Review of Technologies Developed or Utilized in Europe and the Commonwealth of Independent States (CIS) for Use in Long Term Monitoring of Radionuclides and Heavy Metals in Water and Soils

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Introduction

Long-term stewardship corresponds to the physical controls, institutional information and other mechanisms needed to ensure the protection of people and the environment at sites where the United State Department of Energy (USDOE) has completed or plans to complete cleanup. The goal is to avoid, delay, or reduce the frequency or impact of harmful exposures to hazardous substances remaining after DOE cleanup projects and other operations are completed.

Sensors are needed to monitor the performance of remedial actions and engineered solutions, including the potential release and migration of contaminants. Low cost, robust sensors are being sought for remote monitoring of contaminants or other indicators of potential stewardship failures in a variety of media, including water, soils, atmosphere, biota, engineered units, and facilities. In situ, or remote monitoring technologies allow data to be collected as needed at a substantial cost saving. Sensors with the capabilities to automatically detect and monitor hazardous materials in the environment are being sought.

In Europe several related international efforts are in place, e.g.:

- CLARINET: Contaminated Land Rehabilitation Network for Environmental Technologies in Europe [www.clarinet.at]
- NICOLE: Network for Industrially Contaminated Land in Europe [www.nicole.org]
- SENSPOL: Sensors for Monitoring Water Pollution from Contaminated Land, Landfills and Sediments [http://www.cranfield.ac.uk/biotech/senspol/]

Although, according to our knowledge, no other country but the US has initiated a comprehensive program for long term stewardship, there are technologies developed or in the research phase in other parts of the world that might prove to be applicable in the program.

This report contains information on the results of review of technologies developed by scientists/environmental experts, or utilized in Europe and the Commonwealth of Independent States (CIS) for use in long term monitoring of radionuclides and heavy metals in water and soils.

The technologies identified may be adapted or further developed for application for monitoring heavy metals or radionuclides in the vadose zone or groundwater for long term stewardship.

Requirements for monitoring the vadose zone and groundwater for long term stewardship

Principal contaminants of interest are as follows:

<table>
<thead>
<tr>
<th>Metals</th>
<th>Radionuclides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>Plutonium</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td>Strontium- 90</td>
</tr>
<tr>
<td>Mercury</td>
<td>Cesium- 137</td>
</tr>
<tr>
<td>Zinc</td>
<td>Uranium (various isotopes)</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Tritium</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Thorium</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Technetium- 99</td>
</tr>
<tr>
<td>Copper</td>
<td>Radium</td>
</tr>
<tr>
<td></td>
<td>Iodine - 129</td>
</tr>
</tbody>
</table>
For radionuclide monitoring, a system that can monitor gross indicators of contamination, such as gross alpha and gross beta, is needed for both the groundwater and vadose zone. Once the radionuclide contamination has been characterized, gross alpha and beta monitoring may be all that is needed to confirm or question levels between confirmatory sampling events.

For monitoring heavy metals sensors that can measure individual metals as well as the total dissolved metal load are needed.

For effective monitoring, sensors are needed to serve as sentinels for event-related phenomena, monitoring at fixed intervals, early warning systems, or for system validation at a given time.

Expected performance parameters of these sensors are:

- Ability to withstand harsh environments and provide reliable data over the expected range of environmental conditions and events;
- Low power requirements;
- The sensors must be sensitive enough to meet detection limits;
- Rugged, in situ or portable field deployable systems preferred;
- Low or no maintenance required;
- The sensor should provide representative data; and
- Reasonable cost.

Review of technologies developed, or utilized in Europe and the Commonwealth of Independent States (CIS) with the potential for use in long term monitoring of heavy metals or radionuclides in vadose zone or groundwater for long term stewardship.

Over 150 different technologies have been studied from the point of view of applicability for long term stewardship. Out of these, 22 were selected with the potential of applicability for use in long term monitoring of heavy metals or radionuclides in the vadose zone or groundwater for long term stewardship. 17 of the 22 relate to monitoring heavy metals and 5 to radionuclides. 5 of the technologies have been developed in Germany, 5 in Russia, 2 in Norway, 2 in Italy, 2 in the United Kingdom, 1 in Slovakia, the Netherlands, Ireland, the Czech Republic and Croatia. 1 is a German-Russian cooperation. 13 of the technologies can be considered in situ, 7 on-site, 1 involves laboratory analysis and 1 remote sensing. 9 of them target soil measurements, 12 water analysis, and 1 is used currently for waste monitoring. 5 of the technologies are in the development phase while the rest have been in use for some time. The basic technologies used can be categorized into one of the following class of methods: spectrometry, laser induced breakdown spectroscopy, thin film sensors, voltammetry, biosensors, sensor systems, and remote sensing.

Data sheets provided later in this document contain brief descriptions of the technologies, their application for long term stewardship, information on the state of development, whether they are capable for detection only or can provide information on the concentration as well. They provide information on their performance, sensitivity, and cost (when available), and give the technical details including limitations of the technologies. References for further information and contact are given.
Table: Features of the Technologies Identified

| Technology ID no. | 3     | 7     | 8     | 10    | 11    | 12    | 12A   | 12B   | 13    | 14    | 15    | 16    | 17    | 18    | 19    | 24    | 25    | 26    | 26B   | 27    | 29    | 101   | 102   | 103   | 30    |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| country          | D     | D/R   | R     | S     | N     | N     | NL    | UK    | IE    | CZ    | ET    | D     | UK    | I     | CR    | R     | R     | R     | R     | R     | Mo    |       |       |       |       |
| I.1 in situ      | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     |       | x     | x     | x     | x     | x     |       |       |       |       |       |
| I.2 on site      | x     |       | x     | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| I.3 remote sensing | x   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| I.4 laboratory   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| II.1 heavy metals | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |
| II.2 radionuclides |       | x     | x     | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| III.1 soil       | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| III.2 water      | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| III.3 waste      | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| IV.1 in use      | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     | x     |       | x     | x     | x     | x     | x     | x     |       |       |       |       |
| IV.2 u testing   |       |       | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       | x     | x     | x     | x     | x     | x     | x     | x     |       |
| IV.3 u development | x  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| V.1 voltammetry  |       |       |       |       |       | x     |       |       |       |       |       |       | x     |       |       |       |       |       |       |       |       |       |       |       |       |
| V.2 remote sensing |     |       |       |       |       |       |       |       |       |       |       |       |       | x     |       |       |       |       |       |       |       |       |       |       |       |
| V.3 spectrometry | x     | x     | x     | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| V.4 LUS          | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| V.5 film sensor  | x     | x     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| V.6 biosensor    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| V.7 sensor system |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |

The remainder of this report provides data sheets for each technology identified.
Technology ID No.: 3

Sensor system for heavy metals

Technology: Microfabricated Thin-film sensor Array on the basis of Chalcogenide Glass Materials Silicon planar technology, 'electronic tongue' type thinfilm sensor.

Contact information: M.J.Scoening@fz-juelich.de

Application for LTS: detection of Pb, Cd and Cu

State of development: under development

Detect only vs. detect+concentration: detect+concentration

Performance data and sensitivity: Pb, Cd, Cu

Technical details and limitations:
A first step towards a microfabricated potentiometric thin-film sensor array for simultaneous detection of Pb$^{2+}$, Cd$^{2+}$ and Cu$^{2+}$ has been realized. The sensitive layers used are on the basis of chalcogenide glass materials that consists of a mixture of Pb-Ag-As-I-S, Cd-Ag-As-I-S or Cu-Ag-As-Se have been prepared by pulsed laser deposition technique. The developed sensor array has been physically characterized by means of scanning electron microscopy and Rutherford backscattering spectroscopy. The electrochemical sensor characterization has been performed by potentiometric measurements.

Cost data: n.a.

