6020 Analysis Using a Simultaneous ICP MS Without the Need of Reaction or Collision Cells

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Outline

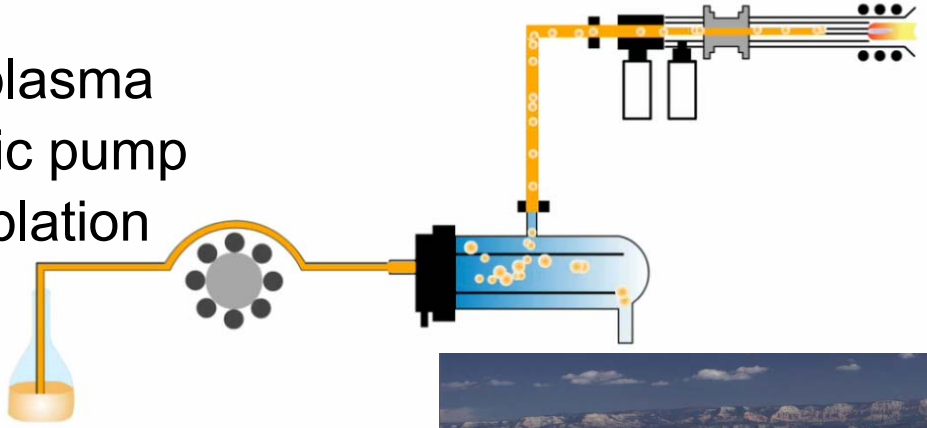
- **Hardware**
  - **ICP-MS**
    - **Advantages of simultaneous ICP-MS**
    - **ICP as Ion source**
    - **Mass spectrometer**
    - **How does the detector work**
- Simultaneous measurements
  - Precision of measurements
  - Interference Correction
- Summary

Why simultaneous detection?

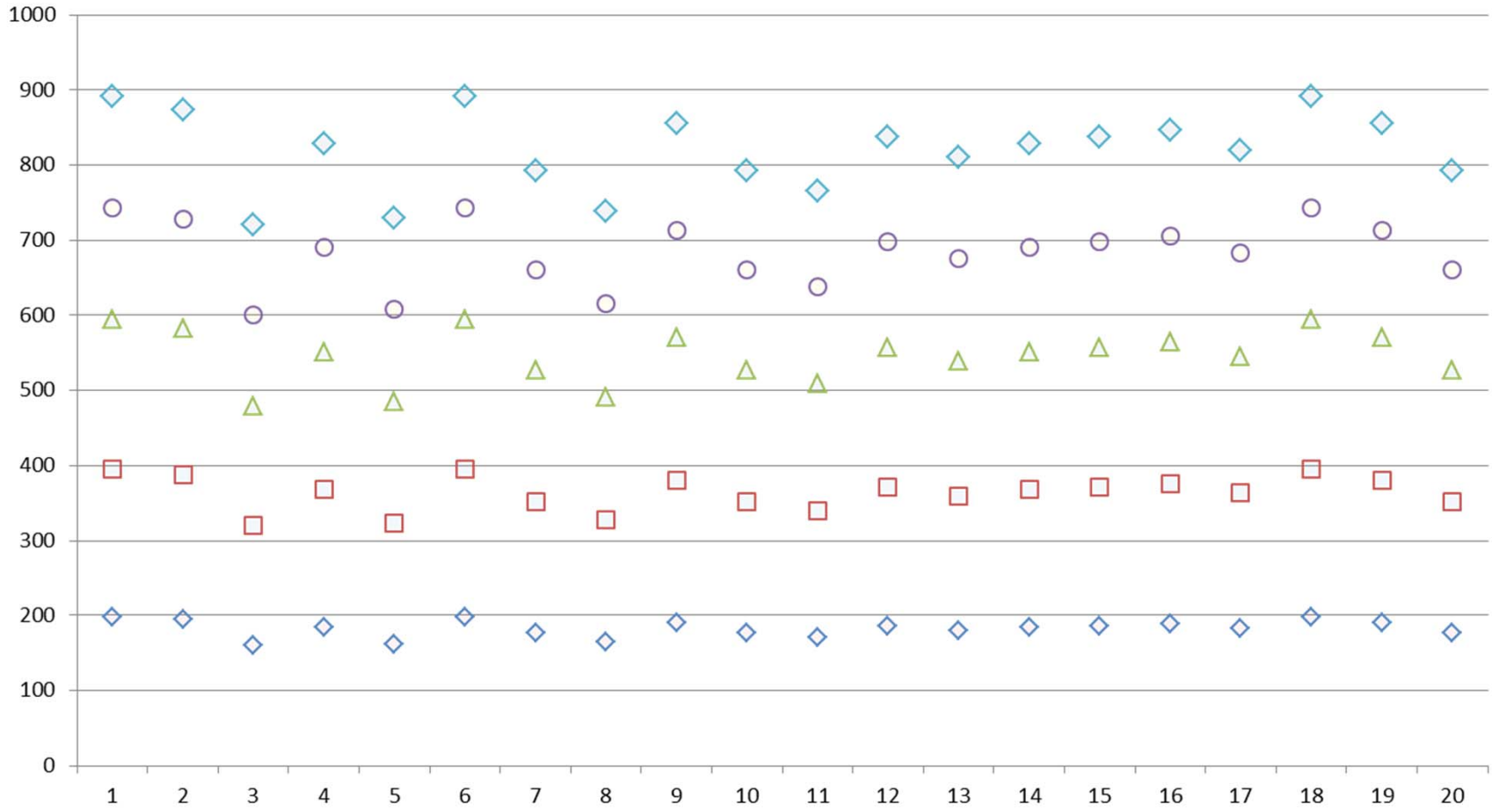
- Get all information in one measurement
  - All isotopes of all elements
  - Low concentrations and high concentrations
- Eliminate noise by using ratio's
  - Isotope ratio
  - Internal standard
- Change the method after the sample is measured
  - Every piece of information is there
  - Compensate the surprises in some samples

Advantages of Simultaneous Detection

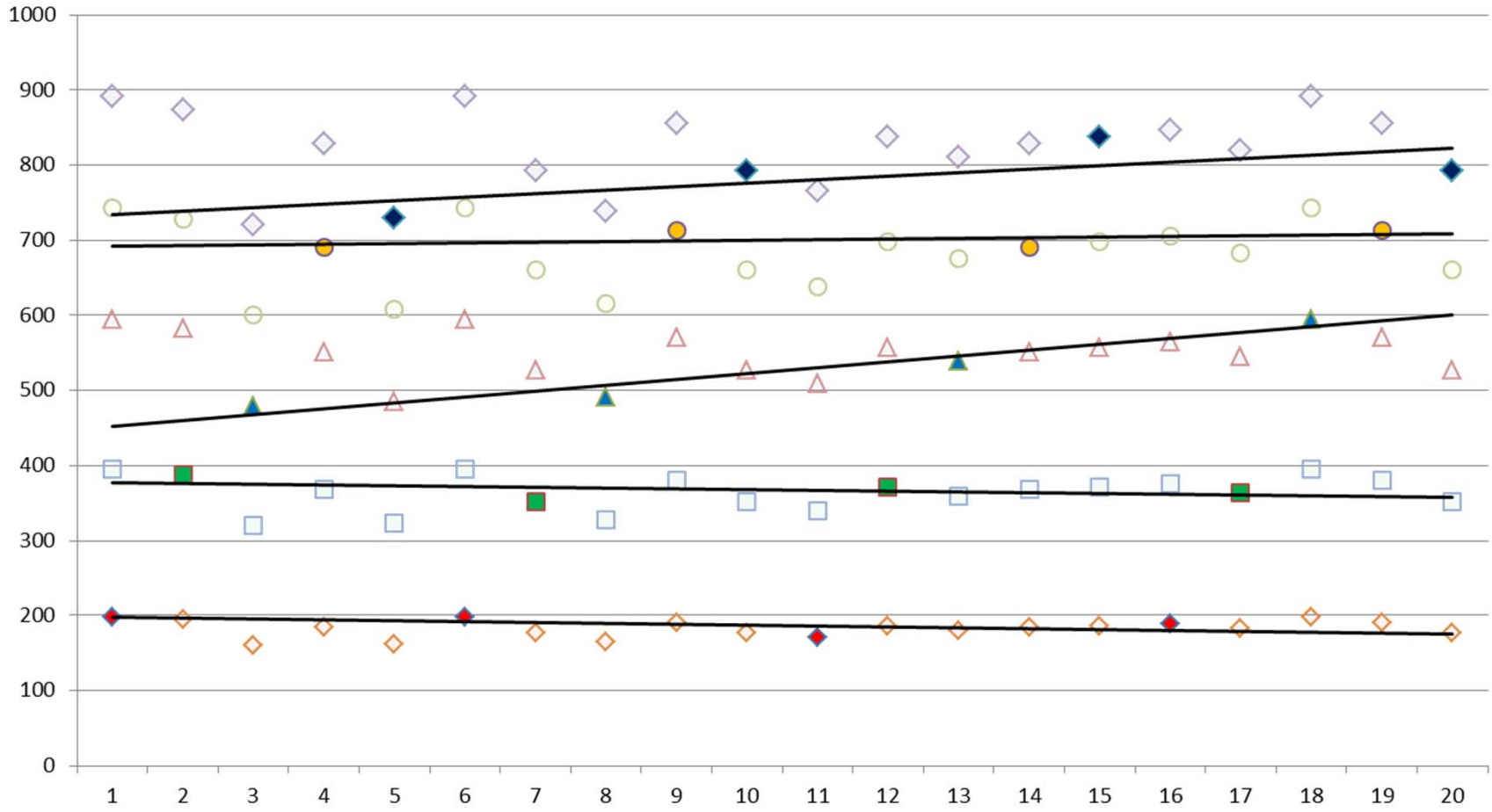
- Calculating the ratio of two signals measured at the same point in time:
  - Elimination of all noise from the sample introduction system
    - Flicker noise from the plasma
    - Pulsation from peristaltic pump
    - Pulsation from Laser Ablation
  - Ratio of 2 signals
    - Isotope ratio
    - Isotope dilution
    - Element ratio (Geology, ex. REE pattern)
    - Quantitative analysis (internal Standard)



