MIKLÓS ZRÍNYI
<u>NATIONAL DEFENCE UNIVERSITY</u>

(LT. COLONEL ENGINEER ÁRPÁD MOLNÁR)

- Automatable integrated radiological and chemical sensors -

(PhD) thesis
Author's review and official reflections

Budapest
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Leader of research:

(Prof. Dr. László Halász DSc, full professor)

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1. DESCRIPTION OF THE SCIENTIFIC PROBLEM

Military-political changes occurred by the end of the 20th century resulted in a situation in which humanity faces threats coming not from conventional armies of the two adverse superpowers or their allies.

Massive armies are gradually being replaced by voluntary armies that are smaller in number and equipped with advanced armament. Wars to be fought by ‘conventional’ countries or their groups have disappeared, and hot conflicts have metamorphosed such warlike conflicts localized to smaller regions of the world in which paramilitary organizations fight against each other or modern and well-equipped armies come into conflict with troops of guerrillas, terrorist or paramilitary bands.

Due to changes in characteristics of military conflicts, and scientific and industrial developments new modes of operations have appeared.

The newest one of them is information operations decisive elements of which are information superiority, information dominance and supremacy in command.

Information superiority can be achieved by acquisition, possession, processing quicker and more effective than enemy’s one, and exploitation and more efficient protection.

Senor systems that can be left unattended fit well in equipment system of information operations, and their operation can not be imagined without special sensors. They are for example radiological and chemical sensors.

Necessity of such sensors is not queried even by the fact that the risk of attacks by mass destruction weapons has decreased due to non-proliferation treaties and disarmament programmes supervised by international organizations.

Unfortunately, on the one hand there are countries which are not involved in these treaties, however possess mass destruction weapons. On the other hand, terrorist organizations – whose locations and activities can be found and followed and observed hard – make effort to obtain mass destruction weapons to be used against symbolic or economic targets.

Therefore, the warning fact remains that because of accidental or intentional activities the environment could become contaminated with chemical or bio warfare agents or toxic industrial materials or materials contaminated with radioactive isotopes from nuclear facilities.

Due to attacks against industrial and/or nuclear facilities, or terrorist activities, materials could get out and endanger large areas; if these materials get into the open air populated areas could be polluted too.

The basic principle is that the NATO plans and accomplishes its operations in the consciousness of threats against its forces. However, even during non-Article 5 crisis management operations it could be a risk that hazardous materials can get out of destroyed industrial or nuclear facilities. Therefore, NATO forces must be capable not only of defence against conventional attacks, but of doing operations during a prolonged period in an environment contaminated with chemical and biological warfare agents and industrial toxic materials, or even in an environment contaminated with radioactive isotopes from nuclear facilities.

Taking into account facts above-mentioned, it is essential to develop capability of defence against these materials in a direction which involves indication, reconnaissance and monitoring of sources of danger, furthermore use of means for individual and collective of protection.

Intensive development of CBRN laboratories all over the world aims at working out simple, quick and reliable procedures for detection and monitoring of impurities content of environmental samples.

Researchers make their significant steps relying on achievements of information technology, biotechnology and nanotechnology.

Biotechnology and information technology are well-known phrases in everyday life. A greater and greater number knows the basis of biotechnology and information technology and enjoys products of them.

Nanotechnology begins to gain ground too; today one can buy refrigerator with bactericidal silver-coating and fruit mixer with nanofilter.

The term ’nanotechnology’ begins to become a vogue word without a more thorough knowing the background. Nano- is a prefix derived from the Greek “nanos” meaning *dwarf* and denoting a factor of a milliardth (1 nm = 10^{-9} m).

Chemists and biologists routinely work with natural or artificial nano-sized objects

Such objects can be the following:

- atom nucleus (diameters: 1–7 fm);
- atom of silicon (its diameter in crystalline structure is 0.24 nm);
- water molecule (maximum diameter is 0.37 nm);
- carbon nanotubes (diameteres are 0.7–3 nm);
- deoxyribonucleic acid (DNA) molecule (diameter is 2 nm);
- proteins (diameter is 6 nm);
- transistor (its size in an integrated circuit is 100 nm);
- animal cell (diameter is 2-20 μm);
- Human hair (its diameter is 50–100 μm).

First popular descriptions of nanotechnology were about nanomechanisms capable of self-assembling after a spontaneous or intentional intervention. In this period there have appeared passive nanostructures (fullerenes, carbon nanotubes).

In our days, active nanostructures such as sensors, or drug delivery means realizing molecule transport have been brought into focus, and also 3D nanostructures and systems have appeared in the horizon of science.

