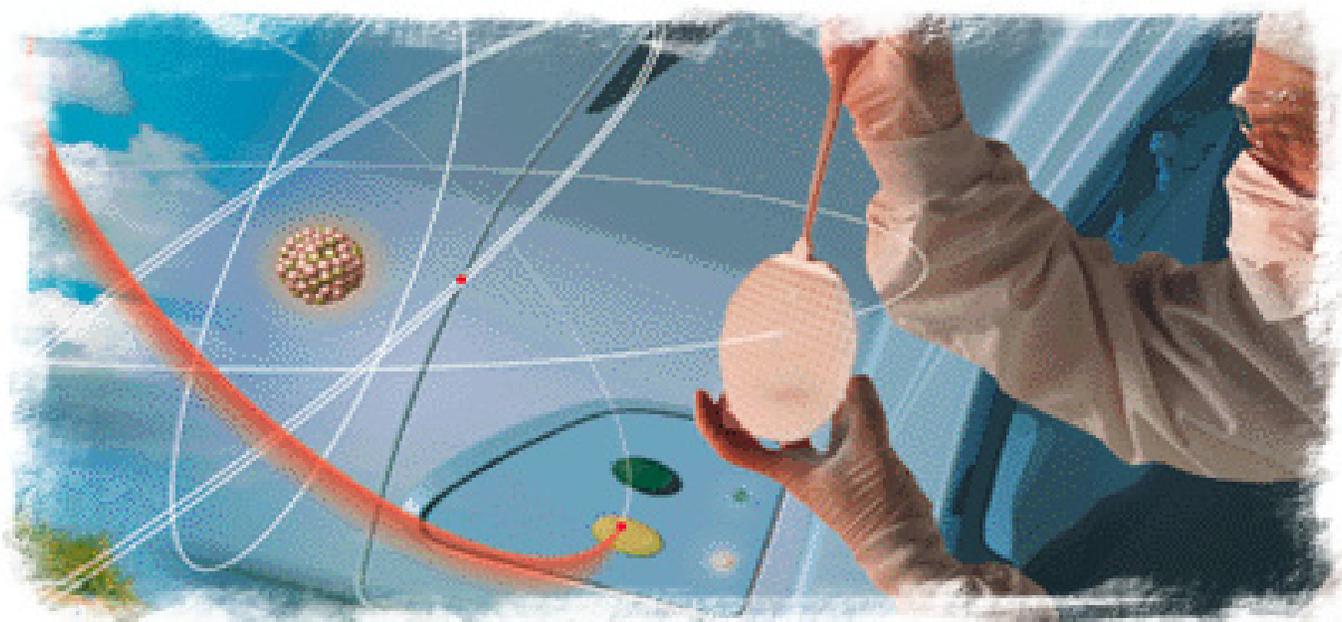


Software Reference Guide

ELAN® 3.4 ICP-MS Instrument Control Software



Hotfix 1
September 2008

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Preface

This Software Reference Guide contains in-depth conceptual information about the use of the application software, as well as software reference information regarding screen components. This guide includes information for multiple instruments in the ELAN® ICP-MS product line. Unless otherwise specified, all functions are available for use on all instruments. If you have any questions or comments about this reference guide, contact our Information Development team at: techpubs@sciex.mdsinc.com

Using this Software Reference Guide

The sections in this guide are structured to provide the information needed to understand the overall operation of the instrument. This includes:

- Procedures for starting and shutting down the instrument and software
- Development of analytical methods
- Calibration, tuning, and optimization
- Information about performing analyses and interpreting results
- Reference information regarding the main software windows and their controls

In addition, a full *Table of Contents* and *Index* provide active links to all sections and concepts in the manual. You can also print all or portions of this guide, using standard 8½" x 11" paper.

Additional Assistance

The ELAN® Inductively Coupled Plasma Mass Spectrometer system includes the following documentation and help materials:

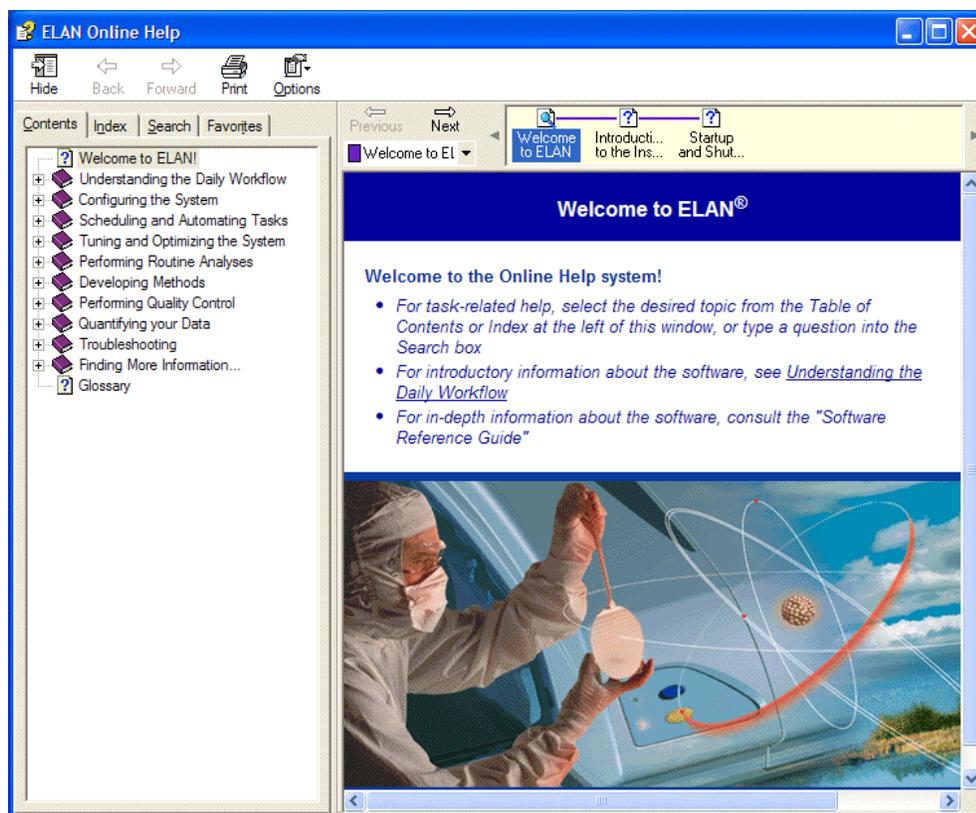
- An Installation Guide containing comprehensive installation instructions. This printed guide ships with the software CD, but is also available in PDF format on the CD
- A Help System providing task-level information for all software procedures. This is available from the software Help menu

- A Hardware Guide containing a detailed description of the instrument hardware system, and instructions for installation, maintenance, and troubleshooting
- A Safety Manual providing important notices and warnings to guide you through the safe operation and maintenance of the instrument
- A series of Maintenance Videos illustrating common maintenance tasks. These are available from the software Help menu
- A CD ROM Maintenance Log containing maintenance spreadsheets in PDF format

Using the Help System

Use the help system to access basic and procedural information while you are working in the software. On the Help menu, click **ELAN Help** to access the full help system, or press **F1** at any time to open a help topic specific to the window or dialog box in which you are working.

At the top of the Help window is a toolbar for common tasks, such as printing and going back to the previous page. The tabbed pane on the left provides several navigational aids to help you find the information you need. The main pane on the right is where the help topics are displayed.



Contents

The Contents tab arranges help topics by subject, just like the Table of Contents in a book. Click a book icon  to display an overview of the topics in that section. Click a topic icon  to display a particular topic.

Index

Use the Index tab to search the online help index for a word. Type the word you want to look up in the text box and click **Display**, or click the topic in the alphabetical list. The chosen topic is displayed.

Search

Use the Search tab to locate a word, phrase, or set of words. The help system uses boolean, wildcard and nested expressions to refine a search. With the AND, OR, NOT, and NEAR operators you can precisely define your search by creating a relationship between search terms. If no operator is specified, AND is used. For example, the query “spacing border printing” is equivalent to “spacing AND border AND printing.”

To search for	Use	Example	Results
More than one term in the same topic	AND	baseline AND correction	Topics that contain both the words “baseline” and “correction”
Either of two terms	OR	spectrum OR spectra	Topics containing either the word “spectrum” or the word “spectra” or both
The first term without the second term	NOT	peak NOT table	Topics containing the word “peak” but not the word “table”
Both terms in the same topic, close together	NEAR	samples NEAR high	Topics containing the word “samples” within eight words of the word “high”

Note: The |, &, and ! characters do not work as boolean operators—you must use OR, AND, and NOT.

To perform a search

1. Type the words or phrase you want to search for in the text box and click **List Topics**. The topics containing the word or phrase are displayed, including a Rank to help you choose the topic you want to view first.
2. Select a topic from the list and click **Display**. The topic you have chosen is displayed in the main window.

Favorites

Use the Favorites tab to quickly find frequently used help topics. You can store the current help topic in a Favorites list by clicking **Add** at the bottom of the Favorites tab, then return to the topic anytime by double-clicking the title on the tab.



1

Introduction to the Software

This section provides a brief overview of the ELAN® ICP-MS Instrument Control Software version 3.4 with Hotfix 1. It introduces the basic techniques for working with the software, including starting and stopping the system.

Topics in this section include:

- ▶ “Supported Instruments” on page 11
- ▶ “Software Layout and Organization” on page 12
- ▶ “Multiple Software Sessions” on page 12
- ▶ “File Locations” on page 13
- ▶ “Startup and Shutdown” on page 15
- ▶ “What to Do if Ignition Is Unsuccessful” on page 17
- ▶ “Automating Daily Tasks” on page 20

Introduction

This guide includes information for multiple instruments in the ELAN® ICP-MS product line. Unless otherwise specified, all functions are available for use on all instruments.

Supported Instruments

The software supports the following PerkinElmer SCIEX® instruments:

- ELAN 6000 series instruments:
 - ◆ ELAN 6000 instrument
 - ◆ ELAN 6100 instrument
- ELAN 9000 instrument
- ELAN DRC™ series instruments:

- ◆ ELAN 6100 DRC instrument
- ◆ ELAN DRC^{Plus} instrument
- ◆ ELAN DRC II instrument
- ◆ ELAN DRC-e instrument

Software Layout and Organization

Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-element technique used to accurately measure the concentration of over eighty elements in a variety of sample matrices. Its analytical potential combines the features of both ICP emission and graphite furnace atomic absorption. This software provides you with many options for optimizing system performance and simplifying operation while performing ICP-MS determinations.

The software is organized around the idea of the *workspace*—a flexible environment configured to suit whatever task you are performing. A workspace contains multiple individual windows simultaneously opened, sized, and positioned so you can see clearly what is happening during operations. You can adjust these windows as needed.

Most of the operations you perform when working with the instrument are carried out through the software system. The software controls the primary hardware components of the spectrometer and the sampling accessories attached to the system. It also manages the data acquisition process and performs all analytical calculations.

Multiple Software Sessions

When desired, you can launch a second session of the software to analyze or reprocess data while the instrument gathers data in the initial session. The first software session is called the Instrument Control session; the second session is called the Edit/Reprocess session. The Edit/Reprocess session can perform the following tasks while the Instrument Control session gathers data and controls the autosampler:

- Reprocess previously acquired data with different compatible methods
- Create new or modify existing file types for Method, Sample, Calibration/Response, and Report Option files
- Review autosampler settings in the Devices window to validate autosampler locations for Methods and Batches
- View reprocessed results in an Interactive Graphics window
- Create new or modify existing workspaces
- Print reports to printer or file
- Print graphics

While running dual sessions of the software, there are no limitations on the Instrument Control session. It has priority over all tasks. As a result, the speed of an Edit/Reprocess session may be impacted. There is no communication between the two sessions. If an error

occurs in one session, the other session is not impacted by the error. Also, the Edit/Reprocess session provides no GPIB communications.

Note: You cannot modify the files used in the Instrument Control session. These files are available on a read-only basis to ensure that files shared between concurrent sessions are not corrupted.

In an Edit/Reprocess session, there is no access to the following windows and tabs:

- Scheduler window
- Realtime Graphics window
- Tuning window
- Instrument window
- Devices window (all tabs *except* the Autosampler tab)

File Locations

The software's file management features include a specific folder setup for data, with several subdirectories unique to the software. These subdirectories are:

- **Autosampler:** This subfolder contains the files for the different types of autosampler that can be used with the instrument.
- **Dataset:** This subfolder comes with a set of pre-defined data folders, wherein files containing the data from your analyses are collected under user-defined filenames. You can also create a Dataset folder outside the default location if you wish.
- **Method:** This subfolder contains any method files developed for analyses. *It also contains a Service subfolder for service-representative-specific information.*
- **Optimize:** This subfolder contains optimization files. The information contained in these files is used to perform the fine-tuning adjustments for the hardware subsystems in the torch/quadrupole assembly of the instrument.
- **ReportOptions:** This subfolder contains the report options files. These files contain the modifications to the report templates that are used to create a hardcopy or file report. You can modify the report template for your needs, name it and save it to this file for future use.
- **ReportOutput:** This subfolder is the default destination for report files if no path is specified in the method.
- **Sample:** This subfolder contains the sample files for sample analysis. These files identify the samples, control the order in which samples are measured and initiate the measurements. In the software, you fill in the Sample window and save a file, with a name you select, to this subfolder.
- **System:** This subfolder contains the calibration files and TotalQuant™ response files.
- **Tuning:** This subfolder contains all default and custom .tun tuning files.

- **Wizard:** This subfolder contains all default and custom SmartTune™ .swz files. *It also contains a Service subfolder for service-representative-specific information.*
- **Workspace:** This subfolder contains all default and custom .wrk workspace files. *It also contains a Service subfolder for service-representative-specific information.*

The Elemental Library

The elemental library contains information on isotopic abundances and polyatomic species. This library applies to all applications except the TotalQuant™ software, which has its own read-only elemental library. The main elemental library is contained in the ELAN.ELM file, located by default in your ELAN root folder.

Startup and Shutdown

This section contains instructions for starting up the instrument for routine operation, and verifying the correct operation of your system before beginning an analysis. It also describes the correct sequence of events for shutting down the instrument after you have finished your determinations.

Starting the Software and Instrument

The software is your main interface to the instrument. It must be running for correct instrument functionality.

To start the software

1. Turn on the computer, monitor, and printer.
2. On the Windows desktop, double-click the **ELAN** icon.

Note: If different users have been set up on the instrument and they do not share project folders, files such as default.tun and default.dac are not shared between users and/or the system administrator.

To start the instrument

This section summarizes the basic steps required to start your instrument, computer system, and accessories for routine measurements. Use this *quick start* procedure only if the instrument has not been shut down for a long time.

Tip: For further information see the *Hardware Guide*.

1. Check the condition of the sample introduction system:
 - a) Check the sampler and skimmer cones. Note any evidence of blockage, deposits and erosion of the edges. Unless the condition of the cones seems severely degraded, do not remove them. If you are unable to obtain satisfactory results when you perform system optimization, you may need to clean or replace the cones.
 - b) Check the ICP torch. Clean it if there are deposits clogging it. If severe wear has occurred, you should replace the torch.
 - c) Check that the load coil is clean. This prevents arcing across the coils. Also, if the humidity in your lab is high, ensure that the coil is dry. If necessary, use a soft cloth to dry it.
2. Check that the sample tubing and drain tubing leading from the peristaltic pump to the spray chamber are properly set up and in good working condition.
3. Place the capillary tubing into a container of deionized water.

4. Open the **Instrument** window, and then click the **Front Panel** tab.

If all system hardware is operating properly and the plasma is ready to be ignited, the System Status indicator indicates **Ready**. If the indicator reads **Not Ready**, there is a fault in the system and the plasma should not be ignited. If this occurs, refer to the instrument's diagnostic display to determine which system component is causing a fault.

5. On the Front Panel tab, click **Plasma Start** to ignite the plasma.

The instrument initiates the ignition process—this takes a minute+ to complete. The progress of the ignition sequence is shown in the Ignition Sequence status bar.

Note: If the plasma does not ignite, wait 15 seconds and then click **Plasma Start** again.

6. After the plasma ignites, allow the instrument to warm up for 45 minutes.

To start the instrument after an extended shutdown

This section presents additional information on the procedures for restarting the instrument after a period of extended shutdown. If the power and vacuum pumps are turned off, the system will need additional time to re-initialize and pump down when the power is turned on. For more information on turning the instrument power on and off, refer to your *Hardware Guide*. The System and Roughing Pumps circuit breakers should remain on, even when the instrument is not in use.

1. Turn on the installed gases and the cooling system.
2. Ensure that the software is running.
3. Ensure that all circuit breakers on the left side of the instrument are in the **On** position. If they are not, allow five seconds before turning on each circuit breaker in the sequence, then slowly, turn on the circuit breakers. For the proper sequence of turning on circuit breakers, refer to your *Hardware Guide*.
4. In the software, click the **Instrument button**, and then click the **Front Panel** tab.

The Control Panel appears. A schematic diagram provides a graphical display of the major operating elements of your instrument. This diagram indicates the status of the plasma, argon flow, cooling system and interlocks.

5. On the Front Panel tab, click **Vacuum Start**.

When a satisfactory vacuum has been achieved, the vacuum chamber in the three-dimensional diagram of the instrument turns green. The System Status indicator should read **Ready** indicating that all the system hardware is operating properly and that the plasma can be ignited. If the indicator reads **Not Ready**, refer to the schematic diagram to find out which system is not prepared for operation.

6. Check the base vacuum pressure. For successful operation of the instrument, the pressure should be in the 10⁻⁶ torr range.
7. Record the instrument readings in the appropriate section of your instrument's Operating Log.
8. Turn on any accessory systems that may be connected to the instrument, such as alternate sampling systems (electrothermal vaporization, flow injection, laser ablation).

Note: To ensure that all standards have been met before the system is turned on, refer to the manuals provided with each accessory.

What to Do if Ignition Is Unsuccessful

The system indicates the progress of the ignition sequence on a bar graph on the Front Panel tab of the Instrument window. If the plasma fails to ignite, due to a component failure, an error message is generated by the system along with a diagnostic display indicating which system component is causing the failure. As a general consideration, the following system interlocks must be satisfied before the plasma can be ignited:

- The torch gas pressure must be achieved
- The vacuum chamber must be locked in the sampling position
- The operating vacuum must be achieved
- The ICP generator must be ready

Additional information can be located on the Instrument window Diagnostics tab, which lists operating conditions for all of the major system components. The following are a series of checks to assist in correcting failure conditions.

Argon Supply

Check the argon supply pressure and record the pressure on the Operating Log Sheet. Ensure that you have enough argon for the amount of time you plan to use the instrument. For information about argon gas requirements, refer to your *Hardware Guide*.

- Check that the argon supply valve is open and the regulator is set at the correct pressure. For the correct pressure setting, refer to your *Hardware Guide*.
- Check for leaks throughout the gas connections.

Cooling System

The cooling system should meet the required specifications and be installed according to the information in your *Hardware Guide*.

- Check that the cooling system is connected at the appropriate points on the instrument.
- Check that all electrical connections have been made. Make sure that the recirculator is turned on and has been filled with coolant. Check the external pressure.
- Check that the coolant supply is turned on and, if necessary, is being properly filtered.
- Check for any leaks in the plumbing connections.

Vacuum System

Check that the vacuum pump oil is clear to amber in color and is at the full level. Change the oil if it is darker. For instructions on changing pump oil, refer to the maintenance section of your *Hardware Guide*.

Torch and Sample Introduction System

Verify that all gas fittings to the torch are finger-tight. Leakage of air into any part of the torch, nebulizer or spray chamber may cause ignition problems. Therefore, be sure to regularly check the following items:

- When using the spray chamber, check that the nebulizer/end cap is tightly secured to the spray chamber.
- When using the spray chamber, check that the sample capillary tubing is attached to the nebulizer sample inlet. The tubing should be clean and in good condition.

- When using the spray chamber, check that the drain fitting is secured on the spray chamber drain. A loose-fitting drain can cause pressure leaks and consequent plasma instability.
- When using dry aerosol sample introduction, check that the transfer tubing connection to the base of the torch is finger tight.
- Check that the drain fitting on the spray chamber drain is secure. Ensure that the pump is properly draining the spray chamber and that the drain liquid is not backing up into the spray chamber. Check that the spray chamber drain leads to the drain bottle. Empty the drain bottle, if necessary. Dispose of waste properly.
- Check that the capillary tubing is attached securely to the nebulizer.

Organic Solvents

If you are analyzing organic solvents and cannot ignite the plasma, run the nebulizer argon for a couple of minutes with the peristaltic pump off to purge the spray chamber.

