Elements & Isotopes: Has ICP-MS delivered all it promised?

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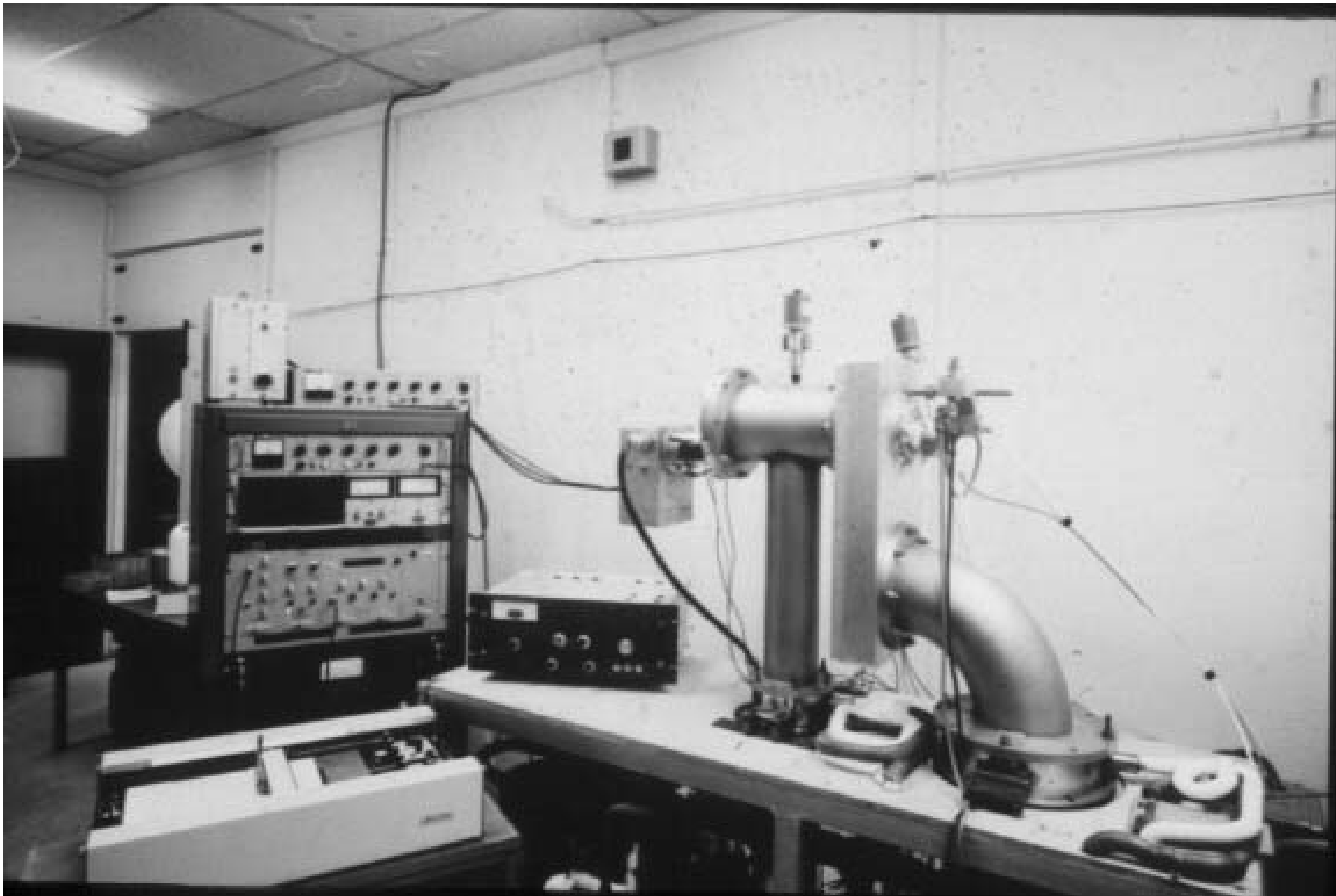
Design requirements for new analytical mass spectrometer – March 1971

- Speed of analysis – 4 to 6 samples per hour
- Mass range – 6 to 238 m/z
- Detection limits for mono-isotopic elements - 0.1 ppm
- Precision - 25% RSD
- Elemental & isotope ratio measurement
- Minimal operator control of excitation source
- Automatic scanning through mass range
- Print out of mass intensity values

Landmarks in development

- Alan Gray Applied Research Laboratories, (1974, 1975)
  - DC plasma
  - 3000-6000K
  - Sufficient to ionise elements <8.5eV
  - Includes U, Th, Pb
  - Requirement for uranium exploration

First DCP 1974



Landmarks in development

- Decision to replace DC plasma with Inductively Coupled Plasma
- Parallel developments in UK, USA and Canada
- First spectra obtained by Alan Gray & Alan Date at Univ of Surrey in 1981
- First commercial instruments ordered in 1983

US Patent 1978

United States Patent [19]

French et al.

[11] **4,121,099**

[45] **Oct. 17, 1978**

[54] METHOD AND APPARATUS FOR FOCUSSING AND DECLUSTERING TRACE IONS

[75] Inventors: **John Barry French; Neil M. Reid, both of Thornhill; Janette A. Buckley, Willowdale, all of Canada**

[73] Assignee: **The Governing Council of the University of Toronto, Toronto, Canada**

[21] Appl. No.: **790,216**

[22] Filed: **Apr. 25, 1977**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 555,202, Mar. 3, 1975, Pat. No. 4,023,398.

