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Measurement technology in mine water applications

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Jouni Tornberg
CTO
Measurepolis Development Ltd

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OUTLINE

- Water management in mines
- Development needs
- State-of-art in water measurements
- Available devices and solutions
- Measurement technology research
- Conclusion

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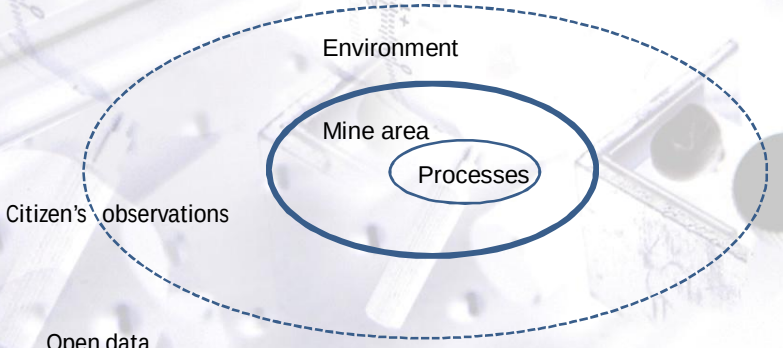
Measurements in Mining



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Management of mine waters

Mine waters

Process waters
– mining and concentration

Waste waters
- mine, grinding
- Waste - flows, leaks
- Exceptional discharge waters (leakages)

Naturally occuring waters
- Rain, smelting

Treatment and recycling

Removing chemicals
Concentration sand
Nitrogen – origin: explosive materials

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Management of mine waters

Concentration process

- flow (water, slurry and chemicals),
- pH, density, redox, quantity,
- mass, temperature, conductivity,
- solution quality
- level, dose, air amount, pressure,
- gas flow, location,
- metal consistencies, solids
- moisture

Environment

- water volumes, levels,
- solids, flows, temperature, metal consistencies,
- air quality, pH, conductivity, etc.

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Mining lisences

- Licences
- Directives
  - EU (2009/90/EY) - cahemical analyses
  - Laboratory standard: EN ISO/IEC 17025 quality system

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Kaivosluvat

Ympäristöluvissa on määrätty metalleille enimmäispitoisuuksia, mitä sallitaan jätevesipäästöissä (taulukko 1). Enimmäispitoisuudet on määrätty sekä kuukausikeskiarvoina että yksittäisten mittausten enimmäispitoisuutena. Raja-arvot vaihtelevat jonkin verran ympäristöluvissa. Tähän saattaa olla syynä niin johdettavien jätevesien määrä kuin purkuvesistön ominaisuudet, jotka on otettava huomioon luparatkaisuissa. Fe-, Mn-, Ca-, Cd-, Cr-, Hg- ja Pb-pitoisuuksille ei ole raja-arvoja, vaikka niitä on määrätty mitattavaksi päästötarkkailuissa.

Taulukko 1. Jätevesien sisältämien metallien enimmäispitoisuuksille annettuja raja-arvoja (Pyhäsalmen, Kittilän Kevitsan, Kemin ja Talvivaaran päätökset).
•annettu neljännesvuosikeskiarvolle ja tavoitearvolle.

Metalli	Kuukausikeskiarvo mg/l	Yksittäinen näyte mg/l
As	< 0,4 ... 1,0	< 1,0 ... 1,7
Cu	< 0,2 ... 0,3 ... 0,5	< 0,6 ... 1,0
Ni	< 0,3 [a]... 0,5	< 1,0 ... 1,5
Zn	< 1,0 ... 1,5	< 2,0
Sb	< 0,5	< 0,8

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Measuring requirements in mining industry

Survey conducted by Measurepolis Development Oy and Prometec Solutions Oy with five different mining companies.

- How the surrounding waters are being measured currently?
- What components are being monitored? Who is responsible of the measurements?
- What should be measured in the future?
- What kind of economic benefits could adopting online-measurements have?

The full world-wide market potential was found difficult to estimate for all of the measurements, but it was concluded that the online monitoring solutions would have considerably large global market potential if the measurement devices was used directly in the process decision-making and control, where the measurements would have the most impact on both the process and wastewaters.

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Development needs and state-of-art of
on-line water quality monitoring technologies in mining industry

Kaivosten ympäristövesien laaduntarkkailun online- mittausteknologioiden kehitystarpeet

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PROMETEC

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Development needs

- Liquid measurements in the mines are important in order to adjust the processes efficiently and to achieve cost savings.
- Important measuring points are located therefore in enrichment processes, as well as in the waste water flows directly from the processes.

