# Analytical Chemistry at Glencore Nikkelverk AS

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Hydrometallurgy Course 2016

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# Agenda

- **Chemical analysis at the Nikkelverk**
- **2** On-line chemical analysis at the Nikkelverk
- **3** On-line Photometry
- 4 On-line Voltammetry
- 5 On-line pH
- 6 On-line Titrimetric Analyzer
- 7 On-line-XRF
- 8 Commercial on-line Analytical Capabilities





## **Online Chemical analysis at the Nikkelverk**

- On-line/at-line Chemical Analysis at The Nikkelverk:
  - > 60 Chemical Analysis
  - 7 measuring prinsipels (Photometry, Voltammetry, titration, pH, Redox, Coulommetric)
- Analytical equipment and methodes developed at the Nikkelverk:
  - Polarographic instruments (not in use any more)
  - Photometric instruments
  - Coulommetric titration
  - Acid titration

Team: Nordnes, Grøntoft, Pedersen, Simonsen (1970 - 2000)



## Absorption spectrum of filtrats at the Nikkelverk



## Photometry Ni-analysis in waste water (0-15 mg/L)





*Foster Dee Snell*; Photometric and fluorimetric methods of analysis, 1978. Del I, side 887 - 899.



### Future spectrometry (CCD-specrometer and PLS/PCR-calibration)



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# Voltammetry (electrochemistry) for trace analysis in the Ni electrolyte ( μg/L)



Collaboration with prof. Øyvind Mikkelsen NTNU.

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### Voltammetry for trace analysis in waste water( µg/L)



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• pH (pondus Hydrogenii) and Nernst equation:

$$E(mV) = E^{\circ} - \frac{2.3 \cdot R \cdot T}{F} pH = konst. - 59 \cdot pH \quad ved 25^{\circ}C$$



• Deviation  $\Rightarrow$  calibration in buffer solutions with known pH

## Who wrong are this poisond pH-elctrodes?



### Daily check of a SOTA-pH-electrode in high Cl<sub>2</sub> cont. NiCl<sub>2</sub>-solution



### Daily check of a pressurized-pH-electrode in high Cl<sub>2</sub> cont. NiCl<sub>2</sub>-solution



### Daily check of a SOTA-pH-electrode in low Cl<sub>2</sub> cont. NiCl<sub>2</sub>-solution



### Daily check of a pressurized-pH-electrode in low Cl<sub>2</sub> cont. NiCl2-solution



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### The pressurized pH-electrodes are more stable then the SOTA pH-electrode



pH-measurement withouth correction. The NiCl solutiond with low Chlorine pH-measurement withouth correction. The NiCl solutiond without Chlorine

### What is happening with new pH-electrodes in concentrated electrolytes?









SOTA

Knick 6 bar

Mettler Toledo 3 bar

pH-electrode pHG201 with separate Ag/AgCI-ref. in a salt bridge (double Junction)

### Change in mV-signal for four new pH-electrodes in a NiCl2-solutions



## **Test of seven pH-electrodes**





## Seven pH-electrodes in high Cl<sub>2</sub> cont. NiCl<sub>2</sub>-soltion



## Seven pH-electrodes in NiCl2-soltion without Cl2



# Halland Instruments AS



- pH-measurements for demanding applications
- The Nikkelverk will install one Halland pH-instument in 2016.

http://hain.no/

## **Titrlyser (On-line Titrimetric Analyzer) from Applitek**



# **Experimenter's XRF Kit from Amptek Inc.**



- Miniature X-Ray-Tube (4W, Ag-anode)
- X-Ray-Spectrometer
  123 SDD (Silicon Drift Detector)
- Software:
- X-Ray -tube Controller
- ADMCA (Spectrometer Controller)
- XRS-FP (XRF-Fundamental Parameter program for quantitative analysis).

## Results from a post-graduate thesis (Liquid samples)





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# **On-line EDXRF at Glencore Nikkelverk**



Flow cell, X-ray tube and SDD-X-ray detector



Amptek DppMCA C:\Hovedoppgave xrf\21.8.2015\2.0M NiCl2 25-10 8mm b.mca - 🗆 X 🚥 Calibrate DP5 (s/n 10812) Tag: Mode live\_d Add NORN Channels 4,096 LLD Thresh 0.88% Replace Fast Thresh 32.18 Peak Time 6.400 Remove Gain Gain Delta 69.06 Remove All Preset Mode Cursor Preset Accum Time 300.00 Centroid Real Time 300.00 Units Plot ... Total Count 5.087. **Calibration Equation** Input Count 6,660, Linear × A + B\*\* Input Rate 22,202 Dead Time 23.621 A=-0.0381188 B=0.0050004 Start: 08/21/2015 09 Auto Calibration (Dt/+F5) Status: disconn Units keV Peak Information Value 2.62 Centroid (N) Peak 2 Value 7.48 EWHM (N) Net Area Uncertainty Net Rate Method 2 Peak Centroid 🔽 Gross Area 5.08 10.20 OK Cancel 223K Det. Temp Cursor Range LOG Sca Det. HV -109V 7.48 -0.04 Set Communication

#### Energy calibration



On-line EDXRF at the Nikkelverk

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## Challenge

#### **1.** Deposition of matter on the polypropylene film.

- 1. Automatic cleaning of flow cell.
- 2. Replacing film.

### 2. Clogging.

Some of the process solutions are hot and saturated with salts, and matter deposits when the solutions are cooled.

- 1. High flow.
- 2. Automatic cleaning of tubes and flow cell.

#### **3.** Difficult to optimize both for main component analysis and trace analysis.

(for this instrument).

- 1. It is not possible to changes filter automatically.
- 2. Hard to optimize detector setting for low and high concentrations in one application.

#### 4. Calibrating the instrument.

1. Best calibration by using single og two element standards.

#### 5. Unstable X-Ray tube

- 1. Wait one day until the tube stabilize.
- 2. Monitor correction (use standard samples or use elements in the cleaning solutions).

#### 6. The Amptek Experimenter's XRF Kit is an instrument for advanced XRF-users.

- On line EDXRF is a promising technique for online multi element analysis of liquid solutions.
- I am sure this will be a technique in more common use in online measurements, and especially at the Nikkelverk.
- I hope we are able to implement an online XRF-instrument in a two years period at the Nikkleverk.

## Courier 5i/6i: Autotec, Finland.



## Metorex 100. Hobre/PANalytical, Netherland.



## XRF Online Instruments, Thermo Fisher Scientific, Australia.



## Boxray. XORE, Sweden.

Boxray 24 (24 sample streams)



### Boxray Compact (16 sample streams)

## NEX-OL. Rigaku, USA.





## **Metrhom Analytical Capabilities**

#### Online

Titration	Ion Selective	Voltammetry	Colorimetry	NIR	ТОС	On-line IC
ppm-%	> 1ppm	ppt-ppm	ppb - low ppm	> 100 ppm	1-500 ppm	ppt-%
LOD<10 ppm	LOD	LOD~1ppt	LOD<5 ppb		LOD<1ppm	LOD<1 ppb
Wide range of inorganics and organics in water and other solvents	Limited number of inorganics	Heavy metals and CVS	Mainly inorganics in water	Organics and water traces	Total amount of organic carbon in liquids.	Anion and cation



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