Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

LA-ICP-MS

- the concept

Laser Energy

↓

Solid sample

↓

Solid vaporization

↓

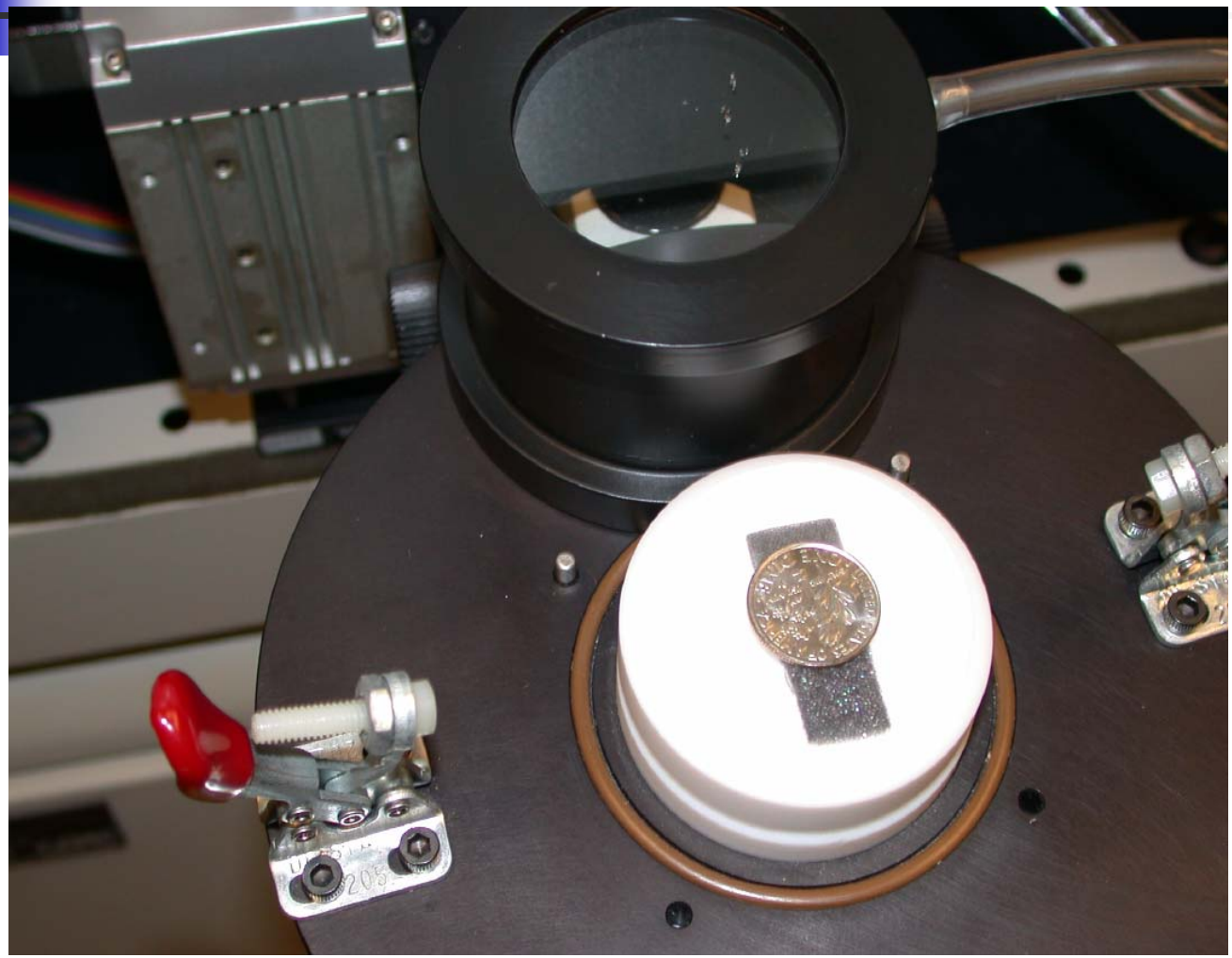
Dissociation

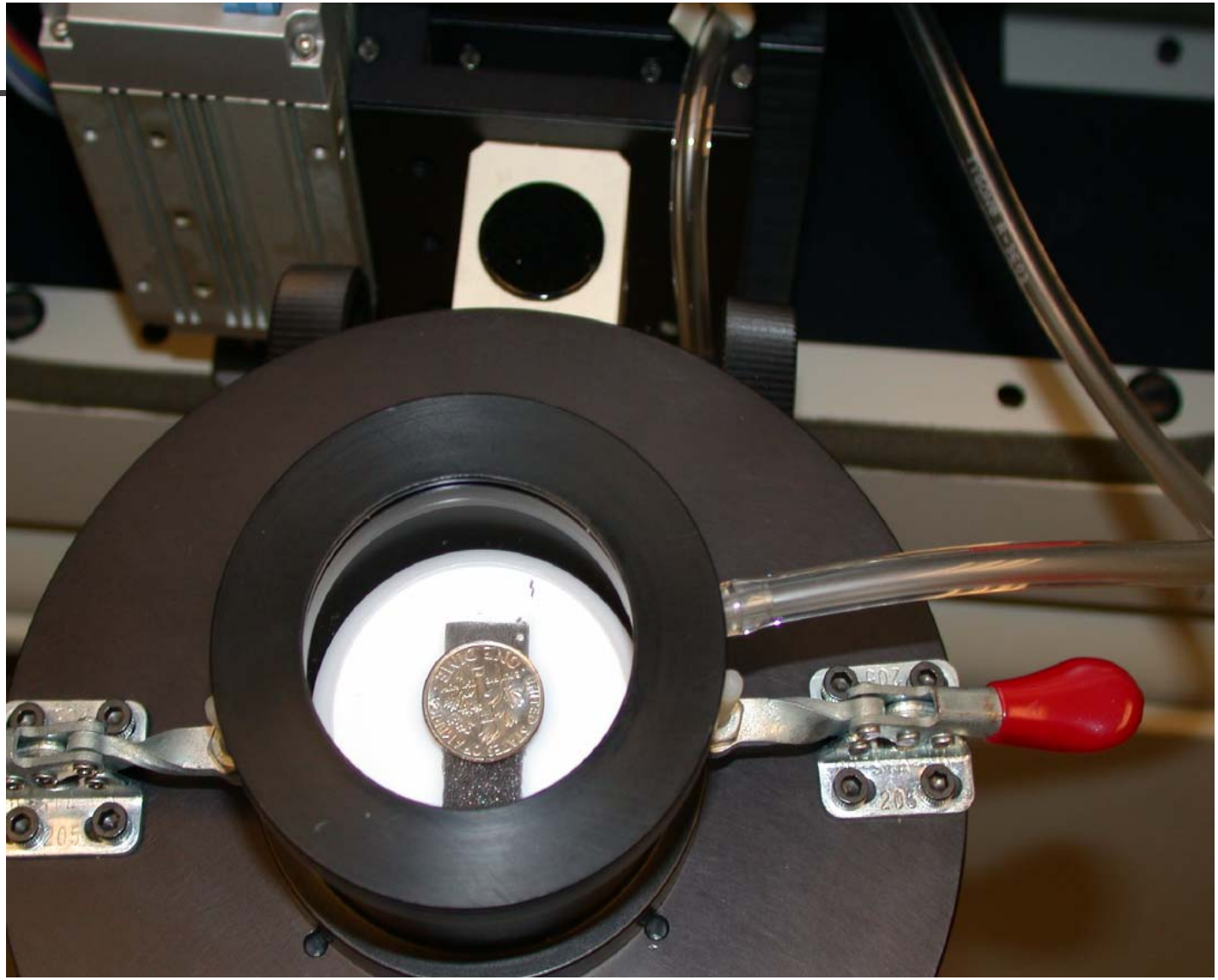
↓

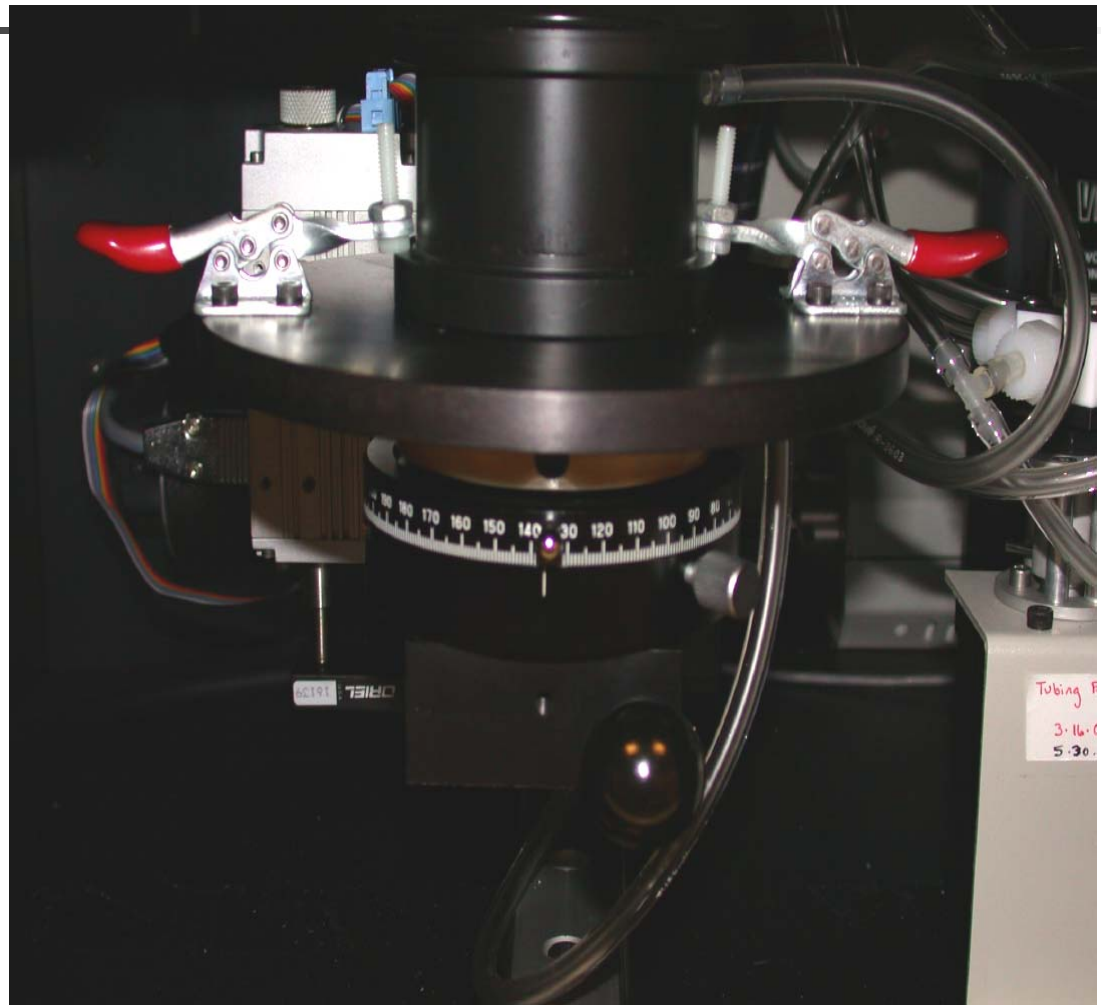
Atomization

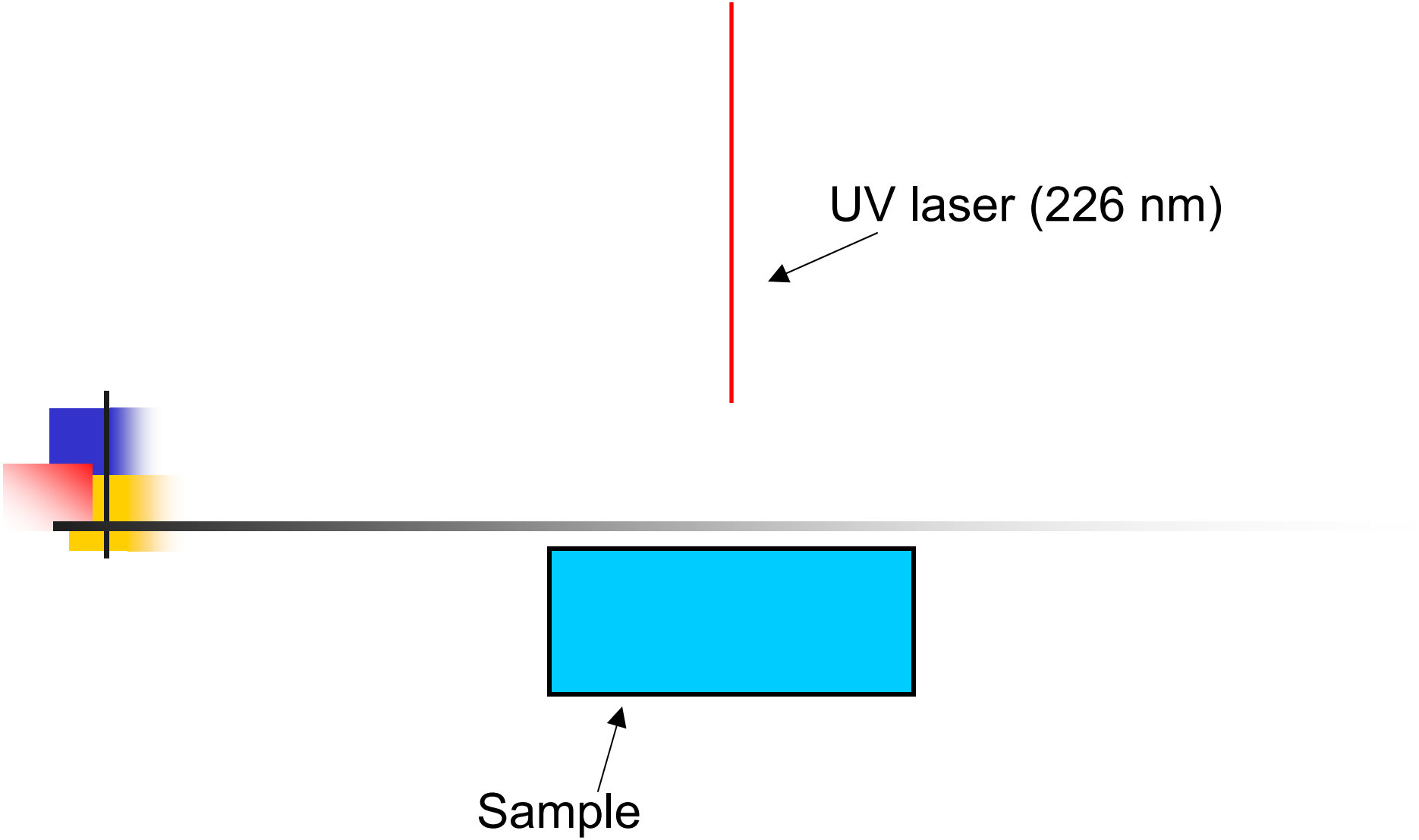
↓

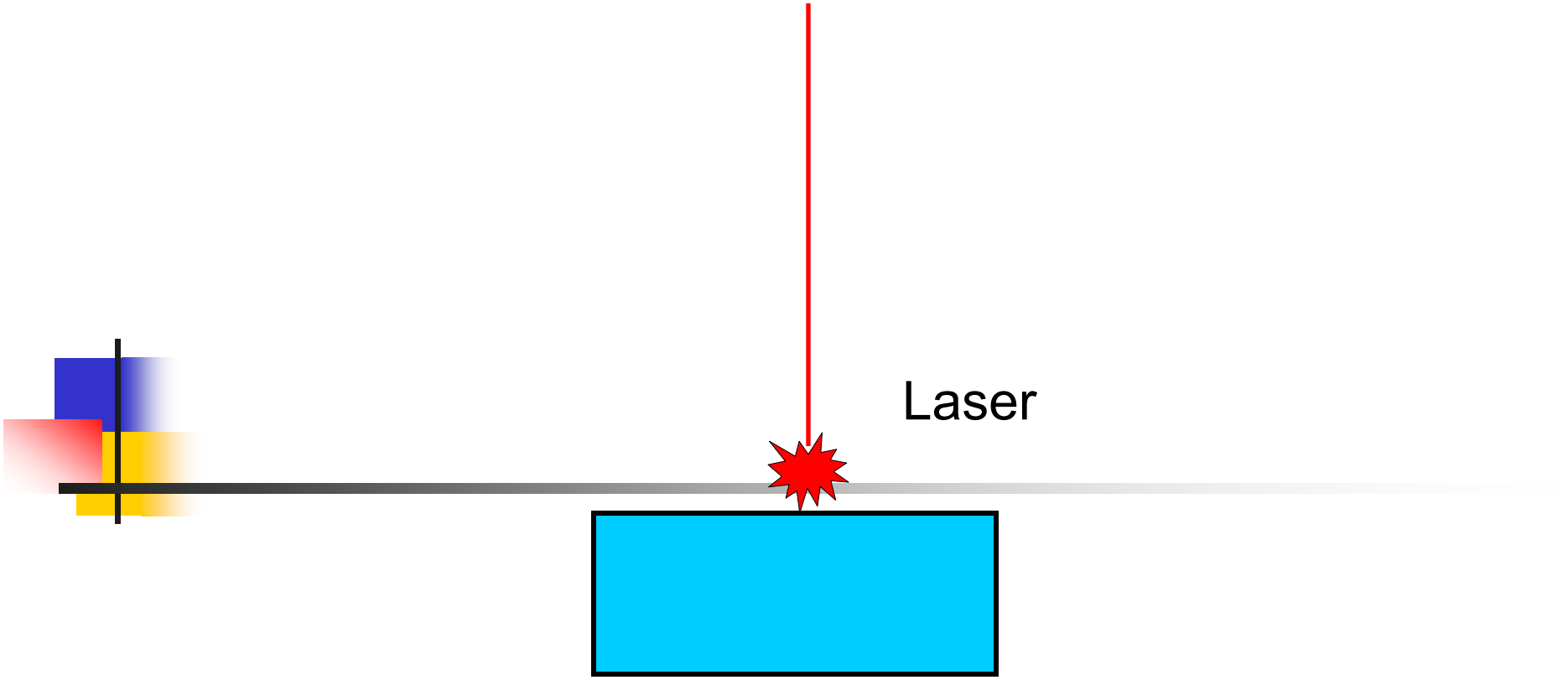
Ionization/Excitation of elements

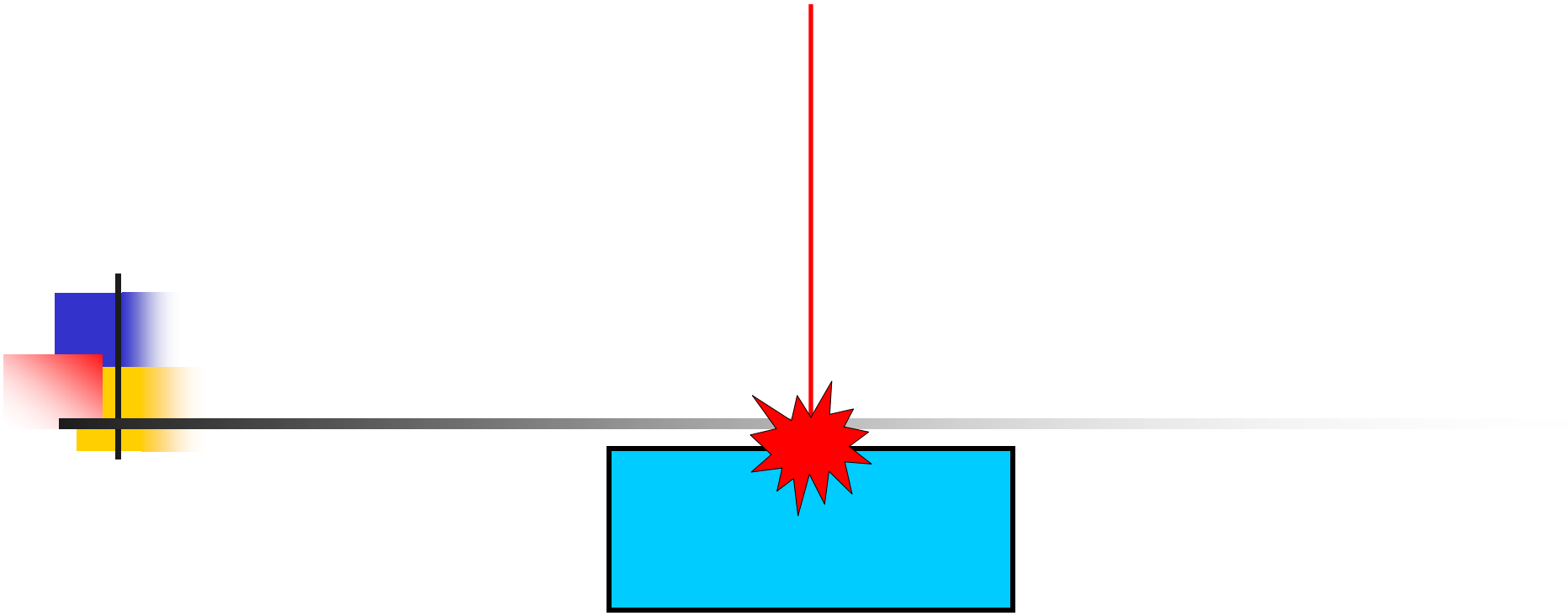