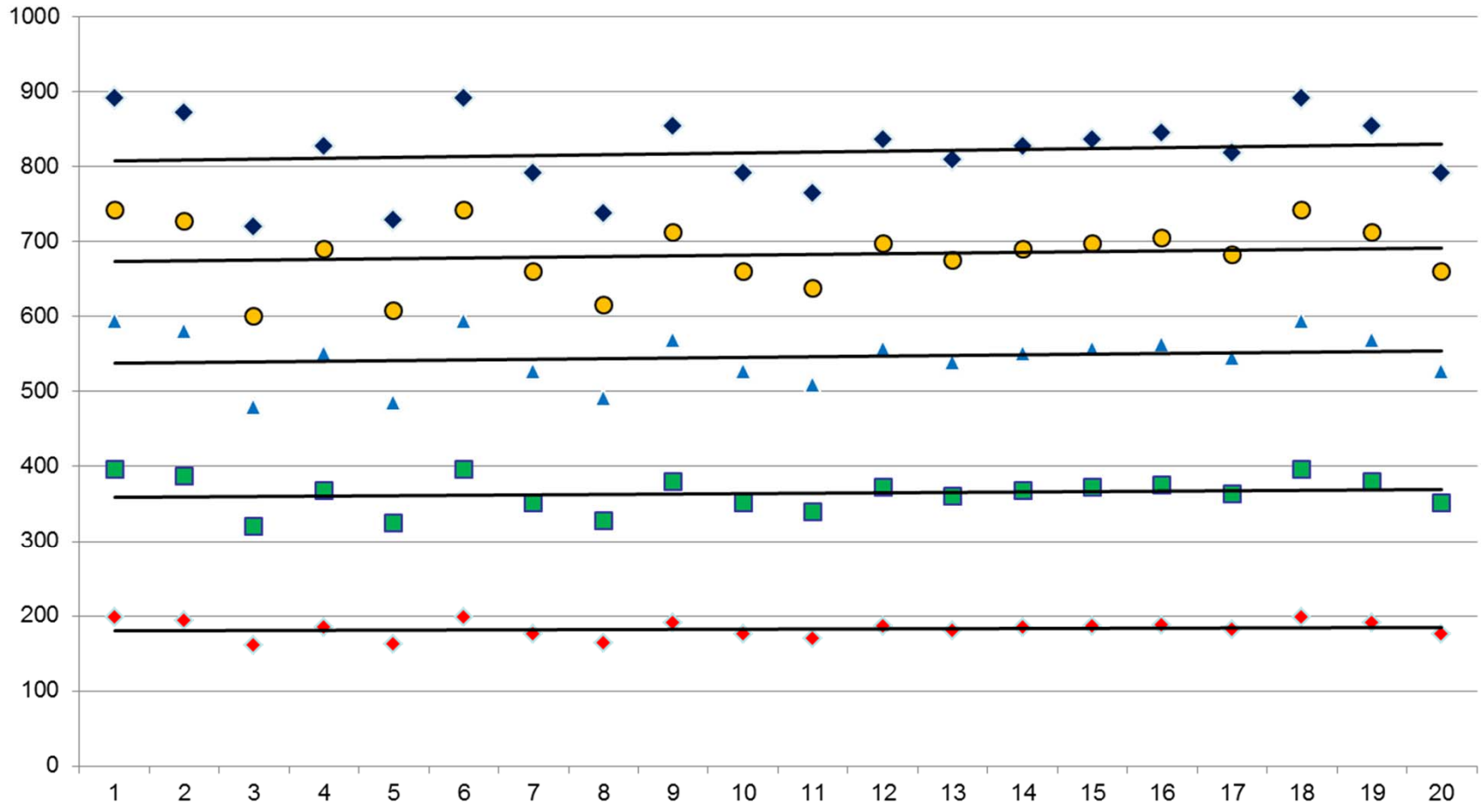
ICP as Ion source: Signal of 5 Isotopes



5 Isotopes Measured Sequentially

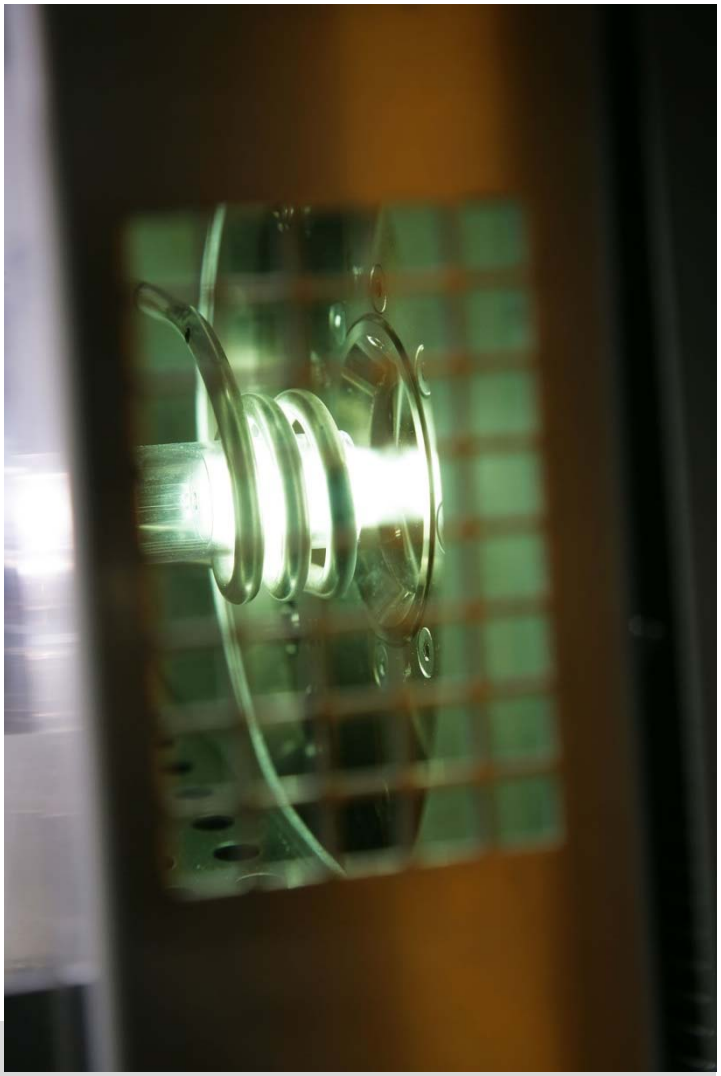


5 Isotopes Measured Simultaneously



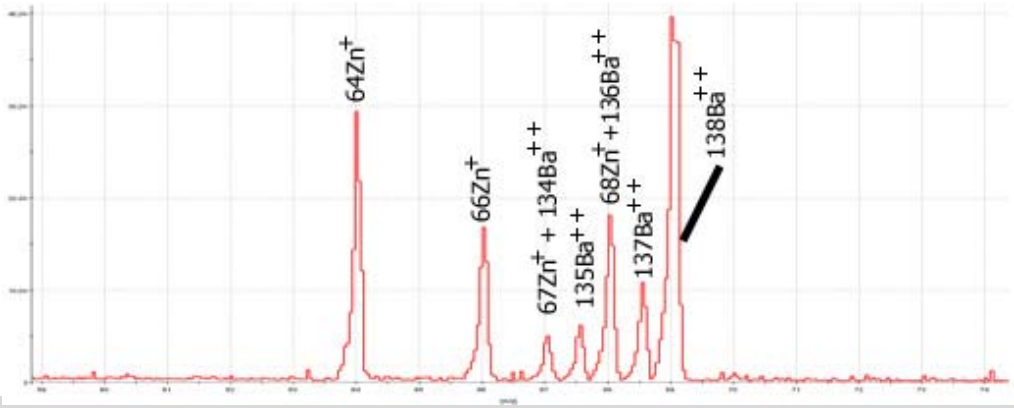
Advantages of Simultaneous Detection

- Precision should be substantially improved
  - In theory by 1 – 2 orders of magnitude



Advantages of Simultaneous Detection

- Always record the complete mass spectrum:
  - Do the method development after the sample is measured
    - See unexpected interferences
    - Detect unexpected elements
    - Include interference corrections after the measurement is completed
  - Review spectra of samples that do not exist anymore



Suitable MS layouts: Mass Spectrographs

- Mattauch-Herzog (1934): double focusing magnetic sector field MS

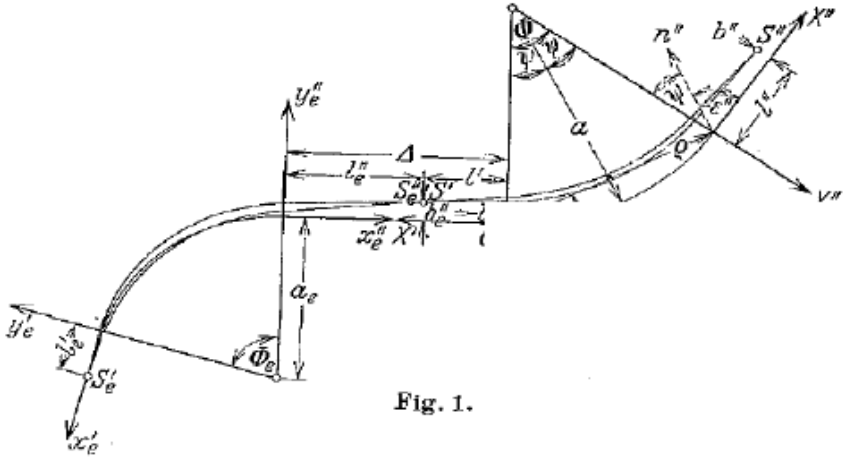


Fig. 1.

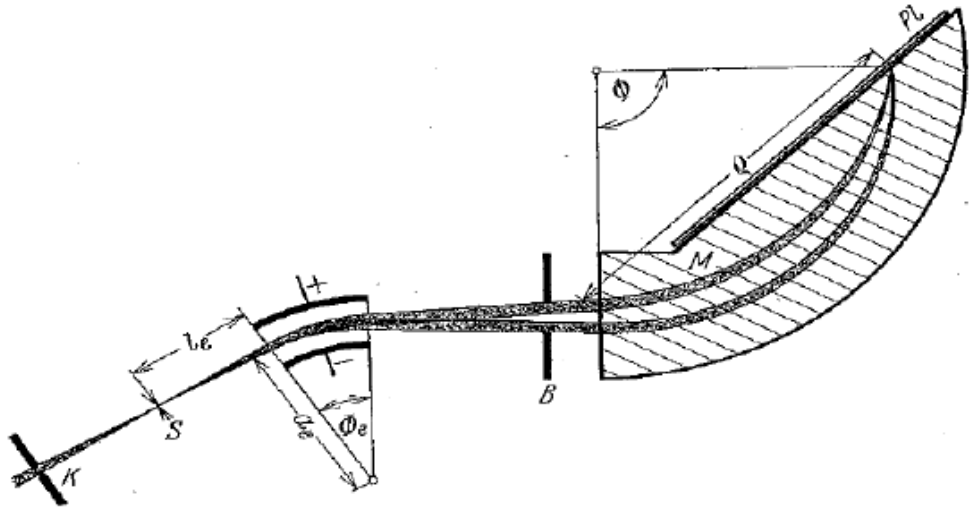


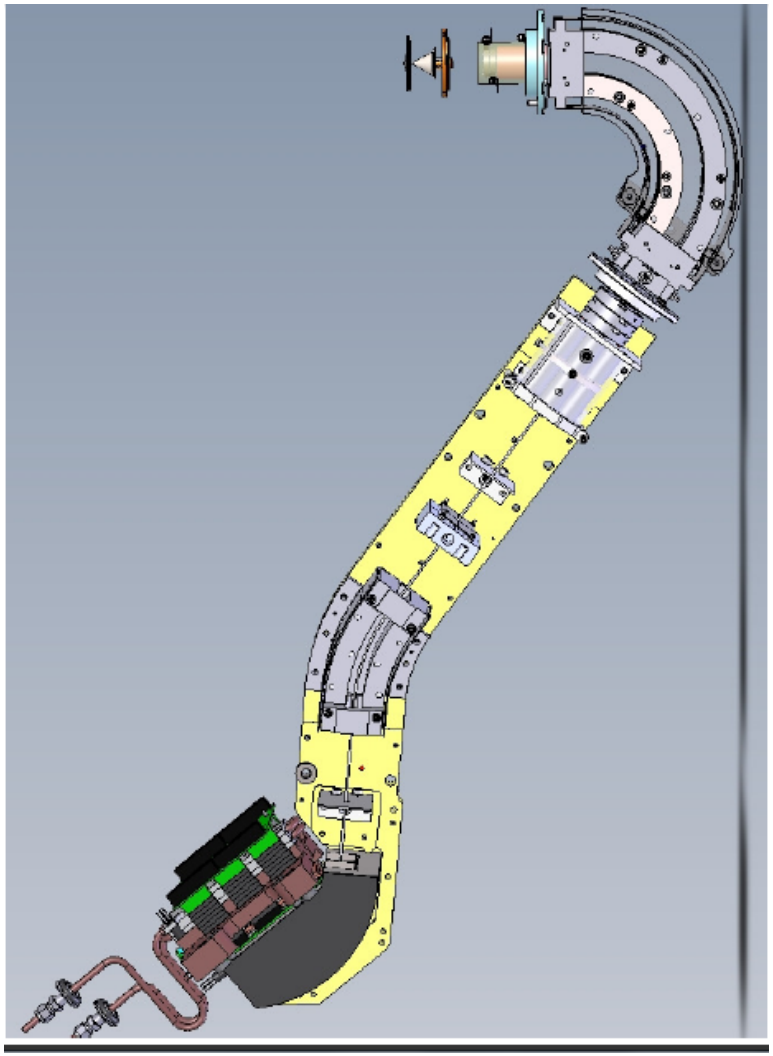
Fig. 3.