- The metal concentration measurements in effluents can be used to monitor the success of the flotation and enrichment process and thus potential production problems can be reacted quickly.

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SURVEY:

An increasing need for online measurements of mine waters

- Reliable, operative online measurements are not available at the moment.
- Their definition limits are too high, the measuring devices need to be cleaned and maintained often, there are malfunctions relatively often, and the rough winter conditions in the mines set very high demands for the measuring devices.
- It was noted by some of the mining companies that the maintenance of laboratory equipment used to analyse the samples from surrounding waters, could be replaced by continuous-time measurements.
- Need for online heavy metal detectors or analysers especially in the multi-metal mines.
- Reliable field meters would also have use in measuring contents of phosphorous, nitrogen, sulphate, fluorite, conductivity and solids in the water.
- Accuracy and reliability should be approved by the environmental authorities.

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SURVEY:

Special interest in heavy metal measurements

- The mining industry has a special interest in real-time monitoring of trace metals, because in the event of leakage an immediate action is required
- Using infrequent laboratory analysis makes early prevention of the hazard virtually impossible.
- Real-time measurement of trace metals in natural environment represents a great challenge, since direct determination of heavy metals is not always possible because of matrix interferences and very low concentrations of metal ions.
- Monitoring wastewater, a detection limit of 0.1 mg/L is commonly considered sufficient, but it is impossible to reach to most conventional methods

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Table 4. The requirements for online measurements of the interviewed mining companies.

Measured Variable	Talvivaara Sotkamo	Sotkamo Silver	FQM Kevitsa Mining	Agnico-Eagle Kittilä	Yara Finland Siilinjärvi
Ni	x		x	x	
Cu	x		x		
Zn	x	x			
Co	x				
Pb		x			
Sb	x	x	x	x	
As				x	
Al				x	
Mn			x	x	
Fe	x		x	x	x
sulphate	x	x	x	x	x
CN				x	
thiocyanate				x	
chloride			x	x	
pH	x	x	x	x	x
conductivity	x	x	x	x	x
flow	x	x	x	x	x
solids	x	x	x	x	x
N	x		x		x
temperature	x	x	x	x	x
redox	x	x	x	x	x
P					x
F					x
ground water surface	x	x	x	x	x

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Development needs

1. Heavy metals
   - Ni, nickel
   - Cu, copper
   - Zn, zinc
   - Co, cobolt
   - Pb, lead
   - Sb, antimone
   - As, arsenic
   - Al, aluminium
   - Mn, manganese
   - Fe, iron
2. Sulphate
3. CN, syanide
4. N, nitrogen
5. P, phosphorus

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Heavy metals

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Table 5. The permit limits for wastewater metal concentrations for the selected group of mines by SYKE. (SYKE 2012)

Metal	Month average mg/l	Individual sample mg/l
As	< 0,4 ... 1,0	< 1,0 ... 1,7
Cu	< 0,2 ... 0,3 ... 0,5	< 0,6 ... 1,0
Ni	< 0,3* ... 0,5	< 1,0 ... 1,5
Zn	< 1,0 ... 1,5	< 2,0
Sb	< 0,5	< 0,8

* Determined as a mean quarter a year or as a targeted value

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Heavy metals - Devices in the market

- Optics/spectroscopy methods
  Laser-induced breakdown spectroscopy (LIBS)
  - Outotec Courier® 8 SL - Advanced online light element analyzer for light & heavy elements. http://www.outotec.com/Global/Products and services/Automation/Advanced online light elementanalyzer for mineral slurry product news.pdf
- Electrochemical methods
  Voltametric breakdown spectroscopy technique:
  - AppliTek: Zinc, Cadmium, Lead, Arsenic, Mercury, Iron and Chromium - Anodic Stripping Voltammetry. http://www.applitek.com/en/offer/analyzers/water-quality/heavy-metals/
  - SensAqua A/S: Copper, Zinc, Mercury, Iron, Lead, Cadmium - Voltammetry. http://www.sensaqua.com/dokumenter/info.pdf
  - Ai-analytical. Online Heavy Metals Measurement. http://www.ai-analytical.com.sg/
  - Trace2O Metalyser Fieldpro hm3000 http://trace2o.com/products/metalyser-field-pro-hm3000/overview~15.html
  - Alta: The Heavy Metals Analyser uses the technology of the polarography. Lead, Copper, Zinc, Cadmium, Nickel, Iron, Chromium 3 and 6. http://www.elta.fr/uk_doc/AML_ENG.pdf
- Colorimetry
  - SEIBOLD – COMPOSER Analysers. Online Analysers for Heavy Metal Measurements in Water. Measurement is based on photometric determination of the intensity of the coloured complex formed by the heavy metal ions and the reagents http://www.seibold-wasser.at/docs/Online Analysers for Heavy Metal Measurements in Water EN.pdf
- Titration
  - Seibold Wasser Titration: http://www.seibold-wasser.at/1157mail.html

