BIDDER'S NAME: Agilent Technologies, Inc.
(Submit with Bid Proposal)

BIDDER'S CHECKLIST

PRODUCT PURCHASE CONTRACT FOR
NEXION 350D INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)
Bid File No. 3424

SUBMIT THIS BIDDER'S CHECKLIST WITH YOUR BID DOCUMENTS. Bidders shall complete and submit all documents marked with an "X" in the "REQUIRED" column. Documents required on the checklist but not included may render your bid nonresponsive and ineligible for award. Bids received by the City by the scheduled bid opening time will be opened and publicly read but are subject to verification that all the required documents have been submitted.

REQUIRED

[X] 1. **BID PROPOSAL PAGES** 1.2 through 1.4.

[X] 2. **BID DEPOSIT** attached to front of Proposal in the form of:

[ ] Certified Check	[✓] Bidder's Bond
[ ] Cashier's Check	[ ] Irrevocable Ltr of Credit
[ ] Certificate of Deposit	[ ] Annual Bidder's Bond

DMC 37306

Note: Company Checks are NOT acceptable

[X] 3. **CERTIFICATION FOR LOCAL PREFERENCE,** if applicable, page 1.5.

[X] 4. **SIGNATURE PAGES** 1.6 and 1.7.

N/A [X] 5. **ADDENDA** - Signature page of all Addenda issued, if applicable.
Addenda No. _____ to _____ (Enter numbers). *N/A*

[X] 6. **LITERATURE/STANDARD WARRANTY.** As required on page 5.0, paragraph (d), any applicable manufacturer's Published Price List or website, and two copies of the manufacturer's descriptive literature and specifications or website, including a copy of the manufacturer's standard warranty.
Please note: Agilent does not have a published price list.

SUBMITTED BY:
Name of Company Agilent Technologies, Inc. Contact Name Georgeann Foster

Address 2850 Centerville Road City Wilmington State DE Zip 19808

Phone No. 800-227-9770 Fax No. 302-993-5941

E-Mail Address: lscabids@agilent.com

BID PROPOSAL

BIDDER'S NAME: Agilent Technologies, Inc.
(Submit with Bid Proposal)

PRODUCT PURCHASE CONTRACT FOR
NEXION 350D INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)
Bid File No. 3424

TO: THE PURCHASING MANAGER OF THE CITY OF FRESNO

The undersigned Bidder hereby proposes to furnish to the City of Fresno, in accordance with the Specifications annexed hereto and made a part hereof, the following item(s) **delivered F.O.B. Destination, Freight Prepaid & Allowed, to the jobsite(s) as specified in the Special Conditions of these Specifications**, and at the prices set forth in the following bid item(s):

BID ITEM	QTY	DESCRIPTION	UNIT PRICE	TOTAL PRICE
1.	01	MANUFACTURER: PerkinElmer MODEL: NexION 350D ICP-MS or an approved equal (see Technical Specifications)	$ 129,653.40	$ 129,653.40
		Agilent Technologies, Inc. is offering Agilent 7800 ICPMS.	SUBTOTAL:	$ 129,653.40
			Sales Tax 8.225%:	$ 10,664.02
2.	01	Training	$ Included	$ Included
3.	01	Delivery	$ Included	$ Included
			Total Net Bid Amount:	$ 140,317.42

The Total Net Bid Amount is One Hundred Forty Thousand Three Hundred Seventeen Dollars and Forty-Two Cents.

Completion of Bid Proposal Form to be Eligible for Award. Bidders must bid all bid items within a section (including any Alternates). The Bidder is non-responsive and ineligible for award in the event Bidder fails to initial this paragraph on the line provided and completely fill in the Bid Proposal Form including, without limitation, all dollar amounts and information called for on this Bid Proposal Form. By his/her initials to the right hereof, Bidder represents he/she has read and understands the consequences of not completely filling in this Bid Proposal Form.

Initial

Agilent Technologies, Inc. (Agilent) is bidding in accordance with attached quotation 1966223. Agilent's quotation is included for configuration purposes. Agilent accepts customer's terms and conditions. Please refer to the quotation and attached literature for details of Agilent's offer. Please refer to the letter dated December 29, 2015 from Margaret Roderick, Atomic Spectroscopy Specialist, for further details.

BIDDER'S NAME: Agilent Technologies, Inc.

(Submit with Bid Proposal)

CONTRACT QUANTITIES. The City reserves the right to increase or decrease quantities in accordance with available funds as appropriated by the City Council. If the City Council has not appropriated funds or sufficient funds are not available to complete the purchase, the City reserves the right to decrease quantities to stay within the budget limitations.

ADDENDA. The City makes a concentrated effort to ensure any addenda issued relating to these specifications are distributed to all interested parties. It shall be the Bidder's responsibility to inquire as to whether any addenda to the Specifications have been issued. Upon issuance by the City, all Addenda are part of the Bid Proposal. Signing the Bid Proposal on the signature page thereof shall also constitute signature on all Addenda.

PRECEDENCE OF BID PRICES. In the event of discrepancies between the bid total, summaries of totals and unit price extensions, the unit price correctly extended will control over the summaries of totals, and the summaries of totals correctly added will control over the total, whether the summaries of totals are extended unit prices or lump sums.

RIGHT TO REJECT ANY AND ALL BIDS. The City reserves the right to reject any and all bids.

TIME PERIOD TO AWARD/REJECT BIDS. The undersigned Bidder agrees that the City may have 90 DAYS from the date bids are opened to accept or reject this Bid Proposal. It is further understood that if the Bidder to whom any award is made fails to enter into a Contract as provided in the Specifications, award may be made to the next lowest responsive and responsible Bidder, who shall be bound to perform as if he/she had received the award in the first instance. No Bid Proposal may be withdrawn prior to award within that time.

AWARD OF CONTRACT. When bids are submitted to the Council, the award will be made to the lowest responsive and responsible bidder, subject to the right to reject any and all bids, pursuant to Fresno Municipal Code section 4-102.

MINOR IRREGULARITIES. The City of Fresno reserves the right to waive any informality or minor irregularity that does not have a monetary consideration when it is in the best interest of the public and of the City to do so. A discrepancy that offers a Bidder an unfair advantage will cause the bid to be nonresponsive.

TIEBREAKER. In the event a tiebreaker is needed to establish the lowest responsive and responsible Bidder, the City shall, unless otherwise agreed upon by all participating parties, utilize a coin toss as a tiebreaker to be administered by a third party chosen by mutual consent of the participants. Such coin toss shall take place within 7 working days from the date of bid opening. If the City determines that a tiebreaker is necessary, each applicable Bidder agrees to participate or to indemnify the City in any litigation resulting from the utilization of the tiebreaker. If a Bidder refuses to timely participate, the City shall conduct the coin toss in a manner determined by the City to be fair to all and the results of such coin toss shall be final.

BIDDER'S NAME: Agilent Technologies, Inc.
(Submit with Bid Proposal)

BID DEPOSIT

Accompanying this bid proposal is a Bid Deposit in the amount of one thousand dollars ($1,000) (or, in bids with Add Alternates, the highest possible combination of the Base Bid plus Add Alternates) in the following form:

[___] Certified Check
[✓] Bidder's Bond
[___] Cashier's Check
[___] Irrevocable Letter of Credit
[___] Certificate of Deposit
[___] Annual Bidder's Bond

Note: Company Checks are NOT acceptable

which is deposited by the undersigned Bidder with the City of Fresno as a guarantee that the Bidder, if awarded all or part of the Contract, will, within 15 calendar days (except in the event federal funding is applicable to this Contract, then 10 working days) from the date the Notice of Award is mailed to the Bidder, execute and return a Contract furnished by the City. If the Deposit is in the form of an Annual Bidder's Bond, the bond must be heretofore registered with the Purchasing Manager and must be in the amount of one thousand dollars ($1,000) in the following form:

Such Deposit is made with the understanding that failure to execute such Contract will result in damage to the City, that the amount of such damage would be difficult to determine and that in the event of such default said Deposit shall become the property of the City; or, if a Bidder's Bond is deposited, the amount of the obligation thereof, but not more than the above stated amount, shall thereupon be due and payable to the City of Fresno as liquidated damages for such default, payment of said amount to be the joint and several obligation of the Bidder and the corporate surety.

BUSINESS LOCATION

(✓) The undersigned Bidder does not maintain a place of business in the City of Fresno.

( ) The undersigned Bidder maintains a place of business in the City of Fresno at:

_____ Fresno, CA _____.

BUSINESS LICENSE

( ) The undersigned bidder has a current City of Fresno Business License Number:
N/A
_____.

BIDDER'S NAME: Agilent Technologies, Inc.
(Submit with Bid Proposal, if applicable)

CERTIFICATION FOR LOCAL PREFERENCE
PRODUCT PURCHASE CONTRACT FOR:
NEXION 350D INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)
Bid File No. 3424

☐ We certify that we qualify as a local business pursuant to Fresno Municipal Code section 4-108(a).

Location of Business:
Please provide street address
(PO Box is not acceptable)

Primary Office [ ]
Branch Office [ ]
(Please mark as applicable)

Address: _____

_____

Phone: _____

****

☐ We certify that we qualify as a local business pursuant to Fresno Municipal Code sections 4-108(a) and (b).

Location of Business:
Please provide street address
(PO Box is not acceptable)

Primary Office [ ]
Branch Office [ ]
(Please mark as applicable)

Address: _____

_____

Phone: _____

Provide total number of employees (includes employees of fixed primary and any branch offices of Bidder): _____

The average annual gross receipts over the previous three calendar years to the city inviting bids herein (includes gross receipts of fixed primary and any branch offices of Bidder)
$_____

Small Business Certification issued by the State of California
Certification Number: _____ Date of expiration: _____

The undersigned Bidder hereby declares under penalty of perjury under the laws of the State of California that the information contained on this CERTIFICATION FOR LOCAL PREFERENCE is correct and complete.

The above Certification is part of the Bid Proposal. Signing this Bid Proposal on the signature page thereof shall also constitute signature of this Certification.

Bidders are cautioned that making a false certification may subject the certifier to criminal prosecution

(Submit with Bid Proposal)

SIGNATURE PAGE

By my signature on this Bid Proposal I certify, under penalty of perjury, that the foregoing statements, pages 1.1 through 1.5, and those contained herein are true and correct.

BID SUBMITTED BY:
(Please follow the instructions for each line, as explained below.)

(1) Agilent Technologies, Inc. (800) 227-9770 (302) 993-5941
Bidding Firm Phone Fax

(2) [✓] Corp: State of Incorporation: Delaware
[ ] Individual
[ ] Partnership
[ ] Other: _____

(3) 2850 Centerville Road
Business Address

Wilmington DE 19808
City State Zip Code

(4) By: Georgeann Foster
Signature of Authorized Person
Georgeann Foster/Business Sales Specialist
Type or Print Name of Authorized Person and Title

Federal Tax I.D. No.: 77-0518772 Date: 01-04-2016

INSTRUCTIONS FOR SIGNATURE PAGE

LINE 1: The name of the Bidder must be the same as that under which a license is issued, if a license is required. If the Bidder is a corporation, enter the exact name of the corporation under which it is incorporated; if Bidder is an individual, enter name; if Bidder is an individual operating under a trade name, enter name and dba (trade name in full); if a partnership, enter the correct trade style of the partnership; if a joint venture, enter exact names of entities joining in the venture.

LINE 2: Identify here the character of the name shown under (1), i.e., corporation (including state of incorporation), individual, partnership, or joint venture.

LINE 3: Enter the address to which all communications and notices regarding the Bid Proposal and any Contract awarded thereunder are to be addressed.

LINE 4: (a) If the Bidder is a corporation, the Bid Proposal must be signed by an officer or employee authorized to sign Contracts on behalf of the corporation evidenced by inclusion of one of the following certified by the secretary of the corporation, authorizing the officer or employee to sign contracts (sample certification attached): a copy of the Articles of Incorporation, a copy of the Bylaws, a copy of the Board Resolution or Minutes authorizing the officer or employee to sign Contracts.

(b) If Bidder is an individual, he/she must sign the Bid Proposal, or if the Bid Proposal is signed by an employee or agent on behalf of the Bidder, a copy of a power of attorney must be on file with the City of Fresno prior to the time set for the opening of the bids or must be submitted with the Bid Proposal.

(c) If the Bidder is a partnership, the Bid Proposal must be signed by all general partners; or by a general partner(s) authorized to sign Contracts on behalf of the partnership evidenced by inclusion of either a copy of the Partnership Agreement or a recorded Statement of Partnership.

(d) If the Bidder is a joint venture, the Bid Proposal must be signed by all joint venturers; or by a joint venturer(s) authorized to sign Contracts on behalf of the joint venture evidenced by inclusion of either a copy of the Joint Venture Agreement or a recorded Statement of Joint Venture; and if the joint venturer(s) is a corporation or a partnership signing on behalf of the Joint Venture, then Paragraphs (a) and c) above apply respectively.

Where Bidder is a partnership or a corporation, the names of all other general partners, or the names of the president and secretary of the corporation, and their business addresses must be typewritten below:

NAME	ADDRESS
Mike McMullen, President and Chief Executive Officer	5301 Stevens Creek Blvd,Santa Clara, CA 95051-7201,USA
Michael Tang, Assistant General Counsel and Secretary	5301 Stevens Creek Blvd,Santa Clara, CA 95051-7201,USA

NOTE: All addresses must be complete with street number, City, State and Zip Code.

SAMPLE CERTIFICATION

Please see Attached Signature Authorization.

I, _____ (Name), certify that I am the secretary of the corporation named herein; that _____ (Name) who signed this Bid Proposal on behalf of the corporation, was then _____ (Title) of said corporation; that said Bid Proposal is within the scope of its corporate powers and was duly signed for and on behalf of said corporation by authority of its governing body, as evidenced by the attached true and correct copy of the _____ (Name of Corporate Document)

By: _____

Name: _____

Title: Secretary

Date: _____

Agilent Technologies

SIGNATURE AUTHORIZATION FOR BIDS, QUOTES, CONTRACTS, BID BONDS AND PERFORMANCE BONDS

RESOLVED: That, effective as of September 17, 2014, the Chief Financial Officer, Secretary and Assistant Secretary, and each of them, is hereby empowered on behalf of the Company to sign bids, quotations, leases and contracts with customers and government agencies, including such bids and performance bonds as may be required in connection with such bids and contracts, and each is further empowered to authorize employees of the Company to sign such bids, quotations, leases, contracts and bid and performance bonds.

I, Hajime Tada, do hereby certify that I am the Vice President and Deputy General Counsel of Agilent Technologies, Inc., a Delaware corporation (the "Company"); that the foregoing is a full, true and correct copy of the resolution adopted by the Board of Directors of the Company on September 17, 2014; and that the resolution has not been annulled, rescinded, or revoked and remains in full force and effect. I, Hajime Tada pursuant to authority granted to me by the Assistant Secretary of the Company, hereby authorize Georgeann Foster to sign bids, quotes, leases, contracts, bid bonds and performance bonds with government agencies and other customers on behalf of the Company, up to the amount of two million five hundred thousand U.S. dollars ($2,500,000).

