Faster, Simpler, More Accurate Semiquantitative Analysis Using the Agilent 7500cx ICP-MS

Application

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Abstract

The new Agilent 7500cx allows the user to achieve the full potential of ICP-MS for semiquantitative elemental screening of a wide range of sample types. Complex, unknown samples can be analyzed with better speed, accuracy, and data integrity than ever before, since all matrix interferences are removed in the Octopole Reaction System (ORS) using helium collision mode. Results are presented for three different certified reference materials.

Introduction

Semiquantitative elemental analysis (semiquant) by ICP-MS is a powerful tool for quick screening of unknown samples for a wide range of trace elements. The ability to perform accurate semiquant is a strength of ICP-MS that is not shared by other elemental analysis techniques. It is based on the fact that the relative response of any element can be estimated from the response of any other element under a given set of conditions. These relative responses are determined by the unique properties of each element as well as the instrument and operating conditions, and can be stored in a semiquant response factor database. The use of internal standards or other calibration elements allows the database to be updated as needed to reflect the specific acquisition and matrix conditions. In practice, however, spectral interferences have limited the usefulness of semiquant for a number of elements in many common matrices.

Collision/Reaction Cell ICP-MS and Semiquant

In most collision/reaction cell (CRC) instruments, specific information about the matrix and target analytes is required in order to set up the correct collision/reaction chemistry to eliminate the interferences. Additionally, the conditions required to eliminate one interference in one matrix are generally not effective for all analytes in all matrices. For this reason, multiple sets of collision/reaction conditions are typically used. However, accurate semiquant response factors cannot be determined for elements acquired under different CRC conditions. As a result, it has not previously been possible to use CRC technology to reduce interferences in semiquant in the same way as in full quantification. However, the unique ability of Agilent's Octopole Reaction System (ORS) to eliminate polyatomic interferences using carefully controlled kinetic energy discrimination (KED) in helium collision mode permits all elements to be acquired under a single, universal set of CRC conditions.

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KED eliminates the transmission of the larger polyatomic ions from the collision cell to the quadrupole by placing an energy barrier between the collision cell and quadrupole. Since polyatomic ions are always larger than atomic (analyte) ions of the same mass (Figure 1), they undergo more energy-reducing collisions with the helium cell gas than do the smaller atomic ions. As a result, the polyatomic ions have insufficient residual energy to cross the energy barrier at the cell exit, and so are excluded from the ion beam. Figure 2 depicts the effects of KED on ion energy. Only the high-energy atomic ions exceed the stopping potential

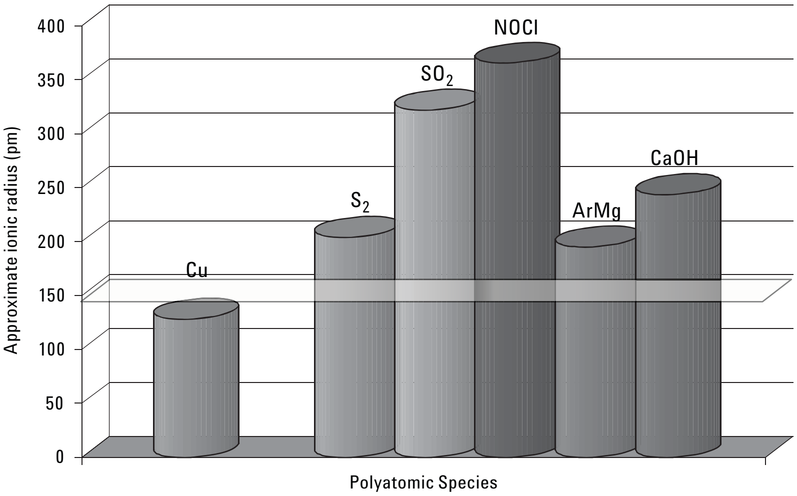

Figure 1. **Graphic representation of the relative diameter of an atomic ion (Cu) compared with the polyatomic ions that can interfere. Most elemental ions are smaller than 150-picometer radius, while most polyatomic ions are larger.**

