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# High-precision GD-MS analysis of Nickel super-alloys: major components and ultra-trace metals

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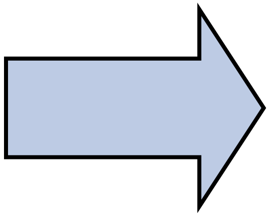
# What is a DC-GDMS good for?

Analysis of conductive and semi conductive samples

# What is a DC-GDMS good for?

| [ppb] | | | | Sample #1 | Sample #2 |
|---|---|---|---|---|---|
| Isotope | Mass | Resolution | Calibration | Conc. [ppb] | Conc. [ppb] |
| Na23(LR) | 23 | LR | STD RSF | 1.1 | 1.2 |
| Mg24(MR) | 24 | MR | Cal | 0.50 | 0.57 |
| Al27(MR) | 27 | MR | Cal | 0.67 | 7.79 |
| Si28(MR) | 28 | MR | Cal | 32 | 14 |
| P31(MR) | 31 | MR | Cal | 1.7 | 2.3 |
| Cl35(MR) | 35 | MR | STD RSF | 408 | 485 |
| K39(HR) | 39 | HR | STD RSF | 1.8 | 1.2 |
| Ca44(MR) | 44 | MR | STD RSF | 2.4 | 4.2 |
| Sc45(MR) | 45 | MR | STD RSF | 0.07 | 0.01 |
| Ti48(MR) | 48 | MR | Cal | 4.7 | 1.7 |
| V51(MR) | 51 | MR | STD RSF | 0.04 | 0.10 |
| Cr52(MR) | 52 | MR | Cal | 0.41 | 0.37 |
| Mn55(MR) | 55 | MR | Cal | 0.06 | 0.08 |
| Fe56(MR) | 56 | MR | Cal | 0.36 | 0.77 |
| Ni58(MR) | 58 | MR | Cal | 0.40 | 0.58 |
| Co59(MR) | 59 | MR | Cal | 0.10 | 0.07 |
| Zn68(MR) | 68 | MR | Cal | 3.8 | 5.2 |
| Ga69(MR) | 69 | MR | STD RSF | 0.43 | 0.40 |
| Ge74(HR) | 74 | HR | STD RSF | 3.4 | 3.5 |
| As75(MR) | 75 | MR | Cal | 1.9 | 0.9 |
| Se77(MR) | 77 | MR | Cal | 15 | 20 |
| Br79(MR) | 79 | MR | STD RSF=1 | 2.8 | 2.4 |
| Rb85(MR) | 85 | MR | STD RSF=1 | 0.06 | 0.07 |
| Sr88(LR) | 88 | LR | STD RSF | 0.07 | 0.10 |
| Y89(MR) | 89 | MR | STD RSF | 0.06 | 0.06 |
| Zr90(MR) | 90 | MR | Cal | 0.18 | 0.20 |
| Nb93(MR) | 93 | MR | STD RSF | 0.02 | 0.07 |
| Mo97(MR) | 97 | MR | STD RSF | 0.71 | 0.64 |
| Ru102(HR) | 102 | HR | STD RSF | 0.52 | 0.81 |
| Rh103(HR) | 103 | HR | STD RSF | 9.4 | 7.4 |

- Analysis of ultra-trace to matrix elements
- Sputtering and ionization are separated processes ⇨ only minimal matrix effects ⇨ semi-quantitative analyses without calibration

