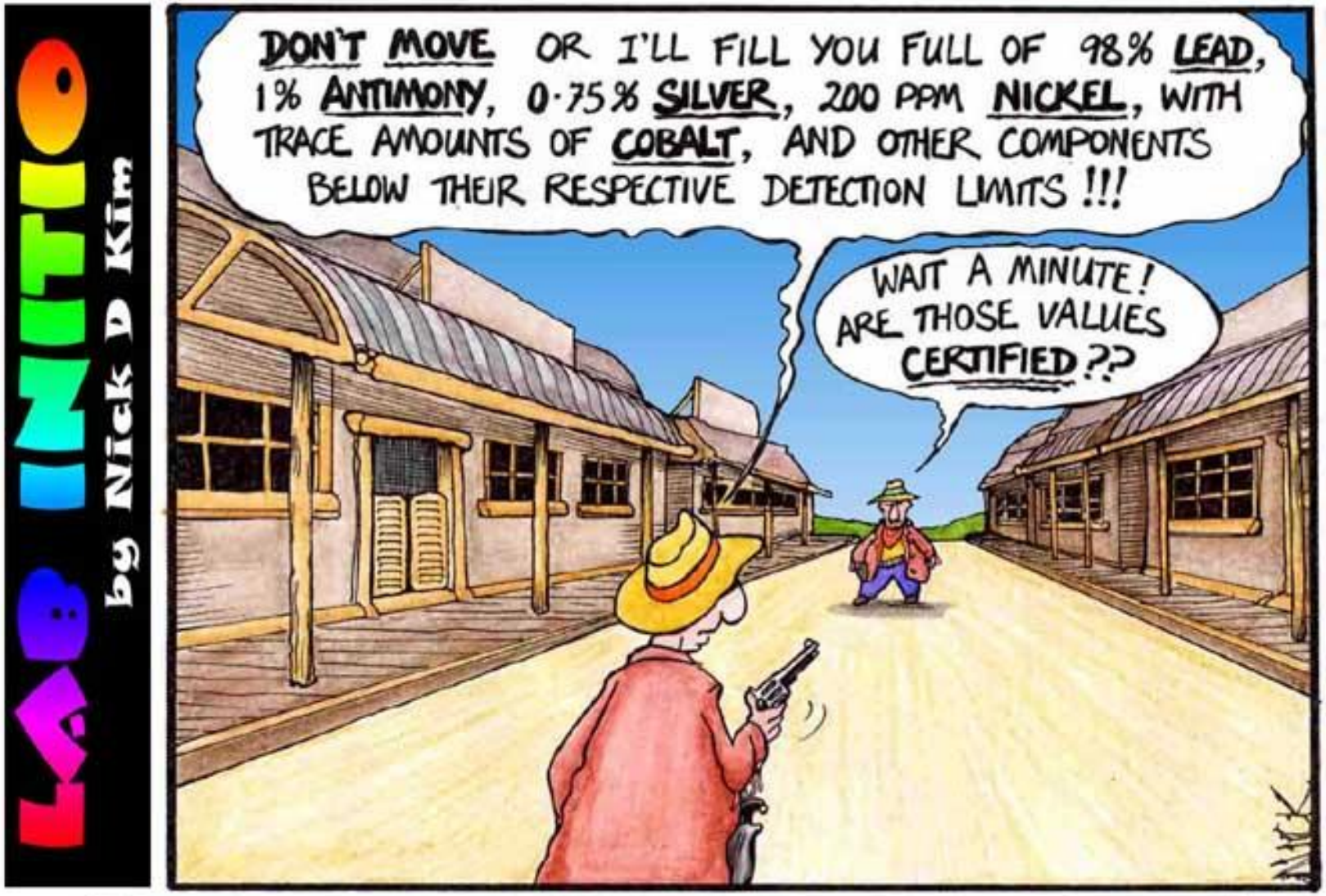

LAB INITIO
by Nick D Kim
DON'T MOVE OR I'LL FILL YOU FULL OF 98% LEAD, 1% ANTIMONY, 0·75% SILVER, 200 PPM NICKEL, WITH TRACE AMOUNTS OF COBALT, AND OTHER COMPONENTS BELOW THEIR RESPECTIVE DETECTION LIMITS !!!
WAIT A MINUTE! ARE THOSE VALUES CERTIFIED ??
NICK
ANALYTICAL CHEMISTS IN THE WILD WEST

