Final Report Summary - INGENIOUS (Innovative Nanostructured Optochemical Sensors)

Executive Summary:

The FP7 project targeted the development of new generation of ultrasensitive optochemical sensor for the detection of benzene, toluene and xylene (BTX) from complex mixtures. Detection of BTX gases is of great social and environmental significance because of their serious medical, environmental, and explosion hazards. The ingenious consortium consists of eight partners. Four prominent European research universities and institutes and four leading Russian institutes from the Russian Academy of Sciences.
Several cutting edge technologies are developed within the project, such as the development of novel sensing fluorophores exhibiting a selective and reversible exciplex formation with monocyclic aromatic hydrocarbons exhibiting a specific shift in the fluorescence spectrum. Solid state detection of BTX with fluorophore was realised by developed nanoporous and hybrid polymer membranes and nanoparticles. The fluorophore doped materials were suitable for integration into plastic waveguides of a few micrometres thick on foils with LED's and photodiodes for the read-out. To enhance the florescence and sensitivity, nanostructured plasmonic structures and nanoparticles specific to this material were developed.

Extensive work was done to optimise the lowest limits of the detection for BTX gases. Concentrations as low as 0.25 ppm for toluene and Xylene and 0.5 ppm for benzene were easily detected. For all gases response and recoveries times in the order of minutes were obtained. Selectively of the system towards a mixture of common interference gases such as hexane and ethanol was investigated. Interferences such gases could easily compensated as they did not exhibit any spectral change.

The discovered fluorophore in combination with the solid supports developed within the Ingenious project offers a new sensor principle capable of selective and reversible detection of BTX at relevant concentration. While further development and validation of the sensor is still required, the relative simplicity and limited cost of the system could enable its widespread use en enhanced safety for the groups at risk of BTX exposure.

Project Context and Objectives:

Benzene, toluene and xylene (BTX) are compounds of great social and environmental significance, as they are widely used in industry in many different applications. However, they can present serious medical, environmental, and explosion dangers. Because they are toxic even at parts per-billion concentrations, it is essential to know their concentration in the air, especially in industrial and populated areas. Measurement of these toxic compounds at trace levels in multi-analyte mixtures is still a challenging task however, and involves the use of expensive laboratory-bound expensive equipment. This severely limits risk analysis and timely initiation of preventive measures in a working environment. The main objective of the INGENIOUS project is the development, evaluation and validation of novel ultra-sensitive and selective nanostructured optochemical sensors for the detection of BTX. Sub-goals involve the different components of such a system; novel fluorescent chemosensing materials, sensitivity enhancing nanostructured transducer substrates and a foil-based optical read-out platform. The central component of such a system will be polymeric or silica nanoparticles combining fluorescence readout probes for volatile organic compounds (VOCs). Information about the recognition event is obtained using either analyte fluorescence or changes in the fluorescent characteristics of molecular probes embedded in imprinted cavities. Nanoparticles selective to different hazardous aromatic compounds such as benzene, toluene and xylenes and PAH's will be investigated. As a second nanotechnological approach, metal enhancement, will be embedded in the sensor system making use of plasmonically active metal nanostructures to enhance the fluorescence signal via enhanced emission, lifetime and stability, enabling a reduction in the lower limit of detection. Significant advances are expected in terms of selectivity, sensitivity and timescale for the detection of a range of important VOC analytes which will enable improved environmental monitoring and more rapid response to leaks in the work-place.
The main scientific and technical objectives of the project are:

Synthesis routes for core-shell nanoparticles having fluorescently active molecularly imprinted polymeric shells.

Optimised nanoparticles for metal enhanced fluorescence.

Fabrication routes for nanostructures on foils for metal enhanced fluorescence.

Stable and robust inkjet-based nanoparticle deposition and patterning processes.

Transducer elements showing fluorescence for detection of target analytes in molecular imprinted core-shell nanoparticles.

Transducer elements based on metal enhanced fluorescence for detection of target analytes by combining molecular imprinted polymers and metal nanoparticles.

A foil based optical readout platform based on organic semiconductor components.

An optical sensor device prototype with detection capabilities for target analytes at concentrations below 25ppb (BTX).