# Recent publication: Pisonero, Fernández, Günther

CRITICAL REVIEW www.rsc.org/jaas | Journal of Analytical Atomic Spectrometry

## Critical revision of GD-MS, LA-ICP-MS and SIMS as inorganic mass spectrometric techniques for direct solid analysis

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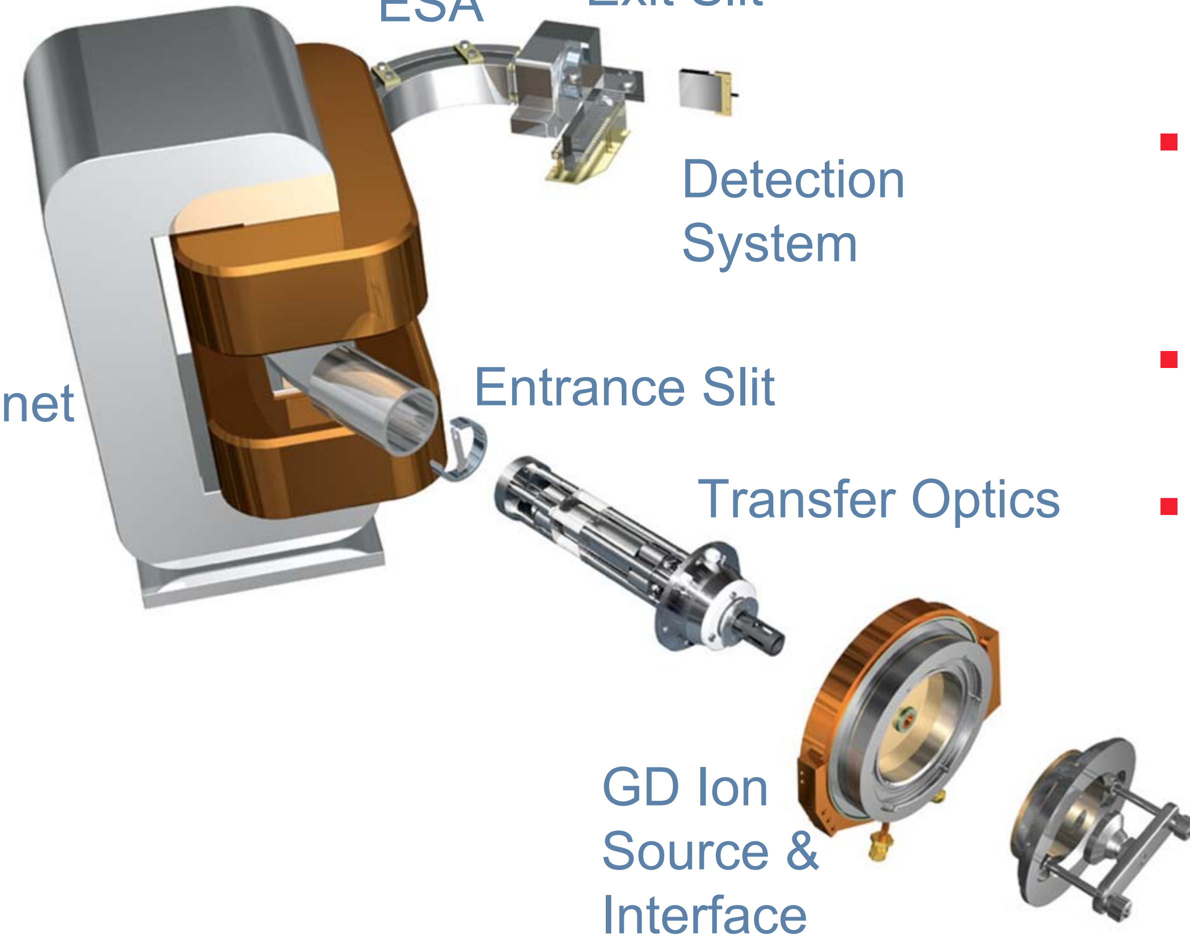
**General capabilities.** The application of glow discharge devices as primary spectrochemical sources for direct solid elemental analysis in mass spectrometry is increasing because they offer several important advantages, such as a high depth resolution (~nm), fast sputtering rate (in the order of µm/min), multi-element capabilities (most of the elements of the periodic table can be determined), isotopic information in a relatively simple spectrum, low matrix effects, low limits of detection (in the range of µg/g-ng/g), and ease of use.

*Absolute and relative sensitivity factors for quantification.* The low matrix dependence of GD-MS in comparison with other solid state analytical techniques provides absolute sensitivity factors which are matrix independent in a first approximation.

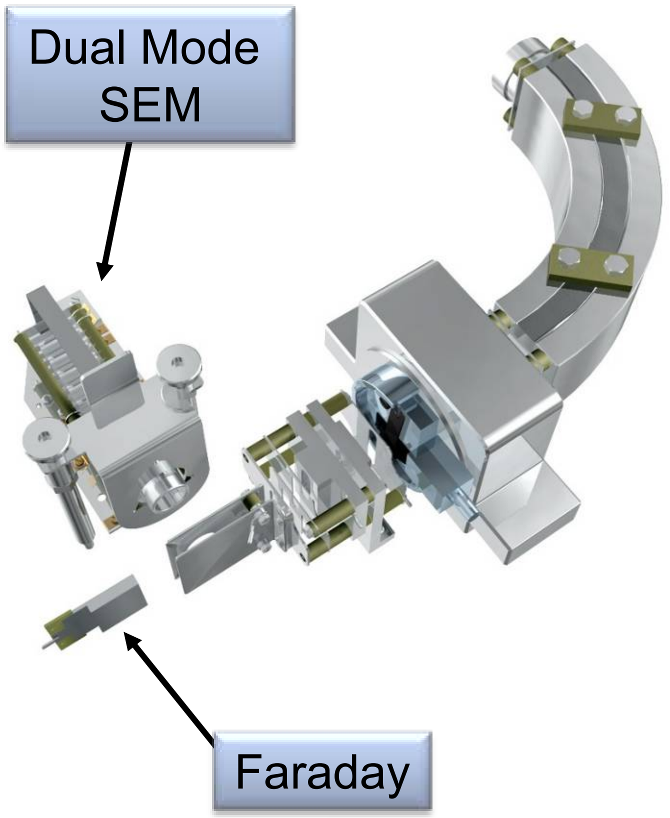
# Components of the Element GD




- Similar to 'Grimm Type' DC source:
  Pump down in 10s
- High power, fast flow ion source:
  High sensitivity
- Anode:
  Plug-in cap
- Flow tube:
  Ion transport to MS

