntheses conducted in a cyclic reactor. Moreover, the work included kinetic tests in homo and heterogenic systems which were essential for a proper design of a microflow system (flow rate, process temperatures, etc.) for nanoparticles synthesis. Fruitful linking of flow parameters in a microreactor with kinetics of metal ions reduction, nucleation and growth allowed control of the size and distribution of the obtained nanoparticles. As a result of conducted experiments, I obtained nanomaterials of higher homogeneity and published 2 works in journals from the Philadelphia List such as: *Chemical Engineering Journal*, *Inorganica Chimica Acta* (App. 4, II A, p.5). The results were presented at 4 international conferences (App. 4, III B, p. from 1 to 4).

After receiving Ph.D. degree I continued works connected with nanomaterials synthesis in microreactors or in microdots. The gained knowledge was applied, among others, to create a catalyser containing nanoparticles of Au, Pd and Pt on carbon carrier such as: active carbon fibre and graphene oxide. I was the originator of a conception of conducting a one-phase process of catalyser creation based on synthesis of catalytic material in a flow microreactor, and then its deposition of active fibres as a catalytic carrier (App. 4, II A, p. 4). In order to do so, I used the flow microreactor again and all the stages: metal ions reduction, nucleation, nanoparticles growth and their deposition on carbon carrier were performed in one cycle of the microreactor. This showed a possibility to automatize the process of catalyser creation based on the kinetic data. I also demonstrated that the process of particles deposition on catalytic carrier is more efficient if conducted in a flow. I continued tests connected with analysing morphology of the synthesised nanomaterials and searching for the key factor determining shape and size of the noble metals particles (App. 4, IIIB, p. 5).

Another aspect of the conducted tests is the use of reaction kinetics for selective separation of metals like platinum and palladium. It is a difficult process because the metals feature similar physicochemical properties. The result of the tests are 3 patents: P.401391 (2013), P.415085(2016), P.415085(2017) (App. 4, II C, p. 1-3) and 1 patent application P-428 274 (2018).

I also took part in tests connected with separation of ions from lanthanide group in the magnetic field (App. 4, II J, p. 3). As a result I am a co-author of a European patent application: 'Microfluidic Device, apparatus and method for enrichment and dilution of magnetic molecular entities', 2019, EP 18 215 771.9. In addition, I participated in the research on the synthesis of silver nanoparticles in the flow microreactor in microdroplets (App. 4, II J, p. 5) and in the studies aimed at validating the new adsorption isotherm model (App. 4, II J, p. 2). The results obtained by me were presented at 8 international conferences (App. 4, II L, App. 4, III B) and presented during the workshops (App. 4, III Q, p. 1).

From 24.01.2018 to 25.01.2019 I was a head of the project 'Miniatura', entitled: 'Spektrofotometryczne oznaczanie śladowych ilości jonów Pd(II), Pt(II) lub Pt(IV) w roztworach wodnych' (Spectrophotometric determining of trace amounts of Pd(II), Pt(II) or Pt(IV) ions in aqueous solutions) (App. 4, II J, p. 1). As a part of the project I elaborated a new method of colorimetric determination of Pd(II) ions in aqueous solutions. The results are the base for a new patent application being prepared. The scientific aim was to elaborate an innovative spectrophotometric method allowing qualitative and quantitative determination of Pd(II), Pt(II) or Pt(IV) ions in aqueous solutions. I used properties of metal ions and compounds containing in their structure the azobenzene group to create complex compounds. The process of creating a metalorganic complex in time was tracked spectrophotometrically. As a result of the tests, the stability constants of the complex Pd-methyl orange were determined which are basic data concerning the process of complex creation. I also verified that ions Pt(IV) and Pt(II) do not create complex compounds with orange which was a base for further studies. Moreover, within the project I investigated the influence of such parameters like pH of the aqueous solution, temperature and presence of other cations (Na^+ , K^+ , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pt^{2+}) on selectivity of the determined metals. The conducted tests showed that qualitative determination of trace amounts of Pd(II) ions in aqueous solutions is possible. Moreover, the spectrophotometric method can be used for quantitative determination of the ions in the examined conditions.