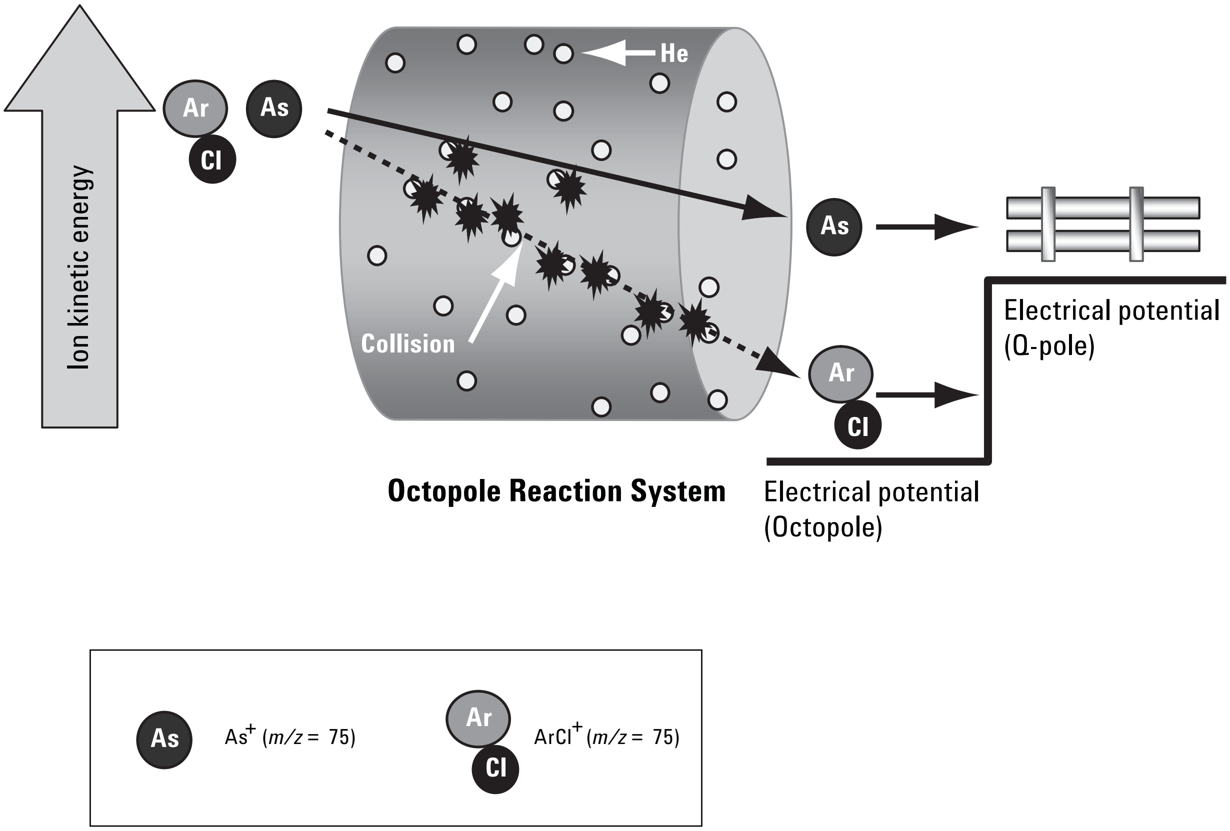

Figure 2. **Diagrammatic representation of Kinetic Energy Discrimination after energy-reducing collisions within the Octopole Reaction System cell.**

and are transmitted. Since helium is a nonreactive gas, no new interferences are formed in the cell and no analyte signal is lost by reaction, as occurs with any reactive cell gas.

The use of helium collision mode with semiquant conveys all the advantages normally associated with the use of CRC technology in full quant. It also solves the previously critical limitations of semiquant due to unresolved interferences. The advantages include:

- Semiquant is simple, fast, accurate, and interference-free for all analytes in any matrix.
- Helium collision mode allows the use of HCl, H_2SO_4, or other acids in digestion without danger of chlorine- or sulfur-based interferences on elements such as As, Cr, Se, V, Zn, etc.
- Improved stability for elements like Ag, Hg, Sb, Sn, and the Pt group due to the ability to add HCl to samples and standards.
- Ability to select the most abundant isotope for the best sensitivity, or multiple isotopes for absolute data confidence.
- Freedom to use any internal standards.

Table 1. Tune Conditions Used for NIST 1640 Semiquant Analysis in Helium Collision Mode

RF power	1550 W
Sample depth	8.0 mm
Carrier gas flow rate	0.90 L/min
Makeup gas flow rate	0.23 L/min
Sample flow rate	0.4 mL/min
Spray chamber temperature	2 °C
Helium flow rate	5 mL/min
KED	2V

Table 2. Semiquant Acquisition Parameters for NIST 1640

Total run time	**170 seconds**
Acquisition mode	Spectrum - peak hopping
Number of masses	250
Integration time[sec] masses 2 - 260	0.1 sec/point
Number of points per mass	1
Acquisition time	50.9 [sec]
Number of replicates	1
Uptake time	20 sec
Stabilization time	60 sec
Post acquisition rinse	30 sec
Preemptive rinse	On (time = 30 sec)

Experimental

The 7500cx ICP-MS was tuned for the same typical robust plasma conditions that are used in routine quantitative analysis (Table 1). No special tuning is required. Semiquant acquisition parameters are listed in Table 2.

A single calibration standard containing 200 ppb of Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Th, Tl, U, V, and Zn made up in 1% HNO_3/0.5% HCl was used to update the semiquant response factor database for a range of elements across the mass range. Non-calibrated elements are updated by interpolating between calibrated isotopes, which the ChemStation does automatically. Any number of calibration elements may be used, but increasing the number of calibration elements will improve semiquantitative accuracy. Internal standardization was applied using a typical suite of internal standard elements distributed across the mass range.

