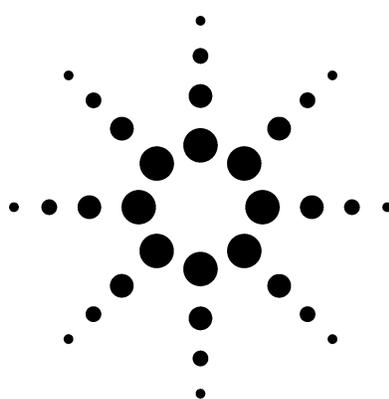


Rapid Analysis of High-Matrix Environmental Samples Using the Agilent 7500cx ICP-MS



Application

Environmental

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Abstract

The new Agilent 7500cx with Octopole Reaction System (ORS) is capable of analyzing most typical environmental samples using only one mode of analysis: helium mode. For the first time, it is possible to analyze an entire environmental suite of elements, including Hg and the major elements such as Na, K, Ca, Mg, Al, and Fe, in less than 2.5 minutes per sample, under conditions that remove or reduce practically all matrix-based interferences.

Introduction

Contract analytical laboratories, particularly those focused on the analysis of environmental samples, face challenges that are significantly different from those of research institutes in government and academia. The samples are typically more numerous, unknown and highly variable in composition, and generally require rapid turnaround. Despite these challenges, the environmental laboratory must ensure that the data produced is of high quality and is supported by extensive analytical quality control (AQC) in order to remain productive and profitable. The recent great improvement in productivity (and, consequently, profitability) of the metals section in contract environmental labs is largely due to the increasing use of ICP-MS, with its rapid multi-element capability, wide elemental cov-

erage and dynamic range, low detection limits, and ease of use. With the advent of collision/reaction cell (CRC) ICP-MS, the ability of the technique to eliminate or significantly reduce the effects of polyatomic interferences in complex matrices has further improved its usability for many applications. However, until recently, the improved accuracy delivered by CRC ICP-MS came at a significant cost to productivity. Typical CRC ICP-MS systems must use reactive cell gases to specifically target known interferences, which requires time-consuming, matrix-specific method development. Furthermore, multiple cell conditions are necessary depending on the matrix and analyte list, which can add minutes to each sample analysis.

Agilent pioneered the use of helium (collision) mode coupled with kinetic energy discrimination (KED) on the 7500c instrument, allowing most polyatomic interferences to be removed using a single set of cell conditions. Subsequent advances in instrument design and in the understanding of the collision mechanisms involved have resulted in the 7500cx, an ICP-MS capable of analyzing typical environmental samples using only helium mode. By eliminating the need for both hydrogen (reaction) mode¹ and no-gas mode, sample throughput is significantly improved and routine operation is greatly simplified. Coupled with improvements in uptake and rinse-out speed through various hardware and software innovations, it is now possible to analyze an entire environmental suite of elements, including Hg and the major elements such as Na, K, Ca, Mg, Al, and Fe, in less than 2.5 min-

¹ Trace level selenium analysis (i.e., below 0.2 ng/mL) requires the use of hydrogen mode to eliminate the Ar₂⁺ interferences on the preferred isotopes at mass 78 and 80.



utes per sample, under conditions that remove or reduce all matrix-based interferences. This application documents the performance of the 7500cx for the high-throughput analysis of long sequences of typical high-matrix environmental samples.

Instrumentation

A standard Agilent 7500cx ICP-MS with a glass concentric nebulizer was used for all analyses. The instrument was tuned for standard robust plasma conditions (Table 1) and the ORS was operated in helium mode only. This means that all elements were measured under identical helium mode collision conditions and no mode switching was necessary. Furthermore, the helium mode conditions used are generic and do not have to be set up or modified for specific sample matrices. Method parameters are shown in Table 1.

