

## *Publishable summary*

The work undertaken during the reporting period was performed according to the initial project plan. Deviations from the project plan and their influence were kept to a minimum. In cases where tasks had to be adjusted, the subsequent changes were found not to change the overall project goals and the overall success of the project.

It is characteristic for the work described in PR3 that by the beginning of this stage the development of main components of NANODETECTOR technology and software was completed, the final prototypes of the device were delivered to the project partners, and a training of coworkers of industrial partners of the project was performed. Therefore, this period was focused on extensive applications of the developed technology for different analytical tasks, on analysis of its limits and application potential. During this project period numerous presentations of this technology in scientific meetings were performed not as a successfully developing scientific project but as a well working, novel and extremely powerful analytical technology which can be immediately applied for a number of practical purposes. Therefore, during the report period an intensive dissemination of the project results was performed. The project was selected to the best ten projects for presentation in NanoForum2015 in Riga. The performed life demonstration of measurements of nanoparticles in real samples has led to a strong interest of the congress audience. Other dissemination events include a co-organization and active participation in the common public workshop in Brussel which was organized together with two other FP7 projects - SMARTNANO and INSTANT. During the reporting period, the project results were reported in 9 scientific conferences and in 7 papers, a number of further papers are in preparation and will be submitted within few month after the end of the project.

Development of theory of plasmonic detection of single nanoparticles was completed. Images of single nanoparticles with different size and refractive index were calculated. A good agreement between the shapes of the images calculated images and experimentally observed images of single nanoparticles were obtained. The theoretical dependence of signal intensity on the refractive index of nanoparticles and on the size of nanoparticles were demonstrated to be very close to the obtained experimental data. The theory developed for single nanoparticles was extended to ensembles of nanoparticles.

Analysis of the performance of NANODETECTOR technology in gas phase was performed. Two approaches were suggested and tested: (i) direct application of the specially developed NANODETECTOR instrument for the measurements in gaseous phases; (ii) extraction of nanoparticles from air to water and subsequent application of the usual NANODETECTOR instrument developed for aqueous media. It was demonstrated that both techniques provide fast analysis of aerosols. In the case of direct measurements of nanoparticles in gaseous phase, an accumulation of nanoparticles on the sensor surface by application of electric field was used. An agreement between the measured value of the adsorption rate and theoretical prediction allows one to apply this technology for nanoparticles of known sizes without calibration. The technology can be used for quantitative analysis of number concentration of nanoparticles in gaseous media. Oppositely, because of possible aggregation of nanoparticles during liquid extraction (which can be principally analyzed using signal magnitude and image shape), this technique can be used now only as a semi-quantitative one. However, a possibility of accumulation of nanoparticles of nanoparticles during liquid extraction allows one to increase sensitivity.

Influence of surface coating, pH and ionic strength on binding of nanoparticles to different surfaces was studied. Unexpected influence of salt concentration on adsorption of

nanoparticles was evaluated. Binding to smooth and rough surfaces was compared. Correlation between literature data on nanotoxicity of nanoparticles and their adsorption to biomimetic surfaces was analyzed.

Software for image analysis was developed. It was demonstrated that SPR images of nanoparticles form characteristic libraries which can be used for identification of size and material of nanoparticles, but also to distinguish adsorption and desorption of nanoparticles. Based on this idea, a number of new applications were developed. Recognition of characteristic images of nanoparticles was applied to improve analytical performance of NANODETECTOR technology in analysis of complex media. For example, within RoundRobin it was demonstrated, that the technique can be used in such complex media as wine, non-transparent fruit juice or diluted sunscreen. Based on this principle, tracking and mapping of nanoparticles was developed, it allows one to follow the fate of each single nanoparticle on the sensor surface (from totally up to a million) and to visualize their movement, adsorption/desorption or electrochemically induced optical conversions. An application of such nanoparticles tracking with electrochemical dissolution of nanoparticles allowed us to distinguish material of nanoparticles.

The technology was been transferred to industrial partners and was successfully applied in real industrial environment.

In conclusion, the results obtained by the consortium during the final project period have demonstrated that the NANODETECTOR-technology (high resolution SPR-microscopy in combination with an advanced image analysis) is a powerful analytical technique for real-time quantitative detection of nanoparticles in liquids as well as in gas media. The technology provides real-time and pretreatment free detection of nanoparticles in liquids at number concentration below 1000 nanoparticles per microliter for 10 seconds measurement time. This value is limited by the number of nanoparticles adsorbed to the sensor surface and therefore can be further improved by increase of the sensor area or detection time. The analysis can be performed also in very complex media, such as wine, juice or diluted sunscreen. The shape of the detected images provides information on the size and refractive index of nanoparticles. The technology can be combined with other analytical techniques. The developed combination of NANODETECTOR with electrochemical methods provides a possibility for electrochemical analysis of nanomaterials.

The results of the project have surpassed initial plans and expectations of the project participants. Already at the current stage of the development of NANODETECTOR technology, it is difficult to find another technique for detection and analysis of nanoparticles in complex media that provides a comparable analytical performance and so wide application possibilities. Themselves, the NANODETECTOR technology has also a strong potential for further development. For example, it may include a combination with a field flow fractionation and surface enhance Raman spectroscopy, incorporation of advanced microfluidics, further development of image analysis and recognition of nanoparticles using libraries of their plasmonic images.