An optical sensor device prototype verified for distinguishing 3 target analytes from mixtures.

Project Results:

The project targeted the development of new generation of ultrasensitive optochemical sensor for the detection of benzene, toluene and xylene (BTX) from complex mixtures. Secondary goals involve the development of components of such a system: novel fluorescent chemosensing materials, sensitivity enhancing nanostructured transducer substrates and a foil-based optical read-out platform. Detection of BTX gases is of great social and environmental significance because of their serious medical, environmental, and explosion hazards. Several cutting edge technologies are involved, such as sensing material based on nanoporous and hybrid polymer membranes and nanoparticles, integrated into plastic waveguides of a few micrometres thick, containing thin film devices for the read-out.

During the project the original methods of synthesis for (1) silica nanoparticles with molecularly imprinted receptor sites (SNMIR) and (2) functional polymeric nanoparticles with shell based on monomers of different chemical nature were developed. Both types of nanoparticles conjugated to a fluorescence dye were characterised and tested as a first sensing material to detect the BTX gases and naphthalene. It has been demonstrated that polymer nanoparticles revealed to be less promising for this type of application than silica nanoparticles. Moreover, the first generation dye did not have strong selectivity to the BTX gases. Therefore a 2nd generation dye system was developed. Due to its particular chemical structure the dye exhibited a particular selective behaviour towards the BTX gases. This unique property of 2nd generation dye was recognised as a solid road towards the selectivity of the Ingenious optochemical gas sensor.

PC-RAS investigated the possibility of differentiating single components form a mixture of gases. To enable differentiation between various BTX gases, PC-RAS developed a deconvolution model based on the various response spectra's for BTX's. They demonstrated that with their model they could differentiate xylene from a mixture of benzene. The use of one single dye system capable of sensing selectively BTX through spectral changes made the development of a large number of sensing materials and therefore sensing nodes unnecessary. The project was therefore adapted appropriately.
In order to enhance the optical response of sensing nanoparticles, new classes of nanoparticles containing metal core were synthesized. For this purpose, the University of Vigo (UVIGO) has worked on synthesising nanoparticles with controlled size and shape. This is a classical road for the enhancement of the fluorescence response in the wavelength spectrum closed to the spectral response of the 1st generation dye which was in the red. As the 2nd generation dye is excited and emitting at a different optical region, new approaches to optical enhancement were undertaken. Novel metal core based nanoparticles were investigated for their suitable in this application. A major difficulty within the project was the quantification of the plasmonic enhancement of the dye grafted to the nanoparticles. As the concentrations of dye onto the particles could not be properly quantified various strategies were undertaken to find alternative methods to quantify the enhancement. Techniques such as etching away the metal core and lifetime measurements of the fluorescence were investigated.

The work on fluorescence enhancement by plasmonics structures was also pursued by Aarhus University (AU within WP2. Various structures (holes, disks, caps, asymmetric caps) and metal dielectric structures (nanosandwiches, multilayer caps and multilayer holes) as well as structured percolation threshold films have been fabricated. Moreover, using their expertise in unconventional lithographical approaches, they transferred their nanostructuring techniques form rigid substrates to flexible substrates. As for UVIGO, AU first developed plasmonic structures for the 1st generation sensing nanoparticles. During the last 18 month their plasmonic structures have been tuned to suit the 2nd generation dye. They have shown that they could plasmonically enhancement the sensing fluorescence of the 2nd generation dye in thin polymer membrane by a factor 5 and by a factor of 50 to 125 at hotspots. To better understand the nature of the enhancement lifetime measurements of the dye in polymer membranes were performed at TNO.

In addition to plasmonic structures, imprint lithography was used within WP2 for creating light incoupling and outcoupling features by means of the nano- and/or micro structuring. Systematic optical measurements and modeling, were performed to improved light incoupling by micromirror features. In parallel TNO investigated the possibility to transfer plasmonic features created by AU to a low cost roll to roll fabrication method. To this end a master of the structures was made by colloidal lithography and they were reproduced via nanoimprint lithography onto foils.