# Requirements on detection system for GD

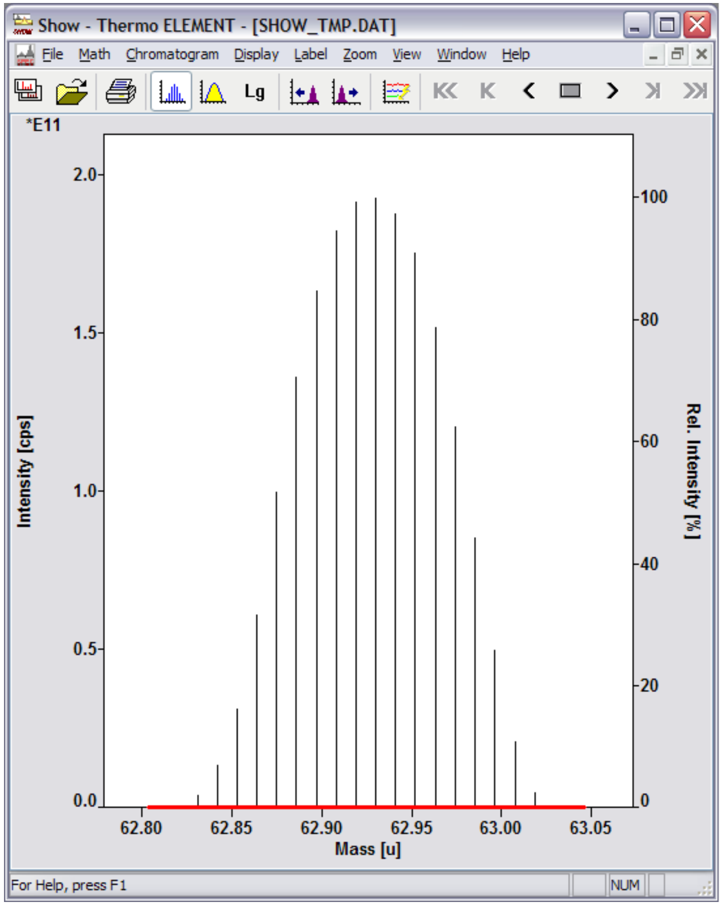
- High dynamic range
  - From <ppb to 100% matrix, i.e. > 12 orders of magnitude
  - Total ion current used for evaluation
  - Low noise
- Linear
  - Semi quantitative results without standards
  - Calibration at higher concentrations than the samples possible