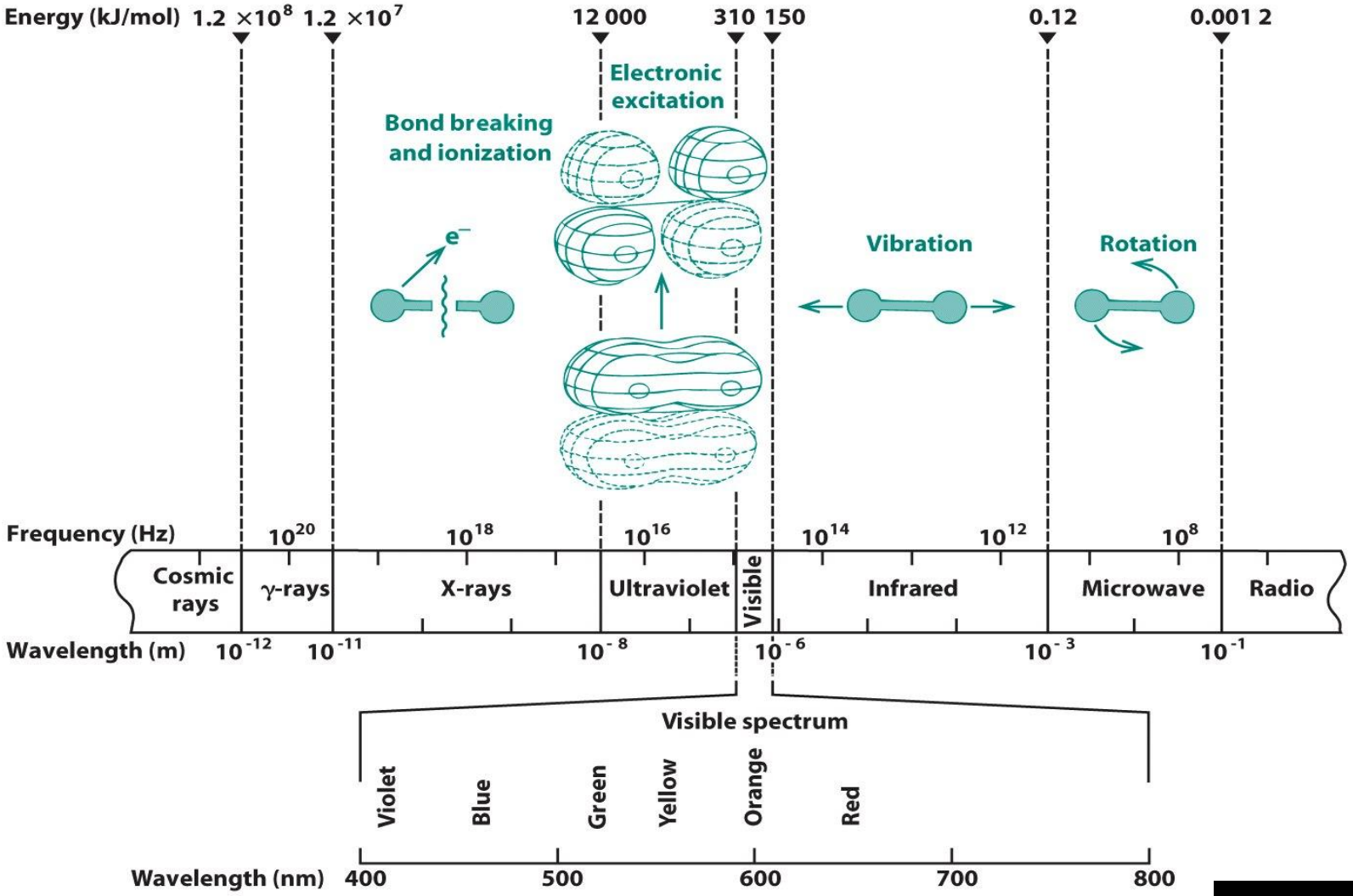
Hg Analysis: Instrumentation

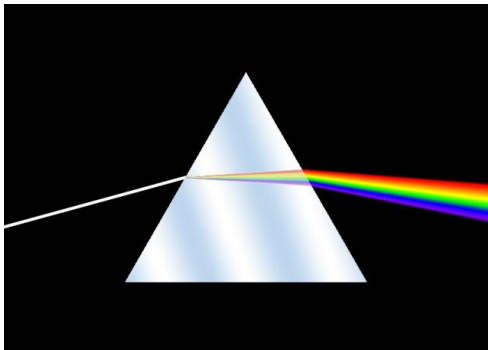
- Atomic Absorption Spectrometry (AAS)
- ***Atomic Fluorescence Spectrometry (AFS)***
- Total Mercury Analyzer (gold trap-pyrolysis-AAS)
- Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Requirements for **AFS** and **AAS**: Hg must be in the elemental form (Hg^0);

→ (Chemical) Reduction of Hg^{2+} prior analysis;