There is a dominance of interdisciplinarity in description of applications of nanotechnology. Nanoscience, nanoengineering, materials fabricated by the use of nanoengineering, biotechnology, supramolecular science and self-assembling – all these come into view at the same time. Taking into account synergic effect of the results of the mentioned fields, emergence of molecule-level nanosystems and self-assembling is expected.

Military applications can be the following:

- mobile nanorobots being molecule-level structures with reproductive capability;

- nanocomputers characterized by high-level artificial intelligence, and capability of automatic building and research;
- manipulated and artificially produced organisms;
- nanorobots which can build in cells, and manipulate DNA and protein synthesis;
- elimination of diseases and ageing;
- nanorobots building in neurons;
- cerebral implants to increase memory and for communication;
- coupling machine and man

Appearance of military nanotechnological applications in the field of NBC defence is expected too.

The role of sensors in detection and diagnostics will significantly increase.

Physical protection will be provided by multifunctional integrated personal protective device supported by sensors.

Decontamination can be carried out by the use of coating surfaces before contamination occurs; or of decontaminating material being emitted by sensors after contamination occurs. We have to continue calculation with a high-volume decontaminating capacity in condemnation of existing stocks of chemical warfare agents.

In medical activities in the field of NBC defence, diagnostics based on nanotechnology characterized by quick results and diagnosis, sensitivity and less false positive evidence, while effectiveness of therapy will be provided by expedient selectivity, gradualness and histic and cytic specificity.

Research and development of automatable integrated radiological and chemical sensors coincides with above-mentioned trend, offering economical and advanced domestic solutions to carry out important NBC tasks.

2. RESEARCH OBJECTIVES

Taking into account the size and complexity of the field of radiological and chemical sensors, I focused my experimental work on chemical sensors.

In my thesis I show my results in the field connected to chemical sensors.

I determined the following research objectives:

- to examine gold sol stabilized with alkyl-thiol as nanostructured chemical receptor coated on interdigital electrodes using Electrochemical Impedance Spectroscopy;
- to work out a new qualification procedure based on examination methods of Transmission Electron Microscopy and Electrochemical Impedance Spectroscopy for testing the production of military automatable integrated chemical sensors;
- to examine military experimental integrated chemical sensors in air contaminated with phosphoric acid esters, using Electrochemical Impedance Spectroscopy;
- to work out a new testing method for qualification materials of military skin-protection devices, using military integrated chemical sensor with alkyl-thiol stabilized gold sol as nanostructured receptor.

3. RESEARCH METHODS

I had given an overview on researches relating to radiological and chemical sensors, after I decided to focus my job on chemical sensors.

On the basis of literature and patent review I have done I found that nanotechnological method is a suitable one to produce receptor.

To observe characteristics of receptor and changes of electrical parameters of interdigital electrodes during sensing, it was necessary to find a method giving better possibilities than those applied by others previously.

The method should facilitate definition of frequency range applicable to materials to be examined.

I found that the suitable method is Electrochemical Impedance Spectroscopy.

I applied the developed procedure to several nerve and blister agents.

In addition to laboratory chemicals and devices, my work required equipment for adjusting dynamic concentration of chemical warfare agents, and many other high-sensitive devices and methods of chemical analysis.

During examinations I checked the adjusted concentration of chemical warfare agents by the use of gas chromatograph-mass spectrometer apparatus.

For characterization of nanostructured materials I used a Transmission Electron Microscope and the method of dynamic light scattering.

4. THE RESEARCH PERFORMED

My thesis resulted from my scientific research consists of five chapters.

In the Chapter 1 I have presented results of a literature review with regard to recent achievements and military aspects of nanotechnology, possible application of several sensors, and with special regard to publications on radiological and chemical sensors, production and tests of them.

In the Chapter 2 I have proved, after examinations carried out with methanol, ethanol and i-propanol using Electrochemical Impedance Spectroscopy, that the chemical sensor coated by nanogold sol stabilized by hexanthiol has a nanostructured receptor which interacts with materials tested.

In the Chapter 3, studying key steps of preparation of military integrated chemical sensors, I have showed the qualification test based on Transmission Electron Microscopy and Electrochemical Impedance Spectroscopy necessary to check and control. The Transmission Electron Microscopy test gives information on applicability the sol produced, but the Electrochemical Impedance Spectroscopy test using reference material toluene provides information about operability of a produced sensor.

In the Chapter 4 I have reported on tests of phosphoric acid esters using experimental military integrated chemical sensors. Utilizing opportunities of Electrochemical Impedance Spectroscopy, on the basis of concentrates tested by gas chromatograph-mass spectrometer I defined characteristic of the sensor on tabun and DFP. In the course of tests I used experience of measurement presented in the Chapter 2 and qualification procedure described in the Chapter 3.