[51] **Int. Cl.²** **B01D 59/44**
[52] **U.S. Cl.** **250/296; 250/281**
[58] **Field of Search** **313/309, 336; 250/281, 250/296**

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,287,749	6/1942	Slayter	313/309
2,611,255	3/1953	Stavro	313/336
3,920,987	11/1975	Anbar et al.	250/281
4,031,397	6/1977	Cardillo	250/281

Primary Examiner—Harold A. Dixon
Attorney, Agent, or Firm—Rogers, Bereskin & Parr

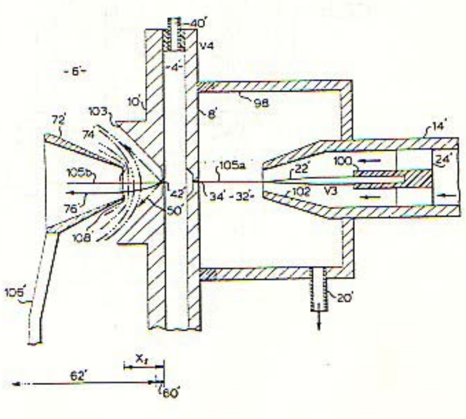
[57] **ABSTRACT**

A method and apparatus for focussing and declustering trace ions travelling from a gas through an orifice into a vacuum chamber and to a mass analyzer in the vacuum chamber. Advantage is taken of the free jet expansion of the gas into the vacuum chamber by applying an electric focussing field in a specific region of the free jet. The region is selected sufficiently close to the orifice that the gas density limits the kinetic energy spread which the ions can acquire under the applied field, typically to 2 ev or less, while the early focussing increases the available ion signal. Declustering can be collision induced in the region by providing a field in the region sufficient to impart an internal energy of between 0.1 and 1.5 ev to ions in the region. The kinetic energy which the ions can acquire under the applied field is still limited by the density of the gas in the free jet, so that the kinetic energy spread which the ions can acquire is still limited. Preferably the focussing and declustering fields are produced by a single conical tapered lens element located at distance X_f from the orifice, where

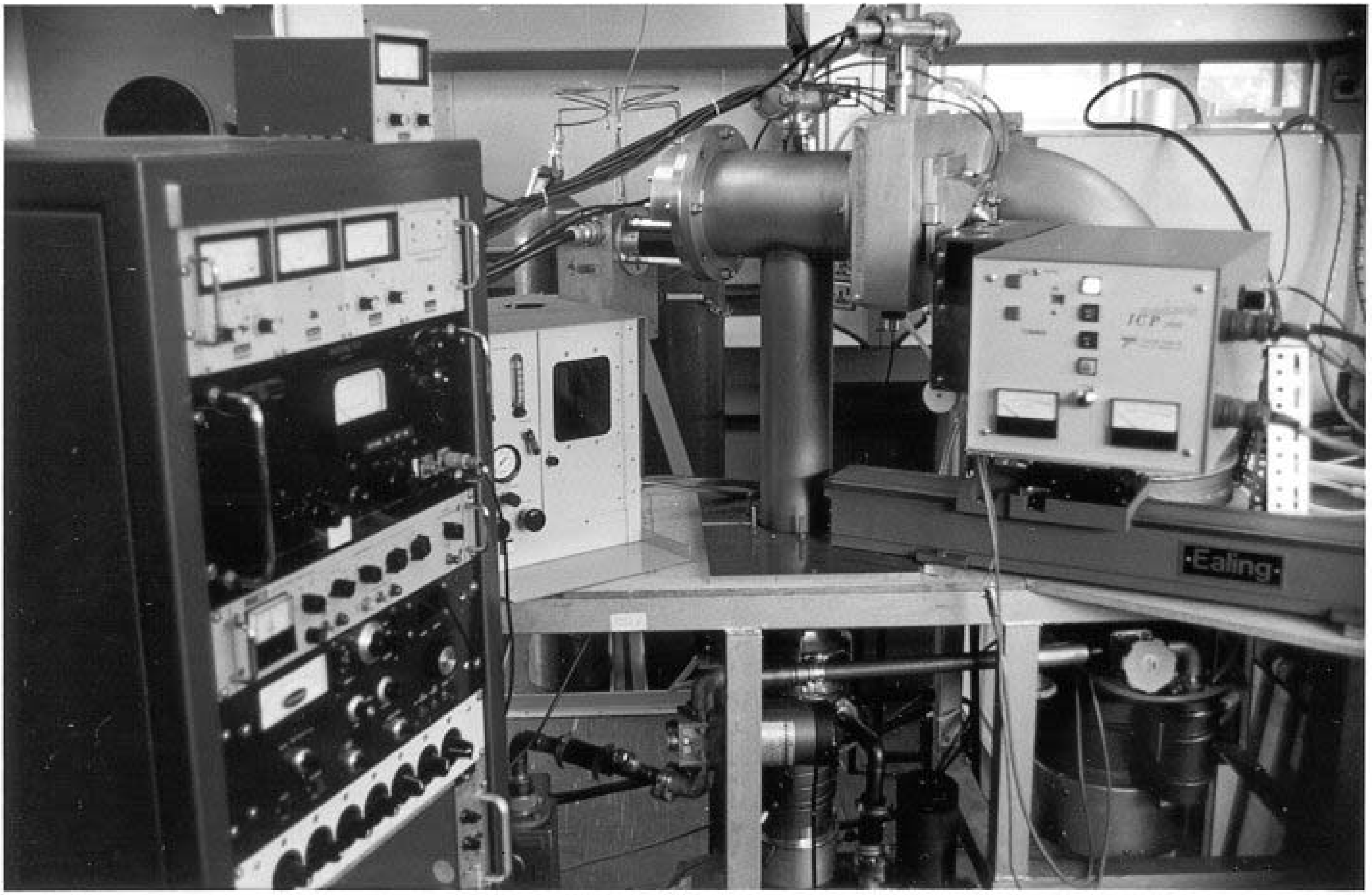
$$X_f = 50D \; [illegible]$$

and D is the orifice diameter, for atmospheric pressure and room temperature source conditions. The electric field between the lens element and the mass spectrometer is then controlled to limit the energy spread imparted to the ions in their travel from the lens elements to the mass spectrometer.

