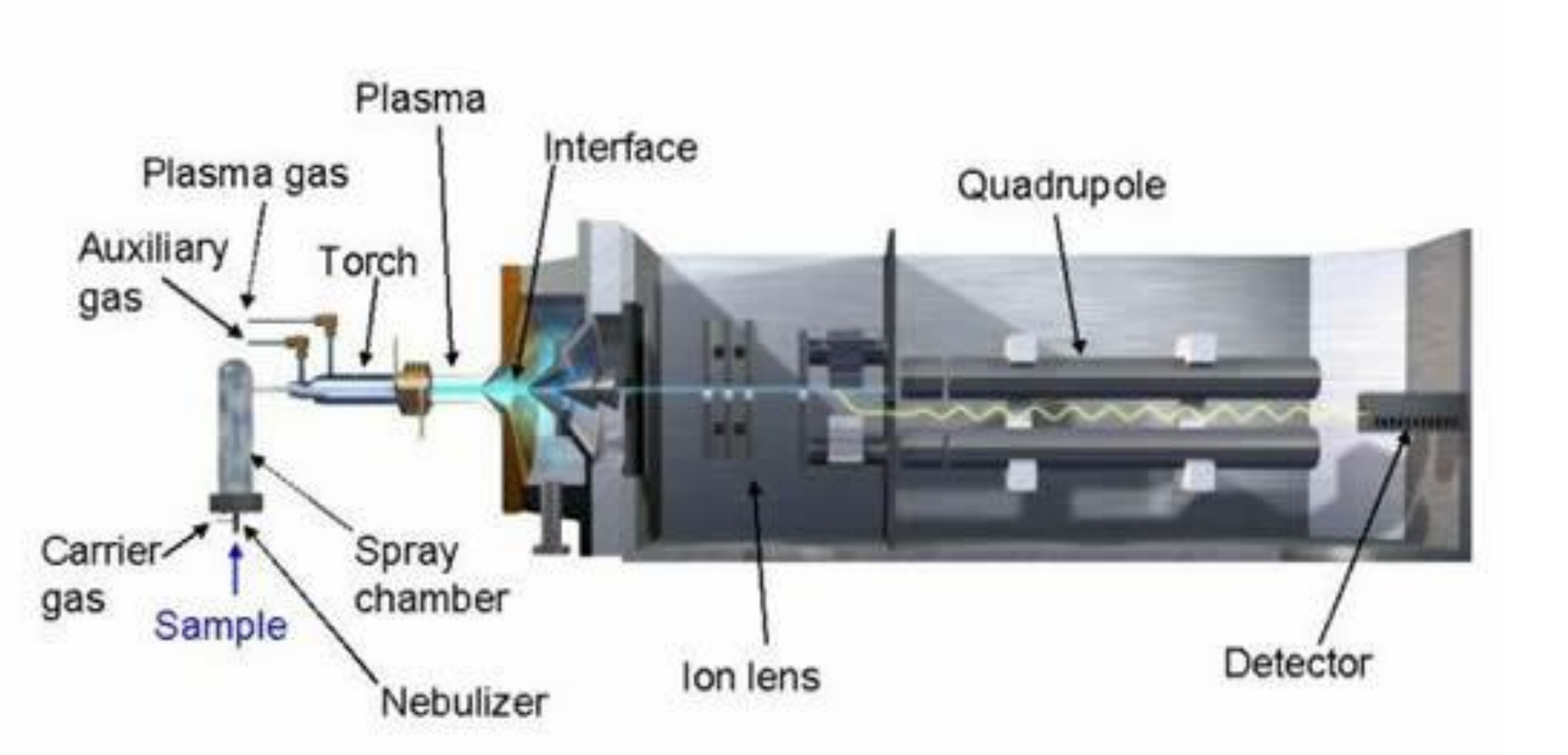
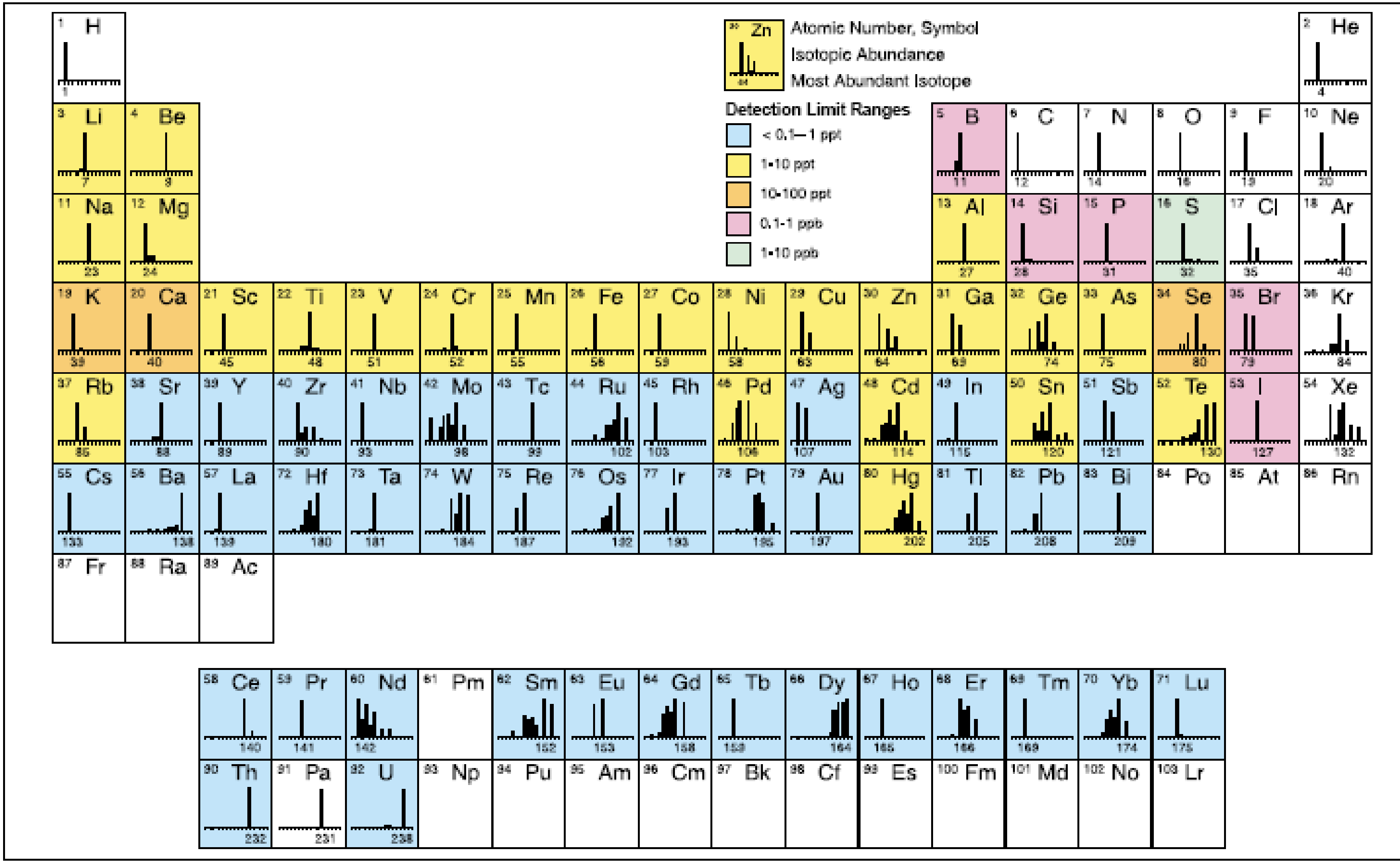
ICP-MS for elemental analysis