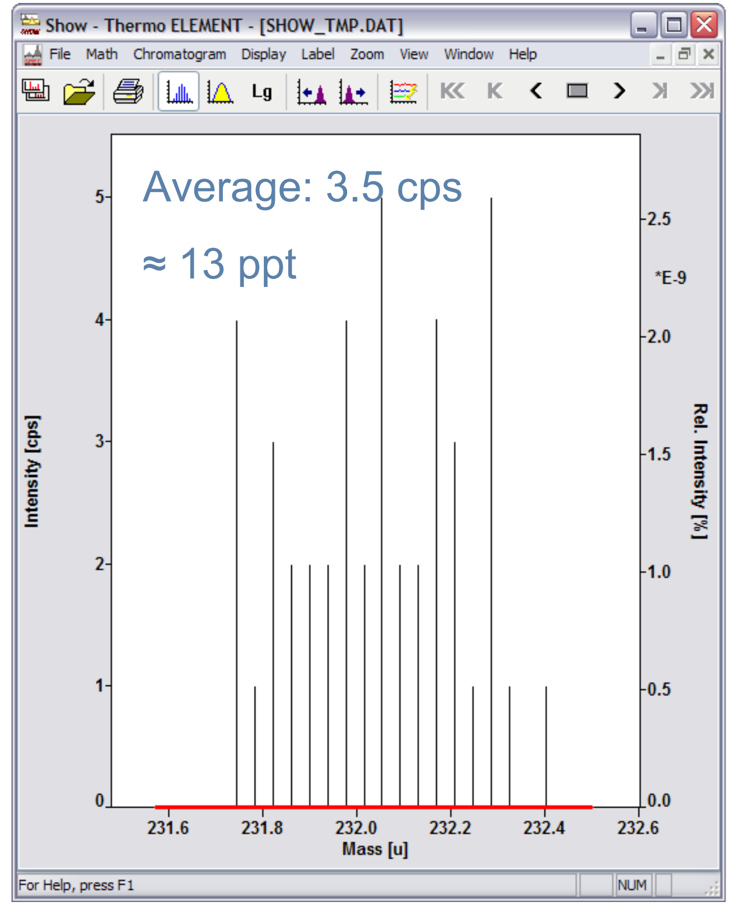


# Detection Power (Th in Copper, Low Resolution)

## Theor. Detection Limit:

## $2 \cdot 10^{11}$ cps Signal@0.2 cps Noise :$DL_{theor.}$ : 1 ppt




Integration time per sample: 100 ms Th, 1 ms Cu; 20 samples per peak; 10 Spectra

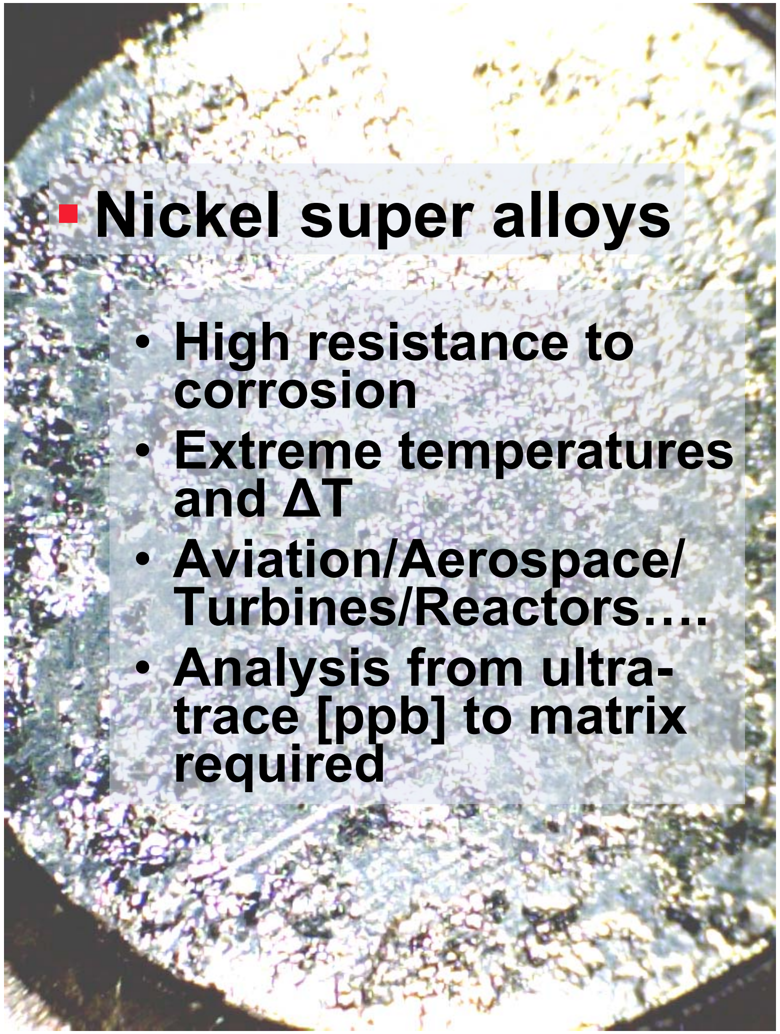
# Applications…

- Overview
- Use of detection system: Analysis of Ni-Alloys (“Super-Alloys”)
- Low detection limits:  solar silicon
- Special aspects of solid sampling at ppb level