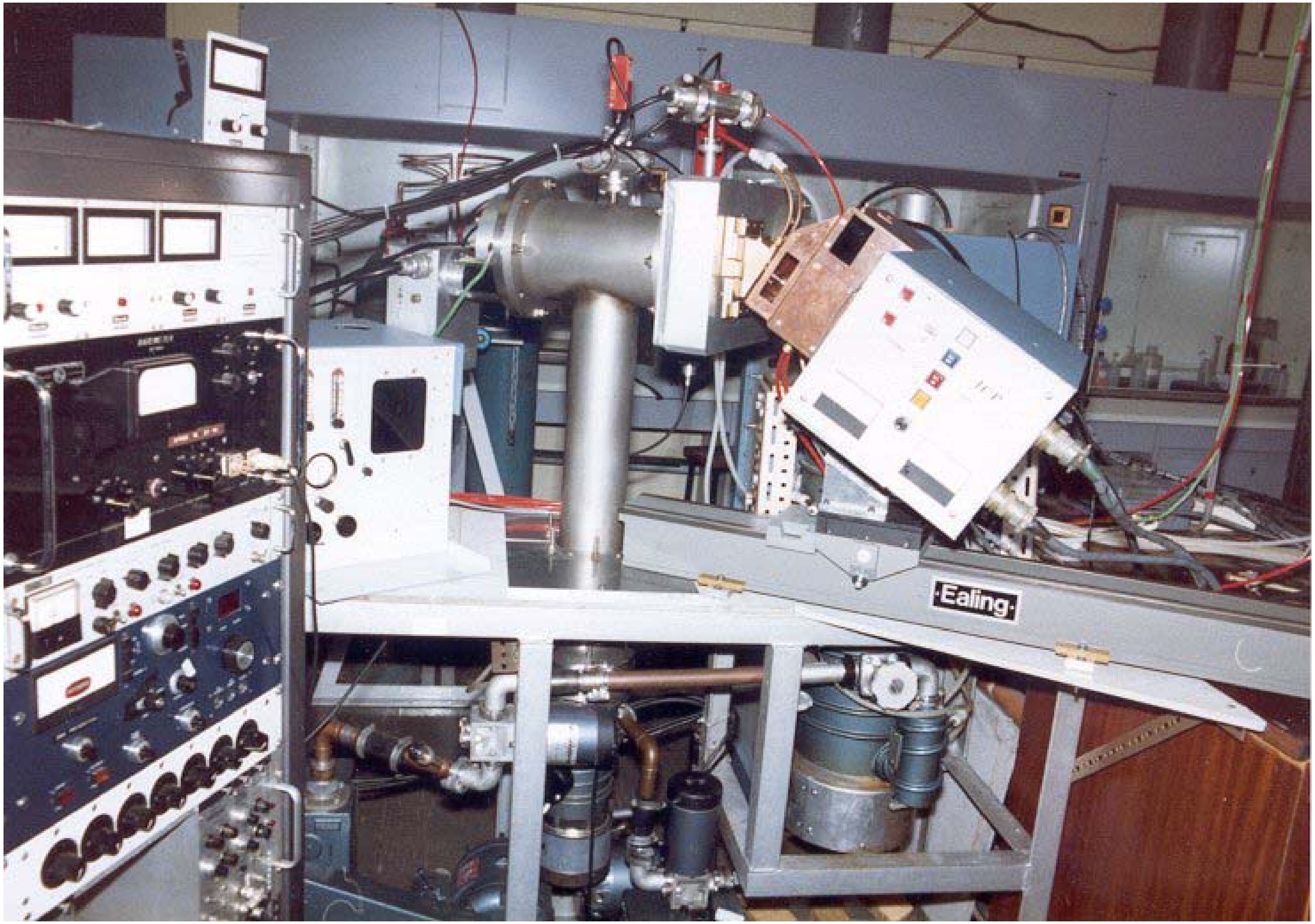
17 Claims, 10 Drawing Figures



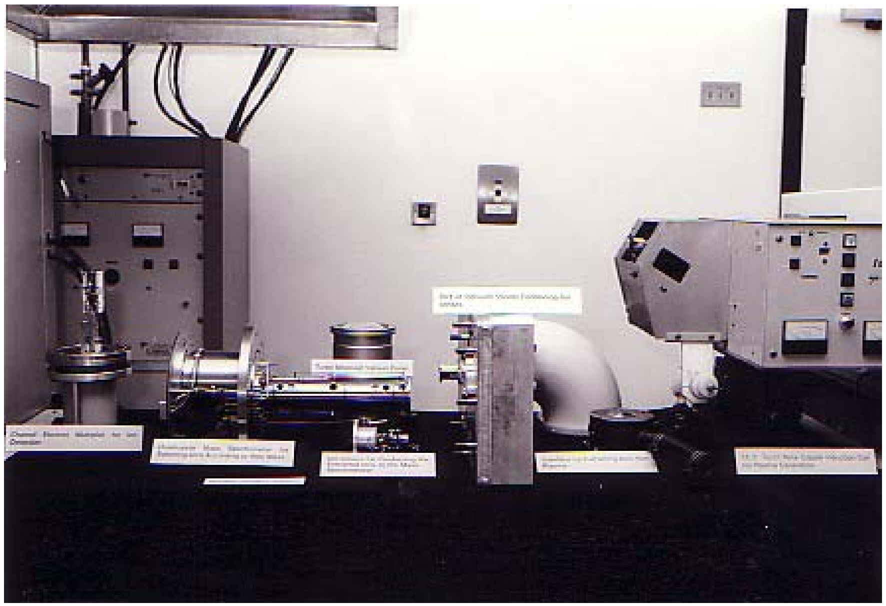
Vertical ICP

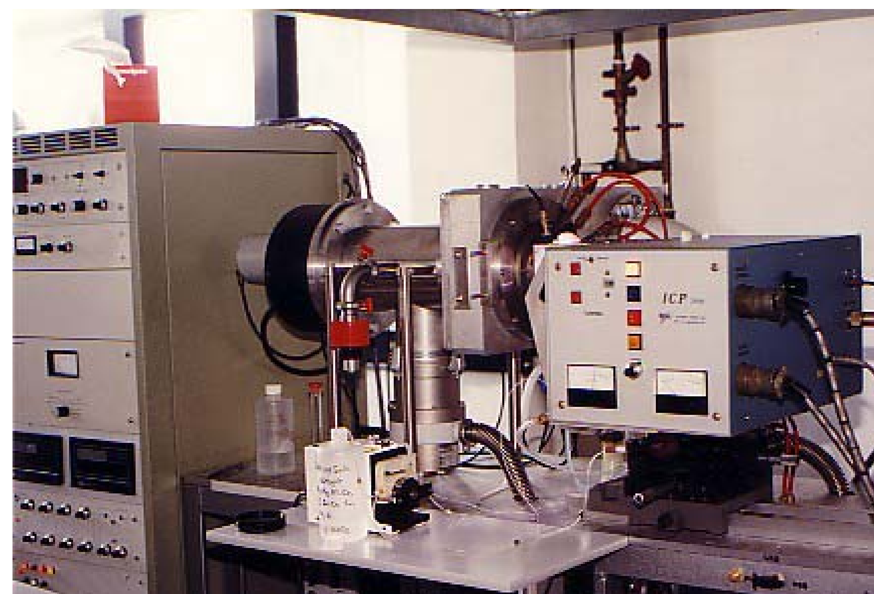


The Angel Plasma!