Components of ICP-MS



ICP-MS

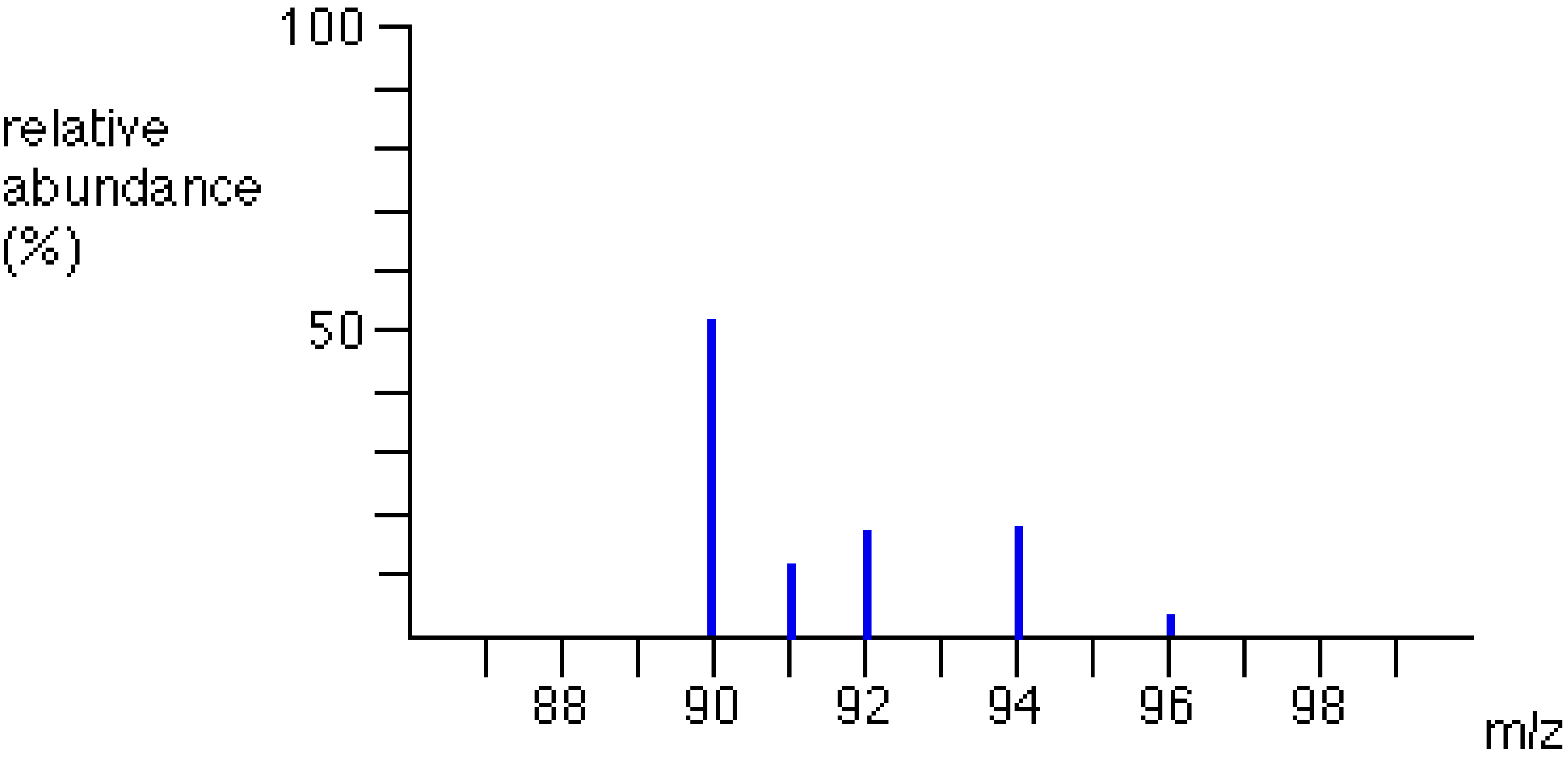
- Developed in the early 1980's
- On-line combination of ICP and MS
- Capable of multi-element trace analysis
- Analysis of liquid samples (solutions) and solids (laser ablation)
- For most elements (90%) of the periodic table



Elements in white: cannot be measured due to poor ionization efficiency.

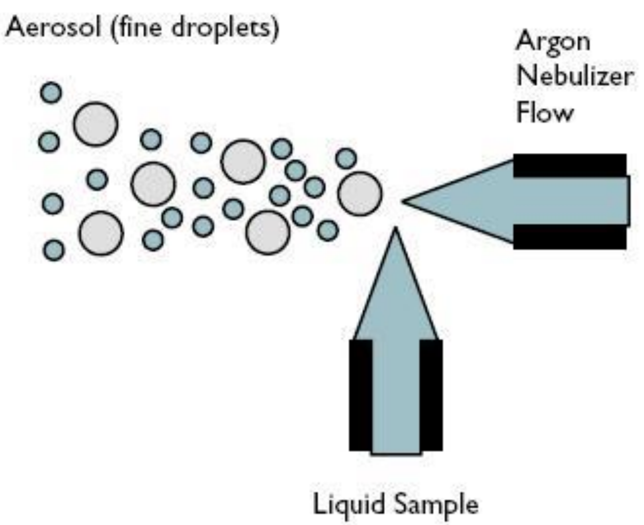
http://crustal.usgs.gov/laboratories/icpms/intro.html

