The New Agilent 7700 Series

The Smallest, Most Powerful ICP-MS Ever Made
Inductively Coupled Plasma Mass Spectrometry

- ICP-MS is a fast, multi-element, high sensitivity trace metals analysis technique
- Key applications are:
  - Environmental
  - Foods
  - Semiconductor
  - Clinical
  - Chemical/Petrochemical
  - Pharmaceutical
  - Consumer Goods
  - Forensic
  - Geological
  - Nuclear
  - Academic/Research
- ICP-MS market continues to grow as technology improves and GFAA and ICP-OES instruments are replaced with ICP-MS
Agilent ICP-MS Instrument Development

Agilent 4500 Series

Agilent 7700 Series
The new face of ICP-MS

Agilent 7500 Series
Agilent’s History of Innovation in ICP-MS – 1987 to 2009

1987 – PMS 100 introduced – First computer-controlled ICP-MS
1988 – PMS 200 introduced – Second generation ICP-MS with off-axis Qpole lens
1989 – 1st ETV accessory for semicon analysis by ICP-MS
1990 – PMS 2000 introduced – Omega off-axis lens. Lowest random background ICP-MS
1992 – ShieldTorch interface developed - Ar interferences virtually eliminated in cool plasma, enabling ppt analysis of K, Ca, Fe by ICP-MS
1994 – 4500 Series introduced - World’s first benchtop system. Hyperbolic profile quad, motorized torch XYZ, cool plasma
1998 – First real time ICP-MS chromatographic software – PlasmaChrom. T-mode reaction interface introduced
1999 – 4500 Series 100, 200 & 300 introduced: 1st applications-specific ICP-MS.
2000 – Agilent 7500 Series introduced - 7500a, 7500i and 7500s - the next generation in ICP-MS instrumentation. 9 orders detector range
2001 – Agilent 7500c launched – 1st generation ORS for high matrix samples.
2003 – Agilent 7500cs launched – 2nd generation ORS for high purity semicon samples.
2004 – Agilent 7500ce launched – 2nd generation ORS for high matrix samples.
2005 – Low flow cell gas MFC’s for Xe NH₃, O₂, etc added to 7500ce/cs.
2006 – Agilent acquires 100% of Agilent/Yokogawa joint venture
2007 – Agilent 7500cx introduced: He only mode ICP-MS
2008 – High Matrix Interface developed – enables 2% TDS samples to be run by ICP-MS
2009 – Agilent 7700 Series introduced – replaces 7500 Series. MassHunter Software introduced - common platform with other Agilent MS. ISIS-DS Discrete sampling system, for ultra high throughput analysis
2012 – Agilent 8800 World’s first ICP-QQQ is introduced
7700 Series – New Product Highlights

New ORS$^3$ Collision/Reaction Cell

- Longer, narrower rods, higher cell pressure and frequency – MUCH better performance in He mode

New RF Generator

- Fast, frequency-matching 27MHz generator, for better tolerance to changing matrix (incl. organics)

Increased Matrix Tolerance

- High Matrix Introduction (HMI) standard on 7700x model

Much smaller cabinet

- >40% smaller footprint than the 7500 ICP-MS

Simple software; reliable Auto-Tuning

- MassHunter software – intuitive and easy to learn. Pre-set plasma conditions and fast lens auto-tuning
Agilent 7700 ICP-MS System in Detail

- High matrix introduction (HMI) dilution gas inlet
- Off-axis ion lens
- Cell gas inlet
- 3rd generation Octopole Reaction System (ORS3)
- Fast, simultaneous dual mode detector (9 orders dynamic range)
- High-frequency (3MHz) hyperbolic quadrupole
- High-performance vacuum system
- Fast, frequency-matching 27MHz RF generator
- Peltier-cooled spray chamber
- Low-flow Sample Introduction
- High-transmission, matrix tolerant interface
In many inorganic labs, several analytical techniques are used, to cover the range of analytes, matrices and detection limits required. This is encouraged by some vendors, who want to sell multiple instruments to each lab!
Inorganic Analysis Techniques in a Typical Laboratory