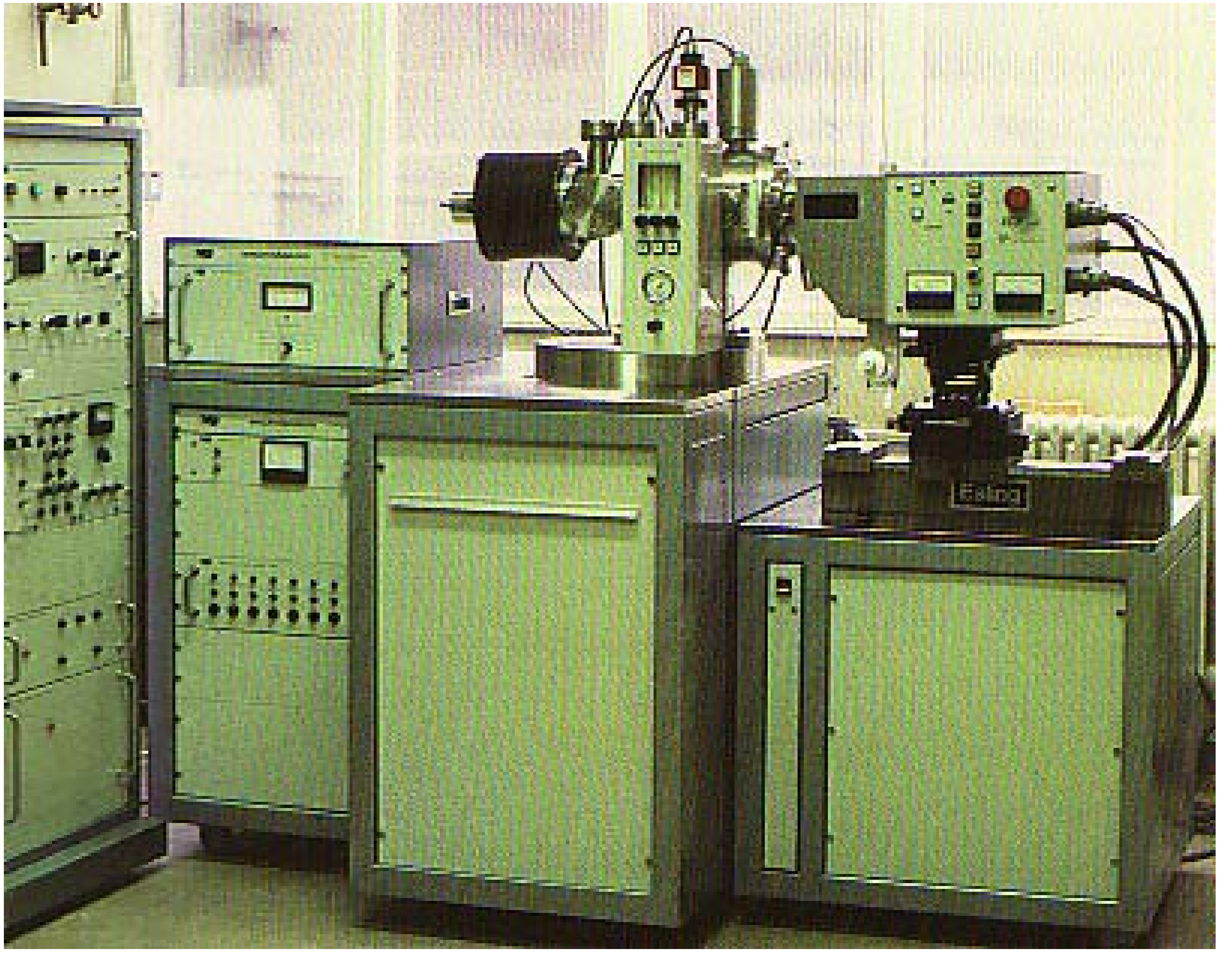


Research Instrument

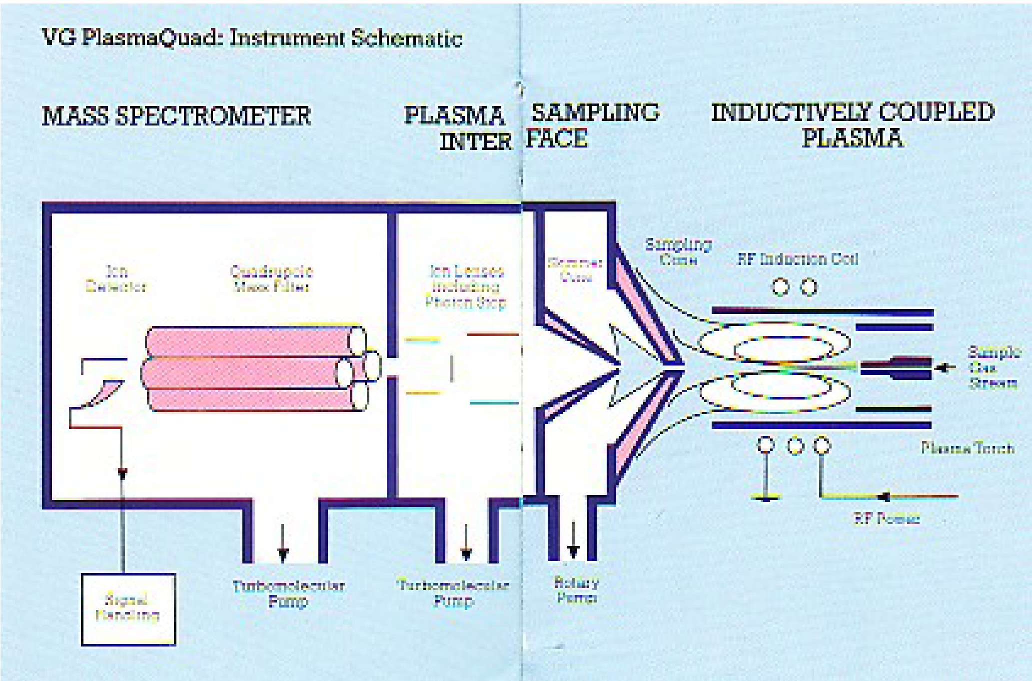


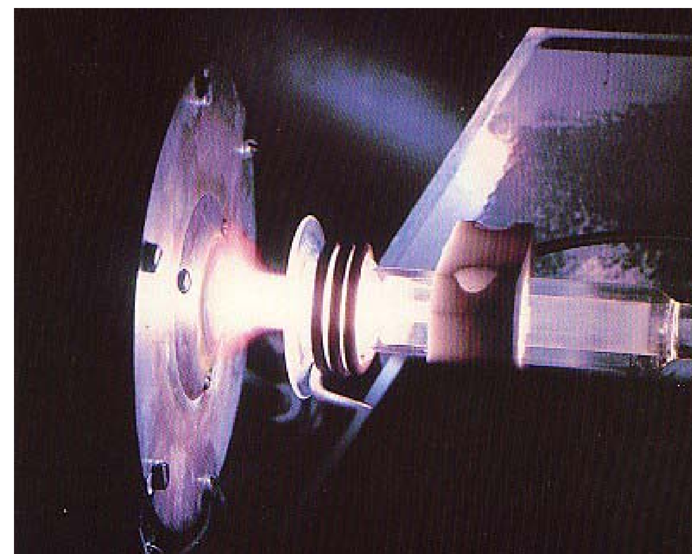


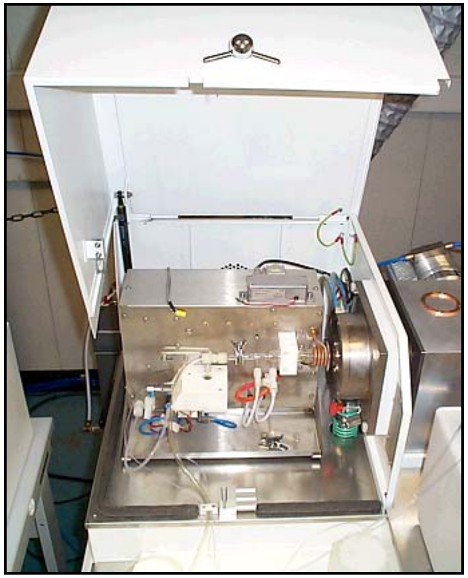
Prototype ICP-MS at BGS Grays Inn Road



The instrument



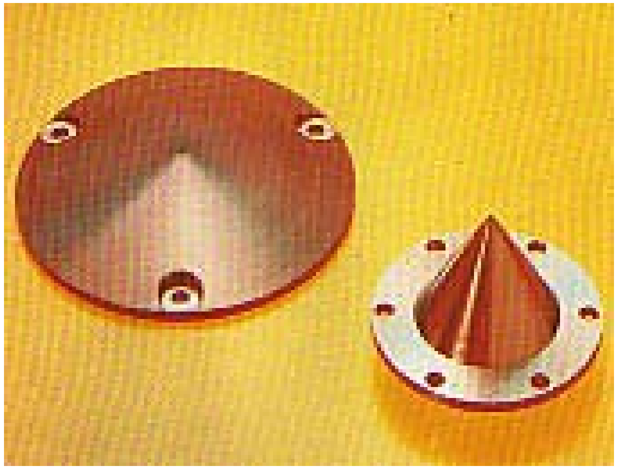


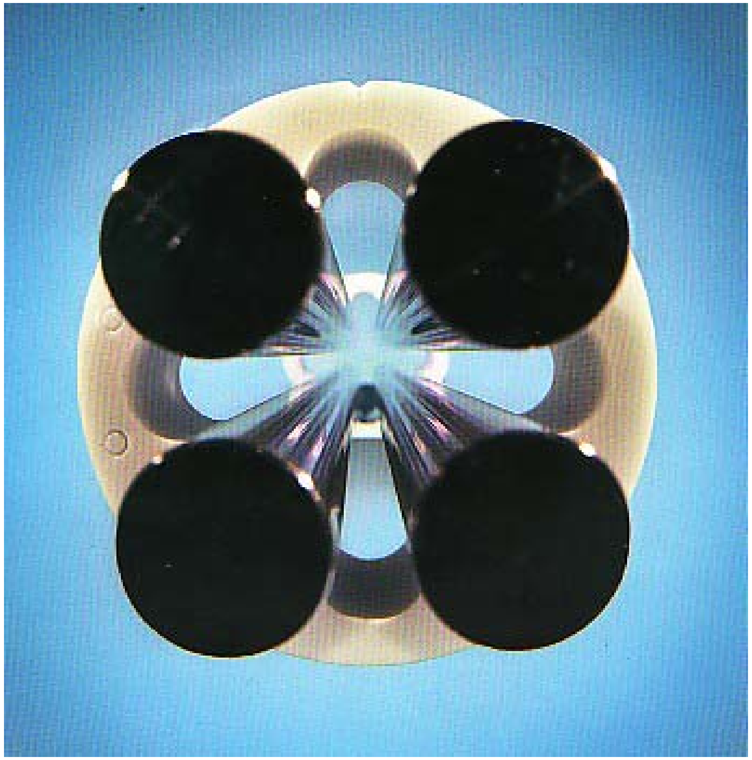


Torch box

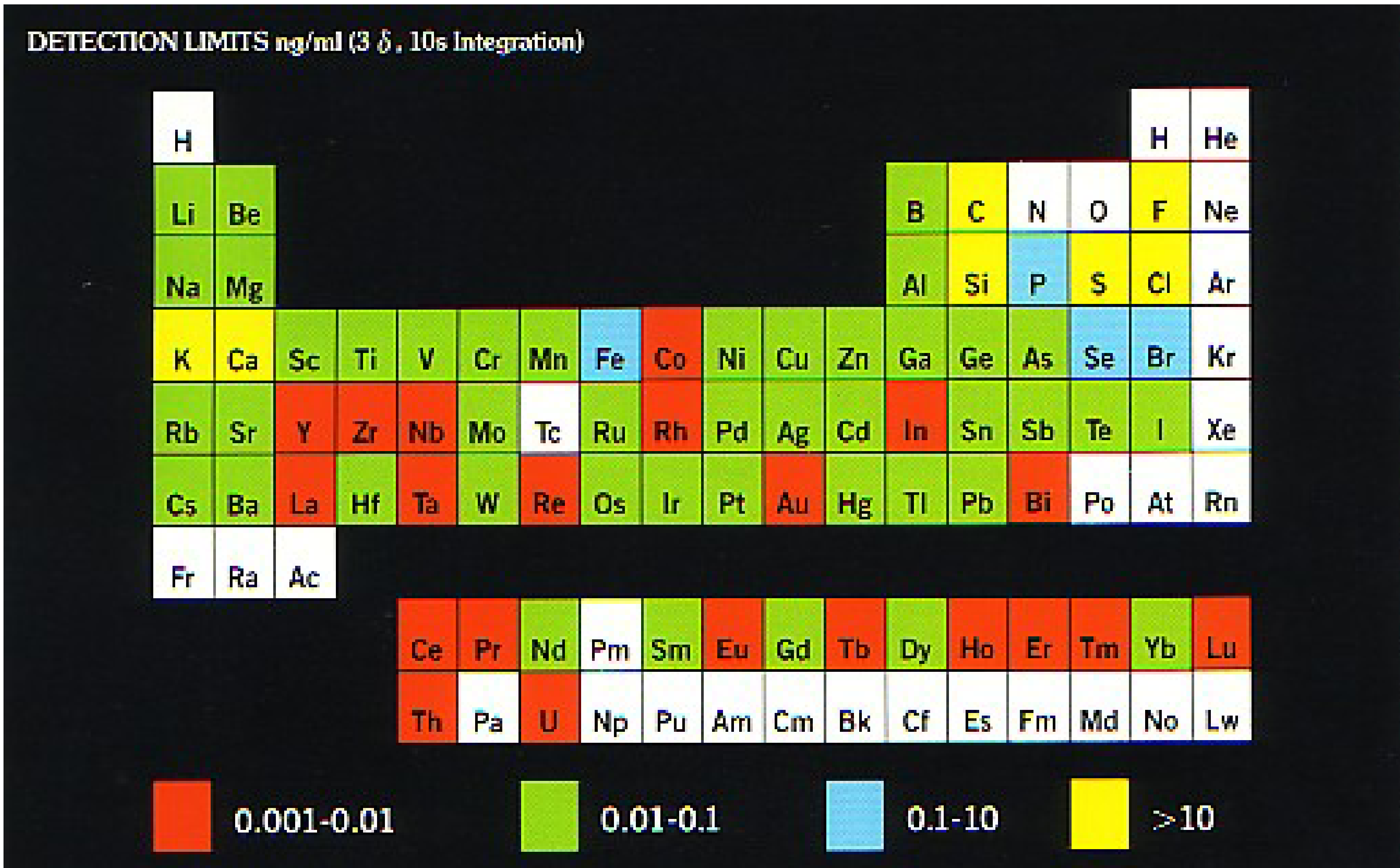
'Ions-eye view' of the quadrupole

Sampling cone & skimmer





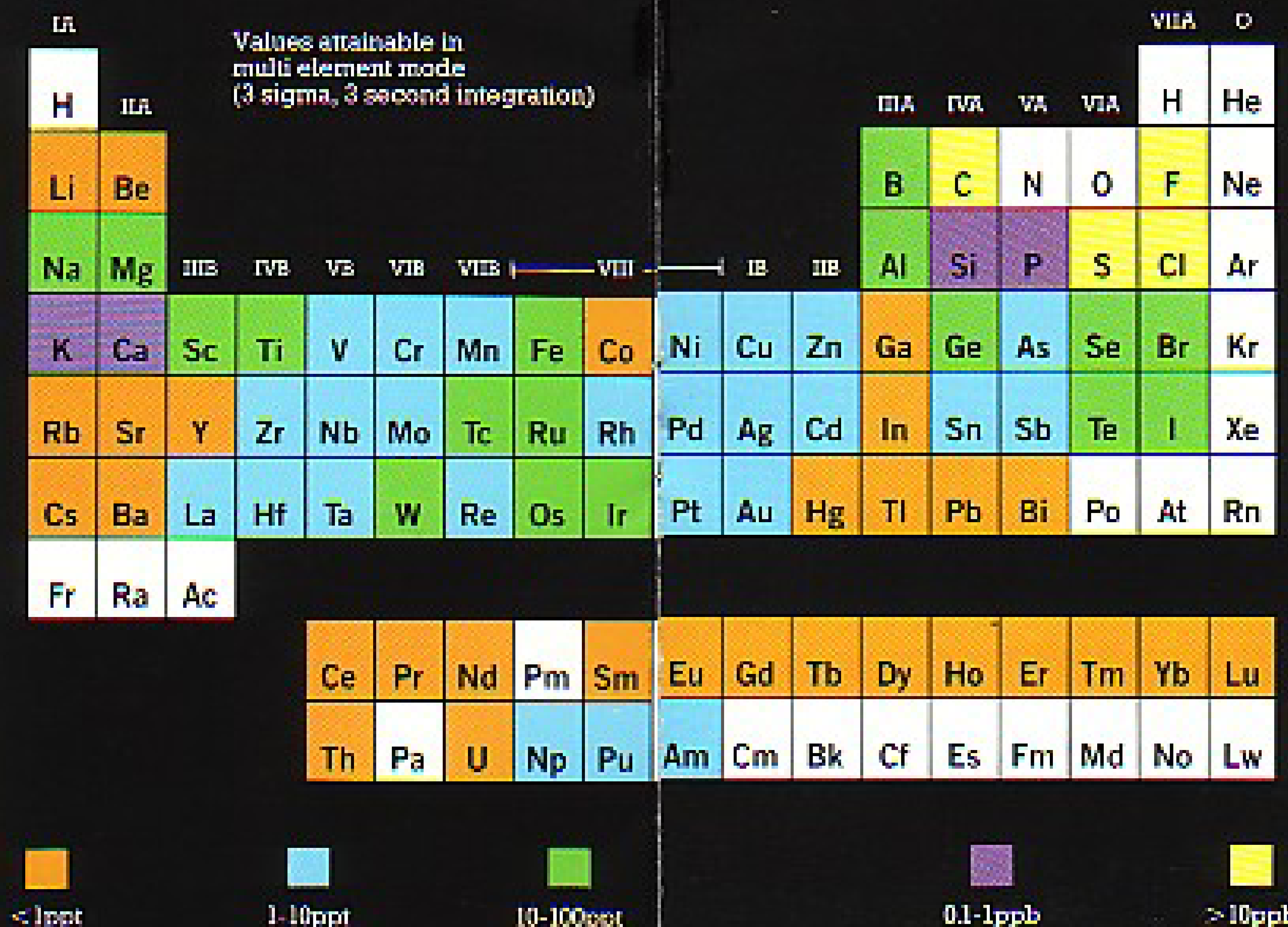
The bottom line



Features of ICP-MS

- Simple spectra
- Most elements ionised in Ar ICP
- Relatively uniform signal response