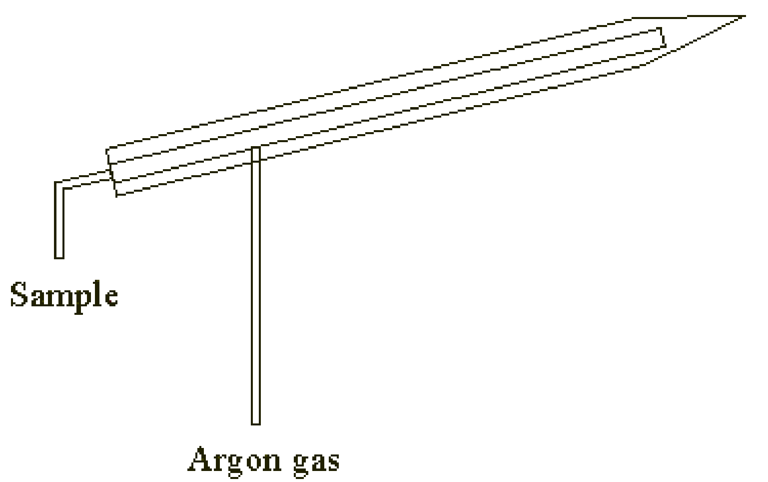
Example: stable isotopes of Zr



Sample Introduction System

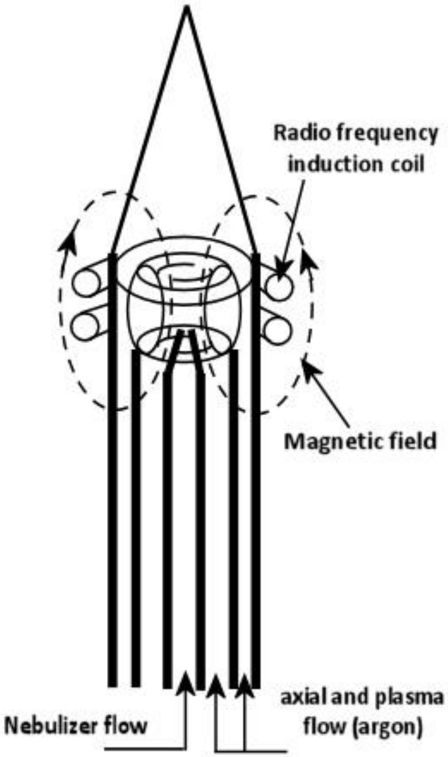
- Involves nebulizer, spray chamber and gas flow
- Nebulizer converts sample into aerosol droplets
- Spray chamber removes larger droplets → waste
- Smaller droplets are swept through plasma





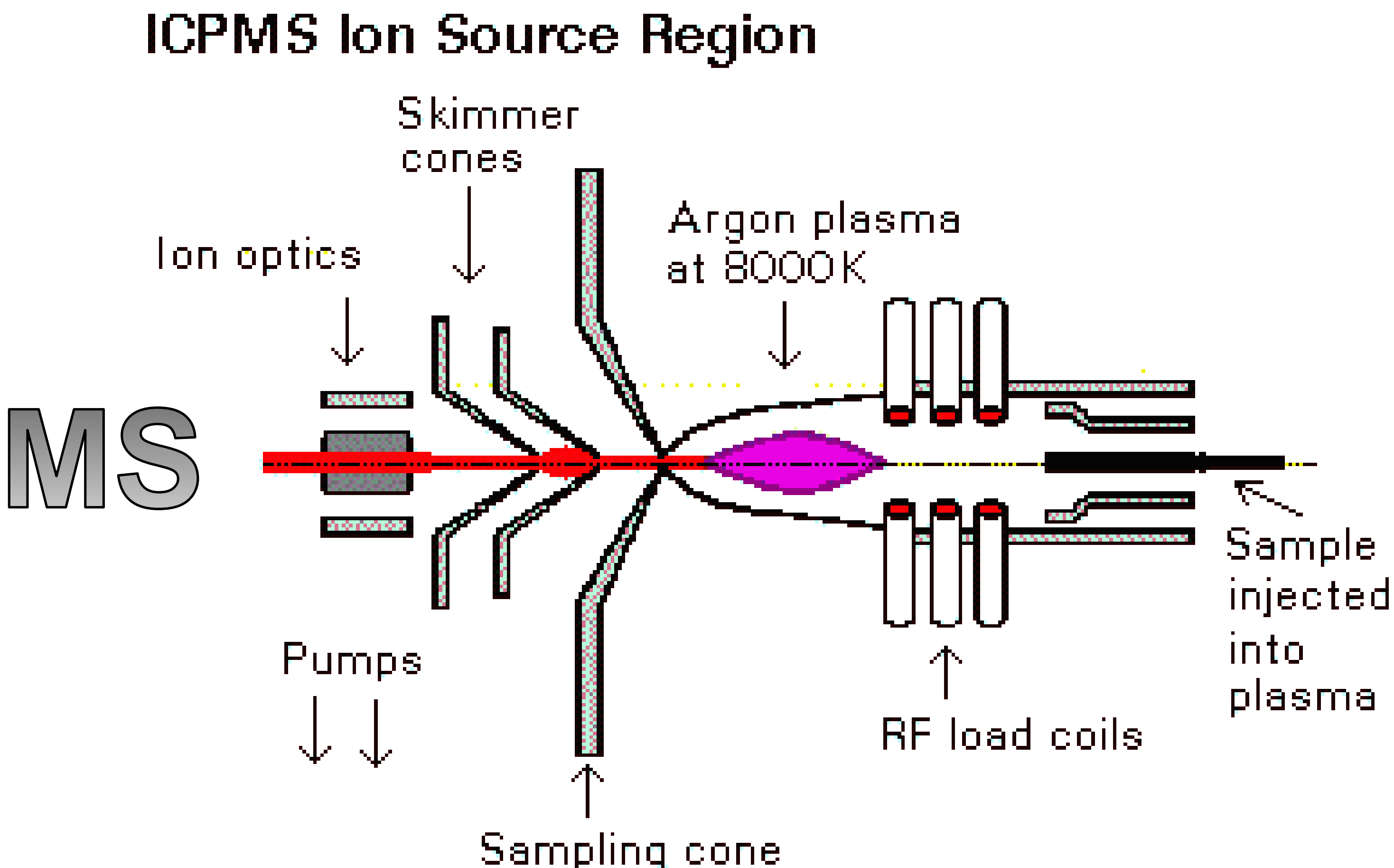
ICP torch

- Aerosol particles mixed with Ar gas
- Ar flow carries vapourized sample into ICP torch where atomization and ionization occur
- Excited atoms and ions enter the interface
- Only ions ions can be analyzed, not neutrals



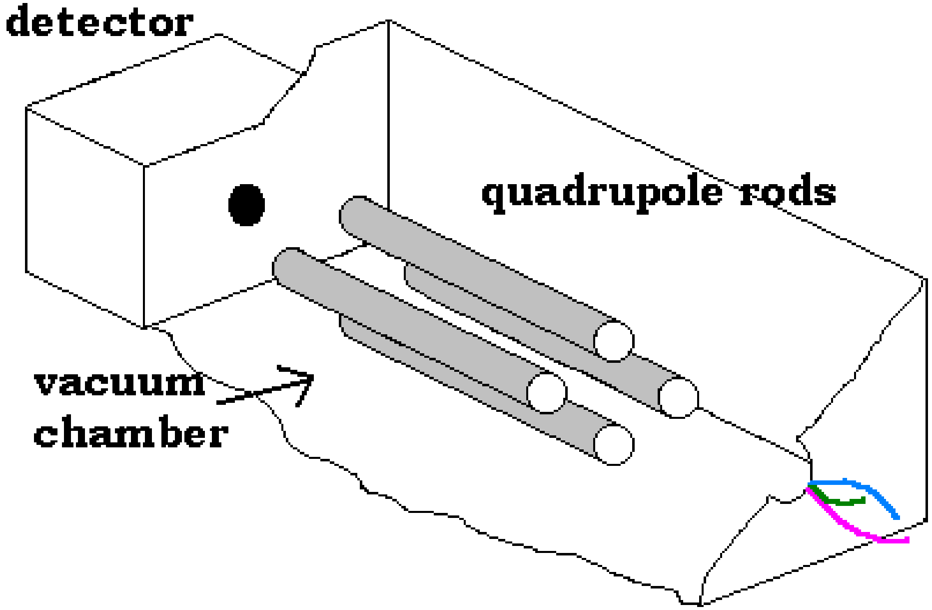
ICP-MS Interface

- Plasma products flow into a vacuum system passing through a few interface skimmer cones
- Skimmer cones are crucial to not disrupt MS vacuum