Optimisation of the sensing layers was performed in WP3, various organic and inorganic supports for the 1st and 2nd generation dyes and nanoparticles were investigated. Techniques such as printed monolayers of nanoparticles were investigated as sensing matrices. It was found that the sensing nanoparticles were not suitable for waveguides and the plasmonic structures as developed by AU. Consequently a versatile toolbox for creating organic sensing membranes was developed based on the 2nd generation dye which could be used in combination with the nanoparticles. A key advantage of the developed polymer membrane is its ease to be up scaled and industrialised.

Within workpackage 4 the sensor platform was developed. First a fabrication process for inplane sensor platforms was developed. Two base technologies for making low cost inplane optical platforms were investigated. One platform was based on solely additive processes such as inkjet printing. The second platform was based on combinations of subtractive methods and hybrid integration. In both cases technologies such as metallization, interconnection and adhesion of components were developed to realise the final platform. In the case of the first platform an inkjet printing technology was developed for
the creation of waveguides. This was demonstrated on various substrates such as PET foils and paper. For the subtractive platform laser scribing technologies in combination with PDMS based waveguides was used. The waveguides were shown to have low optical losses.

As well as developing novel low cost sensing platforms, a significant of work was put by TNO into optimising a conventional read-out platform to obtain the required sensitivity (25 ppb LOD). Via various platform iterations a standard system was build consisting of a small flow cell with a volume reduced to below 30 ml. The electronics, was optimised such that measurement time was decreased to half a microseconds to reduce photobleaching. The LED power and optical filters were optimised to obtain a stable fluorescence signal from the 2nd generation dye.

The validation experiments were performed by CIOP-PIB on the sensor platforms developed by the TNO with materials provided from the Russian partners and TNO. Within WP5 CIOP-PIB developed processes to create reproducible gas concentrations. Regarding the testing of the sensor prototype (WP5), with each new sensor platform, calibrated and reliable gas detection measurements were done according to the EN 45544-1 standard by CIOP-PIB. It was shown that the materials provided by WP1 exhibited selective behaviour to BTX gases.

With their infrastructure CIOP-PIB investigated the lowest limits of the detection for toluene, xylene and benzene. From their measurements concentrations as low as 0.250 ppm could easily be detected for toluene and 0.5 ppm for benzene. For Xylene similar responses as for toluene were obtained. For all gases response times in the order of minutes were obtained. The lowest levels of detection estimated from the signal to noise ratios were 10 ppb for toluene and xylene and 30 ppb for benzene well in line with the project requirements. To verify the selectivity of the system to aromatics against aliphatic compounds the cross selectivity to hexane was tested. Negligible responses were obtained.

Future improvements of the sensor should focus on long term signal stability of the sensor to large variations in relative humidity and to enhance the sensors response to benzene as compared to toluene and xylene. If the two points can be addressed a continuous sensor, capable of detecting individual BTX's at sub ppm ranges without major cross sensitivities from aliphatic volatile compounds could be achieved. Such sensor would have strong intrinsic advantages over all conventional sensors such as PID, metal oxides and reagent tube based sensors. The relative simplicity and low cost of the system would enable widespread use en enhanced safety for a large group of employees occupationally exposed to BTX's in the petrochemical industry and indoor.

Potential Impact:

The FP7 Ingenious project was approved within the theme 4 NMP - Nanosciences, Nanotechnologies, Materials and new Production Technologies and belonged to the special EU-Russia call (Identifier: FP7-NMP-2009-EU-Russia). This call was identified by EU Commission in order strength further the EU-Russia cooperation. A key aspect to this specific project namely the joint Russian-European cooperation was setup to strengthened cross-nation scientific collaboration. In the case of the Ingenious project, former projects already done with the Russian partners considerably facilitated interaction. As an example, the Holst Centre has been for a long time in contact with the Photochemical Centre and Enikolopov Institute of
Synthetic Polymer Materials of the Russian Academy of Sciences. The key to a successful project is building on good communication, mutual trust and beneficial collaboration from both sides. In the case of the Ingenious project, the strong chemical, theoretical and photophysical background from the Russian side was complemented with a solid the expertise in the field of Plasmonics, electronics, sensor verification and system in foil from the European side. Such interdisciplinary cross-national collaborations is at the heart of a successful project. Besides strong willingness to cooperate from both Russian and EU sides, numerous problems are usually met during such a cooperation project from which the language barrier, a strong hierarchical nature at most Russian research organisations and complex decision making process related to the way of working from EU as well as the Russian government for such funded projects.