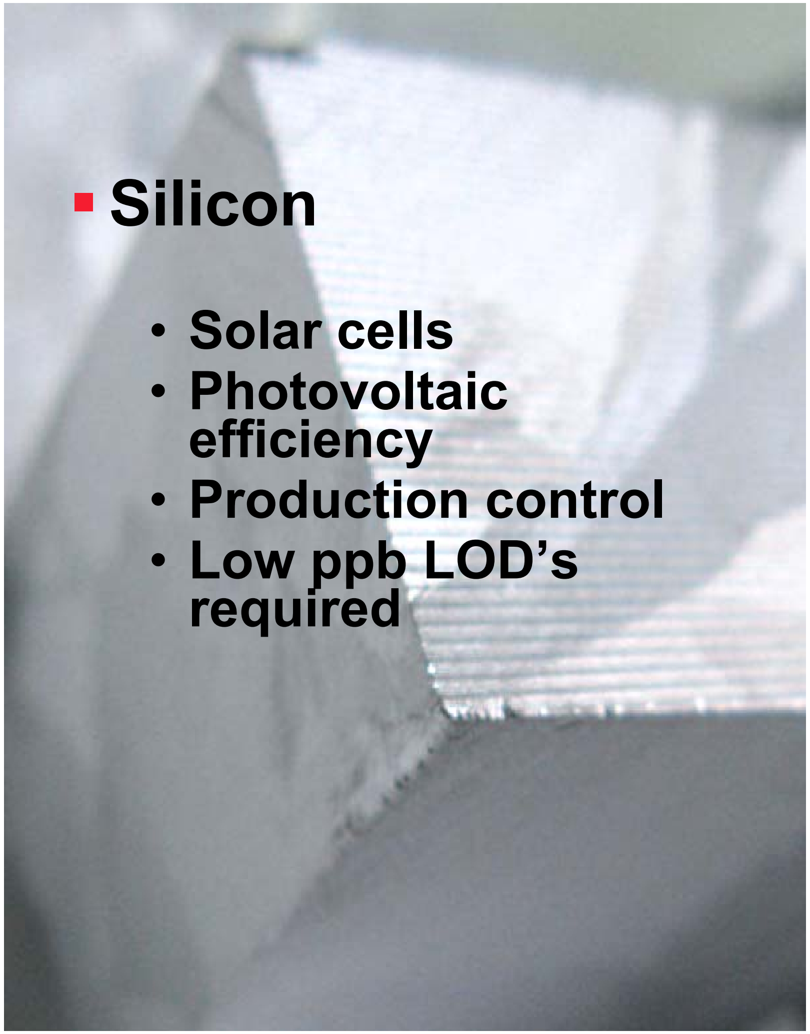
# Overview: sample matrices

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | **Mg** | | | | | | | | | | | **Al** | **Si** | P | S | Cl | Ar |
| K | Ca | Sc | **Ti** | **V** | **Cr** | **Mn** | **Fe** | **Co** | **Ni** | **Cu** | **Zn** | **Ga** | **Ge** | **As** | Se | Br | Kr |
| Rb | Sr | Y | **Zr** | **Nb** | **Mo** | Tc | **Ru** | **Rh** | **Pd** | **Ag** | **Cd** | **In** | **Sn** | **Sb** | **Te** | I | Xe |
| Cs | Ba | La | Hf | **Ta** | **W** | Re | Os | **Ir** | **Pt** | **Au** | Hg | Tl | **Pb** | **Bi** | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |
| | | | **Ce** | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | |

# Application examples



- **Nickel super alloys**
  - High resistance to corrosion
  - Extreme temperatures and ΔT
  - Aviation/Aerospace/ Turbines/Reactors….
  - Analysis from ultra-trace [ppb] to matrix required



- **Silicon**
  - Solar cells
  - Photovoltaic efficiency
  - Production control
  - Low ppb LOD’s required

# Application examples Ni Alloys

## Challenges

- Reliable and routine determination from matrix to ultratrace elements
- Industrial production control
- Large number of alloy components
- Precise calibration with CRM
- Most important: soft metals at ppm/sub-ppm level strongly deteriorate alloy quality

# Repeat GD-MS analysis of NIST 1249 (Inconel 718)

| Element | Unit | Spot 1 | Spot 2 | Spot 3 | Spot 4 | Spot 5 | Spot 6 | Spot 7 | Spot 8 | Spot 9 | Spot 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni | [%] | 56.9 | 56.7 | 57.2 | 57.8 | 57.7 | 57.5 | 56.9 | 57.6 | 57.3 | 56.9 |
| Fe | [%] | 18.0 | 18.1 | 17.9 | 18.0 | 18.0 | 18.1 | 18.1 | 18.1 | 18.1 | 18.1 |
| Mo | [%] | 2.9 | 2.9 | 2.9 | 2.8 | 2.8 | 2.8 | 2.9 | 2.8 | 2.8 | 2.8 |
| Co | [%] | 0.34 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 |
| Cu | [%] | 0.139 | 0.140 | 0.139 | 0.141 | 0.138 | 0.137 | 0.135 | 0.139 | 0.139 | 0.141 |
| P | [%] | 0.018 | 0.018 | 0.017 | 0.018 | 0.017 | 0.018 | 0.017 | 0.018 | 0.018 | 0.017 |
| Sn | [ppm] | 22 | 22 | 22 | 21 | 21 | 21 | 22 | 21 | 22 | 21 |
| Ga | [ppm] | 17.9 | 18.0 | 17.5 | 17.5 | 17.1 | 17.9 | 17.9 | 17.5 | 17.7 | 17.6 |
| As | [ppm] | 17.2 | 17.5 | 16.5 | 16.9 | 16.6 | 16.4 | 16.3 | 16.8 | 16.6 | 16.3 |
| Sb | [ppm] | 3.7 | 3.7 | 3.8 | 3.6 | 3.6 | 3.7 | 3.6 | 3.6 | 3.7 | 3.5 |
| Pb | [ppm] | 0.11 | 0.10 | 0.10 | 0.11 | 0.10 | 0.09 | 0.09 | 0.09 | 0.10 | 0.10 |
| Bi | [ppm] | 0.010 | 0.009 | 0.011 | 0.009 | 0.008 | 0.010 | 0.010 | 0.008 | 0.009 | 0.011 |