IN WITNESS WHEREOF, I have signed my name below.

Dated: May 4, 2015

Hajime Tada

Agilent Technologies

December 29, 2015

City of Fresno Purchasing Division
2600 Fresno Street, Room 2156
Fresno, CA 93721

Bid file Number: 3424

Dear Ms. Rapp,

Agilent Technologies, Inc. will respond to Bid file Number: 3424 with an Agilent 7800 ICPMS. The proposed Agilent 7800 meets and far exceeds the specifications outlined and required by the City of Fresno. The following description and enclosed documents highlight the performance of the Agilent 7800 ICPMS.

When Agilent (HP at the time) introduced its first ICP-MS in the 1994 we had only a small percentage of market share in comparison to Perkin Elmer and Thermo. Over the years our technology has improved as has our understanding of the various analytical markets we support. In 2004 Agilent introduced the 7500ce which was the first high sensitivity collision cell instrument on the market. Up until that time, all other companies had been using either reactive gases or mixtures of reactive gases in helium to effect the removal of polyatomic interferences. The 7500ce successfully removed interferences using only helium, had excellent matrix tolerance and a wide linear dynamic range. It became the mainstay of the environmental industry over the ensuing 5 years of its production. Over this time, Agilent was steadily increasing its worldwide market share in ICP-MS. Agilent incorporated improvements into the successful design of the 7500ce leading to the introduction of the 7700, 7800 and 7900 ICP-MS systems over the last 5 years. The 7800/7900 have become the most successful ICP-MS on the market.

We recently received the latest ICP-MS market share numbers for the US. This information is provided by ALDA which is an impartial organization that provides individual market share information to all companies who participate. **Over the last year, 65% of all ICP-MS systems sold in the US were Agilent**. The combined sales of Perkin Elmer, Thermo and Analytik Jena are approximately half of Agilent sales. There are many reasons for this. Some are outlined below.

The Agilent 7800 ICP-MS combines the simplicity of a single collision cell mode for polyatomic interference removal with the superior matrix tolerance of its unique High Matrix Introduction system. Fourth generation Octopole Reaction System (ORS^4) cell technology provides higher sensitivity and more effective interference removal than ever before in complex, high matrix environmental samples. Helium mode on the ORS^4 is so effective that interference correction equations can also be eliminated. These two factors redefine ease of use in ICP-MS, removing two of the most common causes of errors in multi-element analysis of complex samples.
Environmental samples like aqueous, high matrix soils, waters, seawaters and sediments can be analyzed at ease achieving great detection limits and delivering excellent recovery of certified values.

Agilent Technologies

First you will note that the 7800 Series quadrupole ICP-MS from Agilent Technologies provides unparalleled performance, in the smallest commercial ICP-MS ever made. In fact it is about half the size of the specified PE Nexion ICPMS saving you valuable bench space.

The Agilent 7800 includes a Peltier cooled spray chamber with a temperature range that can be controlled from -5 degrees C to room temperature. This is a thermoelectric cooler with an accuracy of ± 1 degree which is controlled through the ICP-MS software. This is standard on all Agilent ICPMS and provides more stable readouts.

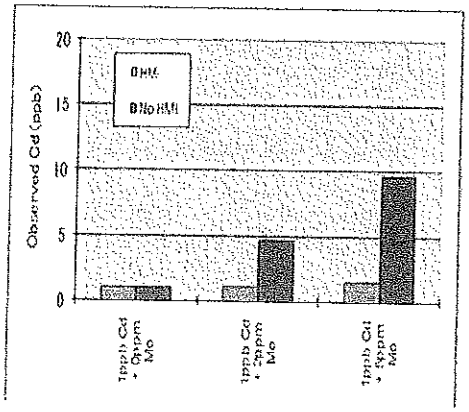
Other systems have problems with high matrix samples (>0.2% TDS), poor sample decomposition (reflected in high CeO/Ce specifications), and signal suppression (shown by internal standard instability and sample deposition on the cones). In addition, other ICPMS's have poor concentration ranges requiring dilutions for samples in only the 100ppm range. The only answer on these systems is to dilute prior to analysis.

Agilent's solution to this is via an optimized ICPMS design. Matrix effects as mentioned above can be reduced by increasing the plasma temperature and reducing the matrix load. How to do? When tuning an ICP-MS, the minimization of interferences is equally important to high sensitivity and low background performance. A low cerium oxide ratio (CeO/Ce) is the most commonly used indicator of plasma robustness and interference formation/reduction. Many factors can influence the reduction of interferences; from a high efficiency RF generator and wide torch injector to low sample uptake rates. The typical ICPMS in the market operates at 2% to 3% CeO/Ce ratios (as does the stated PE Nexion) That means that of all the cerium introduced in the system about 3% will form a polyatomic interference and be shifted to a different mass. The importance of reducing this value while tuning is because this newly formed polyatomic interference can negatively affect the quantitation of other elements. So in high matrix samples the plasma is overloaded and the analyte signal drops (suppression) -- this suppression is worse when the CeO/Ce ratio is higher (plasma temperature is lower). The Agilent ICPMS typically runs at 1% CeO/Ce -- lowest on the market. With ~1% CeO you can calibrate in dilute acids (1/0.5) and analyze unknowns with very high TDS. Signal suppression is minimized. No other ICPMS can do this!

The Agilent's unique and patented technology of the High Matrix Introduction (HMI) accessory enables the Agilent ICP-MS to operate at unprecedented levels of robustness (down to 0.2% CeO/Ce), which greatly reduces matrix suppression, making the analysis of high matrix samples more reliable and accurate than ever before with ICP-MS.
The reduction of CeO from 3% to 0.3% translates into a 90% reduction of interferences.

Agilent Technologies

90% Better Interference Removal with the HMI



Recovery of a 1 ppb Cd spike in increasing Mo concentration (0, 2, 5 ppm Mo). Comparison of 1% oxides (still better than any other ICP-MS) and 0.2% oxides with the Agilent ICP-MS under HMI conditions.

The Agilent ICP-MS with HMI offers >90% better interference removal before the sample reaches the ORS

Assuming 100,000 cps sensitivity for Ce-140

With the HMI 0.2% CeO/Ce

200 cps of CeO-156

Typical ICP-MS = 2%-3% CeO/Ce

2,000 - 3,000 cps of CeO-156

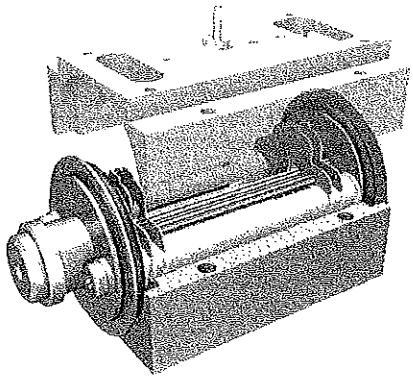
HMI maximizes the plasma robustness of the 7800 ICP-MS through a combination of aerosol dilution and automated plasma temperature optimization. The HMI has a wide range of aerosol dilution and improves sample washout performance allowing **TDS levels of up to 3% to be run** which are 10X greater than any other ICPMS. HMI dilution performs automatically using the dilution factor set by the user, and calibrated by the plasma correction software algorithm to ensure consistent operating conditions. Please refer to enclosed flyer on running waste samples on the Agilent 7800 with HMI. Note the significantly improved recoveries compared to other ICPMS instruments.

7800 Helium Mode Interference Removal and Sensitivity

The 7800 Series incorporates a new, 4th generation cell, the ORS^4, which provides superior interference removal in He mode while maintaining optimal ion focusing. Please refer to the enclosed application note on running waste samples on the Agilent 7800 with He collision cell only. You will note that ammonia gas is not required on the Agilent 7800 in order to achieve interference removal thus simplifying your analysis and making the laboratory safer. Some the highlights include:

- Enables fast analysis with uniform conditions, for stability and consistent interference removal

- Provides both high ion transmission and superior ion focusing, minimizing ion scattering at the high cell pressures required for effective KED
- He cell mode as standard.
  - Only the combination of narrow ion energy distribution (due to ShieldTorch) and the 7800's unique octopole-based cell enables efficient removal of interferences using an inert cell gas (He) and KED. He mode provides several critical advantages compared to reactive cell gases like ammonia.

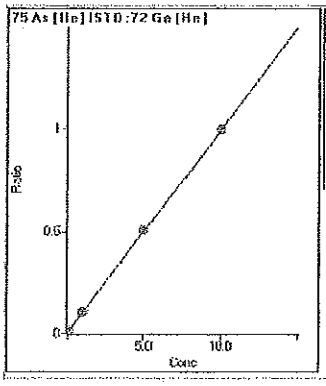


  - He mode is effective for all polyatomic interferences, not just reactive polyatomics
  - The cell gas can be changed with minimal switching time (<5 sec).
  - He is inert, so no new interferences are produced, regardless of the matrix
  - Unlike a reactive cell gas, He does not react with analytes, so consistent and predictable sensitivity is maintained
  - He mode is suitable for all analytes (no-gas mode can be used for un-interfered analytes) and can be used reliably for completely unknown sample matrices - a unique capability of the 7800.

As an example, the calibration curve for arsenic shown below was prepared in a solution of 1% HNO3 and 0.5% HCl at concentrations of 0, 0.1, 1, 5 and 10 ppb. We normally add HCl to our solutions in order to stabilize mercury. However, the presence of HCl will result in the formation of an ArCl polyatomic interference on As-75.

(Prepared in 1%HNO3/0.5% HCl)

Arsenic

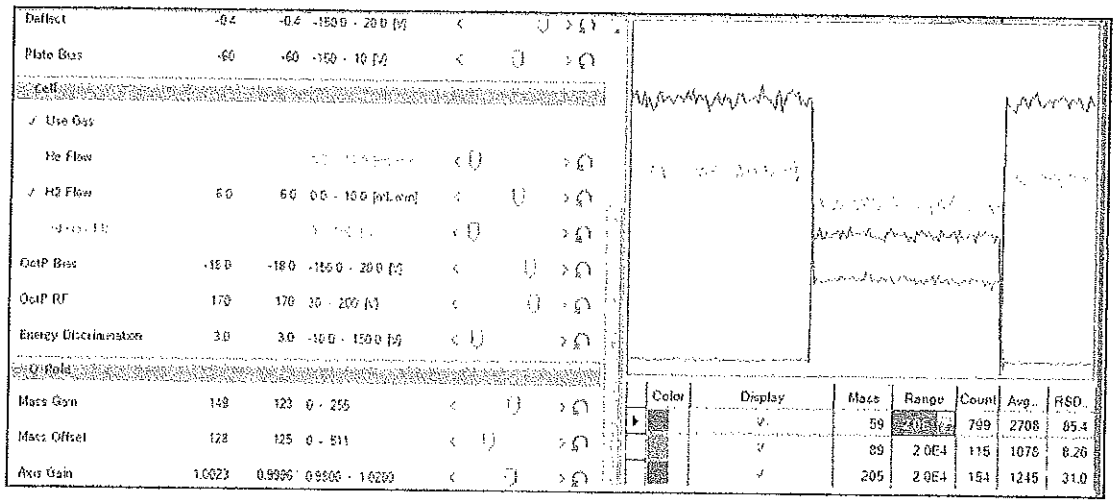


	Rpt	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.000	48.33	0.0007	P	12
2	☐	0.100	0.100	762.35	0.0106	P	7.
3	☐	1.000	1.017	7487.12	0.1021	P	1.
4	☐	5.000	5.041	36872.57	0.5033	P	0
5	☐	10.000	9.078	73250.29	0.9954	P	1
6	☐						

y = 0.0997 * x + 6.637/E-004
R = 1.0000
DL = 0.002449
BEC = 0.006658
Weight: <None>
Min Conc: <None>

As can be seen from the above calibration curve, the ArCl polyatomic interference has been completely eliminated by our helium mode (as evidenced by the curve going through the origin) while at the same time demonstrating a software calculated DL (detection limit) of 0.002 ppb.

The 7800 ORS has the fastest cell gas switch time in the industry. The screen display below shows how quickly the cell stabilizes between turning cell gas on and off. Please note that horizontal scale of the screen capture represents 60 seconds. Transition time in stabilizing both into and out of the cell gas to no cell gas in less than 2 seconds.



Along with the features built into the Agilent 7800, the ISIS 3 discrete sampling valve improves your overall efficiency. Faster discrete sampling (DS) is a key benefit of the 7800 with ISIS 3 (mainly due to the shorter distance between the switching valve and the nebulizer). Of course the sample to sample time will depend on the number of elements, number of gas modes, variability of the samples and required detection limits, but the figure of 60 seconds per sample is typical for EPA method 6020. In addition, it supports an automatic switch between tune and internal standard and supports auto optimization and auto tune.

Agilent's Mass Hunter software brings it all together and automates virtually all aspects of instrument operation. Features such as auto-tuning, automated cone-conditioning and automated detector cross-calibration during the analytical sequence relieve the user of inconvenient and time consuming day to day tasks thus allowing the user to focus on simply loading samples, acquiring the data and reviewing results. In addition, features such as quick-scan semiquant allow the user to collect full spectra for each sample for only two additional seconds of acquisition time. This allows the user to approximate (± ~30%) all of the other elements for which the instrument was not calibrated during the analytical run. Our enhanced resolution autotune allows the user to collect data at half-masses (completely resolved from adjacent masses) which provides the ability to correct for doubly charged interferences of Sr^{++} on Ca, Nd^{++}/Sm^{++} on As and Gd^{++} on Se. Doubly charged interferences can be especially problematic in soil samples. Mass Hunter provides all of the

Agilent Technologies

tools necessary for full compliance and reporting with EPA methods 200.8 and 6020 as well as a variety of software tools for reviewing and exporting data.

Combine the power of HMI, 10 orders of linearity, the simplicity of the He collision cell, the productivity of ISIS 3 and the City of Fresno realizes not only an upfront savings but also Ar savings, consumable savings, waste removal savings, etc. from not having to perform costly dilutions and reruns. If the lab personnel would like to see how easily the Agilent 7800 ICPMS would perform their sample analysis on your samples prior to making a decision, we would be happy to run some samples. I know your analysis would be simplified with an Agilent ICPMS.

Sincerely,
AGILENT TECHNOLOGIES, INC.