Organic Vapors

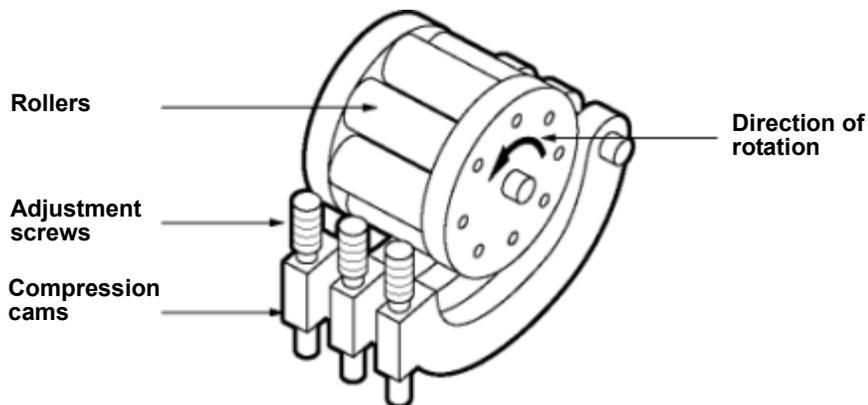
If organic vapors remain in the torch from an earlier analysis, they can sometimes cause ignition problems. If you suspect this, purge the sample introduction system with argon for several minutes.

Instrument Shutdown

To maintain your instrument in proper working condition, you must shut down the different systems and peripherals in the correct order. Simply cutting power to the instrument and peripheral devices may cause damage to your system over time. Also, the software is designed to safeguard your data and minimize the risk of data loss due to closing unsaved files.

To shut down the instrument

1. With the plasma on, flush the system for five minutes using deionized water or clean solvent.
2. Open the **Instrument** window, and then click the **Front Panel** tab.
3. Click the **Plasma Stop** button to extinguish the plasma.
Note: In an emergency, the plasma can be extinguished using the yellow plasma off button on the front panel of the spectrometer console.
4. Remove the sample capillary from the deionized water.



Integrated peristaltic pump

CAUTION! Always remove the sample capillary or autosampler probe from a solution when you are finished using the pump. Otherwise, the solution may siphon into the spray chamber and flood it.

5. Release the compression cams that secure the drain and sample tubing. Loosen the drain and sample tubing. This will increase the usable life of the tubing.

Note: If you are planning to use your instrument on a routine basis, you should leave the system turned on with the vacuum system pumping. This permits quick startup the next time you need to perform determinations. If you are shutting down for longer than two or three days, refer to the disconnection procedures in the *Hardware Guide*.

To exit the software

1. On the File menu, click **Exit**.
You are prompted to save any new or modified files.
2. Click **Yes** to save the files. When all open files have been saved, the software closes.

Automating Daily Tasks

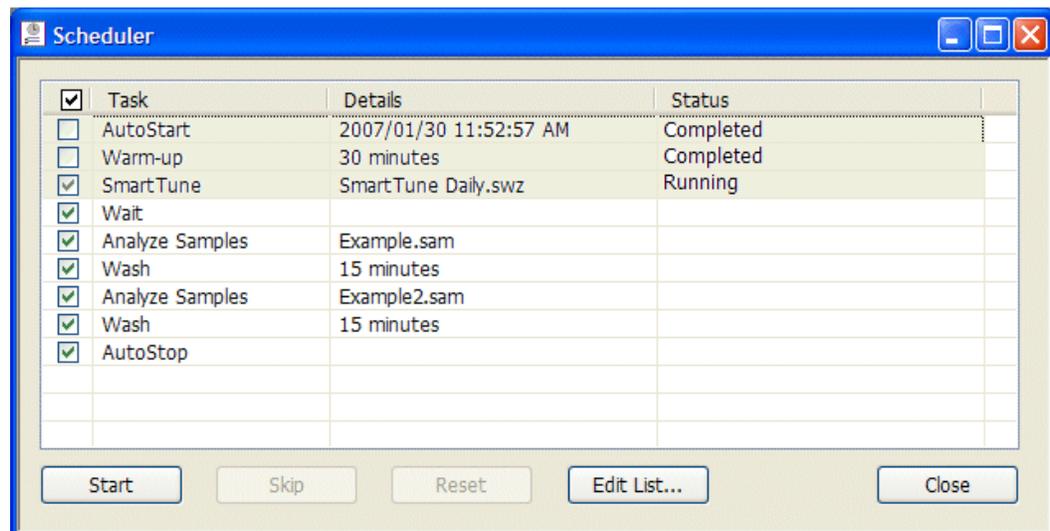
Use the Scheduler function to set up an automated run list of daily tasks. You can automatically start and stop the plasma, and run as many optimizations and analyses as you want completely unattended. You can add multiples of any task type to your Scheduler list. The following tasks are available:

- **AutoStart:** Use to start the plasma. Note that if the plasma is not on and the AutoStart option is not selected, *and* the Scheduler is started, the software alerts you with a *Failed* status.
- **Warm-up:** Add to prepare the instrument for analyses following plasma ignition.
- **SmartTune:** Use to run your daily performance checks and optimizations. Ensure that your SmartTune files are correctly configured and saved before adding to your task list.
- **Wait:** Use to insert a pause between tasks.
- **Analyze Samples:** Use to add one or more sample or batch runs to the task list. Ensure that all methods, samples, and sample batch files are correctly configured and saved before adding to your task list.
- **Wash:** Add to clean the system after an optimization or between sample batches to prevent carry-over.
- **AutoStop:** Use to shut down the plasma after all samples have been run.

Note: You can close the Scheduler window while it is running—the Scheduler status bar provides task progress.

Scheduler Window Software Reference

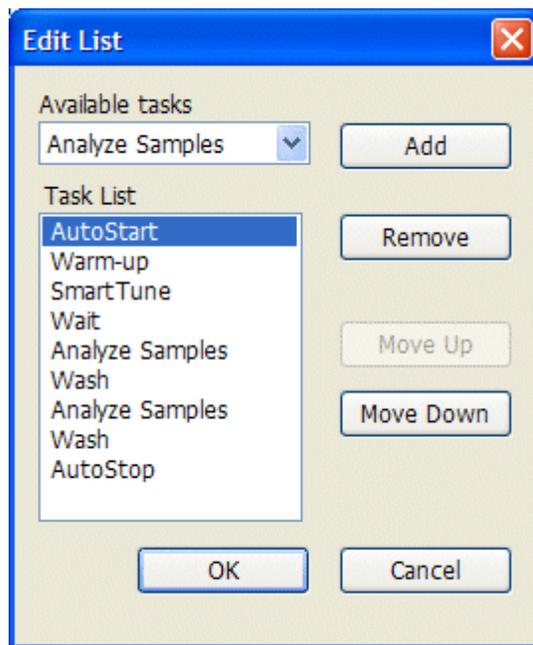
Double-click any task row to access and edit the details for that task. To re-order the tasks, you can drag-and-drop them on the task list, or click Edit List to reconfigure your task list.



Scheduler window

Items on the Scheduler window

- **Check boxes:** Check the boxes beside each task you want to include in the current run. Check the top box (check all) to include all tasks.
- **Task:** Lists all the tasks in the current scheduler run list. Double-click any task row to access and edit the details for that task. To re-order the tasks, you can drag-and-drop them on the task list, or click Edit List to reconfigure your task list. The software prevents you from dragging items above the currently running or last completed task. When started, the Scheduler runs tasks in order from top to bottom.
- **Details:** This column provides additional information about each task. Double-click any task row to access and edit the details for that task.
- **Status:** Provides information regarding what tasks have run, what the current status is, and validation faults (for example, *Invalid file*).
- **Start/Stop:** Toggle button which starts or stops the active Scheduler task run.
- **Skip:** Skips currently running task, (except AutoStart).
- **Reset:** Refreshes the Status column, so you can start a new Scheduler instance or list.
- **Edit List:** Click to access the Scheduler Edit List. Use this dialog box to add and tasks for your Scheduler list. Here you can select the tasks you want the instrument to perform, and use the Move Up and Move Down buttons to put them in the desired order.



Scheduler Edit List window



Method Development

This section discusses creating analytical methods for your instrument.

Topics in this section include:

- ▶ “Analytical Techniques” on page 23
- ▶ “DRC™ Method Development” on page 28
- ▶ “Fundamentals of Data Acquisition” on page 31
- ▶ “Data Processing” on page 36
- ▶ “Fundamentals of Calibration” on page 40
- ▶ “Calibration View Window” on page 46
- ▶ “Method Window Software Reference” on page 47
- ▶ “Global Defaults—Peristaltic Pump Settings” on page 69

Analytical Techniques

Developing a method involves defining your analysis goals, selecting the analytical technique best-suited to achieving those goals, and configuring the method parameters to provide the best possible combination of accuracy, precision, and analysis speed.

The most important consideration when selecting an analytical technique is the degree of precision required in your results. For survey measurements or semi-quantitative testing, TotalQuant™ analyses provide the most convenient method, providing both analytical effectiveness and fast results. However, with the addition of standards in a TotalQuant determination, many quantitative requirements are also satisfied. While Quantitative Analysis methods are generally selected when accuracy and precision are the primary considerations, some applications may benefit from the added precision achievable using an Isotope Dilution method.

The software provides several different ways of managing data acquisition:

- Quantitative Analysis
- TotalQuant III Analysis

- Isotope Dilution
- Isotope Ratio
- Data Only

Quantitative Analysis Methods

This technique accurately determines the concentrations of specific elements in an unknown sample. It is a general-purpose, high-precision analytical tool and is the fundamental tool for most determinations. The technique provides accurate results across a wide range of concentrations and generates results suitable for certification, specification, and litigation work. The software is structured to be simple-to-use, incorporating features such as automatic interference correction through the application of elemental equations.

In Quantitative Analysis, you calibrate the instrument by measuring standards for all the elements you are interested in determining. You analyze standards at different concentrations to ensure that instrument response is accurate across the range of concentrations you are likely to encounter in your sample solutions. As you analyze the standard solutions, the software creates a calibration graph of the measured intensity versus concentration for each element in the standard solution. These individual calibration curves are updated after each standard solution is measured.

After calibration data is acquired, you run your sample solutions. The concentrations for the analytes of interest are automatically calculated. The technique can be used in conjunction with *QC (Quality Control)* procedures to monitor the results of your determination and flag samples which fall outside of pre-defined ranges.

Although Quantitative Analysis methods are suitable for the majority of requirements, should your application require even greater analytical precision, the Isotope Dilution application may offer a slight improvement. However, Isotope Dilution methods require the use of enriched isotopes, making them less suitable for routine use.

TotalQuant™ III Methods

For the rapid analysis of a total unknown, the software provides a unique, fully automated, semi-quantitative method called a TotalQuant analysis. With this technique, you can automatically determine the concentrations of up to 81 elements in a single sample measurement. A TotalQuant analysis measures the entire mass spectrum, so you do not need to specify the individual elements you want to determine. The software automatically corrects for isotopic interferences and interfering molecular species, and produces a comprehensive report listing each element present in your sample and its concentration.

TotalQuant analyses afford an excellent approach to characterizing unknown solutions. They can be used without standards to perform a rapid survey determination, providing a simple means of identifying unexpected components in a solution. After you characterize a solution in this manner, you can select to use a TotalQuant method with standard solutions to improve analytical accuracy, or switch to the Quantitative Analysis technique to focus on specific elements and determine their concentrations with even greater accuracy and precision.

While you can perform a TotalQuant determination without using a series of standards, we recommend you do use standards to adjust the instrument settings for improved accuracy. Unlike Quantitative Analysis methods in which you analyze standards for all the elements you want to determine, TotalQuant calibration is achieved using just a few elements distributed throughout the mass range of interest. The calibration process updates internal response data that correlates measured ion intensities to the concentrations of elements in

a solution. During calibration, the software adjusts this response data to account for changes in the instrument's sensitivity due to variations in the sample matrix.

Isotope Dilution Methods

You can use the Isotope Dilution method for extremely high accuracy and precision measurements of the concentrations of elements in an unknown sample. Isotope Dilution is an absolute means of quantitation based on altering the natural relative abundance of two isotopes of an element by a known amount, and then measuring the results. It is one of the most accurate approaches to elemental analysis.

To use Isotope Dilution, you add a known weight of the spike solution to your sample. Given a known weight for the spike and a sample weight or volume that includes the spike, the software applies natural abundance ratios to calculate the sample concentration. It measures the isotopes in the same sample, eliminating potential errors introduced by sample preparation.

The software uses the following equation to calculate the sample concentration:

$$c = Kx \frac{W (A' - pB')}{M (pB - A)}$$

Where:

- K = natural atomic weight of the element
atomic weight of the spike isotope
- W = weight of the isotopically enriched material added
- M = weight or volume of the sample
- a = element isotope of highest natural abundance
- b = highest abundance isotope in enriched isotope solution
- A, B = natural abundances of sample isotopes a and b
- A', B' = isotopic abundances of a and b in the spike
- p = ratio of isotope a to isotope b measured in the sample

If W is given in micrograms and M in grams, c is the concentration of the element in micrograms per gram by weight.

This technique does have some weaknesses:

- **Requires polyisotopic elements:** Because calculations are based on the ratio of one isotope to another in the same element, the element you are determining must have more than one isotope.
- **Requires certified enriched isotopic standards:** These standards can be expensive, especially those that deviate significantly from the normal isotopic abundance of the element.
- **Does not compensate for spectral interferences:** Although the technique compensates for interferences due to signal enhancements or suppressions, you must subtract a blank to compensate for spectral interferences.

Autodilution Methods

You can use an autodiluter with dilution methods, but be aware of the following issues:

- You can use an autodiluter only when running samples in batch mode.
- Batch mode analysis with more than one method in the batch: In order to use dilution positions sequentially, only the first method in the batch needs to have a rack position entered for the 1st Dil Pos field on the Method window Sampling tab. All methods that follow must have a zero in this field.
- When using internal standards, the diluent must contain internal standard elements at the same concentration as the blank, standards, and samples.
- To prevent uncontrolled mixing of sample and diluent within the dilution probe, the instrument introduces a small air bubble between the two liquids. Each sample is transferred to the dilution tube in quantities that are small enough to keep the air bubble confined within the tubing. The maximum and minimum amounts of sample that can be transferred in one pass is approximately 1.3 mL and 1.7 μ L, respectively. Thus, when small dilution factors are combined with large diluted sample volumes, several passes can be required to transfer sufficient sample to the dilution tube. In order to make a 50 mL diluted sample with a dilution factor of two, 25 mL of sample are needed—this would take 20 passes. Therefore, we recommend that you optimize the dilution factor and dilution volume to reduce multiple passes.
- The autodiluter performs successive dilutions in response to a quality control action until the out-of-limit condition [upper sample concentration, *Shutdown (S)*, or *Elemental Equation Error (EEE)*] is remedied.

Autodilution Controls

The following Method window Sampling tab controls apply specifically to autodilution method development:

- **Dil. Factor:** The system has been designed to operate typically with dilution factors ranging from 2 to 100, with the default set at 10. A dilution factor of **n** should lower the measured intensity by a factor of **n**.
- **Dil. to Vol.:** Specifies the volume of the diluted samples the autodiluter will create. This volume ranges from 2mL to 50 mL, with 10 mL being the default.
- **1st Dil. Pos:** Allows you to specify which tubes should be used when diluted samples are to be created. The first diluted sample will be created in the tube number corresponding to the value entered in the 1st Dil. Pos field, the second in the next higher numbered tube, and so on. To use dilution positions sequentially, only the first method in the batch must have a rack position entered for the 1st Dil. Pos field on the Method window Sampling tab. All methods that follow must have a zero in this field.
- **Probe Purge Pos:** Here you can specify that an empty tube be used for autodiluter initialization. In order to accurately measure the volumes of liquid involved in each dilution, the dilution probe and associated tubing must be full of diluent before any dilutions are done. Ten milliliters of diluent are pumped through the probe into the tube at the Probe Purge Position. The default value for this tube position is *10*.

If the autodiluter is to be under QC control, on the QC Sample tab, right-click in the **Action 1 and Action 2 columns** to view a menu of available actions. For analyte upper limit measurements, the menu item *Wash For X, Dilute, and Rerun Current* is available.

You can also dilute samples before measurement by right-clicking in the **Measurement Action** column on the **Sample window Batch tab** and choosing one of the following actions:

- ♦ *Run Diluted Sample*
- ♦ *Run Blank and Diluted Sample*
- ♦ *Run Stds. and Diluted Sample*
- ♦ *Run Blk, Stds. and Dil. Sample*

Note: The following solution types cannot be pre-diluted: spike, duplicate and dilution pairs, blanks, reagent blanks, calibration standards and QC standards.

Isotope Ratio Methods

This specialized technique enables measurement of the exact ratio of two isotopes of an element. It is a sensitive indicator of age, reaction, or metabolism in nuclear, geochemical, and biomedical applications.

With the Isotope Ratio technique, you compare the isotope of interest to a reference isotope of the same element. For example, you might compare the concentration of Pb204 to Pb206. Alternately, you can compare more than one isotope or all remaining isotopes of an element to your reference isotope, obtaining a ratio for each. For example, you could compare the ratio of Pb204 to Pb206, Pb204 to Pb207, and Pb204 to Pb208. The ratio is presented in the following format: **ratio = isotope of interest / reference isotope**.

Data Only Methods

The Data Only option supports the acquisition and reporting of raw or minimally processed mass spectral data from the instrument. You can apply external data processing routines to analyze your data, to selectively apply a minimum set of the processing routines, and to view and then reprocess the raw data using another analytical technique.

You should use the Data Only technique for advanced method development or when your sample set requires data processing using algorithms other than those supplied in the software processing set. Because the main purpose of the technique is the acquisition and reporting of raw data with minimal processing, it does not support the acquisition of standard solutions—only blank and sample solutions. No concentration calculations are performed as sample data is collected. The system does permit you to specify analytes using either a mass range or individual analyte setting for greater flexibility in defining acquisition than other techniques.

In addition to reporting the raw data, the technique permits you to select from a minimum set of data processing routines, including peak processing, signal profile smoothing, signal profile processing, elemental equations for interference correction, and blank subtraction.

DRC™ Method Development

DRC™ Method Development (DRC MD) incorporates a completely automated simultaneous determination of the DRC gas flows (cell gas A/B) and rejection parameter settings (RPq/RPa) for the isotopes of interest in a specific sample matrix type. The software automatically groups the isotopes according to cell gas flow. The Exclusion Threshold and Optimal Range Factor parameters affect the number of acceptable combinations of cell gas and RPq settings for each isotope. You can use the settings determined by DRC MD as a starting point whenever you add isotopes to existing methods or create methods for new applications. This is not a routine optimization and should be performed only in the initial stages of new method development.

Note: The method file used cannot contain more than 24 analytes for DRC method development. If the software detects more than 24 analytes, a message appears asking that you remove some masses from the method.

DRC™ Method Development Software Reference

DRC method development is centralized in a single window, with a Setup tab for parameter settings, and a corresponding Results tab which is populated following data acquisition or reprocessing.

Setup Tab

Use the Setup tab to configure the parameters you wish to optimize.

The screenshot shows the 'DRC Method Development' software window with the 'Setup' tab active. The window contains the following elements:

- Acquisition ID:** BLD
- Description:** Blood analyses -- baseline
- Range:**

		Start	End	Step
Cell Gas	Cell Gas A	0.1	1	0.1
Rejection Parameter	RPq	0.45	0.8	0.05
- Concentration:**

Analyte	Concentration (ppb)
Ca 39.9626	1
Fe 55.9349	1
Se 77.9173	1
Se 79.9165	1
- Autosampler:**

Procedure	A/S Loc.
Matrix (M)	1
Spiked Matrix (S)	2
- Use Manual Sampling (No Autosampler)
- Buttons:** Advanced..., Get Defaults, Optimize, Create Method..., Browse Datasets..., Reset, Close

DRC Method Development Setup tab

Items on the Setup Tab

Note: Before you begin DRC method development, verify that you have a dual detector calibration in the Optimization window Dual Detector Calibration tab. If not, you must open the SmartTune window, and run a Dual Detector Calibration.

- **Browse Datasets:** To select a pair of existing DRC method development dataset files for reprocessing, click **Browse Datasets**. Note that you must select a matching pair of matrix and spiked matrix files to run an optimization.
- **Acquisition ID:** Type a short identifier to be appended to the resulting dataset file names. This identifier will be appended to the beginning of the resulting dataset files for later identification (for example, the Acquisition ID *BloodBaseline* will result in a matrix dataset file name of *BloodBaseline (M).055* and a spiked matrix file name of *BloodBaseline (S).056*). In the **Description** field, type a meaningful description of the application or sample type being used.
- **Range Group:** Click the **Cell Gas** drop-down list and select an option (*cell gas A* or *cell gas B*). For the cell gas selected, the default Start, End, and Step values will be automatically populated; you can change these if desired.
- **Rejection Parameter:** Click the Rejection Parameters drop-down list and select an option (*RPa* or *RPq*). For the parameter type selected, the default Start, End, and Step values will be automatically populated; you can change these if desired. Note that typically only RPq is varied to determine the optimum DRC settings; RPa is generally set to zero. To reset the Start, End, and Step values to their default settings, click **Get Defaults**.
- **Advanced:** Click to access the Advanced Parameter Settings dialog box. Set the options to the desired settings, and then click OK.

In the **Fixed Parameters** group, enter a fixed value for the cell gas and rejection parameter not being optimized. Note that the RPa value generally remains set to zero.

In the **Exclusion Thresholds** group, enter sensitivity and BEC thresholds beyond which any single analyte should not be considered for grouping. These cells will appear white on the Results grid.