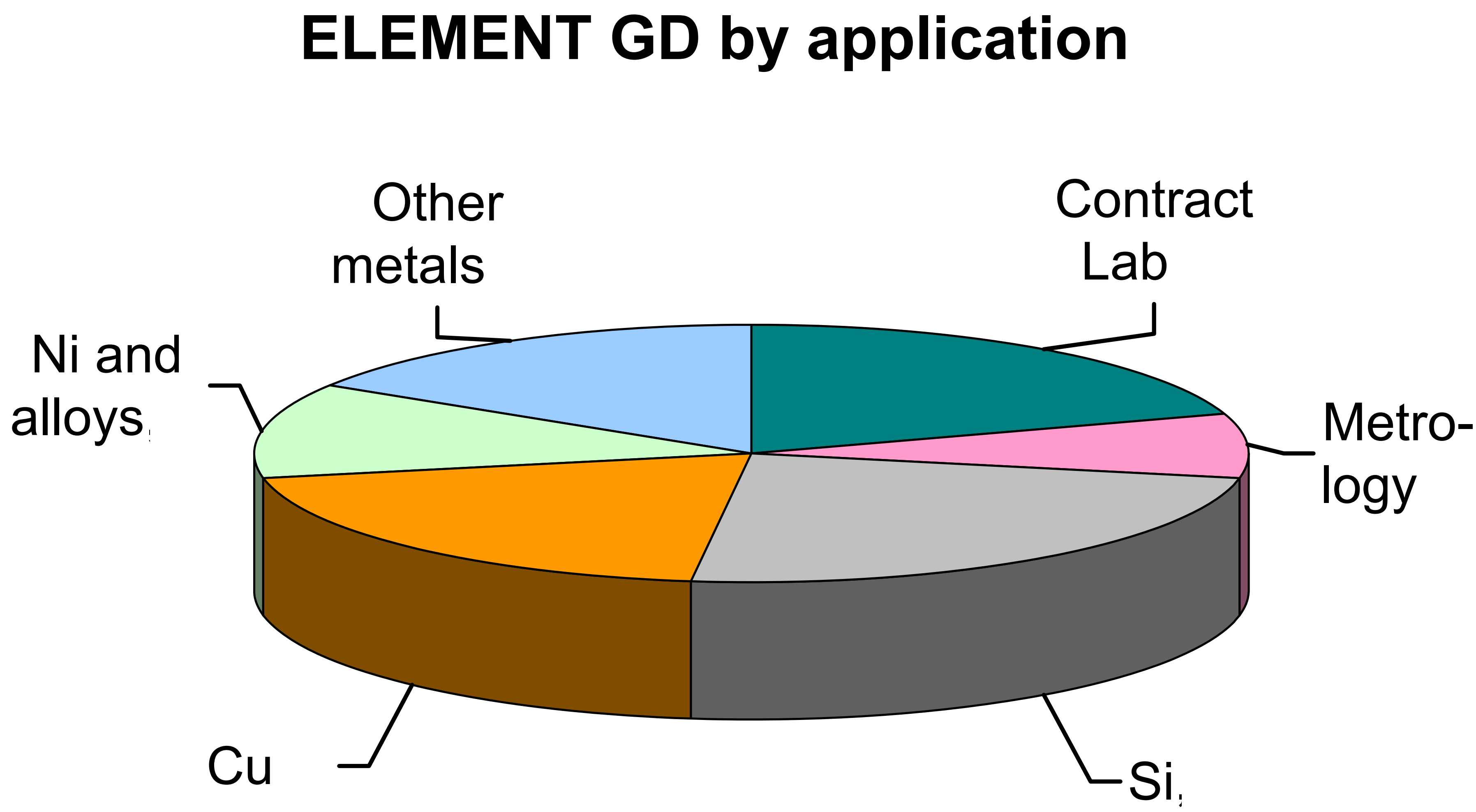
# Repeat GD-MS analysis of NIST 1249 (Inconel 718)

| Element | Unit | Average | STD | RSD |
|---|---|---|---|---|
| Ni | [%] | 57.3 | 0.4 | 0.7% |
| Fe | [%] | 18.0 | 0.07 | 0.4% |
| Mo | [%] | 2.8 | 0.04 | 1.6% |
| Co | [%] | 0.35 | 0.003 | 0.8% |
| Cu | [%] | 0.139 | 0.002 | 1.2% |
| P | [%] | 0.018 | 0.0005 | 2.6% |
| | | | | |
| Sn | [ppm] | 21.5 | 0.6 | 2.7% |
| Ga | [ppm] | 17.7 | 0.3 | 1.6% |
| As | [ppm] | 16.7 | 0.4 | 2.3% |
| Sb | [ppm] | 3.7 | 0.1 | 2.5% |
| Pb | [ppm] | 0.10 | 0.007 | 7.0% |
| Bi | [ppm] | 0.009 | 0.001 | 10.5% |

# Ni alloys: Sensitivity ELEMENT XR vs ELEMENT GD

| | ELEMENT XR [cps] | ELEMENT GD [cps] | GD-MS/ICP-MS |
|---|---|---|---|
| P | 4527 | 199487 | 44 |
| Co | 194322891 | 13100000000 | 67 |
| Cu | 9648 | 766537 | 79 |
| Ta | 64270 | 775730 | 12 |
| Pb | 337 | 3369 | 10 |