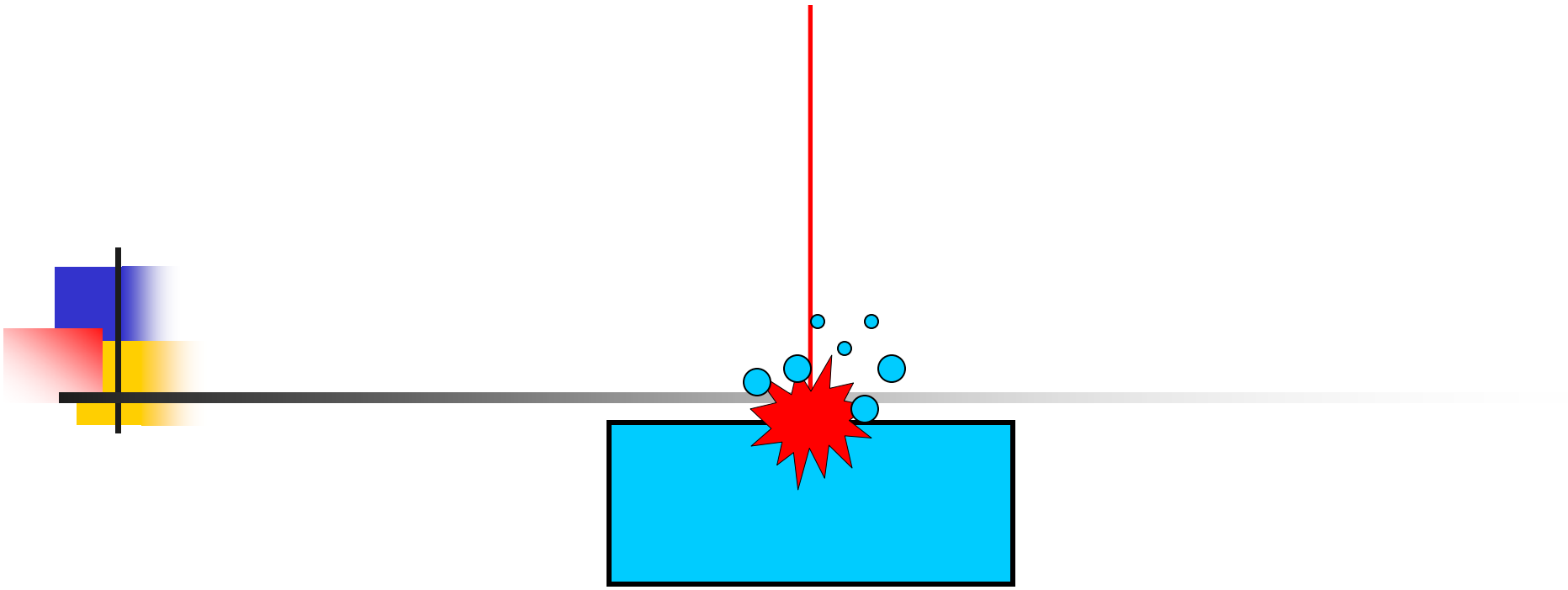


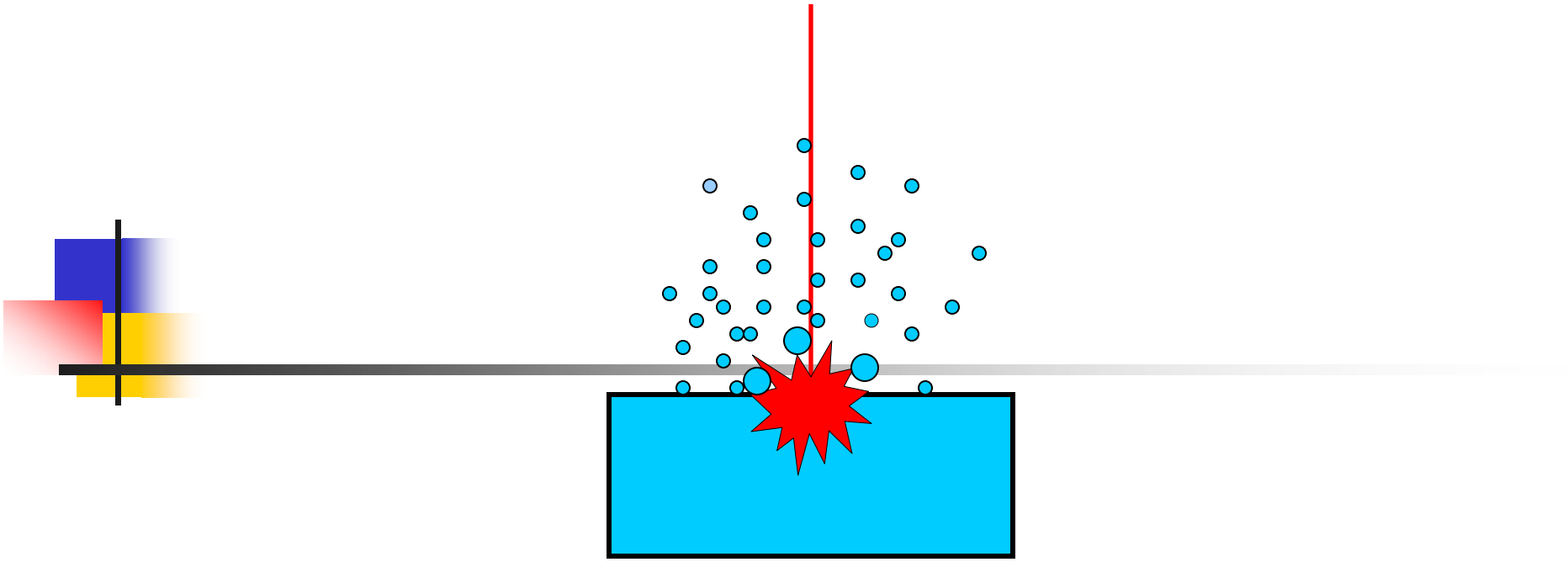

180 170 160 150 140 30 120 110 100 90
ORIEL
Tubing

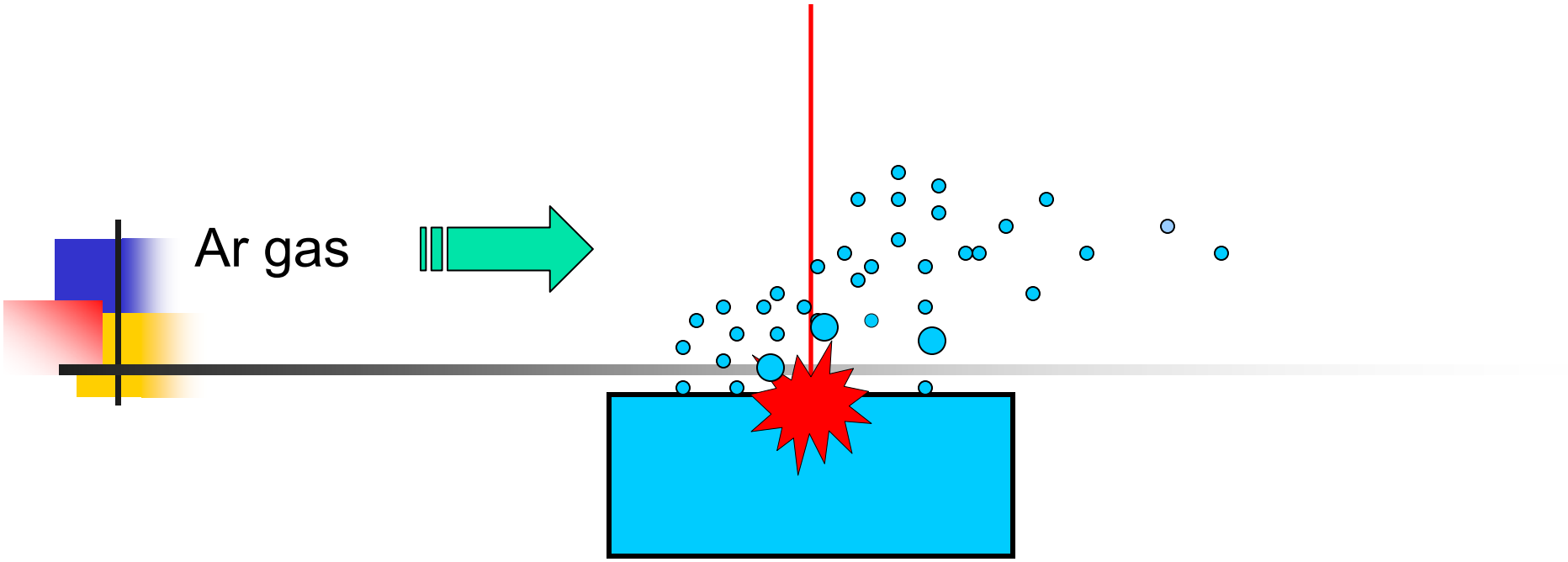

UV laser (226 nm)
Sample

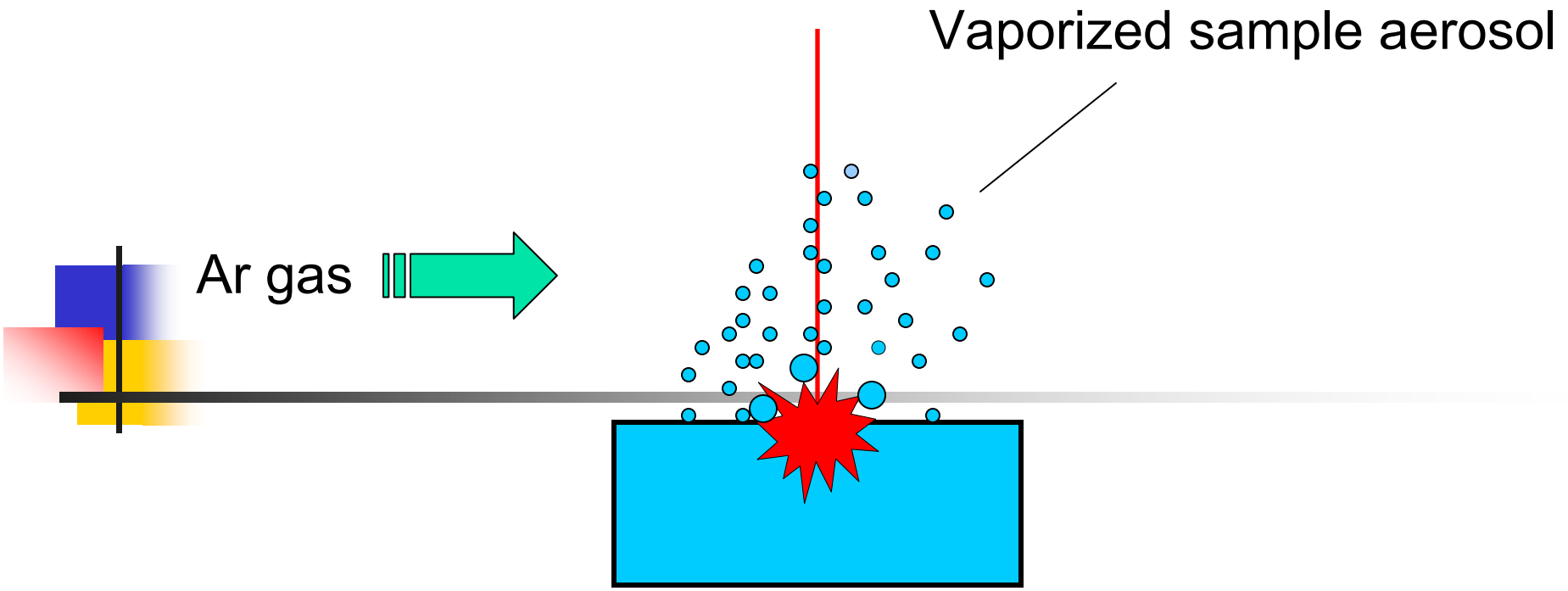

Laser

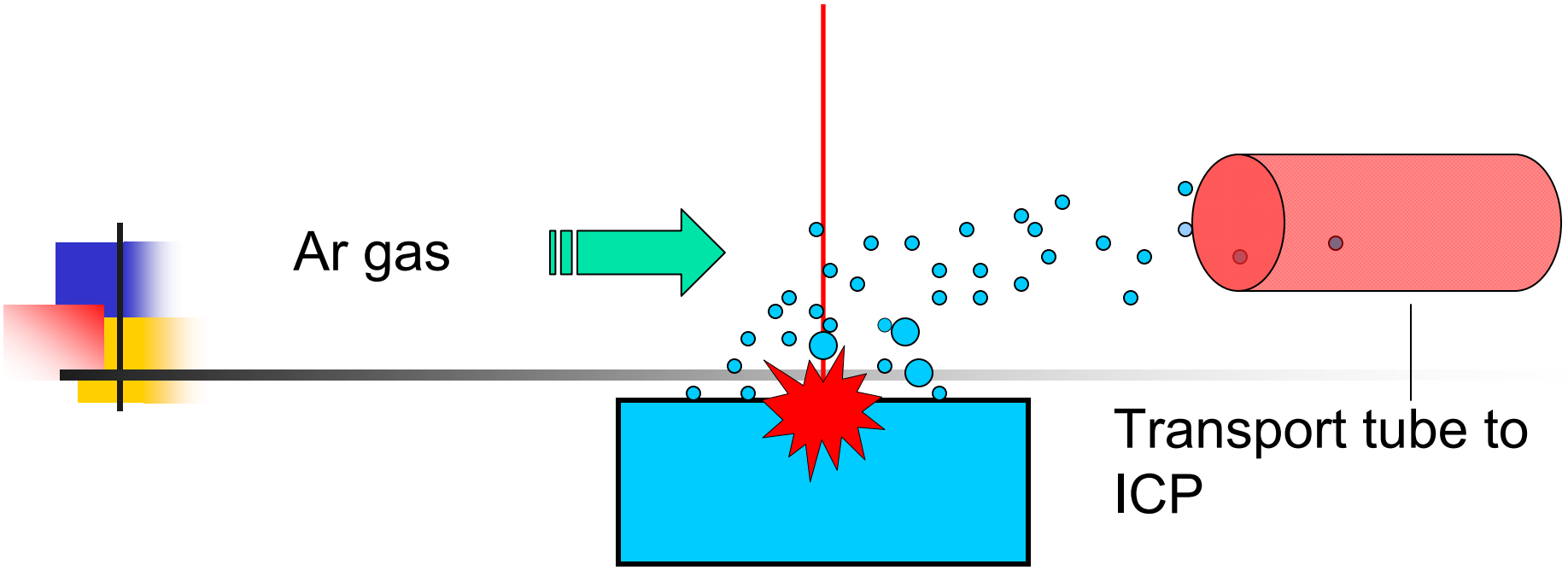


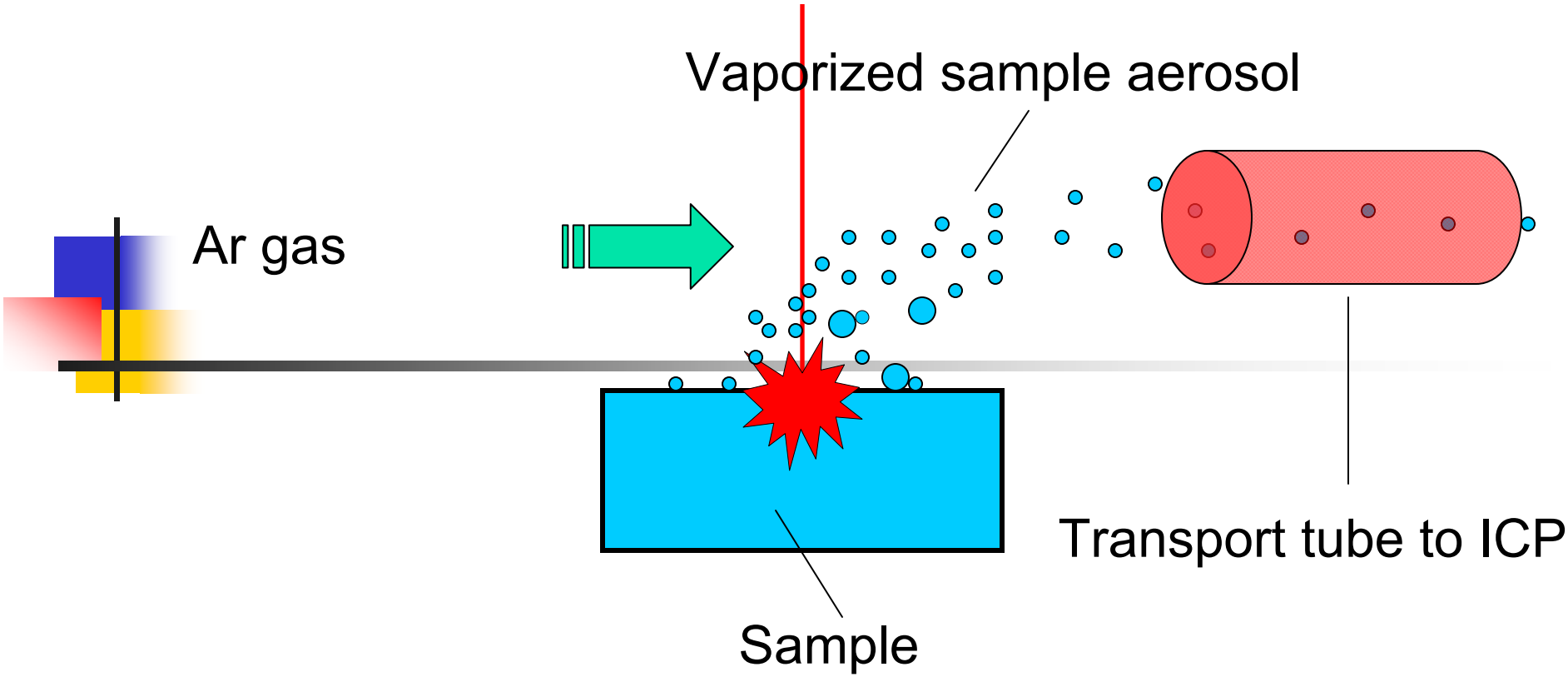


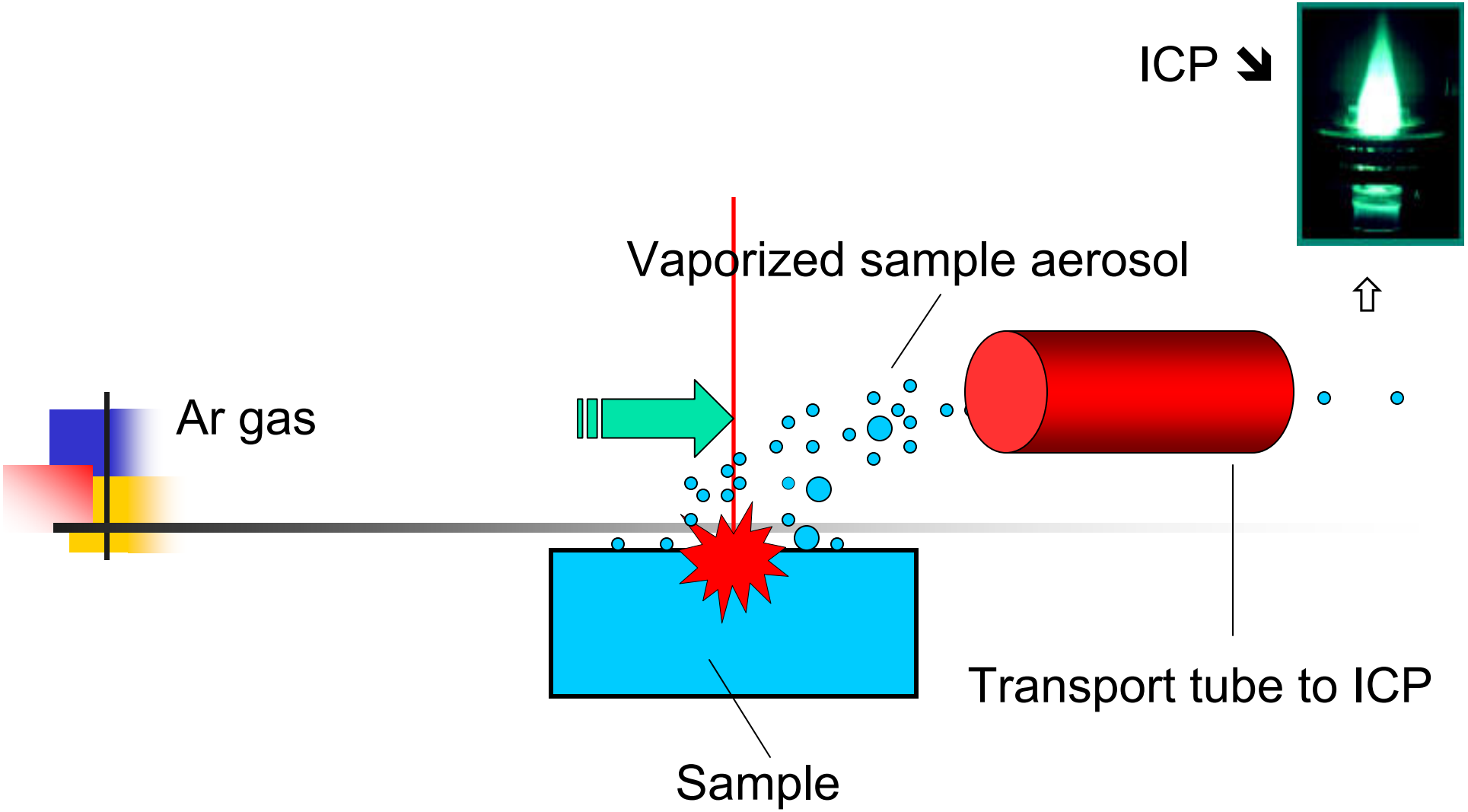


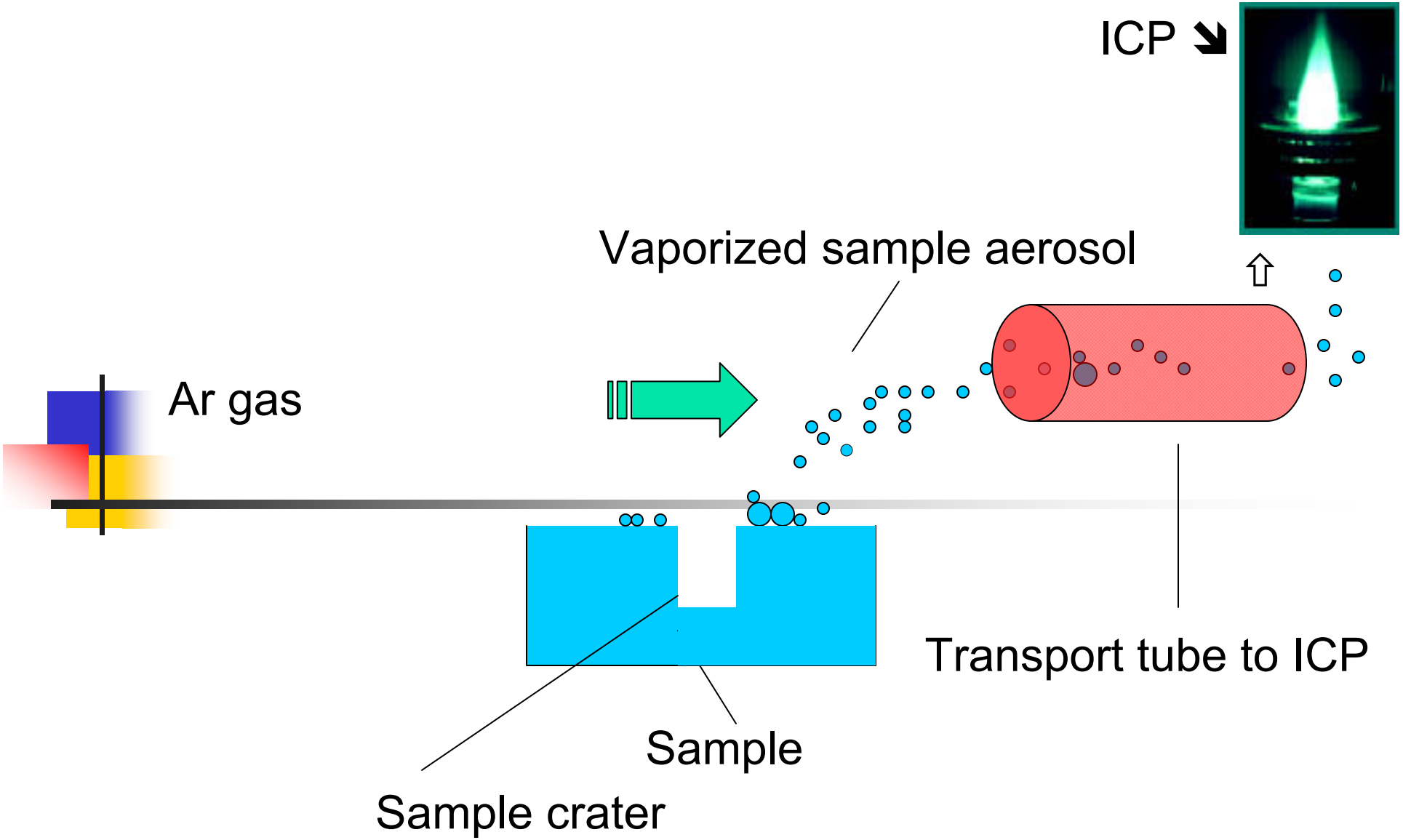

Ar gas