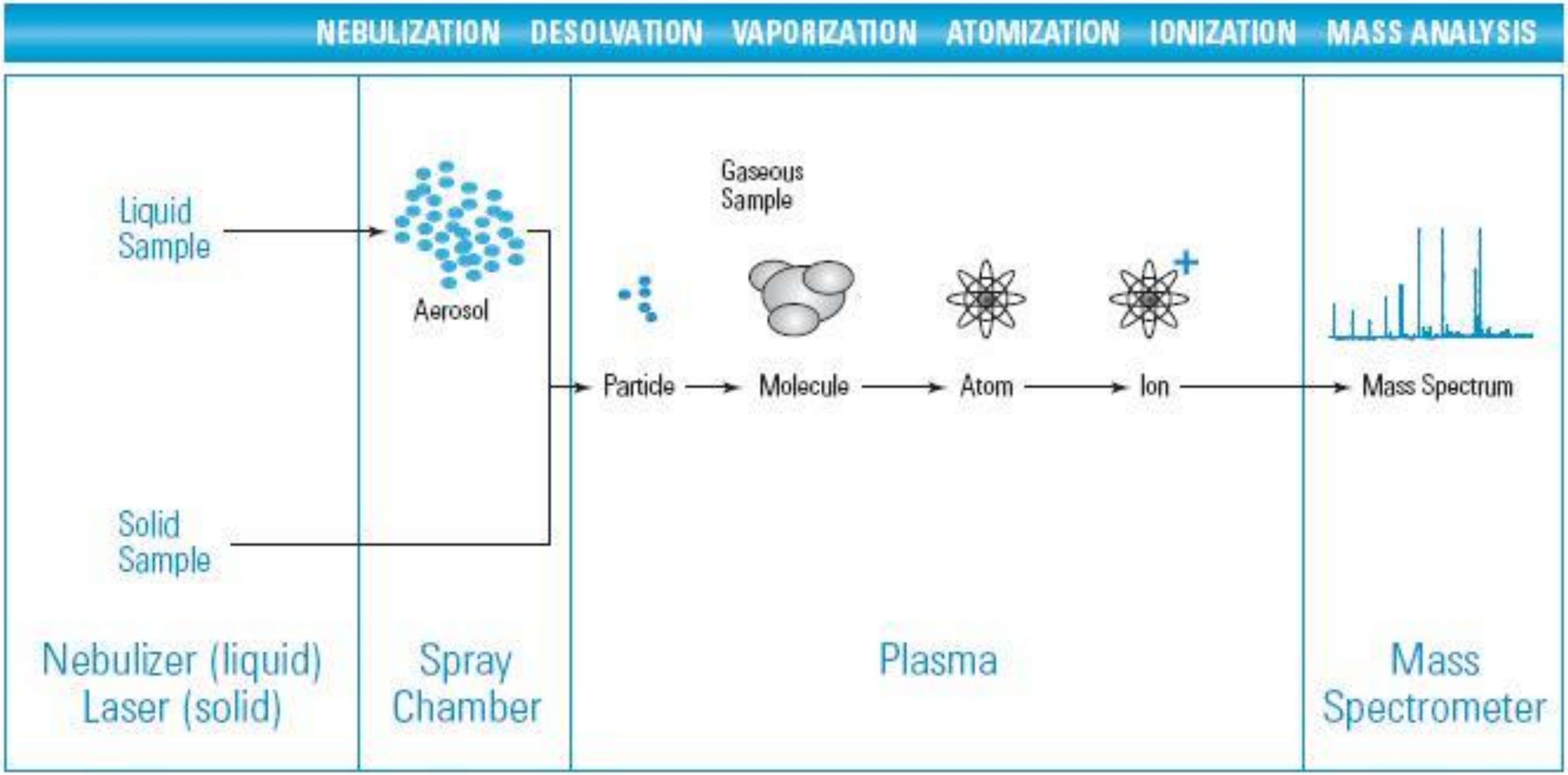


https://www.lhsc.on.ca/lab/metals/icpms.htm

- Mass Spectrometer
  - Quadrupole analyzers are most commonly used



ICP-MS steps



NEBULIZATION
DESOLVATION
VAPORIZATION
ATOMIZATION
IONIZATION
MASS ANALYSIS
Liquid Sample
Aerosol
Gaseous Sample
Particle
Molecule
Atom
Ion
Mass Spectrum
Solid Sample
Nebulizer (liquid)
Laser (solid)
Spray Chamber
Plasma
Mass Spectrometer

Example of application

- Validate the concentrations of elements in human whole blood, plasma, urine and hair
- Assess 27-32 trace elements in samples ranging from 0 to 1000 ng/mL
- 100 healthy volunteers

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Metal and metalloid multi-elementary ICP-MS validation in whole blood, plasma, urine and hair
Reference values

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Table 1
The plasma, the urine and the whole blood sample preparation

	Plasma (ml)	Urine 1 (ml)	Whole blood (ml)	Urine 2 (ml)
Sample	0.3	0.4	0.4	0.6
HNO_3 0.65% (w/v)	2.7	3.6	3.5 (triton 0.1%)	2.3
Triton 0.01% (v/v)				
Butanol 0.5% (v/v)				
Rh (internal standard)				
Standard addition	–	–	0.1	0.1
Centrifugation after hemolysis	No	No	Yes	No
Calibration	Direct		Matrix standard addition	

Analytical validation

According to the French Society of Clinical Biology [18] each element has to show linearity (from limit of detection to 25 ng/ml or to 250 ng/ml depending on the metal) with a correlation coefficient higher than 0.99.