In the **Analyte Grouping** section, type an **Optimal Range Factor**. This value is used to expand the overlap region for analyte groups, as calculated by the software. A value of ≈ 1.3 is typical; a larger number will create a greater area of analyte overlap, and consequently may result in fewer cell gas groups. You can use the Exclusion Thresholds and Optimal Range Factor parameters to achieve the desired balance between fast throughput (fewer groups) and analytical performance.

Click **Get Defaults** if you wish to restore default system values for these settings.

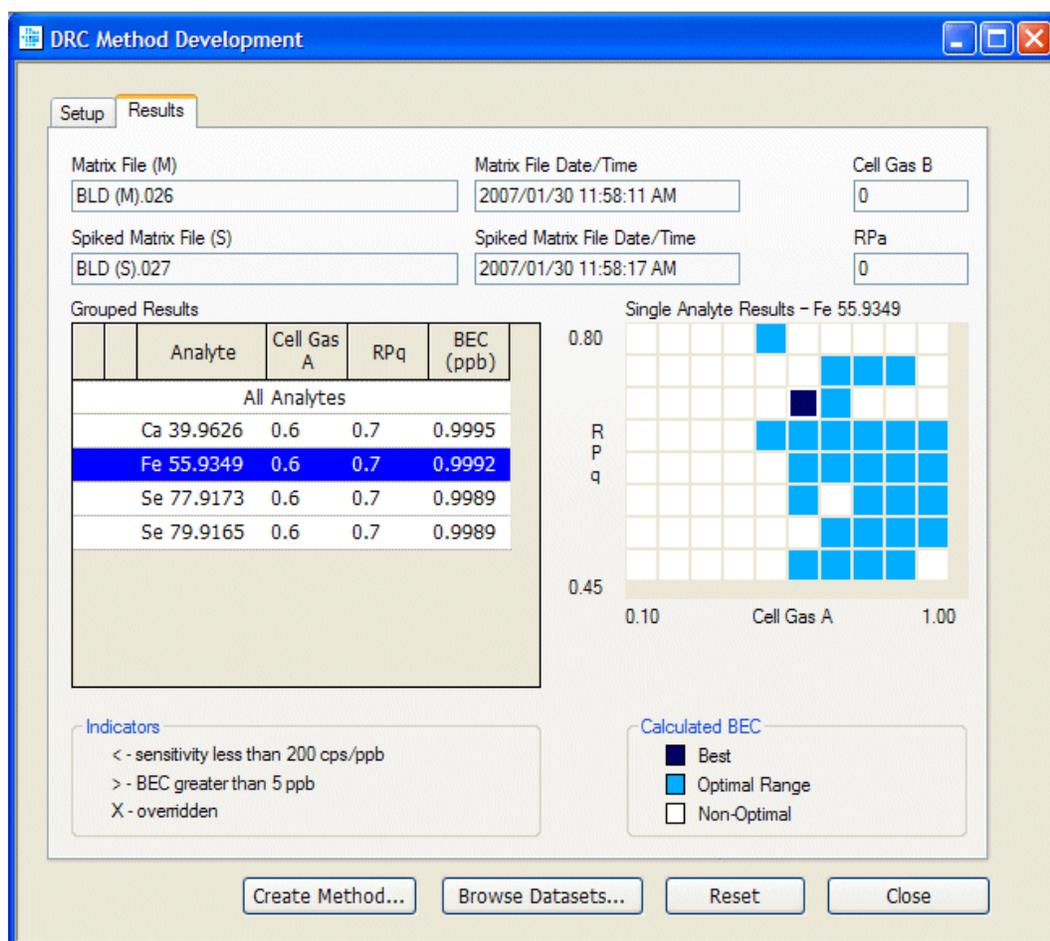
- **Concentration:** Type the concentration of each analyte added to the matrix solution to prepare the matrix spike (this may be different for each analyte).
- **Autosampler:** In the Autosampler group, the default autosampler locations for the matrix and spiked matrix are displayed. You can change these settings here if required. Enable the **Use Manual Sampling (No Autosampler)** check box if you do not plan to use an autosampler.
- **Optimize:** Click to initiate the two-parameter optimization. A Measurement Status window appears displaying the step-by-step progress of the optimization process. Wait for this process to finish. When the optimization is completed, the DRC Results tab appears for you to view the results of the optimization.

Note: If there are any corrections attached to the chosen method, a message will appear asking you to delete them. These corrections are not necessary for the optimization process. Click the Method window Equation tab, and manually clear any entries from the Corrections column.

- **Create Method:** Click when you are satisfied with the results, and then save the resulting Quantitative Analysis method file with a unique name.
- **Reset:** Click to clear the Setup and Results tabs before performing a new optimization.

Results Tab

When optimization is complete, the Results tab appears:



DRC Method Development Results tab

On the Results tab you can review the following information

- **Grouped Results table:** Click **All Analytes** to view analyte overlap results in the grid—the plot represents locations where the analytes’ optimal BEC ranges overlap. Hover your cursor over any cell in the grid to view the corresponding results. The Overlapping Optimal Ranges represent the analytes that have optimal ranges that fall in the same square or section of the grid.

Click any individual analyte listed to view the results for that analyte in the grid. The software determines which analytes can be grouped with the same cell gas flow. The

plot shows the selected best BEC for each analyte, as well as the optimal range based on the multiplier entered in the Advanced dialog box. The light- and dark-blue colored squares represent the points with good or optimal calculated BEC results based on the Exclusion Thresholds and Optimal Range Factor parameter settings. Hover your cursor over any cell in the grid to view the net intensity and BEC for that region.

Double-click any single analyte in the Analyte list to override any optimized settings, as desired.

- **Indicators:** This legend shows what mark appears in the Grouped Results table to alert you when none of the squares in the grid meet the specified threshold criteria.

Tip: If, after reviewing the results, you want to modify the parameters specified (such as the concentration levels, exclusion thresholds, or optimal range factor), return to the Setup tab, enter new concentration values, and click **Reprocess**.

To select a pair of existing DRC method development dataset files for reprocessing, click **Browse Datasets**. Note that you must select a matching pair of matrix and spiked matrix files to run an optimization.

Fundamentals of Data Acquisition

The instrument is comprised of two major components: an Inductively Coupled Plasma source for ion production and a Mass Spectrometer for ion detection and quantification.

For solution analyses, the sample is nebulized into the inductively coupled plasma. Within the plasma, the sample solvent is evaporated and a large percentage of the atoms are ionized by the energetic plasma environment. A fraction of these ions are captured in the interface region of the system and channeled into the mass spectrometer. The mass spectrometer serves as a mass filter and selectively transmits ions according to their mass-to-charge ratio. The ions are then captured by an electron multiplier and quantified by the pulse and analog stages of the dual detector assembly. The entire operation of sample introduction, ionization and detection is controlled and monitored by the system computer, which also generates the final reports on sample composition.

The inductively coupled plasma is usually employed as a means of dissociating sample solutions and generating excited atoms for atomic emission spectrometry. However, ICP is also an excellent ion generator. Under typical plasma conditions (~6000 °C), only a few elements in the periodic table are less than 90% ionized. In addition, the ICP is extremely efficient in the production of singly versus doubly charged ions. Only a few elements possess sufficiently low ionization potentials to permit generation of an appreciable quantity of doubly charged species, and even then, the relative percentage of doubly charged ions is typically less than 2%.

The ELAN® series of products use a classical quadrupole design mass spectrometer, operating in a vacuum of less than 1×10^{-5} torr, as the detection device. This mass analyzer generates a spectrum by linearly varying the RF and DC voltage amplitudes on the quadrupole rods. The mass of the ions that reach the detector is a linear function of the applied voltage. The entire mass range from 1 to 269 atomic mass units (amu) may be scanned in milliseconds. The software allows you to select scanning over the entire mass range, over a portion of the mass range, or scanning of only the individual masses of interest while intervening masses are skipped.

Mass Discrimination and Spectral Scanning

During a measurement, the instrument measures signal intensity by counting the rate at which ions of each mass reach the detector system. By skewing the charge conditions across the quadrupole rods, the mass spectrometer selectively passes ions through to the detector according to their mass-to-charge ratio. This mass filtering process is not conducted in discrete fashion, that is, the spectrometer actually passes ions distributed over a range of mass-to-charge ratio-varying from slightly below to slightly above the actual mass of interest.

The width of the range is determined by the resolution settings in the Tuning file. Generally, resolution is set to 0.7 atomic mass unit (amu) per mass, covering from half an amu below the actual mass to half an amu above the mass. Resolution is also individually adjustable by atomic mass, meaning that you can selectively narrow the range of masses to less than one amu to help compensate for spectral interferences. The primary consideration in narrowing the resolution for an individual mass is the reduction in the total counts, and therefore, the signal-to-noise ratio for that mass. If you set too narrow a resolution, you will adversely impact the precision of the acquired data.

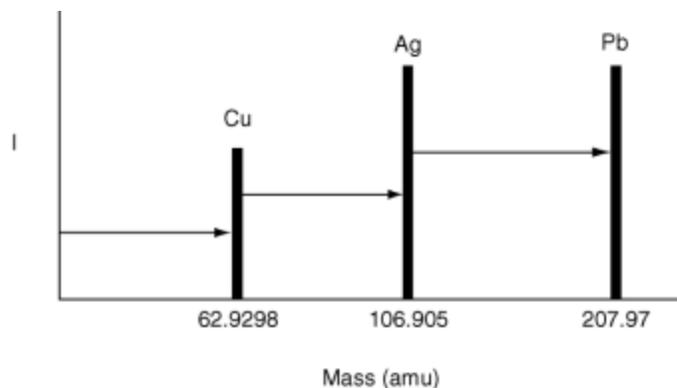
To this point, we have described operations that physically discriminate ions according to their mass-to-charge ratios. Mass discrimination defines a spectrum of intensity values. If you sampled all the possible data for each measurement you made, you would end up acquiring a vast amount of data. In any method, you instruct the instrument how to scan across this spectrum while acquiring only the data of importance to your analysis.

The software provides two different modes for acquiring mass spectral data during a determination:

- Peak hopping
- Scanning

Peak Hop Acquisition

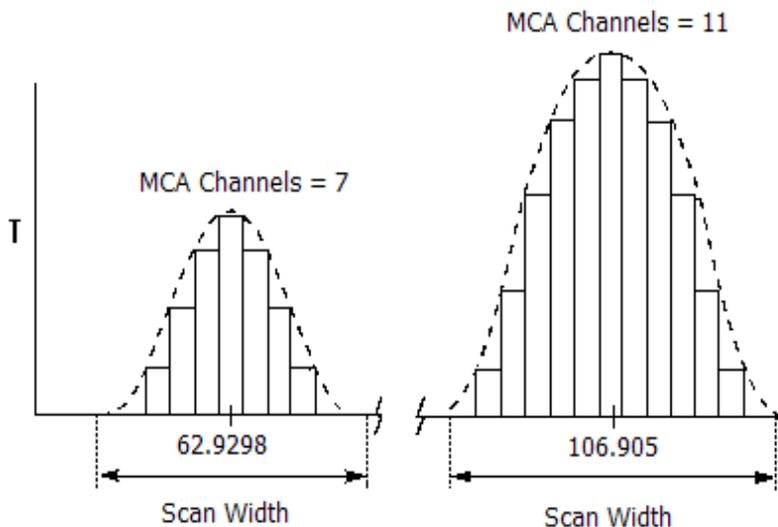
The most common method for ICP-MS data acquisition is peak hopping. In peak hop mode, the instrument measures the signal intensity at only the center point in the mass range defined for each element of interest. The spectrometer spends a specified amount of time, the *dwelt time*, measuring signal intensity at this point, and then *hops* to the next element in the method. The data from each measurement constitutes a reading. Multiple sweeps through the mass range can be set, with the data from each of the individual sweeps averaged into a single final value for each atomic mass.



Single Sweep Peak Hop Acquisition

Scanning: Data Acquisition

Acquiring a single point directly at each atomic mass of interest is the most time efficient means of acquiring data. However, this approach does not provide information about potential interferences from adjacent peaks. To more accurately characterize the mass spectrum and identify potential interferences during data acquisition, scanning is commonly employed. Scanning acquires data from multiple points in the mass range defined for the element being measured. The spectrometer *ramps* (steps incrementally) through the mass range, acquiring intensity data at each point. The number of data points acquired in the range is determined by the number of MCA channels, which can be set from 1 to 20, centered around the exact mass for the element being measured.

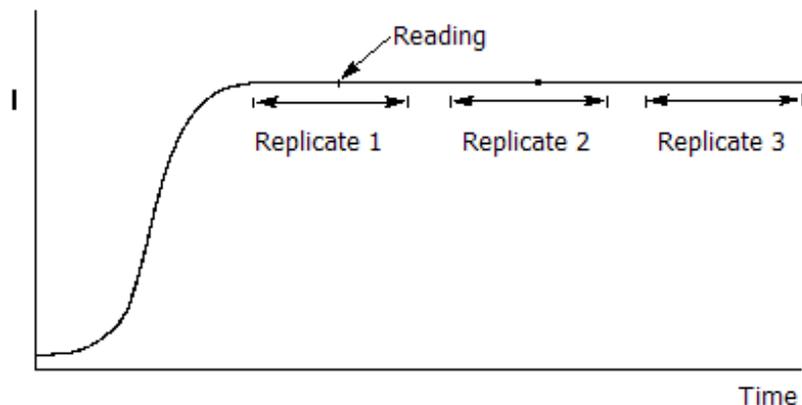


Scanning Data Acquisition

During scanning, because the total number of data points being acquired is larger, the time spent acquiring each point is shorter relative to the time spent during peak hop mode. The total time spent at each element is determined by the Dwell Time value. The time spent acquiring each individual data point is therefore the dwell time divided by the number of MCA channels being measured. As in Peak Hop mode, multiple Sweeps/Reading can be acquired to improve measurement precision.

Signal Profile and Scanning

In a traditional ICP-MS determination, the sample solution is continuously nebulized into the ICP torch during a measurement. As sample introduction begins, the signal strength gradually increases until the system reaches a steady-state condition at maximum signal intensity. At this point, the signal measurements are taken. Under steady-state conditions, the peak maximum can be measured at any time after the steady-state is achieved.



Steady State Signal

In the preceding illustration, one Reading/Replicate was used to collect several data points along the signal. Because the sample is continuously aspirated, the Readings parameter is typically set to one, as there is no reason for multiple sample injections.

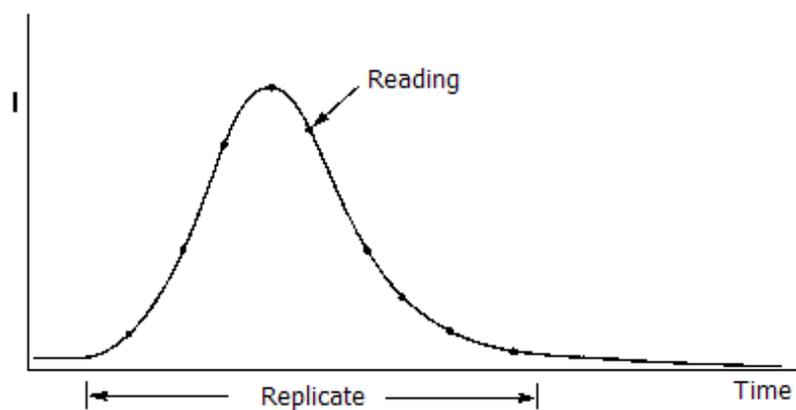
Although it is the most common, a peristaltic pump is only one of the sampling techniques used to continuously introduce sample into an instrument. Other commonly used techniques include:

- Electrothermal vaporization
- Flow injection
- Laser ablation

Both electrothermal vaporization and flow injection use transient signals.

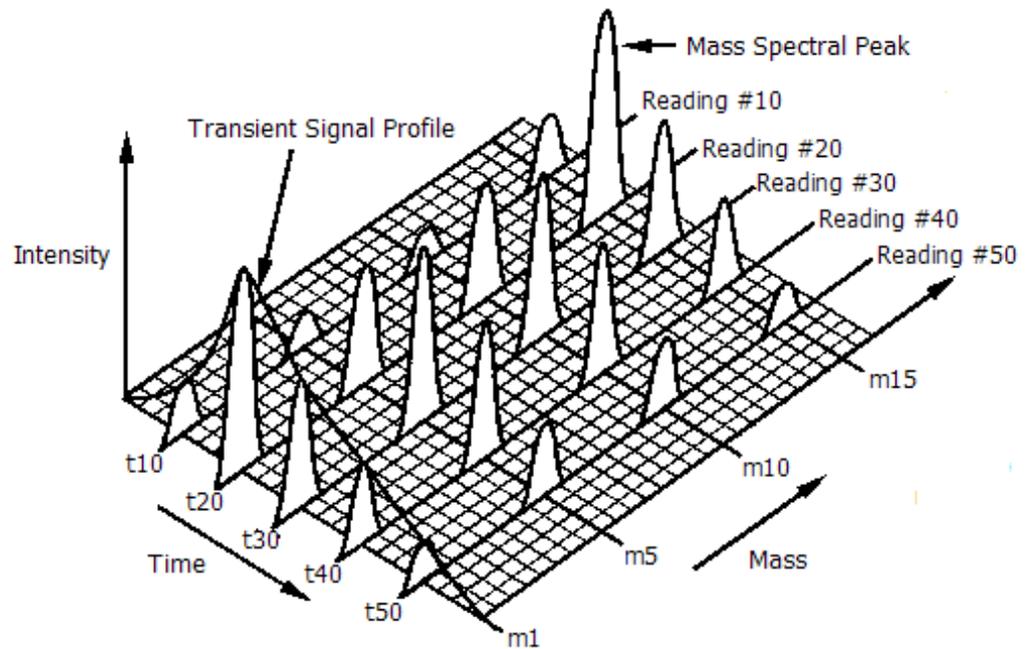
Transient Signal Processing

Electrothermal vaporization and flow injection introduce a discrete volume of sample into the ICP-MS system. In these situations, the signal intensity gradually increases to a maximum intensity, then decreases back to zero; this is termed a transient signal.



Transient Signal

For a transient signal, you must acquire enough readings to accurately profile the shape of the signal before it disappears. This means careful evaluation of the timing parameters, balancing Dwell Time, Sweeps/Reading, and Readings/Replicate to complete data acquisition in the available time. This is especially crucial if scanning is used.



Data processing in a transient analysis

Note: The signal profile is a representation of the composite mass spectral peaks—that is, behind each point along the signal profile is a set of mass spectral data.

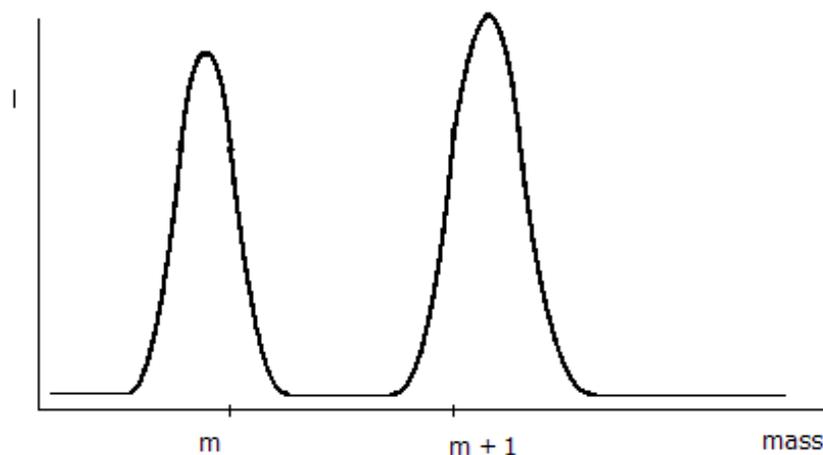
Data Processing

The raw data acquired during a determination must be processed before it is passed along for the analytical technique-specific calculations. Making the correct selections requires you to consider the mixture of the analytes, the sample matrix, instrument conditions and analytical requirements. The processing functions are divided into two broad classes:

- Functions used to process the mass spectral data
- Functions used to process the time-based signal profile

Spectral Peak Processing

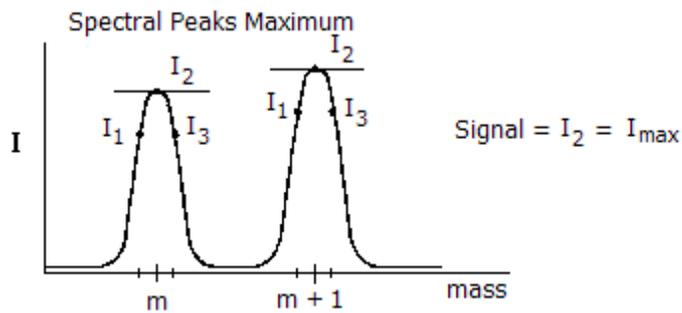
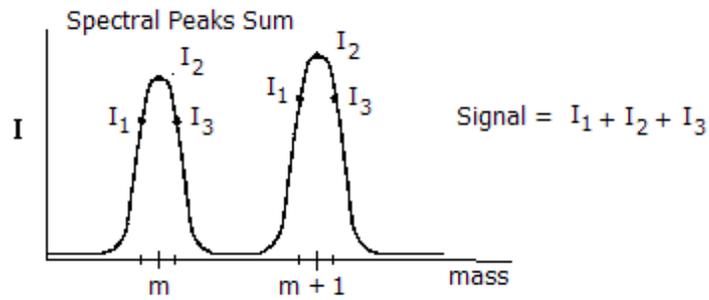
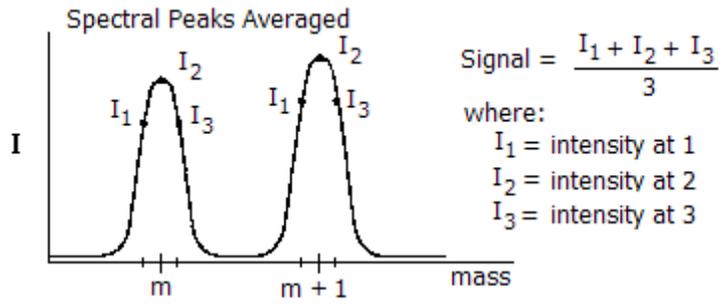
Mass spectral peaks are actually a set of individual data points whose spacing is based on the resolution and the number of points per peak.