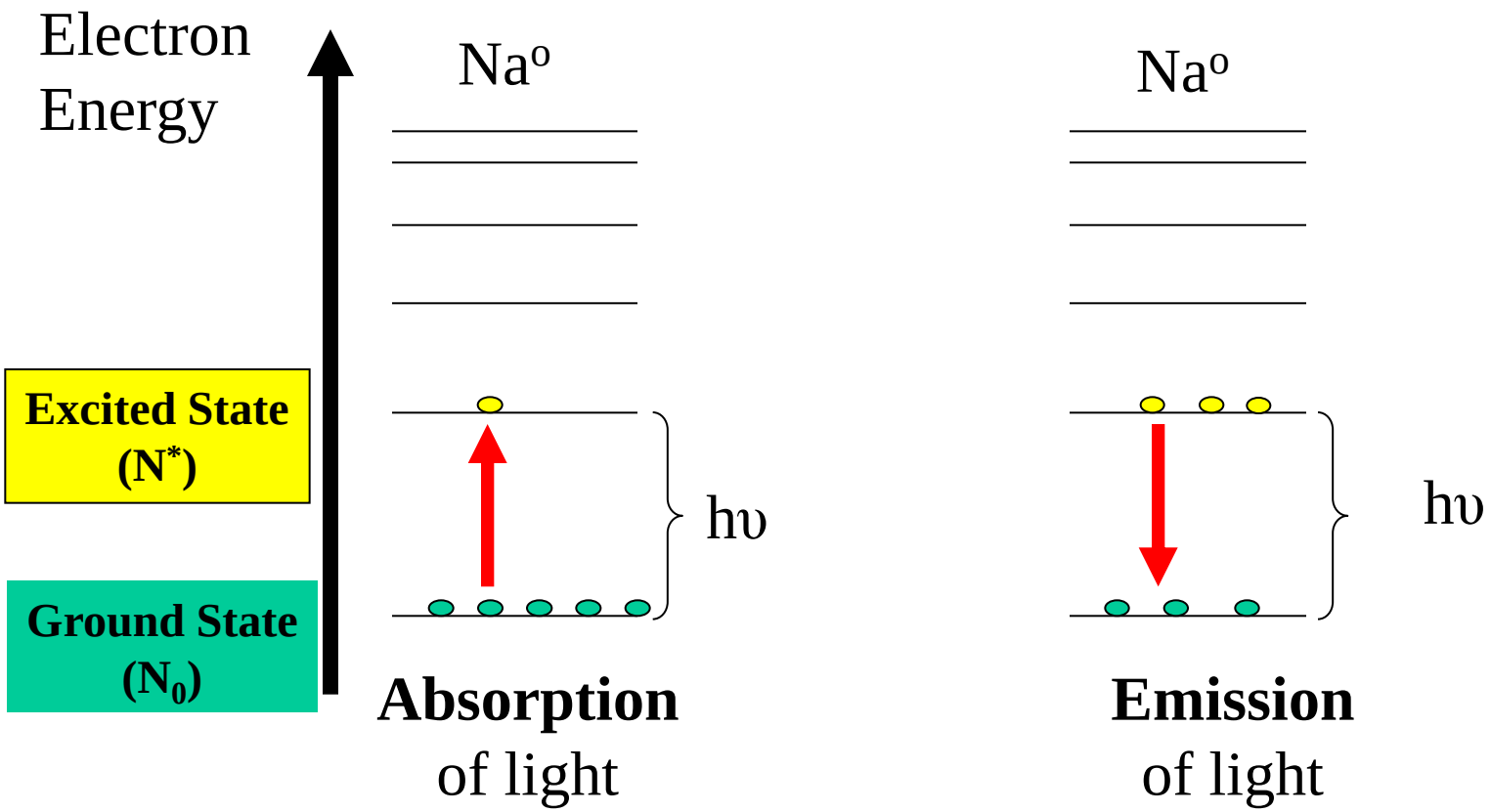
→ (Pyrolytic) Reduction and breaking Hg-C bond of MeHg prior analysis


Energy (kJ/mol)
1.2 ×10^8
1.2 ×10^7
12 000
310
150
0.12
0.001 2
Electronic excitation
Bond breaking and ionization
e⁻
Vibration
Rotation
Frequency (Hz)
10^20
10^18
10^16
10^14
10^12
10^8
Cosmic rays
γ-rays
X-rays
Ultraviolet
Visible
Infrared
Microwave
Radio
Wavelength (m)
10^-12
10^-11
10^-8
10^-6
10^-3
10^-1
Visible spectrum
Violet
Blue
Green
Yellow
Orange
Red
Wavelength (nm)
400
500
600
700
800