As it can be seen from the Ingenious partner distribution, half the partners belonged to the Russian Academy of Sciences and half belonged to European research institutes and universities. The establishment of efficient interaction mode and proper communication between the Russian partners and EU partners was extremely important for the success of this project due to the large number of Russian and European partners. The differences in social, cultural and work organisation habits between the Russian and EU partners could strongly affect the actual outcome of the project therefore required additional care. Communication between parties could be described as efficient with all monthly conference calls and half-yearly project meetings, which were organised within Ingenious project. For all the meetings, a representation was always present from the Russian as well as from all EU side. This was even the case when the project was effectively finished from the Russian side. While running the Ingenious project, it was found efficient to communicate predominantly to only to one representative of Russian partners (Russian coordinator) and subsequently dissipate the information within the Russian partners internally. Moreover, the Russian partners as well as EU partners participating in this project understood well their role in the project and the tasks they are expected to carry out. Equally, the internal SharePoint site setup for the project, was heavily used by Russian as well as EU partners for sharing the documents. Communication to the outside was arranged via the website [http://www.ingenious-project.eu](http://www.ingenious-project.eu)

From a European scientific perspective, the project supported leading European groups in the field of plasmonics such as the Colloid Chemistry Group of the University of Vigo (Spain) and Nanobiointerfaces Group at the University of Aarhus (Denmark) as well as leading research institutes such as Holst Centre (The Netherlands) and Central Institute for Labour Protection â?? National Research Institute (Poland). In addition the project opened up the possibility to a multidisciplinary consortium to venture in the new area of plasmonically enhanced fluorescent gas sensors for the detection of aromatic compounds. Direct educational tasks strengthening the knowledge position of the EU can be clearly exemplified by the two PhD's programs setup during the Ingenious program (Thomas Schmidt and Marcin Grzelczak) and Post Doc employee involved in the project. The project gave numerous students the opportunity to perform their master project at a leading research institutes and the universities (Jeroen Schram, Sami Sabik, Rafay Ahmed and Juan Diego Arias Espinoza).

With respect to travelling and staffs exchange, the representatives of all EU partners went to Moscow for the project kick off meeting. The meeting was attended by the project coordinator Dr Albert van Breemen, and Dr Herman Schoo from Holst Centre/TNO), Prof. Luis Liz-Marzajín (UVIGO), Prof. Duncan Sutherland (AU) and Dr Magorzata Poaniak, (CIOP-PIB) and additional researchers. Numerous visits to the Russian
Academy of Sciences were planned. The first regular 6th month meeting of the Ingenious project, organised on the EU side was in Eindhoven, Netherlands hosted by the Holst Centre/TNO on the 29th to the 30th of March 2010. It was attended by 4 colleagues from Russian side with key responsible such as Prof. Viatcheslav Sazhnikov and the Russian coordinator Dr D. Ionov present. Such regular meetings between the Russian and European partners were important to update and reinforce interaction within the project. Subsequently the first annual meeting was hosted by Holst Centre and took again place in Eindhoven from the 6th to the 8th of October 2010. It was combined with the Exploitation Strategy Seminar as suggested by the EU commission in order to brainstorm on the exploitation of the project results. From the Exploitation strategy seminar clear goals on possible intellectual property were set. The seminar was highly appreciated from the EU as well as the Russian partners and raised particular awareness on the importance of exploitation of the results. The meeting was attended from the Russian side of the project noticeably by Prof. A. Muzafarov (Enikolopov Institute), Dr D. Ionov and additional Russian participants as well by the European partners and members of the advisory board. During this period of time the project coordinator from the EU side was transferred from Dr Albert van Bremen to Dr Iryna Yakimets. The 18 months review meeting was organised by the University of Vigo from 13th to 15th of April 2011 and was combined with first workshop on ‘Nanostructured Materials for Sensing’. The workshop, which was public, was well attended by numerous students from the university of VIGO and clearly contributed to the dissemination of results obtained within the project. Speakers involved in the project together with invited speakers, gave an extensive overview of the current developments in the field of nanostructured materials for sensing applications. From the Russian side a delegation of 4 researchers attended the meeting, particularly Prof. Viatcheslav Sazhnikov, participated to the meeting. The members of the advisory board attended the meeting in addition to all EU members of the project. The 2nd year meeting was organized in Moscow from the 5th to 7th October 2011 and was hosted by the Photochemical Centre of the Russian Academy of Science. It was combined with the second workshop from Ingenious project. Again the workshop was made public as to increase the project awareness within Russia. All EU partners were represented during this meeting. Members of the advisory board attended the meeting, indicating the overall interest of the project from the industrial advisory board point of view. The 30th month meeting was held in Warsaw, Poland from the 28th to the 30th 2012 of March and was preceded by an open workshop on ‘Nanomaterials in Chemical and Biomedical Applications’. At this point in time the project was finished from the Russian side, to show their support and commitment to the project. The Russian partners sent a representative to attend the meeting at their own expense. From the EU, all partners attended as well as members from the advisory board. The final project meeting took place in Aarhus, Denmark on the 23rd to the 25th of September 2012. All European partners participated as well as one representative from the Russian side were present. The meeting was combined with a public workshop on the topic of ‘Applications of Plasmonic and Nanostructures’. During these last meeting the project finalisation was discussed as well as the commitment to future exploitation of the results. Final project results and outcome were presented to the European Coordinator on the 28th of September 2012 in a joint meeting with the other two European-Russian collaboration project. Key scientific outcome as well as future dissemination of the results were presented. The intent and status of a start-up exploiting the results from the Russian side was presented during this meeting.