Results and Discussion

Tables 3 and 4 show the results of a semiquantitative screen of three standard reference materials, NIST 1640 water, LGC 6010 hard drinking water,

Table 3. Results of Helium Collision Mode Semiquant Anaysis NIST 1640 Standard Reference Water

Element	NIST 1640 certified value	SQ conc.	Unit	Recovery (%)
9 Be	34.94	33.42	µg/L	95.6
11 B	301.1	335.83	µg/L	111.5
23 Na	29.35	22.25	**mg/L**	75.8
24 Mg	5.819	4.24	**mg/L**	72.9
27 Al	52	48.92	µg/L	94.1
39 K	994	919.17	µg/L	92.5
42 Ca	7.045	5.81	µg/L	82.4
51 V	12.99	12.83	µg/L	98.8
52 Cr	38.6	36.58	µg/L	94.8
55 Mn	121.5	121.67	µg/L	100.1
56 Fe	34.3	30.92	µg/L	90.1
59 Co	20.28	19.75	µg/L	97.4
60 Ni	27.4	25.83	µg/L	94.3
63 Cu	85.2	81.17	µg/L	95.3
66 Zn	53.2	51.83	µg/L	97.4
75 As	26.67	27.75	µg/L	104.0
78 Se	21.96	24.08	µg/L	109.7
88 Sr	124.2	122.50	µg/L	98.6
95 Mo	46.75	46.17	µg/L	98.8
107 Ag	7.62	7.31	µg/L	95.9
111 Cd	22.79	21.50	µg/L	94.3
121 Sb	13.79	12.83	µg/L	93.1
137 Ba	148	139.17	µg/L	94.0
208 Pb	27.89	23.5	µg/L	84.3

Table 3 has been simplified to show only those elements with some reference values, although many other elements were determined in each reference material.

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Table 4. Results of Helium Collision Mode Semiquant Analysis of LGC 6010 Hard Drinking Water and LGC 6177 Landfill Leachate Standard Reference Materials

	LGC 6010 hard drinking water			LGC 6177 landfill leachate		
Element	LGC certified value (µg/L)	SQ conc. (µg/L)	Recovery (%)	LGC certified value (µg/L)	SQ conc. (µg/L)	Recovery (%)
10 B	N/A	83	N/A	9,800	6,700	68.4
23 Na	21,900	20,000	91.3	1,750,000	1,500,000	85.7
24 Mg	4,200	3,700	88.1	73,500	62,000	84.4
27 Al	208	160	76.9	N/A	110	N/A
31 P	N/A	670	N/A	11,500	12,000	104.3
39 K	5,100	5,100	100.0	780,000	810,000	103.8
44 Ca	83,200	73,000	87.7	74,800	77,000	102.9
52 Cr	48	51	106.3	180	160	88.9
55 Mn	48	45	93.8	140	130	92.9
56 Fe	236	240	101.7	3,800	3,300	86.8
60 Ni	48	42	87.5	210	170	81.0
66 Zn	542	540	99.6	260	250	96.2
75 As	55	49	89.1	N/A	86	N/A
78 Se	9.5	13	136.8	N/A	< 16.00	N/A
107 Ag	6.2	4.3	69.4	N/A	1.8	N/A
121 Sb	11.9	13	109.2	N/A	5	N/A
137 Ba	116	110	94.8	N/A	770	N/A
208 Pb	95	92	96.8	N/A	17	N/A

Table 4 has been simplified to show only those elements with some reference values, although many other elements were determined in each reference material.

and LGC 6177 landfill leachate. No attempt was made to matrix-match; tune conditions used were as shown in Table 1; and all elements were acquired in helium collision mode. In all cases, for every certified element, the semiquantitative result was within ± 40% of the certified concentration, from as low as 7 ppb for Ag in NIST 1640 to over 1700 ppm for Na in the LGC 6177 landfill leachate.

Conclusions

Semiquant has always been a powerful tool available to the ICP-MS analyst for quickly estimating the concentration of unknown, uncalibrated elements in a variety of simple matrices. However, in complex matrices, polyatomic interferences could render the results for many elements useless. Collision/reaction cell technology, which requires more than one set of conditions for all masses, cannot be used since it would result in deviation from the standard relative response tables upon which semiquant is based. Helium collision mode coupled with kinetic energy discrimination in the Agilent 7500cx can overcome these limitations. By effectively removing polyatomic interferences, rapid, accurate, semiquantitative screening of a wide range of sample types for most analyte elements is possible. In this work, a full mass range, 250 isotope semiquant screen was performed in less than 3 minutes total sample-to-sample time with accuracy comparable to full quantification, for most elements, when measuring three different certified reference materials.

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