Ion Intensity vs. Mass plot

The raw data for each mass is processed to produce a single value for that mass by using one of three algorithms: Average, Sum, or Maximum. The Average function calculates the average intensity value of the channels acquired for the mass. The Sum function is a mathematical summation of the individual intensity values in counts. The Maximum function determines the maximum intensity channel for each mass being determined.

To improve analytical precision, you can acquire more than one sweep through the mass spectrum for each reading. The spectral peaks from each sweep are summed to create the final reading. This reading is then plotted as a function of time to create the signal profile.



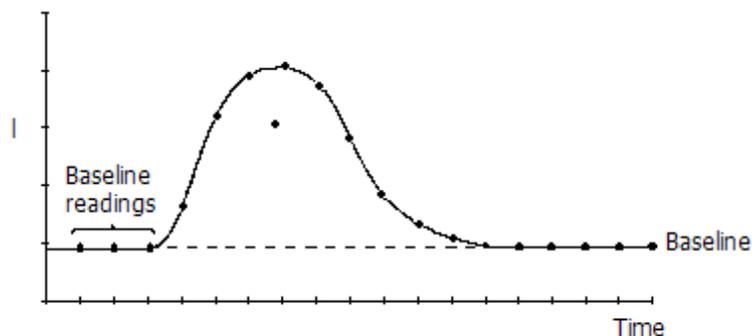
Mass Spectral Peaks

Signal Profile Processing

Following acquisition, the data consists of a series of intensity data readings plotted against time. This intensity versus time signal profile is processed to produce a final intensity value used in the analytical technique calculations. The software provides three options for processing the signal profile data: Average, Sum, and Maximum.

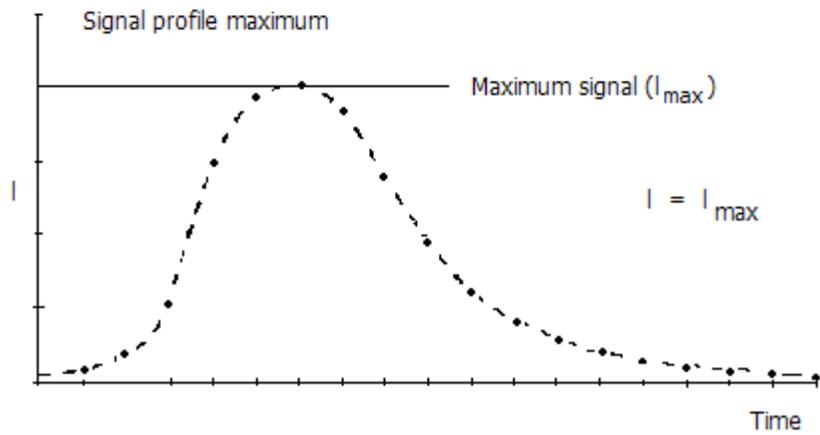
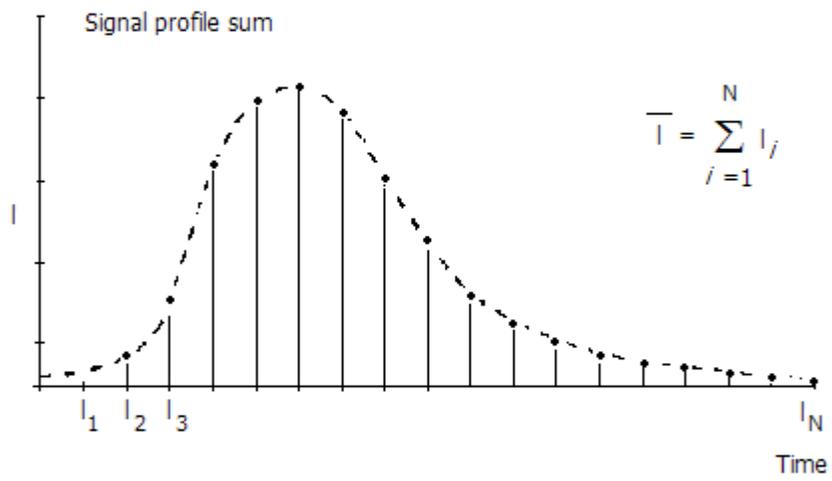
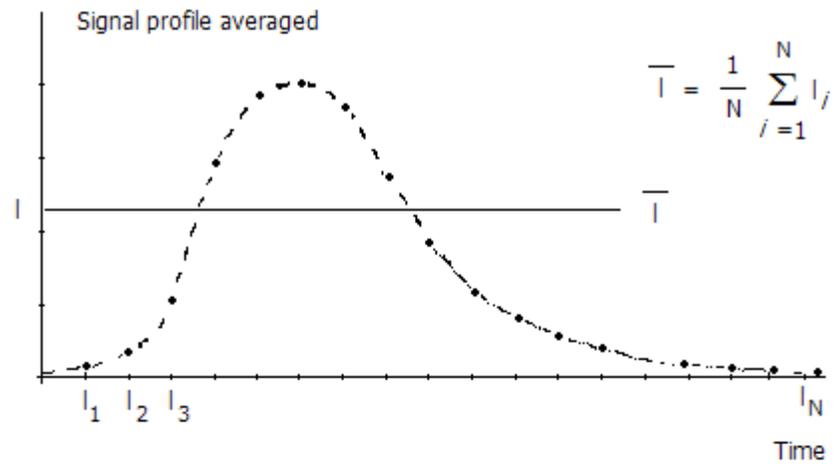
The Average function calculates the average intensity for all readings in a replicate. The Sum function calculates the total counts measured for all readings, a particularly useful option when a low number of readings per replicate have been specified. The Maximum option identifies the reading with the largest intensity value and selects it for use in further calculations.

In situations where the sample matrix causes a high background reading, greater precision may be achieved by adjusting the background level before performing signal profile processing. The Baseline Readings entry in the Process Signal Profile group is used to designate a specific number of readings at the start of each acquisition as background points. These readings are then used to set the baseline level for all subsequent readings.



Baseline Readings set to 3

Finally, for measurements with a low signal-to-noise level or in other cases where the signal profile readings are subject to baseline shift effects, the software permits you to smooth data before applying the signal profile processing algorithm. The Smooth Signal Profile option uses a Savitzky-Golay moving point average over a defined number of readings to reduce the effects of noise on the signal profile.



Signal Profile Data for an individual replicate

Fundamentals of Calibration

Calibration is a fundamental part of acquiring the best possible data from your instrument. In Quantitative Analysis, you calibrate the instrument by analyzing standards for all the elements you are interested in measuring. You analyze standards at different concentrations to ensure that instrument response is accurate across the range of concentrations you are likely to encounter during your determinations.

As you measure standard solutions, the software plots the measured intensity versus the concentration for each element in the standard solution. These individual calibration curves are updated as each subsequent standard is measured. The calibration curves can be viewed and edited using the Calibration window. If a point seems aberrant, that point can be removed and the curve recalculated. All calibration data can be stored and used for future determinations.

In a TotalQuant determination, the instrument uses stored response tables to correlate measured ion intensities with known concentration values. This internal response data indicates how many ions per second should be observed for a concentration of one milligram/Liter for each element in a sample. The response table takes into account variations in instrument sensitivity to different elements. However, changes in overall instrument sensitivity can occur from day to day. Because instrument sensitivity for all elements generally changes to the same degree, you can update the responses for all elements by measuring the responses for a few calibration elements.

Both Isotope Dilution and Isotope Ratio are effectively self-calibrating techniques. In Isotope Ratio, you compare the isotope of interest to a reference isotope of the same element. For example, you might measure Pb204 compared against Pb206. Because this ratio can be calculated from within a single sample measurement calibration is not required, although it is recommended to run a standard of known isotopic composition to verify that the instrument is not biasing the results due to mass discrimination.

One additional calibration technique, internal standardization, is commonly employed in methods. Internal standards allow you to correct for changes in instrument hardware response or for sample-to-sample variations in sensitivity. An internal standard is a non-analyte isotope that is added to the standards and samples before you analyze them. During the determination, the software uses the ratio of analyte and internal standard intensities to adjust the final analyte intensity values. Internal standards are used in both Quantitative Analysis and TotalQuant methods. Isotope Ratio methods use the principles of internal standardization as the basis for ratio measurement. Isotope Dilution measurements do not require internal standards.

Calibration in Quantitative Analysis

The instrument offers these methods of calibration in the Quantitative Analysis technique:

- External standardization
- Standard addition
- Addition calibration (as a variant of standard addition)

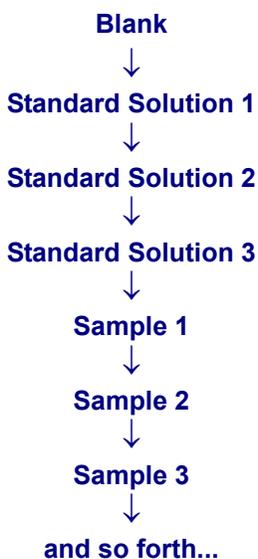
The method you select defines how you prepare and run your samples. The following descriptions should be used to help you select the calibration method best-suited to your analytical requirements.

External Standardization

For samples that are not subject to sample-specific matrix interferences that change the overall instrument sensitivity between measurement of the standards and samples, external standardization is a simple and effective way to calibrate your instrument.

External standardization involves measuring a blank solution followed by a set of standard solutions to create a calibration curve over the concentration range of interest. Typically, you run two or three standard solutions containing different concentrations of all the elements you are determining. Increasing the number of points on the calibration curve—that is, increasing the number of standard solutions—may improve accuracy in circumstances where the calibration range is very broad. However, it is seldom necessary to run more than five standard solutions. After the standards have been measured, you continue with the measurements of your unknowns.

The following figure summarizes the measurement procedure when using external standardization:

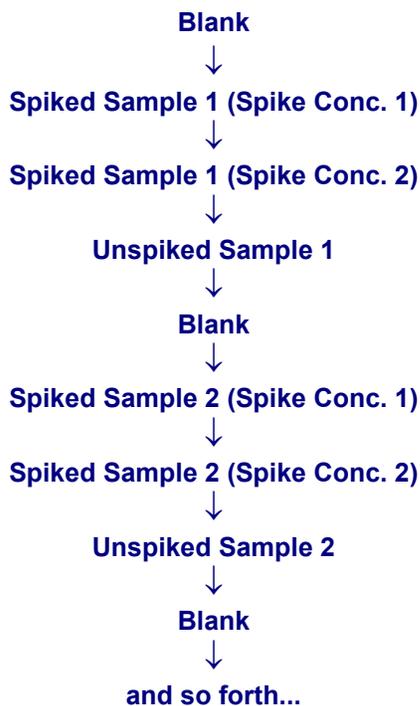


Standard Addition Calibration

Standard addition calibration provides an effective way to minimize sample-specific matrix effects through the use of spiked samples.

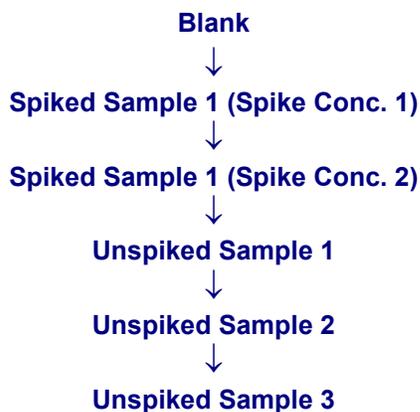
In standard addition calibration, you first measure a blank solution. Next, you measure the sample solution *spiked* with a known concentration of each element you want to determine. The software measures the response for the spiked samples and creates a calibration curve for each element for which a spike has been added. This curve is based on the known concentration values which you entered. The calibration curve plots the measured intensity of each spike element against its concentration. Based on the slope of the calibration curves, the software can determine the unspiked concentration of the analytes in your unknown. After creating the calibration curve, you run your unspiked sample solution.

The following figure summarizes the measurement procedure when using standard addition calibration:



Addition Calibration

Addition calibration is a variant of standard addition. It is used when all samples have a similar matrix. The following figure summarizes the measurement procedure when using standard addition calibration:



Calibration in TotalQuant™ Methods

The software uses response tables to correlate measured ion intensities with known concentration values. The data in these tables can be updated by calibrating the instrument. You can calibrate the full mass range using just a few calibration solutions.

Two response tables are supplied with the software: ELAN.rsp and current.rsp. The ELAN.rsp table contains reference response data for the instrument. When you perform a calibration, changes to the response table are automatically saved in the file current.rsp. Response tables can be saved under a user-defined name so that you can recall them for future determinations on similar samples.

The software offers two methods for updating the internal response data:

- External calibration
- Sample addition calibration

External Calibration

Use external calibration when you are interested in a few specific elements or when you are running a large number of samples of simple composition with little sensitivity variation between samples. By updating the calibration of the elements you are most concerned with, you ensure that the instrument measures those elements with the highest accuracy possible. Although it is typical to use three to six elements for external calibration, the software permits calibration using up to 100 elements. The more elements you use, the more accurate your results will be.

Using external calibration, you measure a blank, then a calibration solution containing known quantities of specific elements prior to measuring your unknowns. You identify the elements in the calibration solution and their concentrations into the software.

The software determines the intensities for each of the calibration elements and the software calculates the response based on the concentrations you have specified. It then adjusts the response factors in the response table for all elements in proportion to the calibration elements.

For example, using cobalt and rhodium in the calibration solution, the software finds the response for cobalt at mass 59 to be 5% greater than the internally recorded response and the response for rhodium at mass 103 to be 15% greater. It adjusts these elements by 5% and 15% respectively. For other elements that have isotopes between cobalt and rhodium, the adjustment is based on the relative mass difference between the measured analyte and the calibration elements. The adjustment value for an individual element (**c**) is calculated as follows:

Adjustment = a + [(b-a) * (c-d) / (e-d)] where:

a = % difference for calibration element with lower mass

b = % difference for calibration element with higher mass

c = mass of element

d = mass of lower calibration element

e = mass of higher calibration element

For example, the adjustment for arsenic at mass 75 is:

Adjustment = 5 + [(15-5) * (75-59)/(103-59)] = 8.6%

For the most accurate results for all detectable elements, use a calibration solution that contains five or six elements from a wide mass range, with the elements concentrated at the lower masses. This provides reference points for adjustments across the entire spectrum. A typical calibration solution might contain 1µg/L of Li, Mg, Co, In, Tb, and Pb.

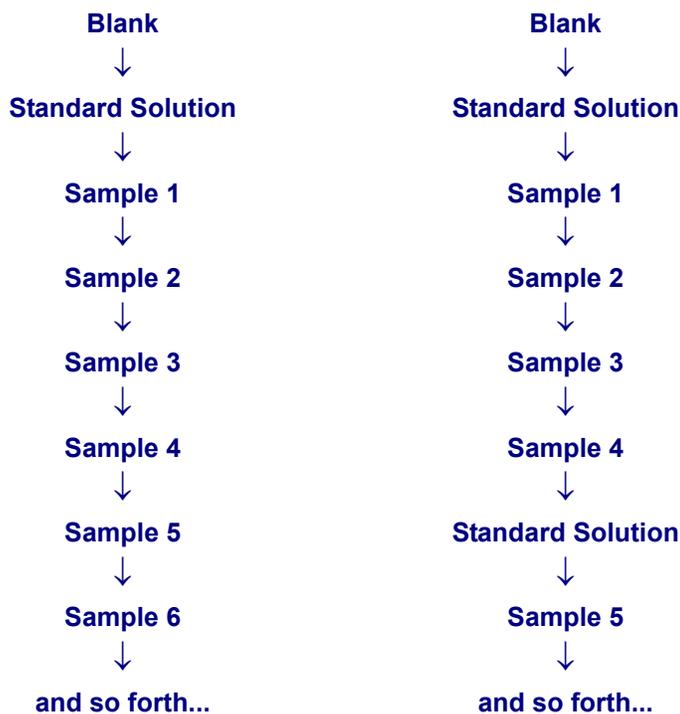
You can measure your standard solution once during a determination, after measuring the blank, or periodically during the determination, as shown in the following figure. The protocol on the right could be applied to correct for time-dependent drift in response or to re-standardize between groups of samples with dissimilar matrices.

When you change the software's internal response data through external calibration, the changes remain in effect until you update the response data again. That means the updated response information will be used for all subsequent samples until you perform another external calibration or load a new calibration file that has been stored in memory.

Sample Addition Calibration

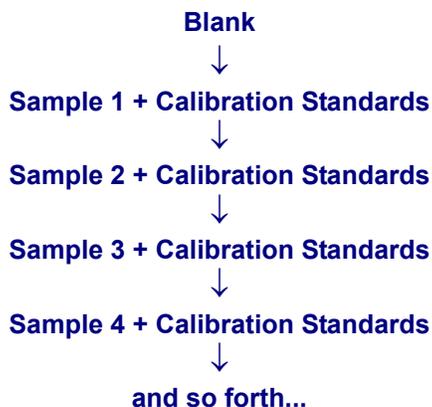
Sample addition calibration corrects for sensitivity changes that are specific to each individual sample. If you expect the physical or chemical characteristics of individual samples to affect instrument sensitivity, use sample addition calibration. For example, if a sample has a high concentration of ions, instrument sensitivity will not be accurate because the high ion concentration alters the readings for all ions in the sample.

By performing a sample addition calibration, you ensure the highest possible accuracy for each sample in your analysis.



Sample addition calibration involves adding known quantities of specific elements to your unknown sample before measuring it, or requires that you know the concentration of some elements in the sample. If you are adding elements, the elements you add must not already be present in significant quantities in the unknown. As with external calibration, you identify the elements that you are adding or the elements that you know the concentrations

of, identifying the concentrations for each of these elements. The software calculates the response data based on the concentrations you specify. It then adjusts the internal response data for all remaining analytes relative to the calibration elements.



When you modify the software's internal response data using sample addition calibration, the changes remain in effect for the individual sample only. However, the response data can be saved for later use. You can correct any sensitivity drift that may occur during a determination by measuring each sample using sample addition calibration. However, because you have to add calibration elements to each sample you measure, this technique can be time-consuming. Generally, sample addition calibration is only applicable when performing determinations on complex samples of unknown concentration.

Internal Standards

An internal standard is a non-analyte isotope added to standards and samples before a determination. Internal standards allow you to correct for changes in instrument hardware response or for sample-to-sample variations in sensitivity.

The implementation protocol for internal standards varies according to the analytical technique in which it is used. For Quantitative Analysis methods, the Internal Standard entry clusters elements with similar ICP-MS response characteristics into a standard group, then specifies which element within the group will serve as the standard or reference isotope. The software assumes that all elements within the standard group are similarly affected by instrument drift or matrix interferences. Therefore, changes in the measured intensity of the internal standard are used to create the ratios for correcting measured intensities of the analytes.

For example, during the measurement of Pb in water, you must account for the effect of salinity. High Na concentrations typically result in a matrix interference. For these measurements, Bi (mass 209) can be used as an internal standard to correct the measured intensities of Pb (mass 208).