I also attended a 3-month internship in the industry (from 04.2015 to 06.2015) in 'Tacon Chem sp. z o.o.' within the project: 'Innowacyjny Transfer' (App. 4, III A, p.1), co-financed by the EU within EFS, Program Operacyjny Kapitał Ludzki (Human Capital Operational Programme). During the internship I worked out complete documentation i.e. Instruction concerning production of CuO with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with three technologies.

In order to raise my competences as a scientist, I took part in seminars and trainings (App. 4, III Q, p. 2a, b and 3a).

Moreover, in 2018 I received The Chancellor Team Award 1st grade for didactic activities (App. 4, III D, p. 1).

5.2. Scientific, research and expert activity

Since the beginning of my work at the faculty of Non-Ferrous Metals, I have been engaged in the statutory activities as an executor of individual tasks (App. 4, III Q, p. 4) and in research and development projects. In the years 2010-2013 I was the main executor of the project 'POIG' (App. 4, II J, p. 6). As a result about 10 publications were elaborated with me as a corresponding author and one monography (App. 4, II E, p. 7). I was also engaged in projected financed by Ministerstwo Nauki i Szkolnictwa Wyższego (Ministry of Science and Higher Education) and Narodowego Centrum Nauki (National Science Centre).

Summarising, in the years 2010-2019 I was a head or executor in 11 projects, and in 9 of them as Ph.D. (App. 4, II J, p 1-5 and App. 4, III Q, p. 4b-g) and in 2 projects before I received the degree (App. 4, II J, p. 6 and App. 4, III Q, p. 4a).

Since 2010 I have cooperated with Prof. Volker Hessel (co-author of 453 publications by Scopus and 10 books) from the University of Adelaide (Australia). The cooperation started with my stay in the Institute of Microtechnique in Mainz (Germany) and is still continued. It comprises both chemical engineering issues and materials synthesis using flow microreactors as well as application of flow microreactors as 'Novel Process Window' in metals separation processes, processes intensification, improvement of the produced materials parameters etc. Within the frames of the cooperation the following publications appeared in Chemical Engineering Journal (App. 4, II A, p. 1), Micromachines (App. 4, II A, p. 13). Currently, two other publications are being prepared.

Moreover, since 2018 I have cooperated with the group of Dr Edit Csapo from University of Szeged (Hungary), which resulted in publications in Micromachines (App. 4, II A, p. 13) and Microchemical Journal (App. 4, II A, p. 16).

For many years I have cooperated with Mennica Metale Szlachetne in Radzymin (Noble Metals Mint), in the area of search for alternative methods for currently applied noble metals recovery and separation of platinum and palladium. The aim of the cooperation is to minimise

losses of noble metals in processes of their recycling and minimising their content in waste solutions.

I also cooperate with Polish research centres, including Jagiellonian University (Pharmaceutic Department) within potential application of the synthesised nanomaterials (two publication form the Philadelphia List, app. A4, A5) for medical purposes, Faculty of Chemistry to identify newly synthesised metalorganic complexes with methods of nuclear magnetic resonance (NMR), with Akademickie Centrum Materiałów i Nanotechnologii AGH (Academic Centre of Materials and Nanotechnologies AGH) within microscopic analysis (TEM) of the synthesised nanomaterials, Discrete Fourier Transform analysis of noble metals complexes, metalorganic compounds, with Warsaw University of Technology within HRTEM analysis of the synthesised materials.

As for my scientific activity, I am currently a co-author and author of 43 scientific works, 41 of them are from the MNiSW (Ministry of Science and Higher Education) list, 26 of them (App. 6b) were published in journals from the JCR list (App. 4e, I B, II A) and I am a co-author of two monography (App. 4, II E, p. 7, 14). Data concerning number of citations, Hirsch index and summary IF of the publications are to be found in the Table 1.

Table 1. Data on scientific accomplishment according to Scopus (App. 6b) and Web of Science (App. 6a).