ICP-OES
- Multi-element
- ~2 min/sample
- 10's ppb to 1000's ppm
- Few Elements/Samples

ICP-MS – for trace elements and clean samples
- Multi-element
- ~4 min/sample
- Single ppt to 10's ppm
- GFAAS
- Single element
- ~6 min/sample
- 10's ppt to 100's ppb
- Many Elements/Samples

Uniquely, the Agilent 7700 can replace all these separate techniques, providing high throughput, matrix tolerance, wide elemental coverage and low LODs in a single run.
Unique Performance of the 7700

Better matrix tolerance than any other ICP-MS
- Higher plasma temperature (lower CeO/Ce ratio) under standard conditions than any other system

Best performance with Helium cell gas – eliminates need for reaction gases in all common applications
- 7700 ORS³ improvements - removes all polyatomics in He mode, giving accurate results in complex or variable sample types – impossible on ICP-MS systems that use reactive cell gases or mixtures

Wider dynamic range than any other quadrupole ICP-MS
- Full 9 orders dynamic range at the detector – linear to 500ppm without changing conditions or hardware
7700 Series Sample Introduction

• Low-flow (typically 0.15mL/min)
• Temperature stabilized (Peltier cooled spray chamber)
• Wide Torch Injector ID (2.5mm)
• No O-rings in spray chamber end-cap – reduced risk of contamination
• Auto-alignment of torch after maintenance
• Fast frequency-matching RF generator
• Simple setup, using “pre-set” plasma conditions and auto-tuning

Provides most robust plasma of any ICP-MS under standard conditions
Comparison of Plasma Loading/Cooling

ICP-MS plasma must produce ions – neutral atoms cannot be measured (unlike ICP-OES where many of the best emission lines are atomic). Sample introduction must maintain high plasma temperature – monitored using CeO⁺/Ce⁺ ratio.

Conventional ICP-MS
0.5 - 1.0mL/min, 1.8-2.0 mm Injector, no water vapor removal $\dagger$ Low central channel temperature

Optimized ICP-MS (7700)
0.10 - 0.25mL/min, 2.5mm Injector, water vapor removed $\dagger$ High central channel temperature

Hottest part of plasma ~ 8000K
Sample channel is at ~6700K
Residence time is a few milliseconds

By sample cone, analytes present as $M^+$ ions
Highest $M^+$ population should correspond to lowest polyatomic population
Atoms are formed and then ionised

Aerosol is Dried
Particles are decomposed and dissociated

High sample load, narrow central channel $\dagger$ poor matrix decomposition
Low sample load, wide central channel $\dagger$ good matrix decomposition
CeO/Ce Ratio – Effect on Matrix Suppression

When a high sample matrix (e.g. 1/10 seawater) is introduced, the plasma is overloaded and analyte signal drops (suppression). Suppression is worse when the CeO/Ce ratio is higher (plasma temperature is lower).

Spike recovery in a high matrix is better with a robust plasma (low CeO/Ce ratio).

7700 has the lowest CeO/Ce ratio in standard conditions of any ICP-MS (<1%)
Other Benefits of High Plasma Temp.

- Reducing CeO\(^+\)/Ce\(^+\) ratio from 3.0% to 1.0% (3x reduction) removes ~70% of many matrix-based interferences (ArCl\(^+\), ClO\(^+\), CaO\(^+\), etc).
- Hotter plasma is less affected by a variable matrix (more robust).
- Better matrix decomposition reduces interface and lens contamination and therefore reduces maintenance.
- Hotter plasma improves the ionization of poorly ionized elements, so MUCH lower LODs possible for Be (right), B, As, Se, Cd, Hg (below), etc.

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>BEC (ppt)</th>
<th>LOD (ppt)</th>
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<tbody>
<tr>
<td>201 Hg</td>
<td>9.49</td>
<td>1.51</td>
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<table>
<thead>
<tr>
<th></th>
<th>Be</th>
<th>BEC (ppt)</th>
<th>LOD (ppt)</th>
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<tbody>
<tr>
<td>9 Be</td>
<td>0.465</td>
<td>0.235</td>
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Sub ppt Be detection limit!
High Matrix Introduction (HMI) – How it Works

HMI is a sample dilution technique but, uniquely, it dilutes the sample in the gas state, using aerosol dilution.