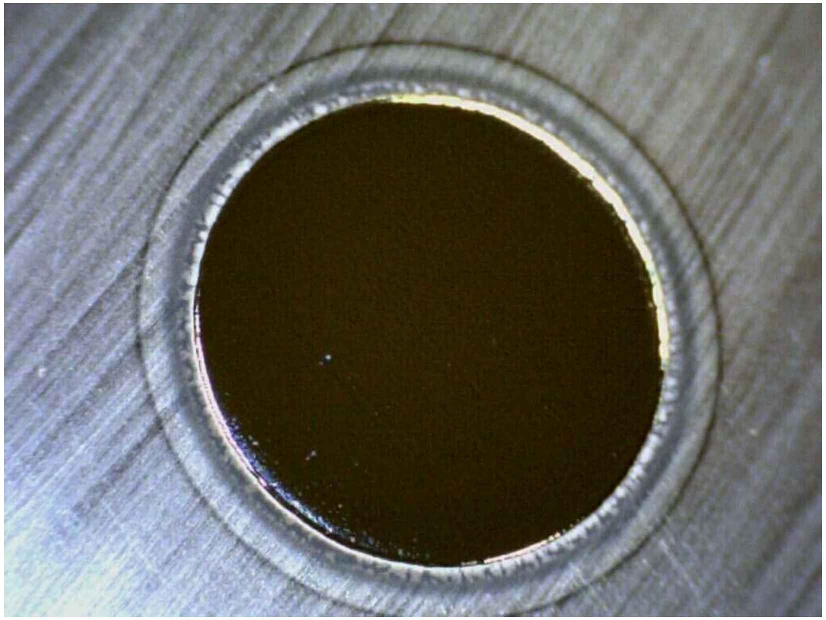
# ELEMENT GD by application



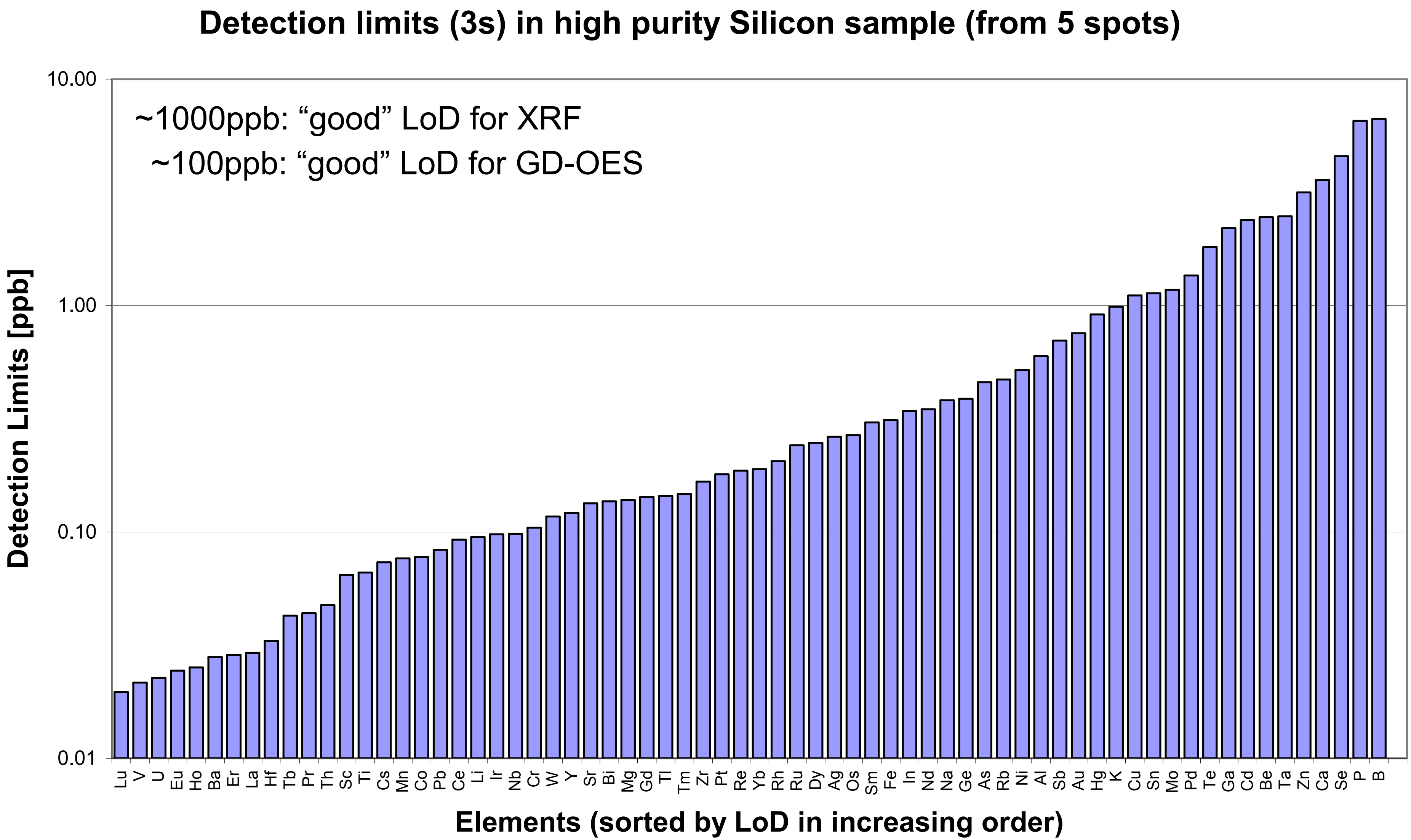
# Application examples Solar Cell Silicon

## Challenges

- Routine determination of sub-ppm and sub-ppb concentrations
- High sputter yield required
- BEC & Memory
- Calibration
    - Mostly semiquant