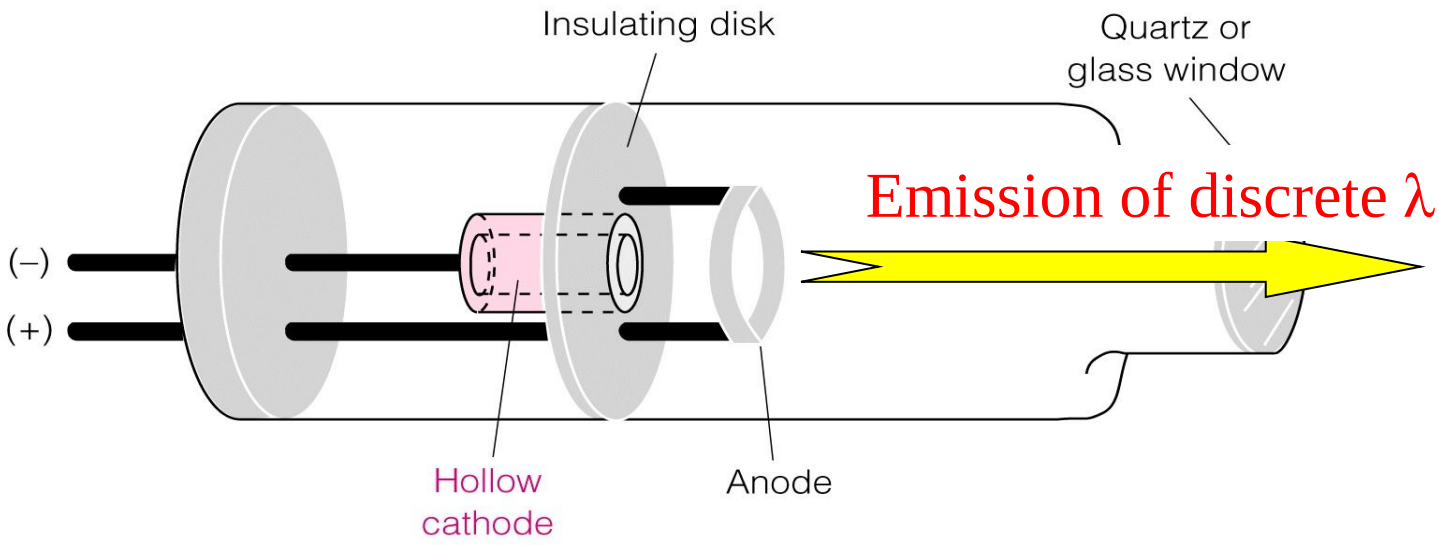
Atomic Spectrometry

- In atomic spectrometry, we use the excitation state of electrons in an **ATOM**



- In atomic fluorescence spectrometry, we excite the electron by applying the appropriate wavelength, then ***measure*** the light subsequently emitted (Atomic Emission) by the Hg Atom

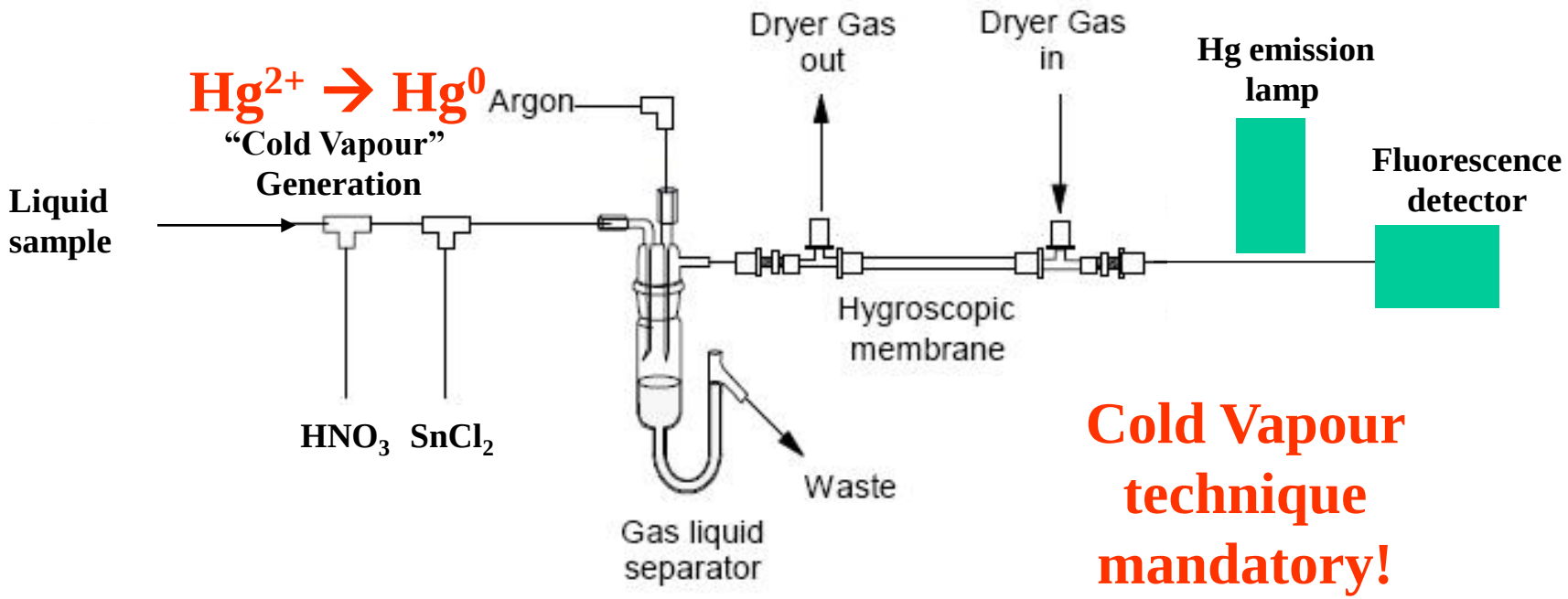
Light Source: Hollow Cathode Lamp



- Hollow cathode made of element of interest (e.g. of Na to measure Na! Selectivity of AAS!)
- Potential of 100-400 V ionizes Ne (glow discharge)
- Ne^+ hit the cathode and excite the element
- Emission lines are generated.
- Low pressure and filled with Neon (Ne)