Further information: http://www.mdpi.net/sensors/papers/s20900356.pdf

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Technology ID No.: 7

Sensor system for heavy metals

Technology: Rapid On-Line Detection of Additives in Technical Polymers

Contact information: General information is given by Mr. A. Bauer or by letter to: Fraunhofer Institute for Lasertechnology ILT Steinbachstr. 15 D-52074 Aachen Germany Tel.: +49(0)241/8906-0 Fax: +49(0)241/8906-121 email: info@ilt.fraunhofer.de

Dipl.-Phys. M. Stepputat Tel.: 0241 / 8906 - 124

Dr. R. Noll Tel.: 0241 / 8906 – 138
Application for LTS:

Two main factors determine the economics of the recycling of technical polymers: purity of the sorted fractions and throughput. The purity of the materials to be recycled is important for deciding whether the recycled material has the same properties and thus a similar monetary value as the initial material. Due to their hazardous properties, heavy metal and halogenated additives are a major problem, both during the recycling process and in the final product. Hence, waste pieces containing these substances need to be identified and separated from the waste material before recycling.

It is worth considering application of the technology, has been developed for on line monitoring of recycled waste for monitoring heavy metals in soils.

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: heavy metals

Technical details and limitations:
A multi-sensor-system based on optical spectroscopy was developed within the scope of a joint European project. The polymer is structurally analyzed by two infrared sensors operating in the near and middle infrared ranges. The concentration of heavy metals and halogens is analyzed by a LIBS sensor (LIBS = laser-induced breakdown spectroscopy) which was developed by Fraunhofer ILT. The distance from the LIBS sensor to the surface of the waste pieces varies while the waste pieces pass the LIBS sensor. An incorporated autofocus unit with a measuring range of 50 mm compensates these distance variations with 50 focusing actions per second. The LIBS sensor detects the heavy metals Pb, Cr, Cd and Hg contained in pigments and stabilizers. The identification of the brominated flame retardants by infrared sensors is validated via the detection of Br or by the detection of Sb as a component of the widely used synergist Sb₂O₅. The determined element concentrations are classified into four categories: < 100 µg/g, 100 - 1000 µg/g, 1000 - 2000 µg/g, > 2000 µg/g.

The developed multi-sensor-system has been integrated into a pilot sorting system for end-of-life waste electric and electronic equipment (EOL-WEEE). During the tests of the sorting systems the LIBS sensor characterized the concentration of halogens and heavy metals in waste monitor housings moving on a belt conveyor at a speed of 0.5 m/s with high reliability. Future applications of the LIBS analyzer for on-line material identification, e.g. for the recycling of aluminum, are planned.

Cost data: n.a.


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**Application for LTS:** Chemical sensors for environmental monitoring and for continuous *in situ* measurements.

**State of development:** under testing

**Detect only vs. Detect+concentration:** detect only

**Performance data and sensitivity:** Cu, Cd, Hg

**Technical details and limitations:** Chemically stable chalcogenide and chalcohalide glasses and thin films for chemical sensing of Cu$^{2+}$, Cd$^{2+}$, and Hg$^{2+}$ ions were investigated. It was found that chalcogenide glasses appear to be promising membrane materials for chemical sensors and microsensors. Developed Cu$^{2+}$ chemical sensors were applied for continuous *in situ* monitoring of the waste water treatment at the VITON factory (St. Petersburg, Russia). Further improvement of the sensor properties can be expected by using ion-conducting materials. $^{64}$Cu and $^{110}$Ag tracer diffusion experiments, electrical conductivity studies, $^{129}$I-Mössbauer spectroscopy and EXAFS measurements showed very promising transport characteristics and structure features of CuI-based glassy systems which can be used for this purpose.

New Hg$^{2+}$ chemical microsensors based on thermally evaporated AgBr-Ag$_2$S-As$_2$S$_3$ thin films showed high sensitivity with a low detection limit of $10^{-8}$ M (2 ppb), excellent potential reproducibility, high selectivity and long-term stability. XPS studies and tracer measurements of ionic processes at the sensor surface showed that at least 2 different mechanisms are responsible for Hg$^{2+}$ ion sensitivity of the devices. No commercially available Hg$^{2+}$ sensors are presently at the market.

New Cd$^{2+}$ chemical microsensors based on thermally evaporated CdS-AgI-Sb$_2$S$_3$ thin films showed high sensitivity of these materials.

Investigations of bulk membrane transport and membrane local structure as well as tracer measurements of ion-exchange at the solution/membrane interface and surface spectroscopy studies of the membrane surface appear to be extremely important to understand sensing mechanism of chemical sensors, to optimize the existing and to develop new membrane materials for chemical sensors. It was found that there is a definitive correlation between membrane local structure and bulk transport properties, on the one hand, and surface ion-exchange characteristics and ionic sensitivity mechanism, on the other hand. It means that there exists a possibility to synthesize new chalcogenide glass membranes with improved ions-selective properties, better durability and response stability.

**Cost data:** n.a.


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**Technology ID No.: 10**

**Emission spectral analysis for heavy metals**

**Technology:** emission spectral analysis using the computer technology ECOSCAN for the monitoring of derelict mining territories

**Contact information:** [http://librara.iem.ac.ru](http://librara.iem.ac.ru)
Journal of the Institute of Experimental Mineralogy (IEM)

**Application for LTS:** ecological and geochemical monitoring of derelict mining territories.
State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: Li, W, Sn, Be

Technical details and limitations:
In order to estimate the environmental situation and organize the monitoring, the probing of rocks, soil and vegetation was carried out. The probes were analyzed by the emission spectral analysis. Using the computer technology “ECOSCAN”, worked out in IMGRE, maps of typical geochemical associations of the elements in the probed media were constructed.

The soil and vegetal cover (birch leaves) on the most portion of the region are characterized by near-phonic contents. The polluted areas occupy up to 35% of the region. It is important that elevated contents of elements were not identified on the territory of the Novoorloskii village. The natural-technical system (NTS), were all the probed media (rocks, soils and vegetation) show close typical association of chemical elements, are the NTS of the mine, the NTS of spoil banks, (Li-Be-W), and the NTS of tailing dump (W-Sn). The objects for the monitoring are phonic and technogenically changed territories. Among the latter, the greater attention must be paid to the NTS both with elevated contents of elements and with the distribution of elements between the natural media, which is different from the phonic one.

During the ecological and geochemical monitoring of the NTS, the special attention must be paid to the elements, whose distribution between the media is different from the phonic distribution. The media of the NTS, which are more vulnerable to the influence of these elements, must be intensely observed. The most technogenically changed NTS of the mining territories are the NTS of mine and spoil banks and the NTS of tailing dump. During the monitoring of NTS of mines and spoil banks of REE-granite deposits, the most attention must be paid to Li, W and Be, especially Be in soil. During the monitoring of the NTS of tailing dumps, the most attention must be paid to Sn and W, especially Sn in vegetation. After ceasing of mining, the monitoring must be continued. The redistribution of elements between the NTS components must be studied and the further accumulation of elements in the most vulnerable components must be controlled.

Cost data: n.a.

Further information: http://library.iem.ac.ru/exper/v10_1/152-155.pdf

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Technology ID No.: 11

Biosensor for heavy metals

Technology: Highly Sensitive Protein-Based Capacitive Biosensors

Contact information: Lund University, Faculty of Technology
Getingevägen 60, SE-221 00 Lund

Application for LTS: monitoring heavy metals in soil

State of development: under development

Detect only vs. Detect+concentration: detect only

Performance data and sensitivity: mercury (copper, cadmium, zinc, lead)
Technical details and limitations:
Highly sensitive biosensors were developed for environmental and medical applications. The biosensors were based on bioengineered proteins as biorecognition elements coupled to a highly sensitive capacitive transducer.

Heavy metal binding proteins like the metallothionein SmtA, regulatory protein MerR, periplasmic protein MerP and the synthetic phytochelatin EC20 were used for designing, constructing, and characterising biosensors for the determination of various heavy metal ions, i.e. mercury, copper, cadmium, zinc and lead, in a wide concentration range (fM-mM). The developed heavy metal biosensors had a useful storage stability (about two weeks) and could be regenerated using EDTA. The developed and optimised biosensors were assessed in two practical applications, namely monitoring mercury ions in contaminated soil samples, and measuring inducer molecules.

The SmtA based biosensor was successfully used to monitor heavy metals in soil samples originating from a contaminated agricultural site in Denmark. The obtained results were compared to those given by a bacterial biosensor, a plant sensor, and the total amount of mercury contained in the soil. Both the protein-based and the bacterial biosensor proved to accurately monitor the ion content, giving results well in agreement with those shown by the total amount.