27 elements in whole blood

Table 2
One hundred blood multi-elementary healthy volunteers analytical validation and proposed reference range (ng/ml = µg/l)

Compound	*r*	LOD	LOQ	CV% (1)	CV% (2)	Median	Reference range 5th–95th percentile
Beryllium	0.9996	0.042	0.14	2.61	2.78	0.02	0.02–0.09
Boron	0.9995	1.33	4.4	3.55	5.18	26	14–44
Aluminum	0.9995	2.55	8.1	4.56	8.97	1.3	1.28–6.35
Manganese	0.9999	0.027	0.09	2.22	3.33	7.6	5.0–12.8
Cobalt	1.0000	0.017	0.06	2.52	7.34	0.25	0.04–0.64
Nickel	0.9999	0.188	0.63	3.71	9.99	2.1	0.09–4.18
Gallium	0.9997	0.013	0.04	1.24	7.23	3.5	2.65–4.71
Germanium	0.9999	0.05	0.17	2.18	9.39	16	10.8–19.5
Arsenic	0.9998	0.032	0.11	3.36	5.35	5.0	2.6–17.8
Selenium	0.9996	0.49	1.6	1.70	2.39	119	89–154
Rubidium	0.9994	0.019	0.06	1.65	7.00	1680	1289–2358
Strontium	1.0000	0.007	0.02	1.02	2.36	16	9–41
Molybdenum	0.9993	0.02	0.07	4.66	9.74	2.9	0.77–7.86
Palladium	0.9998	0.012	0.04	2.59	9.28	0.08	0.01–0.71
Silver	0.9995	0.081	0.27	4.09	6.10	1.4	0.69–4.51
Cadmium	1.0000	0.011	0.04	2.18	2.87	0.31	0.15–2.04
Tin	0.9999	0.022	0.07	3.46	6.74	1.1	0.11–1.75
Antimony	0.9997	0.008	0.03	1.61	3.79	0.08	0.05–0.13
Tellurium	1.0000	0.019	0.06	3.02	5.83	0.16	0.11–0.45
Barium	0.9998	0.057	0.19	1.38	5.45	59	46.4–77.6
Tungsten	0.9999	0.008	0.03	1.58	7.33	0.006	0.004–0.082
Platinum	0.9994	0.004	0.01	1.85	5.83	0.002	0.002–0.010
Mercury	0.9998	0.079	0.26	3.09	4.23	3.0	0.94–8.13
Thallium	0.9999	0.002	0.005	2.76	3.43	0.02	0.011–0.035
Lead	0.9998	0.019	0.07	2.92	4.77	26	11.4–62.8
Bismuth	0.9997	0.002	0.007	3.00	2.62	0.001	0.001–0.007
Uranium	0.9999	0.001	0.002	1.89	3.59	0.004	0.002–0.006

r: correlation coefficient, LOD: limit of detection, LOQ: limit of quantification, CV% (1) = intra-assay imprecision, CV% (2) = inter-assay imprecision.

27 elements in plasma

Table 3
One hundred plasma multi-elementary healthy volunteers analytical validation and proposed reference range (ng/ml = µg/l)

Compound	*r*	LOD	LOQ	CV% (1)	CV% (2)	Median	Reference range 5th–95th percentile
Lithium	0.9999	0.19	0.63	1.03	5.71	3.4	1.8–18.8
Beryllium	0.9999	0.03	0.10	0.85	5.20	0.015	0.015–0.103
Boron	0.9997	1.26	4.2	1.66	3.26	36	19–79
Aluminum	0.9991	2.30	7.7	1.25	13.8	3.1	1.2–17.3
Manganese	0.9999	0.024	0.08	0.60	2.59	1.12	0.63–2.26
Cobalt	0.9997	0.085	0.28	0.86	4.24	0.49	0.30–1.02
Nickel	0.9874	0.08	0.28	1.58	5.13	2.20	0.04–5.31
Copper	0.9978	0.14	0.47	0.49	2.35	1075	794–2023
Zinc	0.9982	0.63	2.1	0.27	2.36	726	551–925
Gallium	0.9992	0.16	0.52	0.74	3.57	6.24	5.03–8.82
Germanium	0.9996	0.026	0.09	0.89	3.22	5.06	3.70–6.17
Arsenic	0.9997	0.038	0.13	0.22	3.44	6.2	4.4–14.2
Selenium	0.9998	0.66	2.0	1.42	1.61	112	79–141
Rubidium	0.9995	0.014	0.05	0.26	3.06	147.8	101–358
Strontium	0.9998	0.016	0.05	0.35	2.14	28.8	18–75
Molybdenum	0.9997	0.026	0.09	1.09	2.46	0.956	0.67–1.68
Cadmium	0.9998	0.008	0.03	2.64	2.88	0.03	0.01–0.05
Tin	0.9979	0.29	0.97	0.86	2.03	1.82	0.15–2.70
Antimony	0.9996	0.006	0.02	3.23	4.03	0.11	0.03–0.15
Tellurium	0.9999	0.013	0.04	1.18	2.35	0.057	0.02–0.13
Barium	0.9998	2.09	7.0	0.75	2.91	111	90–154
Tungsten	0.9997	0.19	0.62	2.17	4.05	0.239	0.09–0.75
Platinum	0.9977	0.007	0.02	0.97	4.50	0.3855	0.016–0.92
Thallium	0.9996	0.003	0.01	1.51	4.43	0.06	0.01–0.24
Lead	0.9991	0.028	0.10	1.96	6.70	0.062	0.014–0.25
Bismuth	0.9994	0.004	0.01	1.88	5.19	0.002	0.002–0.401
Uranium	0.9997	0.001	0.002	2.28	5.70	0.007	0.004–0.011

r: correlation coefficient, LOD: limit of detection, LOQ: limit of quantification, CV% (1) = intra-assay imprecision, CV% (2) = inter-assay imprecision.

30 elements in urine

Table 4
One hundred urine multi-elementary healthy volunteers analytical validation and proposed reference range (ng/ml = µg/l)

Compound	*r*	LOD	LOQ	CV% (1)	CV% (2)	Median	Reference range 5th–95th percentile
Lithium	0.9998	0.006	0.02	0.23	6.03	12	4.6–219
Beryllium	0.9998	0.015	0.05	3.74	7.44	0.01	0.008–0.042
Boron	0.9997	0.25	0.82	4.47	3.42	647	282–2072
Aluminum	0.9996	0.32	1.1	2.02	7.14	1.9	0.16–11.2
Vanadium	0.9999	0.04	0.15	2.19	3.40	3.3	1.4–10.2
Manganese	0.9999	0.010	0.03	1.22	5.14	0.31	0.11–1.32
Cobalt	0.9999	0.017	0.06	1.15	2.87	0.30	0.16–1.14
Nickel	0.9999	0.063	0.21	1.59	3.50	1.8	0.59–4.06
Copper	0.9999	0.047	0.16	1.40	3.35	6.9	4.3–12.1
Zinc	0.9999	0.506	1.7	1.09	8.25	195	44–499
Gallium	0.9999	0.006	0.02	2.02	3.88	0.07	0.02–0.28
Germanium	0.9994	0.023	0.08	2.40	8.87	2.0	1.17–3.37
Arsenic	0.9999	0.030	0.10	0.72	3.91	19	2.3–161
Selenium	0.9995	0.647	2.2	3.55	5.52	20	10.5–45.5
Rubidium	0.9992	0.018	0.06	2.77	5.46	1211	433–2698
Strontium	0.9995	0.004	0.01	2.15	2.84	90	20–413
Molybdenum	0.9999	0.060	0.20	8.87	7.85	20	7–50
Palladium	0.9995	0.14	0.45	0.83	7.31	0.07	0.07–0.64
Cadmium	0.9999	0.007	0.02	1.06	2.95	0.16	0.06–0.79
Tin	0.9997	0.008	0.03	0.80	1.96	0.32	0.05–2.28
Antimony	0.9999	0.003	0.009	0.74	3.13	0.04	0.02–0.08
Tellurium	0.9999	0.021	0.07	1.43	7.02	0.23	0.10–0.52
Barium	0.9999	0.022	0.07	1.54	7.72	0.89	0.17–3.85
Tungsten	0.9999	0.012	0.04	1.90	3.77	0.03	0.01–0.09
Platinum	0.9999	0.004	0.01	2.89	5.75	0.005	0.002–0.036
Mercury	0.9996	0.29	0.95	5.26	5.44	0.59	0.14–2.21
Thallium	0.9997	0.14	0.47	4.91	3.45	0.15	0.07–0.84
Lead	0.9999	0.017	0.06	4.71	3.39	0.55	0.01–2.14
Bismuth	0.9997	0.0009	0.003	4.07	4.36	0.001	0.0005–0.009
Uranium	0.9994	0.0003	0.001	5.41	5.58	0.002	0.0002–0.008