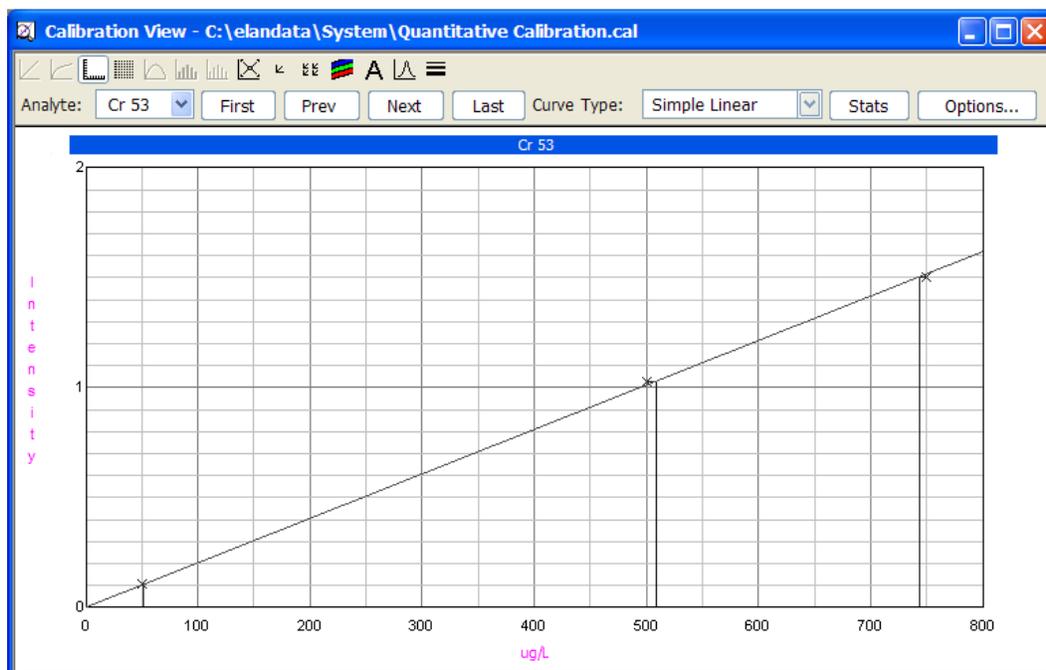
Quantitative Analysis Internal Standard Example

	Tl	Pb	Bi
Standard Solution			
Intensity	4.078	6.117	2.039
Sample Solution			
Measured Intensity	4.820	6.234	1.78
Adjusted Intensity	5.521	7.141	

For TotalQuant determinations, the internal standard function is similar in purpose, but somewhat different in implementation. A TotalQuant internal standard is used to continuously compensate for instrument drift or for interferences for a defined mass range. If you use a single internal standard, it is used to cover all the masses selected for the determination. You can also define more than one internal standard which is valuable when conducting measurements over a large mass range. When multiple internal standards are used, the software interpolates any resulting adjustment to intensity values according to the distance in mass between the analyte and the nearest internal standard element.

Calibration View Window

Use the Calibration View window for post-acquisition viewing and interpretation of calibration curves generated from measurement of your standard solutions. The Calibration View window allows you to evaluate the quality of the calibration by viewing both the graphic plot of the calibration points and reviewing statistical information on the curve fit. You can also evaluate the effect of eliminating individual calibration points or of inserting recalculated calibration data.



Calibration View window

Items on the Calibration View window

The following controls are available on this window:

- **Graphics Display Toolbar:** This toolbar controls display and printing parameters for the graphs shown in the window
- **Analyte:** Select the isotope for which you want to view calibration data
- **First/Prev/Next/Last:** Use these buttons to view calibration data for the first, previous, next, or last analyte
- **Curve Type:** Select the algorithm used to calculate the calibration line. The options are *Simple Linear*, *Linear Through Zero*, and *Weighted Linear*

- **Stats:** Click this button to view statistical data on the quality of the calibration fit, such as a correlation co-efficient. When you toggle a point out of the calibration calculations, the statistics are automatically updated to reflect the change
- **Options:** Click this button to change the range of the X- and Y-axes. Select **Display Apparent Concentration** in this dialog box to show the analyte concentration of each point on the calibration curve

Method Window Software Reference

All method development takes place within the Method window sections of the software. Here you can describe the analytes you want to measure during a determination and set the data acquisition, processing, and calibration information that will be used to control the determination. The Method window is also used to specify any quality control checks that will be employed during automated quantitative analysis determinations.

Method Window Tabs

There are nine tabs used by all of the analytical methods. The Devices and QC (quality control) tabs have further sub-tabs accessed from within each.

- **Timing:** Specifies the isotopes and/or mass ranges that you want to measure and defines the parameters used to control the acquisition of data from the mass spectrometer, including the amount of time for measuring each isotope in the sample and how many times to repeat each measurement.
- **Processing:** Specifies which detector system will be used in the determination and defines how the software will manage the processing of the raw signal data.
- **Equation:** Defines the equations used to correct for interferences in your determinations.
- **Calibration:** Specifies the compositions of the standard solutions, including any internal standards, and defines the calibration type to be used for quantitative calculations.
- **Sampling:** Describes the type of sampling system to be used for sample introduction and specifies the peristaltic pump speed setting to introduce sample solution to the instrument. Also contains read delay and pump speeds for the blanks and standards.
- **Devices:** Specifies the sample introduction control program for various sampling systems. Each system has its own sub-tabs: for example, the FIAS™ option specifies the sample introduction control program when using a flow injection sampling system. Only accessible when specified in the Sampling field on the Sampling tab.
- **QC:** Specifies the quality control functionality. The QC parameters are used to check on the data acquisition quality and to flag out-of-range results during automated quantitative analysis measurements.
- **Report:** Specifies the report options template that will be used for creating reports and defines the destination for the report output (printer, file, or serial port). This tab is located on the right side of the Method window.
- **Notes:** Used to enter notes about the analytical method. This tab is located on the right side of the Method window.

Timing Tab

Use this tab to specify the isotopes or range of isotopes to look for in your samples. You also use this tab to identify the internal standards within the sample, adjust the analysis time spent on an individual element and to specify the Tuning and Optimization files to use during determinations.

Note: In software version 3.0 or higher, reaction cell parameters are stored directly in the Method file to simplify the transferability of methods. As a result, for most applications, the Default.dac file can be selected in the method timing table. During data acquisition, the reaction cell parameters in the Timing tab are used. The reaction cell parameters in the Optimization window are no longer used during data acquisition, except for optimization. During optimization, the cell parameters corresponding to the analyte in the Auto Optimize tab are applied.

	Int Std	Analyte (*)	Mass (amu)	Scan Mode (*)	MCA Channels	Dwell Time per AMU (ms)	Integration Time (ms)	Corrections	Cell Gas A	Cell Gas B	RP a	RP q	Mode
1		Mg	23.985	Peak Hopping	1	50	3000		0	0	0	0.25	Standard
2		In	114.904	Peak Hopping	1	50	3000		0	0	0	0.25	Standard
3		U	238.05	Peak Hopping	1	50	3000		0	0	0	0.25	Standard
4		Ce	139.905	Peak Hopping	1	50	3000		0	0	0	0.25	Standard
5		CeO	155.9	Peak Hopping	1	100	6000		0	0	0	0.25	Standard
6		Ba	137.905	Peak Hopping	1	50	3000	La, Ce	0	0	0	0.25	Standard
7		Ba++	68.9525	Peak Hopping	1	100	6000		0	0	0	0.25	Standard
8		Bkgd	220	Peak Hopping	1	100	6000		0	0	0	0.25	Standard
9		Bkgd	8.5	Peak Hopping	1	100	6000		0	0	0	0.25	Standard
10													
11													

Method Window Timing tab

Timing Tab Controls

- **Sweeps/Reading:** This entry determines the number of sweeps through the mass spectrum that will be averaged to yield each data point (reading). The acceptable range of values is from 1 to 1000. The default value is 1. A sweep is counted each time that the instrument scans from the lowest to the highest mass specified in the table on the Timing tab. The software averages the results of multiple sweeps and saves this average as the data for one reading. A series of consecutive readings constitute a replicate. Increasing the number of sweeps/reading is one way to increase analytical precision. However, with transient signals, you will typically use one sweep/reading and multiple readings/replicate to measure several elements in a sample.
- **Readings/Replicate:** This entry defines how many individual readings will be acquired during the course of a single sample injection (for a transient signal) or during the course of a steady-state determination. The acceptable range of values is from 1 to 25000. The default value is 1. The Readings/Replicate entry is especially important during determinations with transient signals. To create an accurate picture of the shape of the transient profile depends on selecting an appropriate number of

readings. Selecting too few readings will lead to a poorly shaped peak that does not accurately portray the true data signal. Selecting too many readings results in excessive total analysis time and very large data files. The optimum number of Readings/Replicate with transient signals is partially dependent on the sample technique being employed. With a FIAS measurement, a 30-second peak might require 25 to 50 Readings/Replicate in peak hop mode. During steady-state determinations, the signal profile is approximately constant once steady-state conditions are achieved, and one Reading/Replicate can satisfactorily define signal intensity.

- **Replicates:** Determines the number of times the instrument will repeat a measurement for an individual sample. This entry is typically set between 1 and 3. When performing a determination with a transient signal, this value corresponds to the number of repeat sample injections. The acceptable range of values is between 1 and 1000. The default value is 1.
- **Est. Reading Time:** Displays an estimate of the time required to complete each reading, based on the current timing parameters set in the table and the value entered for the number of Sweeps/Reading. The values in this field are read-only. The calculation of estimated time is updated whenever a change is made to the Sweeps/Reading or Dwell Time entry, as soon as you click in another entry on the tab.

Note: *DRC series instruments*

If one or more elements is defined in Standard mode and one or more in DRC mode, the estimate reflects the estimated time required to complete all readings. This is an estimate because of delays required for gas flow changes and is therefore unavailable if two or more modes are required in the method. The delay time between flow rate changes will be significant (that is, tens of seconds). Short settling times are permitted in Standard mode only.

- **Est. Replicate Time:** Displays the total time required to measure a single replicate, based on the timing parameters set in the table and the values for the Sweeps/Reading and Readings/Replicate. The values in this field are read-only. The calculation of estimated time is updated whenever a change is made to the Readings/Replicate, Sweeps/Reading, or Dwell Time entry, as soon as you click in another entry on the tab.

Note: *DRC series instruments*

If one or more elements is defined in Standard mode and one or more in DRC mode, the estimate reflects the estimated time required to complete all replicates. This is an estimate because of delays required for gas flow changes and is therefore unavailable if two or more modes are required in the method. The delay time between flow rate changes will be significant (that is, tens of seconds). Short settling times are permitted in Standard mode only.

- **Est. Sample Time:** Displays an estimate of the total time to analyze a single sample based on the current timing parameters set in the table and the values for the Sweeps/Reading, Readings/Replicate, and Replicates entries. The values in this field are read-only. The calculation of estimated time is updated whenever a change is made to the Replicates, Readings/Replicate, Sweeps/Reading, or Dwell Time as soon as you click in another entry on the tab.

Note: *DRC series instruments*

The calculation of estimated time is also updated whenever a change is made to the Cell Gas A and Cell Gas B entries.

- **Tuning File:** Specifies the name of the tuning file used to calibrate the instrument during determinations made with the method. Every method must have a tuning file specified. The default file is default.tun.
- **Enable QC Checking:** Activates the quality control functions. The software includes a comprehensive set of quality control checks for verifying data integrity when performing quantitative analysis measurements. This option is available for Quantitative Analysis methods only.
- **Optimization File:** Specifies the name of the optimization file that will be used during determinations made with the method. The optimization file contains important hardware settings for your instrument, including nebulizer flow, ICP power, and dual detector calibration information. Every method must have an optimization file specified. The default file is default.dac.
- **Get Cell Parameters:** *DRC series instruments only.* Click this button to copy the Cell Gas A, Cell Gas B, RPa, and RPq parameters from the Optimization window Cell Parameters tab into the Method Timing table. You can also edit these columns in the Method Timing table.

Timing Table: Quantitative Analysis

The Timing Table is used to identify the isotopes that you want to measure during your determinations along with details of the measurement timing conditions. This table must include at least one Analyte entry and its associated measurement specifications.

When completing the table, a set of default parameters is automatically filled in once you specify an Analyte. These default parameters provide a standard starting point for developing a method. The conditions should provide reasonable data, permitting you to analyze the results and determine what type of modifications are required to yield the best possible data on your specific sample system.

You can sort the analytes in the Timing table by mass or analyte name in either ascending or descending order by selecting a Sort option from the Edit menu.

DRC series instruments:

Groups can be sorted by selecting Sort and then Gas Flows Ascending from the Edit menu. If Gas Flows Ascending and another sort option are selected (that is, Mass Descending or Analyte Ascending), the analytes will be sorted within the group. If Gas Flows Ascending is not selected, sorting occurs on the entire spreadsheet. Analytes in the Timing table with the same Cell Gas A, Cell Gas B (optional), Rejection Parameter a (RPa) and Rejection Parameter q (RPq) are grouped together. These values are specified on the Optimization window Cell Parameters tab.

Quantitative Analysis Table

- **Internal Standard:** Lists the standard groups and internal standards that have been defined in the method.
- **Analyte (*):** Specifies the element and/or isotope that the instrument will determine in each measurement. Valid entries include the atomic symbols for all naturally occurring elements, and the atomic symbol followed by “++”, such as Ca++, which acquires data for the most abundant isotope, but at half the listed mass. Molecular names for polyatomic species, such as ClO and ArN are also valid entries. If you enter only the atomic symbol, the system defaults to the exact mass for the most abundant isotope (except for Ca, Ti, Ni, Zn, Cd, and Sn). For example, if you type Pb, the system will enter 207.977 in the Mass column. You may also enter the atomic symbol followed by the specific isotope of interest. For example, if you type Pb206, the system will enter 205.975 for the mass.

- **Mass (amu):** Specifies the mass at which the isotope will be measured. This entry normally does not need to be made, because the system automatically fills in a mass setting based on the analyte specified. If the Scan Mode is set to Scanning, this entry represents the center of the measured peak.
- **Scan Mode (*):** Specifies whether the system will use either peak hop data acquisition or peak scanning. Two options are available:
 - ♦ *Peak Hopping:* The instrument acquires data at the specified mass only, then jumps directly to the mass for the next analyte in the method. Peak hopping allows you to spend more time at each mass. This usually helps to reduce the number of sweeps / reading that are required to achieve satisfactory precision.
 - ♦ *Scanning:* The instrument acquires data at a number of data points around the specified mass, based on the value of the MCA Channels entry.
- **MCA Channels:** Determines the number of multichannel analyzer channels that are assigned to an analyte when using scanning mode. The MCA Channels setting is always 1 when using peak hopping. Valid entries are between 1 and 20 for scanning. The default value is 1. Spectra are scanned by rapidly and repetitively sweeping the quadrupole across all of the channels within the mass range set by the Analyte/Mass entries. During each sweep, the spectrometer acquires data for a length of time determined by the dwell time, and the ion count rate is measured and stored in an MCA channel buffer. The use of a multichannel analyzer permits enhanced analytical precision by permitting rapid scanning of the defined mass range, with all elements measured closely to one another in time.
- **Dwell Time per AMU (ms):** Determines the length of time spent measuring the analyte during a single sweep. The Dwell Time per AMU is the total time spent at the mass range corresponding to the individual analyte listed. If more than one MCA channel is being used, this time is divided by the number of MCA channels to determine the length of time spent at each MCA channel. The acceptable range of settings is between 0.1 and 1800000. The default setting is 100 in both peak hop and scanning modes. The Dwell Time per AMU setting applies only to the individual analyte listed in the same row of the table. The optimum dwell time setting depends upon your analysis conditions and your sample. Typical dwell time values for peak hopping are between 20 and 100 ms using multiple sweeps per reading for a total integration time of 1000 ms. A longer dwell time measures the analyte more precisely at the expense of total analysis time. The use of shorter dwell times is recommended only for transient analysis when determining a large number of analytes. However, attempting to determine too many analytes using very short dwell times in a short-duration transient signal will adversely affect accuracy and precision.

Note: *DRC series instruments*

For analytes that are in DRC mode with a Rejection Parameter a (RPa) value of 0, the minimum dwell time is automatically raised to 10 ms. If an analyte is in DRC mode and the RPa value is not 0, the minimum dwell time is automatically raised to 33 ms. If an analyte's flow rate or RPa value is changed, putting the analyte in DRC mode, and the dwell time becomes invalid, the dwell time will be automatically changed by the software.

- **Integration Time (ms):** Displays the total amount of time that the analyte listed in the same row of the table will be measured during one replicate, based on the setting for Dwell Time per AMU, Sweeps/Reading, and Readings/Replicate as follows:

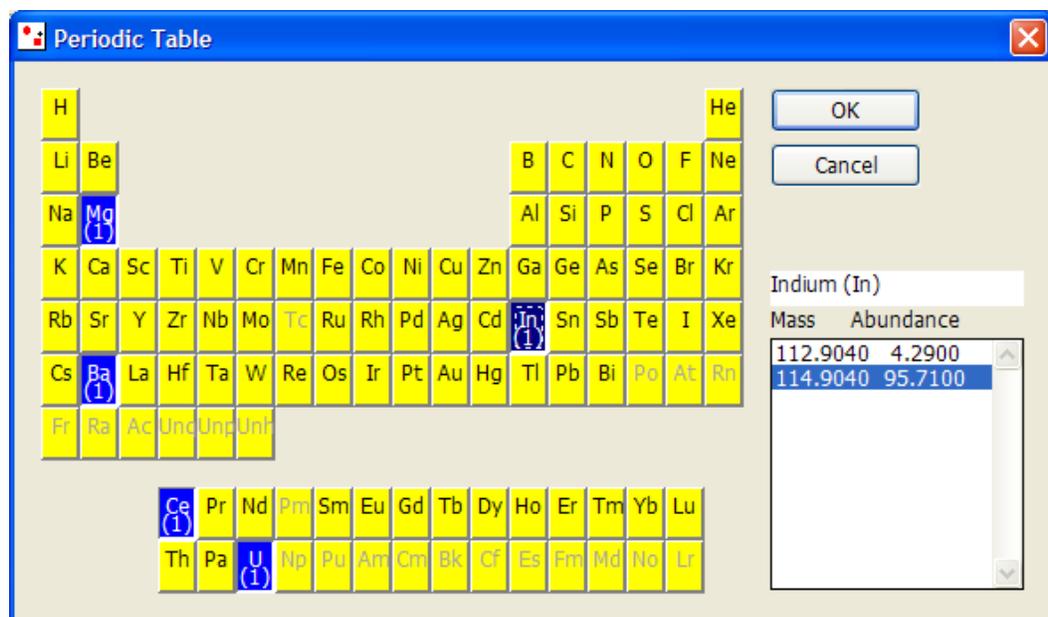
$$\text{Integration Time} = \text{Dwell Time} * \text{Sweeps/Reading} * \text{Readings/Replicate}$$

This is a read-only entry and is designed to permit a quick assessment of the time the quadrupole will spend measuring the individual analyte.

- **Corrections:** This entry is used for all methods except TotalQuant analyses. Shows that inter element or polyatomic ion corrections are being applied to this analyte. The interferent species used in the correction is listed in this entry.
- **Cell Gas A:** (*DRC series only*) Displays the flow rate for the reaction gas as specified in the Optimization window Cell Parameters tab. The default value is 0.
- **Cell Gas B:** (*DRC series only*) Displays the flow rate for the reaction gas as specified in the Optimization window Cell Parameters tab. The default value is 0.
- **RPa (Rejection Parameter a):** (*DRC series only*) Displays the RPa voltage for all the analytes as specified in the Optimization window Cell Parameters tab. The default value is 0.
- **RPq (Rejection Parameter q):** (*DRC series only*) Displays the RPq voltage for all the analytes as specified in the Optimization window Cell Parameters tab. The default value is 0.25
- **Mode:** (*DRC series only*) This entry is read-only. It displays the mode (Standard or DRC mode) in which the instrument is working. The mode also appears in the Status bar at the bottom of the tab. If Cell Gas A or B is 0, the instrument is in Standard mode. If either Cell Gas A or B is above 0.08 ml/min, the instrument is in DRC mode.

Periodic Table Dialog Box

Use this dialog box to select analytes from a graphical display of the Periodic Table of elements.



Periodic Table dialog box

The analyte buttons in the Periodic Table dialog box can assume one of several states depending on whether the analyte has been selected for the method and whether the analyte is currently *in focus* in the dialog box.

Periodic Table button states

Selected	Text color	Button color	Button state	Dotted box
No	Black	Yellow	Up	No
Yes	White	Bright blue	Down	No
Yes	White	Dark blue	Down	Yes

Timing Table: TotalQuant™ Methods

The Timing tab includes a table that is used to identify the isotopes or mass range that you want to measure during your determinations. This table must include at least one Begin Mass/End Mass entry and its associated measurement specifications. When completing the table, a set of default parameters is automatically filled in once you specify a beginning and end mass range. These default parameters provide a standard starting point for developing a method. The conditions should provide reasonable data, permitting you to analyze the results and define what type of modifications are required to yield the best possible data on your specific sample system.

The following entries are included in the TotalQuant Timing table:

- **Internal Standard:** Lists the internal standards that have been defined in the method. When using internal standards with TotalQuant methods, these entries are used to calibrate the TotalQuant response table for optimal accuracy during analytical measurements.
- **Begin Mass (amu):** Defines the start of an atomic mass range for each measurement. The scanning range defined by a single row in the table is the range between the Begin Mass and End Mass values set in that specific row. The total mass range that the instrument will scan during an individual replicate is defined by all the entries in the table. Valid entries are between 1 and 270 amu. To enter a Begin Mass value, click in the desired cell in the table and type the value that you want to use. In TotalQuant analyses, detectable isotopes for the naturally occurring elements range from mass 6 (Li) to mass 238 (U). Because TotalQuant methods use all the information available in the mass range, you must gather data over the entire mass range that provides useful information in your specific samples. The following additional rules should be observed when setting Begin Mass and End Mass values:
 - ♦ Because of the large amount of oxygen present in solution samples, the measured intensities for the oxygen isotopes (16, 17, 18) are usually beyond the working range of the instrument. It is generally best to avoid acquiring data in this mass range, unless you are working with laser sampling or other techniques that do not introduce water vapor into the mass spectrometer.
 - ♦ Exclude masses 40 and 41 from the detection range. These masses represent ^{40}Ar and ^{41}ArH , both of which are present in concentrations beyond the working range of the instrument.
 - ♦ It is not usually necessary to collect data for masses above 209, except for masses 232 to 238 where thorium and uranium occur, because no stable element isotopes occur in that range.
 - ♦ If you specify a mass range that omits all the isotopes for an element, you will receive no reported concentration for that element. However, if you include a range that covers at least one isotope of an element, then concentration results will be reported for that element.
- **End Mass (amu):** Defines the end of an atomic mass range for each measurement. The scanning range defined by a single row in the table is the range between the Begin

Mass and End Mass values set in that specific row. The total mass range that your instrument will scan during an individual replicate is defined by all the entries in the table. Valid entries are between 1 and 270 amu. To enter an End Mass value, click in the desired cell in the table and type the value that you want to use.