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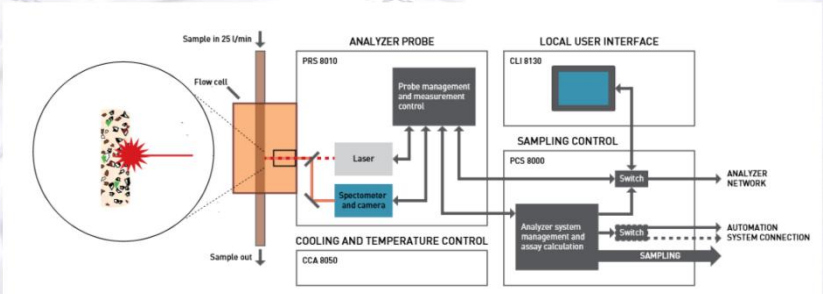
Outotec Courier 8 SL



A small portion of the sample is heated into hot plasma in the Courier 8 SL flow cell by a short laser pulse. The light spectrum emitted by the atoms and ions in the cooling incandescent plasma is measured after a short time delay. The concentrations of the elements in the sample are calculated from averaged spectra using calibration equations based on the laboratory assays of calibration samples.

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ADI 2045TI Process Analyzer

You want to bring your laboratory analysis online in your process? Metrohm Applikon can do that for you!

The analytical system uses high quality Metrohm analysis modules like the Titrando range of titrators. Combining Metrohm's knowledge and experience in laboratory analysis and Applikon's experience in process control instrumentation results in an analyzer that can perform nearly every ON-line or AT-line wet chemical analysis in the most difficult environments. It's unique modularity design makes it possible to adapt the analyzer to the specific needs of the application. Multi-parameter and multi-stream analyses are easily implemented as well as analog and digital communication with other devices.

Analysis capabilities

- Titration for a broad range of application
- Karl Fischer titration for water determination in liquids
- Dynamic Standard Addition with Ion Selective Electrodes
- Absorbance Colorimetry for water quality analysis & plating solutions
- Direct Measurements for measuring pH, conductivity, redox and temperature
- Third party devices such as density, flow, refraction, turbidity,..
- Special applications are available on request!

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MODERNWATER

Trace Metals Products

On Line Monitor – OVA7000 and OVA7000 Dual

- Unique on-line monitor
- Voltammetry-based
- Low detection limits (0.5 µg/l)
- Programmable for a variety of metals and sample types
- 24/7 on-line monitoring with process control

Portable Analyser – PDV6000 *ultra*

- Portable heavy metal analyser for field and laboratory
- Fast results down to low ppb levels
- Suitable for water and soil

OVA7000

OVA7000 DualCell

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Promising technologies

[http://www.urbanwateralliance.org.au/publications/UWSRA-tr10.pdf]

- Currently, there are two main research approaches available
  - **Voltammetric sensors** are promising candidates for real-time, simultaneous measurements, as they can acquire continuous information with minimal or limited sample pre-treatment
  - **Potentiometric sensors** and **biosensors** that may also be viable alternatives.

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Measurement principles in development

Technologies:
electrochemistry, optics/spectroscopic, colorimetric

- Electrochemical determination, screen printed electrode, Ni, Cemis-Oulu (electrochemical) Mari Jaakkola
- MEAN Square Wave Anodic Stripping Voltammetry (Cu, Zn, Pb, Cu, …), Cemis-Oulu (electrochemical), Mika Mahosenaho
- Stand-alone LIBS Measurement System, Fe, Mn, Ni, VTT (spectroscopic) Kimmo Solehmainen
- LIBS, Ni, Zn, Pb, TTY (spectroscopic) Juha Toivonen
- Aztec, Fe, Mn, Cu, ABB (colorimetric) Jussi Laitinen 050 33 27278
- PHD Nordic Oy, Fe, (colorimetric) Ville Rautiainen
- Chemetrics, Fe, Mn, Cu (soluble), (colorimetric) Hanna Runtti
- Fenno-Aurum (XRF), Arto Niemelä
- MPES (microplasm-emissionspectrometry) Anssi Mäkynen, OY