Margaret Roderick/g

Margaret Roderick
Atomic Spectroscopy Specialist

Agilent Technologies

Quotation

Laura Rapp
Buyer
City of Fresno
5607 W Jensen Ave
FRESNO CA 93706-9458

Quote No.	Create Date	Delivery Time	Page
1966223	12/17/2015	6 Weeks	1 of 7

Contact	Phone no.	Valid to
Margaret Roderick	415-990-7621	02/15/2016

To place an order: Call 1-800-227-9770 Option 1
For Instruments Fax : 302-633-8953
For Consumables Fax : 302-633-8901
Email : LSCAinstrumentsales@agilent.com
For Genomics Fax: 512-321-3128
Email : orders@agilent.com
For additional instructions, see last page

Second year warranty and training included

Product/Description	Qty/Unit	Unit List Price	Discount Amount	Extended Net Price
G8421A Agilent 7800 ICP-MS mainframe with He cell gas line With the following configuration: Ship-to Country : USA Advanced Acquisition Installation (44K) Familiarization at Installation (44L)	1.000 EA	172,613.00 USD	74,223.59-	98,389.41
Special discount of 43.00 % is applied.				
G7215C ICP-MS Workstation PC bundle for 7700, 7800, 7900 and 8800. Includes PC, Windows 7 64 bit OS, Monitor and Printer but does not include ICP-MS MassHunter software for operation of instruments. With the following configuration: Ship-to Country : USA MassHunter Software For 7800 ICP-MS Installation (44K) 1 Year SW Update/Phone Assist (44W)	1.000 EA	14,634.00 USD	6,292.62-	8,341.38
Special discount of 43.00 % is applied.				
G7206C ICP-MS MassHunter Intelligent Sequence Quality Control software option. Provides comprehensive real-time QC actions in ICP-MS MassHunter for the 7700 and 7900.	1.000 EA	2,999.00 USD	1,289.57-	1,709.43

Agilent Technologies

Quotation

Quote No.	Create Date	Delivery Time	Page
1966223	12/17/2015	6 Weeks	2 of 7

Contact	Phone no.	Valid to
Margaret Roderick	415-990-7621	02/15/2016

To place an order: Call 1-800-227-9770 Option 1
For Instruments Fax : 302-633-8953
For Consumables Fax : 302-633-8901
Email : LSCAinstrumentsales@agilent.com
For Genomics Fax: 512-321-3128
Email : orders@agilent.com

Laura Rapp
Buyer
City of Fresno
5607 W Jensen Ave
FRESNO CA 93706-9458

Product/Description	Qty/Unit	Unit List Price	Discount Amount	Extended Net Price
With the following configuration: Ship-to Country : USA Installation (44K) Familiarization at Installation (44L)				
Special discount of 43.00 % is applied.				
G3292A PolyScience Model 6106T Recirculating Chillers. With the following configuration: Ship-to Country : USA	1.000 EA	5,441.00 USD	2,339.63-	3,101.37
Special discount of 43.00 % is applied.				
5185-5850 ICP-MS Checkout Solutions Installation checkout solutions kit required by the Agilent installation engineer to validate the Agilent 7700 performance on site. Contains tuning solution, dual mode (1), dual mode(2),wash and water blank solutions	1.000 EA	592.00 USD	254.56-	337.44
Special discount of 43.00 % is applied.				
5188-6524 PA tuning solution set, 2 bottles of 100mL: 20ppm each of zn, be, CD, As, 10PPM of Ni, Pb, Mg, 5ppm of Tl, NA, Al, U, Cu, Th, Ba, Co, Sr, V, Cr, Mn, Li, Sc, In, Lu, Bi 2.5ppm of Y, Yb in 2- 2.5% HNO3	1.000 EA	717.00 USD	308.31-	408.69

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Special discount of 43.00 % is applied.				
G8415A SPS 4 autosampler for ICP-MS products. Optional cover kit not included. With the following configuration: Dual Port Reservoir Kit (004) : Selected Ship-to Country : USA SPS 4 Dual Port Reservoir Kit Installation (44K) Familiarization at Installation (44L)	1.000 EA	11,314.00 USD	4,865.02-	6,448.98
Special discount of 43.00 % is applied.				
RMSH-2 Big Universal Trap, 1/8inch fttgs,Helium	1.000 EA	325.00 USD	139.75-	185.25
Special discount of 43.00 % is applied.				
5080-8751 Fittings 1/8" stainless steel 20/PK 1/8" stainless steel Nuts, front and back ferrules	1.000 PK	312.00 USD	134.16-	177.84
Special discount of 43.00 % is applied.				
7157-0210 Stainless Steel Tubing, 1/8 in, 20ft	1.000 EA	124.00 USD	53.32-	70.68
Special discount of 43.00 % is applied.				

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Product/Description	Qty/Unit	Unit List Price	Discount Amount	Extended Net Price
~~0101-1536~~	~~1.000 EA~~	~~314.00 USD~~	~~135.02-~~	~~178.98~~
Gas regulator, Helium for ICP-MS. 2 stage, brass body, stainless steel diaphragm, CGA580 Inlet 3000psi, 15psi outlet, 30psi gauge + 1/8" Swagelok.				
Special discount of 43.00 % is applied.				
G8411A ISIS 3 for Agilent 7900 ICP-MS	1.000 EA	13,462.00 USD	5,788.66-	7,673.34
With the following configuration: Ship-to Country : USA				
Installation (44K) Familiarization at Installation (44L)				
Special discount of 43.00 % is applied.				
5184-3566 ICP-MS Tuning Sol 10ug/mL 2x 500mL Contains 10 ppb Li, Y, Ce, Tl, Co in 0.2 wt % HNO3	1.000 EA	273.00 USD	117.39-	155.61
Special discount of 43.00 % is applied.				
NON AGILENT PROD 72 inch bench	1.000 EA	2,475.00 USD		2,475.00

Please note that above product 72 inch bench is not manufactured by
Agilent Technologies which hereby disclaims any liability for the performance,

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For Genomics Fax: 512-321-3128
Email : orders@agilent.com

Product/Description	Qty/Unit	Unit List Price	Discount Amount	Extended Net Price

~~quality, reliability or delivery of the items. The standard~~
warranty,INCLUDING INDEMNIFICATION FOR INTELLECTUAL PROPERTY INFRINGEMENT, is to be supplied by manufacturer unless otherwise specified on
the Agilent Technologies quotation.

Gross Amount	: $	225,595.00
Total Discount	: $	95,941.60
Net Amount	: $	129,653.40
Sales Tax	: $	10,664.02
Total	**: $**	**140,317.42**

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4) Or you can mail your order to:
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   2850 Centerville Road BU3-2
   Wilmington, DE 19808-1610

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TERMS AND CONDITIONS:

- Pricing: Web prices are provided only for the U.S. in U.S.dollars. All phone prices are in local currency and for end use. Applicable local taxes are applied.
- All Sales Tax is subject to change at the time of order.
- Shipping and Handling Charges: Orders with a value less than $4000 or those requiring special services such as overnight delivery may be subject to additional shipping & handling fees. Some of these charges may be avoided by ordering via the Web
- Payment Terms: Net 30 days from invoice date, subject to credit approval.

* Quotation Validity: This quotation is valid for 60 days unless otherwise indicated.
* Warranty period for instrumentation is 1 year. The Warranty period for columns and consumables is 90 days.

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It is Agilent Technologies intent to ship product at the earliest available date unless specified otherwise.

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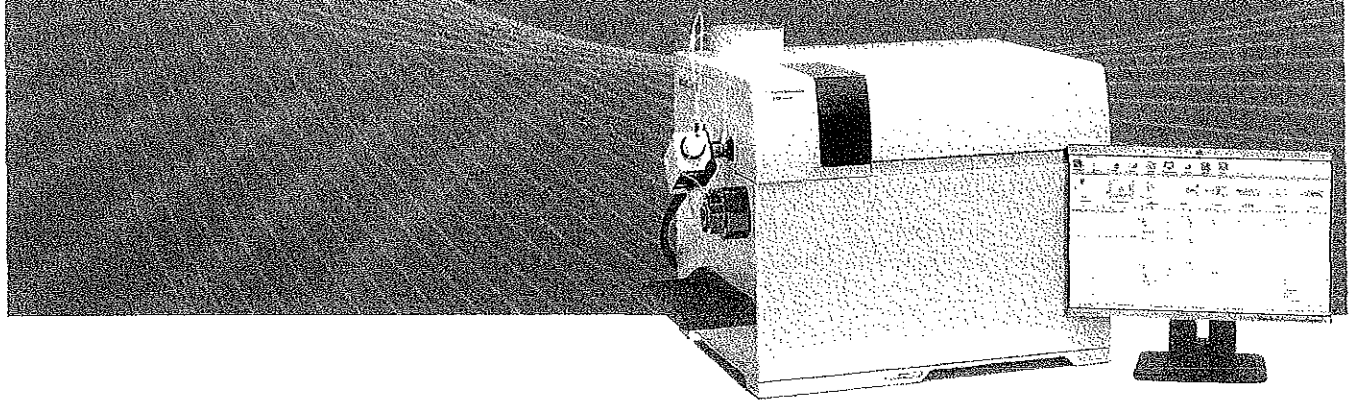
WARNING: This product contains a chemical known to the State of California to cause cancer or birth defects or other reproductive harm.

Agilent 7800 Quadrupole ICP-MS

FAST-TRACK YOUR METALS ANALYSIS WITH SOLUTION-READY ICP-MS

The Measure of Confidence



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AGILENT 7800 QUADRUPOLE ICP-MS

TAKE A NEW LOOK AT ROUTINE METALS ANALYSIS

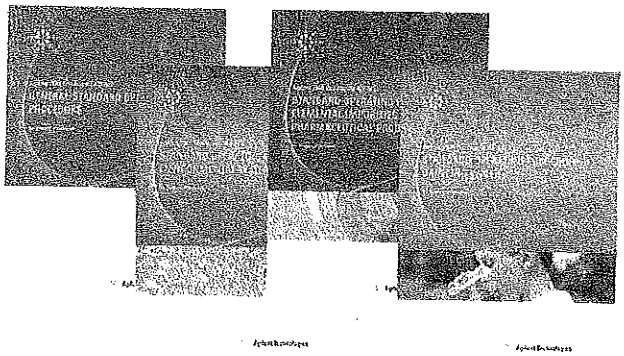
The new, Solution-Ready Agilent 7800 ICP-MS combines proven, robust hardware, auto-optimization tools, and Pre-set Methods to simplify routine analysis, making your laboratory more productive, and your results more reliable.

What's more, with high matrix tolerance, wide dynamic range, and effective control of polyatomic interferences, the 7800 ICP-MS takes the uncertainty out of analyzing complex or variable sample matrices.

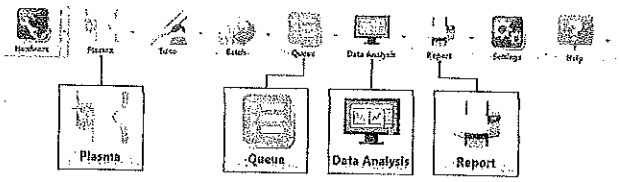
The 7800 ICP-MS is extraordinarily easy to set up and use, so you can quickly produce reliable results in the widest range of sample types.

Fast track your ICP-MS method development

- New ICP-MS MassHunter software provides fast system setup, robust auto-optimization tools and extensive system status monitoring, to ensure consistent high performance.
- Many common methods can simply be loaded and run, with settings – from plasma conditions to analyte integration times and internal standards – predefined in a Pre-set Method. Where a specific new method is needed, the Method Wizard simplifies the setup process.
- The software includes performance, tune, QC, and sample report templates with operator tutorials for refresher or new-user training.
- Standard operating procedures (SOPs) for several common applications, guide new users in system setup and routine operation, setting you on the fast track to accurate analysis.



Solution-Ready ICP-MS
The 7800 ICP-MS includes SOPs for common applications, including drinking water, environmental waste analysis, and Elemental Impurities in pharmaceutical products.



Simplify your method setup
ICP-MS MassHunter software uses an intuitive layout with graphical toolbar Gadgets, making it easy to learn and use. The innovative Method Wizard builds a fully functional method based on your sample type and application.

AGILENT 7800 QUADRUPOLE ICP-MS

UP TO THE AGILENT 7800 ICP-MS SUPPORTING YOUR ANALYTICAL WORKFLOW

Maximize throughput and productivity

The optional Integrated Sample Introduction System (ISIS 3), shown, and new SPS 4 autosampler lower your cost per analysis, without compromising data quality.

Reduce sample preparation and minimize suppression

Agilent's unique High Matrix Introduction (HMI) technology, standard on the 7800 ICP-MS, lets you analyze samples containing up to 3% total dissolved solids (TDS) without dilution, reducing sample preparation and saving time.

HMI also reduces signal suppression, so high matrix samples can be measured accurately without requiring matrix matched calibration standards.

Ensure accurate data with effective interference removal

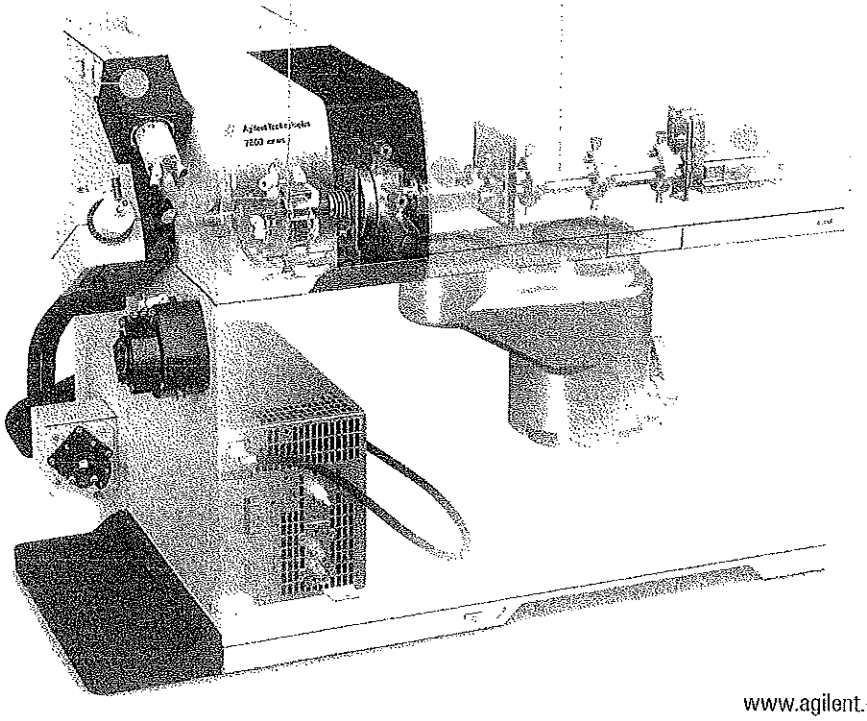
Helium (He) collision mode simplifies method development and routine operation by removing all polyatomic ion interferences under a single consistent set of conditions.

He mode avoids the need for matrix-specific or analyte-specific reaction cell conditions.