In the Chapter 5 I have studied possibilities of testing materials of skin-protection devices by the use of experimental military integrated chemical sensors. On the basis of concentrates tested by gas chromatograph-mass spectrometer I defined characteristic of the sensor on sulfur mustard. During examination I relied on results and experience gained from the previous Chapters.

5. SUMMARIZED CONCLUSIONS

On the basis of literature and patent review I have done I found that nanotechnological method is a suitable one to produce receptor and to carry out experimental work with chemical sensors, taking into account the size and complexity of the two fields.

To observe characteristics of receptor and changes of electrical parameters of interdigital electrodes during sensing, I used the Electrochemical Impedance Spectroscopy method that can be used to define frequency ranges applicable to materials examined; and in this sense it is a method providing better possibilities than those applied by others previously.

In addition to laboratory chemicals and devices, I used not only equipment for adjusting dynamic concentration of chemical warfare agent, but many other high-sensitive devices and methods of chemical analysis.

Throughout examinations on methanol, ethanol and i-propanol I presented that Electrochemical Impedance Spectroscopy method can be applied to examine hexanthiol-stabilized gold sol as nanostructured receptor coating on interdigital electrodes.

Exploiting possibilities of Transmission Electron Microscopy and Electrochemical Impedance Spectroscopy, I worked out a qualitative procedure to check and control the key steps of preparation of military chemical sensors on the basis of the two methods.

I applied this procedure for several phosphoric acid esters and blister agent.

I defined characteristics of experimental military automatable integrated chemical sensors with nanostructured receptor which is hexanthiol-stabilized nanogold sol.

I worked out a new test method using characteristics of hexanthiol-stabilized gold sol nanostructured sensing material on test materials used for examination of material of military protective devices.

6. NEW SCIENTIFIC RESULTS

1. I examined nanogold sol stabilized with hexanthiol as nanostructured receptor coating on interdigital electrodes special by the use of Electrochemical Impedance Spectroscopy.
2. I worked out a qualitative procedure based on Transmission Electron Microscopy and Electrochemical Impedance Spectroscopy to control preparation of military automatable integrated chemical sensors with nanostructured receptor which is hexanthiol-stabilized nanogold sol.
3. I was the first researcher who examined a military experimental integrated chemical sensor in air contaminated with phosphoric acid esters, using Electrochemical Impedance Spectroscopy.
4. Using military integrated sensor with nanostructured receptor which was hexanthiol-stabilized nanogold sol I worked out a new examination method for testing material of military protective devices.

7. PRACTICAL APPLICABILITY OF RESEARCH RESULTS

Electrochemical Impedance Spectroscopy for examination of nanogold sol stabilized with hexanthiol as nanostructured receptor coating on interdigital electrodes can be applied to research and development of new nanostructured materials.

The qualitative procedure for controlling thepreparation of military integrated chemical sensors will be usable for testing preparation of integrated sensors.

Experience gained during examination of experimental military integrated chemical sensors in air contaminated with phosphoric acid esters can be used for development of an detector operating on the basis of an integrated chemical sensor.

The examination procedure using experimental military integrated chemical sensors for testing material of military skin-protective devices can be used to define material development results and protective capability of military devices of protection.

8. PROPOSALS

I recommend material of my thesis

- to those specialists of the Ministry of Defence and Hungarian Defence Forces who deal with military technological research and development of chemical and radiological sensors;
- to the Miklós Zrínyi National Defence University, as teaching background material;
- to those specialists who are involved in military technological research and development of materials of devices of NBC protection.

9. LIST OF THE AUTHOR'S PUBLICATIONS CONCERNING THE THESIS

Articles published in edited journals

[1] Molnár Á., Halász L.: Arany szol bevonatú vegyi érzékelők vizsgálata diizopropil-fluorofoszfonáttal szennyezett légtérben
HADMÉRNÖK, 4, 4 (2009) (59-69)

[2] Molnár Á., Halász L.: Aranyszol bevonatú vegyi érzékelők alkalmazhatósága a katonai egyéni védőeszközök védőképességének vizsgálatára
HADMÉRNÖK, 4, 4 (2009) (70-82)

Articles published in foreign language publications

[3] Vincze Á., Halász L., Solymosi J., Ágai B., Kása I., Molnár Á., Sáfrány Á.: Development of an extractive-scintilating chromatographic resin for the detection of radioactive isotopes
Journal of Radioanalytical and Nuclear Chemistry Vol. 273 No.3 (2007) 615-619)