Table 1. Instrument Tune and Acquisition Conditions Used

Instrument	7500cx
Sampler	Ni (standard)
Skimmer	Ni (standard)
Nebulizer	MicroMist (standard)
Plasma torch	Quartz, 2.5 mm (standard)
Integration Time	
Li, Be, As, ⁷⁸ Se, ¹¹¹ Cd	0.3 sec x 1 point
All other	0.1 sec x 1 point
Tune Parameters	
RF power	1550 W
Sample depth	8.5 mm
Carrier gas	0.80 L/min
Makeup gas	0.23 L/min
Extract 1	0V
Extract 2	-120 V
Energy discrimination	2 V
Reaction gas	He 5.0 mL/min
CeO/Ce	0.52%
Ce ⁺⁺ /Ce	2.06%

Sensitivity in Helium Mode

Real sensitivity, as determined by practical limits of detection (LOD), is a function of signal to background (high signal, low background) and the precision of the background measurement. The greatest analytical benefit in using helium mode will be realized for analytes that suffer from polyatomic ion overlaps (essentially every isotope of every element from mass 45 to 82). However, it is important to assess the possible degradation in performance for elements that do not suffer from polyatomic interference where helium mode is used for all analytes. Poorer signal to noise for

noninterfered elements is a possibility, as any ICP-MS operating with the cell pressurized (in collision or reaction mode) will suffer some loss of signal for low-mass elements when compared with no-gas mode. This signal loss occurs as a result of collisions between analyte ions and gas molecules in the cell. However, in most cases, the reduction in background more than compensates for the loss of signal, so real detection limits for noninterfered elements are not significantly impacted. In order to measure actual sensitivity under helium conditions, signal-to-background ratios and 3 sigma instrument detection limits (IDLs) were determined in helium mode for all commonly measured elements². For nearly all elements, IDLs are in the low- to sub-ppt range. More important for environmental applications are the background equivalent concentrations (BECs) and IDLs for those elements that typically suffer from interferences in high-matrix samples. Table 2 compares the BECs, IDLs, and equivalent concentration of interferences for several critical elements in no-gas and helium mode in USEPA Interference Check Solution (ICS-A³ - see Table 3 for composition). Note the significant reduction in all three measurements for all isotopes, showing that helium mode is capable of simultaneously removing interferences on multiple elements (and even multiple isotopes) in complex matrices.

Interference Removal in Helium Mode

USEPA Method 6020 specifies an interference check sample (ICS-A) designed specifically to monitor the effect of polyatomic interferences resulting from high concentrations of common matrix components. Traditionally, these interferences have been compensated for through the use of mathematical correction equations. However, experienced ICP-MS users know that in the case of multiple interferences on a single analyte or interferences from uncommon matrix components, mathematical correction is unreliable. Additionally, many polyatomic interferences cannot be corrected mathematically because of the lack of a free mass at which to monitor the interferent. A common example is the interference from ⁴⁰Ar²³Na on ⁶³Cu. This is a significant interference in saline matrices, but because Na is monoisotopic (at mass 23), it is not possible to derive a mathematical cor-

² Performance characteristics of the Agilent 7500cx ICP-MS. Agilent application note 5989-6663EN.

³ ICS-A is the USEPA-specified "Interference Check Solution" designed to alert the user to the possibility of isobaric, doubly charged, polyatomic and memory interferences in high-matrix samples. ICS-AB is the same high-matrix solution spiked with 100 to 200 ppb of each analyte element in order to measure the effects of high matrix on analyte recovery. In this work, the target analytes were spiked much lower (20 ppb, ICS-AB Modified) in order to test the effectiveness of interference removal at trace analyte levels.

Table 2. Comparison of No-Gas Mode and Helium Mode on BEC, IDL, and Measured Concentration in ICS-A Solution (Note the much higher measured concentration values obtained in no-gas mode due to polyatomic interferences. Se 77 and 78 values do not agree in no-gas mode, and V gives a negative concentration reading.)

	No Gas Mode			Helium Mode		
	BEC (ppt)	IDL (ppt)	Measured conc (ppb)	BEC (ppt)	IDL (ppt)	Measured conc (ppb)
⁵¹ V	1461	143	-1.35	107	45	0.13
⁷⁵ As	1945	186	3.23	120	149	0.70
⁷⁷ Se	9973	540	12.31	401	204	0.50
⁷⁸ Se	9738	313	3.84	342	162	0.43

reaction based on the abundance of a second ArNa polyatomic ion. This has typically led ICP-MS users to select the alternative (and much lower abundance) Cu isotope at mass 65. However, ⁶⁵Cu suffers from a much higher level of S-based interferences (S₂ and SO₂) than ⁶³Cu as well as a significant ²⁵Mg⁴⁰Ar interference, so switching to ⁶⁵Cu to avoid the ArNa overlap can result in compromised data quality in many sample types.