Analyze major and trace analytes in a single run

The wide dynamic range orthogonal detector system (ODS) enables direct analysis of major elements (100s or 1000s of ppm) and trace level analytes (single- or sub-ppt) in a single run, simplifying methodology.

The high upper concentration limit reduces sample reruns caused by overrange results.



For more information

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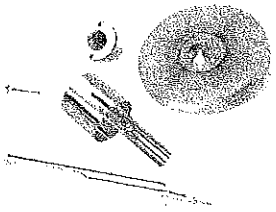

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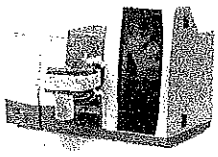
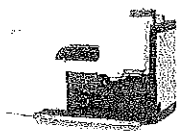
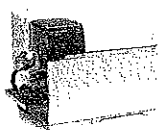


Agilent AA

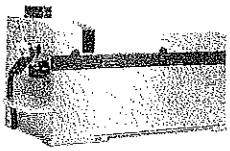


Agilent MP-AES

Agilent ICP-OES



Agilent ICP-MS



Agilent ICP-QQQ

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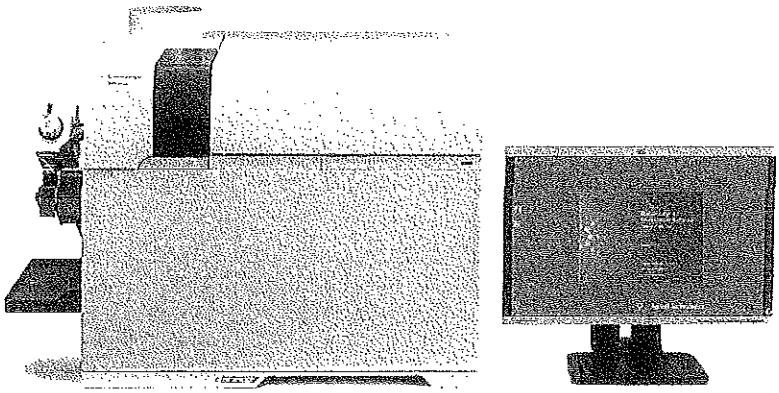
Agilent 7800 ICP-MS

Specifications and Typical Performance



Fast track metals analysis with Solution-Ready ICP-MS

The Solution-Ready Agilent 7800 Quadrupole ICP-MS combines proven, robust hardware, auto-optimization tools, and pre-set methods to simplify routine analysis, making your laboratory more productive, and your results more reliable.

What's more, with high matrix tolerance, wide dynamic range, and effective control of polyatomic interferences, the 7800 ICP-MS takes the uncertainty out of analyzing complex or variable sample matrices.

The 7800 ICP-MS is extraordinarily easy to set up and use, so you can quickly produce reliable results in the widest range of sample types.

Specifications

Sample introduction system	Peristaltic pump	10-roller, 3 channels
	Nebulizer	MicroMist (borosilicate glass)
	Spray chamber	Scott-type double-pass (quartz) Controlled temperature range: –5 °C to +20 °C
	High Matrix Introduction system (HMI)	Included
Plasma	RF generator	Solid state digital drive 27 MHz Variable-frequency impedance matching 500 W to 1600 W
	Torch	One-piece (quartz) 2.5 mm id injector ShieldTorch system
	Torch position	Horizontal and vertical position: ±2 mm, in 0.1 mm steps *Sampling depth: 3 to 28 mm, in 0.1 mm steps*
	Mass flow controllers (Ar)	4: Plasma, Aux., Carrier, Make up/Dilution
	5th gas line for alternative carrier gas	Optional
Interface	Sampling cone	1 mm diameter orifice Standard: Ni-tipped with Cu base Optional: Pt-tipped with Cu base
	Skimmer cone	0.4 mm diameter orifice Standard: Ni Optional: Pt-tipped with Cu base
Ion lens	Lens system	Extraction lens Off-axis Omega lens
Octopole Reaction System (ORS)	He (collision) cell gas line	Included
	H_2 (reaction) cell gas line	Optional
	3rd cell gas line (low- or high-flow rate)	Optional
Mass analyzer	Quadrupole	Frequency: 3 MHz Hyperbolic rod profile
	Mass range	2–260 u
	Mass resolution	Variable from 0.3 u to 1.0 u
	Typical mass calibration stability	< 0.05 u per day < 0.1 u per 6 months
	Abundance sensitivity (at Cs)	Low mass side: $\leq 5 \times 10^{-7}$ High mass side: $\leq 1 \times 10^{-7}$

Detector	Configuration	Orthogonal Detector System (ODS)
	Detector	Dual-mode discrete dynode electron multiplier
	Dynamic range	10 orders (0.1 cps to 4 Gcps)
	Minimum integration time	100 µs
	Minimum dwell time (TRA mode)	3 ms
Vacuum system	Configuration	Three-stage differential vacuum system
	Vacuum pump	Single split-flow turbo molecular pump Single external rotary pump
	Vacuum pump hose length	1.5 m, 3 m (optional)
Software	Instrument contol software	ICP-MS MassHunter Workstation software
	User access control software	Optional
	Chromatographic software	Optional
	Single nanoparticle application module	Optional
	Intelligent sequencing software	Optional
	Three offline user licenses	Optional

Accessories and Peripherals

Autosamplers	Agilent SPS 4 Autosampler Agilent Integrated Autosampler (I-AS)
Sample introduction	Integrated Sample Introduction System 3 PFA Inert Sample Introduction Kit Organic Solvent Introduction Kit Humidifier
Speciation kits	LC-ICP-MS Speciation Kits Arsenic Speciation Kit Chromium Speciation Kit Capillary LC Interface Kit GC-ICP-MS Interface
Peripherals	Water recirculator Water chiller Optional hood Quiet cover for rotary pump

Instrument Performance

The factory shipping specifications that are confirmed at the factory represent minimum requirements for shipping approval. The actual performance of the Agilent ICP-MS is invariably much higher. The two tables below provide the typical performance of the Agilent 7800 ICP-MS, together with the factory shipping specifications.

No Gas mode		**7800 Factory Specifications[1]**	**7800 Typical Performance[2]**
Sensitivity (Mcps/ppm)	^{7}Li	50	110
	^{59}Co		180
	^{89}Y	160	270
	^{115}In		320
	^{205}Tl	80	340
	^{238}U		540
Background	*m/z* 9	<1 cps	<0.3 cps
Detection limits	^{9}Be	<0.5 ppt	<0.1 ppt
	^{115}In	<0.1 ppt	<0.04 ppt
	^{209}Bi	<0.1 ppt	<0.04 ppt
Oxide	CeO/Ce	<1.5%	<1.8%
Doubly charged	Ce^{2+}/Ce	<3%	<2.5%
Stability	20 min	<2.0% RSD	<1.0% RSD
	2 hr	<3.0% RSD	<1.2% RSD
Isotope ratio precision	^{107}Ag/^{109}Ag	<0.1% RSD	<0.1% RSD

He Gas mode		**7800 Typical Performance[2]**
Sensitivity (Mcps/ppm)	^{59}Co	47
Background	*m/z* 9	<0.2 cps
Interference reduction factor[3]	^{59}Co/^{61}ClO	>30
Oxide	CeO/Ce	<0.5%
Detection limits[3]	^{75}As	<10 ppt

1. 7800 Factory Shipping Specifications. These specifications are detailed in the Agilent publication: Agilent 7800 ICP-MS, Specifications (Publication number: 5991-5927EN).

2. The typical performance values are not checked during the standard installation.

3. Performed in a matrix of 2% HNO_3 + 0.5% HCl.

Site Requirements and Safety

Dimensions

Mainframe	Width	730 mm (main cabinet, excluding peri-pump)
	Depth	600 mm (main cabinet, excluding power cord)
	Height	595 mm (main cabinet, excluding exhaust chimney)
	Weight	100 kg
Largest shipping container	Width	1,020 mm
	Depth	1,120 mm
	Height	1,000 mm
	Weight	148 kg

Environmental

Operating temperature	Range	15–30 °C
	Rate of change	<2 °C/hr (max. change 5 °C)
Operating humidity	Range	20-80% (non-condensing)

Utilities

Electricity supply	Voltage	Single Phase, 200-240 V, 50/60 Hz
	Current	30 A
Cooling water	Inlet temperature	15-40 °C
	Minimum flow rate	5 L/min
	Inlet pressure	230-400 kPa
Argon gas supply	Minimum purity	99.99 %
	Maximum flow rate	20 L/min
	Supply pressure	500-700 kPa
Cell gas supply	Minimum purity	99.999%
	Maximum flow rate	12 mL/min for He and 10 mL/min for H_2
	Supply pressure	90-130 kPa for He 20-60 kPa for H_2
Exhaust duct	Vent Type	Single vent, 150 mm diameter
	Flow rate	5-7 m^3/min

Regulatory Compliance

Safety	IEC 61010-1:2001 / EN 61010-1:2001 IEC 61010-2-061:2005 / EN 61010-2-061:2003 IEC 61010-2-081:2001+A1:2003 / EN 61010-2-081:2002+A1:2003 Canada: CAN/CSA C22.2 No. 61010-1-04 Canada: CAN/CSA C22.2 No. 61010-2-061-04 Canada: CAN/CSA C22.2 No. 61010-2-081-04 USA: UL 61010-1 (2nd Edition)
EMC	IEC 61326-1:2012 / EN 61326-1:2013 Canada: ICES-001:2006
ISO	Manufactured at an ISO 9001 and ISO 14001 certified facility

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Published October 26, 2015
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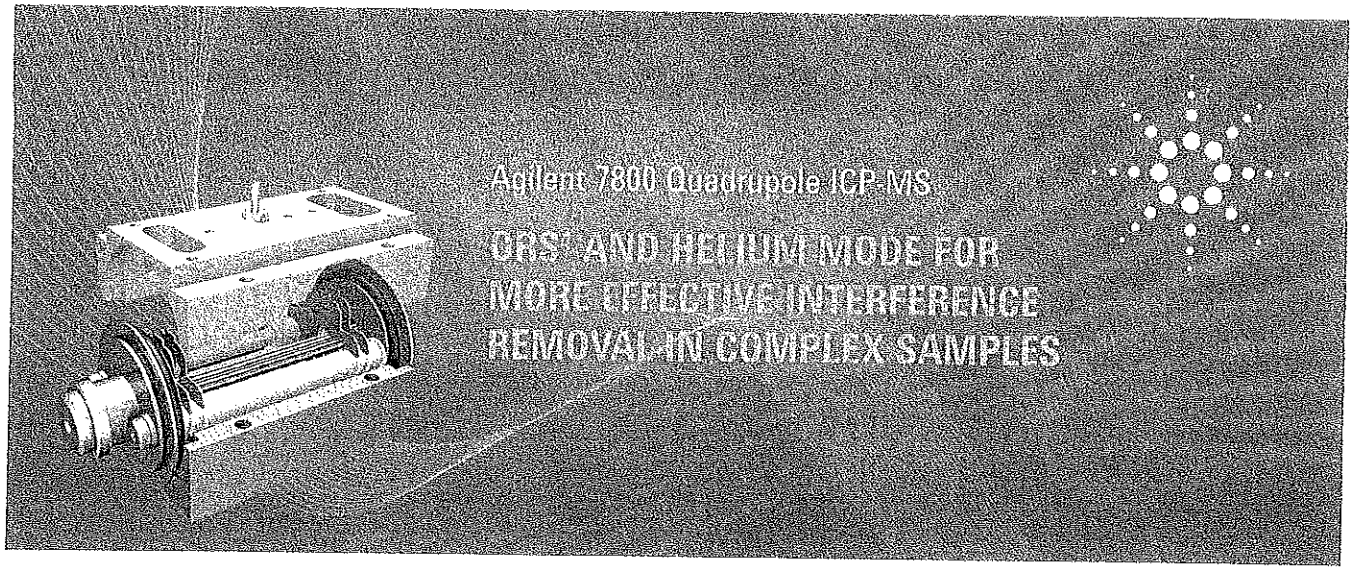

Benefits of helium mode

- Helium is inert, so no new reaction product ion interferences are formed
- Helium does not react with analyte ions, so loss of sensitivity by reaction does not occur
- Helium is effective against all polyatomic overlaps, so method development is simple, and accurate multi-element analysis is possible in complex matrices

Reaction mode

Collision/Reaction Cells (CRCs) in ICP-MS can operate as reaction cells (when a reactive gas is used) or as collision cells (when an inert gas is used). While the hardware used for these two approaches is similar, the mode of operation is very different.

With a reactive cell gas, interference removal is based on the relative reaction rates of the cell gas with the analyte and interfering ion. To choose which reactive gas should be used, the interference must therefore be identified, which means the matrix composition must be known in advance. Reaction mode is also typically only effective against one specific interfering ion.

However, in most applications the sample matrix is unknown, variable, and often complex, so multiple polyatomic ions may interfere at each analyte mass. Under these circumstances, reactive cell gases will lead to serious analytical errors:

- Each reaction gas only reacts with specific interferences; unreactive interferences remain, leading to errors.
- Reaction gases create new cell-formed reaction product ions causing new, matrix-dependent polyatomic interferences.
- Reaction gases react with some analyte ions, leading to severe signal loss and poorer detection limits.

With an inert cell gas, interference removal is mainly by kinetic energy discrimination (KED). This process works because polyatomic interferences are molecular ions, and so have a larger ionic cross section than analyte (single atom) ions at the same mass. Polyatomics collide more often with the cell gas and lose more energy, and so can be prevented from passing into the analyzer by applying a KED bias voltage at the cell exit.

The key benefits of collision mode are that it can remove multiple interferences on multiple analytes, no new polyatomic interferences are produced regardless of the sample matrix, and selective analyte signal loss by reaction does not occur.

The 4th generation Octopole Reaction System (ORS^4) used in the Agilent 7800 ICP-MS is optimized for high performance in helium (He) collision mode. The ShieldTorch System provides a narrow initial ion energy spread, and the small internal volume, octopole-based ORS^4 cell maintains high ion transmission at the high cell gas pressure needed for effective KED.

He mode in the ORS^4

Figure 1 compares the effectiveness of the different cell modes for the removal of multiple interferences on the 1st row transition elements, in a blank matrix mix containing 5% HNO_3, 5% HCl, 1% H_2SO_4, and 1% IPA. All spectra are shown on the same intensity scale. In no gas mode (Figure 1, top) the complex polyatomic interferences created in this matrix mix are obvious. In H_2 reaction mode (Figure 1, middle) some (unreactive) polyatomics remain, and several new ones are created. By contrast, He mode (Figure 1, bottom) effectively removes all the polyatomic interferences in this complex matrix. High sensitivity is maintained in He mode, as shown by the inset spectrum of a 10 ppb spike measured under the same conditions.