Overview

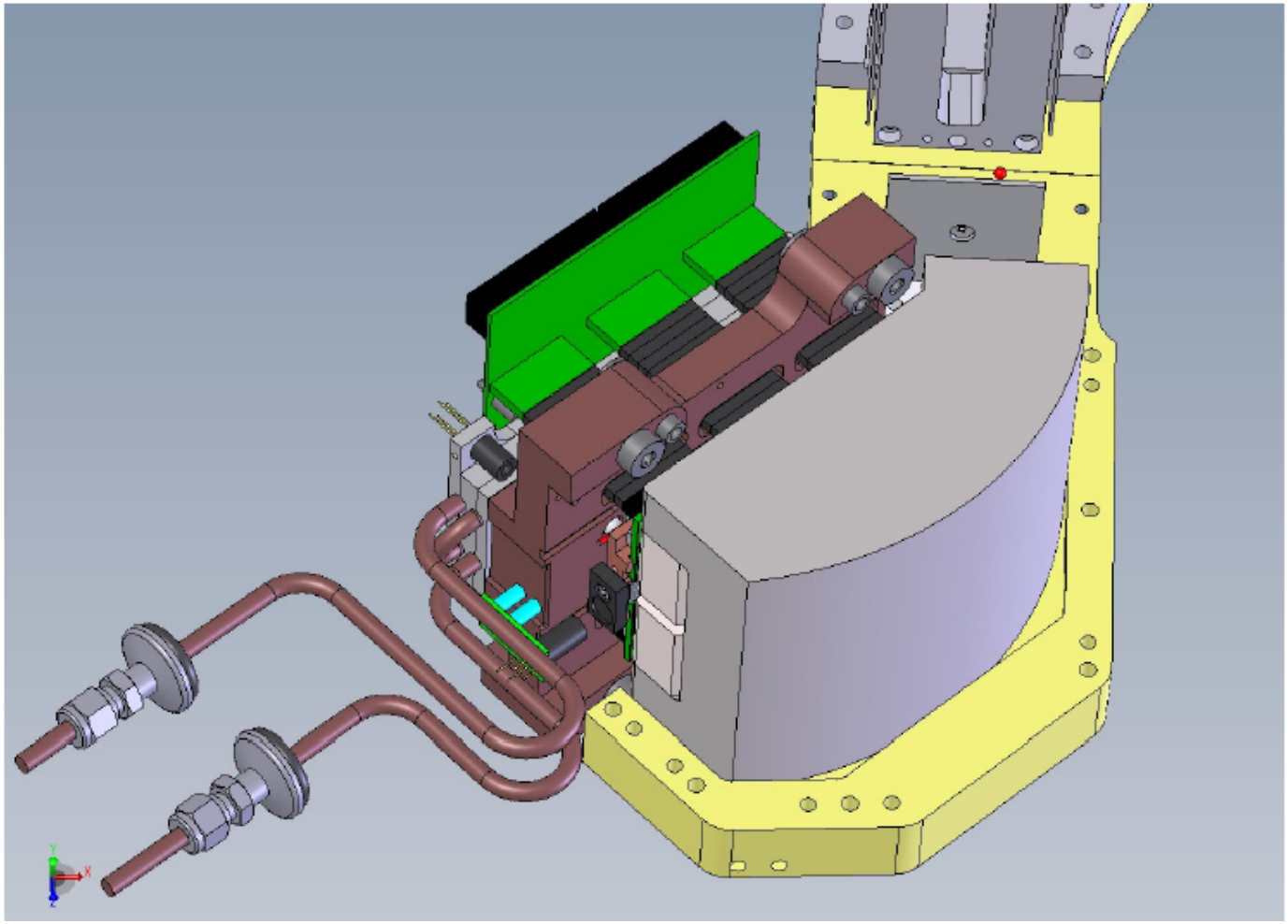
Ion Optic

Mass spectrometer

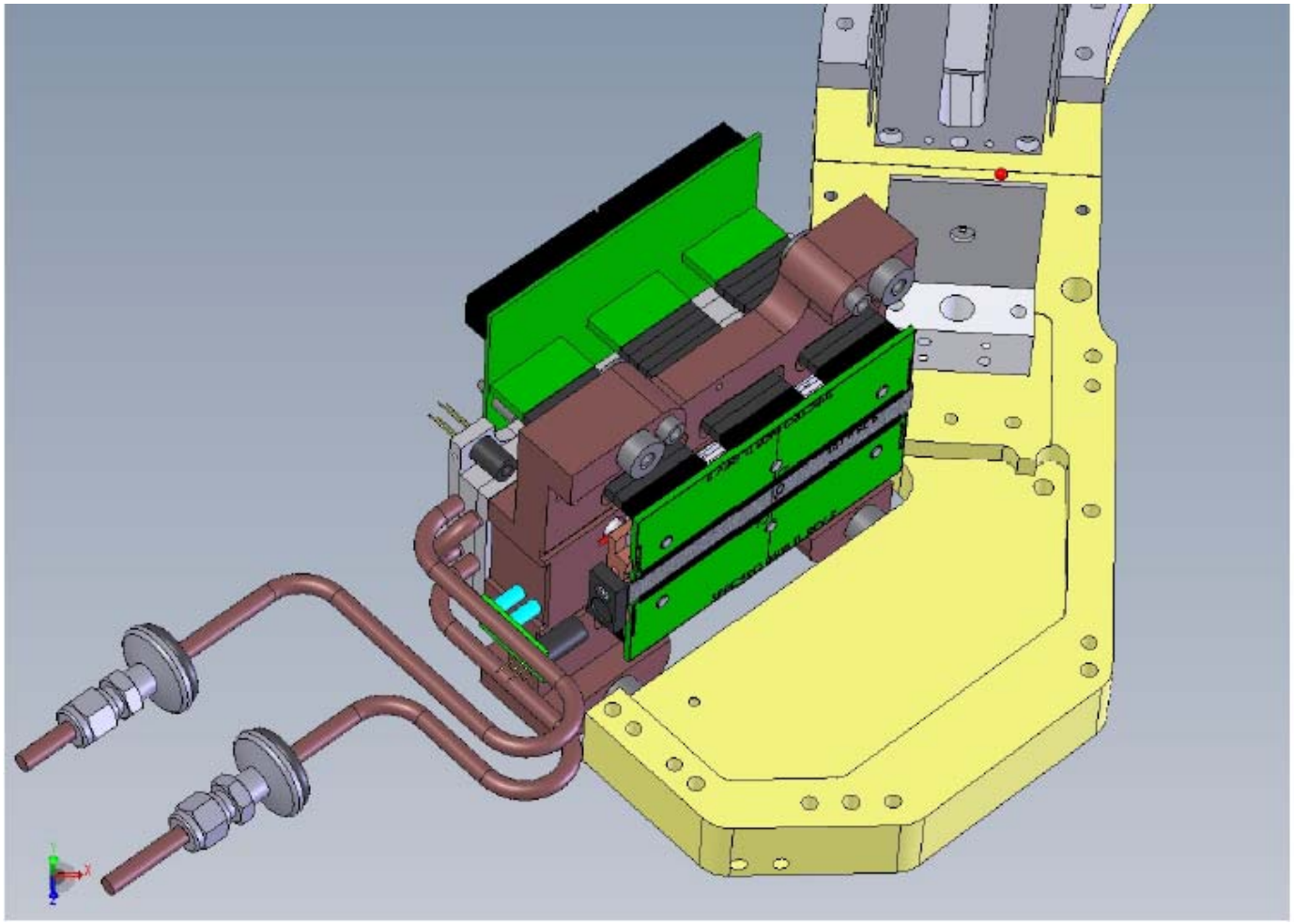
Detector



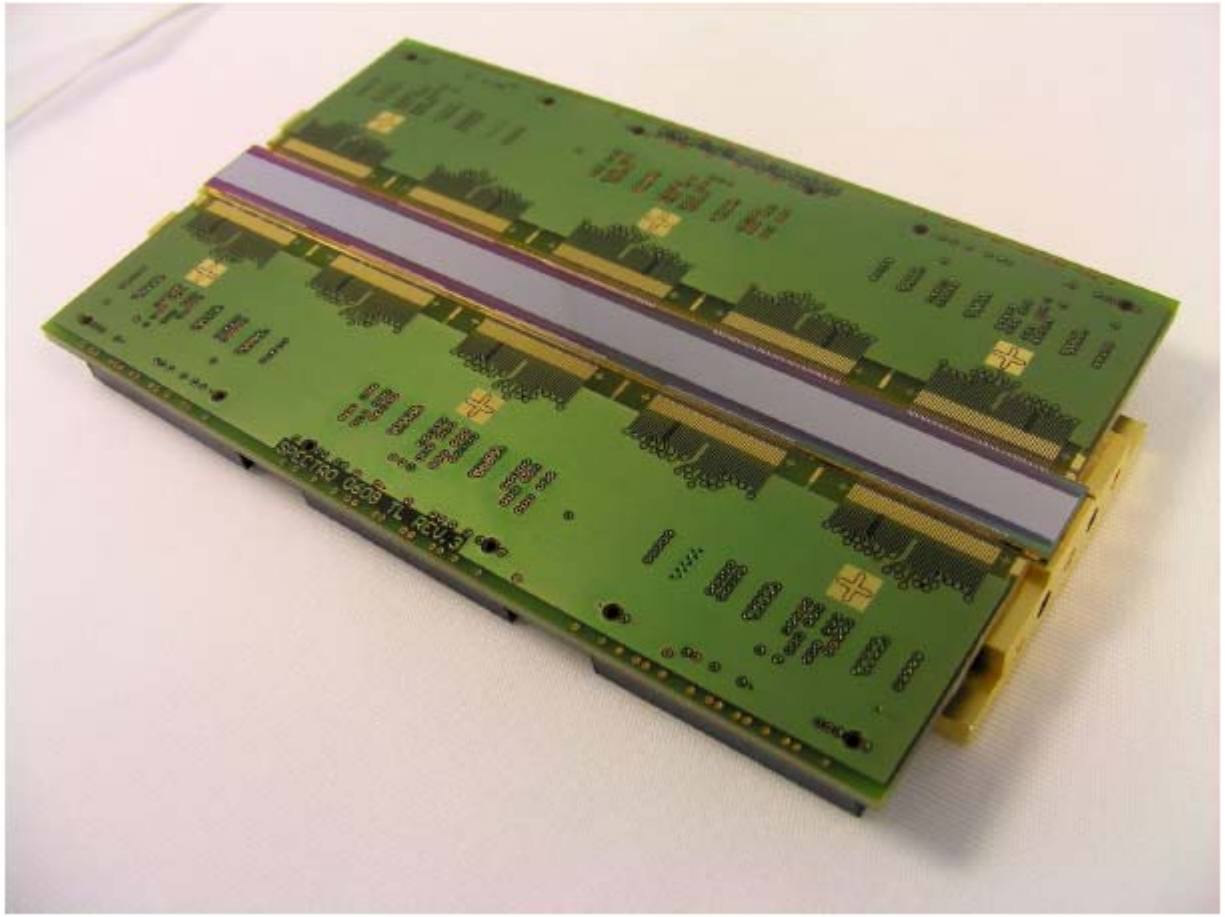
Magnet and Detector with Detector cooling system



Detector with Cooling System



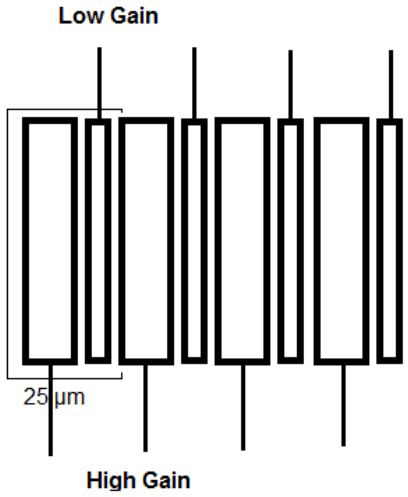
Semiconductor Direct Charge Detector “Ion 120”



- CMOS (Complementary Metal Oxide Semiconductor) technology
- 120 mm sensor
- 4800 channels
  - Two fixed gains
- Cooling to -17°C
- Designed for SPECTRO

Semiconductor Direct Charge Detector “Ion 120”

- Very robust detector
  - Survival after ion dose rates of 10^{13} ions/sec
    - The detector is not be expected a consumable
  - No cross talk
    - Located between every high gain strip is a low gain strip
    - High and low gain part is connected to different sides of the detector



Semiconductor Direct Charge Detector “Ion 120”

- How does the detector work?
  - Every incoming ion is discharged and converted into an atom
    - Depending on the properties of this element, the atom:
      - Is pumped out as a gas or stays on the surface as a metal
    - The connected electronic is amplifying this current of electrons to the detector channels
      - This information is stored in different capacitors
      - The information is checked every basic integration cycle