# GD-MS Analysis of Solar Cell Silicon



# Special aspects of solid sampling at ppb level

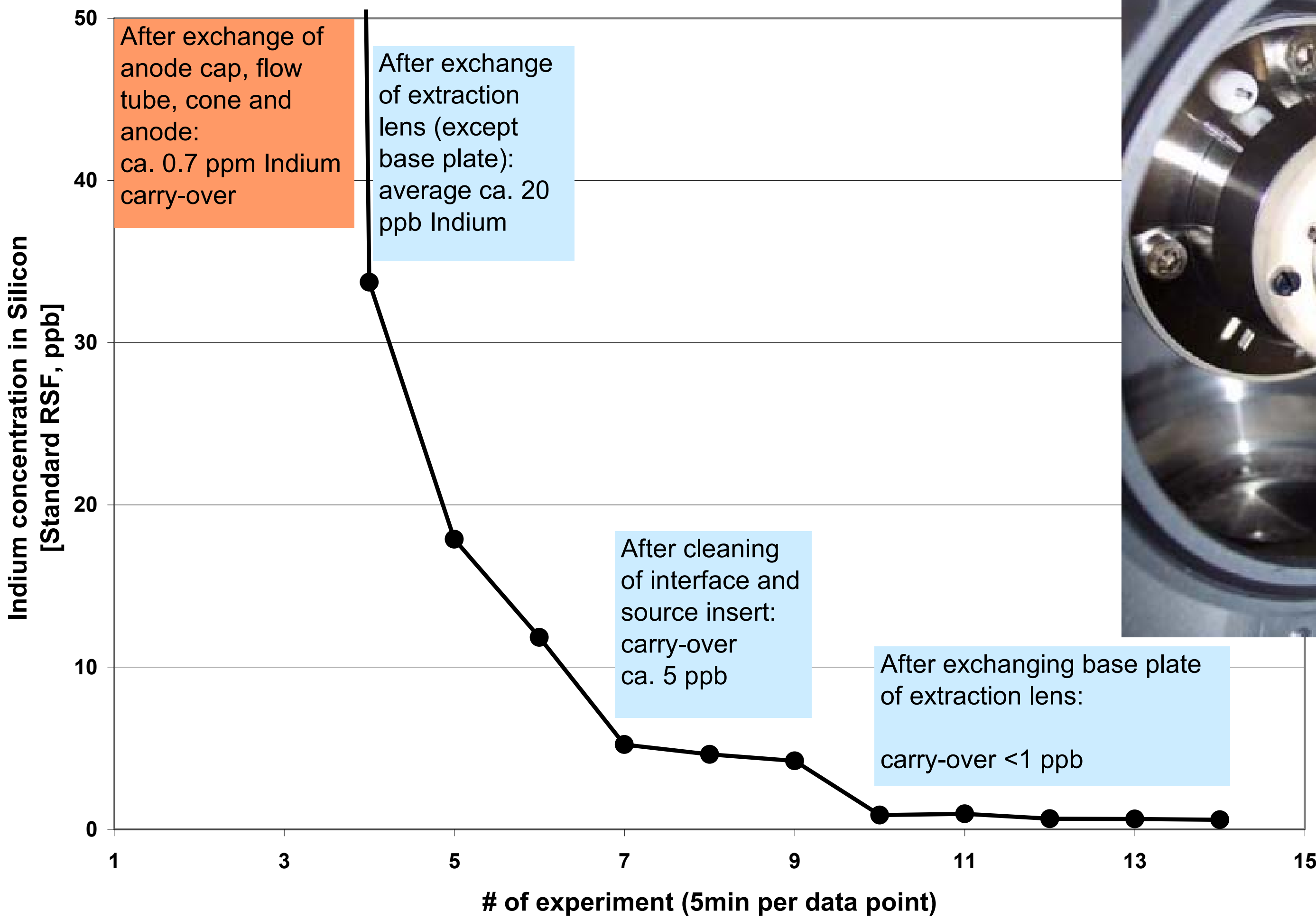
**Input from GD source parts: made from graphite**

- High purity material available
- Very low sputter probability
- Lowest detection limits

# Input from Memory effects

- Experiment: Analyses of Si after sputtering of an In sample
- Finding: Major contribution (> 98 %) from deposits on extraction lens
- Solution: Plug-in extraction lens
  - Exchange by user within a few minutes through slide valve
  - Venting with Ar avoids moisture in vacuum system: instrument back in operation after 1.5 h

# Tracking the source of memory effects




# Input from previous sample: Plug-in cone

… and let it snap into position.

Mount clean cone
in holding ring…

# Conclusion

- ELEMENT GD keeps HR-GDMS alive
  - Around 30 instruments within 4 years
  - Increasing demand from new markets, e.g. super alloys, solar cell industry
- ELEMENT GD is fast
  - Became a routine tool with > 5-6 samples/hour
- ELEMENT GD is a routine and powerful technique
  - Accepted technique (e.g. contract labs)
  - Used for a variety of samples
  - Used for matrix to ultra-trace determination
  - Easy to use; software based on HR-ICP-MS software