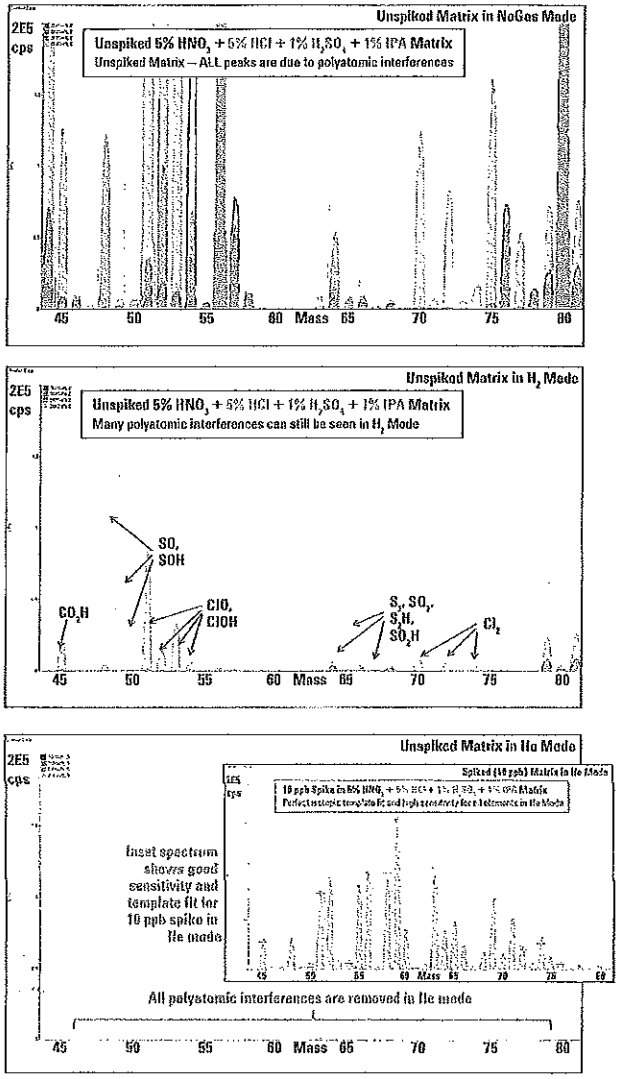

Figure 1. Mixed matrix blank in no gas, H_2 and He mode (inset: Same matrix with 10 ppb spike in He mode).

For more information visit:
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Published June 1, 2015
5990-7574EN

Simple, Reliable Analysis of High Matrix Samples According to US EPA Method 6020A using the Agilent 7700x/7800 ICP-MS

Combining the advantages of helium mode and aerosol dilution for superior performance

Application Note

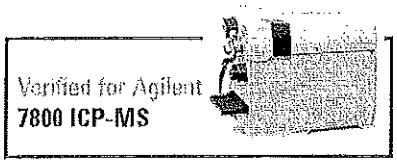
Author

Steve Wilbur
Agilent Technologies, Inc.
1615 75th Street SW, Suite 210
Everett, WA 98203

Craig Jones
Agilent Technologies, Inc.
5301 Stevens Creek Blvd
Santa Clara, CA 95051

Abstract

The Agilent 7700x/7800 ICP-MS combines the simplicity of a single collision cell mode (helium mode) for polyatomic interference removal with the superior matrix tolerance of its unique High Matrix Introduction (HMI) system. Octopole Reaction System (ORS) cell technology provides higher sensitivity and more effective interference removal than ever before in complex, high matrix samples, eliminating the need for reactive cell gases in routine analysis. Helium mode on the ORS is so effective that interference correction equations can also be eliminated. These two factors redefine ease of use in ICP-MS, removing two of the most common causes of errors in multi-element analysis of complex samples. A challenging 15-hour sequence of high matrix soils, waters, seawaters and sediments was analyzed according to US Environmental Protection Agency (EPA) Method 6020A. The Agilent 7700x ICP-MS delivered excellent recovery of certified values for six standard reference materials, with no quality control failures throughout the entire sequence.



Agilent Technologies

Introduction

US EPA Method 6020A (Rev 4, February 07) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. The EPA has carried out multi-laboratory studies to validate Method 6020A for 23 elements in aqueous and solid wastes (Table 1).

*Table 1. Elements Currently Validated by EPA for Method 6020A. *Chemical Abstract Services Registry Number*

Element	CASRN*
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Thallium (Tl)	7440-28-0
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

However, the method can be used for the analysis of any element(s) for which the performance can be shown to meet the project data quality objectives. Unlike Method 200.8 for drinking water compliance, Method 6020A does not place any restrictions on the use of advancements in ICP-MS technology such as collision/reaction cells (CRCs) for the removal of polyatomic interferences. As a result, Method 6020A permits the use of helium (He) mode on the Agilent 7700x/7800 ICP-MS to provide simple, efficient removal of all polyatomic interferences, even in complex and unknown sample types.

This is especially important for Method 6020A, due to the wide variety of sample types and concentrations for which the method is applicable. Table 2 illustrates the challenges presented by the range of samples typically analyzed using Method 6020A. Nearly every element from scandium through selenium is subject to multiple polyatomic interferences in common environmental matrices. No reactive cell gas can simultaneously remove all these interferences, but He mode is universal. It uses the size difference between polyatomic (interfering) and monatomic (analyte) ions to remove all polyatomic interferences, eliminating the need for unreliable interference correction equations.

Table 2. Polyatomic Interferences on Elements Between Mass 40 and 80 Resulting from a Common Mixed Matrix Containing Na, Ca, C, S, P, Cl in Nitric Acid

Isotope/ Element	Common Polyatomic Interferences in Mixed Matrix Samples
^{45}Sc	$^{13}C^{16}O_2$, $^{12}C^{16}O_2H$, ^{44}CaH, $^{32}S^{12}CH$, $^{32}S^{13}C$, $^{33}S^{12}C$
^{47}Ti	$^{31}P^{16}O$, ^{46}CaH, $^{35}Cl^{12}C$, $^{32}S^{14}NH$, $^{33}S^{14}N$
^{49}Ti	$^{31}P^{18}O$, ^{48}CaH, $^{35}Cl^{14}N$, $^{37}Cl^{12}C$, $^{32}S^{16}OH$, $^{33}S^{16}O$
^{50}Ti	$^{34}S^{16}O$, $^{32}S^{18}O$, $^{35}Cl^{14}NH$, $^{37}Cl^{12}CH$
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$
^{52}Cr	$^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{16}OH$, $^{37}Cl^{14}NH$, $^{34}S^{18}O$
^{53}Cr	$^{36}Ar^{16}OH$, $^{40}Ar^{13}C$, $^{37}Cl^{16}O$, $^{35}Cl^{18}O$, $^{40}Ar^{12}CH$
^{54}Fe	$^{40}Ar^{14}N$, $^{40}Ca^{14}N$, $^{23}Na^{31}P$
^{55}Mn	$^{37}Cl^{18}O$, $^{23}Na^{32}S$, $^{23}Na^{31}PH$
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$
^{57}Fe	$^{40}Ar^{16}OH$, $^{40}Ca^{16}OH$
^{58}Ni	$^{40}Ar^{18}O$, $^{40}Ca^{18}O$, $^{23}Na^{35}Cl$
^{59}Co	$^{40}Ar^{18}OH$, $^{43}Ca^{16}O$, $^{23}Na^{35}ClH$
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$
^{61}Ni	$^{44}Ca^{16}OH$, $^{38}Ar^{23}Na$, $^{23}Na^{37}ClH$
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{12}C^{14}N^{37}Cl$, $^{31}P^{32}S$, $^{31}P^{16}O_2$
^{64}Zn	$^{32}S^{16}O_2$, $^{32}S_2$, $^{36}Ar^{12}C^{16}O$, $^{38}Ar^{12}C^{14}N$, $^{48}Ca^{16}O$
^{65}Cu	$^{32}S^{16}O_2H$, $^{32}S_2H$, $^{14}N^{16}O^{35}Cl$, $^{48}Ca^{16}OH$
^{66}Zn	$^{34}S^{16}O_2$, $^{32}S^{34}S$, $^{33}S_2$, $^{48}Ca^{18}O$
^{67}Zn	$^{32}S^{34}SH$, $^{33}S_2H$, $^{48}Ca^{18}OH$, $^{14}N^{16}O^{37}Cl$, $^{16}O_2{}^{35}Cl$
^{68}Zn	$^{32}S^{18}O_2$, $^{34}S_2$
^{69}Ga	$^{32}S^{18}O_2H$, $^{34}S_2H$, $^{16}O_2{}^{37}Cl$
^{70}Zn	$^{34}S^{18}O_2$, $^{35}Cl_2$
^{71}Ga	$^{34}S^{18}O_2H$, $^{35}Cl_2H$, $^{40}Ar^{31}P$
^{72}Ge	$^{40}Ar^{32}S$, $^{35}Cl^{37}Cl$, $^{40}Ar^{16}O_2$
^{73}Ge	$^{40}Ar^{32}SH$, $^{40}Ar^{33}S$, $^{35}Cl^{37}ClH$, $^{40}Ar^{16}O_2H$
^{74}Ge	$^{40}Ar^{34}S$, $^{37}Cl_2$
^{75}As	$^{40}Ar^{34}SH$, $^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{37}Cl_2H$
^{77}Se	$^{40}Ar^{37}Cl$, $^{40}Ca^{37}Cl$
^{78}Se	$^{40}Ar^{38}Ar$
^{80}Se	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$, $^{32}S_2{}^{16}O$, $^{32}S^{16}O_3$

Additionally, samples analyzed by Method 6020A can range from very low to very high Total Dissolved Solids (TDS) and a single sequence may cover the entire TDS range. The ICP-MS method must therefore accommodate both the wide range of unknown matrix interferences and the wide range of analyte concentrations; and for the method to be simple and routine,

this must all be achieved without any prior knowledge about the samples. The Agilent 7700x/7800 ICP-MS achieves this through the use of advanced helium collision technology (ORS) coupled with a unique High Matrix Introduction (HMI) system that is fitted as standard.

Experimental

A sequence of samples representing the types of matrices typically encountered by a contract environmental laboratory was analyzed according to Method 6020A requirements. The sequence consisted of a range of water (NIST, Gaithersburg MD, USA), soil, and sediment standard reference materials (High-Purity Standards, Charleston SC, USA), analyzed at both 1/10 and 1/50 dilutions, as well as synthetic seawater (SPEX Certiprep, Metuchen NJ, USA) and spiked seawater, (Figure 1). Additionally a set of low-level standards was analyzed to calculate the method detection limits (MDL). In total, 156 samples, standards and blanks were analyzed over the course of almost 15 hours, after a single initial calibration. Continuing calibration blanks (CCBs) and continuing calibration verification (midpoint) standards (CCVs) were automatically run after every 10 samples. Low level CCVs (LLCCVs) were also analyzed with each CCV block, as required by this most recent update to Method 6020A.

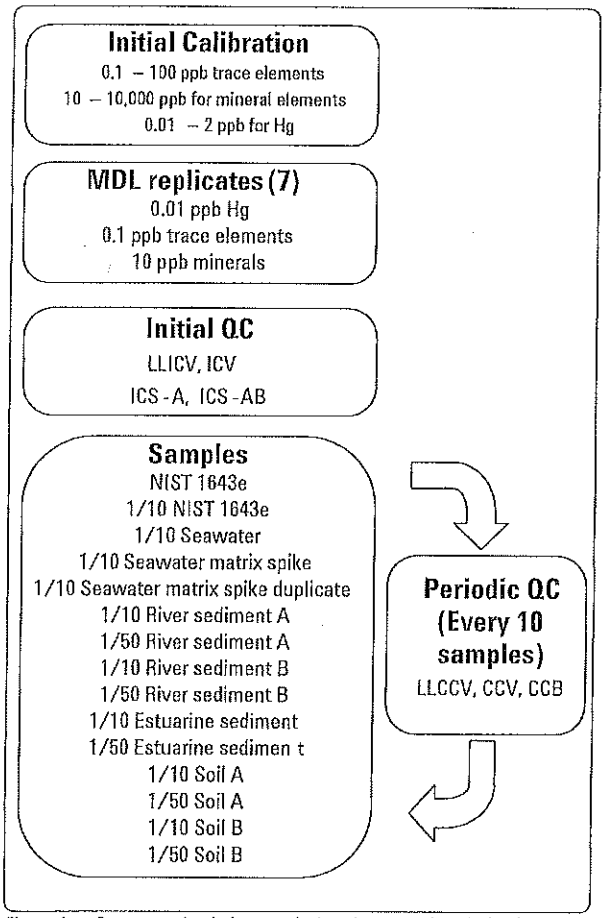


Figure 1. Sequence simulating a typical environmental analysis of a complex mixture of samples, analyzed according to the requirements of EPA Method 6020A.

Instrument Acquisition Parameters

The Agilent 7700x ICP-MS was operated in standard robust plasma conditions (less than 1% CeO/Ce) using the integrated HMI system to effectively eliminate matrix suppression and maintain long term stability in high matrix samples (Table 3). All analytes were acquired using He mode with the exception of the low and high mass elements that do not suffer from polyatomic interferences in any common matrices; these elements were acquired in no gas mode. Table 4 lists the acquisition mode for each element.

Note that the preferred, most abundant isotope was used for every analyte, and the reliable removal of interferences in He mode means that the same isotopes are used regardless of the sample matrix; furthermore, no interference correction equations were applied for any analyte in any matrix. This provides simplified method setup across a wide range of sample types.

*Table 3. 7700x ICP-MS Operating Conditions Used for Both No Gas Mode and He Mode (*He Flow for Se and V = 12 mL/min)*

Parameter	Value No gas mode	Value He mode
Forward power (W)	1550	same
Sample depth (mm)	8	same
Nebulizer pump speed (rps)	0.1	same
Carrier gas (L/min)	0.6	same
Dilution gas (L/min)	0.4	same
Dilution mode	On	same
Extract 1 (V)	0	same
Kinetic Energy Discrimination (KED) (V)	3	4
Cell gas flow (mL/min He)	0	4*

Results

Method Detection Limits

Table 4 shows the 3 sigma MDLs (µg/L) determined from seven replicates of a low level multi-element standard (3-5 times the estimated MDL for each analyte) measured immediately after the initial calibration. In nearly all cases, single digit to low double digit ppt MDLs were achieved, significantly below the typical requirements for this analysis. Even the common mineral elements, Na, K and Ca showed single digit ppb MDLs.