- **Scan Mode (*):** Specifies whether the system will use either peak hop data acquisition or peak scanning. To select a Scan Mode, right-click in the desired cell of the table. The options are:
 - ♦ *Peak Hopping:* The instrument acquires data at the specified mass only, then jumps directly to the mass for the next analyte in the method. Peak hopping allows you to spend more time at each mass. This usually helps to reduce the number of sweeps/reading that are required to achieve satisfactory precision.
 - ♦ *Scanning:* The instrument acquires data at a number of data points around the specified mass, based on the value of the MCA Channels entry.
- **MCA Channels:** Determines the number of multichannel analyzer channels that are assigned to an analyte when using scanning mode. The MCA Channels setting is always 1 when using peak hopping. Valid entries are between 1 and 20 for scanning. The default value is 1. To enter an MCA Channels value, click in the desired cell in the table, then type in the value that you want to use. Spectra are scanned by rapidly and repetitively sweeping the quadrupole across all of the channels within the mass range set by the Analyte/Mass entries. During each sweep, the spectrometer acquires data for a length of time specified by the dwell time, and the ion count rate is measured and stored in an MCA channel buffer. The use of a multichannel analyzer permits enhanced analytical precision by permitting rapid scanning of the defined mass range, with all elements measured closely to one another in time.
- **Dwell Time per AMU (ms):** Determines the length of time spent measuring the analyte during a single sweep. The Dwell Time per AMU is the total time spent at the mass range corresponding to the individual analyte listed. If more than one MCA channel is being used, this time is divided by the number of MCA channels to define the length of time spent at each MCA channel. The acceptable range of settings is between 0.1 and 1800000. The default setting is 100 in both peak hopping and scanning modes. To enter a Dwell Time value, click in the desired cell in the table, then type in the value that you want to use. The Dwell Time per AMU setting applies only to the individual analyte listed in the same row of the table. The optimum dwell time setting depends upon your analysis conditions and your sample. Typical dwell time values for peak hopping are between 20 and 100 ms using multiple sweeps per reading for a total integration time of 1000 ms. A longer dwell time measures the analyte more precisely at the expense of total analysis time. The use of shorter dwell times is recommended only for transient analysis when determining a large number of analytes. However, attempting to determine too many analytes using very short dwell times in a short-duration transient signal will adversely affect accuracy and precision.
- **Integration Time (ms):** Displays the total amount of time that the analyte listed in the same row of the table will be measured during one replicate, based on the setting for Dwell Time per AMU, Sweeps/Reading, and Readings/Replicate as indicated below:

$$\text{Integration Time} = \text{Dwell Time} * \text{Sweeps/Reading} * \text{Readings Replicate}$$

This is a read-only entry designed to permit a quick assessment of the time the quadrupole will spend measuring the individual analyte.

Timing Table: Isotope Ratio and Isotope Dilution

The Timing table is used to identify the isotopes that you want to measure during your determinations along with specifics about the measurement timing conditions. This table must include at least one Analyte entry and its associated measurement specifications.

When completing the table, a set of default parameters is automatically filled in once you specify an analyte. These default parameters provide a standard starting point for developing a method. The conditions should provide reasonable data, permitting you to analyze the results and define what type of modifications are required to yield the best possible data on your specific sample system.

The following entries are included in the Isotope Ratio and Isotope Dilution Timing table:

- **Reference Mass:** Specifies the Reference Mass to be used in the ratio calculations. When you use Isotope Ratio, you compare the isotope of interest to a reference isotope of the same element. For example, the concentration of Pb204 to Pb206. Alternatively, you can compare more than one isotope or all remaining isotopes of an element to your reference isotope and obtain a ratio for each. The formula for the ratio is as follows:

$$\text{Isotope Ratio} = \text{Analyte Isotope} / \text{Reference Isotope}$$

Where:

Analyte Isotope is set using Analyte and Mass entries
Reference Isotope is set using the Reference Mass

- **Analyte (*):** Defines the atomic mass of the isotope that the instrument will determine in each measurement. The simplest way to specify entries is by using the Periodic Table dialog box. To use this dialog box, right-click in any cell in the Analyte column. Select the desired elements and isotopes in the Periodic Table dialog box that appears. If you are not using the Periodic Table dialog box to specify analytes, click in the appropriate cell, then type an element's atomic symbol to determine the intensity for that element in the sample. Valid entries include the atomic symbols for all naturally occurring elements. If you enter only the atomic symbol, the system will default to using the exact mass for the most abundant isotope (except for Ca, Ti, Ni, Zn, Cd, and Sn). For example, if you type Pb, the system will enter 207.977 in the Mass column. You may also enter the atomic symbol followed by the specific isotope of interest. For example, if you type Pb206, the system will enter 205.975 for the Mass.
- **Mass (amu):** Specifies the mass at which the isotope will be measured. This entry normally does not need to be made, because the system automatically fills in a mass setting, based on the analyte that you specified. If the Scan Mode is set to Scanning, this entry represents the center of the measured peak.
- **Scan Mode (*):** Specifies whether the system will use either peak hop data acquisition or peak scanning:
 - ♦ *Peak Hopping:* The software acquires data at the specified mass only, then jumps directly to the mass for the next analyte in the method. Peak hopping allows you to spend more time at each mass. This usually helps to reduce the number of sweeps/reading that are required to achieve satisfactory precision
 - ♦ *Scanning:* The instrument acquires data at a number of data points around the specified mass, based on the value of the MCA Channels entry
- **MCA Channels:** Determines the number of multichannel analyzer channels that are assigned to an analyte when using scanning mode. The MCA Channels setting is always 1 when using peak hopping. Valid entries are between 1 and 20 for scanning.

The default value is 1. Spectra are scanned by rapidly and repetitively sweeping the quadrupole across all of the channels within the mass range set by the Analyte/Mass entries. During each sweep, the spectrometer acquires data for a length of time determined by the dwell time, and the ion count rate is measured and stored in an MCA channel buffer. The use of a multichannel analyzer permits enhanced analytical precision by permitting rapid scanning of the defined mass range, with all elements measured closely to one another in time.

- **Dwell Time per AMU (ms):** Determines the length of time spent measuring the analyte during a single sweep. The Dwell Time per AMU is the total time spent at the mass range corresponding to the individual analyte listed. If more than one MCA channel is being used, this time is divided by the number of MCA channels to determine the length of time spent at each channel. The acceptable range of settings is between 0.1 and 1800000. The default setting is 100 in both peak hop and scanning modes. The Dwell Time per AMU setting applies only to the individual analyte listed in the same row of the table. The optimum dwell time setting depends upon your analysis conditions and your sample. Typical dwell time values for peak hopping are between 20 and 100 ms using multiple sweeps per reading for a total integration time of 1000 ms. A longer dwell time measures the analyte more precisely at the expense of total analysis time. The use of shorter dwell times is recommended only for transient analysis when determining a large number of analytes. However, attempting to determine too many analytes using very short dwell times in a short-duration transient signal will adversely affect accuracy and precision. In Isotope Ratio, it is important to collect enough analyte ions of each isotope for an accurate determination of the true ratio. The dwell time of a minor isotope should be increased such that an equivalent number of ions are counted for each isotope.
- **Integration Time (ms):** Displays the total amount of time that the analyte listed in the same row of the table will be measured during one replicate, based on the setting for Dwell Time per AMU, Sweeps/Reading, and Readings/Replicate:

$$\text{Integration Time} = \text{Dwell Time} * \text{Sweeps / Reading} * \text{Readings / Replicate}$$

This is a read-only entry designed to permit a quick assessment of the time the quadrupole will spend measuring the individual analyte.

- **Corrections:** This entry is used for all methods except TotalQuant analyses. It shows that inter element or polyatomic ion corrections are being applied to this analyte. The interferent species used in the correction is listed in this entry.
- **Mode:** (*DRC series only*) This entry is read-only. Displays the mode (Standard or DRC mode) in which the instrument is working. The mode also appears in the Status bar at the bottom of the tab. If Cell Gas A or B is 0, the instrument is in Standard mode. If either Cell Gas A or B is above 0, the instrument is in DRC mode.
- **Cell Gas A:** (*DRC series only*) This entry is read-only. Displays the flow rate for the reaction gas as specified in the Cell Parameters tab in the Optimization window.
- **Cell Gas B:** (*DRC series only*) This entry is read-only. Displays the flow rate for the reaction gas as specified in the Cell Parameters tab in the Optimization window. This entry is available only if Cell Gas B is installed.

- **RPa (Rejection Parameter a):** (*DRC series only*) This entry is read-only. Displays the reaction cell voltage for all the analytes as specified in the Cell Parameters tab in the Optimization window.
- **RPq (Rejection Parameter q):** (*DRC series only*) This entry is read-only. Displays the reaction cell voltage for all the analytes as specified in the Cell Parameters tab in the Optimization window.

Timing Table: Data Only

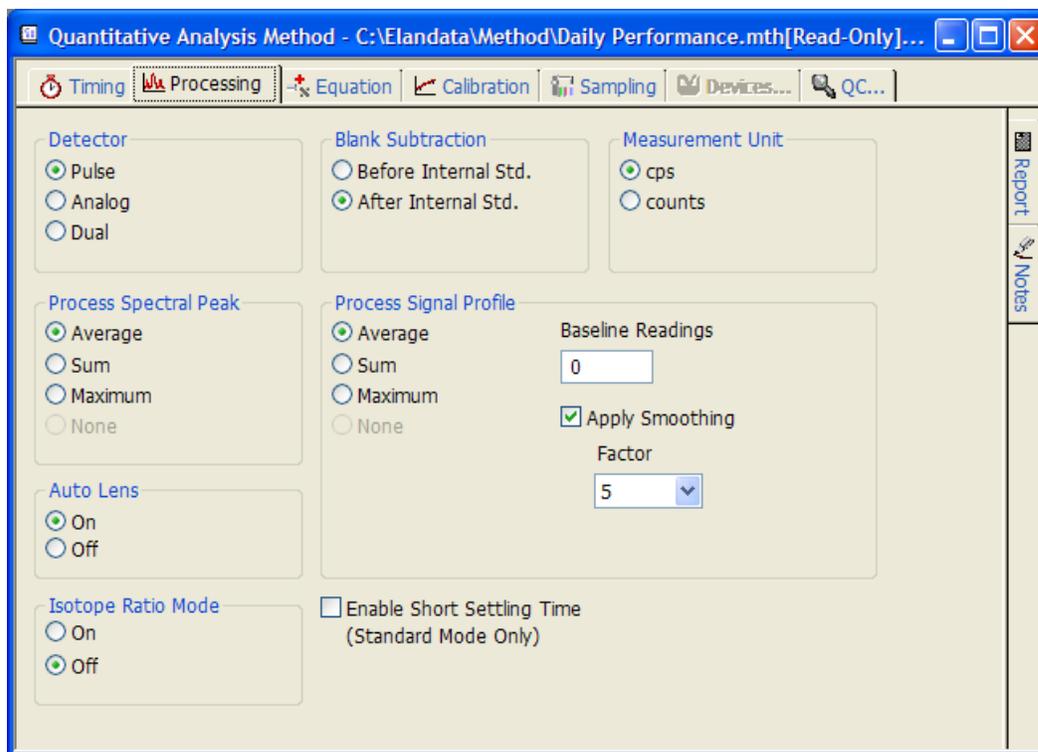
The Timing tab includes a table that is used to identify the isotopes or mass range that you want to measure during your determinations. This table must include at least one Analyte entry and its associated measurement specifications.

When completing the table, a set of default parameters is automatically filled in once you specify an analyte. These default parameters provide a standard starting point for developing a method. The conditions should provide reasonable data, permitting you to analyze the results and determine what type of modifications are required to yield the best possible data on your specific sample system.

The entries in the Timing table for the Data Only method are similar to those found in the Quantitative Analysis method, except a Begin Mass and End Mass can be used (similar to TotalQuant methods). When an analyte is defined in the first column, the exact mass of the isotope is measured.

Processing Tab

Use this tab to specify which detector signals to monitor, and to define the manner in which raw signal data will be managed by the software. These settings include important handling options for both the signal profile and spectral peak data.



Method window Processing tab

Detector Group

The Detector group is used to specify which detector signal should be used during a determination. The system incorporates SimulScan which automatically measures two signals simultaneously from a single, dual-stage, discrete dynode detector. High-level signals are measured as an analog current at the midpoint of the detector, while low-level signals are measured using pulse counting at the base of the detector. The detector system can also be used in either mode exclusively, however, in normal operation, you will usually elect to operate in the dual detector mode. Detector options are as follows:

- **Pulse:** Specifies use of the detector's pulse counting signal option only. This option is applicable if you are performing a measurement on a sample likely to produce a very low signal level.
- **Analog:** Specifies use of the detector's analog signal measurement option. This option is applicable if you are performing a measurement on a sample likely to produce a very high signal level.
- **Dual:** Specifies instrument operation in SimulScan mode, with the detector measuring both the pulse count and analog signals. This is the default value for the Detector group.

Process Spectral Peak

The Process Spectral Peak group defines the manner in which spectral peak data will be handled during ICP-MS determinations. The raw spectral data collected during a measurement is not a smooth curve but rather a series of points, the number of which is determined by a number of acquisition parameters. The raw data for each mass is processed according using the method specified in this group. The available spectral peak processing algorithms are as follows:

- **Average:** Averages the values of all the MCA channels for each peak
- **Sum:** Adds the values of all the MCA channels to create a total ion count for each peak
- **Maximum:** Selects the MCA channel of the maximum value for each peak

AutoLens™ Scan

You can synchronously scan the ion lens with the actual quadrupole mass scan, permitting dynamic adjustment of the lens voltage for optimum ion throughput. The AutoLens control on the Processing tab permits you to manually turn this function off/on. The default condition in a new method is for the AutoLens function to be Off.

To use the AutoLens feature, you must first perform an AutoLens calibration in the SmartTune™ window. For maximum effectiveness, the AutoLens system should be recalibrated when sample matrices change significantly.

Isotope Ratio Mode

An Isotope Ratio method is a specialized technique that enables you to measure the exact ratio of two isotopes of an element in a sample. This technique is a sensitive indicator of age, reaction or metabolism in nuclear, geochemical or biomedical applications. In addition to providing an accurate ratio of isotope concentration, these measurements are also highly precise. The status of the Isotope Ratio mode is automatically controlled by the type of method applied to a data acquisition. The Isotope Ratio Mode settings control the operation of the *Axial Field Technology (AFT)* during certain types of data acquisition. The Isotope Ratio Mode can be set to either On or Off when you are working with Data Only and Quantitative method acquisitions. During all other acquisition methods, the Isotope Ratio Mode is controlled automatically by the software. In order to optimize data

acquisition, the Isotope Ratio Mode defaults to the on position during Isotope Ratio and Isotope Dilution methods.

Blank Subtraction

The Blank Subtraction group shows that the subtraction of the blank signal will occur before or after signal correction based on your internal standards.

Process Signal Profile

Signal profile characterization is used primarily for transient signals. When the instrument has completed the acquisition of data for a measurement replicate, the data consists of a series of intensity data points (readings) plotted against time. This intensity/time signal profile can be processed to yield a final intensity value for use in quantitative calculations. The Process Signal Profile group is used to define the manner in which signal data will be handled during ICP-MS determinations. The available signal processing algorithms are as follows:

- **Average:** Calculates the average intensity for all the readings in the replicate.
- **Sum:** Adds the total ion counts measured for all readings.
- **Amplitude:** Determines the maximum intensity point for all the readings acquired.
- **None:** Specifies that no signal processing should be performed on the acquired data.

You can then set the number of Baseline Readings and a Smoothing Factor, if desired. The Baseline Readings entry is used to define the number of readings that will be used in baseline correction. The number set in this field defines the number of readings.

Beginning with the first reading acquired. This reading will be used to calculate a baseline intensity value that is subsequently subtracted from all measurements in the replicate. This baseline count can be used to correct for solvent effects or other sample induced intensity shifts. To enter a value, click in the Baseline Readings field, and then type in the value for the number of readings that you want to set.

The Apply Smoothing function specifies whether to apply a Savitzky-Golay moving point average smoothing function to the signal profile data. Smoothing tends to reduce the effects of measurement noise in low signal-to-noise measurements. The number of points used in the moving point average calculation is determined by the value of the Factor entry. The minimum number of points allowable equals 5. The larger the value selected, the greater the smoothing effects.

Enable Short Settling Time

This option applies to Standard mode elements only for DRC series instruments, and to all elements for the ELAN 6000, 6100, and 9000 instruments. By selecting this option, the settling time for the quadrupole becomes much shorter (for example, 200 microseconds). This disables the Extended Dynamic Range feature; only the pulse stage of the detector is used.

Measurement Unit

The Measurement Unit group defines the manner in which the raw data will be measured:

- **cps:** Data is displayed using counts per second (cps) as the raw data
- **counts:** Data is displayed using total counts as the raw data

Equation Tab

Use this tab to view isotope abundance information, to identify potential interferences for your analytes, and to define interference corrections for use during determinations.

Note: The fields that appear on this tab vary, depending on the type of method.

The screenshot shows the 'Equation' tab in the software. It features a toolbar with icons for Timing, Processing, Equation (active), Calibration, Sampling, Devices..., and QC... Below the toolbar is the 'Isotope Information' section, which lists isotopes with their mass, abundance, and interferences. The main part of the window is a table with columns for Int Std, Analyte (*), Mass (amu), Corrections, and Potential Interferences. The 'Mg' analyte is highlighted in the first row of the table.

Isotope Information				
Isotope	Mass	Abundance	Interferences	
Mg 24	23.9850	78.990000	LiO, NaH, Ti++, Ti++, Ca++	
Mg 25	24.9858	10.000000	BeO, NaH, LiO, Ti++	
Mg 26	25.9826	11.010000	CN, BO, BeO	

	Int Std	Analyte (*)	Mass (amu)	Corrections	Potential Interferences
1		Mg	23.985		LiO, NaH, Ti++, Ti++, Ca++
2		In	114.904		Sn, MoO
3		U	238.05		
4		Ce	139.905		
5		CeO	155.9		Gd, Dy, BaO, LaO
6		Ba	137.905	- 0.000903 * La 139 - 0.002825 * Ce	La, Ce
7		Ba++	68.9525		Ga, ArP, ClO2, VO, La++, Ce++, La++
8		Bkgd	220		
9		Bkgd	8.5		
10					
11					

Method window Equation tab

Items on the Equation Tab

- Isotope Information:** Displays the mass, natural abundance, and known interferences for all of the isotopes of the analyte that is currently selected in the Equations table. This listing helps you to develop elemental equations for interference correction by making important isotopic information readily available. To display information for a different element, click a different analyte in the Equations table. If the element you are interested in is not currently listed in the table:
 - Click in an empty cell in the Analyte column of the Equations table.
 - Type in the atomic symbol for the desired element, or right-click the mouse and select the element from the Periodic Table dialog box. The information for that element is displayed in the Isotope Information listing. If you enter an analyte in this manner, and do not want to include the analyte in your measurements with the current method, remember to delete the element from the Equations table.
- Equations Table:** The Equation tab includes a table that is used to list the elements/isotopes. This table is also included in the method and for entering the elemental equations. It will be used to correct for interferences during data acquisition. Each element/isotope that is listed on the Timing tab of the Method window is automatically listed on the Equation tab. The table also automatically lists the known potential interferences for each isotope listed, and lists any pre-programmed elemental equations that are included in the software. When working in the Equations table, the default parameters (pre-programmed equations) are generally

acceptable as a starting point for many determinations. However, the specific equations that may be required are a function of your sample.