r: correlation coefficient, LOD: limit of detection, LOQ: limit of quantification, CV% (1) = intra-assay imprecision, CV% (2) = inter-assay imprecision.

32 elements in hair

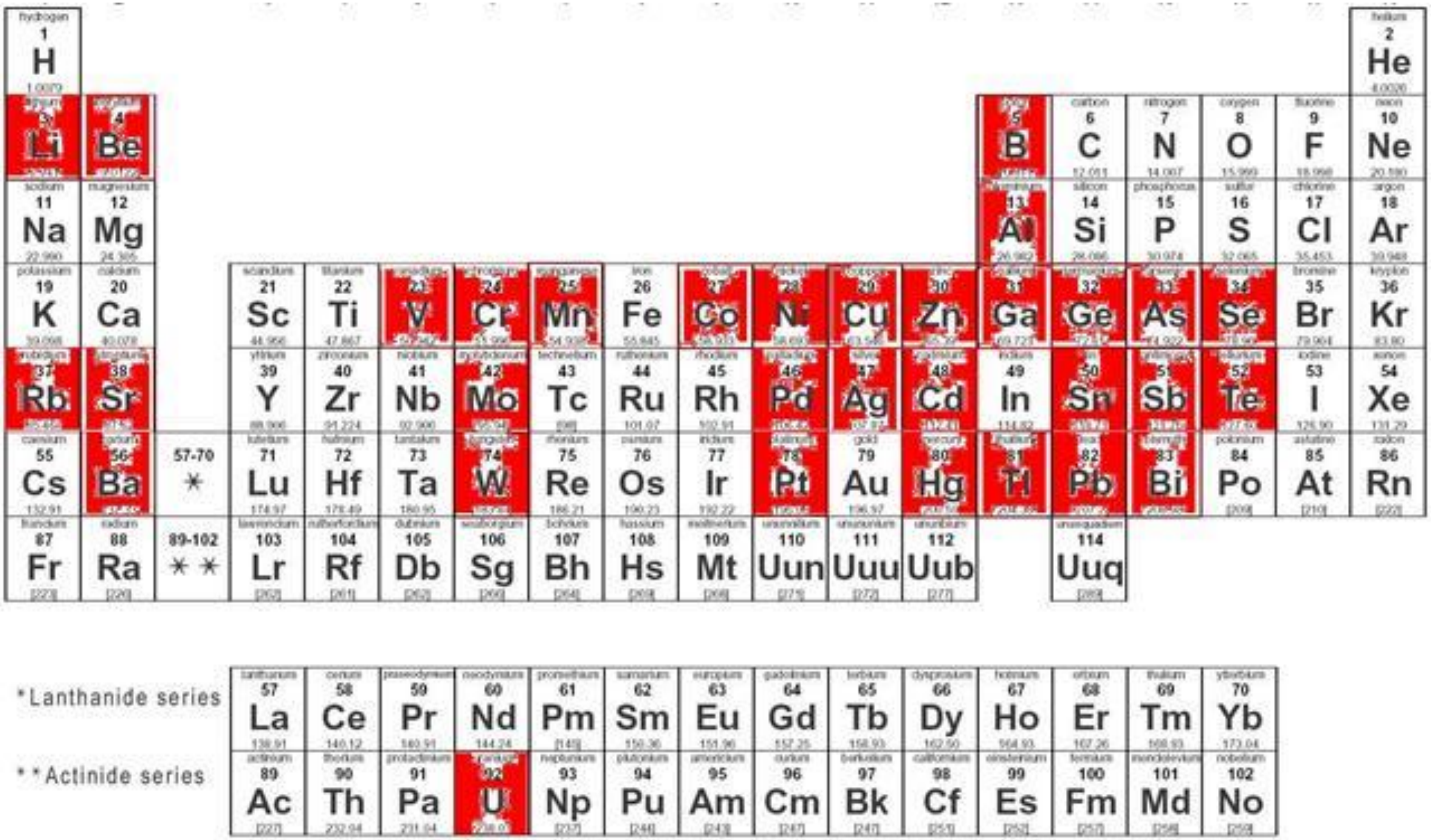
Table 5

Forty five hair multi-elementary healthy volunteers analytical validation and proposed reference range (ng/mg)