By using the same sensing principle, biosensors based on lac repressor protein were developed for monitoring of different inducer molecules, e.g. IPTG, ONPG, and lactose, or DNA. The biosensor could differentiate between lac operator DNA contained in linearized plasmid DNA and circular plasmid DNA, and genomic DNA.

Cost data: n.a.

Further information: http://www.lub.lu.se/cgi-bin/show_diss.pl?db=global&fname=tec_564.html

Technology ID No.:  12A

Sensor system for heavy metals

Technology: Sensor system for the analysis and surveillance of metals in aqueous liquids

Contact information:  Morten Roalkvam
E-mail: m.roalkvam@oceanor.no
Phone: +47 51634334
Mobile: +47 90873842

Application for LTS:  Run-off from waste treatment sites and polluted ground Environmental monitoring (lakes, rivers and ground water)

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity:  Zn, Pb, Cd, Ni, Co, Tl, Cu
Technical details and limitations:

- Quantification of various metals using the same sensor (for example Zn, Pb, Cd, Ni, Co, Tl, Cu)
- Quantification of various metal forms (species)
- Environment friendly electrodes
- Solid state reference electrode
- High sensitivity, resolutions 1 ppb (1 mg/L)
- Stable over time
- Short analysis time (2-3 minutes)
- Small sample volume (65 ml)
- Compact
- Low operating costs
- Simple maintenance
- Automatic electrochemical cleaning of electrodes
- User friendly calibration
- Simple and user friendly software for equipment control and presentation of results
- Automated sampling pretreatment and analysis
- Real time/on-line data presentation

APPLICATIONS

- Process control (electrochemical, chemical, textile, electroplating and water treatment industries)
- Product control (water, wine, beer, spirits)
- Pollutant discharge control
- Run-off from waste treatment sites and polluted ground
- Environmental monitoring (lakes, rivers and ground water)
- On-line surveillance
- Laboratory analyses
- Field measurements

Cost data: n.a.

Further information:  [http://www.oceanor.no/products/sensors/trace_metal_monitor.htm](http://www.oceanor.no/products/sensors/trace_metal_monitor.htm)
Technology ID No.: 12B

Radioactivity sensor with spectrometer

Technology: Sea and onshore radioactivity sensor with spectrometer

Contact information: OCEANOR Main office
ADDRESS: Pir-Senteret, N-7462 Trondheim, Norway
PHONE: +47 73545200
FAX: +47 73545201
E-MAIL: oceanor@oceanor.no

Application for LTS: in situ monitoring of radioactivity, salt and freshwater sensor with spectrometer

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: $^{137}\text{Cs}$

Technical details and limitations:
- Same sensitivity and detection level as in laboratory analysis
- RS232 communication or internal data logging
- Special housing reduces the temperature gradients during deployment and recovery

Possible pollution from nuclear powered vessels, power plants, test sites and waste deposits increase the need for radioactivity surveillance. RADAM is developed to provide accurate and updated information about radioactivity in the environment whether on land or in water.

RADAM, the miniaturized GENI computer, communication link, are all assembled within the same robust housing. The external temperature is measured, and gain control eliminates temperature drift in the spectrum. A user friendly Windows interface is available. The sensor can be connected to other instrumentation or operate as a standalone unit.

Cost data: n.a.

Further information: http://www.oceanor.no/products/sensors/radam.htm

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Technology ID No.: 13

Electrochemical sensor for heavy metals

Technology: Electrochemical sensor interface

Contact information: Dr. Kees van Velzen
Palm Instruments BV Ruitercamp 119
3992 BZ Houten The Netherlands
Tel.: +31 30 2459211 Fax.: +31 30 2459212
info@palmsens.com
**Application for LTS:**  
Sensors for heavy metal determinations with sensors from IVA (Russia)  
- Determination of Cu, Cd, Pb, Zn, Sn, Ni, Cr, Mn, Mo, W and Hg,  
- Analysis without addition of mercury,  
- Batch and flow-through systems.

**State of development:** in use

**Detect only vs. Detect+concentration:** detect+concentration

**Performance data and sensitivity:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Description</th>
<th>Concentration range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>EPA method</td>
<td>7063 0.3 – 300 µg/l</td>
</tr>
<tr>
<td>Mercury</td>
<td>EPA method</td>
<td>74720 1 – 10000 µg/l</td>
</tr>
<tr>
<td>Lead, cadmium, copper and zinc</td>
<td>Ir-microelectrode</td>
<td>(sub-) nanomolar</td>
</tr>
<tr>
<td>Lead, cadmium and copper</td>
<td>Screen-Printed sensor</td>
<td>&gt; 5 µg/l</td>
</tr>
<tr>
<td>Lead, cadmium and bismuth</td>
<td>film on GCE</td>
<td>10 – 100 µg/l</td>
</tr>
</tbody>
</table>

**Technical details and limitations:**

The PalmSens instrument is used for sensors or cells with two or three electrodes. The wide dynamic range allows application of micro- as well as macroelectrodes. The response time of the instrument is short enough to apply fast techniques as square wave voltammetry. Its noise level is low enough to measure dc-currents with a resolution of a picoam.

The applicable techniques are:
- differential pulse and square wave (stripping) voltammetry;  
- normal pulse and ac voltammetry;  
- stripping chronopotentiometry or PSA;  
- amperometric and pulsed amperometric detection; and  
- linear sweep and cyclic voltammetry.

PalmSens is controlled by a Pocket PC. The Pocket PC software provides easy control of PalmSens. All relevant parameters can be edited. The measured curves as well as the calibration plots are graphically displayed. The software allows determination by means of standard addition or using a calibration curve.

The instrument has connections for control of external equipment like valves or a stirrer. PalmSens is expandable with an optional module. This provides the possibility to modify the instrument for specific electrochemical sensors but also to develop a complete integrated analytical instrument with flow control etc.
Cost data:

PalmSens with Pocket PC (Compaq iPAQ) EUR 3000
- PalmSens instrument
- Compaq iPAQ Pocket PC with cradle
- Ac-adapter for PalmSens
- Serial cable
- Sensors cable with 2 mm crocodiles
- Testsensor
- Manual
- CD-ROM

Standard sensor EUR 2
Aluminum case EUR 120
CH8 Multiplexer EUR 1200
Desktop PC Software (from IVIUM) EUR 950

Further information: http://www.palmsens.com/

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Technology ID No.: 14

Biosensor for heavy metals

Technology: Plants as biomarkers for monitoring heavy metal contaminants on landfill sites using sequential extraction and inductively coupled plasma atomic emission spectrophotometry.

Contact information: J.Barker@kingston.ac.uk

Application for LTS: Vegetation can be used as a biomonitor of site pollution, by identifying the mobilization of heavy metals and by providing an understanding of their bioavailability

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: Pb, Cu, Zn

Technical details and limitations:
The results suggest that the analysis of bramble leaves, nettle leaves and roots can be used to monitor the mobility of Pb in soil, with nettle, bramble and sycamore leaves to monitor Cu and Zn. Analysis of the vegetation reflects well, the variation in the mobility of Pb, Cu and Zn between each location. Utilizing the knowledge of plants as indices of metal contamination, the monitoring of metal mobility in soil can be studied by determining the metal uptake balance between plants and soil. This analog with the impetus of new legislation, is of great importance given the specific requirement for continuous monitoring. The basis for the future risk assessment of bioavailability in contaminated land will place emphasis upon the metals’ mobility, and not be solely reliant on total metal concentration.

Cost data: n.a.