- ♦ **Internal Standard:** (*Quantitative Analysis methods only*) Lists the standard groups and internal standards that have been defined in the method.
- ♦ **Analyte (*):** Defines the atomic mass of the isotope that the instrument will determine in each measurement. The simplest way to specify entries is by using the Periodic Table dialog box. To use this dialog box, right-click in any cell in the Analyte column. Select the desired elements and isotopes from the Periodic Table dialog box that appears. If you are not using the Periodic Table dialog box to specify analytes, click in the appropriate cell, then type an element's atomic symbol to determine the intensity for that element in the sample. Valid entries include the atomic symbols for all naturally occurring elements. You may also type the atomic symbol followed by “++”, such as Ca++, which acquires data for the most abundant isotope, but at half the listed mass. Molecular names for polyatomic species, such as ClO and ArN are also valid entries. If you enter only the atomic symbol, the system will default to using the exact mass for the most abundant isotope (except for Ca, Ti, Ni, Zn, Cd, and Sn). For example, if you type Pb, the system will enter 207.977 in the Mass column. You may also enter the atomic symbol followed by the specific isotope of interest. For example, if you type Pb206, the system will enter 205.975 for the Mass.
- ♦ **Mass (amu):** Here you specify the mass at which the isotope will be measured. This entry normally does not need to be made, because the system automatically sets a mass setting based on the analyte specified. If the Scan Mode is set to Scanning, this entry represents the center of the measured peak.
- ♦ **End Mass (amu):** (*Data Only methods only*) Specifies the end of an atomic mass range for each measurement. The scanning range defined by a single row in the table is the range between the Begin Mass and End Mass values set in that specific row. The total mass range that the instrument will scan during an individual replicate is defined by all the entries in the table. Valid entries are between 1 and 285 amu. To enter an End Mass value, click in the desired cell in the table and type the value you want to use.
- ♦ **Reference Mass:** (*Isotope Ratio methods only*) Displays the reference mass used in the ratio calculations. The Isotope Ratio compares the isotope of interest to reference isotopes of the same element.
$$\text{Isotope Ratio} = \text{Analyte Isotope} / \text{Reference Isotope}$$
- ♦ **Elemental Equation** (*TotalQuant methods only*) Lists any preprogrammed elemental equations included with the software.
- ♦ **Corrections:** This setting defines the elemental equations to be used for interference correction. Many quantitation problems produced by spectral interferences can be compensated for by using an elemental equation.
- ♦ **Potential Interferences:** This column lists the known interferences, isotopes and polyatomic ions, for an isotope listed in the Equations table. The software includes a comprehensive listing of the potential interferences for a determination, helping you to define problems more easily and to simplify correction. These standard equations correct for isotope interferences, not for molecular interferences that may occur.

Calibration Tab

Use this tab to set up a calibration for use in your determinations. The entries on this tab allow you to define the composition of your standards and to specify the concentrations of each analyte in each standard solution. Up to 30 standards may be defined in a single calibration. This tab is used with all methods except the Data Only method.

The screenshot shows the Calibration tab in a software window. The window title is "Quantitative Analysis Method - C:\Elandata\Method\Daily Performance.mth[Read-Only][Mo...]" and the active tab is "Calibration". Other tabs include "Timing", "Processing", "Equation", "Sampling", "Devices...", and "QC...".

At the top of the tab, there are two radio buttons: "External Std." (selected) and "Std. Addition".

Below the radio buttons is a table with the following columns: Int Std, Analyte (*), Mass (amu), Curve Type (*), Sample Units (*), Standard Units (*), Std 1, and Std 2. The table contains 10 rows of data:

Int Std	Analyte (*)	Mass (amu)	Curve Type (*)	Sample Units (*)	Standard Units (*)	Std 1	Std 2
1	Mg	23.985	Linear Thru Zero	ug/L	ug/L		
2	In	114.904	Linear Thru Zero	ug/L	ug/L		
3	U	238.05	Linear Thru Zero	ug/L	ug/L		
4	Ce	139.905	Linear Thru Zero	ug/L	ug/L		
5	CeO	155.9	Linear Thru Zero	ug/L	ug/L		
6	Ba	137.905	Linear Thru Zero	ug/L	ug/L		
7	Ba++	68.9525	Linear Thru Zero	ug/L	ug/L		
8	Bkgd	220	Linear Thru Zero	ug/L	ug/L		
9	Bkgd	8.5	Linear Thru Zero	ug/L	ug/L		
10							

On the right side of the window, there are buttons for "Report" and "Notes".

Method window Calibration tab

Items on the Calibration Tab

- Calibration Type:** The Calibration Type group is used to specify the type of calibration that is being defined on the Calibration tab: External Std. or Std. Addition. The solutions listed on this tab are run whenever the Calibration Action for a sample solution listed in the Sample window specifies that the standards should be run. To specify a Calibration Type, click the desired calibration method. For samples that are not subject to sample-specific matrix interferences that change the overall instrument sensitivity between the samples and the standards, external standardization is a simple and effective means of calibrating your instrument. External standardization involves measurement of a blank solution followed by a set of standard solutions to create a calibration curve that covers the concentration range of interest. Typically, two or three standard solutions are run, each containing different concentrations of all the elements that are being determined in the analysis. Increasing the number of points on the calibration curve (that is, increasing the number of standard solutions) may improve accuracy in circumstances where the calibration range is very broad. Standard addition calibration provides an effective means of minimizing sample-specific matrix effects through the use of spiked samples. In standard addition calibration, you begin by measuring a blank solution. Next, you measure the sample solution *spiked* with a known concentration of each element that you are determining. You may perform the spike measurements at one or more spike concentrations, depending on the accuracy required in your determinations. You then measure the unspiked sample solution. The software measures the responses for the spiked samples, and creates a calibration curve for each element for which a spike has been added, based on the known concentration values which you have entered. Based on

the slope of the calibration curves, the software can determine the unspiked concentrations of the analytes in your unknown.

- **Concentration Unit:** The concentration of the sample or standard in selectable units (for example, ppm or mg/L). This is available for TotalQuant methods only.
- **Conversion Factor:** All units are calculated internally using ppm. The conversion factor is used to create the displayed value from the internal value. This is available for TotalQuant methods only. For example, the conversion factor for ppm is 1; the conversion factor for ppb is 1e-3.

Parameters in the Calibration Table

The Calibration tab includes a table that is used to list the elements/isotopes that are included in the method and for entering the information that will be used to specify the composition of your standard solutions. Each element/isotope that is listed on the Timing tab of the Method window is automatically listed on the Calibration tab. In addition, any internal standards that were defined on the Timing tab are also shown here. You may also use the Int. Std. field in the Calibration table to specify an internal standard.

The following entries appear in the Calibration table:

- **Internal Standard:** Lists the standard groups and internal standards that have been defined in the method.
- **Analyte (*):** Defines the atomic mass of the isotope that the instrument will determine in each measurement. This entry lists all the isotopes that are listed in the Analyte column on the Timing tab of the Method window. You may specify additional isotopes on this tab, however, it is preferable to enter new isotopes on the Timing tab, because the timing parameters may need to be adjusted from their default values. The simplest way to specify entries is by using the Periodic Table dialog box. To use this dialog box, right-click in a cell in the *Analyte* column and select the desired elements and isotopes from the dialog box that appears. If you are not using the Periodic Table dialog box to specify analytes, click in the appropriate cell and type an element's atomic symbol to determine the intensity for that element in the sample. Valid entries include the atomic symbols for all naturally occurring elements. You may also type the atomic symbol followed by “++”, such as Ca++, which acquires data for the most abundant isotope, but at half the listed mass. Molecular names for polyatomic species, such as ClO and ArN are also valid entries. If you enter only the atomic symbol, the system will default to using the exact mass for the most abundant isotope (except for Ca, Ti, Ni, Zn, Cd, and Sn). For example, if you type Pb, the system will enter 207.977 in the Mass column. You may also enter the atomic symbol followed by the specific isotope of interest. For example, if you type Pb206, the system will enter 205.975 for the mass.
- **Mass (amu):** Specifies the mass at which the isotope will be measured. This entry normally does not need to be made, because the system automatically fills in a mass setting, based on the analyte that you specified. To enter a mass value, click in the desired cell in the table, then type in the value that you want to use. If you want to modify the mass setting which the system enters, click in the appropriate cell and type the exact mass (using up to four decimal places) at which the isotope should be measured. If the Scan Mode is set to Scanning, this entry represents the center of the measured peak.
- **Curve Type (*):** Specifies the type of calibration curve that will be constructed from the calibration information for the specific analyte listed on the same row of the Calibration table. Three curve types are available in the software: Simple Linear, Linear Thru Zero, and Weighted Linear. The default setting is Simple Linear. To select

a curve type, right-click in the Curve Type field and click the desired type from the list that appears. The following definitions describe each of the curve type options:

- ♦ **Simple Linear:** Uses standard linear regression for curve calculation, with equal weighting applied to all calibration solutions
- ♦ **Linear Thru Zero:** Uses linear regression with a forced zero—that is, the curve includes a point at the origin of the calibration graph
- ♦ **Weighted Linear:** Uses a linear regression algorithm that incorporates a standard, concentration-dependent weighting factor to emphasize measurements in the low concentration region of the calibration curve. The weighting factor (w) equals the inverse of the square of the concentration of the standard.
- **Sample Units (*):** Specifies the concentration units for the sample solutions. The following concentration units are available:
 - ♦ ppm: parts per million
 - ♦ ppb: parts per billion
 - ♦ ppt: parts per trillion
 - ♦ mg/L: milligrams per liter
 - ♦ $\mu\text{g/L}$: micrograms per liter
 - ♦ ng/L: nanograms per liter
 - ♦ $\mu\text{g/g}$: micrograms per gram
 - ♦ ng/g: nanograms per gram
 - ♦ mg/dL: milligrams per deciliter
 - ♦ $\mu\text{g/dL}$: micrograms per deciliter
 - ♦ ng/dL: nanograms per deciliter
 - ♦ $\mu\text{g/mL}$: micrograms per milliliter
 - ♦ ng/mL: nanograms per milliliter
 - ♦ pg/mL: picograms per milliliter

Sampling Tab

Use this tab to define the sampling device parameters for all analytic solutions within the method. The information entered here includes general information about the type of autosampler, plus information about pumping rates and times. Only one device, in addition to the peristaltic pump, can be active.

	Time (sec)	Speed (+/- rpm)
Sample Flush	35	-24.0
Read Delay	15	-20.0
Analysis		-20.0
Wash	45	-24.0

Standard	Solution ID	A/S Loc.	Wash Override (sec)
1	Blank		
2	Standard 1		
3	Standard 2		
4	Standard 3		
5	Standard 4		
6	Standard 5		

Method window Sampling tab

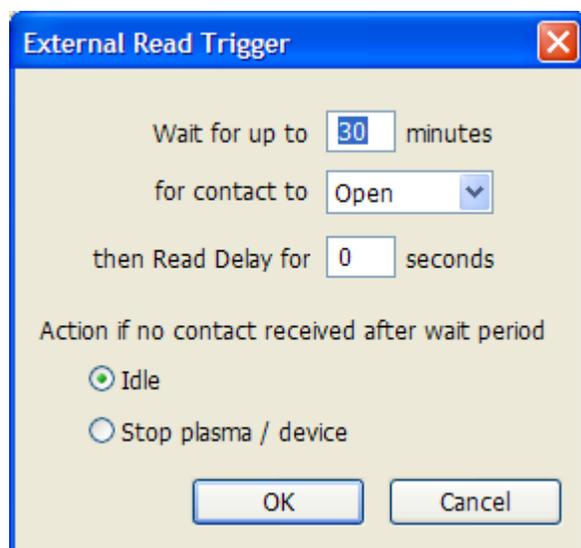
Items on the Sampling Tab

- **Peristaltic Pump Controls:** These parameters are imported from your global pump settings (see “[Global Defaults—Peristaltic Pump Settings](#)” on page 69). You can modify them here if you want to override the global defaults for this method.
- **Peristaltic Pump Under Computer Control:** Select this check box if you want the peristaltic pump speeds to be automatically controlled by the software. If this box is not selected, you will need to control pump speeds manually.
- **Autodiluter Controls:** When the Cetac ADX-500 is selected as the sampling device, the following fields become available:
 - ♦ **Dil. Factor:** Controls dilution factors ranging from 2 to 1000, with the default set at 10. A dilution factor of n should lower the measured intensity by a factor of n.
 - ♦ **Dil. To Vol.:** Allows you to specify the volume of the diluted samples which the autodiluter will create. This volume ranges from 2 mL to 50 mL, with 10 mL being the default.
 - ♦ **1st. Dilution Pos.:** Allows you to specify which tubes should be used when diluted samples are to be created. The first diluted sample will be created in the 1st. Dilution Pos. tube, the second in the next higher numbered tube and so on.
 - ♦ **Probe Purge Pos.:** Allows the specification of a tube to be used for the autodiluter initialization. In order to accurately measure the volumes of liquid involved in each dilution the probe and associated tubing must be full of diluent before any dilutions are done. Ten milliliters of diluent are therefore pumped into the probe, and the tube at the Probe Purge Pos. is used to collect any spillage. The default position for this probe is 10.

- **Sampling Device:** Specifies the use of a sampling device such as External, HGA, or a FIAS™ device.
 - ♦ If you select the HGA or FIAS option, the Devices tab becomes active and the related sub-tabs become available. Complete the parameters on the appropriate sub-tabs; use the Device Control window to manually control the device.
 - ♦ If you select the External option, an external sampling device, such as a liquid or ion chromatograph or laser, may interface with the instrument. When you click this option, the External Read Trigger dialog box appears. The external sampling device must use a contact closure/opening with the instrument before it begins its measurements—define the type of external read trigger needed. External devices also require a connector cable to communicate between the external sampling device to the instrument.
- **Autosampler and Tray:** Display the autosampler and tray selected on the Device Control window Autosampler tab.

External Read Trigger Dialog Box

An external sampling device must use a contact closure/opening with the instrument before it begins its measurements—use this dialog box to define the type of external read trigger needed. External devices also require a connector cable to communicate between the external sampling device to the instrument.



External Read Trigger Dialog Box

Items on the External Read Trigger Dialog Box

- **Wait and Read Delay Controls:** Type in Wait and Read Delay times, and select a Contact action (*Open* or *Close*) from the drop-down list. The Wait time is how long the system will wait for the external device contact to open or close, as selected. When the Contact action takes place, the system performs the specified Read Delay. If the Contact action does not occur within the prescribed wait time, the system proceeds to the selected time-out option (see following).
- **Action if no contact received after wait period:** Select the action you want the instrument to perform if no contact is made during the defined wait period.

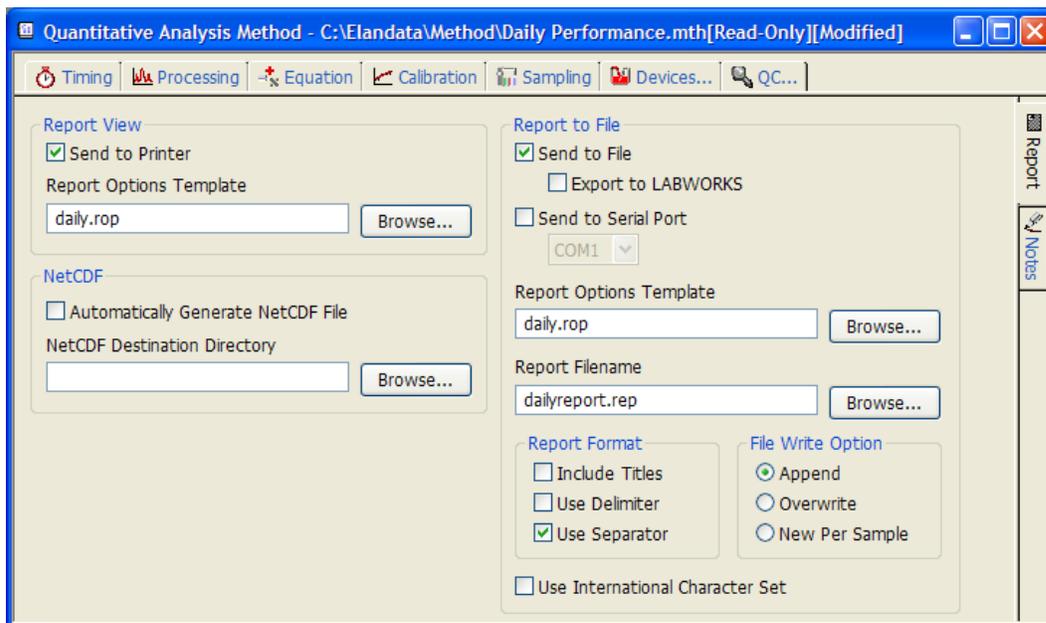
Sampling Table Controls

These entries contain information for the blank and standards.

- **Solution ID:** This field allows you to specify the Solution ID for Calibration Standards and Blanks. The contents are stored in the Method file, and are displayed as the Sample ID in reports if specified, during acquisition in the measurement status window and/or run list, and in the dataset. If you do not have a solution ID specified, the instrument uses the default sample IDs.
- **A/S (Autosampler) Location:** Lists the autosampler location for the blank or standard. This is the location that the solution occupies in the autosampler tray. For standard additions calibration, enter the autosampler locations for the blank and the two standards here. Use negative numbers, indicating the location of the blank and standards relative to the sample location. This entry is ignored if a manual analysis with no autosampler is being performed.
- **Wash Override (sec):** Specifies the time in seconds that the autosampler probe is in the wash solution before it moves to the next solution to be analyzed. Any positive value is valid, including zero. Use this function to provide a longer wash time than specified in the peristaltic pump settings for specific solutions.

Report Tab

The Report tab is located at the right side of the Method window. Here you can specify the type of report you want to produce and the report template to be used. You can also specify the creation of a results file in tab- or comma- delimited ASCII format.



Method window Report tab

Items on the Report Tab

- **Report View group:** The Report View group lists the name of the Report Options template that will be used to format the results from your determinations
- **NetCDF group:** NetCDF files are used to export data to chromatographic data handling software, such as TotalChrom®. The software automatically creates the NetCDF file after each sample is run.
- **Report Concentration group:** These controls apply to TotalQuant™ methods only.
 - ♦ *Concentration Unit:* The concentration of the sample or standard in selectable units—for example, ppm or mg/L.
 - ♦ *Conversion Factor:* All units are calculated internally using ppm. The conversion factor is used to create the reported value from the internal value. For example, the conversion factor for ppm is 1; the conversion factor for ppb is 1e-3.
- **Report to File group:** Select the file where you want to store the data from the determination, send the file to a serial port, or export the file in PKI LabWorks format.
- **Report Format group:** The following options are available in the Report Format group:
 - ♦ *Include Titles* adds section and control titles to the report.
 - ♦ *Use Delimiter* causes a tab-delimited format to be used for the report. This means that a tab character is inserted between each field.
 - ♦ *Use Separator* causes a comma-separated variable format to be used for the report. This means that a comma (,) is inserted between each field.
 - ♦ *Use International Character Set* allows international characters to be displayed and printed on the report.
- **File Write Option group:** The following options are available in the File Write Option group:
 - ♦ *Append* adds the data to the end of the existing file.
 - ♦ *Overwrite* causes all current data in the file to be erased and replaced with the new data.
 - ♦ *New Per Sample* sends the data to a new file for each sample.

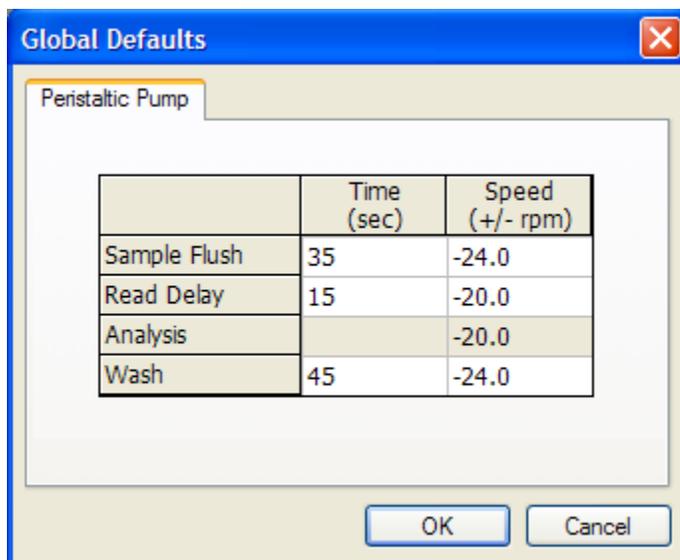
Notes Tab

The Notes tab is located on the right side of the Method window. Use the Notes tab to record notes about the method or about specific procedures that may be required when using the method.

Global Defaults—Peristaltic Pump Settings

The values entered on the Peristaltic Pump tab set the default peristaltic pump settings for the Scheduler and SmartTune™ functions. They also automatically populate the Peristaltic Pump group on the Method window Sampling tab when you create a new method.

Note: If you leave the wash override settings in the method empty, the software uses the wash value specified during acquisition. If you set a wash override value, it overrides that specified in the method. This lets you specify longer washes to prevent residue when running high-concentration samples.



Global Defaults Peristaltic Pump tab

Default peristaltic pump settings

instrument	sample flush (sec)	sample flush speed	read delay (sec)	delay & analysis speed	wash (sec)	wash speed
ELAN® 6000 instrument	35	-48	15	-24	45	-48
ELAN® 6100 instrument	35	-48	15	-24	45	-48
ELAN® 6100 DRC™ instrument	35	-24	15	-18	45	-24
ELAN® 9000 instrument	35	-48	15	-26	45	-48
ELAN® DRC II™ instrument	35	-24	15	-20	45	-24
ELAN® DRC Plus™ instrument	35	-24	15	-18	45	-24
ELAN® DRC-e™ instrument	35	-48	15	-26	45	-48



3

Performing Analyses

This section presents instructions for performing an analysis using a stored method file. The material describes steps for analyzing samples with standard sample introduction.