Compound	*r*	LOD	LOQ	CV% (1)	CV% (2)	Median	Reference range 5th–95th percentile
Lithium	0.9999	0.002	0.007	6.5	6.1	0.016	0.003–0.042
Beryllium	0.9998	0.002	0.007	3.9	8.8	0.007	0.003–0.012
Boron	0.9991	0.14	0.46	3.6	8.9	0.54	0.26–1.87
Aluminum	0.9993	0.02	0.08	2.3	7.7	1.63	0.26–5.30
Vanadium	0.9998	0.001	0.003	1.7	9.0	0.016	0.001–0.051
Chromium	0.9999	0.06	0.20	3.5	9.3	0.20	0.11–0.52
Manganese	0.9996	0.001	0.004	1.7	6.6	0.067	0.016–0.57
Cobalt	0.9998	0.0003	0.001	2.3	7.9	0.023	0.004–0.14
Nickel	0.9998	0.01	0.05	1.8	6.4	0.23	0.08–0.90
Copper	0.9999	0.01	0.03	1.3	10.4	20.3	9.0–61.3
Zinc	0.9996	0.01	0.04	1.1	8.1	162	129–209
Gallium	0.9998	0.0003	0.0009	2.2	8.9	0.011	0.002–0.068
Germanium	0.9999	0.001	0.002	1.8	7.6	0.004	0.001–0.039
Arsenic	0.9997	0.01	0.02	3.5	6.4	0.05	0.03–0.08
Selenium	0.9997	0.02	0.06	2.6	7.8	0.54	0.37–1.37
Rubidium	0.9995	0.0003	0.001	2.0	5.8	0.006	0.003–0.03
Strontium	0.9995	0.0002	0.0007	1.0	7.0	0.89	0.17–4.63
Molybdenum	0.9998	0.0004	0.001	3.9	8.2	0.021	0.01–0.028
Palladium	0.9995	0.001	0.003	2.9	22.3	0.01	0.004–0.049
Silver	0.9998	0.0005	0.002	0.7	9.9	0.08	0.02–1.31
Cadmium	0.9998	0.0003	0.0009	0.7	5.9	0.011	0.004–0.17
Tin	0.9998	0.001	0.002	1.0	5.9	0.046	0.007–0.34
Antimony	0.9998	0.0003	0.001	1.0	5.2	0.008	0.003–0.13
Tellurium	0.9997	0.0006	0.002	6.7	6.1	0.0003	0.0003– 0.001
Barium	0.9998	0.001	0.003	0.8	5.5	0.28	0.05–1.58
Tungsten	0.9998	0.0002	0.001	2.1	7.2	0.0013	0.0001–0.007
Platinum	0.9999	0.0001	0.0002	1.5	6.2	0.00035	0.0004–0.0008
Mercury	0.9986	0.004	0.013	0.4	9.5	0.66	0.31–1.66
Thallium	0.9995	0.00005	0.0002	3.7	4.7	0.0002	0.0001–0.0004
Lead	0.9997	0.0003	0.001	0.7	4.4	0.41	0.13–4.57
Bismuth	0.9997	0.0008	0.003	1.4	5.3	0.009	0.0004–0.14
Uranium	0.9998	0.00004	0.0002	2.0	7.2	0.009	0.002–0.03

r: correlation coefficient, LOD: limit of detection, LOQ: limit of quantification, CV% (1) = intra-assay imprecision, CV% (2) = inter-assay imprecision.

Elements observed in study



Conclusions

- Required very small amount of samples
- Each element showed linearity R^2 ~0.99
- Clinical applications were reported
  - Individual revealed lead exposure
  - Whole blood content showed 120 μg/l (normal < 63 μg/l)
  - Home tap water discovered as source of lead: 111 μg/l(normal <25 μg/l)
- ICP-MS used for unexplained cases of deceased individuals when toxicological analysis is negative

Other applications of ICP-MS

- Forensic Sciences
- Geological and Environmental Sciences
- Health Sciences (toxicology)
- Industry (materials)
- Biochemistry (metalloproteins)

Applications in Forensic Science

ICP-MS is used to help solve crimes where microscopic specimens are left behind, or picked up, by criminals.

- glass
- bullets
- Ink
- paint

Advantages

- Information on isotope distribution for each element studied
- Wide elemental coverage
- Simple sample preparation
- Good precision and accuracy
- Very specific

Weaknesses

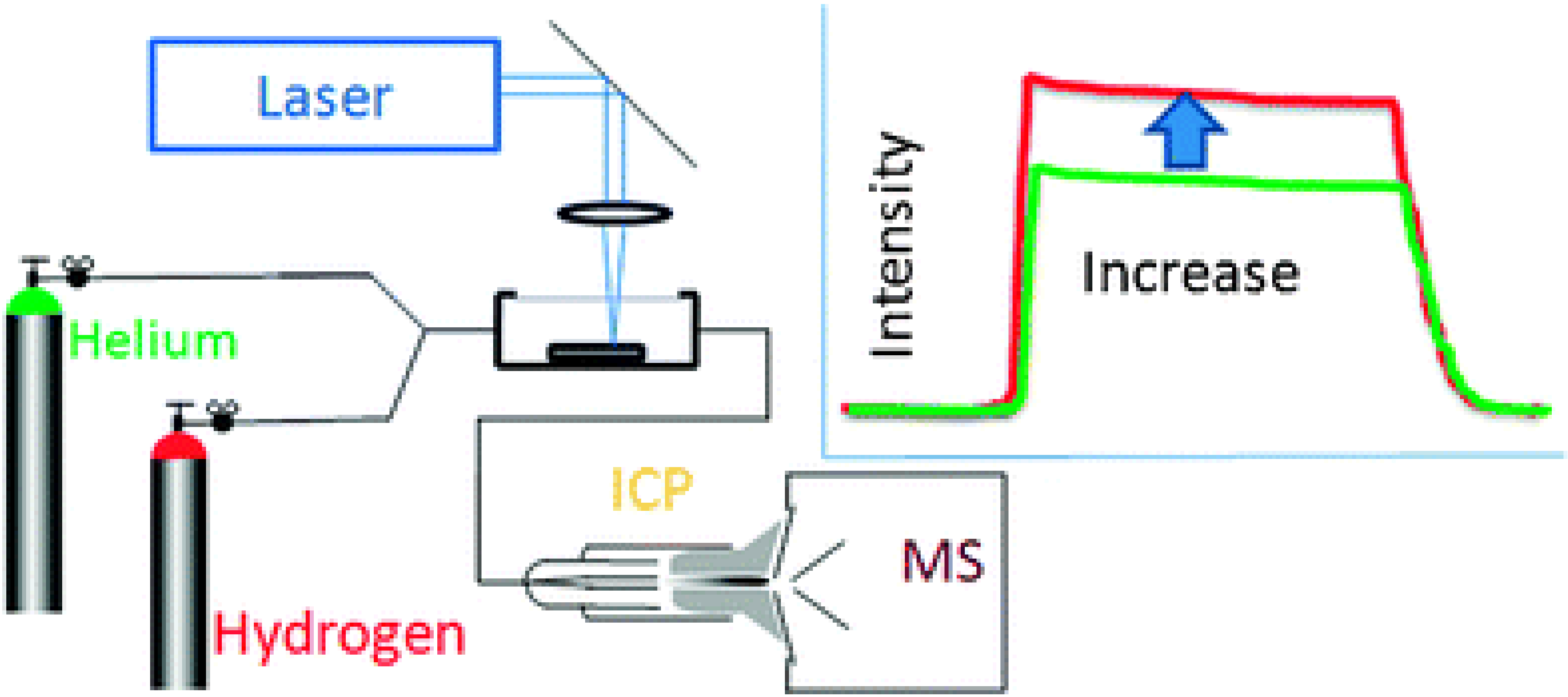
- Prone to spectral interferences
  - Oxides
  - Small organic molecules
- Cost (MS + high vacuum pumps)
- High maintenance

Additions to ICP-MS

"Hyphenated" ICP-MS:

- Laser Ablation ICP-MS (LA-ICP-MS)
- Gas Chromatography-ICP-MS (GC-ICP-MS)
- Liquid Chromatography ICP-MS (LC-ICP-MS)

Laser ablation ICP-MS



http://pubs.rsc.org/EN/content/articlelanding/2007/ja/b709489b#!divAbstract

Questions

1.