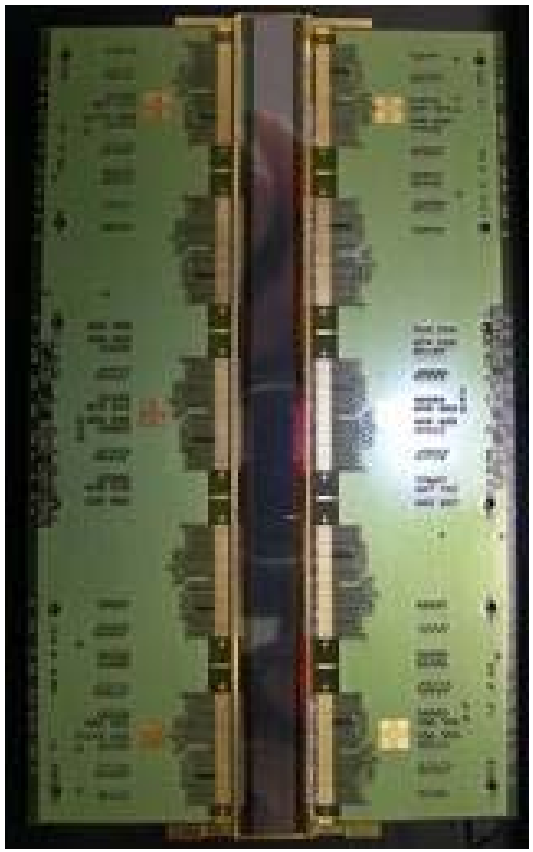
- A potential change on the detector does not change the property of the detector to deliver one electron per incoming ion.
- → the detector is not expected to age
- → The detector is not expected to be a consumable

Detector Readout

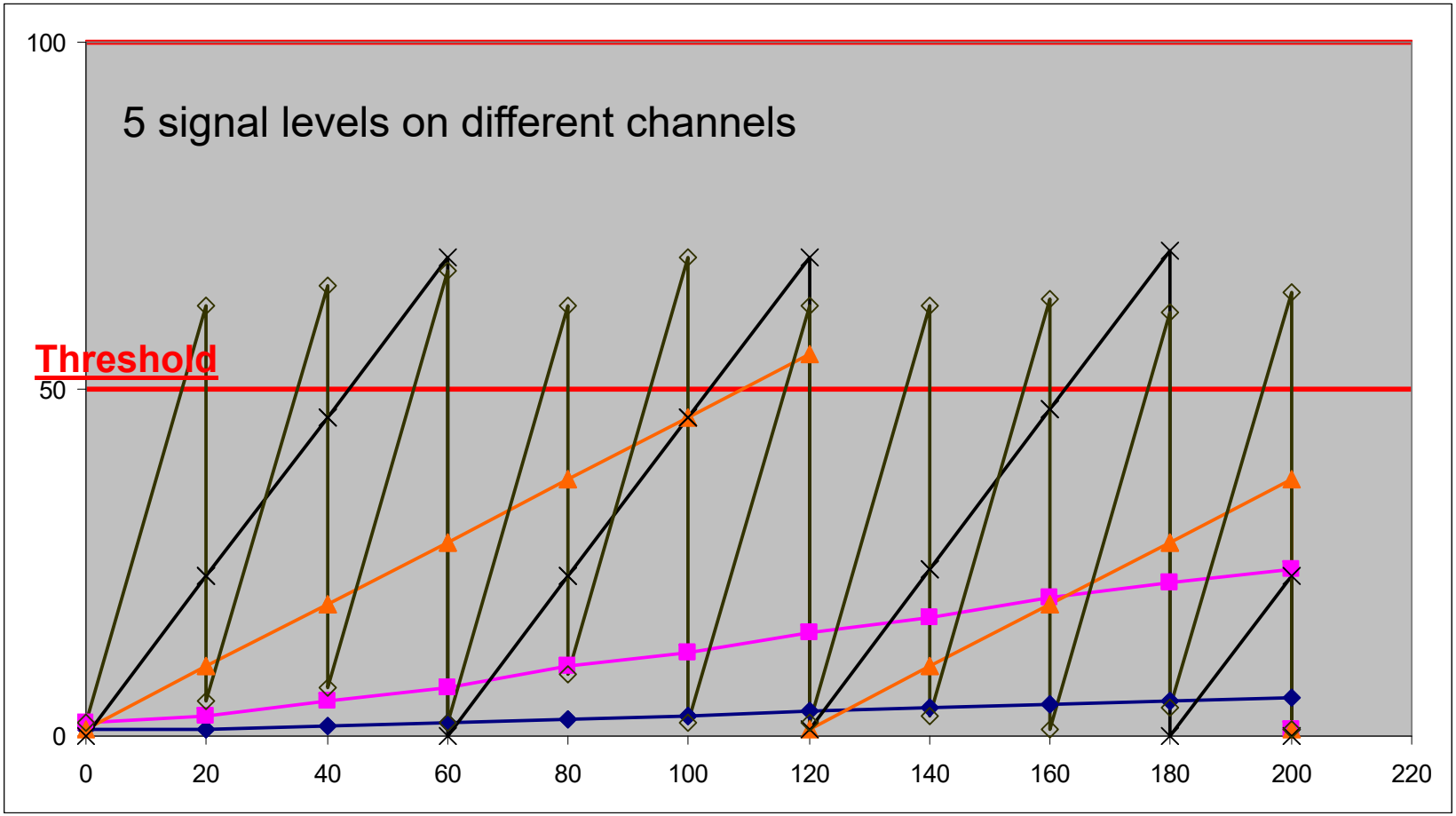
- Two possibilities available in the software
  - Counter Mode
    - Forced readout every basic integration cycle
    - Every 20 ms readout,
    - Data transfer every 100 ms
  - Threshold mode
    - Check if a readout if required every 10 ms
    - Data transfer after replicate is complete

Non destructive read out, threshold mode

- Every basic integration cycle, the camera makes a non destructive readout of each channel and detector
- Only, when a certain threshold is exceeded, the channel goes through a reset
- If a channel is reset, a second readout happens immediately.
  - Correlated double sampling
  - Second readout acts as baseline for next readout



Threshold Mode with Correlated Double Sampling



The total measurement time can be adjusted

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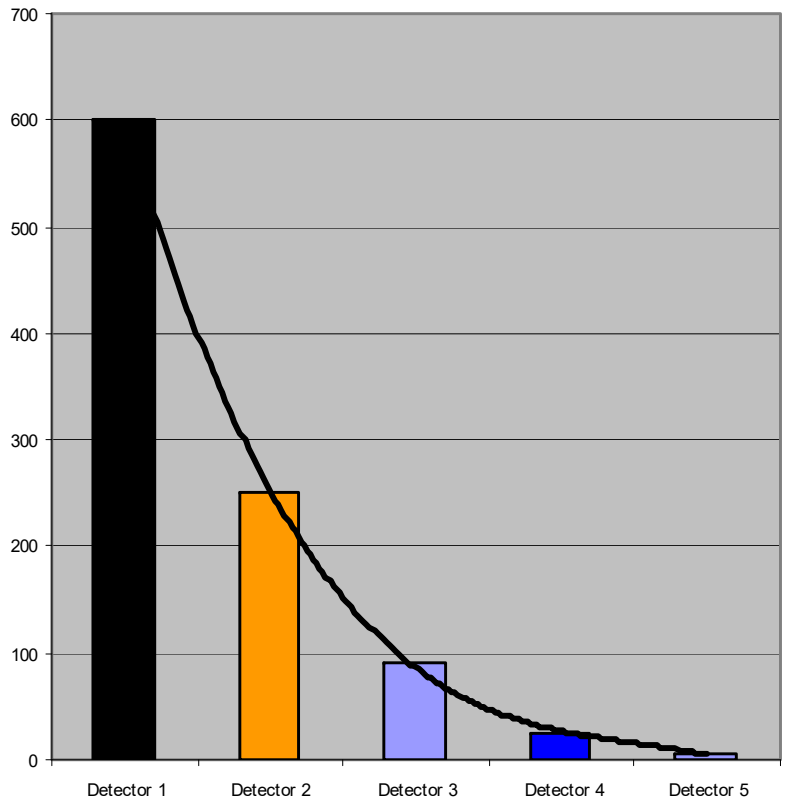
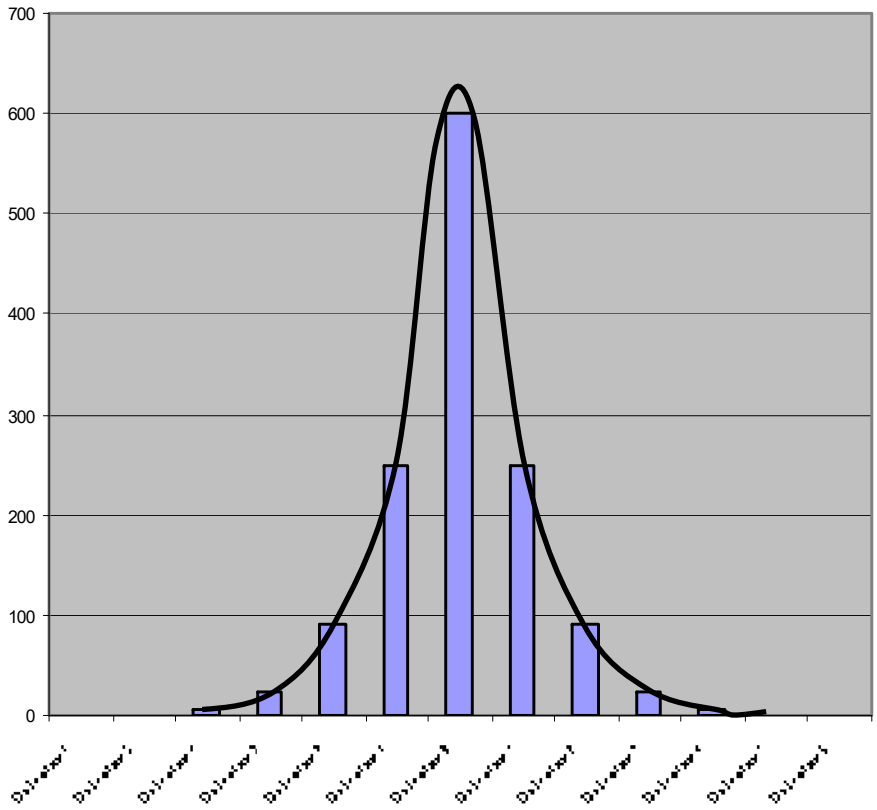
Threshold Mode with Correlated Double Sampling



Detector 1	600	10*60	10 reset
Detector 2	230	3*69 + 23	3 reset
Detector 3	90	1*54+36	1 reset
Detector 4	24	24	
Detector 5	5	5	