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Quantity ranges

Metal	Month average [	Individual sample [mg/l]
As	<0,4...1,0	<1,0...1,7
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Ni	<0,3*...0,5	<1,0...1,5
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Sb	<0,5	<0,8

* Determined as a mean quarter a year or as a targeted value

The permit limits for wastewater metal concentrations for the selected group of mines by SYKE

s. 27 MMEA raportti

	Metallit							
Mittarit	Fe	Mn	Ni	Sb	As	Cu	Zn	Pb
SPE, OY			0,5 ppm -->					
MEAN, OY						<ppb	x	x
LIBS, TTY	ppb	ppb	>60 ppb eli 0,06 ppm		ppb (ei kovin tarkka)	ppb	>50 ppb eli 0,05 ppm	>60ppb eli 0,06 ppm
LIBS, VTT	>1 ppm	>1 ppm	>1 ppm					
AZTEC, ABB	0,005-5ppm	0,020-10 ppm tai 0,001-0,1						
Metalyser, LTY (jenkkimittari)		1-200 ppb eli 0,001-0,2 ppm	10-100 ppb eli 0,01-0,1 ppm		1-500 ppb eli 0,001-0,5 ppm	20-100 ppb	1-500 ppb	1-500 ppb
PHD Nordic	2-20 ppm				kehitteillä			
Chemetrics Kit	esim. 0,10-2,50 ppm	2,0-30,0 ppm				0,25-7,00 ppm		

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Some project descriptions

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Measuring Sulphates from Mine Waters
Using Different Measurement Technologies

Merja Rautiainen, Measurepolis Development Oy
Report 2/2014

CLEEN
Cluster for Energy and Environment

mmea
Measurement, Monitoring and Environmental Assessment

MEASUREPOLIS DEVELOPMENT LTD | Kehräämöntie 7 | Technology Park Box 103 | FIN-87400 KAJAANI, FINLAND

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Sulphate measurement campaign

- Find and test different technologies to measure sulphates from mine waters and mine waste waters.
- Evaluate reliability, functionality and possible suitability of technologies for online use.
- Sulphates were measured in five different technologies and elemental sulphur was measured in one technology from different mine water fractions.

- Reference: ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and IC (Ion Chromatography).
- Titration technology by Metso
- CE (Capillary Electroforesis) by Cemis-Oulu
- VTT commercial Raman spectroscopy device (VTT has also developed time-gated Raman spectroscopy – Later Timegate Instruments Oy.)
- The Sulfate Vacu-vials® test kit (commercial) based on the turbidimetric method.

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Results of mine waters/waste waters measurements

SULPHATE MEASUREMENTS									
	Technology								
Näytteet	Calculated sulphate from ICP-OES results [mg/L]	Ion Chromatography [mg/L]	Titration Technology [mg/L]	Capillary Electrophoresis [mg/L]	Test Kit (turbidimetric) [mg/L]	ICP-OES (sulphur, mg/L)	Time-gated Raman [mg/L]	pH	Conductivity [mS/m]
Mine 1 Sample 1.1	4973	4000	5422	4435	4567	1660		7,7	692
Mine 1 Sample 1.2	3985	3500	4927	3653	3776	1330		8,4	517
Mine 1 Sample 1.3	2756	2700	3324	2678	2524	920		8,8	431
Mine 2 Sample 2.1	2487	2400	3255	2300	2341	830		7,7	396
Mine 2 Sample 2.2	479	430	403	406	343	160		7,3	193
Mine 2 Sample 2.3	419	350	377	361	306	140		7,6	153
Mine 3 Sample 3.1	869	780	954	762	729	290		7,8	162
Mine 3 Sample 3.2	9258	9000	17480	9350	10325	3090		7,9	1038
Mine 3 Sample 3.3	4824	4400	13566	4875	4889	1610		8,3	701