In ICP, two detectors can be used in line: an OES system and a mass spectrometer. What is the main advantage of this combination?

a) All elements M produce M^+ ions and emit light at the same wavelength
b) Elements that have the same mass emit light at different wavelengths
c) The OES can be used only in the axial configuration, yielding more intensity
d) It is not possible to combine ICP with both OES and MS
e) No calibration is needed

2

The graph below was obtained by ICP-MS using the method of standard additions. The x-axis represents the different concentrations of standard once added to the unknown, and the y-axis is the measured signal in arbitrary units. Determine the concentration of the unknown.

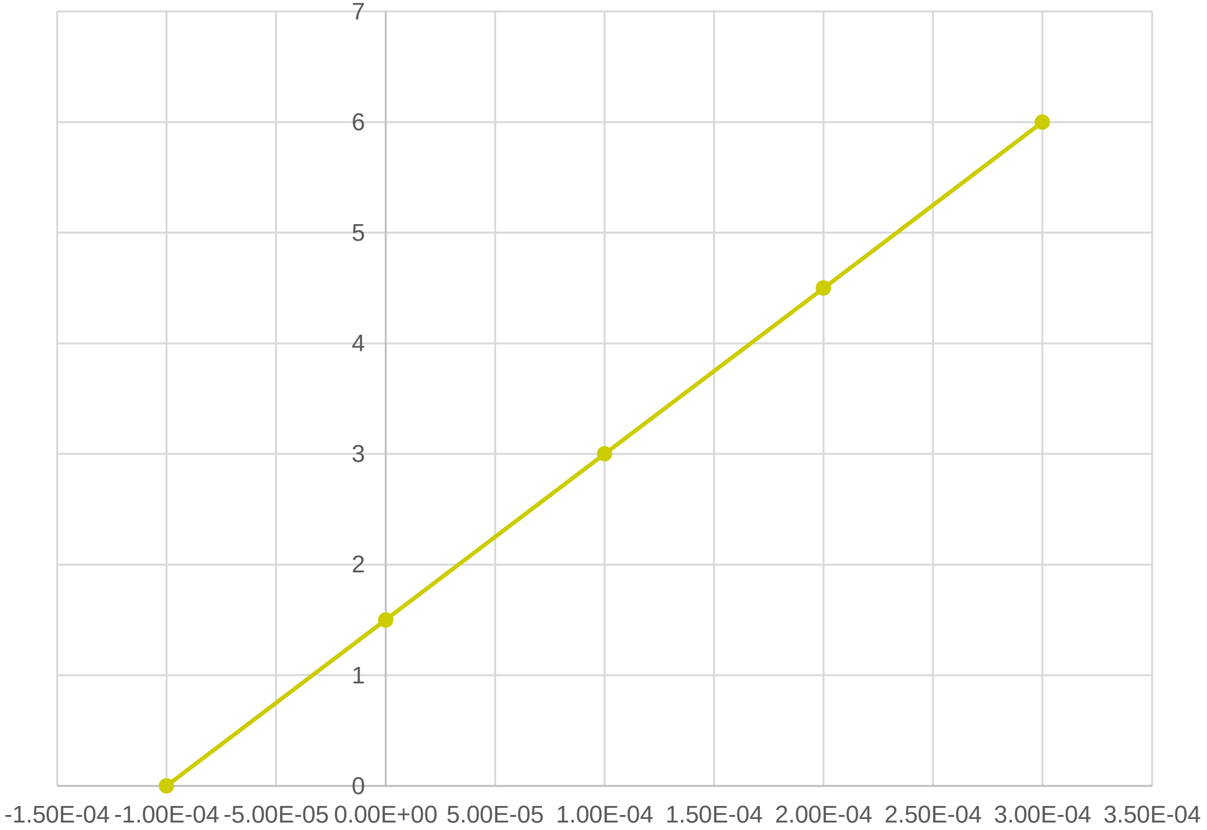
a) 1.5 M

b) 10^{-4} M

c) 5×10^{-5} M

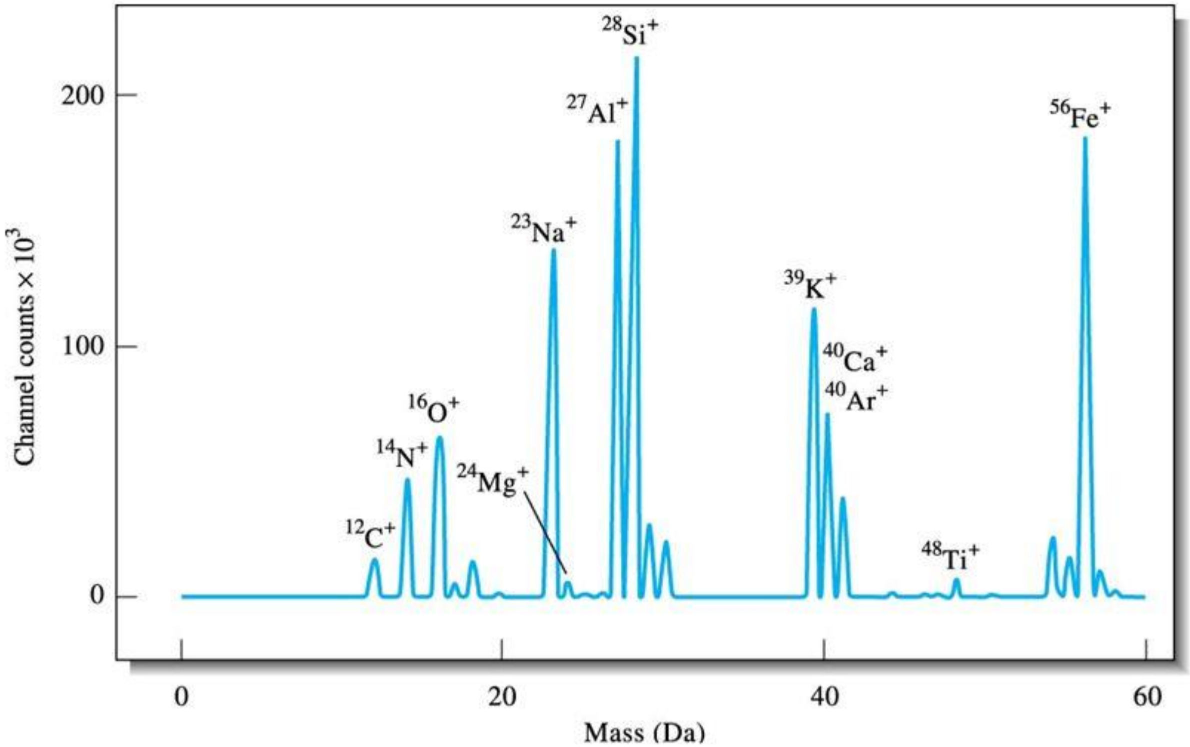
d) 3×10^{-4} M

e) unsolvable



3.

The mass spectrum below was obtained by laser ablation ICP-MS. Interference between Ar and Ca is observed at *m/z* 40. Assuming that the background Ar^+ peak remains constant in all analyses, suggest and describe a method for the determination of Ca^+. Justify.



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The mass spectrum of a standard rock sample obtained by laser ablation / ICP-MS.