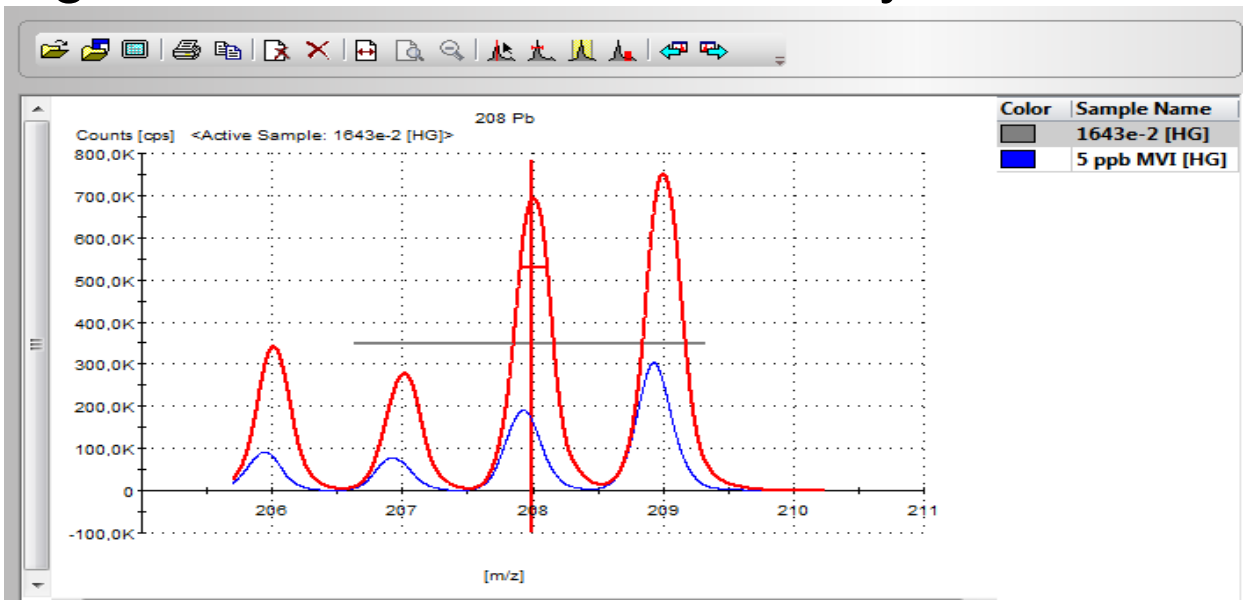
10 Channels



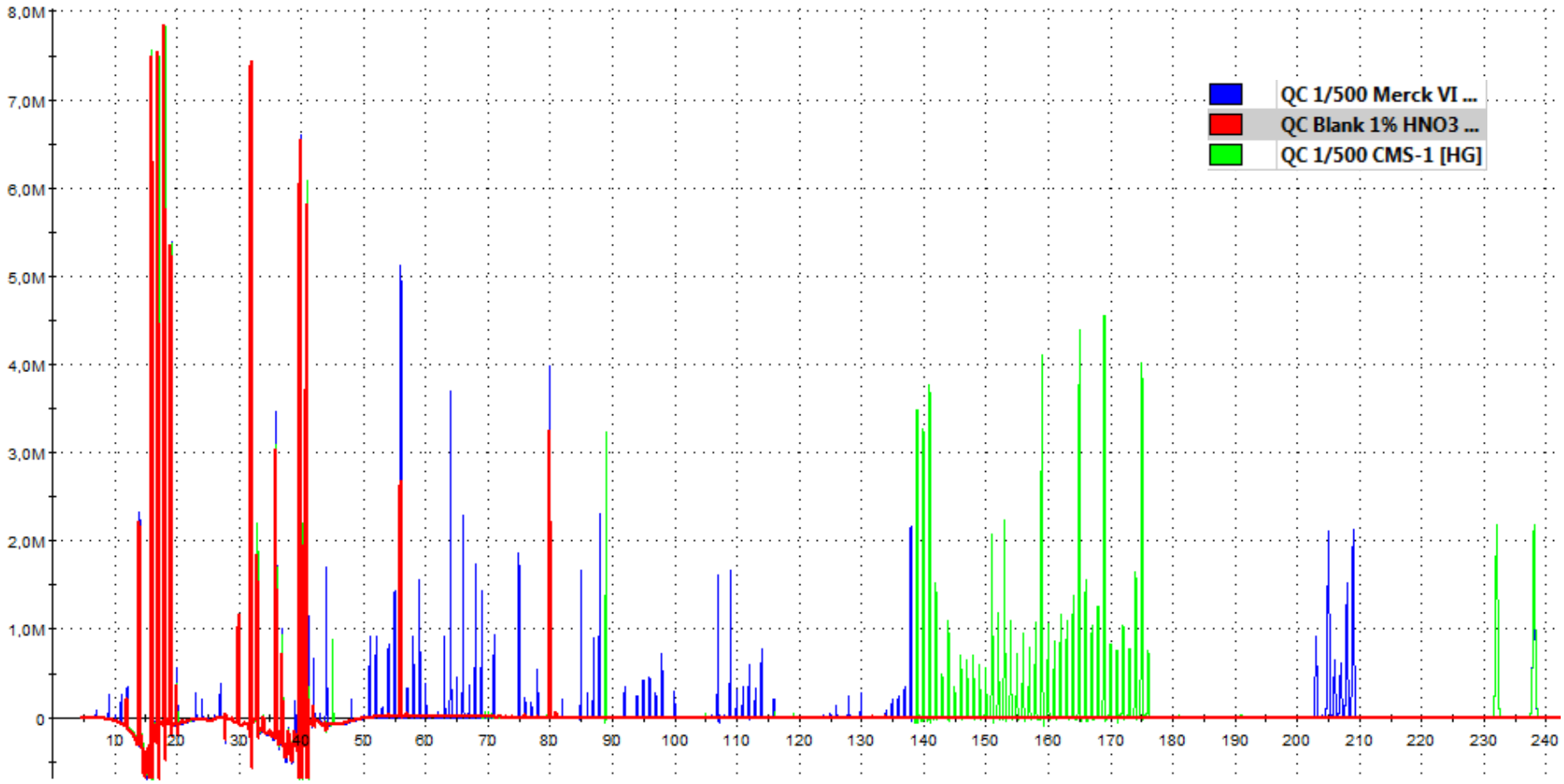
- Average 20 channels/amu
- Multiple datapoints/peak
  - Set peak maximum
  - Set integration range
    - Whole peak for best precision
  - Set background correction

Peak definition for method

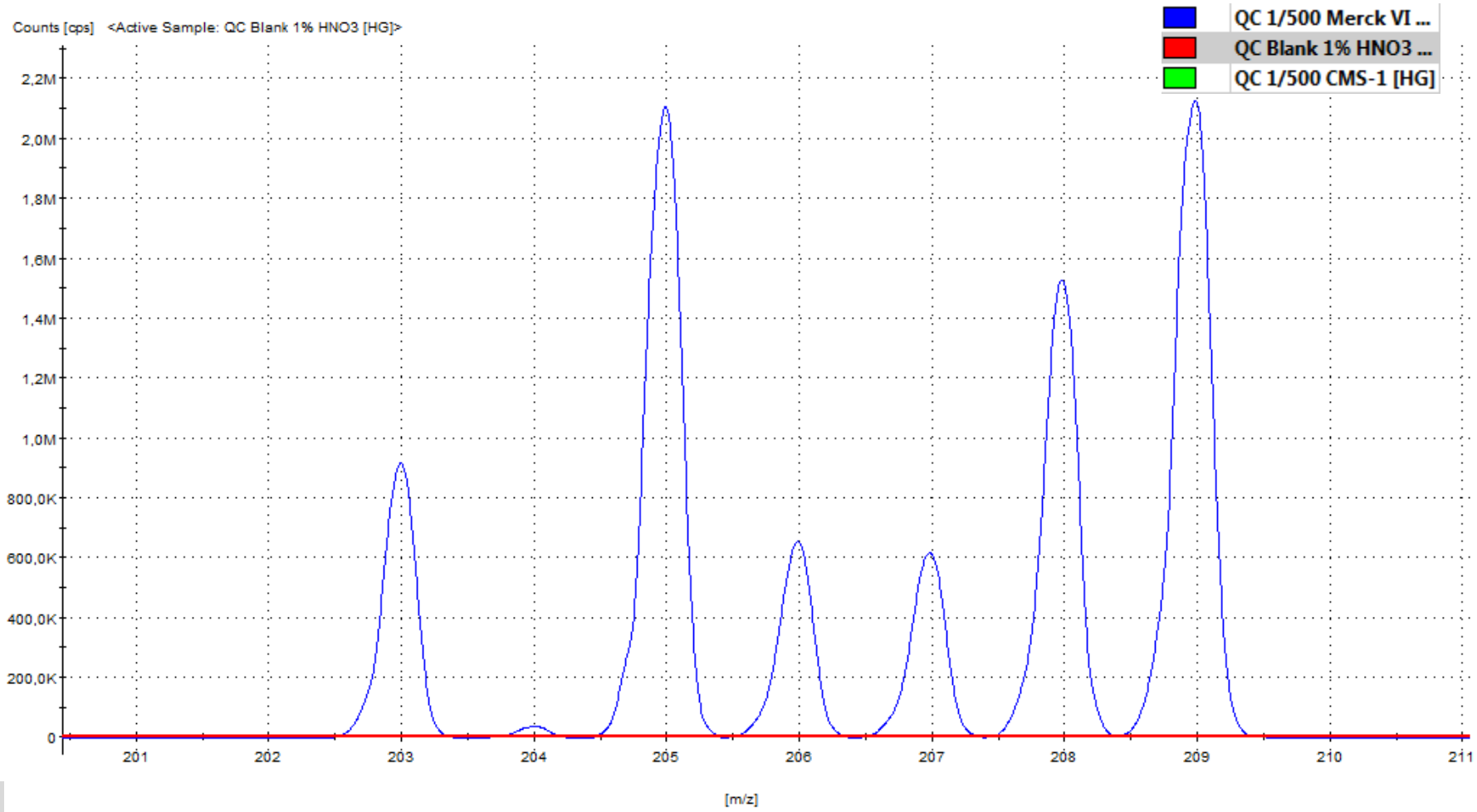
- Peak maximum
  - ICAL procedure
- Integration range
- Background correction if necessary



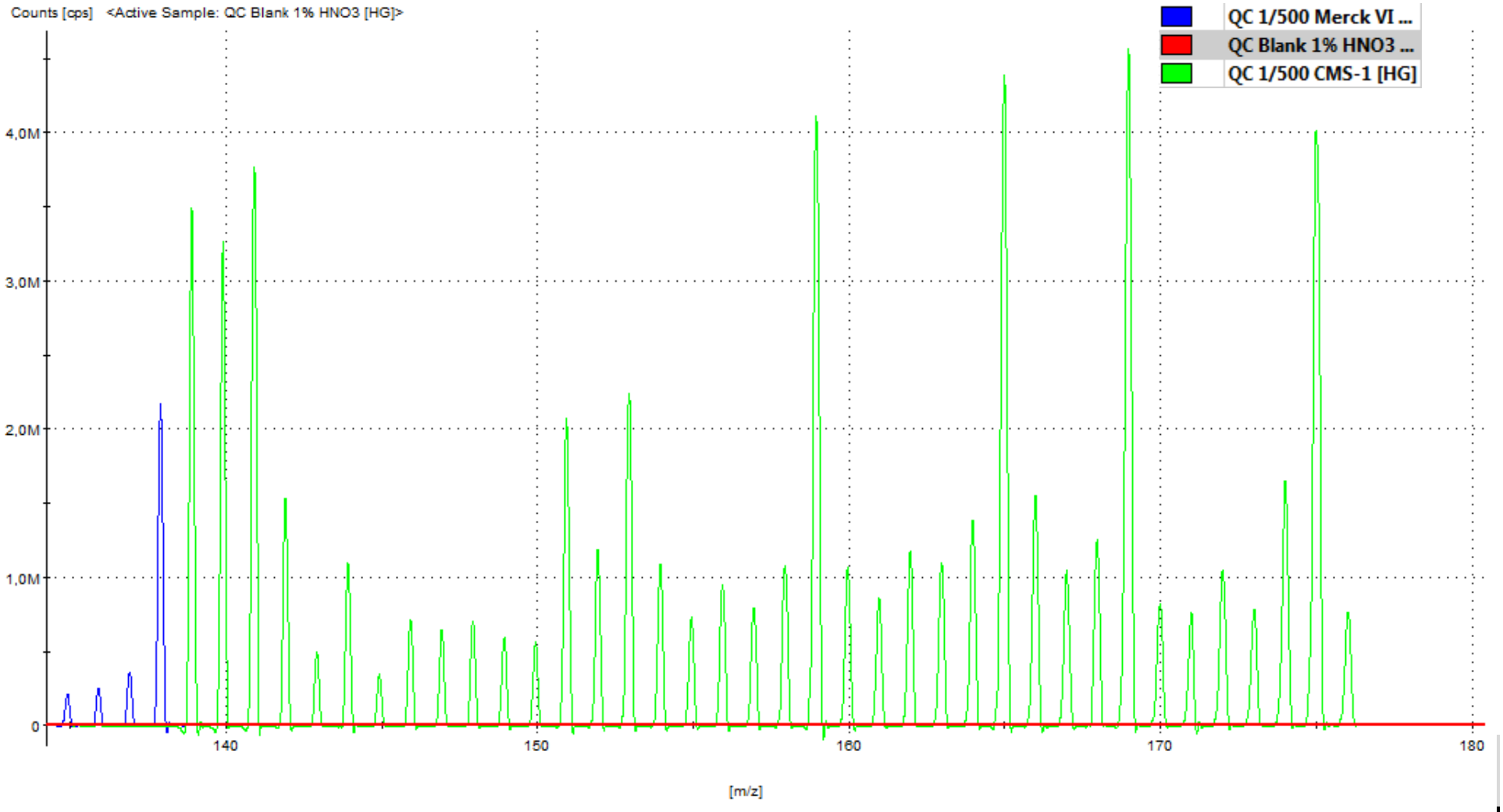
Simultaneously measured mass spectra 10 sec