Cr is another example of an element that commonly suffers from polyatomic interferences (⁴⁰Ar¹²C, ³⁵Cl¹⁶OH, ³⁶Ar¹⁶O, and ³⁸Ar¹⁴N on ⁵²Cr, and ³⁷Cl¹⁶O, ⁴⁰Ar¹³C, and ³⁶Ar¹⁶OH on ⁵³Cr), which cannot be reliably corrected mathematically due to the lack of a free reference mass. For these reasons, helium mode, with its ability to remove all polyatomic interferences regardless of sample matrix composition, is vastly more reliable and more widely applicable than the use of mathematical corrections⁴.

Figure 1 shows overlaid spectra for USEPA ICS-A, measured from mass 73 to 82 in no-gas, helium, and hydrogen modes. The spectra have been normalized on the bromine peak at *m/z* 79 to compensate for differences in sensitivity between modes. The differences in spectral complexity are clear, with almost every mass showing some level of interference in no-gas mode, while helium mode has reduced all of these interferences to background levels.

Table 3. Composition of ICS-A and ICS-AB (modified)³ (ICS-AB was prepared by spiking ICS-A with a 20-ppb standard containing all analyte elements of interest.)

Component	ICS-A concentration (mg/L)	ICS-AB concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.02
Cd	0.0	0.02
Cr	0.0	0.02
Co	0.0	0.02
Cu	0.0	0.02
Mn	0.0	0.02
Hg	0.0	0.02
Ni	0.0	0.02
Se	0.0	0.02
Ag	0.0	0.02
V	0.0	0.02
Zn	0.0	0.02

⁴ Note that because helium mode works only on polyatomic interferences, it is not capable of removing elemental isobaric interferences (e.g., ⁴⁰Ar on ⁴⁰Ca) or doubly charged interferences. Fortunately, these types of interferences are rare, and simple methods are available to avoid them, such as choosing an alternative analyte isotope.

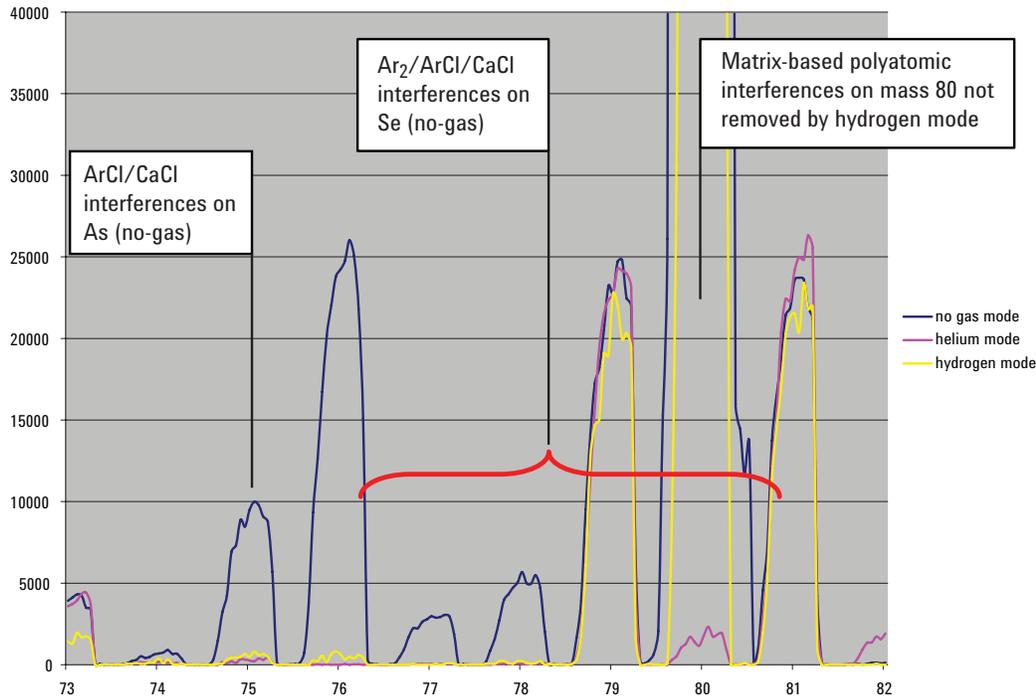


Figure 1. Overlaid spectra of ICS-A obtained in no-gas, hydrogen, and helium modes over the range from mass 73 to 82 to show interferences on As and Se. Spectra normalized on Br signal at m/z 79. Note that while H_2 mode is effective for the removal of the Ar_2^+ overlap at mass 80 (main isotope of Se) in simple matrices, it is not effective for several other interferences at this mass in ICS-A ($ArCa$, Ca_2 , S_2O , SO_3 , etc.). Ar_2^+ is completely removed by H_2 mode at m/z 78, which is therefore the preferred isotope.