[4] Molnár Á., Halász L.: Qualitative Procedure Applicable in Course of Preparation of Military Chemical Sensors Coated with Gold Sol, AARMS befogadva

[5] Kása I, Solymosi J, Molnár Á.: Preparation and investigation of thermoluminescence properties of CaSO4:Dy,Cu Radiation Protection Dosymetry Vol. 65, Nos. 1-4, pp. 313-316, 1996

Paper published in conference proceedings

[6] Vincze Á, Ágai B, Halász L, Kása I, Solymosi J, Molnár Á: Extrakciós-szcintillációs szenzor radioizotópok kimutatására, Vegyészkonferencia 2004, Magyar Kémikusok Egyesülete, Balatonföldvár 2004

Hungarian patent, invention

[7] Dékány I, Nagy L, Németh J, Patzkó Á, Molnár Á: Monokationos agyagásvány-félvezető fém-oxid és/vagy -hidroxid nanokompozitok, eljárás ezek előállítására, és ezek alkalmazása környezetre káros szerves anyagok fotooxidációs lebontására 225 845, Budapest, 2008

Evaluated study for a Call

[8] Molnár Á.: A nanotechnológia új lehetőségei az ABV védelmi kutatás-fejlesztésben (Tanulmány HM FLÜ TI/386-5/2009 Budapest 2009)

[9] Gyulai G., Molnár Á.: Kémiai redukcióval előállított nanoporok eljárásainak és katonai alkalmazási lehetőségeinek irodalmazása, a katonai igények felmérése, elemzése
NKFP-07-A2-METANANO-0-0710120730 Budapest, 2008. július

10. AUTHOR'S PROFESSIONAL-SCIENTIFIC BIOGRAPHY

Personal data

Name:	Árpád Molnár
Rank:	Lt. Colonel Engineer
Date of Birth:	6 May 1962
Place of Birth:	Budapest
Mother's maiden name:	Irma Dróth
Address:	Ministry of Defence
Office:	Development and Logistics Agency H-1135 Budapest, Lehel u. 35-37
Nationality:	Hungarian
Marital status	married, two children

Qualifications	Radiochemical engineer1985 (75/1985)
	Dipl. Chemical engineer 1994 (32/1994)
Languages:	English – medium level 1997 (684/1997)
	Russian – basic level 1985

Educations

1977-1981	Miklós Radnóti School of the Loránd Eötvös University (ELTE), Budapest
1981-1985	Máté Zalka Military Technical College, Budapest
1991-1994	Chemical Industry Branch of Organic Biology, Faculty of Chemical Engineering, Technical University of Budapest
2003-	Military Technical Doctoral School of the Miklós Zrínyi National Defence University (PhD student)

Duties

1985-1987	14th Mechanized Infantry Regiment, NBC platoon commander
1987-1990	14th Mechanized Infantry Brigade, NBC company commander
1990-1992	14th Mechanized Infantry Brigade, NBC Operations Officer (in charge of chief of NBC defence)
1994-1996	Hungarian Defence Forces, Institute of Military Technology, research-worker
1996-2001	MoD Institute of Military Technology, engineer-developer
2001-2002	MoD Technology Agency, engineer-developer
2002-2006	MoD Technology Agency, senior officer (project manager)
2007-	MoD Development and Logistics Agency, Technology Directorate, senior officer (project manager)

Activities

- Scientific Students' Associations: Modelling some chemical effects using computer, third place,1985
- Preparation and examination of $CaSO_4$: Dy,Cu thermoluminescence phosphorus 1993-1994

Project manager for the following R&D topics:

- Examination of imported chemical detectors 1995-1997
- Development of a simple chemical indicator 1997-1999
- Development of D-class dry-powder and fire extinguisher 1999-2001
- Research on new type decontaminating solutions 1998-
- Development of Indicating probe kit 1998-2003
- Development of a simple biological indicator 1999-2003
- Development of a flexible NBC container 1999-2003
- Development of an individual decontamination kit 1999-2003
- Examination of carbon nanotubes 2002
- New type decontaminating material (nanocomposite) 2006-
- Broad-spectrum chemical indicator 2006-

Call for Proposals:

2008-2010 Leader of the project „Development of noble metal nanopowder-based innovative products (filters, sensors, catalyst) for environment protection and safety engineering purpose (Anyos Jedlik Programme, National Office of Research and Development)

Membership:

Hungarian Association of Military Sciences, Section of Military Technology 2003-

31/1/2010, Budapest

Lt. Colonel Engineer Árpád Molnár