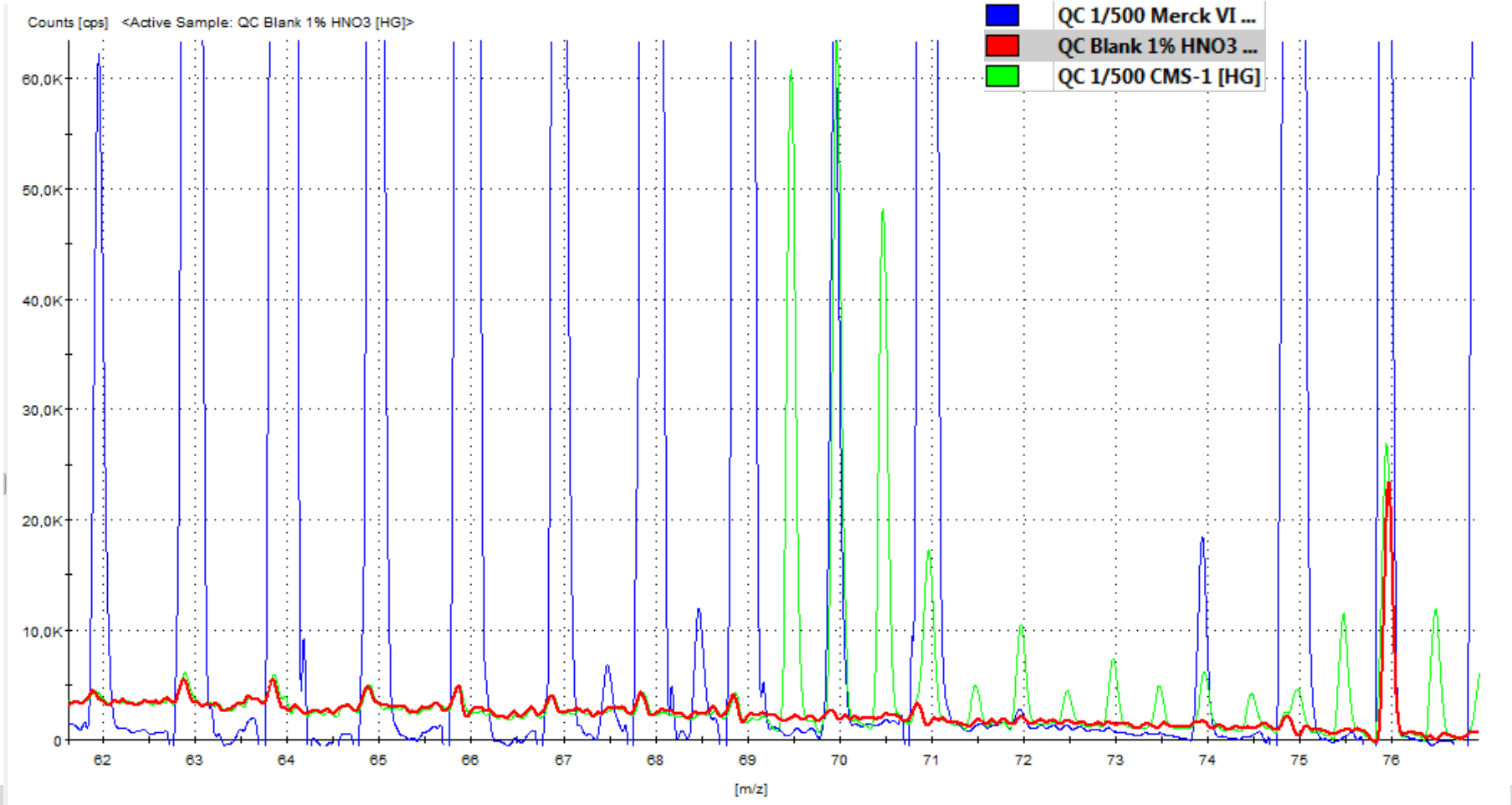
Simultaneously measured mass spectra 10 sec



Simultaneously measured mass spectra 10 sec



Simultaneously measured mass spectra 10 sec



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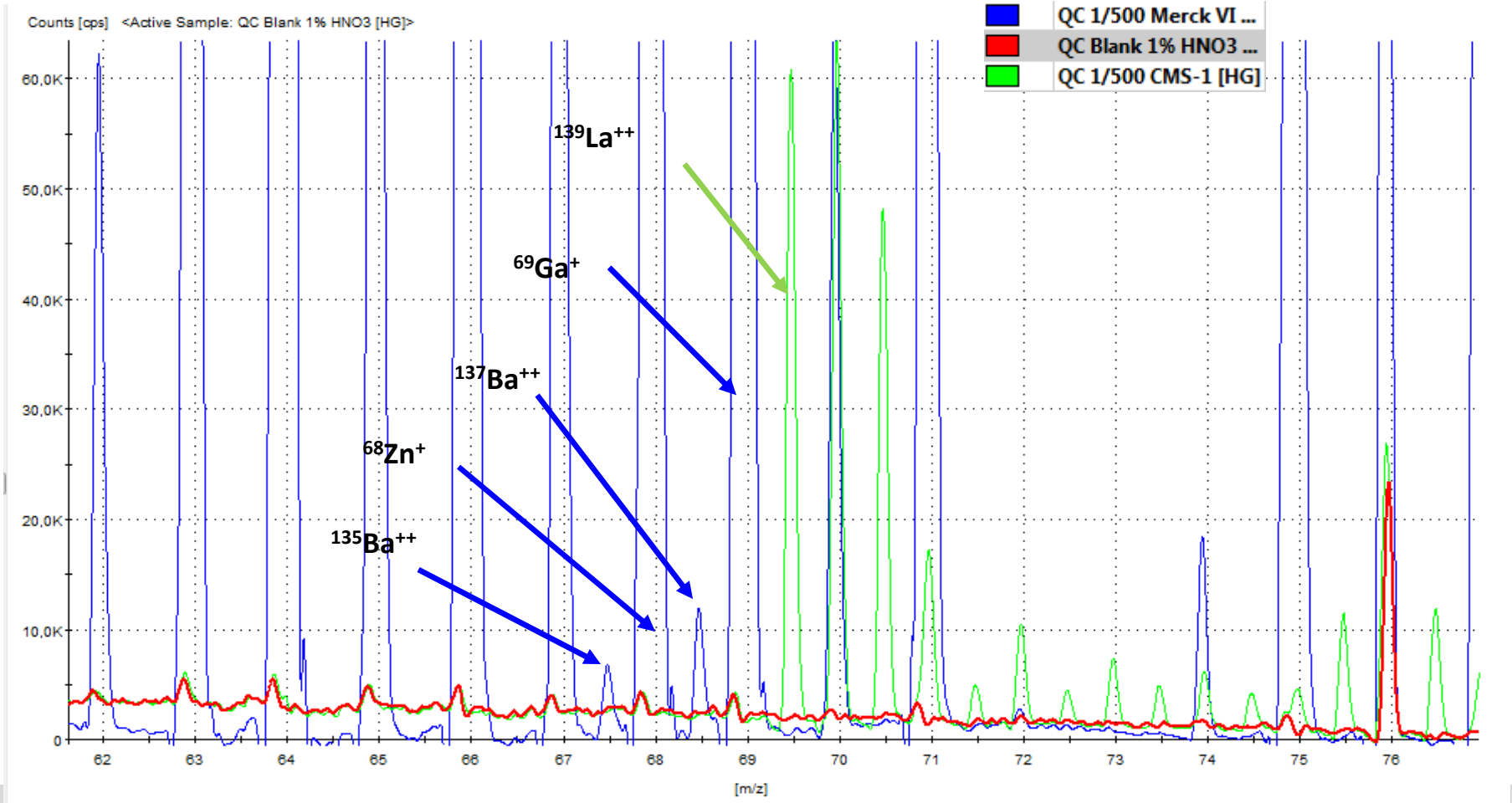


www.spectro.com

When you have the complete spectrum

- **Let the software do the job**
  - Subtract the blank spectrum
  - Let the software rebuild the measured net spectrum with the isotopic pattern of the elements and interferences
    - About 220 datapoints for 100 elements plus interferences
  - Get qualitative results for elements never calibrated and a standard is not available
  - See the unexpected

Fully simultaneous now means

- **On every measurement**
  - **Every mass from 6 to 241**
    - Li to Uranium
      - 241 as limit is set by the German BAFA
  - **Low concentration to high concentration**
    - Compared to most simultaneous ICP-OES

Outline

- Hardware
  - ICP-MS
    - Advantages of simultaneous ICP-MS
    - ICP as Ion source
    - Mass spectrometer
    - How does the detector work
- **Simultaneous measurements**
  - **Precision of measurements**
  - **Interference Correction**
- Summary

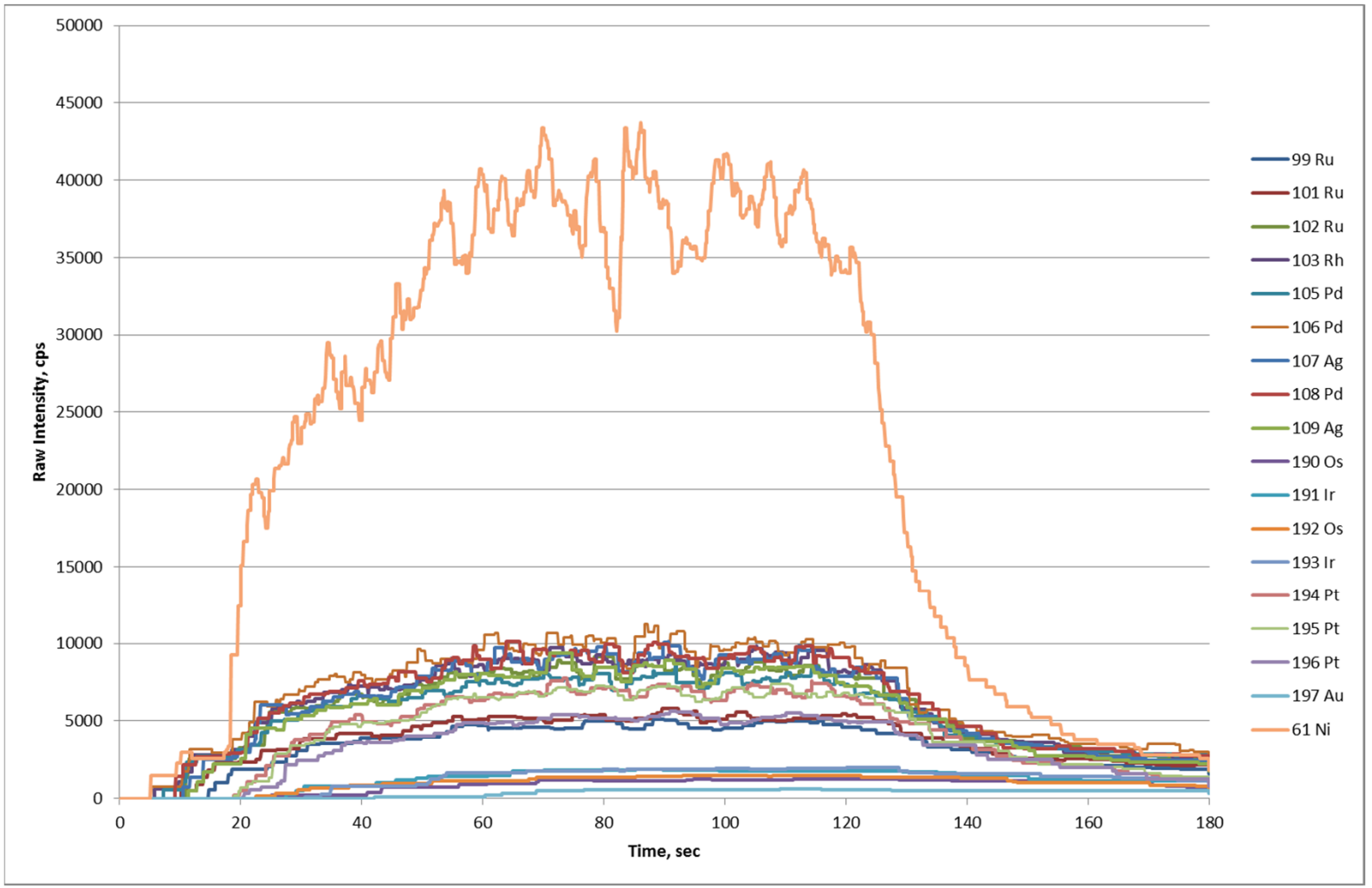
Precision: PGE Determination

	101Ru [µg/L]	103Rh [µg/L]	106Pd [µg/L]	108Pd [µg/L]	185Re [µg/L]	191Ir [µg/L]	193Ir [µg/L]	194Pt [µg/L]	196Pt [µg/L]	197Au [µg/L]
Sample 1	0.58	0.60	0.66	0.64	0.61	0.68	0.65	0.64	0.64	0.85
RSD %	0.66	0.25	0.70	0.99	0.29	0.56	0.34	0.59	0.71	3.01
Sample 2	5.81	5.66	5.94	5.87	5.77	5.95	5.98	6.03	6.02	6.04
RSD %	0.21	0.32	0.22	0.17	0.14	0.16	0.16	0.26	0.21	1.00