Experimental

A 12-hour, 300-sample sequence, representing a typical environmental batch, was analyzed after a single initial calibration consisting of a blank and standards at 1, 10, 50, and 100 ppb (Figure 2). The sequence consisted of repeated blocks of 10 samples, including NIST 1640 standard reference water, ICS-A, ICS-AB, and two commercially available high total dissolved solids (TDS) mineral water samples. After each block, blank check and calibration check samples (USEPA sample types continuing calibration blank [CCB] and continuing calibration verification [CCV]) were automatically inserted to check for memory effects and calibration accuracy. No recalibrations were performed during the 12-hour run.

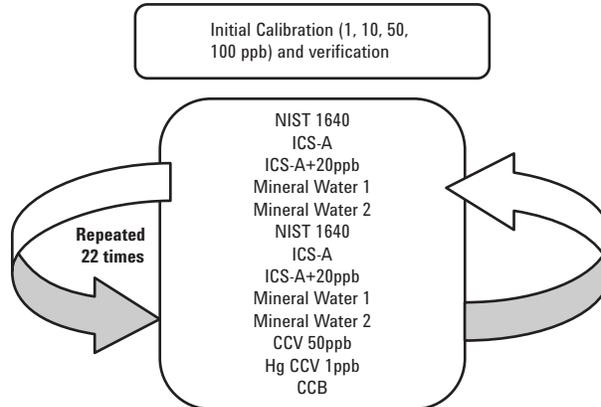


Figure 2. Schematic of analytical sequence. 300 sample analyses were performed, including an initial calibration and 22 repeated analyses of a block of samples containing 10 samples followed by 2 CCV samples and a CCB.

Long-Term Stability

Analysis of CCV Samples

As a check on calibration stability for all analyte elements, a CCV standard (50 ppb for all analytes except Hg – 1 ppb) was analyzed repeatedly throughout the sequence. USEPA Methods 200.8 and 6020 require that the measured CCV values fall within $\pm 10\%$ of the true value in order to report samples. Figure 3 shows the results of 25 measurements of the CCV sample over the 12-hour sequence, indicating no failures throughout the run, despite the fact that no recalibrations were performed after the initial calibration.

Analysis of High-Matrix Samples

In order to simulate difficult, high-matrix sample types, ICS-A and ICS-AB were each analyzed twice

in each 10-sample block (giving a total of 48 replicate analyses of each), in addition to the two high-TDS mineral water samples. ICS-A and ICS-AB were selected because they are well characterized and were specifically designed by the USEPA to challenge the ICP-MS's ability to handle high-matrix samples in terms of controlling interferences, managing ionization suppression, eliminating memory effects, and maintaining long-term stability. Long-term precision and accuracy for trace-level measurement in high-matrix samples can be determined by examining the results of repeated analysis of ICS-AB. Recoveries ranged from 97 to 104% with %RSDs ranging from less than 1% to approximately 5% over the 12-hour sequence (Figure 4).