Table 4. 3-Sigma Method Detection Limits in µg/L (ppb) Calculated from Seven Replicate Analyses of a Low Standard at the Beginning of the Sequence

Mass	Element	Mode	MDL (µg/L)
9	Be	no gas	0.019
23	Na	He	2.134
24	Mg	He	0.582
27	Al	He	0.214
39	K	He	1.873
44	Ca	He	3.171
51	V	He	0.007
52	Cr	He	0.012
55	Mn	He	0.012
56	Fe	He	0.157
59	Co	He	0.004
60	Ni	He	0.011
63	Cu	He	0.012
66	Zn	He	0.028
75	As	He	0.013
78	Se	He	0.034
95	Mo	no gas	0.016
107	Ag	no gas	0.007
111	Cd	no gas	0.009
121	Sb	no gas	0.008
137	Ba	no gas	0.015
201	Hg	no gas	0.005
205	Tl	no gas	0.005
208	Pb	no gas	0.005
232	Th	no gas	0.009
238	U	no gas	0.004

Low Level Performance Verification – LLCCV

A new requirement for Method 6020A (Feb 2007) is the analysis of a low level continuing calibration verification (LLCCV) sample in order to verify that the system continues to accurately measure samples at the reporting limit over the course of the entire sample sequence. The recommended recovery limits are ±30% of the actual value. A LLCCV sample was included in the periodic QC block along with the CCV and CCB standards. The LLCCV concentration was 0.5 ppb for most elements, 50 ppb for the mineral elements (Na, K, Ca, Mg and Fe) and 0.05 ppb for Hg. The LLCCV was analyzed five times over the 15-hour sequence. RSDs for the five replicates were mostly <3% and recoveries were easily within the ±30% limits (mostly within ±10%) for all elements (except Hg, due to low level contamination) (Table 5). This demonstrates the superior sensitivity and accuracy of the Agilent 7700x ICP-MS, and its exceptional long-term stability.

Dynamic Range

In order to provide the simplest, most accurate analysis, the instrument must possess a dynamic range sufficient to analyze typical samples without excessive dilution or over-range results. Table 4 establishes the lower end of the dynamic range as single digit ppt for nearly all elements under typical environmental laboratory conditions, validated by the LLCCV recoveries shown in Table 5.

*Table 5. Precision (%RSD) and Accuracy (% Recovery) of Replicate Low Level CCV (LLCCV) Analyses Over the Duration of the 15 hour Sequence. *Some Contamination was Evident in the Hg LLCCV, Expected Value = 50 ppt*

	Mean n=5 (µg/L)	%RSD	Recovery (%)
Be	0.492	4.1	98.4
Na	43.146	11.6	86.3
Mg	48.160	0.9	96.3
Al	0.416	17.6	83.2
K	48.106	6.7	96.2
Ca	39.387	9.3	78.8
V	0.489	0.9	97.9
Cr	0.504	1.7	100.8
Mn	0.485	1.5	97.1
Fe	49.210	1.4	98.4
Co	0.489	2.0	97.8
Ni	0.509	3.0	101.9
Cu	0.508	2.3	101.6
Zn	0.433	4.1	86.7
As	0.498	1.1	99.7
Se	0.482	5.3	96.4
Mo	0.470	2.4	94.0
Ag	0.471	2.2	94.2
Cd	0.489	0.9	97.8
Sb	0.479	1.2	95.8
Ba	0.492	4.9	98.4
Hg	0.068	10.4	135.7*
Tl	0.461	1.5	92.1
Pb	0.480	1.3	96.0
Th	0.461	1.6	92.3
U	0.461	1.6	92.1

The upper limit is established either by the highest calibration concentration (100 ppb for trace elements and 10 ppm for minerals), or by linear range standards. In this work, any of the certified reference materials (CRMs) can be used as a linear range standard. The certified concentrations for the six CRMs are listed in Table 6. The highest concentration for each element is shown in the "Maximum" column. For those samples that were diluted 1/10, the on-instrument concentration is shown in the final column. Documented dynamic range under the simple conditions used in this work ranged from 2 ppt to more than 120 ppm, while other work has shown upper range in excess of 1000 ppm for some elements [1].

Accuracy and Precision

Recovery of Certified Values

In all, six CRMs were analyzed repeatedly over the course of the 15-hour sequence (Table 6). These included NIST 1643e (water), and High-Purity Standards CRM-ES (estuarine sediment), CRM-RS-A, CRM-RS-B (river sediments), CRM-Soil-A and CRM-Soil-B (soils). All CRMs were analyzed without further preparation, either undiluted (NIST 1643e), diluted ten times in 1% HNO_3/0.5% HCl (NIST 1643e, and all High Purity Standards CRMs), or diluted 50x (all High Purity Standards CRMs). The results are shown in Table 7.

Table 6. Composition of Six Certified Reference Materials Analyzed (µg/L in Original Aqueous Solutions as Provided). The Last Two Columns Show the Highest Concentration by Element Across the Six CRMs to Illustrate the Dynamic Range Encountered in this Sequence.

	NIST 1643e (µg/L)	CRM-ES (µg/L)	CRM-RS-A (µg/L)	CRM-RS-B (µg/L)	CRM-Soil-A (µg/L)	CRM-Soil-B (µg/L)	Maximum (µg/L)	Diluted 1/10 (µg/L)
Be	13.98	20	0	0	0	0	20	2
Na	20740	200000	0	50000	70000	100000	200000	20000
Mg	8037	100000	70000	120000	70000	80000	120000	12000
Al	141.8	700000	250000	600000	500000	700000	700000	70000
K	2034	150000	150000	200000	200000	210000	210000	21000
Ca	32300	80000	300000	300000	350000	125000	350000	35000
V	37.86	1000	250	1000	100	800	1000	100
Cr	20.4	800	300000	15000	0	400	300000	30000
Mn	38.97	4000	8000	6000	100	100000	100000	10000
Fe	98.1	350000	1200000	400000	200000	350000	1200000	120000
Co	27.06	100	100	150	0	100	150	15
Ni	62.41	300	500	500	300	200	500	50
Cu	22.76	200	1000	1000	300	3000	3000	300
Zn	78.5	1500	15000	5000	1000	70000	70000	7000
As	60.45	100	600	200	200	6000	6000	600
Se	11.97	50	20	10	10	0	50	5
Mo	121.4	0	0	0	0	0	121.4	12.14
Ag	1.062	0	0	0	0	0	1.062	0.1062
Cd	6.568	0	100	30	0	200	200	20
Sb	58.3	0	500	40	30	400	500	50
Ba	544.2	0	500	4000	5000	7000	7000	700
Tl	7.445	0	10	10	0	0	10	1
Pb	19.63	300	7000	2000	400	60000	60000	6000
Th	0	100	20	100	100	100	100	10
U	0	0	10	30	10	250	250	25

Table 7 *Recovery of Certified Values for 6 Certified Reference Materials. Note Excellent Agreement Between Both 10x Diluted and 50x Diluted Samples Indicating Excellent Sensitivity, Matrix Tolerance, Precision and Linear Range.*

	NIST 1643o	NIST 1643e (10×)	Estuarine Sediment (10×)	Estuarine Sediment (50×)	River Sediment "A" (10×)	River Sediment "A" (50×)	River Sediment "B" (10×)	River Sediment "B" (50×)	Soil "A" (10×)	Soil "A" (50×)	Soil "B" (10×)	Soil "B" (50×)
9 Be	107.6%	106.6%	95.8%	102.1%								
23 Na	94.9%	92.9%	96.7%	96.8%			102.8%	117.1%	95.0%	97.8%	91.9%	93.4%
24 Mg	101.5%	91.7%	101.0%	101.9%	97.8%	94.8%	102.2%	104.9%	99.5%	93.2%	96.4%	90.6%
27 Al	103.9%	105.9%	99.6%	100.9%	100.8%	99.1%	101.8%	104.1%	98.0%	100.1%	96.1%	97.0%
39 K	99.7%	88.5%	100.5%	99.5%	99.3%	103.9%	102.8%	104.0%	97.8%	98.7%	95.5%	95.6%
44 Ca	101.9%	100.1%	97.3%	99.4%	100.1%	101.7%	97.7%	99.7%	97.2%	100.0%	96.7%	99.0%
51 V	102.3%	100.0%	97.8%	97.2%	99.8%	102.0%	97.3%	98.2%	99.3%	99.3%	96.8%	96.5%
52 Cr	103.5%	102.1%	96.5%	97.5%	102.7%	106.1%	101.8%	104.8%			94.3%	96.1%
55 Mn	101.4%	98.5%	104.2%	95.8%	105.9%	100.1%	104.5%	97.7%	99.1%	100.9%	98.5%	99.6%
56 Fe	104.0%	108.8%	99.2%	100.8%	101.1%	104.4%	98.8%	101.5%	97.8%	99.9%	96.1%	97.8%
59 Co	99.0%	96.7%	99.4%	100.9%	112.4%	116.9%	98.1%	101.4%			99.4%	101.3%
60 Ni	101.8%	100.7%	96.8%	100.0%	101.2%	105.7%	96.0%	100.3%	96.0%	99.4%	96.8%	100.4%
63 Cu	100.5%	98.8%	94.6%	98.6%	98.1%	102.5%	94.6%	99.1%	94.6%	98.0%	100.4%	97.1%
66 Zn	98.7%	101.8%	94.5%	99.2%	105.1%	102.5%	94.4%	100.1%	96.2%	100.5%	100.0%	106.2%
75 As	101.0%	102.1%	99.9%	101.8%	101.7%	105.6%	100.0%	102.1%	100.2%	102.2%	99.3%	100.7%
78 Se	94.9%	101.0%	98.2%	101.4%			93.6%	95.0%	93.8%	94.3%		
95 Mo	107.3%	96.5%										
107 Ag	93.1%	91.3%										
111 Cd	99.2%	100.9%			99.6%	101.3%	97.8%	100.3%			96.8%	98.4%
121 Sb	102.2%	99.7%			100.6%	100.5%	100.0%	99.2%	101.2%	99.5%	101.8%	101.5%
137 Ba	107.9%	99.8%			100.0%	101.2%	107.9%	101.4%	107.1%	99.9%	105.5%	98.0%
205 Tl	95.5%	94.1%			88.0%	95.7%	84.0%	95.1%				
206 Pb	101.3%	104.6%	94.2%	98.6%	107.4%	110.6%	104.3%	101.6%	102.1%	99.8%	104.8%	108.8%
232 Th			94.6%	97.8%	98.4%	98.9%	93.9%	94.8%	96.5%	97.9%	97.3%	98.8%
238 U					97.1%	98.1%	91.3%	93.6%	94.1%	96.6%	107.7%	97.4%

no certified value

Matrix Spike (MS) and Matrix Spike Duplicates (MSD) in 1/10 Seawaters

Seawater is a challenging matrix for several reasons. Neat seawater contains approximately 3% total dissolved solids, mainly NaCl, which can accumulate on the nebulizer tip, torch injector, and interface cones, causing signal instability and gradual loss of sensitivity. Additionally, Na is an easily ionized element (first ionization potential (IP) = 5.14 eV) that can significantly reduce the response of higher IP elements such as Zn, As, Se, Cd and Hg in non-robust plasmas. Synthetic seawater (3% high purity NaCl) was diluted 1/10 and spiked in duplicate (MS and MSD) with the calibration standard mix at 10 ppb (1 ppm for mineral elements). Each MS and MSD was measured four times over the course of the sequence. The mean results of the four measurements are presented in Table 8. Most recoveries were well within ±10%, and %RSDs over the 15-hour sequence were typically a few percent. In all cases, the RPD values were within the EPA limit of ±20%.

Table 8. 1/10 Seawater Matrix Spike (MS) and Matrix Spike Duplicate (MSD) Results for 10 ppb Spike (1 ppm Ca, Fe) Showing Mean Value of Replicate Measurements (n=4), %RSD and % Recovery of Both MS and MSD Samples. RPD = Relative Percent Difference Between the Mean MS and Mean MSD values.

	Matrix Spike			Matrix Spike Duplicate			
	Mean	%RSD	%Recovery	Mean	%RSD	%Recovery	RPD
9 Be	10.513	4.0	105.1	10.572	4.4	105.7	-0.6
24 Mg	928.493	5.4	92.8	921.914	5.4	92.2	0.7
44 Ca	892.134	5.8	89.2	905.386	10.0	90.5	-1.5
51 V	10.246	3.8	102.5	8.848	1.7	88.5	13.6
52 Cr	9.82	6.6	98.2	8.71	1.8	87.1	11.3
55 Mn	9.557	4.9	95.6	9.433	1.9	94.3	1.3
56 Fe	886.110	2.0	88.6	905.780	1.8	90.6	-2.2
59 Co	9.205	3.0	92.1	9.098	2.8	91.0	1.2
60 Ni	9.144	3.1	91.4	9.216	3.6	92.2	-0.8
63 Cu	8.895	4.6	89.0	8.835	4.3	88.3	0.7
66 Zn	9.470	5.1	94.7	8.833	5.0	88.3	6.7
75 As	10.220	1.1	102.2	8.099	0.4	81.0	20.8
78 Se	9.241	6.4	92.4	8.799	2.5	88.0	4.8
95 Mo	9.859	2.6	98.6	8.349	1.5	83.5	15.3
107 Ag	8.826	1.2	88.3	8.774	0.8	87.7	0.6
111 Cd	9.268	1.0	92.7	9.146	2.7	91.5	1.3
121 Sb	9.741	2.5	97.4	9.687	3.1	96.9	0.6
137 Ba	9.990	1.8	99.9	9.998	0.7	100.0	-0.1
205 Tl	8.708	5.4	87.1	8.707	6.0	87.1	0.0
208 Pb	8.879	7.3	88.8	8.698	6.8	87.0	2.0
232 Th	9.397	6.6	94.0	9.316	7.6	93.2	0.9
238 U	9.447	7.6	94.5	9.229	8.2	92.3	2.3

Precision and Long Term Stability

Long term precision was measured by calculating percent relative standard deviation (%RSD) for all replicates of the repeated samples over the course of the 15-hour sequence. The CCV and NIST 1643e were analyzed most frequently (n=8 and n=6 respectively). %RSD values in the range of a few percent indicate excellent precision over a long sequence, without the need for recalibration (Table 9).

Table 9. Long Term Precision (%RSD) Over the Course of the 15-hour Sequence, for Both the Continuing Calibration Verification (CCV) Standard (Mid-Point of the Calibration Range), and for NIST 1643e Water (Undiluted).