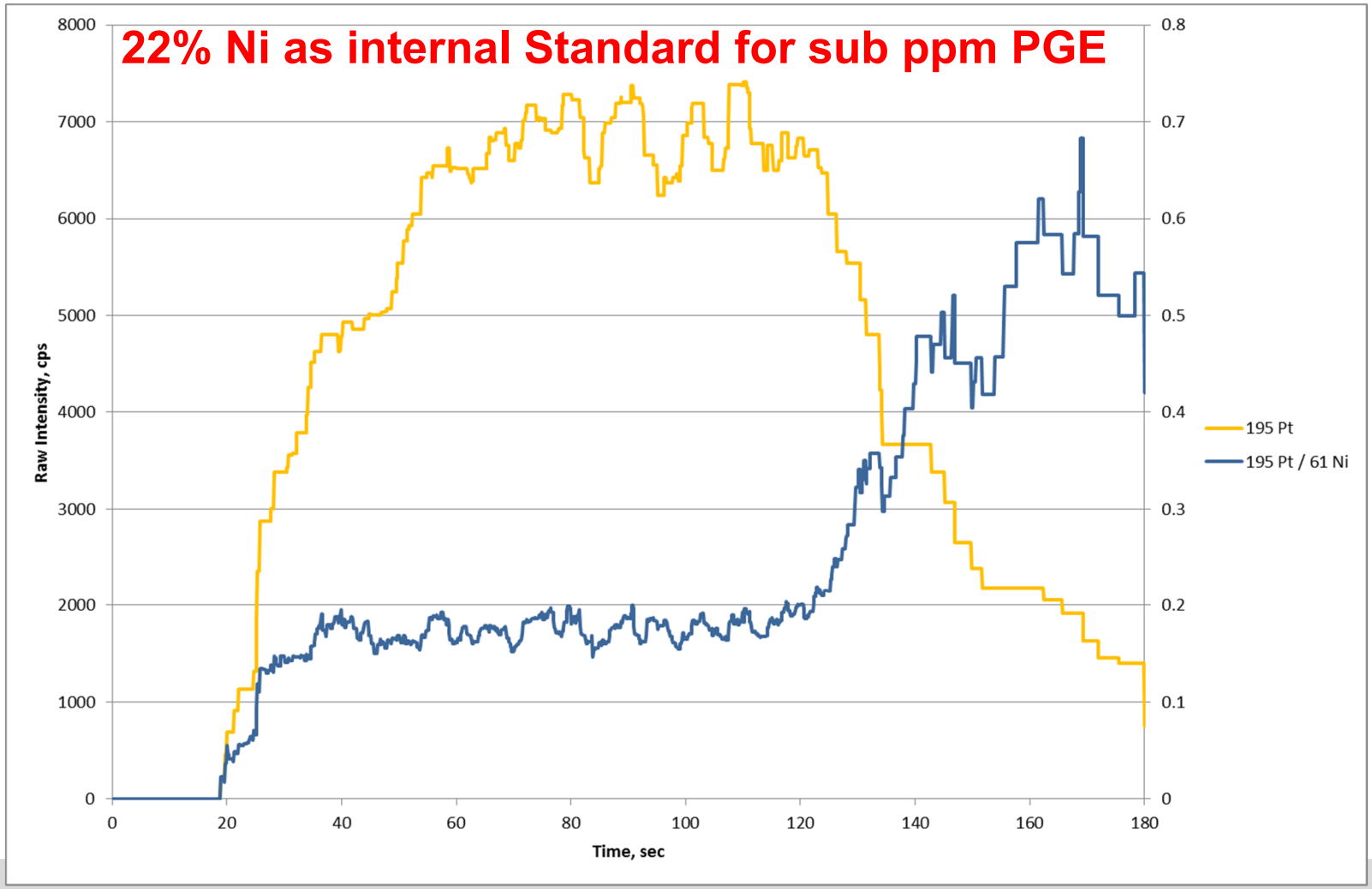
Results for synthetic samples with typical precious metal concentrations, Sample 1: 0.6 µg/l, Sample 2: 6 µg/l

20 sec per replicate, In as internal Standard

Precision: Transient Signals

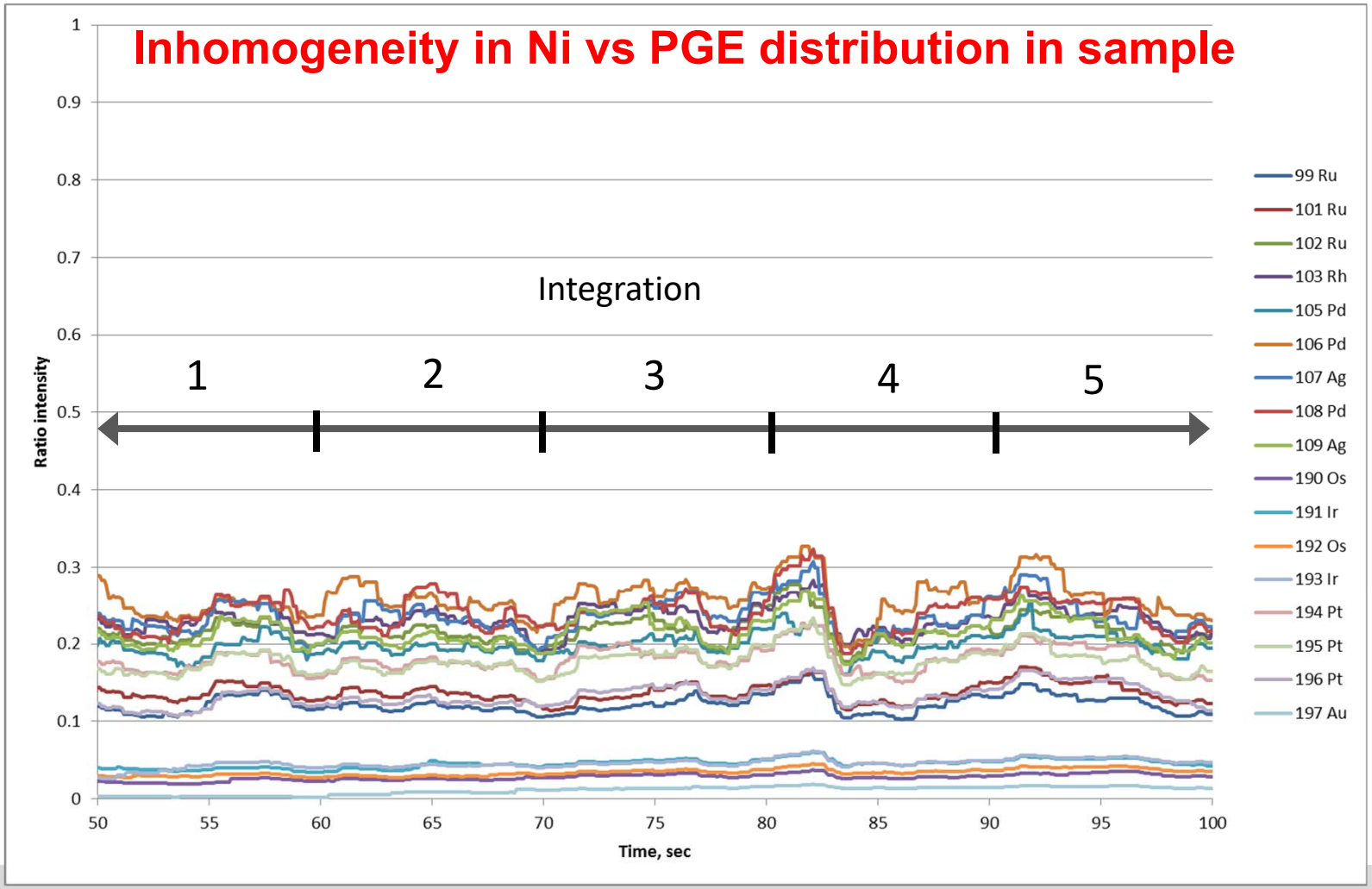


Precision: Transient Signal Ratio



Precision: Transient Signal Ratio

Inhomogeneity in Ni vs PGE distribution in sample



Multielement Isotope Ratio

Ratio	Li 6/7	B 10/11	Sr 86/88	Sr 87/88	Ag 107/109	Pb 204/208	Pb 206/208	Pb 207/208
1	0.08031	0.24503	0.11687	0.08578	1.08513	0.02491	0.45227	0.43387
2	0.08039	0.24516	0.11694	0.08591	1.08541	0.02499	0.45267	0.43350
3	0.08038	0.24515	0.11699	0.08592	1.08465	0.02494	0.45216	0.43396
Average	0.08036	0.24511	0.11693	0.08587	1.08506	0.02495	0.45237	0.43378
Standard Deviation	0.000044	0.000072	0.000060	0.000078	0.000384	0.000040	0.000268	0.000244
RSD%	0.054	0.030	0.052	0.091	0.035	0.162	0.059	0.056

100 µg/l multi-element solution (B at 1000 µg/l) with a sample uptake rate of 0.8 ml/min and 3 replicates, each of 30 seconds measurement time

Total sample consumption : <2 ml

Isotope Ratio Uranium

Instrumentation	SPECTRO MS

Instrument settings	
Plasma torch	Standard Quartz, fixed 1.8mm injector tube
Nebulizer	Standard Seaspray
Spray Chamber	Cyclonic baffled
Power	1500 W
Coolant gas	12 L/min
Auxiliary	2.5 L/min
Nebulizer	0.94 L/min
Sample aspiration rate	1.5mL/min
Readtime	200 sec (10*20 sec)
Replicates	12
Sample	Uranium solution MVI 20ppb

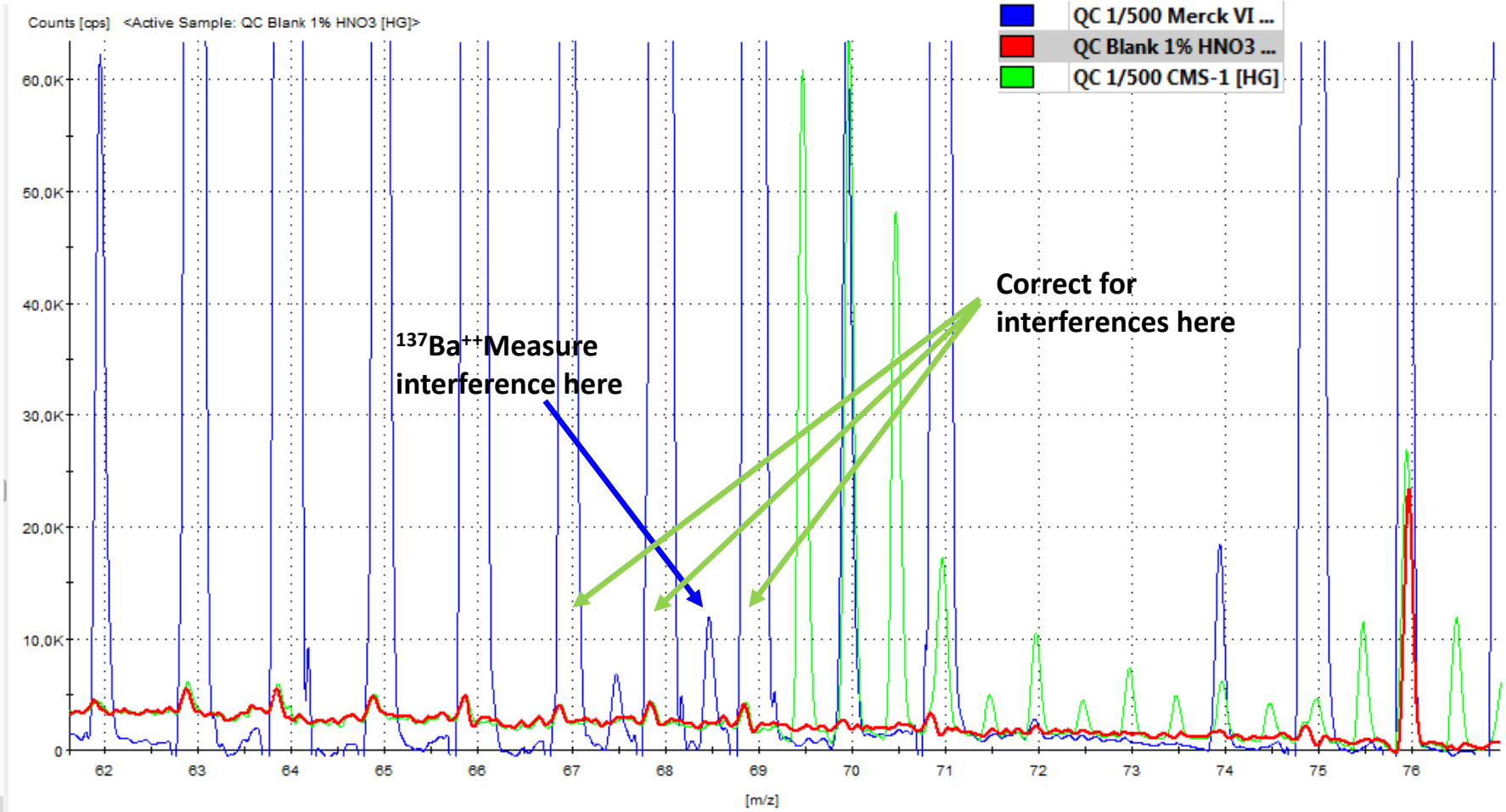
	238 U BGC Intensity	235 U BGC Intensity	Abundance U238	Abundance U235
<x>	925798	2657.2	99.7138	0.2862
sd	9876	24.2	0.0001	0.0001
rsd	1.1	0.92	0.0001	0.0524