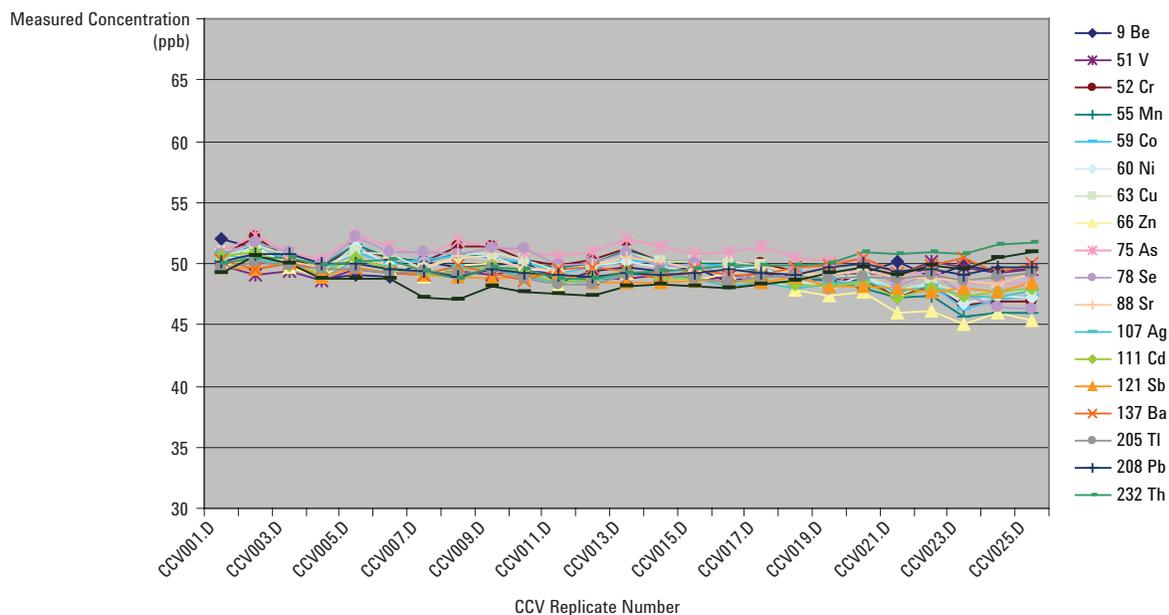


Figure 3. Measured values of 50 ppb CCV samples (n = 25) over the course of the sequence. USEPA criteria are $\pm 10\%$ (i.e., 45 to 55 ppb).

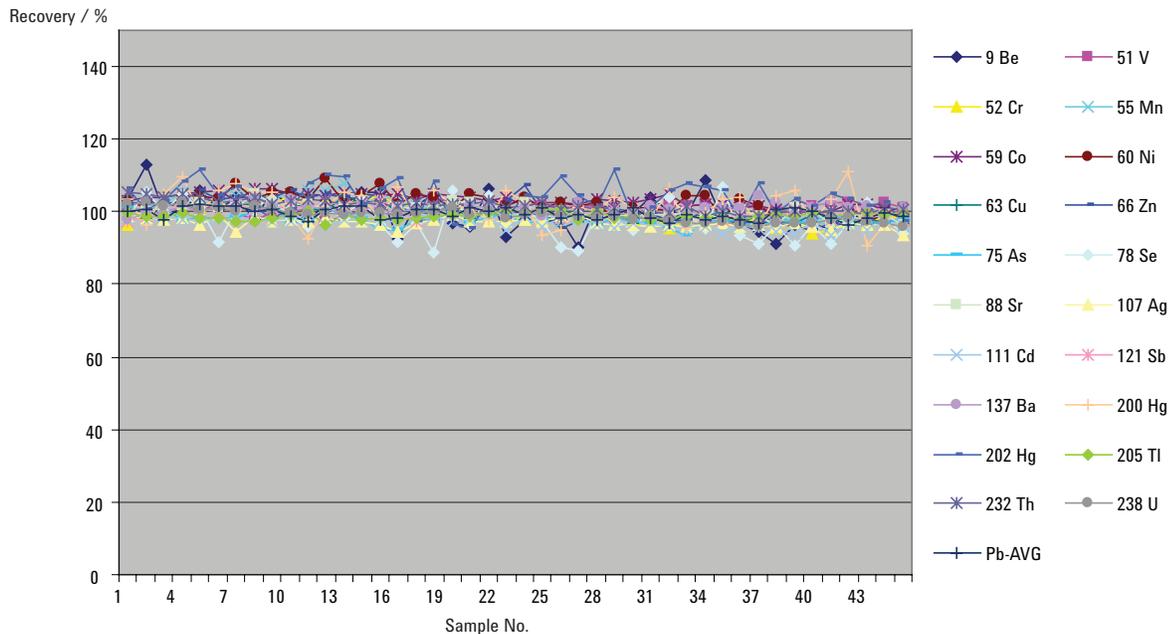


Figure 4. Spike recovery (20 ppb, 1 ppb Hg) for ICS-AB over 12 hours (n = 44).

Analysis of Certified Reference Material

NIST 1640 certified reference water was analyzed repeatedly (n = 44) as part of the sequence. Results are shown in Table 4.