Hg Analysis

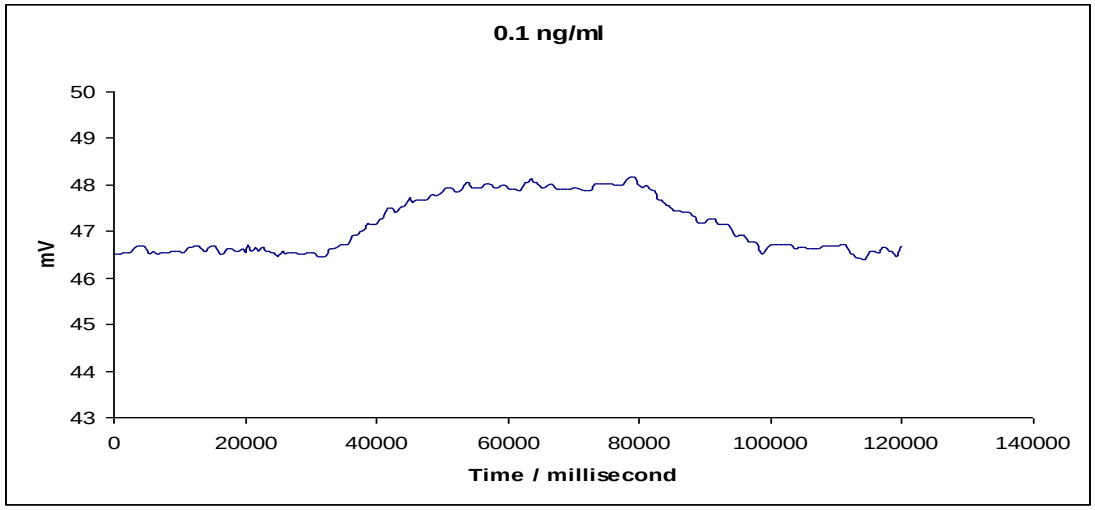
Principle of ***Atomic*** Fluorescence Spectrometry (AFS)

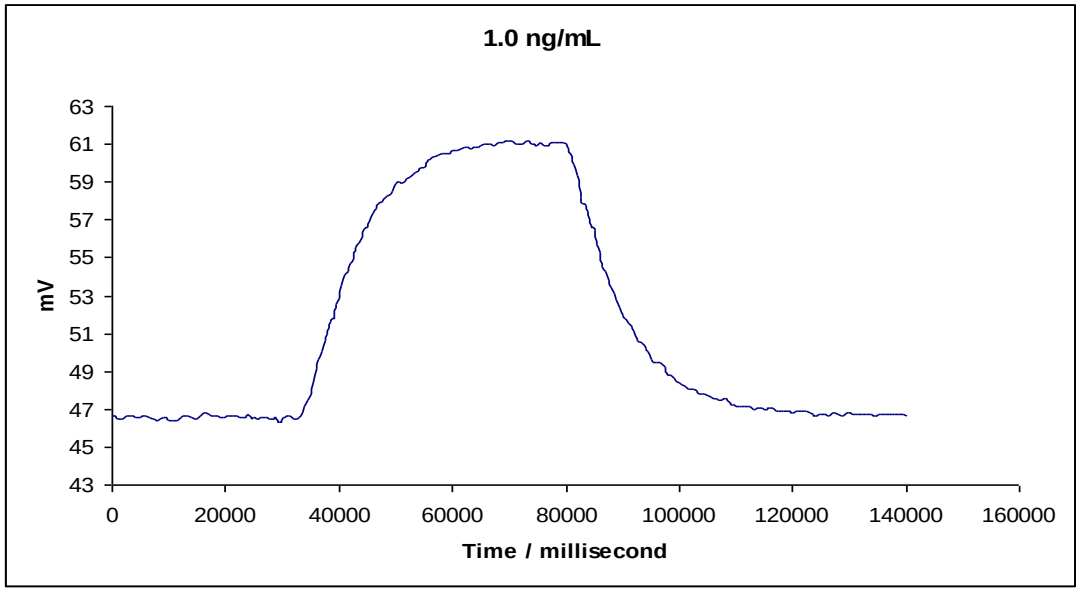


Cold Vapour technique mandatory!