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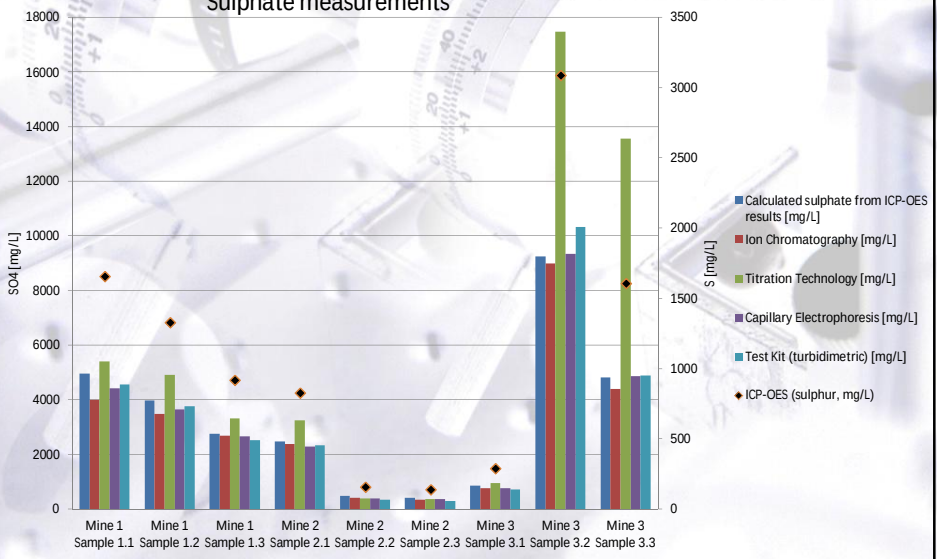
Sulphate measurements



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Sulphate measurement campaign

- When evaluating measurement results, the best technology was CE. The second best results were achieved by sulphate test kits when sulphate amount was over 500 mg/L. In turn, when sulphate amount was below 500 mg/L, the titration technology gave more reliable results than test kits.
- Traditional Raman spectroscopy recognized sulphates as peaks in spectrum but did not react to sulphate amounts as reference measurements. These results were published in MMEA and Sulka projects.

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Heavy metals

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NICK - Novel methods for online monitoring environmentally critical substances (primarily nickel) in process and waste water streams

Project summary

Duration: 1.2.2012 – 31.12.2013

Budget: 500 000 €

Coordination: Jarkko Räty, CEMIS-Oulu

Main aims of the project are to create state-of-the-art methods and pilot instrumentation to monitor low nickel contents coming from the mining site discharge waters. Targeted detection limit is below 0.1 ppm.

Consortium will use Laser Induced Breakdown Spectroscopy (LIBS) and sensor based approach in order to achieve the proposed aims.

VTT

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Stand-Alone LIBS Measurement System

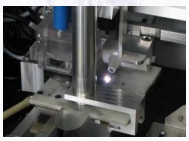
Pre-concentration and measurement scheme

1. Dispense a 0.03ml droplet of sample liquid

Graphite disk →

2. Dry the droplet using hot air circulation

3. Do LIBS measurement on the dry residue



Reference:

Sarkar et al. *Determination of sub-ppm levels of boron in ground water samples by laser induced breakdown spectroscopy*, Microchim Acta, December 2009

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Real-time elemental analysis of water droplets using laser-induced breakdown spectroscopy

Samu Järvinen, Sampo Saari, Jorma Keskinen and Juha Toivonen

Tampere University of Technology, Department of Physics, Tampere, Finland

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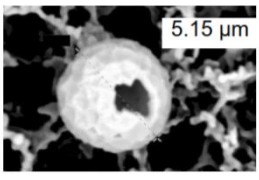
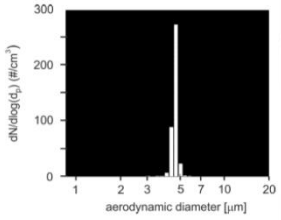
LIBS with droplet preconcentration

Fast conversion from liquid to monodisperse aerosol particles

- 0.6 g/l NaCl added to water sample
- 50-60 µm droplets dried to monodisperse 4-5 µm solid particles where metals are present as dopants
- Metals **preconcentrate** as the droplet evaporates
- LIBS analysis of a single particle using low pulse energy
- Average of many single-shot spectra
- Stable sodium matrix can be utilized in the signal processing