Table 4. Results of Repeated Analysis of NIST 1640 (n = 44) Over a 12-Hour Sequence

Element	Mean (n = 44)	RSD (%)	Certified value (µg/L)	Recovery (%)
⁹ Be	32.36	4.72	34.94	92.6
²⁷ Al	48.62	3.90	52.00	93.5
⁴² Ca	6652.25	2.59	7045	94.4
⁵¹ V	12.66	1.40	12.99	97.4
⁵² Cr	36.14	3.19	38.60	93.6
⁵⁵ Mn	114.96	3.87	121.50	94.6
⁵⁹ Co	19.64	2.27	20.28	96.8
⁶⁰ Ni	26.76	2.86	27.40	97.7
⁶³ Cu	84.95	2.16	85.20	99.7
⁶⁶ Zn	52.64	2.66	53.20	99.0
⁷⁵ As	25.28	1.52	26.67	94.8
⁷⁸ Se	20.69	4.61	21.96	94.2
⁸⁸ Sr	118.03	1.31	124.20	95.0
¹⁰⁷ Ag	7.15	1.67	7.62	93.8
¹¹¹ Cd	21.31	1.26	22.79	93.5
¹²¹ Sb	13.48	1.68	13.79	97.7
¹³⁷ Ba	140.78	1.03	148.00	95.1
²⁰⁰ Hg	0.10	12.23	—	—
²⁰² Hg	0.10	9.83	—	—
²⁰⁴ Pb	26.98	3.62	27.86	96.9
²⁰⁵ Tl	0.01	54.91	—	—
²⁰⁶ Pb	25.04	1.06	27.86	89.9
²⁰⁷ Pb	26.94	1.11	27.86	96.7
²⁰⁸ Pb	26.17	0.86	27.86	94.0
²³² Th	0.05	45.36	—	—
²³⁸ U	0.73	2.90	—	—

Average Analysis Time

One of the major goals of using a single ORS mode is to improve productivity. To ensure that this end was met:

- Integration times were kept short, typically 0.1 second per point.
- A single point per mass was used.
- Intelligent and pre-emptive rinse functions were employed (minimizes wasted time in uptake and rinseout and ensures that carryover could not occur).

Figure 5 graphically shows the time savings possible. In a conventional CRC system, after sample uptake and initial stabilization, acquisition occurs in the first of several CRC modes, followed by cell evacuation, repressurization, and restabilization (top). The process continues until all necessary modes have been completed (typically 3). In the 7500cx helium mode (bottom), initial uptake and stabilization are the same. After that, helium mode acquisition can begin immediately, since no cell evacuation or repressurization is necessary, followed by rinse. Pre-emptive rinsing begins up to 60 seconds before acquisition has finished, and intelligent rinse monitors rinseout, ensuring complete washout without any wasted time. The total acquisition time for all analytes and internal standards was 9.7 seconds per replicate. Three replicates were acquired according to USEPA methods,

resulting in a total acquisition time of 29.2 seconds. Overall, the average run-to-run time based on 300 runs beginning at 4:44 p.m. and ending at 5:04 a.m. the following morning was 2.46 minutes per run. As the data in Table 4 illustrate, despite the short acquisition time, precision was not compromised and all data returned excellent %RSDs over the 12-hour period.

Conclusions

Since helium mode is universal, all interferences are removed without prior sample knowledge. Tuning is simplified and problems associated with reactive cell processes such as the creation of new interferences or loss of analyte or internal standard are avoided. Stability is not compromised since cell conditions are static and run times are

markedly improved through the elimination of multiple cell conditions along with the associated stabilization times.

For many applications, particularly commercial analysis of high-matrix environmental samples, the use of helium mode offers significant benefits in productivity, data reliability, and ease of use.

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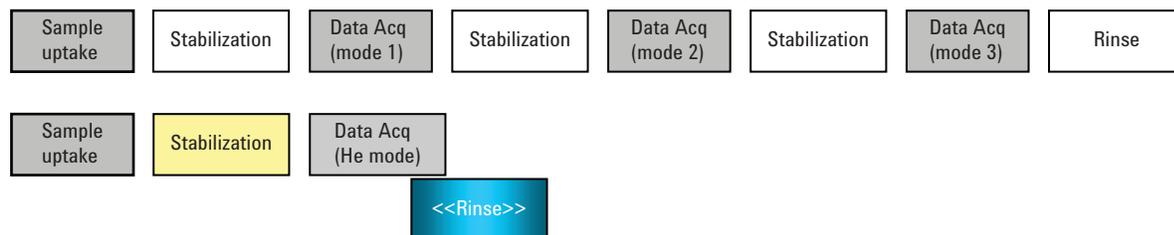


Figure 5. Typical multimode CRC operation (top), and 7500cx using helium mode and pre-emptive rinse software (bottom).

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Printed in the USA
September 20, 2007
5989-7297EN