Vaporized sample aerosol
Ar gas


Ar gas
Transport tube to
ICP


Vaporized sample aerosol
Ar gas
Transport tube to ICP
Sample


ICP
Vaporized sample aerosol
Ar gas
Transport tube to ICP
Sample


ICP
Vaporized sample aerosol
Ar gas
Transport tube to ICP
Sample
Sample crater

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS

Plasma?

- Partially ionized gas
  - Ar^o, Ar^+, and e^-
- Temp: 10,000 K
- Three concentric quartz tube
- Argon plasmas are most common
  - Ar flow rates : 10-15 L/min;
  - Auxiliary < 2 L/min
- Analytical observation region (on top)
- Water cooled rf (radio frequency) load coil

Fate of the Sample Aerosol

Desolvation $H_2O_{(l)} \rightarrow H_2O_{(g)}$

↓

Vaporization $MX_s \rightarrow MX_l \rightarrow MX_g$

↓

Atomization $MX_g \leftrightarrows M_g + X_g$

↓

Excitation $M_g \rightarrow M_g^*$

↓

Ionization $M_g \rightarrow M_g^{n+} + ne^-$

Ions

- 54 elements > 90% are ionized
- Metalloids As, P, Se

- Plasma ions: $Ar \rightarrow Ar^{+} + e^{-}$
- Water -> H^{+}, OH^{-}, O^{-}
- Analyte Ions -> M -> $M^{+} + e^{-}$
  - Doubly charged ions (M^{2+})
    - Depends on the second ionization energy
    - 10% of the total analyte ions
    - Possible suspects: Ba^{2+}, rare earth elements (REE)

Ion Extraction

M^+

Collect

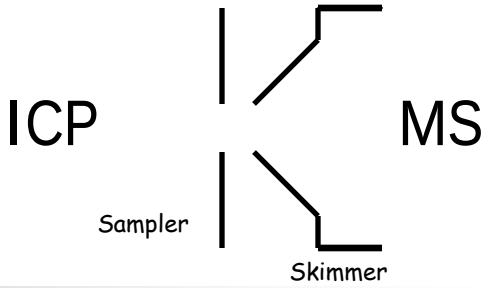
Focus

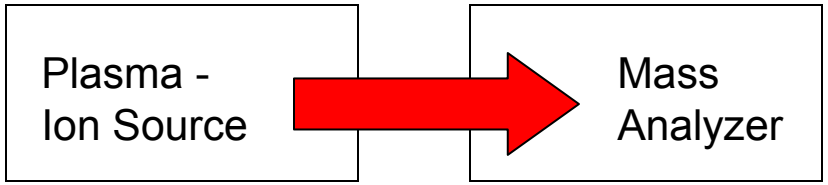
Transmit to the mass analyzer

Detector

(channeltron electron multiplier, faraday cup)

ICP-MS interface





- Ambient pressure to low pressure (vacuum)
  - Two stage interface
    - Sampling cone (pressure drops to 2.5 mbar)
    - Skimmer cone (pressure drops to *c.a.* 10^{-4} mbar)
  - A Slide valve for close the interface hole when the instrument is not in use

Plasma → Sampler → Skimmer → MS

Sampler:

Sampler (r=1.0 mm) water cooled cone

Ions are sampled from the central region of the plasma

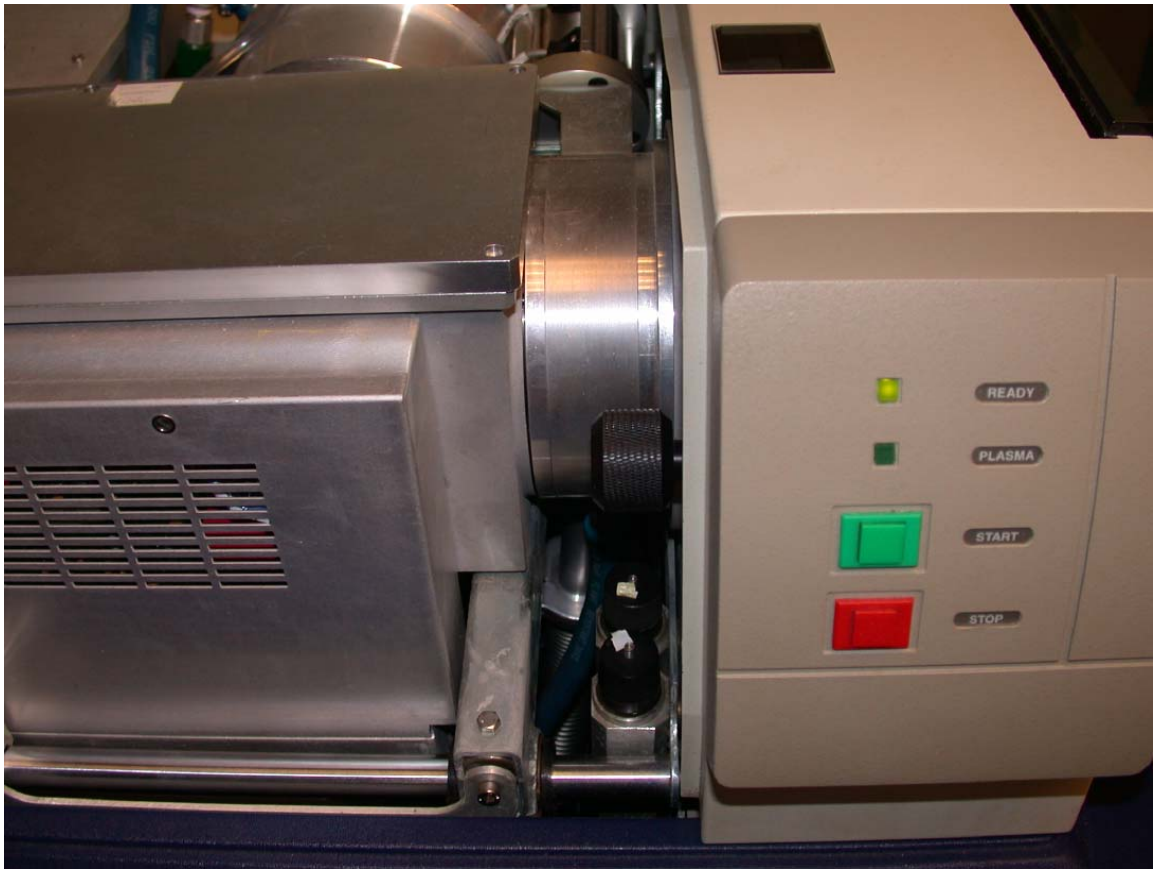
Formation of oxides

Condensation of solids

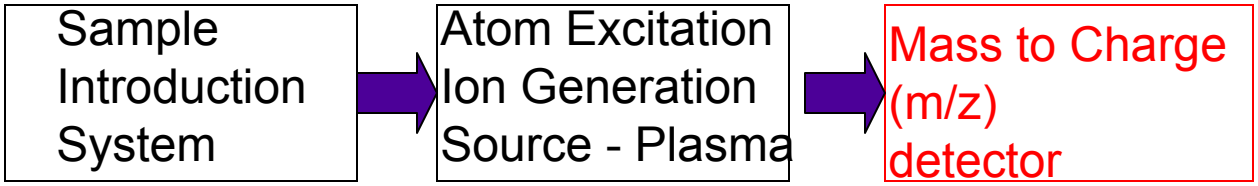
'supersonic' jet' expansion

P=2.5 torr

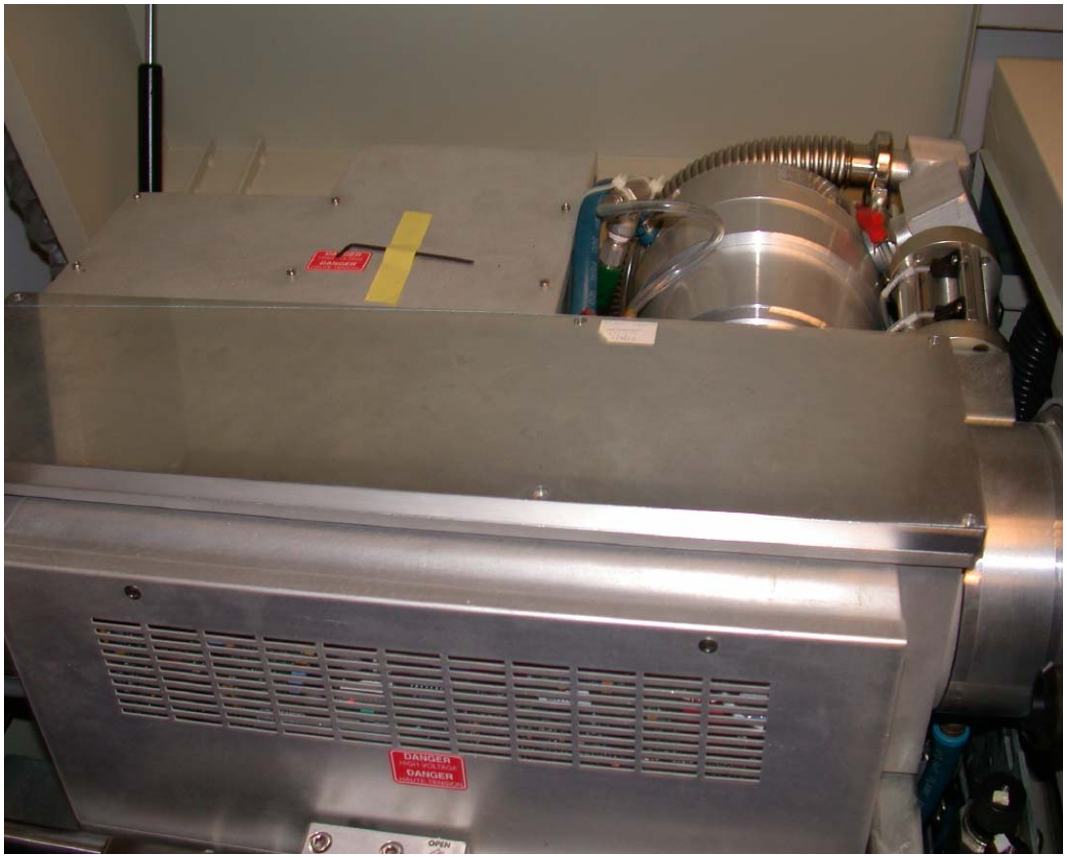
Interface



Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)



Quadrupole mass analyzer



Mass Analyzers

- Quadrupole mass analyzer (m/z range 1-300)
- Magnetic sector mass analyzer
  (for high precision measurements)
- Time of the Flight (TOF) mass detectors

Quadrupole mass analyzers

- Rapid scanning
  - Mass to mass jump (peak hop)
  - Takes only few µs
  - Real-time scanning ability
  - Thus, great for scanning of chromatographic and laser profiles

Isotopic abundances

^{40}Ca	99.600%	^{204}Pb	1.4%
^{42}Ca	0.647%	^{206}Pb	24.1%
^{43}Ca	0.135%	^{207}Pb	22.1%
^{44}Ca	2.086%	^{208}Pb	52.4%
^{46}Ca	0.004%		
^{48}Ca	0.187%		

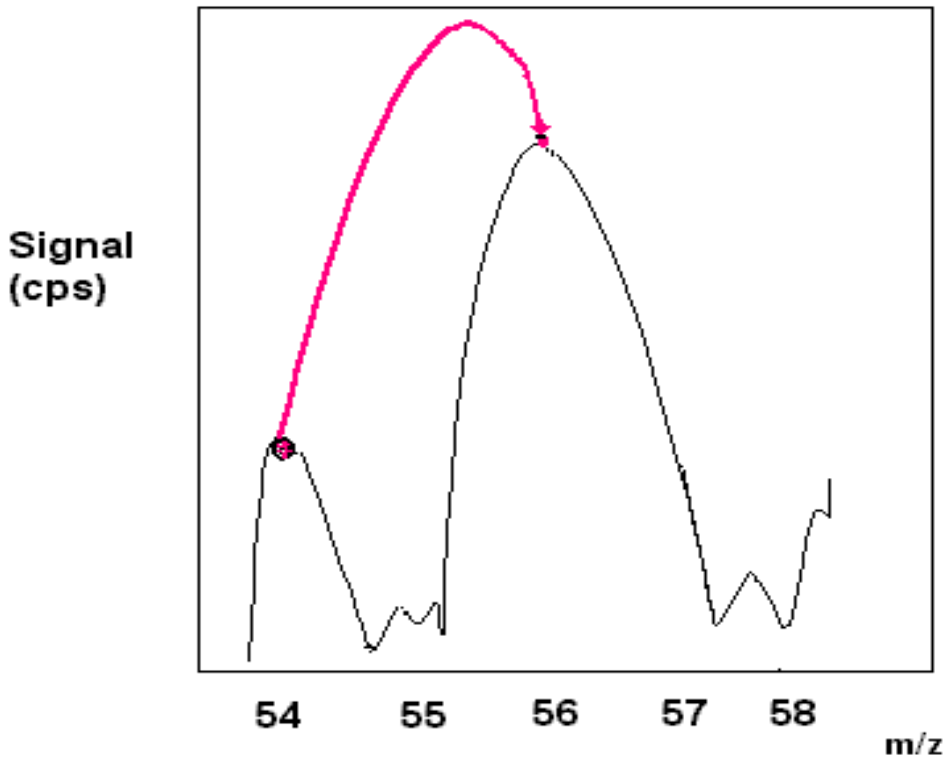
Mass to Charge ratio (m/z) measurements

- mass (m)/charge(z)
  - For :- $^{48}Ca \rightarrow Ca^{+} + 1e^{-}$
    - m/z = 48/1 = 48
  - Doubly charged ions:
    - $^{134}Ba^{2+}$ = 134/2 =67