1) **Bring sample into liquid form**
2) **$Hg^{2+} + Sn^{2+} \rightarrow Hg^{o} + Sn^{4+}$**

Signal of 0.1 ng/mL and 1.0 ng/mL

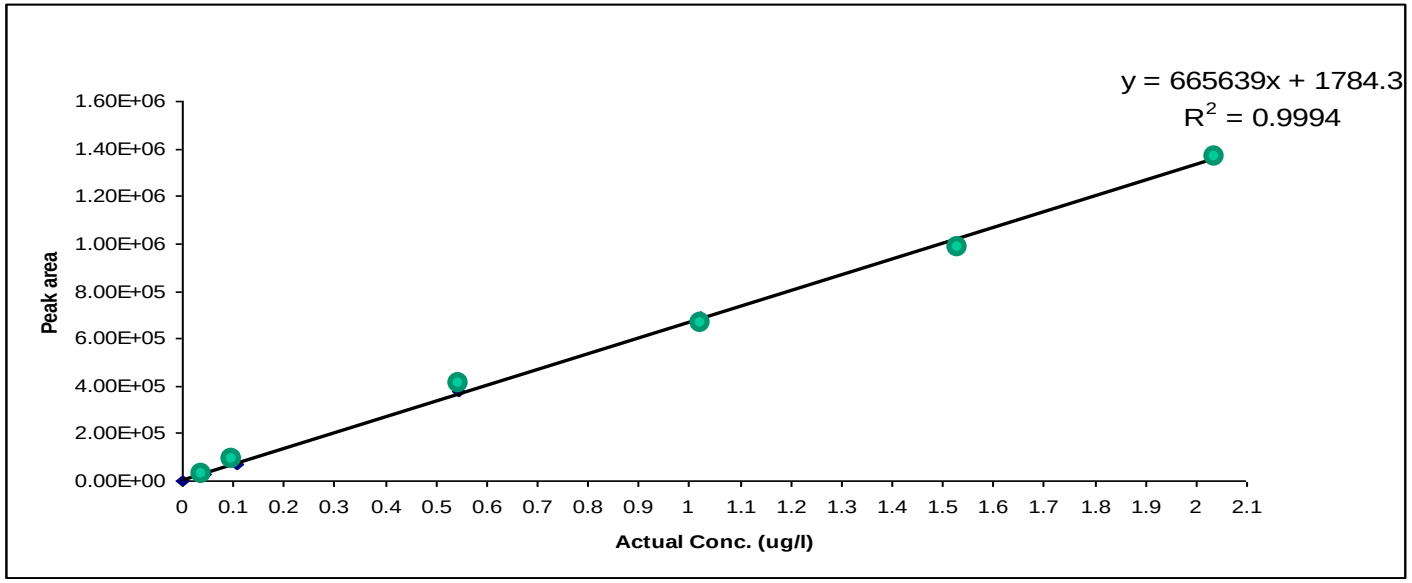




Instrument Calibration

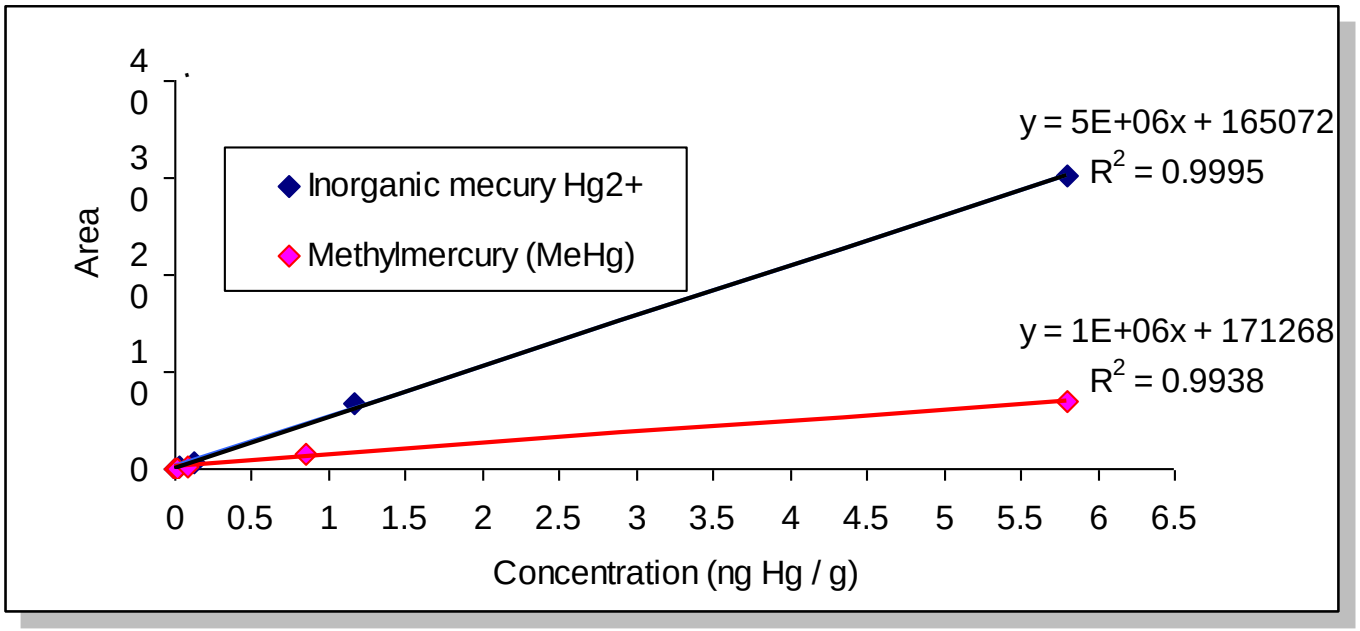
Six standards points were prepared for calibration curve:

0.05 - 2 μg/L in 5% HNO_3



Limit of Detection (LOD) based on 3 σ: 0.05 ng Hg /mL

The effect of carbon- mercury bond (Hg-C)



- Slope (Hg^{2+}) > slope (CH_3Hg) means not all Hg-C has been cleaved in the digestion because
  - $Hg^{2+} + Sn^{2+} \rightarrow Hg^{o} + Sn^{4+}$
  - $CH_3Hg^{+} + Sn^{2+} \rightarrow$ XXXX (no volatile product!!)

Strong digestion methods for Hg analysis in hair: Validation with CRM

No	Digestion method	Total mercury *Results are given as average ± standard deviation (n=3)				
		CRM 085 Certified value µg/g	Measured *value µg/g using 2% $SnCl_2$	**Recovery (%) @ 2% (w/v) $SnCl_2$**	Measured *value µg/g using 3 % $SnCl_2$	**Recovery (%) @ 3%(w/v) $SnCl_2$**
1	5 ml HNO_3+ 1ml H_2O_2 (microwave)		19.28 ± 0.5	83.10	21.76 ± 0.2	93.79
2	5 ml Aqua regia (microwave)		32.25 ± 0.2	139.0	31.23 ± 0.3	134.61
3	5 ml HNO_3 (autoclaved @ 100ºC)	**23.2 ± 0.8**	22.50 ± 0.2	96.98	23.19 ± 0.1	99.96
4	3 ml HNO_3+ 2 ml H_2O (autoclaved @ 100ºC)		6.94 ± 0.4	28.62	7.54 ± 0.3	32.50

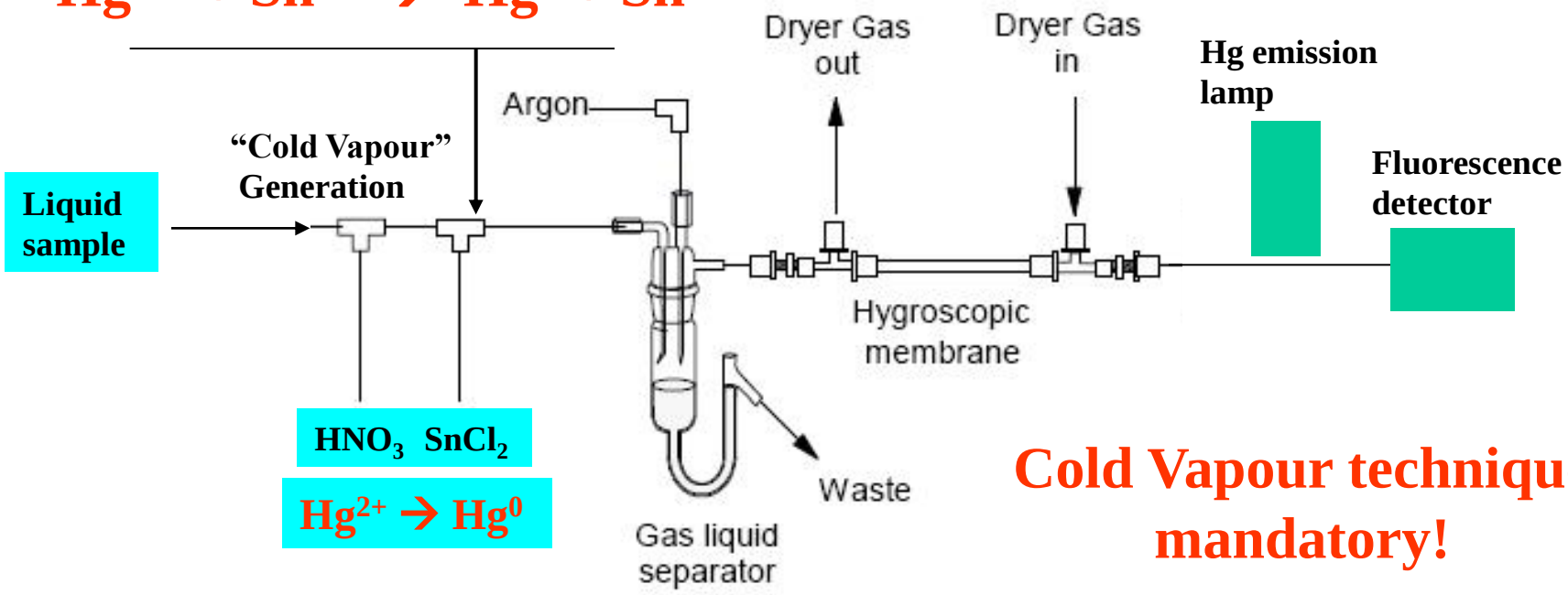
* Results are given as average ± standard deviation (n=3)