Mathematical interference correction

- Lower formation of interferences formed by recombination in the interface
  - Different kinetic energy means different efficiency for transport to the detector
- Better precision of the mathematical correction due to simultaneous measurement
  - Depending on counting statistics
  - Calculations are based on concentrations

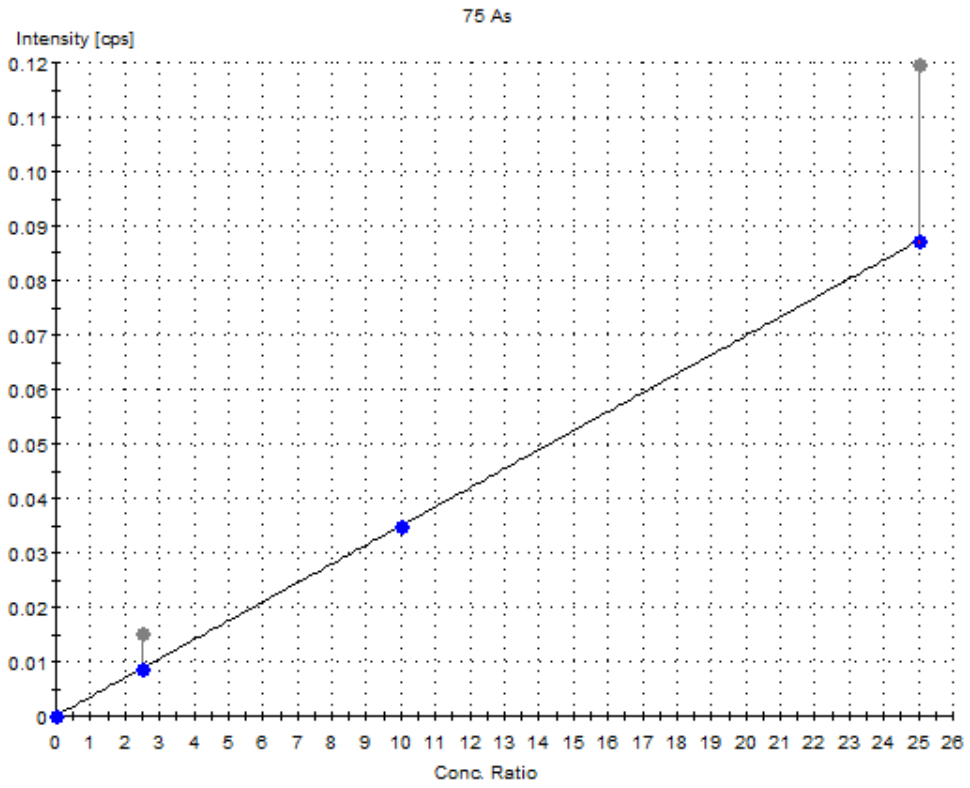
Doubly charged interference's

use the isotopes with uneven masses



Polyatomic interferences: Cl interference‘s

- Addition of Cl to some defined As standards



Coef. A0:	-0.0097467
Coef. A1:	286.65
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Mass Range:	0.0211 µg/l - 30 µg/l
Isotope Info:	
BEC:	3.86 µg/l
DL:	0.0211 µg/l
Std.Error:	0.0182 µg/l
Corr.Coef.:	1
Dist.Factor:	Factors defined in Conc/Conc

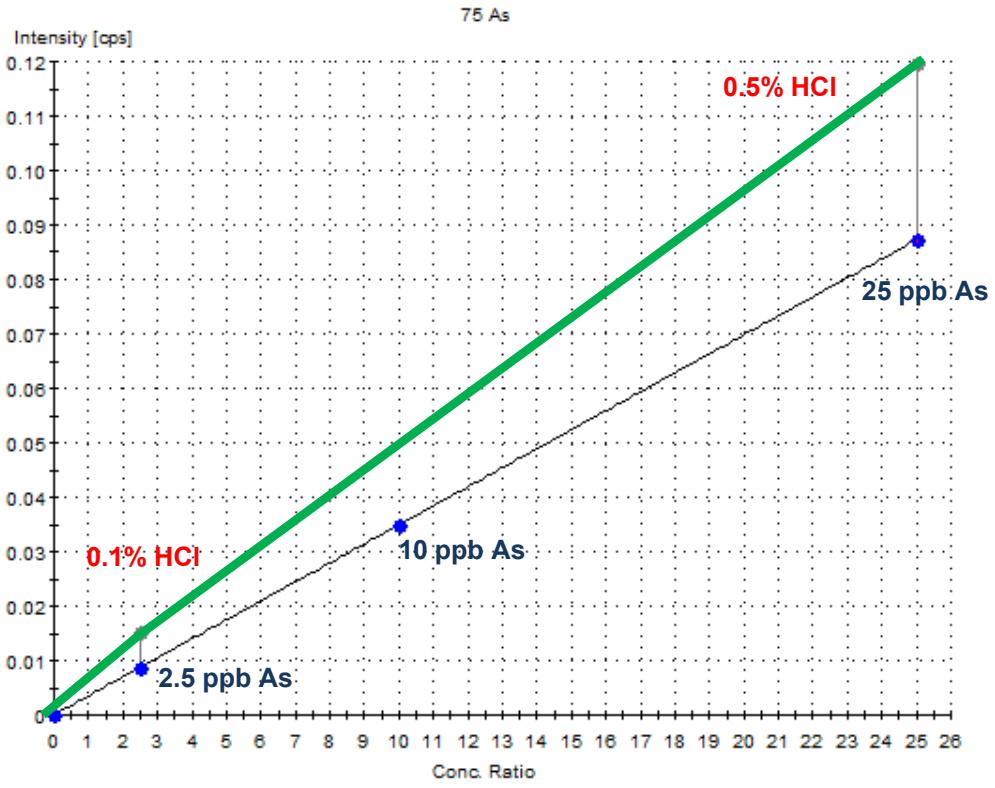
Detection Limit:	0.02113	[µg/l]	Lock
Conc. Min:	0.02113	[µg/l]	Lock
Conc. Max:	30	[µg/l]	Lock

Dist. Ion	Type	Factor	Use	Lock
Cl	+	6.214e-006	Yes	No

Measure As on m/z 75 in High Gain
Measure Cl on m/z 35 in Low Gain

Polyatomic interferences: Cl interference

- Addition of Cl to some defined As standards or as a single Std



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Corr.Coef.:	1
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.02113	[µg/l]	Lock
Conc. Min:	0.02113	[µg/l]	Lock
Conc. Max:	30	[µg/l]	Lock

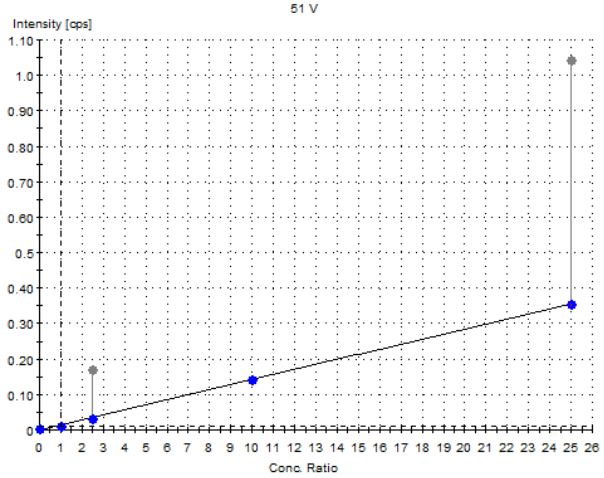
Dist. Ion	Type	Factor	Use	Lock
Cl	+	6.214e-006	Yes	No

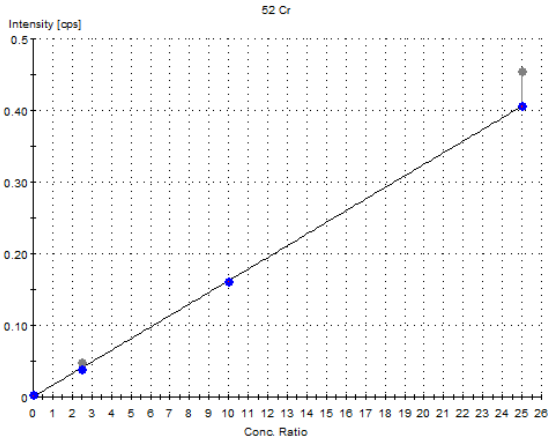
Do the rest at the same time

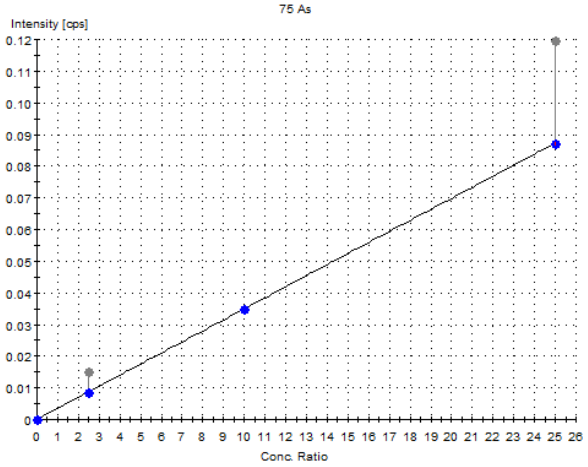
- Results

Sample	51 V	52 Cr	75 As
	µg/l	µg/l	µg/l
Certificate	**3.786**	**2.04**	**6.045**
Nist1643e 0.1%HCL	3.885	2.007	6.096
Recovery	**102.6**	**98.4**	**100.8**
Nist1643e	3.845	2.002	6.122
Recovery	**101.6**	**98.1**	**101.3**
0.2% HCL 10ppb STD	9.92	9.99	9.74
10ppb STD	10.34	10.03	9.91

NIST 1643e was diluted 1:10







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Summary

- **SPECTRO MS**
  - Measure the complete inorganically relevant mass range with every replicate in every sample
    - Get all information you want
    - Get all the additional information you need
    - Get all information you might need now or in the future
      - Think beyond what you are doing now
    - Method development after the sample is measured
    - Post measurement reprocessing for additional quantification
      - Quantitative mode or in Semi Quantitative mode
    - Never reanalyze a sample

Summary

- **SPECTRO MS**
  - Interferences: Keep it simple
    - Low transmission of interferences to detector
    - A simple mathematical correction can often do the job
      - » Can be added to the sample after the measurement
    - A more precise correction compared to sequential measurements is possible due fully simultaneous measurements

- **Thank you very much for your attention**

- **Questions**