

## INTRODUCTION

The aim of this thesis is to obtain new optical sensors for ions, especially sensors using metallic nanostructures. Metal cations and inorganic anions were selected as the analytes, since they are widespread chemical species. They play various roles in our surroundings: as fundamental electrolytes in bodies of living organisms (e.g. sodium or potassium cations, chloride anions), food additives (nitrates, carbonates) and even pollutants (heavy metal cations, sulphates, phosphates). Detection of ions is essential in, just to name a few: quality control of food products, testing environmental samples, industrial waste monitoring, as well as rapid detection of diseases.

Due to the presence of ion in so many areas, lots of effort is put into development of diverse sensors. Apart from well-known electrochemical sensors, optical sensors gain popularity. In principle, information about the environment is in this case carried by a light beam. The analyte has an influence on interactions between the light and the reporter molecule (a molecule sensitive to the presence of a detected substance). Fluorescence spectroscopy, UV-Vis absorption spectroscopy and techniques based on oscillation spectroscopy are the main techniques employed for the optical detection. We live in a world driven by miniaturization: it comes as no surprise that analytical methods reach out to nanotechnology. This trend stimulates development of nanosensors based on surface enhanced Raman scattering (SERS). In SERS spectroscopy, intrinsically weak inelastic light scattering (Raman scattering) – is enhanced due to a giant increase of electromagnetic field intensity near the surface of metallic nanostructures. When placed in this area, a molecule is exposed to electric field of extremely high amplitude, which gives rise to a strong SERS signal – with sensitivity reaching down to a single molecule (so called single molecule SERS). More details on SERS spectroscopy, as well as PM-IRRAS spectroscopy, which accompanied SERS in research on anion detection, can be found in *Chapter 1*.

Nanometric size of such systems lets the researchers reach such unattainable places as the inside of a cell and its compartments. What is more, confinement of the SERS phenomenon to the direct vicinity of a metal nanoparticle gives promise to obtaining resolution much higher than diffraction limit, as it would be determined solely by the size of the nanoparticle (NP) itself. All these features, as well as optical character of work and, consequently, non-invasive way of passing information about the surroundings, make such sensors particularly useful

in biological applications. However, while there are many known systems based on SERS spectroscopy which are sensitive to such biological parameters as pH value or redox potential, efficient ion determination in live cells with SERS still poses a challenge. Although this issue has seemingly been examined: equilibrium concentrations of inorganic ions are already commonly known, their distribution inside the cell, transport and accumulation mechanisms inside organelles have yet to be elucidated. Research on fabrication of such sensors will contribute to development of analytical methods already in use, as well as will open up new perspectives for detection of ions, and in consequence, of disorders in their metabolism paths as well as diseases caused by them. *Chapter 2* contains current state of the art in the subject of optical nanosensors.

It is worth pointing out that metal cations, as one-atom species, are undetectable by vibrational spectroscopies. As they have no vibrational fingerprint, their detection must be made indirectly by observation of the impact they have on the signal of a reporter molecule. Changes may concern total intensities of the spectrum, relative intensities of some bands or the energy shift of bands. In the thesis, 2-mercaptoethanesulphonate anion (MES) is selected as a Raman reporter molecule. Two components of the  $\text{SO}_3^-$  symmetric stretching vibrations are chosen to be marker bands – bands, whose changes are related to the presence of the analyte. Their intensity ratio is used to determine a cation concentration, while the energy shift of one of these two bands makes differentiation between cations possible. *Chapter 3* presents the effort to use MES molecules adsorbed on silver nanoparticles as Ag-MES nanosensor. Its sensitivity towards heavy metal cations and more biologically relevant cations of alkali and alkaline earth metals is described there. In *Chapter 4*, tests of performance of the Ag-MES nanosensor in biological systems can be found. Cells incubated in a cell medium containing the nanoprobe are proved to absorb Ag-MES NPs and the distribution of internal potassium concentration is deduced based on SERS mapping. Well studied system of Ag-MES NPs was employed in the further research on permeation of cations through a thick silica shell. Discussion on these results collected for silica covered Ag-MES nanosensors: Ag-MES@SiO<sub>2</sub> is given in *Chapter 5*. Synthesis of other types of biocompatible nanoparticles based on gold nanostars: i) Janus nanoparticles of gold nanostars and Fe<sub>3</sub>O<sub>4</sub> and ii) gold nanostars encapsulated in mesoporous silica – both types additionally covered with a thin layer of silver – are included in *Chapter 6*. In case of Janus NPs, the effect of magnetic field on the intensity of SERS spectra is examined. *Chapter 7* refers to anion detection with use of brand new type of carbazole derivatives

deposited on metal surfaces. Surface-attached diamidocarbazoles are proved to be able to bind sulphates from the solution.

The scope of the thesis has already been published in two original articles (*Sensors and Actuators B: Chemical* and *Journal of Physical Chemistry C*) and one chapter in a book (*Optical Spectroscopy and Computational Methods in Biology and Medicine*, publ. Springer Netherlands); another article is being prepared for a prompt submission.