Further information: http://pubs.rsc.org/ej/EM/2000/B005594H.pdf?&Yr=2000&VOLNO=%26nbsp%3B%3Cb%3E%26nbsp%26nbsp%3C%2Fb%3E%26nbsp%3C%26nbsp%3E%26nbsp%3Cbp%621%Ef%627%Ef%JournalCode=EM&Iss=6

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Anodic stripping voltammetry for detecting heavy metals

Technology: Anodic stripping voltammetry (ASV)

Contact information:
Centre for Environmental Engineering and Sustainable Energy School of Engineering
The Robert Gordon University, Schoolhill, ABERDEEN, AB10 1FR
Tel: +44 (0)1224 262352
Fax: +44 (0)1224 262317

Application for LTS: analysis of heavy metals in the marine environment

State of development: under testing, under development

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: Pb,Cd,Cu

Technical details and limitations:
Anodic stripping voltammetry (ASV) is a precise and sensitive analytical method with excellent limits of detection. The technique is particularly useful for the determination of heavy metals in a wide range of applications. Stripping voltammetry has several advantages over spectroscopic methods for metal determination since less processing of the sample is often necessary. Consequently the use of such electrochemical sensors could minimise the risk of sample contamination, loss of the analyte and avoid expensive and time-consuming procedures such as sample acquisition and storage. For these reasons stripping voltammetry is a particularly desirable technique for monitoring pollutants in the aquatic environment. The Centre for Environmental Engineering and the Optoelectronics Research Centre have developed 3-electrode-sets (counter, reference and working electrode) screen printed on different substrates (glass, polycarbonate and alumina) for analysis of heavy metals in the marine environment (figure 1).

Figure 1: Screen printed electrode sensor
Good results were achieved with the screen printed and plated electrodes under conditions optimised for each electrode material. The electrode stability, reproducibility of single measurements and the limit of detection obtained for Pb were very promising e.g. using 3-electrode-sets with a gold plated WE on glass was a limit of detection of $7 \times 10^{-7}$ mol/l was achieved after only 60s of deposition (figure 2).

Figure 2: ASV peaks obtained using 3-electrode-sets with a screen printed carbon and a gold plated WE - $C_{Pb}=10^{-5}$ mol/l

The development of these heavy metal sensors were part of a project is investigating the development of a multi-capability optical sensors for the realtime in situ monitoring of three key marine environmental and offshore/oil parameters: hydrocarbons, synthetic based fluids and heavy metals. This work was funded under the Dti/NERC link Seasense programme in collaboration with Halliburton Manufacturing and Services, Hook and Tuckers Instruments and Central Research Laboratories.

Cost data: n.a.

Further information:  http://www2.rgu.ac.uk/subj/mes/cee/main/Research.htm

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Technology ID No.: 17

Sensor system for heavy metals

Technology: Spectroscopy using Optical Fibers in the Marine Environment

Contact information: Prof. Brian MacCraith, bdm@physics.dcu.ie

Application for LTS: sensor system for real-time and in situ sensing of heavy metal ions in water, screening either for a selected metal ion or as a general pollution warning detection of metals.

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: heavy metal, polyaromatic hydrocarbons and chlorinated hydrocarbons (Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+})

Technical details and limitations: see next page
Development of a fluorescent probe for Pb\(^{2+}\) sensing in Seawater

X. Potenza, T. Glanze, M. Hesler, B.D. MacCraith
NCSR, Dublin City University
Dublin, Ireland

1 Spectroscopy using Optical Fibers in the marine Environment: the SOFIE project (EU - MAST III)

Seawater analysis for research and monitoring purposes is a challenging task because many constituents of interest are to be measured at trace level in a very complex matrix. The classical method of performing chemical analysis in seawater is to take statistically spatially and temporally distributed samples followed by laboratory analysis on board ship or on shore. Alteration of the sample upon transport and storage is one of the main flaws inherent in this sampling approach. The objective of SOFIE is the development of a modular all-fibre optic measurement device for real-time and in-situ monitoring of diverse hazardous chemicals in the marine environment.

2 Luminescence optode

A sensor system has been developed for the optical detection of the heavy metal ion Pb\(^{2+}\) in seawater. The optical sensing is based on the continuous monitoring of the fluorescence spectrum of an immobilized metal-sensitive dye system using the lock-in technique. The metal ions diffusing into the layer are extracted and the fluorescence properties of the dye are changed. The intensity of the fluorescence level can therefore be directly linked to the concentration of the chosen analyte.

A polyethylenimine based on co-extraction was assigned with three main components: an optically active (Pyridine), a pH indicator and a protolytic group. It is clear that the concentration ratio of these active components is crucial in creating a reliable and stable sensor and therefore loss of components from the membrane into the aqueous solution cannot be tolerated.

The pH dye used in such a system has a very important effect on the overall membrane response. It determines the magnitude and duration of the membrane signal and also the dynamic range of the device. Oregon Green \(488:\) Rhodamine 6G, 70,000 ppm, around 530 nm - 545 nm presents the advantage of a highly fluorescent quench at the pH of study (-7.5).

3 Results and Discussion

- No leakage of the dye was observed, the large Debye (polyethylenimine) derivative efficiently anchors the dye in the membrane and prevents leakage. Furthermore, no photobleaching was observed, an excellent long span of the membrane for sensor purposes was therefore achieved. Lifetime of the membrane was found to be excellent so no noticeable leakage of the main components was observed.
- Reproducibility was also achieved over a long period of time as the same membrane was used for multiple trials without change in response time, limit of detection and signal linearity. It is also important to note that no interference was observed upon the use of seawater.
- The sensitivity of the Pb\(^{2+}\) has been obtained in the same range, the response behavior as a time integration of the fluorescence signal of the membrane shows a remarkable signal linearity related to the concentration of Pb\(^{2+}\) in seawater. The study range varying from 0 to 20 ppm shows a perfect match between the integrated signal and the concentration of Pb\(^{2+}\) in the sample.
- A lower detection limit of 1 ppm (1 mg/l) has been found. (\(\lambda_{	ext{ex}} = 475 \text{ nm} \); \(\lambda_{	ext{em}} = 500 \text{ nm} \) time integrated fluorescence signal in real).

4 Conclusion

An excellent linearity response and good lifetime can give an extremely reliable sensor for Pb\(^{2+}\) sensing.

*The problem lies in regard to the required dynamic range which is clearly above 0.05 ppm (average natural abundance of lead in seawater in the ppb order). Consequently, the actual detection limit is not sufficient to efficiently quantify lead in seawater. Nonetheless, the optode developed here shows that it could be an appropriate tool as a lead pollution warning system for continuous in-situ and real-time monitoring where critical levels of lead are encountered (e.g., estuaries...).

Cost data: n.a.

Further information: http://www.physics.dcu.ie/OSL/projects/SOFIE/
Technology ID No.: 18

Remotely Sensed and Geophysical Data for Detecting Radionuclides

Technology: Detecting Environmental Impacts of Uranium Mining with the use of Remotely Sensed and Geophysical Data

Contact information: Petr Dobrovolný (1), Lubomil Pospíšil (2), Otakar Pazdírek (2)

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Application for LTS: method for detection of contamination due to uranium mining and connected activities

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: $^{40}\text{K}$, $^{238}\text{U}$, $^{232}\text{Th}$

Technical details and limitations:
Digital processing of remotely sensed data is based above all on multispectral approach. It means that with the help of several images of the same area, acquired in different but precisely defined intervals of electromagnetic spectrum, it is possible to recognize specific processes, even such ones, which can not be directly seen in the environment. This is based on the assumption that the searched processes are connected with the characteristic features in their spectral response. The typical example of such features can be the change of spectral response of vegetation cover due to various kinds of stress.

Possible approaches to the contamination detection connected with uranium mining with the help of remotely sensed data can be summarized briefly. In some circumstances direct observation of rocks and minerals is possible. This approach seems to be very promising, especially with the help of hyperspectral data. Contaminated areas can show specific spectral response. On the other hand rocks and minerals are covered with the vegetation mostly.
In some cases, processes of contamination can be enhanced with the help of various kinds of spectral enhancements. This group of image processing techniques transforms original multispectral data to a new set of images. Changes in vegetation condition can be stressed using e.g. principal component analysis, color transformations or multispectral classification. Some methods of enhancement and classification allow to combine imagery with a different kinds of data - DEM (contamination can be spread in the area through drainage network), or geological map (contamination can be controlled by faults of specific direction). Principal component analysis for the detection of polluted areas due to uranium mining has been successfully used by NEVILLE (1996). The author proved, that some transformed images - principal components (PCs) - correlate with the occurrence of specific rocks and minerals or even with the occurrence of contaminated areas.
Radioactive pollution due to uranium mining can be studied directly with the help of geophysical remote sensing. Concentrations of the most radionuclides can be measured using airborne gamma-ray spectrometry. This kind of investigation has been used in Czech Republic for aerial monitoring of the environment in the uranium mining area Stráž pod Ralskem - Hamr (JURZA 1994).