- Similar detection limits for all elements
- Analysis of solutions and solids (using laser ablation)

VG PlasmaQuad ICP-MS Detection Limits



Data obtained on VG PlasmaQuad PQ2 Turbo Plus

Isotopic applications - 1988

- Boron - geological
- Lithium - medical
- Iron - medical
- Zinc - medical
- Osmium - geological
- Lead - environmental
- Uranium - nuclear

- Natural variation in rocks & minerals
- Isotope tracer studies in medical applications
- Isotopic variation in fabricated materials

Precision of single isotope limited to ~2% RSD

Precision on isotope ratio limited to ~0.1% RSD

Pb isotopes

	$^{204}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Certified value	0.05904	0.9146	2.168
Measured	0.05965	0.9179	2.159
Bias	+1.03%	+0.36%	-0.40%
Experimental RSD	1.29%	0.35%	0.32%
Counting stats RSD	1.10%	0.38%	0.31%

From Gray, 1988

Result of high dissolved solids

Matrix effect on isotope ratio

Na (ppm)	$^{10}B/^{11}B$
1000	4.044
1500	4.040
2000	4.042
3000	4.124
4000	4.205
5000	4.286
6000	4.367

Data from Gregoire, 1987

Limitations to isotope ratio measurement by quadrupole ICP-MS

Mains frequency ‘noise’

+

Sample introduction ‘noise’

+

Interface ‘noise’

+

Gas flow ‘noise’