	% Relative Standard Deviation	
Element	CCV (n=8)	NIST 1643e (n=6)
9 Be	3.7	7.0
23 Na	5.5	5.9
24 Mg	4.1	5.0
27 Al	2.1	4.6
39 K	4.1	9.4
44 Ca	3.5	5.4
51 V	1.3	1.1
52 Cr	4.1	3.9
55 Mn	3.4	4.0
56 Fe	3.3	3.1
59 Co	3.0	2.5
60 Ni	4.0	3.0
63 Cu	4.2	3.1
66 Zn	3.0	2.2
75 As	0.9	0.5
78 Se	0.8	2.0
95 Mo	3.0	2.2
107 Ag	3.2	2.1
111 Cd	1.5	1.3
121 Sb	0.8	3.7
137 Ba	1.9	1.0
205 Tl	3.7	3.6
208 Pb	3.1	4.3
232 Th	4.6	N/A
238 U	5.3	N/A

Calibration accuracy and precision were measured by repeated analysis of the continuing calibration verification (CCV) sample, which is at the midpoint concentration of the calibration curve. Figure 2 shows the percent recoveries for all elements for each of the eight CCV samples. No CCV failed the EPA limit of ± 10% for any analyte. Absolute long term stability (absence of drift) is measured by comparing raw internal standard responses from the beginning of the sequence to the end. Internal standard responses also indicate the degree of suppression from high matrix samples. EPA Method 6020A requires that the internal standard responses be greater than 70% compared to the calibration blank for all samples (lower dashed line – Figure 3). If the internal standard response in

any sample falls below 70%, that sample must be diluted and reanalyzed until the internal standards exceed the 70% limit. Figure 3 shows the percent recovery of the raw internal standard responses for the entire 15-hour sequence normalized to the calibration blanks. A single blank recalibration at run # 118 (CCB) compensated for the slight change in internal standard responses due to gradual conditioning of the cones and interface. All samples passed the >70% test, and no samples required additional dilution as a result of an internal standard failure. In addition, the generally flat slope of the internal standard recovery curve shows that there was no gradual loss of sensitivity over time, even when running these high matrix samples.

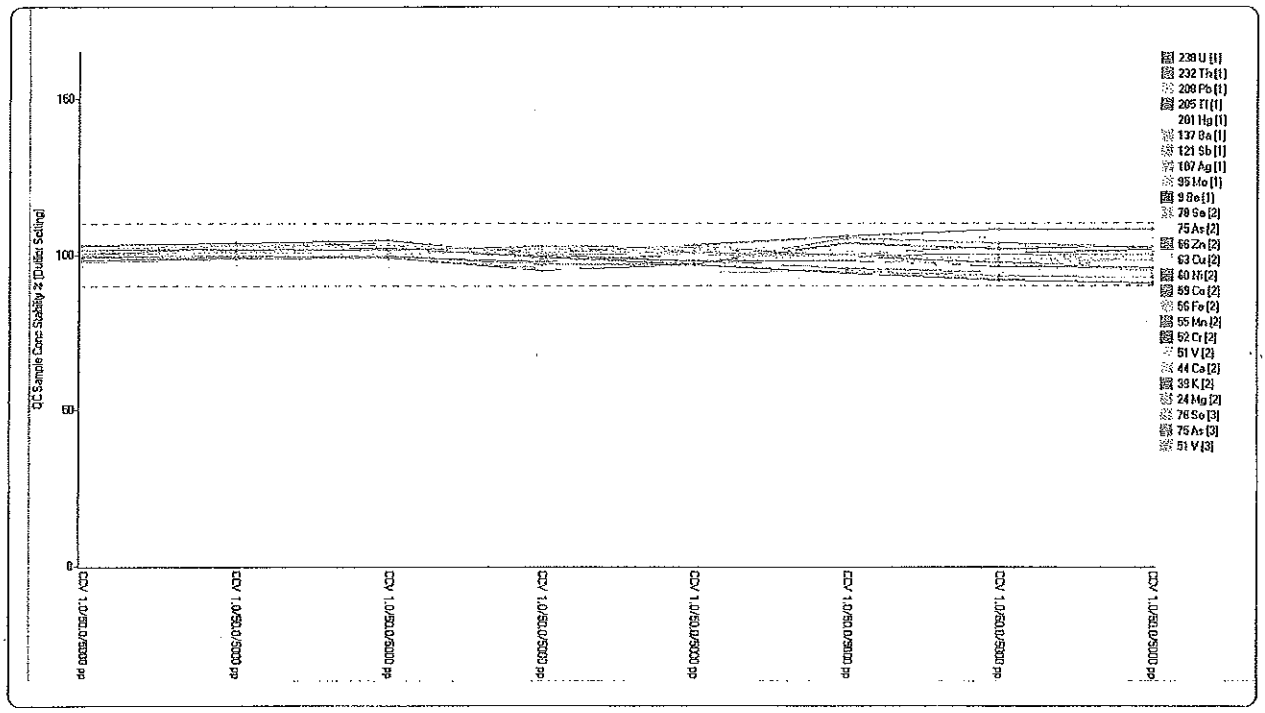


Figure 2. CCV recoveries – all analytes (1 ppb Hg, 50 ppb trace elements, 5 ppm minerals). Control limits at +/- 10% are indicated in by the dashed line.

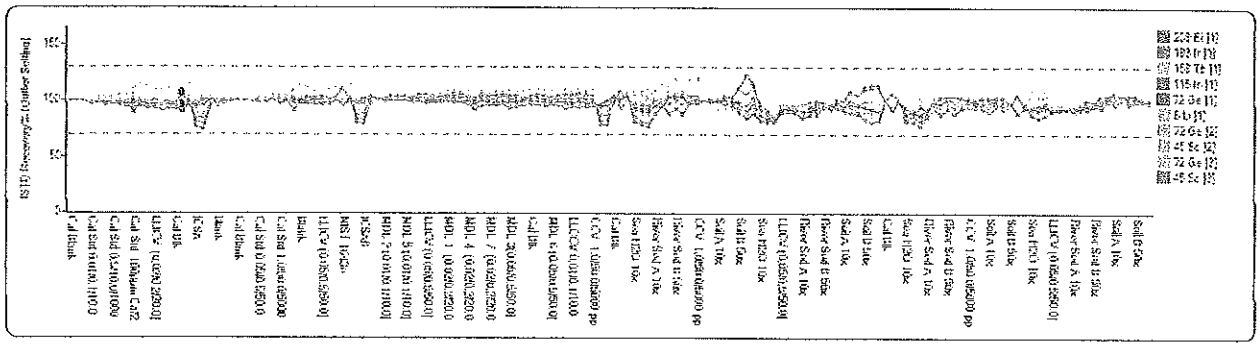


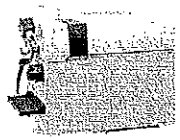
Figure 3. ISTD stability over 156 runs, 14.8 hours. EPA 6020A lower control limit is 70% (lower dashed line). While there is no upper limit specified in EPA 6020A, 130% is displayed as the upper limit. Due to space limitations, not all sample names are shown.

Conclusions

EPA Method 6020A is applicable for a wide range of elements in samples ranging from clean waters to highly contaminated soils or sludges. Because of this, contract laboratories running Method 6020A may not have detailed information on the composition and concentration of samples analyzed together in a single sequence. The Agilent 7700x/7800 ICP-MS is uniquely qualified to perform this difficult application for a number of reasons. All samples, regardless of composition or concentration can be analyzed using a single cell gas mode (helium mode), and no prior knowledge of the sample is necessary. The built-in High Matrix Introduction system (HMI) allows most samples to be analyzed without the need for further dilution after initial sample preparation. Additionally, the HMI significantly improves plasma robustness, which minimizes internal standard failures and extends the number of samples that can be run between calibrations. All of these benefits translate into simpler, faster, more reliable analysis of com-plex environmental samples.

Reference

1. Steven Wilbur and Emmett Soffey, "Meeting Worldwide Regulatory Requirements for the Analysis of Trace Metals in Drinking Water Using the Agilent 7500c ICP-MS", Agilent Application Note 5988-8902EN



Verified for Agilent
7800 ICP-MS

Results presented in this document were obtained using the 7700x, but performance is also verified for the 7800 ICP-MS.

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Printed in the USA, June 1, 2015
5990-5514EN

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Using Qualifier Ions to Improve ICP-MS Data Quality for Waste Water Analysis

Application Note

Environmental

Authors

Wim Proper
Eurofins Analytico
Gildeweg 44
3771 NB Barneveld
Netherlands

Naoki Sugiyama
Agilent Technologies
Tokyo Analytical Division
9-1 Takakura-cho
Hachioji, Tokyo 192-0033
Japan

Steve Wilbur
Agilent Technologies, Inc.
1615 75th Street SW, Suite 210
Everett, WA 98203
USA

Abstract

Researchers at a commercial environmental laboratory have developed an effective method for validating high throughput multi-element data from high matrix waste water samples. The method used an Agilent 7700x ICP-MS with High Matrix Introduction (HMI)[1] capability and third generation Collision Reaction Cell (CRC) operating in helium (He) mode to simultaneously remove the polyatomic interferences from all isotopes of each analyte. This gives access to secondary isotopes for many analytes, and simply checking the agreement between the results from the primary and secondary isotope provides a quick and easy means to confirm the accuracy of the analytical data. The new method was validated by analyzing approximately 6000 samples over a 21-week study period.

[1]The High Matrix Introduction System is patented by Agilent Technologies, US Patent number 7,671,328 B2

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Introduction

Commercial analytical service laboratories must meet strict client and ISO 17025 demands for data quality, while maintaining acceptable turnaround and profitability. Typical performance testing and quality control protocols are based largely on the analysis of periodic calibration checks, and reference samples or synthetic mixes that simulate the expected sample matrices to be analyzed. However, this approach does not confirm the actual analyte results measured in each of the unknown samples, and so may result in errors when sample matrices are variable. A technique that can validate the quality of the analytical results for each unknown sample, without adding significant cost or time provides a competitive advantage to the laboratory.

Eurofins Analytico, a branch of Eurofins Scientific, which is an international group of testing laboratories, uses a simple yet powerful method to confirm the routine multi-element results reported on their ICP-MS instruments. They have developed a method for secondary isotopes (or "qualifier" ions) as a fast quality check in their wastewater method using the Agilent 7700x ICP-MS. While the use of qualifier ions for quantitative confirmation is well established in organic mass spectrometry, the approach hasn't been widely applied in conventional ICP-MS due to the presence of polyatomic interferences on secondary (and many primary) isotopes.

The Agilent 7700x/7800 ICP-MS use an Octopole Reaction System (ORS) cell operating in helium (He) mode to effectively remove the polyatomic interferences on both primary and secondary isotopes under the same cell conditions. This allows secondary isotopes to serve as qualifier ions for many elements, providing a fast and simple way to validate the analytical result. This method does not require any additional sample analysis or sample preparation for calibration or quality control.

Effective Interference Removal

Agilent's ORS collision cell is unique in operating effectively with He cell gas and Kinetic Energy Discrimination (KED) to remove spectral interferences caused by polyatomic ions. He mode on the ORS separates analyte ions from interfering polyatomic ions using the difference in ionic radius (polyatomic ions are always larger than monatomic analyte ions of the same mass), so the method is universal. As a result, HE mode works with all polyatomic ions, regardless of the sample matrix. This eliminates the need for interference correction equations, and the complicated matrix-, analyte- or isotope-specific optimization and method development characteristic of cells that use reactive gases. This makes He mode the most suitable CRC technique for the elimination of unpredictable interferences that arise in the analysis of complex and variable environmental samples such as wastewater. Figure 1 shows the results of preliminary interference tests investigating the applicability of the qualifier ion technique. A clean seawater matrix was diluted ten times to give a major element composition of approximately: Cl 2000 ppm, Na 1100 ppm, Mg 130 ppm, S 90 ppm, Ca 40 ppm, K 40 ppm, Br 7 ppm, and C 3 ppm. This solution was analyzed, and the apparent quantitative results measured at both the primary and secondary isotopes were examined. Figure 1 demonstrates that He mode removed the matrix-based interferences effectively, reducing the quantitative error and enabling the use of all primary and secondary isotopes. By contrast, the results for no gas mode showed that significant interferences were present on most primary and secondary isotopes of the analytes studied.

Experimental

An Agilent 7700x ICP-MS, which includes the High Matrix Introduction (HMI) system, was used for this study. The fully integrated HMI provides unparalleled plasma robustness through automated aerosol dilution and preset plasma conditions. For these high-matrix wastewater samples, maximum plasma robustness (Ultra Robust setting) was selected, along with midlevel aerosol dilution. The analytical conditions used for Analytico's waste water method are shown in Table 1. Method validation for high throughput wastewater analysis consisted of:

- Analyte recoveries in a NaCl matrix
- Determination of method detection limits (MDL)
- Recovery and precision of low and high concentration spikes
- Accuracy and precision of measurement of certified reference materials (CRM)
- Accuracy and precision of continuing calibration blanks and calibration checks (CCB, CCV)
- Determination of linear dynamic range

For brevity, not all results from the method validation are presented in this application note.

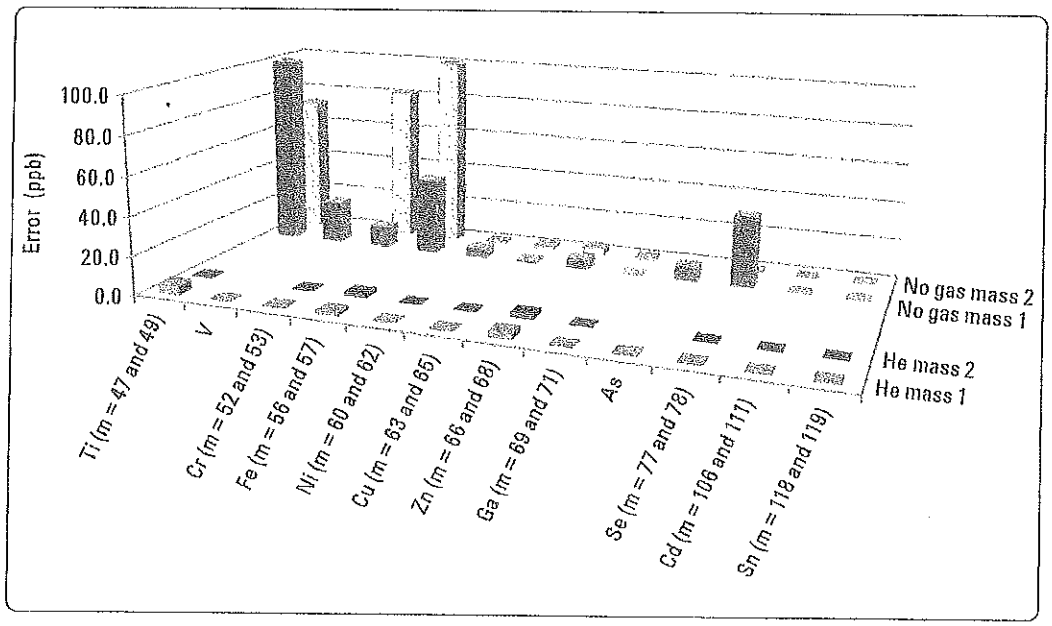


Figure 1. Quantification error in tenfold diluted seawater matrix. Apparent concentrations due to interferences are shown for two isotopes in both cell modes (no gas and He). V (51) and As (75) don't have secondary isotopes available.