For identification of contamination connected with the uranium mining activities in the area of Dolní Rožinka and surroundings, geophysical data were used along with the correlation with LANDSAT TM data. From gamma-ray spectrometry records it is evident, that higher concentrations of $^{40}$K, $^{238}$U, and $^{232}$Th are more or less restricted on the mine shafts, mine tailings and tailing ponds. These concentrations of the radioactive isotopes sharply decrease with the increasing distance from the mentioned spots. It is clearly evident especially in the case of uranium $^{238}$U (see Fig. 2). Average natural concentration of $^{238}$U is about 2-4 ppm. The highest concentrations of this isotope in the processed area are more than 30 ppm. In case of thorium the average natural concentration is about 8-12 ppm. In the study area the concentrations of $^{232}$Th reach more than 24 ppm. At this time it is not possible to prove some dynamics in polluted areas. Temporal changes in spatial distribution of contaminated areas can be defined with the help of series of spectrometry measurements. On the other hand, in case of good correlation with gamma-ray spectrometry this dynamic aspect can be traced using multispectral satellite imagery. Relations between the two types of data are discussed further on. Using LANDSAT Thematic Mapper imagery the mining areas are clearly visible even on a suitable enhanced RGB color composites, especially on those ones where channels from the middle infrared part of the electromagnetic spectrum are included. Further identification of mining areas is possible using spectral enhancements. As a suitable method principal component analysis can be designated. In this project several combinations of input original channels was tested. It was possible to delineate specific features in a transformed output channels (PCs). Some of them were restricted on mining areas only. So that they correlate well with the contaminated areas, which were defined using geophysical data. Other specific classes are not connected neither with mining areas nor with the specific land cover features. This holds especially about higher order PCs (see FIG. 3). Bright spots on the image show good spatial correlation with the higher concentration of uranium and thorium and therefore with the areas of mining activity (compare with Figure 1 and 2).

The second approach how to localize contaminated areas on LANDSAT TM imagery was ISODATA classification. This widely used clustering algorithm was used for definition as many as 50 fine spectral classes. Through subsequent aggregation of the spectral classes only those were preserved which classified...
pixels in the areas of mining activities. Such classes again show good correlation with the polluted areas denoted from gamma-ray spectrometry.

Figure 3: Example of the 3rd principle component (PC3) transformed from the original LANDSAT imagery (TM1-TM5, TM7)

**Cost data:** n.a.


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**Technology ID No.:** 19

**Biosensor for heavy metals**

**Technology:** recombinant sensor bacteria

**Contact information:** [http://www.kbfi.ee](http://www.kbfi.ee)

**Application for LTS:** detection of heavy metals

**State of development:** field research phase

**Detect only vs. Detect+concentration:** detect only
Performance data and sensitivity: heavy metals

Technical details and limitations:
The recombinant sensor bacteria consists of: plasmid with a regulator (R) sensitive to a desired analyte (e.g. heavy metal), promoter (P) and reporter gene (e.g. luciferase gene).

How does a luminescent recombinant bacterial sensor for the detection of heavy metals work? When the suitable heavy metal (analyte) is not present in the growth media, transcription of the luciferase gene (reporter gene) is repressed by the regulator and very little luminescence (signal) can be measured. When the suitable heavy metal is present in the growth media, the regulator allows the transcription of the luciferase gene. The mRNA will be then translated to the enzyme luciferase (reporter protein) and high levels of luminescence can be measured. The more heavy metal in the growth media the higher the signal until the heavy metal reaches concentration toxic for the cell. After that luminescence decreases.

Cost data: n.a.

Further information: http://www.kbfi.ee/Mol_gen/Homes/Anne/Sensorbacteria_eng.htm

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Technology ID No.: 24

Spectrometry for radionuclides

Technology:
- high resolution gamma spectrometry
- high resolution alpha spectrometry
- integral alpha and beta counting
  - in situ gamma spectrometry

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Application for LTS: Wisutec offers measurement devices in the areas of radiation protection, environmental monitoring (water, air)

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: radionuclides
Technical details and limitations:
Field measurement methods:
- measurement of the ambient dose rate (measured quantities: H*(d); Hx);
- surface activity determination (total alpha activity, alpha/beta activity);
- determination of radon exhalation rates as well as of radon concentration and radon decay products (Cpot) in air;
- dust measurements and measurements of air-borne long-lived alpha emitters; and
- measurement of diffusion parameters in the media air and water in situ gamma spectrometry.

Lab measurement methods
- high resolution gamma spectrometry;
- high resolution alpha spectrometry; and
- integral alpha and beta counting.

Cost data: n.a.

Further information: http://www.wisutec.de/english/index2_engl.htm

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Technology ID No.: 25

Anodic stripping voltammetry for detecting heavy metals in water

Technology: Anodic Stripping Voltammetry

Dual-cell ASV  http://www.maran.co.uk/technologies/dera/sensors/asv/dual.htm
Multiple cells for simultaneous ASV  http://www.maran.co.uk/technologies/dera/sensors/asv/multi.htm
Reagent-free operation of ASV electrodes  http://www.maran.co.uk/technologies/dera/sensors/asv/reagent.htm
Reagent dosing system for ASV and other applications  http://www.maran.co.uk/technologies/dera/sensors/asv/dosing.htm

Contact information:
- General: contact@maran.co.uk
- Technologies: technologies@maran.co.uk

Application for LTS: detecting heavy metals in water

State of development: in use

Detect only vs. Detect + concentration: detect concentration

Performance data and sensitivity: heavy metals

Technical details and limitations:
Anodic Stripping Voltammetry (ASV) is an important electrochemical measurement technology that is highly sensitive, easy to use, and has recently been extended to measure a wide range of aqueous ions and organic materials.

The instrumental assay of aqueous ions has almost entirely replaced other methods. Techniques such as UV/visible spectroscopy, ion chromatography, and anodic stripping voltammetry (ASV), in particular, have all played a part in this change.
ASV is not just a technique for ions, however. It is also now also being applied increasingly to monitoring molecular species, especially organic chemical pollutants in water.

This group of related patents stems from a major long-term research programme at DERA Porton Down laboratories. Commercial companies supplying instrumentation to the scientific world, manufacturers of pollution monitoring equipment and companies supplying the water industry or the food industry will find this technology particularly interesting.

ASV is increasingly used commercially because it uses only simple small scale equipment, yet is capable of yielding analysis of contaminants at the level of 1 part per billion (1:109) or even 1 part per trillion (1:1012).

ASV avoids the main problems of mercury drop polarography, from which it was originally derived. It does not need a supply of liquid mercury to operate, and the mercury film electrode used in ASV releases essentially no mercury into the environment and is automatically regenerated during use. ASV is increasingly being incorporated into continuous flow or quasi-continuous flow analysers. Unlike many rival techniques ASV is suitable for portable use, e.g. in pollution monitoring.

Originally ASV technology was only appropriate for the assay of heavy metal ions. However, in recent years the capabilities of the mercury film electrode have been extended to other ions - including anions and a surprisingly large range of the more reactive organic chemicals of interest, including organochlorines and DDT.

ASV methods have been developed for many important naturally-occurring organic compounds from simple aldehydes and quinones to complex molecules like some vitamins.

**Dual cell ASV**

The full analysis of samples containing complex mixtures of contaminants will always be problematic, and this is as true for ASV as for other single methods.

Even with samples containing a few contaminants there are often difficulties with ASV: from dissolved oxygen and interference between different metal ions, for example. Furthermore, even if only one species is being monitored, if there is complex mixture of ions and molecules in the sample 'matrix', ASV can be unusable. The technique devised here is so effective at dealing with this that it is usable even in very complex matrices like sea water, and can achieve part per billion (ppb) sensitivity.

The inventor devised a dual cell technique that gives a difference signal for the determination of ionic species (Sn, Pb, Cd for example) and molecular species. The background ions and matrix effects are largely avoided, so that electronic amplification can be employed to boost the sensitivity of the method.

The sample stream is split into two, and one ASV cell is used to analyse the sample as it arrives. The other half of the sample stream has the species of interest removed in some way, and it is then passed through an identical ASV analysis cell. The dual cell approach also has other benefits. For example, with suitable cell construction, it can present balanced capacitances to the electronic part of the system, which has advantages in the speed and accuracy of measurement.