This removes the main problems of liquid sample dilution:

- Time
- Reagents
- Errors
- Contamination
HMI ‡ Robust Plasma → Low Oxide Interferences

Recovery of a 1 ppb Cd spike in increasing Mo concentration (0, 2, 5 ppm Mo). Comparison of standard 7700x (1% oxides) and 7700x under HMI conditions (0.2% oxides)
HMI – Effect on Matrix Suppression

HMI dilutes aerosol density & water vapour, as well as sample matrix. Gives much higher plasma temp; much better matrix decomposition. Matrix suppression is almost eliminated.

Plot shows % recovery in undiluted seawater vs aqueous calibrations.

With HMI, ALL results are within +/- 15% recovery (shaded area)
Without HMI, ALL results are below 60% recovery
Other Benefits of HMI

HMI increases sample throughput
- Reduces sample prep time (no manual or auto-dilution)
- Reduces number of over-range samples which have to be repeated

HMI decreases routine maintenance
- HMI dilution reduces the matrix loading on the plasma
- This decreases the amount of matrix which reaches the interface cones and so less maintenance (cone cleaning) is required
- Lower matrix loading also improves long-term stability, which decreases the need to run repeated calibrations
  - Further increases sample throughput
New interface provides simple access for maintenance – remove and refit cone without any tools

Provides good ion transmission and matrix tolerance

7700 Series standard interface provides high sensitivity and good matrix tolerance as standard – no need for a separate set of low-sensitivity cones for high matrix samples!
7700 Series Ion Lens

- Ion Lens focuses ions into the cell, and rejects photons and neutrals
- 7700 uses a combined Extraction/Off-axis Lens – located outside high-vacuum region, so easy to access for maintenance
- Provides ideal combination of high transmission across the mass range, low random background, and protection from matrix contamination in the high vacuum region
- No need to set up variable voltages to increase ion transmission at specific masses – all masses are transmitted all the time!

7700 Series has the highest ion transmission across the mass range of any ICP-MS, in standard, matrix tolerant conditions
7700 Quadrupole & Abundance Sensitivity

3MHz, hyperbolic quadrupole with alignment tolerance to 1 micron

- Winner of 2006 Bill Hewlett Innovation Award
- U.S. Patent #6,926,783: Manufacturing Precision Multipole Guides and Filters
- "This invention is the most significant advance in quadrupole mass filter technology in 40 years."
  Jerry Dowell, Agilent Senior Staff Scientist

Best Abundance Sensitivity Specification of any ICP-MS – no need to set up custom resolution to separate adjacent peaks – all peaks are separated under standard conditions!

(Factory performance certificate ships with every 7700 Series instrument)

<table>
<thead>
<tr>
<th></th>
<th>Agilent 7700</th>
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<tbody>
<tr>
<td>Low Mass Side</td>
<td>$5 \times 10^{-7}$ (Cs)</td>
</tr>
<tr>
<td>High Mass Side</td>
<td>$1 \times 10^{-7}$ (Cs)</td>
</tr>
</tbody>
</table>
7700 – 9 Orders Detector Dynamic Range

Original ICP-MS pulse-count detectors gave 6 orders dynamic range (up to 2Mcps)

Analog mode typically adds a further 2 orders dynamic range (up to 400Mcps), equivalent to about 50ppm

Agilent 7700 Series detector adds another order of dynamic range in analog mode – up to 4,000Mcps or around 500ppm

Upper range is even higher for mineral elements in He mode, as low-mass signal is reduced when cell is pressurized.

*7700 electronics increase detector lifetime to >2 years (around 6 months on other ICP-MS)*
7700x – Largest Analytical Range of any ICP-MS

Calibration ranges
Hg (10 – 200ppt) – NoGas Mode
As (10 – 200 ppt) – He Mode
Se (10 – 200 ppt) – He Mode
Na (0.05 – 1000 ppm) – He Mode

Overall calibration range 10ppt (Hg, As, Se) to 1000 ppm (Na) in a single method
- without attenuating ion transmission to increase working range

Na
Typically, ICP-MS cannot measure above 200ppm Na without changing quad resolution or ion lens settings

Hg
Hg LOD on 7700x is about 2ppt – 7700x can QUANTITATE at 10ppt!