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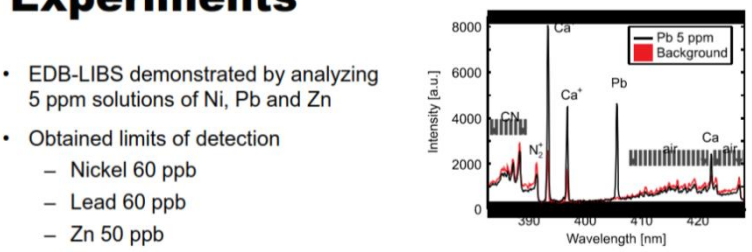
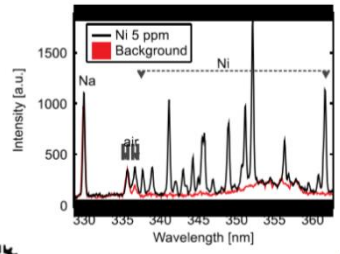
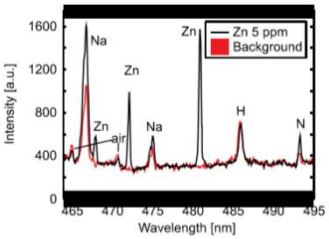
Experiments

- EDB-LIBS demonstrated by analyzing 5 ppm solutions of Ni, Pb and Zn
- Obtained limits of detection
  - Nickel 60 ppb
  - Lead 60 ppb
  - Zn 50 ppb







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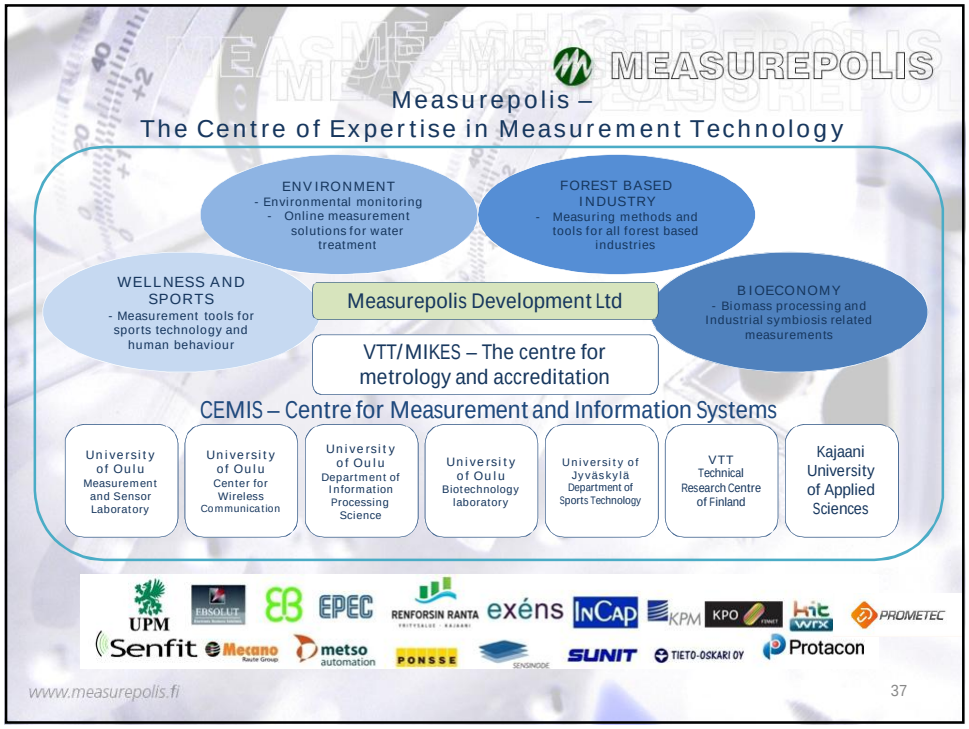
CONCLUSION

- Measurement technology exists
- Have they tested and applied
- Measurement business -alone- always difficult
- Focus to be directed to process measurements
- Environment monitoring measurement business logic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- Environmental monitoring
- Online measurement solutions for water treatment
FOREST BASED INDUSTRY
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WELLNESS AND SPORTS
- Measurement tools for sports technology and human behaviour
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BIOECONOMY
- Biomass processing and Industrial symbiosis related measurements
VTT/MIKES – The centre for metrology and accreditation
CEMIS – Centre for Measurement and Information Systems
University of Oulu Measurement and Sensor Laboratory
University of Oulu Center for Wireless Communication
University of Oulu Department of Information Processing Science
University of Oulu Biotechnology laboratory
University of Jyväskylä Department of Sports Technology
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