Samples were prepared as follows: CRM samples were prepared by digesting 0.5 g sample plus 25 mL water with 2 mL HNO_3 and 6 mL HCl. After digestion, samples were diluted to 50 mL with ultrapure water. Since the final acid concentration of the samples was quite high (4% HNO_3 and 12% HCl), an optional Ni plated sampling cone was fitted. The method used two cell gas modes: He and hydrogen (H_2) mode. H_2 was needed for low level analysis of sulfur in the method. Sulfur is a difficult element for ICP-MS because of its high ionization potential and intense interference from polyatomic ions such as O_2^+. Though xenon cell gas has been widely used for sulfur analysis, H_2 also gives good performance by allowing sulfur to be detected as the reaction product, SH^+. He mode was operated in both conventional KED mode and high energy mode which offers enhanced sensitivity for selenium. H_2 mode was also operated in two modes, because the measurement of sulfur at SH requires that energy discrimination be turned off to allow transmission of the SH polyatomic for measurement. In Table 2, all measured isotopes are shown. As illustrated, most of the elements measured have at least two isotopes available; the primary isotope used for quantification and a second isotope for use as a qualifier. All isotopes except those underlined were analyzed using He mode. Underlined isotopes were analyzed using H_2 mode.

Table 1. The Agilent 7700x ICP-MS Configuration and Operating Conditions for Wastewater Analysis

Equipment				
Nebulizer	Mira Mist nebulizer - PTFE (Agilent G3161-80000)			
Sampler/skimmer	Ni plated sampler (Agilent G3280-67061)/Ni skimmer			
ISTD	^{6}Li, ^{45}Sc, ^{103}Rh and ^{193}Ir added 1:1 to sample via online ISTD kit			
Plasma setting	Ultra Robust/Mid-level Aerosol Dilution			
Forward power	1600 W			
Carrier gas	0.6 L/min			
Dilution gas	0.4 L/min			
Extract 1	0 V			
Parameter	**He Mode**	**He Mode (high energy)**	**H_2 Mode**	**H_2 Mode (sulfur)**
Cell gas flow (mL/min)	4.3	10	6	8
KED (V)	3	4	3	0

Results

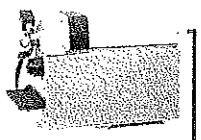
Table 2 summarizes the MDL and reference sample (BCR-145R - sewage sludge, FeNeLab - Dutch soil) results obtained during the method validation. The MDLs were calculated using a synthetic digested wastewater (a digested clean water sample was used to calculate the MDLs for the matrix elements), spiked at a low level (a few times the required MDL concentration), measured on 10 different days, over a period of 30 days. MDLs (3 sigma of the 10 replicates) for all elements met the required reporting limits despite the high matrix. Quantification results of two CRMs are shown for both the primary ion (isotope 1) and qualifier ion (isotope 2). Relative Percentage Difference (RPD) values in the table show the difference between the quantitative results reported from the primary and qualifier ions. If the RPD exceeds ±20%, the analyst is automatically alerted. In this way, both human and analytical errors are detected and can be corrected. For example, while the quantified concentration using the primary ion shows good recovery for almost all certified elements, the RPD exceeded the ±20% criteria for Ce in both CRMs and Ti in BCR-145R. These differences were not, however, due to residual polyatomic interferences, but the fact that the secondary isotopes of both elements (^{142}Ce and ^{48}Ti) suffer from direct isobaric interferences from another element (^{142}Nd and ^{48}Ca, respectively). This illustrates the importance of isotope selection when considering choices for secondary or qualifier ions in ICP-MS. While He mode has been demonstrated to remove polyatomic interferences effectively, it cannot remove isobaric (same-mass) overlaps from an isotope of another element. In this case, ^{49}Ti might be another option as a secondary isotope for Ti analysis.

While the CCV/CCB test showed good stability during the method validation, long term stability throughout routine analysis of real samples is also essential. Figures 2 and 3 show the internal standard (ISTD) stability in real sample sequences. Figure 2 shows the normalized internal standard recoveries compared to the calibration blank for a single sequence consisting of 160 high-matrix wastewater samples. Figure 3 shows the raw internal standard response at the end of each day's sequence over the course of the 21-week study period. During this period, nearly 6000 samples were analyzed. These plots demonstrate the excellent robustness provided by the HMI and the exceptional stability of the Agilent 7700x ICP-MS, despite the high matrix and high acid concentrations. This exceptional matrix tolerance and stability contributes significantly to the laboratory's productivity by minimizing both recalibration overhead and maintenance downtime.

Table 2. MDL and CRM Test Results

	Measured Isotope (*m/z*)				FeNeLab "Dutch Soil"					BCR-145R "Sewage Sludge"				
	#1	#2	MDL µg/L	Reporting Limit µg/L	Certified mg/kg	Measured #1 mg/kg	Measured #2 mg/kg	Recovery %	RPD %	Certified mg/kg	Measured #1 mg/kg	Measured #2 mg/kg	Recovery %	RPD %
Be	9		0.8	1	1.52	1.68		110			0.41			
B	11	10	25.6	60	35.10						18.72			
Na	23		120	200	316	325		103			652			
Mg	24	26	30	100	9400	9147	9427	97	3.1		5316	5473		3.0
Al	27		50	100	25600	28424		111			21484			
P	31		30	50	2520	2451		97			11804			
S	34	33	570	1000	1230	911	1004	82	−9.2		12329	11977		2.9
K	39		180	200	5250	6417		122			1363			
Ca	40	44	170	200	36500	34516	34385	95	−0.4		43499	43319		−0.4
Ti	47	48	10.0	20	504.79	556.35		10.2			204.64	268.13		31.0
V	51		2.8	10	55.8	64.03		115			28.82			
Cr	52	53	1.9	5	180	193.66	191.91	108	−0.9	300	289.57	289.94	97	0.1
Fe	56	54	40.0	50	35.54	35.25	35.80	99	1.6		12.85	13.36		−3.9
Mn	55		0.004	20	1.05	1.03		99		0.145	0.14		96	
Ni	60	61	2.0	5	54.6	56.81	57.00	105	0.3	251	224.33	220.81	89	−1.6
Co	59		2.0	10	18.4	19.03		103		5.3	4.83		91	
Cu	63	65	1.0	5	153	151.27	151.56	99	0.2	707	652.40	646.36	92	−0.9
Zn	66	68	6.0	10	1020	1019.1	1028.8	100	1.0	2140	1963.8	2002.1	92	1.9
As	75		1.7	2	41.6	44.62		107			8.01			
Se	78	77	1.8	2	1.71	1.80	1.74	105	−3.3		6.08	6.36		4.6
Sr	88	86	3.6	10	129	139.35	139.88	108	0.4		295.02	294.20		−0.3
Mo	95	98	0.002	10	0.0014	0.0014	0.0014	100	0.0		0.01	0.01		0.3
Ag	107	109	0.4	2	2.75	3.06	3.04	111	−0.6		13.39	13.48		0.6
Cd	114	111	0.3	0.4	8.24	8.30	8.33	101	−0.3	3.43	3.10	3.18	93	−2.4
Sn	118	120	1.8	10	22.2	24.32	24.35	110	0.1		58.22	59.18		−0.1
Sb	121	123	1.4	2	3.28	2.56	2.63	78	2.8		12.00	12.03		0.3
Te	125	126	0.9	1		0.29					0.06			
Ba	135	137	4.5	10	797	857.95	858.54	108	0.1		2446.6	2450.4		0.2
Ce	140	142	3.6	10		46.96	89.62		90.9		9.94	18.90		90.1
Hg	201	200	0.1	0.1	3.81	3.67	3.68	96	0.4	1.99	1.83	1.85	92	1.2
Tl	205	203	3.1	10	1.19	1.25	1.21	114	−3.2		0.16	0.15		−2.1
Pb	208	206	2.7	5	282	295.52	291.08	105	−1.5	282	262.46	256.17	93	−2.4

MDLs shown were calculated from 3-sigma of a low level spiked sample based on the primary isotope (mass 1) of each element. # 1 - *m/z* of primary isotope, # 2 - *m/z* of qualifier isotope. Underlined isotopes analyzed in H_2 mode, all other isotopes analyzed using He mode.



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Printed in the USA, June 1, 2015
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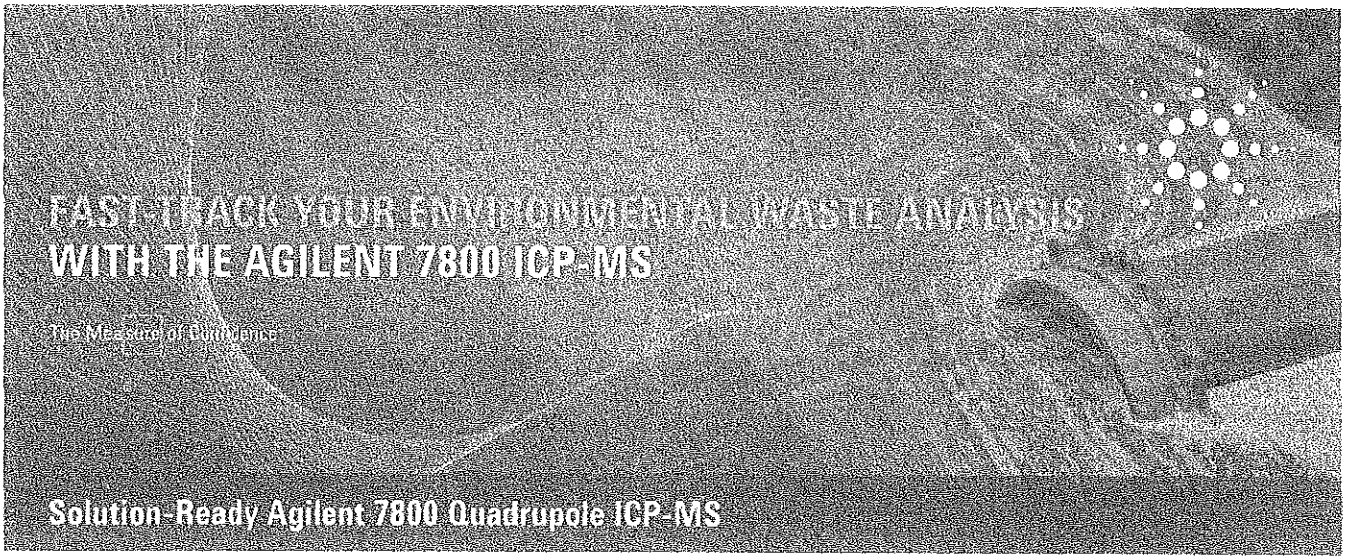
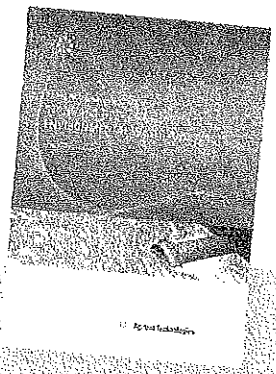


When Pre-set Methods and productivity tools combine with high-performance ICP-MS, the results are extraordinary

Waste analysis, from treated wastewater to contaminated soil, presents many challenges for routine analysis by ICP-MS. Sample matrices are often high, with many major elements at 100s or 1000s of mg/L, with percent levels of other matrix components such as chloride, sulphate, and carbon. This leads to signal suppression and the formation of many polyatomic interferences in the ICP-MS spectrum, a problem compounded by matrix levels that vary from sample to sample, and so the interferences are unpredictable.

Contract labs must analyze many regulated and non-regulated samples with fast turnaround times. Consequently, routine waste analysis requires a robust method that produces reliably accurate results for many elements, in variable matrices, without requiring extensive method development for each sample type.

The new Agilent 7800 ICP-MS comes with Pre-set Methods for waste analysis, auto-optimization tools, and a standard operating procedure (SOP). ICP-MS has never been easier to use. The robust plasma, unique high matrix introduction (HMI) technology, wide dynamic range, and helium cell mode, let you quickly produce reliable results, even in highly variable waste samples.



Waste analysis with the Agilent 7800 ICP-MS

SOP includes:

- Waste method summary and analytes
- Controlling interferences
- Sample preparation details
- Pre-set Method parameters
- Calibration and Quality Control
- Method validation
- Troubleshooting guide

For more, go to
www.agilent.com/chem/7800icpms

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Accurate, reliable, quantitative results for all regulated elements in wastes

Two key issues must be solved to simplify routine waste analysis and ensure accurate results with variable, high-matrix samples:

- Suppression (signal loss) caused by high and variable sample matrices must be avoided or corrected
- Spectral interferences, caused by polyatomic ions formed from the matrix elements, must be reduced

High matrix introduction (HMI) technology on the 7800 ICP-MS reduces the sample matrix load on the plasma, and so much higher matrix levels are analyzed routinely (up to 3% total dissolved solids (TDS)). This means that additional sample dilution is avoided, and unknown samples are measured with confidence, simplifying laboratory workflow.

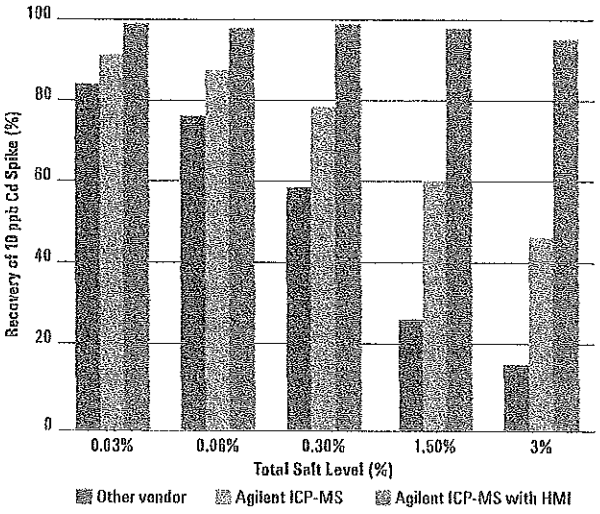
On the 7800 ICP-MS, the octopole-based collision/reaction cell works so effectively in helium (He) mode that a wide range of matrix based polyatomic interferences are eliminated with one set of cell conditions. This provides method simplicity, and delivers reliable and accurate quantitation of all elements at the regulated levels, without the added complexity involved in methods that use a reactive cell gas.

Simplify waste analysis workflow

- Standard operating procedure
- Auto-optimization tools
- Pre-set Method for waste analysis
- QC, tune, and sample analysis reports
- Optional ISIS 3 for fast discrete sampling

High matrix introduction (HMI)

The 7800 ICP-MS uses unique HMI technology to reduce matrix suppression, and so variable samples can be measured reliably against simple aqueous standards.



Cd recovery in samples up to 3% TDS. HMI ensures recovery is consistent in variable matrices, so matrix-matching of calibration standards is not required

High throughput discrete sampling

The Agilent Integrated Sample Introduction System (ISIS 3) provides high throughput discrete sampling (DS) for the 7800 ICP-MS, reducing sample run times to <90 s, while still maintaining effective interference removal in He mode for complex samples.

For more information, go to:
www.agilent.com/chem/7800icpms

This information is subject to change without notice.

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Printed in the USA June 1, 2015
5991-5877EN

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