Where as the project related travels and exchanges were discussed above, the project results were extensively disseminated at various conferences and forums. For instance, Dr Herman Schoo (Holst centre/TNO) strongly involved in setting up the Ingenious project, attended the RUSNANOTECH Forum...
which took place in Moscow from 1st to 3rd November 2010. This Forum has been initiated by RUSNANO in 2007 and attracted more than 11000 people for its last event. This forum was organised in order to assist the Russian nanotech industry to strengthen its international links, which will help its advance to the global market. Therefore, the main goal of RUSNANO is to develop the partnerships with the world’s leading nanotechnology centres. Subsequently, the ingenious project served as a global platform for the discussion of issues related to innovation development and on-going formation of the Russian nanotech industry. It was extremely important to attend such event in order to strengthen further the EU-Russia cooperation in the area of nanotechnology and promote the Ingenious project. Likewise, the Russian partners presented the work which has been done within the frame of Ingenious project at the international conferences which took place in the EU countries. For instance, development of nanoparticles for sensing was presented in Greece (BIONANOTOX Symposium in Heraklion, Crete, Greece, 3-9 May, 2010) and in Poland (7th International Workshop of Silicon-Based Polymers, Lodz, Poland 27th-30th June 2010). Work related to plasmonics was extensively disseminated by UVIGO as well as AU. Oral and/or poster presentations were given at top conferences such as ACS Spring Meeting, NanoBio Conference, ACS National Meeting, SPP5, Gordon Research Conference on Supramolecular Materials, Nano Today Conference, Yamada Conference, Gordon Research Conference on Noble Metal Nanoparticles, ACS Fall National Meeting and the International Conference of Near-field Optics, Nanophotonics and Related Techniques. Whereas work specifically related to the optical platform as developed by Holst Centre/TNO and characterized by CIOP-PIB was presented in acclaimed sensor and optics conferences such as SPIE Photonics West, EuronanoForum, Photonics Europe, EMRS, IMCS and Eurosensors. In addition to all conferences attended, it was decided to participate in global FP7 EU-Russia cooperation initiative which brings together 3 EU-Russia cooperation projects in the sensors research area: Ingenious, 3S and SAWHOT. The RF/EU Satellite workshops were organized to discuss and share experiences acquired from the RF/EU collaborations and provide feedback on the process to the EU. Within this initiative three events took place namely S3 Summer School 2011 organised on Igora/Konevets Island in Russia. A joint meeting of S3, SAWHOT and Ingenious and workshop was scheduled from 3rd - 4th of September 2011 in Athens in conjunction with the EUROSENSORS 2011 conference. Finally a S3, SAWHOT and Ingenious workshop was held in May 2012 in Nuremberg in connection with the IMCS 2012 conference.