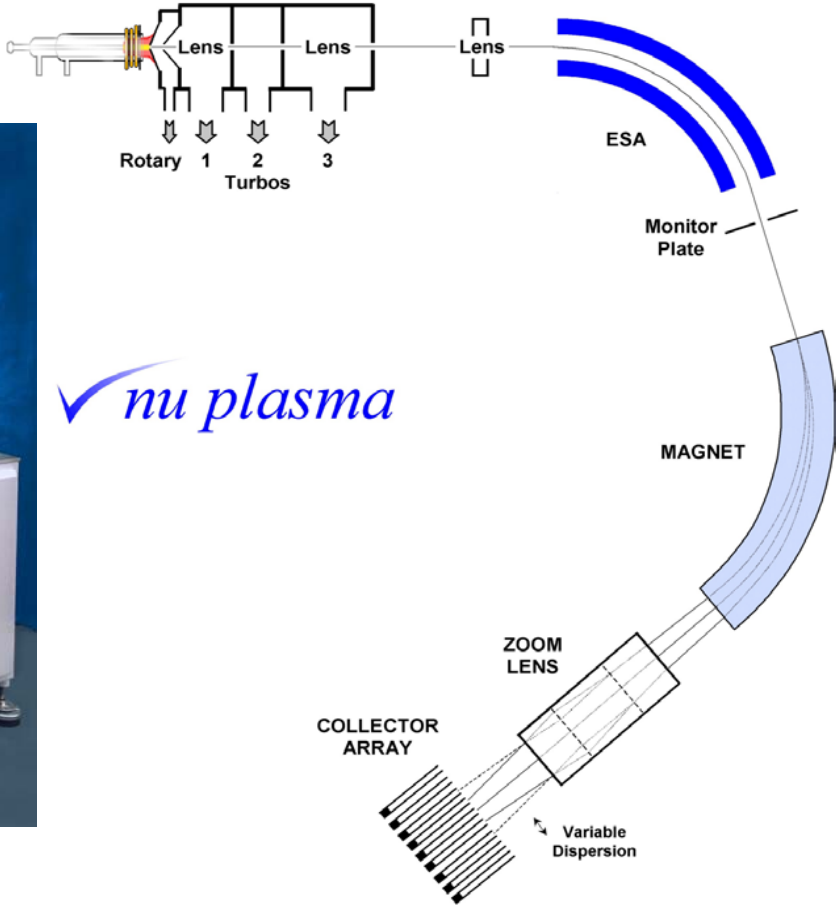
+

Sequential measurement of isotopes

=

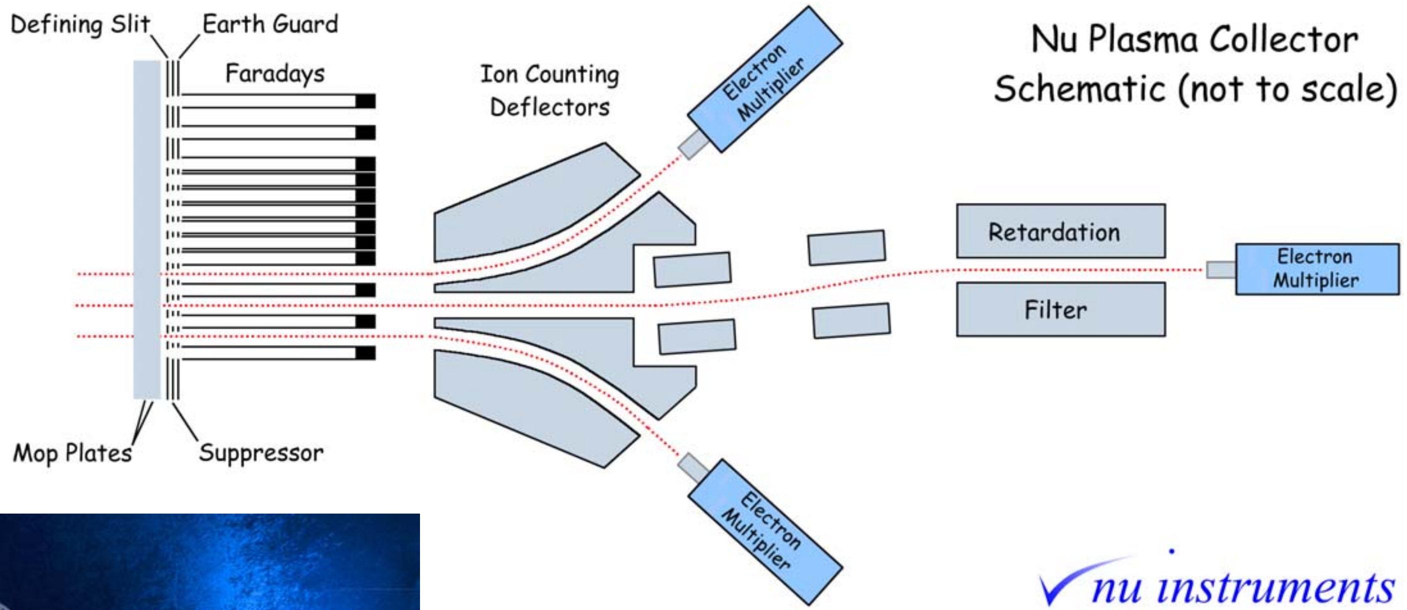
>0.1% RSD $^{107}Ag/^{109}Ag$

Multi-collector ICP-MS

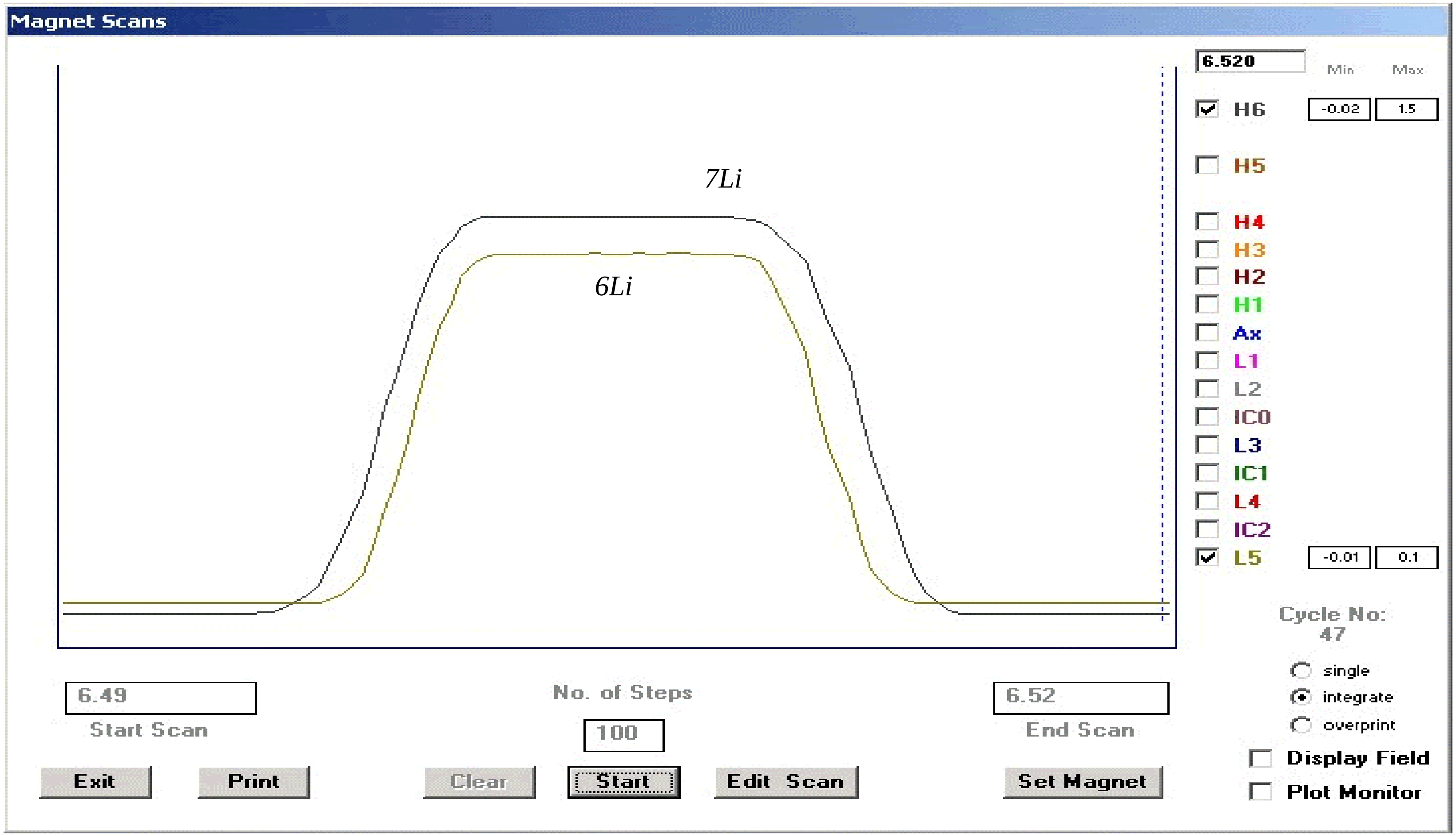


nu plasma

Multi-collector array



Flat topped peaks



NIST 981 Pb isotopic standard

	n	207/206	±	RSD (%)	208/206	±	RSD (%)	206/204	±	RSD (%)
Collerson et al (2002)	114	0.91461	18	0.02	2.16740	70	0.03	16.941	6	0.04
Thirlwall et al (2000)	11	0.91469	7	0.008	2.16770	21	0.009	16.941	2	0.01

Has ICP-MS delivered all it promised?