- Good agreement was found between the certified value and measured value as determined by procedure No 3, total recovery being between 96 and 100%

Cold vapour – AFS for Hg determination

Principle of Atomic Fluorescence Spectrometry (AFS)

$Hg^{2+} + Sn^{2+} \rightarrow Hg^{o} + Sn^{4+}$



Cold Vapour technique mandatory!

CV-AFS is a very sensitive method for Hg determination with detection limits (in solution) in the lower ng/L range (ppt). Sensitivity can be even enhanced by applying amalgamation on gold support (gauze, gold coated silica etc.)

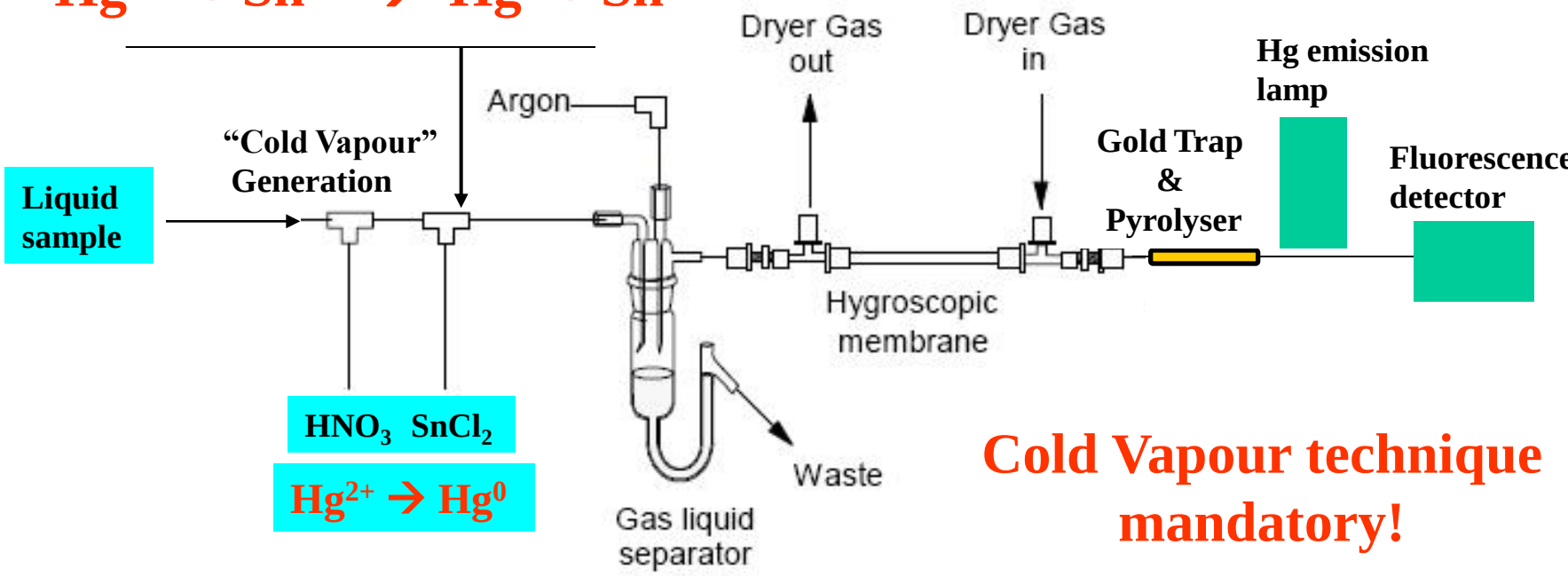
Gold traps for Hg accumulation

- Mercury amalgamates with gold, and gold traps have often been used for the collection and enrichment of mercury and mercury species.
- All volatile mercury species can be collected on gold traps → gold traps are not species specific!
- Use of gold traps: Improvement of LOD by enrichment; Direct gas sampling;
- Pyrolysis system needed for AFS or AAS detection after gold trapping!

Cold vapour – AFS for Hg determination

Principle of Atomic Fluorescence Spectrometry (AFS)

$Hg^{2+} + Sn^{2+} \rightarrow Hg^{o} + Sn^{4+}$



Cold Vapour technique mandatory!

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