7700x can do both of the above in the same run!

These 4 plots were obtained under the same analytical conditions on the 7700x – only the gas mode (NoGas for Hg) changed

- Mercury
- Arsenic
- Selenium
- Sodium

Good fit at 0.2ppm
All New Octopole Reaction System (ORS\textsuperscript{3})

The 7700 uses a completely new collision/reaction cell, with:

- 18% longer rods
- 15% smaller ID

and operates at

- 16% higher pressure
- 20% higher frequency

ORS\textsuperscript{3} also operates with a much larger energy discrimination step.

Result is much more effective removal of interferences in He mode with KED

*Major improvement compared to 7500 Series, which already offered by far the best He mode performance of any ICP-MS*
At cell entrance, analyte and polyatomic ion energies overlap. Energy spread of both groups of ions is narrow, due to ShieldTorch System.

Energy loss from each collision with a He atom is the same for analyte and polyatomic ion, but polyatomics are bigger and so collide more often.

By cell exit, ion energies no longer overlap; polyatomics are rejected using a bias voltage “step”. Analyte ions have enough residual energy to get over step; polyatomics don’t (energy discrimination).
Acid Matrices and IPA in NoGas Mode

\[(HNO_3 + HCl + H_2SO_4 + IPA)\]

NoGas Mode

Unspiked 5% HNO_3 + 5% HCl + 1% H_2SO_4 + 1% IPA Matrix

Unspiked Matrix – ALL peaks are due to polyatomic interferences

Multiple polyatomic interferences affect almost every mass – Interferences are matrix-dependent

What happens to all these polyatomics in He Mode?
Single Acid Matrices and IPA in He Mode
(HNO₃ + HCl + H₂SO₄ + IPA) – same scale as NoGas

Unspiked 5% HNO₃ + 5% HCl + 1% H₂SO₄ + 1% IPA Matrix
ALL polyatomic interferences are removed in He Mode (same cell conditions)

All polyatomic interferences are removed in He Mode

How does this compare to Reaction (H₂) Mode?
Many polyatomic interferences remain (or new ones are created) in H$_2$ Mode.

Interferences are different in each Matrix!

Reaction mode is used on ALL other ICP-MS

**Unspiked 5% HNO$_3$ + 5% HCl + 1% H$_2$SO$_4$ + 1% IPA Matrix**

Many polyatomic interferences can still be seen in H$_2$ Mode
Se Calibration (in 2% HCl + 100ppm Ca)

Calibration for $^{78},^{80},^{82}$Se at 0, 0.5, 1, 10ppb

Improved performance for Se with ORS$^3$ in He mode – eliminates the need for reaction mode in routine applications.

No SeH or BrH formation (affects all reaction gases)

Sub-ppb LOD shows interference removal on all Se isotopes – essential for accurate isotope ratio or isotope dilution measurement

<table>
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<tr>
<th>Isotope</th>
<th>BEC (ppt)</th>
<th>LOD (ppt)</th>
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<tbody>
<tr>
<td>78</td>
<td>7.95</td>
<td>N/A</td>
</tr>
<tr>
<td>80</td>
<td>301</td>
<td>133</td>
</tr>
<tr>
<td>82</td>
<td>252</td>
<td>210</td>
</tr>
</tbody>
</table>

Isotope BEC (ppt) LOD (ppt)

78 7.95 N/A
80 301 133
82 252 210
Agilent 7700 with ORS$^3$ – The Most Powerful ICP-MS for the Routine or Research Lab

• Effective removal of polyatomic interferences using He mode only, even in unknown and variable sample matrices
• Simple method development – same conditions used for all elements and all sample types
• No new interferences and no loss of analyte signal by reaction
• Highest data integrity in unknown matrices
• Unmatched sensitivity across the mass range
• Widest dynamic range – low ppt to 1000ppm

The 7700x simplifies ICP-MS operation, while improving matrix tolerance and providing unparalleled interference removal in complex and variable samples