The molecular substances which can be analysed include a variety of herbicides and pesticides of great commercial interest in pollution monitoring. The control stream is typically passed through a resin-filled adsorber column designed to adsorb the species of interest, although electrochemical polishing (the deposition of the contaminant of interest in an auxiliary electrode system) can also be employed.

The patent specification also describes how the sensitivity of the method can be enhanced by the use of complexing agents, and how a cathodic stripping mode can be used for molecules.

View patent: [http://www.maran.co.uk/technologies/dera/sensors/asv/p0906.pdf](http://www.maran.co.uk/technologies/dera/sensors/asv/p0906.pdf)
P0906: Anodic stripping voltammetry. Inventor: Dobson JV. Priority: 22.08.91 Ref: EP 0 529 155 B1
Multiple cells for simultaneous ASV

This new technique allows on-line quasi-continuous reading instrumentation for multiple ion analysis by ASV.

ASV analysis for a number of different ions or molecules typically involves changing cells, perhaps by using slightly different reagents or analysis timing. This technique developed for DERA Porton Down incorporates a number of ASV cells, all running at different conditions and hence optimised to assay for different ions or molecules.

The test fluid is directed into the ASV cells. The cells must be electrically isolated from each other so that each cell is free from interfering current conducted from the other cells. This is achieved by flowing the fluid in isolated drops from one cell to another, so that volumes of fluid are interrupted by free space.

As the commercial use of ASV expands, instrumentation companies are keen to provide on-line continuous monitoring: this technique provides a simple and elegant basis to enable them to do so.

View patent:  http://www.maran.co.uk/technologies/dera/sensors/asv/01p_2186.pdf

Reagent-free operation of ASV electrodes

Mercury film electrodes are an important general feature of the ASV technique. Conventionally they require the addition of small amounts of a mercury salt to the sample.

This can be avoided by an elegant method developed for DERA Porton Down for the generation of the mercury film electrodes needed by ASV. Instead of adding a mercury salt, controlled electrolysis at a separate electrode is used to add mercury ions from behind a semi-permeable membrane into a flowing stream. These mercury ions are then deposited on the test electrode to create the mercury film.

This is a very convenient technique and provides very close control of the amount of mercury used. It will be highly desirable in the manufacture of commercial ASV instruments for many key markets. It is more suitable than conventional ASV technology for use by unskilled operators, for field use, and for continuous monitoring.

View patent  http://www.maran.co.uk/technologies/dera/sensors/asv/01p_2188.pdf

Reagent dosing system for ASV and other applications.

This is a simple technique for introducing small amounts of reagent to an ASV sample. It is particularly useful for continuously operating ASV systems.

The reagent is introduced via a small aperture that leads to a housing containing the reagent in bulk. This is an improvement on the direct addition of reagent tablets to the fluid stream. It results in less reagent being consumed and a greater consistency of reagent concentration in the sample.

View patent  http://www.maran.co.uk/technologies/dera/sensors/asv/01p_2189.pdf

Cost data:  n.a.

Further information:  http://www.maran.co.uk/technologies/dera/sensors/asv/intro.htm
Technology ID No.: 26A

Voltammetric In-line Analyzer for heavy metals

Technology: Voltammetric In-line Analyzer

Contact information:
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Application for LTS: on-site reliable concentration measurements of various fractions of trace elements at the ppt level

State of development: in use

Detect only vs. Detect+concentration: detect+concentration

Performance data and sensitivity: Cu, Pb, Cd, Zn, Mn, Fe

Technical details and limitations:
The technical and analytical advances of the VIP submersible voltammetric probe have been used to develop a compact portable Voltammetric In-line Analyzer (VIA-Field). It provides on-site reliable concentration measurements of various fractions of trace elements at the ppt level in minutes, eliminating problems associated with conventional sampling, storing and laboratory analyzing and thus significantly reducing the cost, time and difficulties of testing. Battery-powered, lightweight and weatherproof, the VIA-Field is ideal for stationary source testing and hazardous waste site investigation.

Engineered for the field, the VIA-Field is designed to withstand harsh testing environment. It consists of a voltammetric analyzer module, a mini-flow injection module, an optional multiparameter probe and reagent/waste containers integrated in an unbreakable, corrosion proof and airtight protective case. The electronic stainless steel housing of the different modules were designed under given similar specific format, to facilitate their integration and minimize at maximum the size of the whole system.

Voltammetric analyzer module
The voltammetric analyzer module consists of the VIP flow-through plexiglas cell (incorporating the unique VIP microsensors), a cell holder and an electronic housing. The electronic housing is based on mechanical modification and adaptation of the VIP voltammetric probe housing and electronic boards. The hardware and firmware, similar to those of the VIP probe, allow to manage: i) the voltammetric measurements, ii) the interfacing of the optional field-portable multiparameter probe via an RS232C interface, the mini-flow injection module and finally iii) the data acquisition and data transfer, via RS232C interface to a portable PC or via cellular phone to a control station. Data files are stored in an internal non volatile memory having its own battery which guaranty high data retention and protection. The flow-through voltammetric cell is screwed on the cover of the cell holder. The cell holder incorporates a preamplifier for the microsensor. It is made of a POM cover, on which is screwed the flow-through cell, and shielded housing.

Mini-flow injection module
The mini-flow injection system consists of a peristaltic pump, a multi-way rotary valve and filters. It enables to perform in laboratory or on-field:

- The renewal of the microsensor Hg layers;
- The calibration of the system;
- The sampling of the natural waters; and
- The direct measurements of unmodified natural water samples, i.e. specific measurements of the mobile fraction of trace metals defined as free metal ions and small labile complexes with size of
few nanometers. The measurements of in-line chemically modified natural samples, e.g. acidified raw or filtered samples for the determination of colloidal and particulate forms of the trace elements.

**Analytical specifications:**

Measurable elements or compounds: Cu(II), Pb(II), Cd(II), Zn(II), Mn(II), Fe(II), extension to other elements or compounds is possible and metal speciation (see text)

Lowest detection limits:
50 pM (10 ppt) (15 minutes deposition time)

Measurement range:
0.2 nM to 500 nM (5 minutes deposition time)
40 ppt to 1000 ppt (5 minutes deposition time)

Measurement techniques:
Chronoamperometry
potential range: ± 2048 mV
Cyclic Voltammetry (CV) Linear Sweep Voltammetry (LSV)
Anodic Stripping Voltammetry (ASV)

potential range: ± 2048 mV

scan rate:
1 mV/s to 1 V/s
Square Wave Voltammetry (SWV) Square Wave Anodic Stripping Voltammetry (SWASV)

potential range: ± 2048 mV

pulse amplitude: 1 to 250 mV

step amplitude: 1 to 250 mV

pulse frequency: 1 to 1000 Hz (period: 1 ms to 1 s)

**CALIBRATION DECK UNIT SPECIFICATIONS**

Allows laboratory and on-site conditioning and calibration operations. It incorporates the computer controlled six position rotary valve and the peristaltic pump. The unit is provided with a holder containing (up to four) solution bottles; each bottle is equipped with cap, micro-filter and vent hole. The Calibration Unit is complete with a wall-cube power supply able to power, in laboratory, the Voltammetric Probe.

Dimensions: 130 x 270 x 86 mm. Weight: 1 kg.

**SURFACE DECK UNIT SPECIFICATIONS**

The function of the PORTABLE DECK UNIT is to power and interface, by telemetry, the Voltammetric Probe with a portable Personal Computer. This unit contains a rechargeable lead battery (12V - 6.5 A/h) which allows about 35 hours of continuous operation even without external power (100, 110 or 220V AC, 50/60 Hz). The PORTABLE DECK UNIT is provided with an adjustable power supply to power the Probe, an internal power supply to recharge the 12 V internal battery and a transceiver able to transform commands coming from the PC and data coming from the probe into an RS232C asynchronous transmission format, HALF-DUPLEX mode.

Dimensions: 275 x 250 x 75 mm. Weight: 4.5 kg.