Data on: 18.04.2019			
	Scopus	Web of Science	
No of citations (Lc)	307	299	
Lc without self-citations	193	231	
Hirsch Index	10	10	
	Before Ph.D.	After Ph.D.	Total
Number of publications	8	35	43
Summary IF	7.8	51.3	59.1
Summary points of the Ministry	146	712	858

Since 2013 I have reviewed 15 publications from the JCR group of journals. Such titles should be mentioned among them: ACS Omega, Chemical Engineering Journal, International Journal of Chemical Kinetics, Inorganica Chimica Acta (App. 4, III P).

5.3. Organisational activity

Since 2007 I have actively participated in the Festival of Science in Cracow which is annually organised in the city Main Square (App. 4, III I, p. 1). Since 2014 I have participated in the Małopolska Noc Naukowców (Night of Scientists), which is organised at the Faculty of Non-Ferrous Metals (App. 4, III I, p. 2). Moreover, since 2017 I have participated in AGH Open Days to present the University, Faculty and different subjects as well as research and development labs, devices and even unusual experiments (App. 4, III I, p. 4). Moreover, this year (12.04.2019) during the Open Days I will give a lecture: 'Złoto- niejednen ma kolor' (Gold can be of different colours) which will show the world of nanoparticles and their unbelievable physicochemical properties to the visitors.

My latest venture (since Nov 2017) is organising a cycle of chemical workshops: 'Czary-mary, Hokus-pokus' (Abracadabra, Hocus Pocus) within the AGH Junior program to promote science in the youngest groups of children (App. 4, III I, p. 3). During the workshops children draw inconspicuous pictures which start to shine under an impulse induced by UV light. The participant can also make the flower leave shine purple, a popular drink will get heavenly colours and a kitchen herb will reflect light. Moreover, they have a chance to see, among others, magic ink or garden that does not require any plants, they try to squeeze current from a lemon and create an artificial lung. The main aim of the workshop is to induce curiosity in children with science and get them familiar with interesting phenomena we live next to. Studying surroundings and observations, concluding on the bases of observations of presented experiments, or conducted on their own. The workshops also prove that it is not necessary to be a chemist, or have an access to fully-equipped lab, to be able to discover and explain what is not so clear with the use of simple objects or even herbs found in a kitchen.

Additionally, since 2013 I have been the Social Labour Inspector at the Faculty of Non-Ferrous Metals which is connected with obeying safety of work regulations and reacting to potential threats. Since 2016, I am also the supervisor of the science and didactic laboratory.

5.4. Didactic activity

During my work at the Faculty of Non-Ferrous Metals at the AGH University of Science and Technology I have led lab and project classes and arithmetic exercises in different subjects. They were mainly connected with chemistry (App. 4, III Q, 5, p. a-c), mass transfer (Zał. 4, III Q, 5, poz. d) and synthesis of modern materials (Hydrometallurgical methods for transition metals, nanomaterials and nanocomposites, Principles of nanotechnology for engineers). In case of lab classes run in English: Hydrometallurgical methods for transition metals, nanomaterials and nanocomposites, I am a co-author of the syllabus and classes instructions for which I received the Chancellor Team Award 1st grade in 2018 (App. 4, III D). Moreover, I was an author or co-author of didactic materials and elaborations for students (auxiliary materials, for arithmetic or lab classes) and research stations.

In my didactic career I have supervised two master degree diploma papers (they both were distinguished in an annual contest 'Diamonds of AGH' (2016, 2018) (App. 4, III J, p. 1) and 12 engineering papers (App. 4, III J, p. 2). In this period of time I reviewed 6 engineering works. In addition, in 2014/2015 I was a trainee mentor from the company under the project "Innovative Transfer" (App. 4, III Q, p. 6).

In order to increase my didactic competence I take part in trainings organised by the e-Learning Centre at AGH, and so far I have taken part in three trainings: Nie bój się i Moodle! (Oct 2017), OZE Rentgen and E-learning akademicki – certifying training (March 2018), (App. 4, III Q, p. 3b-d).

Magdalena Duby-Flacio