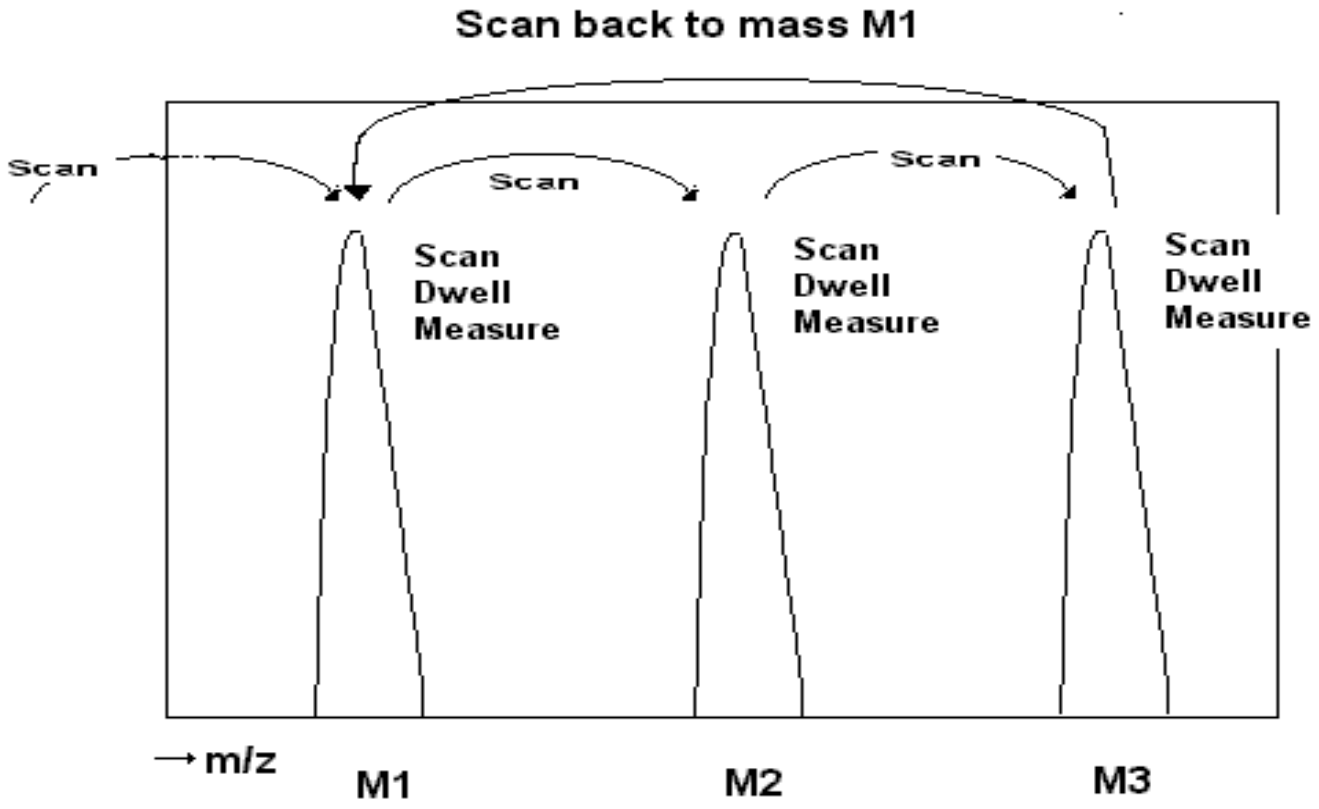
      Interferes with $^{67}Zn^{+}$

Peak-hopping approach

Measurement of ^{54}Fe and ^{56}Fe



ICP-MS Multielement Measurement Routine



Potential interferences

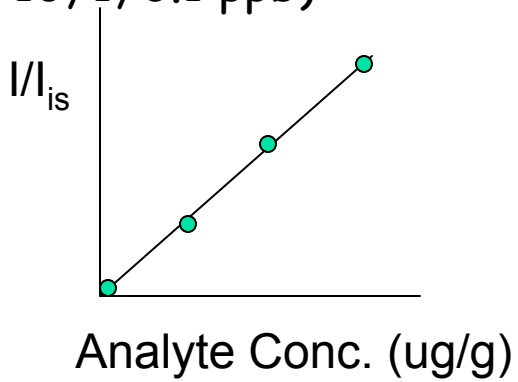
Interferences	on
➢ Isobaric	$^{40}Ar^{+}$	$^{40}Ca^{+}$
➢ Polyatomic	$^{40}Ar^{16}O^{+}$	$^{56}Fe^{+}$
	$^{40}Ar^{35}Cl^{+}$	$^{75}As^{+}$
➢ Background spectrum	$^{38}Ar^{14}N^{+}$	$^{52}Cr^{+}$
	$^{40}Ar^{40}Ar^{+}$	$^{80}Se^{+}$

Types of Analysis

- Bulk analysis
- Surface analysis
- Chemical speciation
- Size fractionation
- Isotopic information

Analytical Information

- Quantitative Analysis with low detection limits
  - Multielement (M_1, M_2, M_3 ….) standards (i.e., 100, 10, 1, 0.1 ppb)
  - Linear calibration curves
  - Very low detection limits (ppt)



- Isotopic abundance ratio information
- Isotope dilution analysis (high precision measurements)

Lead isotopes

Isotope	*Natural Abundance*
^{204}Pb	1.4% (primordial)
^{206}Pb	24.1% (non-radiogenic)
^{207}Pb	22.1% (non-radiogenic)
^{208}Pb	52.4% (non-radiogenic)

All are stable isotopes

Radiogenic lead isotopes

^{232}Th ----- → ^{208}Pb

$(6He + 4\beta)$ $\quad t_{\frac{1}{2}} = 14 \times 10^9$ y

^{235}U ----- → ^{207}Pb

$(7He + 4\beta)$ $\quad t_{\frac{1}{2}} = 0.7 \times 10^9$ y

^{238}U ----- → ^{206}Pb

$(8He + 6\beta)$ $\quad t_{\frac{1}{2}} = 4.5 \times 10^9$ y

Due to the radiogenic origin of these lead isotopes, lead does not have a fixed isotopic abundance in the nature

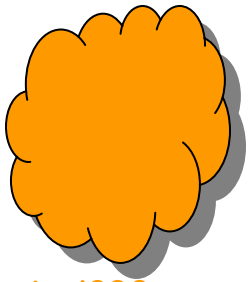
Lead isotope signatures

$^{232}Th/^{238}U$

$\therefore\ ^{208}Pb/^{206}Pb$

$^{232}Th/^{238}U$

$\therefore\ ^{208}Pb/^{206}Pb$



$^{232}Th/^{238}U$

$\therefore\ ^{208}Pb/^{206}Pb$

$^{208}Pb/^{206}Pb$	1.95-2.15
$^{207}Pb/^{206}Pb$	0.78-0.86
$^{204}Pb/^{206}Pb$	0.05-0.06

LA-ICP-MS Analysis

- Hair samples were mounted on a sticky glue tapes
- Laser ablation mode – single spot method,
- Nd(YAG)– 266 nm
- Laser Energy: 0.85
- Average hole size – 48 ± 5 μm
- Ablation depth – 16 μm
- Hair samples were analyzed for

  ^{64}Zn, ^{208}Pb, ^{75}As, ^{12}C and ^{32}S

- Ion intensity (cps) *vs.* Time (s) signals were collected