**Cost data:** n.a.

**Further information:** [http://www.idronaut.it/metals_monit/main4.html](http://www.idronaut.it/metals_monit/main4.html)
Technology ID No.: 26B

Votametric *In Situ* Profiling System for heavy metals

**Technology:** Votametric *In Situ* Profiling System (VIP System)

**Contact information:** IDRONAUT S.r.l
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Tel. ++39 039 879656/883832
e-mail idronaut@idronaut.it

**Application for LTS:**
The only existing submersible voltammetric probe for *in situ* trace element monitoring and profiling

**State of development:** in use

**Detect only vs. Detect+concentration:** detect+concentration

**Performance data and sensitivity:** Cu, Pb, Cd, Zn, Mn, Fe

**Technical details and limitations:**

:: simultaneous multi-element analysis
:: possible extension to other compounds
:: original, long-term reliable gel protected micro-sensor
:: wide dynamic range (ng/l to mg/l)
:: chemical speciation capability
:: easy combination with CTD, oxygen, pH, redox sensors
:: flexibility of operation: spot or long-term monitoring
:: autonomous data analysis and transmission to land
:: profiling capability between 0 and 500 metres
:: advanced computer controlled analysis
The whole VIP system consists of several units: the submersible voltammetric probe based on a unique micro-sensor, a submersible on-line O₂ removal module, a submersible Ocean Seven 316 multiparameter probe, a calibration deck unit, a surface deck unit and a management software running on WINDOWS PCs.

It allows simultaneous measurements of Cu(II), Pb(II), Cd(II) and Zn(II) with a sensitivity at the ppt level, as well as Mn(II) and Fe(II) with a sensitivity at the ppb level (extension to other elements and organic compounds are foreseen). It is usable in sea and fresh water down to 500 m. It is controlled either by an operator from the surface or in autonomous mode, under pre-set sequences. When interfaced with an automatic Buoy Profiler, the VIP System allows the whole water column to be automatically monitored for at least one week, at prefixed periods.
Unique micro-sensor
The heart of a VIP is its sensor. It measures a signal intensity, produced by the chemical reaction at its surface, which is proportional to the concentration of the analytes. However, to perform automatic measurements over extended periods in complex media such as natural waters, most of the currently available sensors are not reliable nor sensitive enough for monitoring very low concentration of chemical compounds. In addition, fouling problem, due to the adsorption of organic and inorganic matters at the sensor surface, is an important limitation of direct voltammetric measurements in complex matrices. The VIP sensor is a unique micro-sensor which has been developed by CABE and IMT (University of Neuchatel-Switzerland) to solve all the above problems. It is produced by thin film technology on chips and photolithographic technique. It consists of an array of 5 x 20 interconnected Iridium microdiscs, having a diameter of 5 µm and a centre to centre spacing of 150 µm, coated by Hg layers and covered by an hydrophilic protective gel membrane. Measurements with this gel-integrated micro-sensor are performed in two successive steps:
a) equilibration of the gel with the sample (typically 5 minutes for a membrane thickness of 300 µm); and
b) voltammetric analysis inside the gel.

Cost data:
Voltammetric probe USD 29,000
Optional in situ on-line oxygen removal module USD 2,500
Ocean Seven 316 probe provided with RS232C output USD 15,000
Optional pressure transducer USD 2,000
Titanium mooring frame USD 1,800
Calibration deck unit USD 3,750
Cable Ø9mm Polyurethane USD 8/meter
Electro-mechanical sea cable termination USD 500
Laboratory power supply USD 270
Portable deck unit for telemetry option USD 3,700
Coaxial armored cable Ø5mm, Ø7mm USD 5/meter
Manual portable winch with slip-ring USD 1,800
Windows VIP management software USD 3,000

Further information:  http://www.idronaut.it/index_prodotti.html

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Technology ID No.:  27
Voltammetry for heavy metals

Technology: Automation of voltammetric measurements by polarographic analyzer,

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CROATICA CHEMICA ACTA
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Ruder Boskovic Institute Zagreb,  PO BOKSZ 1016 HR 10001 Croatia
**Application for LTS:** determination of dissolved Cd, Pb and Cu concentrations in groundwater, determination of dissolved copper species in seawater

**State of development:** field deployed

**Detect only vs. Detect+concentration:** detect+concentration

**Performance data and sensitivity:** Cd, Pb, Cu, Co

**Technical details and limitations:**
The measurement system consisting of polarographic analyzer PAR384B and a personal computer using a new software package EARSOFT is particularly advantageous for automated data assessment. The system performs automatic routine analyses of dissolved trace metal easily and rapidly. The possibility of long duration of automatic measurements (overnight or even for days, without an operator) is very useful for the methods utilizing repetitive measurements and systematic change of one or two electrochemical parameters (such as pseudopolarography). Measurements performed using an automatic system provide more reliable and reproducible data (avoiding the possibility of personal errors). The EARSOFT is easy to handle and enables numerous routine for automatic and manual data analyses as well as graphic presentation.

**Cost data:** n.a.


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**Technology ID No.:** 29

**Stripping voltammetry for heavy metals**

**Technology:** Sensors (electrodes) for flow-through, batch and field Stripping Analysis

**Contact information:** [http://www.iva.usue.ru](http://www.iva.usue.ru)

**Application for LTS:** monitoring of technological processes, environment, biological and clinical entities, and various industrial materials. The determination of concentrations of toxic elements) in the environment

**State of development:** in use

**Detect only vs. Detect+concentration:** detect+concentration

**Performance data and sensitivity:** copper, lead, cadmium, chromium, zinc, nickel, mercury, molybdenum, tungsten, manganese, arsenic and selenium
Technical details and limitations:

A rapid development and wide application of stripping electroanalytical methods (SEAM) and, in particular, of stripping voltammetry (SV) that have taken place in recent decades are explained by a low detection limit, high sensitivity, selectivity and speed of the methods, low cost of equipment. They provide a successful tackling of the problems associated with monitoring of technological processes, environment, biological and clinical entities, and various industrial materials. The methods lend themselves rather easily to automation. The methods are particularly important in Environmental restoration, numerical simulation and prediction of crisis’s, that can not be successful without monitoring systems. These systems require sensors special hardware and software.

That is why increasing application of on-line stripping analysis and field (portable) variants of the method is expected in the near future.

Development of voltammetry and stripping voltammetry in particular is connected with the use of mercury and carbon containing electrodes. The main problems in the use of these electrodes are:

- toxicity of mercury and its soluble salts; and
- short life-time of solid electrodes, the necessity of surface regeneration, that is the result of changing of the electrode surface in the measuring process.

Possible solutions:

- thick film graphite sensors (for example, for determination of Ni, Cr, W, Se, Mn, Mo)(TFGE);
- modified thick film graphite sensors (for determination of Cd, Pb, Cu, Zn, As, Hg, Se)(MTFGE);
- carbon-containing screen-printed electrode (CSPE);
- carbon-containing modified screen-printed electrode (MCSPE);
- new long-living renewable sensors (for determination of Ni, Cr in flow-through systems) (LLCSPE); and
- modified long-living renewable sensors (for determination of Cd, Pb, Cu, Zn in flow-through systems) (MLLCSPE).

Nonmodified sensors can be preplated with mercury or work in situ mercury plated mode.

Of great interest are modified sensors for determination of amalgam-forming elements without the use of metallic mercury or introduction of mercury ions into the test solution. As to their analytical characteristics, these sensors differ little from usual ones coated with mercury preliminarily or in situ.

Some of above mentioned sensors can be used in Adsorptive Stripping Voltammetry, what is the essential advantage in comparison with glassy carbon ones. Thick film graphite electrodes can be used with laboratory or field (portable) instruments. Long-living renewable sensors are designed for batch and online flow systems, FIA, for example. As we know there are no analogous sensors in the market. Software and hardware based on the sensors proposed are developed. Besides, sensors can be used with different voltammetric analyzers on condition that special software will be supplied. The sequence “electrochemical sample pre-treatment - analysis” is realized in stripping voltammetric four-electrode sensors that are developed in portable and flow-through variants. They are designed to be used in laboratory, portable and
flow-through systems for on-site and on-line determination of copper, lead and cadmium concentrations in waters of different genesis.

**Immunosensor**
A new electrochemical immunosensor was proposed, which uses the interaction between encephalitis viruses and specific antibodies, and between the latter and protein A labeled with colloid gold. The signal is due to the electrochemical reaction of gold ion reduction. Thick-film graphite are used as the basis of the sensor.