In addition to the regular meetings, numerous bilateral visits took place during the project. The availability of certain characterisation techniques, training, development of setups and fabrication procedure required numerous visits of researchers to numerous nodes. At the end of the project the sensors developed during the process were tested externally at potential customers interested in exploiting the results.

Possible foreseen socio-economic impact of the project

Within the Ingenious project, insights on suitable markets and exploitation strategies were investigated during the Exploitation Strategy Seminar (ESS). From an early stage of the project the focus was placed more on BTX. CIOP-PIB, strongly involved in sensor validation indicated that the interest for BTX could be substantially larger than that for PAH. They also indicated the limitations of current sensor systems and which elements should be focus on to obtain exploitable results at the end of the project. This information was used as the basis to setup a Plan of Use. During the course of the project the relevance of detecting specifically BTX’s was further exemplified by news coverage’s on series of benzene leaks throughout 2011 and 2012 in Rijnmond (the Netherland) where the responsible companies and authorities had great
difficulty in tracing the origin of substantial benzene leaks. Whereas disposable sensors are available, reversible and selective BTX detection at relevant concentration and cost is still lacking. We have therefore set reversibility as an additional constraint to the project deliverable. We have addressed this issue by focusing on a reversible sensor, with an intrinsic selectivity to BTX's and worked on having detections limits below the exposure limits.

Analysis of the proposed sensor compared to the state of the art

A range of portable and stationary devices is currently used for the detection and measurement of BTX gas concentration in air: disposable indicative handset, portable and fixed gas detectors. Many stationary devices are combined into complex monitoring and control system, situated in the oil refineries. To date, there is no simple, inexpensive, portable, wearable device for the real time detection of BTX and its individual components in the mixture. The nearest analogue are the one-time use indicator tubes. Current existing selective real time portable devices are bulky, extremely expensive. Lightweight instruments for monitoring the individual components of a mixture of BTX in real time are not available. The technology developed in the course of the Ingenious project, based on the use of fluorescent sensors, could in the future allow the realisation of a compact device that can be used to monitor mixtures of BTX in real time without suffering from interferences such as hexane and ethanol. Based on the case exemplified above we can conclude that there is an urgent demand for products with these characteristics.

The expected product would initially consist of an optical sensor system for detecting BTX. Optical chips containing the active sensor material could be used for a certain moment of time. It could be envisaged that employees at a refinery could use the system for a full week of continuous monitoring with a sampling rate of 1 min. Continuous measurement for a month can be achieved by simply increasing the measurement intervals to 5 minutes which would make it suitable for indoor air quality monitoring of BTX. The fabrication cost of such a chip should however remain low. The verified sensor detection limits are at this moment for Benzene <0.5 ppm, Toluene < 0.25 ppm, Xylenes < 0.5 ppm however further developments should allow even lower and more reliable detection limits and better selectivity of the individual BTX compounds.

Another market perspective, where so far no sensor has been suitable either due to cost or to selectivity issues, is for indoor air quality monitoring of specifically toluene. Here the detection of toluene from predominantly nonaromatic compounds such as ethanol is required. Our sensor is well suited for this application. From literature survey's, not many other concepts have so far emerged capable of reconciling low cost and selectivity.

With the currently developed technology two possible large markets scenarios can be addressed. The first case is the selective detection of BTX at sub-ppm detection limits for the petrochemical industry. Although the sensor will be exposed to harsh environment and strict certification will be required, the size of the market and the seriousness of the problem make it an interesting case where quality oversees costs. At this point in time further developments will be required to selectively detect traces of benzene from high concentrations of toluene and xylene. The second case consists of the indoor air quality monitoring. In this case the detection of toluene is required at low ppm concentrations. The requirements are less strict and interference form benzene and xylene are of lesser importance. The sensor at this moment could very
quickly be implemented for this application as the sensitivity to toluene is higher and it's sensitivity to relevant interference low. However the sensor cost will need to be kept low.

Project website: http://www.ingenious-project.com

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Last update: 29 April 2013
Record number: 55943

Permalink: https://cordis.europa.eu/project/id/248236/reporting

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