**Laboratory equipment**
**Analyser IVA-5**

![Analyser IVA-5](image)

**Configuration:**
- **electronic unit**
  Electronic unit controls analysis process: sample preparation, magnetic stirrer, analyte accumulation, measurement, data collecting and data processing, electrode surface regeneration
- **magnetic stirrer**
  Electrochemical unit contains magnetic stirrer, electrochemical cell (electrolyzer) and collector for electrodes. Electrochemical cell (electrolyzer) includes 3 (or 4) electrodes: working (impregnated graphite or thick film graphite), auxiliary (glassy carbon) and reference (silver-silver chloride) ones. Additional (the 4th) electrode is introduced for sample preparation if need arises.
- **software**
  The software works in the Windows operational environment. The program assigns values of all input parameters necessary for realization of the analysis procedure, provides mathematical processing of analytical signals (responses), and computes the concentration of test substances (analytes). The measured concentration (g/l) is displayed on the monitor screen. The software stores in the computer memory all information about the analysis process including graphics (recorded voltammograms), data on the origin and composition of samples, concentration of standard additions, analysis conditions, and parameter values. The experimental results can be printed out or sent to the clipboard for use by other applications. A personal computer controls parameters of the whole analytical system, records and processes the experimental data (voltammograms).

**Application of sensors (electrodes) and instruments**
The determination of concentrations of toxic elements (copper, lead, cadmium, chromium, zinc, nickel, mercury, molybdenum, tungsten, manganese, arsenic and selenium) in the environment (natural, drinkable and waste waters), food, and biological materials (blood, urine and serum).

The sensors and instruments offered are universal which fact will give one a chance to use them in different fields, for example, in hydrochemistry, ecology, waste water, biology, medicine and food analysis, in technological process monitoring.
Basic technical characteristics of the instrument:

- low detection limit (0.5 ppb, in some cases 0.1 ppb);
- elimination of mercury and amalgamated metallic electrodes;
- solid-state (graphite), disposable or modified electrodes are used as sensors;
- electrochemical regeneration of the electrode surface;
- registration of the signal without removal of dissolved oxygen;
- electrochemical unit for electrochemical sample preparation;
- analysis of high saline waters without matrix separation; and
- low cost.

Certified Methods of Analysis (Russia):  http://www.iva.usue.ru/methodseng.htm

Type UFOM-500 UV irradiator-mineralizer for sample pretreatment

The irradiator-mineralizer is intended for destruction of dissolved surface-active and complexation organic substances, which impede determination of the microelemental composition of natural, drinkable, and waste waters. The irradiator ensures rapid and efficient pretreatment of samples of aqueous solutions containing up to 500 mg/dm³ of organic compounds. The irradiator applies to the field of analytical chemistry.

Basic Technical Characteristics
Sample volume up to 15 ml
Sample pretreatment time 60 to 120 min
Temperature of the test solution 60 to 95 °C
Number of samples treated concurrently 7 to 9

Overall dimensions:
control unit 260? 140? 340 mm
irradiator 300? 200 mm
Weight max. 10 kg
Power requirements 210 to 230 V, 50 Hz
Computer-aided flow-through discrete analyzer type IVA-7

The flow-through discrete on-line system type IVA-7 for automatic monitoring of water quality is designed to measure concentrations of heavy metals (copper, lead, cadmium, zinc, nickel, chromium) in natural water and processing solutions under a real-time operation mode.

The software automatically realizes methods of analysis, controls all functional units of the on-line system, and also processes and stores the experimental results.

**Cost data:** n.a.

**Further information:** [http://www.iva.usue.ru/ourdevelop.htm](http://www.iva.usue.ru/ourdevelop.htm)

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**Technology ID No.: 30**

**Stationary gamma monitor for radionuclides**

**Technology:** stationary gamma monitors

**Contact information:** [www.iaea.or.at](http://www.iaea.or.at) IAEA Marine Environment Laboratory Monaco

**Application for LTS:** monitoring of marine radioactivity

**State of development:** under development

**Detect only vs. Detect+concentration:** detect+concentration

**Performance data and sensitivity:** Tritium, Cesium, Strontium, Plutonium

**Technical details and limitations:**
An innovation in the monitoring of the marine radioactivity using stationary gamma monitors with satellite data transmission has been conceived at IAEA-MEL’s Radiometrics laboratory.

The sensors were deployed a few meter bellow of the sea surface on a structure attached to a floating buoy. They generated a long-term continuous records of gamma activity in seawater, salinity, temperature and current speed and direction. The monitoring system performed well over the testing period and reached the projected sensitivity of 4 Bq per cubic meter for cesium-137 concentration in water.
Further work recently completed in the Irish Sea is \textit{in situ} gamma-mapping of seabed sediments from the Sellafield (reprocessing plant) discharging point to about 15 kilometers from the coast. The total sea area covered was about 400 square kilometers. A high resolution map of the distribution of cesium-137 in the sediment was obtained. This would have required hundreds of sampling points and thousands of analysis of sediments if the data for the map had been obtained by laboratory work.

\textbf{Cost data:} n.a.

\textbf{Further information:} \url{http://www.iaea.or.at/worldatom/Press/Events/RadWaste/mel.pdf}

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\textbf{Technology ID No.: 101}

**Biosensor for heavy metals**

\textbf{Technology:} phytotoxicity of water and soil polluted with heavy metals, pesticides, and other pollutants is estimated from the number of dead cells of duckweed leaflets after staining

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\textbf{Application for LTS:} Method for biologically testing water and soil for pollution

\textbf{State of development:} patent

\textbf{Detect only vs. Detect+concentration:} detect only

\textbf{Performance data and sensitivity:} heavy metals

\textbf{Technical details and limitations:} phytotoxicity of water and soil polluted with heavy metals, pesticides, and other pollutants is estimated from the number of dead cells of duckweed leaflets after staining. Using thus obtained results pollution appraisal scale drawn.

\textbf{EFFECT:} increased determination accuracy and rapidity. 1dwg, 1tbl

\textbf{Cost data:} n.a.

\textbf{Further information:} \url{http://ep.espacenet.com}

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\textbf{Technology ID No.: 102}

**Biosensor for radionuclides**

\textbf{Technology:} line of spreading industrial solar pollutants is determined by analyzing stratal water sampled from reference points. Concentration of calcium and/or magnesium ions in stratal water is measured and results of measurements are used to determine migration of industrial solar pollutants

\textbf{Contact information:} Sibirskij khimicheskij kombinat
Semenov E.N., Dzjubenko V.I., Zubkov A.A., Mikhailova N.A.
Application for LTS: monitoring migration of radionuclides and other components of waste in veneer of the crust.

State of development: patent

Detect only vs. Detect+concentration: detect only

Performance data and sensitivity: radionuclides

Technical details and limitations:
Line of spreading industrial solar pollutants is determined by analyzing stratal water sampled from reference points. Concentration of calcium and/or magnesium ions in stratal water is measured and results of measurements are used to determine migration of industrial solar pollutants. Timely detection of increase in concentration of calcium and/or magnesium ions compared with natural level enables instant determination of direction and distance of spreading industrial solar pollutions to take measures for eliminating spreading pollutants over earth surface.

EFFECT: facilitated procedure.

Cost data: n.a.

Further information: http://ep.espacenet.com

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Technology ID No.: 103

Plannar simulating for determining content of radionuclides

Technology: planlar simulating for determining content of radionuclides

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Application for LTS: radiation monitoring of building materials, environment, miscellaneous loose and crushed materials, and soil parts

State of development: patent

Detect only vs. Detect+concentration: detect only

Performance data and sensitivity: radionuclides

Technical details and limitations:
Method involves use of enclosed planar simulating source as internal standard which is placed directly in analyzed sample coaxially to detector without contacting sample material by active substance. Simulating source is standard source wherein surface-distributed point sources simulate activity of homogeneous three-dimensional sample which makes it possible to take into account geometry of measurements and absorption of gamma-ray photons in analyzed sample material.

EFFECT: enlarged functional capabilities, facilitated procedure.

Cost data: n.a.

Further information: http://ep.espacenet.com