Topics in this section include:

- ▶ “Analyzing Samples” on page 71
- ▶ “Analysis Order for DRC™ Instruments” on page 72
- ▶ “Creating a Sample File with a Text Editor” on page 73
- ▶ “Sample window Software Reference” on page 76

Analyzing Samples

This section provides an overview to the use of the software for routine measurements using a stored procedure. Virtually all the parameters required for controlling a determination are contained within the analytical method file. After selecting the method to be employed for the determination, you set up and optimize the instrument. Next, you use the Sample window to identify the samples, control the order in which samples are measured, and initiate the determination. In most cases, the Sample window serves as the principle interface between you and the instrument.

The Sample window provides two tabs that allow you to control sample introduction during an analysis in two different ways:

- **Manual:** Sample solutions are introduced manually into the spectrometer
- **Batch:** Blank, standards and samples are placed in the optional autosampler and the samples are introduced automatically into the spectrometer

Following a determination, you can generate a report on the results of the measurement, review/analyze the results in either report or graphical form, reprocess the data, or export the results to another computer for final analysis and reporting.

Files Required During an Analysis

During a determination, a number of files must be open for data acquisition and processing to occur properly. These files include:

- An analytical Method
- A Calibration file, if you are not acquiring new calibration data as part of the current determination (except in TotalQuant™ analyses, where you use a Response file instead)
- A Dataset for storing the results from the determination
- A Tuning file is specified in the method and needs to be changed only if you want to use a different file from the one associated with the method
- An Optimization file is specified in the method and needs to be changed only if you want to use a different file from the one associated with the method
- A Sample file containing the names of your solutions and specific instructions for performing the determination

You can open these files individually or using a workspace. Using a workspace to set up an analysis is a quick way to access the main files needed. Use the default Quantitative Analysis and TotalQuant workspaces as guides to create your own application-specific workspaces.

Analysis Order for DRC™ Instruments

This section covers the correct order of analyses performed on DRC series instruments.

Mode Change Switching and Sampling delays

During instrument operation, if the sum of the Read Delay and Sample Flush delay is greater than the STD mode to DRC mode pressurization delay, the DRC mode analytes are always acquired before STD mode analytes for each sample analysis.

If the sum of the Read Delay and Sample Flush delay is less than the STD mode to DRC mode pressurization delay, the following actions occur:

- If the instrument is currently in the STD mode:
 - ♦ The first sample STD mode analytes are acquired before the DRC mode analytes.
 - ♦ The second sample DRC mode analytes are acquired before the STD mode analytes.
 - ♦ The third sample STD mode analytes are acquired before the DRC mode analytes.
 - ♦ The alternating process continues.

- If the instrument is currently in the DRC mode:
 - ♦ The first sample DRC mode analytes are acquired before the STD mode analytes.
 - ♦ The second sample STD mode analytes are acquired before the DRC mode analytes.
 - ♦ The third sample DRC mode analytes are acquired before the STD mode analytes.
 - ♦ The alternating process continues.

Creating a Sample File with a Text Editor

You can use the following information to create a software Sample file (*.sam) using a word processor, barcode reader, or other ASCII text editor. After you have created the file, open it in the ELAN software and save it before running your analyses.

Sample file format

The Sample Information File (*.sam) is an ASCII text file with each field delimited by a comma. When formatted as described in this section, the file can be created using any text editor, saved as an ASCII file, and then read directly by the software.

The sample information has three sections: header, body, and footer. Each section must be separated from the others by a carriage return (blank line). The header and footer format must be the same for all sample files. The body consists of multiple columns of information for each sample, which should be entered in successive rows.

Header Section:

```
[Begin SampleFile]
FileType=ElanSample
FileVersion=3
```

Body Section:

```
[Begin Samples]
```

Column number	Information	Entry format
1	Row number (batch index)	An integer value, starting at zero, incremented by one
2	Batch ID	Text in double quotes
3	Sample ID	Text in double quotes
4	Autosampler position	Positive integer
5	Sample type	Select one of the following: 0 = Sample 1 = QC Spike 2 = QC Dilution 3 = QC Duplicate 4 = QC Reagent Blank 5 = TotalQuant Addition 6 = QC Duplicate Spike

Column number	Information	Entry format
6	Spike table number	When column 5 = 1, then a positive integer indicating the spike table for this sample. Otherwise = 0
7	Dilution factor	Positive integer or zero
8	Initial sample quantity (mg)	Positive, floating point number. If the box is to be left blank, use n/a
9	Sample prep volume	Positive, floating point number. If the box is to be left blank, use n/a
10	Aliquot volume (ml)	Positive, floating point number. If the box is to be left blank, use n/a
11	Diluted to volume (ml)	Positive, floating point number. If the box is to be left blank, use n/a
12	Solids ratio	Positive, floating point number. If the box is to be left blank, use n/a
13	Description	Text in double quotes
14	Method name	Text in double quotes
15	Calibration/measurement action	Select one of the following: 0 = Run Sample 1 = Run Blank, Standards, and Sample 2 = Run Blank and Sample 3 = Run Standards and Sample 4 = Run diluted Sample 5 = Run Blank and diluted Sample 6 = Run Standards and diluted Sample 7 = Run Blank, Standards, and diluted Sample
16	QC parent raw number (batch index)	Positive integer. Applicable to QC Dilution, Spike, Duplicate, and Duplicate Spike samples only. For other samples, use n/a
17	Wash override time (sec)	Positive integer or zero. If box is to be left blank, use n/a

Footer Section:

[End Samples]

[End SampleFile]

Example Text File

[Begin SampleFile]

FileType=ElanSample

FileVersion=3

[Begin Samples]

0, "stability", "stab001", 1, 0, 0, 0, 0.1, 10, 100, 1000, 0.11, "Stability test", "stability.mth",
0, n/a, 2

1, "stability", "stab002", 2, 1, 8, 0, 0.2, 20, 200, 2000, 0.22, "Stability test", "stability.mth",
1, 0, 4

2, "stability", "stab003", 3, 2, 0, 77, 0.3, 30, 300, 3000, 0.33, "Stability test",
"stability.mth", 2, 1, n/a

3, "stability", "stab004", 4, 5, 0, 0, n/a, n/a, n/a, n/a, n/a, "Stability test", "stability.mth", 3,
n/a, 8

4, "stability", "stab005", 5, 4, 0, 0, n/a, n/a, n/a, n/a, n/a, "Stability test", "stability.mth", 4,
n/a, 10

5, "stability", "stab006", 6, 3, 0, 0, n/a, n/a, n/a, n/a, n/a, "Stability test", "stability.mth", 5,
2, n/a

6, "stability", "stab007", 7, 6, 0, 0, n/a, n/a, n/a, n/a, n/a, "Stability test", "stability.mth", 6,
3, 14

7, "stability", "stab008", 8, 0, 0, 0, n/a, n/a, n/a, n/a, n/a, "Stability test", "stability.mth", 7,
n/a, 16

[End Samples]

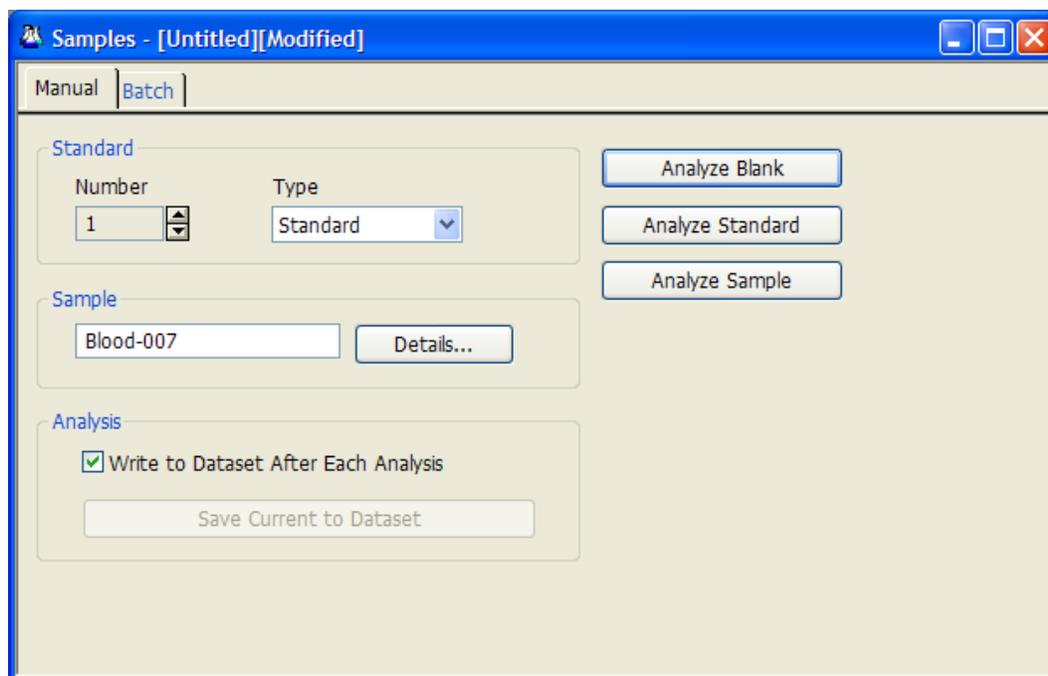
[End SampleFile]

Sample window Software Reference

Use the Sample window to identify the samples in a determination, control the order in which samples are analyzed, and initiate measurements.

Sample Window Manual Tab

Use the Manual tab to individually identify samples for manual control of a determination. This tab is the measurement control interface on instruments configured without an autosampler. You can also use this tab to control individual sample measurements on systems that have an autosampler attached.



Sample window Manual tab

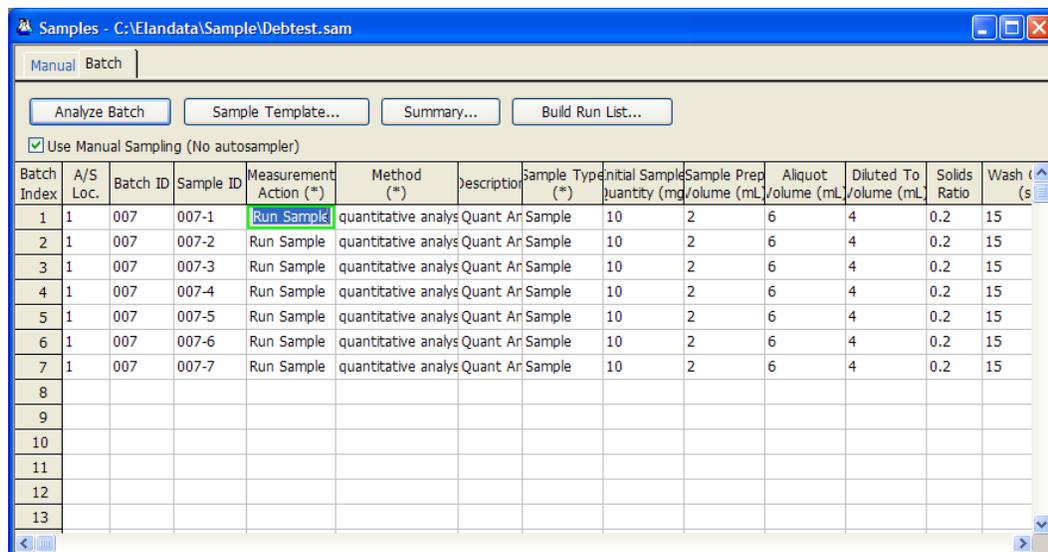
Items on the Sample Window Manual Tab

- **Standard Number:** Identifies the number of the standard solution to be measured when the Analyze Standard button is clicked. To change the value, use the arrows. Valid numbers correspond to the number of standards defined in the active method. For example, you cannot select the number **12** if there are only three standards defined in the method.
- **Standard Type:** Identifies the type of standard solution to be measured. The following options are available from the drop-down list:
 - ♦ *Standard:* Use this option with a normal standard solution
 - ♦ *QC Standard:* Use this option if your solution is a QC standard used in QC checking
- **Analyze Blank:** Initiates a measurement on the blank solution listed in the active method. The measurement parameters are determined by the active method—that is, the method currently open in the Method window.

- **Analyze Standard:** Initiates a measurement on a standard solution. The standards are defined in the active method. The number of the standard to be measured is determined by the Standard No. entry on this tab. The measurement parameters are determined by the active method—the method currently open in the Method window.
- **Analyze Sample:** Initiates a measurement on a sample solution. The sample is described by the Sample ID entry on this tab, and by any information entered in the Sample Details dialog box. The measurement parameters are determined by the active method—the method currently open in the Method window.
- **Sample:** Identifies each sample with a unique name. Type any alphanumeric combination as an individual Sample ID. Example: **Sample01, Water 6-94**
- **Sample Details Dialog Box:** Here you can enter specific information about each sample. It contains the same entries as those on the Batch tab. Note that this information does not change if you alter the Sample ID on the Manual tab, unless you edit the information.
- **Write to Dataset After Each Analysis:** When selected, saves all data acquired to the current dataset following each analysis.
- **Save Current to Dataset:** Saves all information from the last data acquisition to the current dataset. Available only when Write to Dataset After Each Analysis is not selected.

Sample Window Batch Tab

Use the Batch tab to identify a group of samples for an automated determination, to control the order in which samples are measured, and to initiate the measurements. This tab is the primary measurement control interface on an instrument configured with an autosampler.



Sample window Batch tab

Items on the Sample Window Batch Tab

- **Analyze Batch:** Analyzes all of the samples that are selected (highlighted) in the Sample window. When you click Analyze Batch, the Run List dialog box appears and displays the currently running batch samples. To set plasma AutoStop options, insert a priority sample into a running batch, or append additional samples, see “Build Run List” in this section.
- **Sample Template:** Automatically enters values in the Sample ID and Autosampler Location (A/S Loc.) fields for a batch of samples.
- **Summary:** Specifies the summary report type and the destination to which it will be directed.
- **Build Run List:** Click to open the Run List dialog box, where you can review the sequence of samples prior to running them, set plasma AutoStop options, insert priority samples into a running batch, or append additional samples.
- **Use Manual Sampling (No Autosampler):** Enable this check box if you do not use an autosampler. Note that, if using manual sampling, you must aspirate each sample in turn.

Items in the Batch Table

- **A/S (Autosampler) Location:** Lists the autosampler position for the sample—the location that the solution occupies in the autosampler tray. Type the number corresponding to the position in the autosampler tray where the sample solution will

be placed or, on the Edit menu, click Generate Default Sample to automatically enter a Sample ID for a group of samples.

- **Batch ID:** Identifies a group of samples with a batch label. Type a name (any alphanumeric combination) to enter an individual Batch ID or, on the Edit menu, click Fill Down to automatically enter a Batch ID for a group of samples.
- **Sample ID:** Identifies each sample with a unique name. Type a name (any alphanumeric combination) to enter an individual Sample ID or, on the Edit menu, click Generate Default Sample to automatically enter a Sample ID for a group of samples.
- **Measurement Action (*):** Specifies when to run standard and blank solutions, in addition to specifying the running of the sample solution. To select a calibration action, right-click the appropriate cell of the Samples data table to open the drop-down menu and click the desired Measurement Action. The following options are available:
 - ♦ *Run Sample:* Runs only the sample solution that is on the same line of the Samples data table.
 - ♦ *Run Blank, Stds. and Sample:* Runs the solvent blank, the standards that are specified on the Method window Calibration tab, and the sample solution that is on the same line of the Samples data table.
 - ♦ *Run Blank and Sample:* Runs the solvent blank solution and the sample solution that is on the same line of the Samples data table.
 - ♦ *Run Standards and Sample:* Runs the standards that are specified on the Calibration tab of the Method window and the sample solution that is on the same line of the Samples data table. Typically used with Additions calibration.
 - ♦ *Run Diluted Sample:* Runs the specified diluted sample. This is applicable only if using an autodilution device.
 - ♦ *Run Blank and Diluted Sample:* Runs the solvent blank solution and the specified diluted sample. This is applicable only if using an autodilution device.
 - ♦ *Run Standards and Diluted Sample:* Runs the solvent standards and the diluted sample as specified. This is applicable only if using an autodilution device.
 - ♦ *Run Blank, Standards and Diluted Sample:* Runs the solvent blank and the specified standards and diluted sample. This is applicable only if using an autodilution device.
- **Method (*):** Specifies the method to be used for measuring the related sample solution and for all following samples, until a different method is specified. Right-click to browse for the desired method file.
- **Description:** Type additional information/comments about an individual sample solution.
- **Sample Type (*):** Identifies samples being used for a quality control determination or as part of the TotalQuant calibration sequence. This entry is required when using either a Quantitative Analysis method with a QC function or when performing TotalQuant measurements using standard additions calibration. Right-click the Sample Type field. The Sample Type dialog box appears. Select the appropriate option for your sample:

- ◆ *Sample*: Identifies the solution as a sample.
- ◆ *QC Spike*: Identifies the sample as a spike. When selected, a dialog box appears that allows you to select the Spike Table you want to use for the spike, and the parent (Spike Of) sample reference location. You create a Spike Table using the Spike Tables window in the method. The Sample Type field displays Spike - X of Y as the Sample Type, where Y is the sample batch row number.
- ◆ *QC Dilution*: Identifies the sample as a dilution. When selected, a dialog box appears that allows you to select the Dilution Factor, and the parent (Dilution Of) sample reference location. The Sample Type field displays Dilution - DF:X of Y as the Sample Type, where Y is the sample batch row number.
- ◆ *QC Duplicate*: Identifies the sample as a duplicate. When selected, a dialog box appears that allows you to select the parent (Duplicate Of) sample reference location. The Sample Type field displays Duplicate of Y as the Sample Type, where Y is the sample batch row number.
- ◆ *QC Reagent Blank*: Identifies the sample as a reagent blank. If you select this option, the system will subtract the concentration from all subsequent samples until the next reagent blank. If you specify several reagent blanks in succession, the system calculates the average concentration of the set, then subtracts the average concentration from all subsequent samples.

Note: QC Reagent Blank data will be cleared and the *Analysis>Clear QC Reagent Blank* option disabled when you:

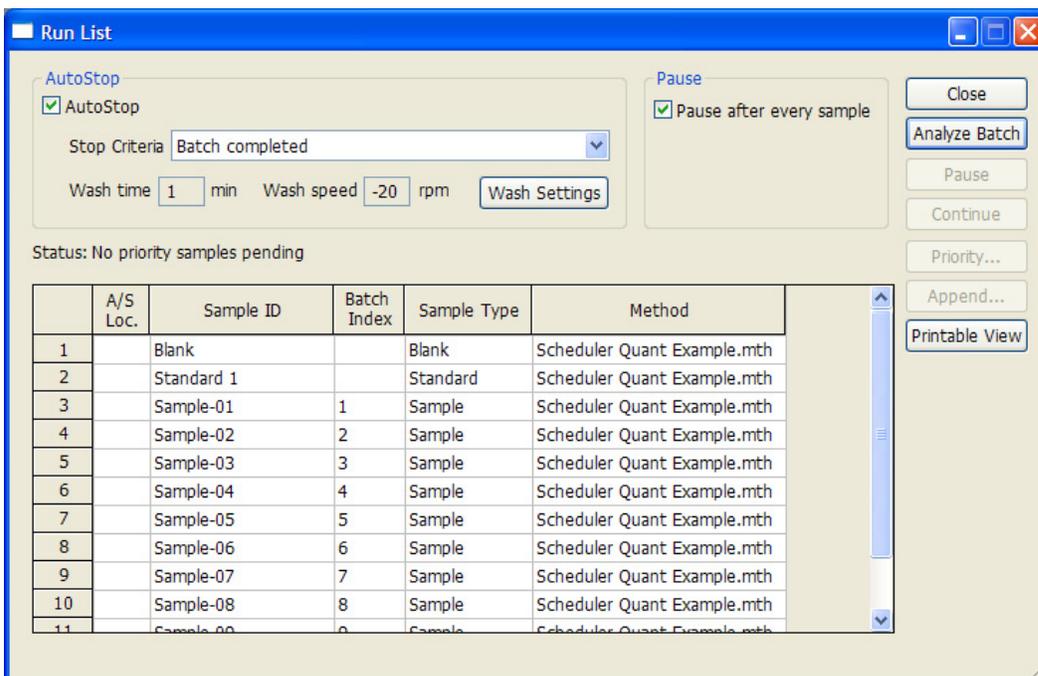
- ❖ Load a new calibration file.
- ❖ Load a Quantitative Analysis method that does not have the *Enable QC Checking* option selected.
- ❖ Load a method type other than Quantitative Analysis.
- ❖ Clear the blank using the *Analysis>Clear QC Reagent Blank* option.
- ❖ Select *Restart QC* from the Analysis menu.
- ❖ Clear all blank and calibration data via a message box.
- ◆ *TQ Addition*: Specifies that the sample contains specific added calibration elements in known quantities, as required during a Sample Addition calibration in TotalQuant analyses. This is necessary to allow the instrument to properly calculate intensity values using the TotalQuant algorithms.
- ◆ *QC Duplicate Spike*: Identifies the sample as a QC duplicate spike. When selected, a dialog box appears for you to select the parent QC spike sample (Duplicate Spike Of) reference location. The reference location is the sample batch row number that the parent spike appears on. The software performs a relative percentage difference (RPD) calculation based on the results for the parent QC spike and the QC duplicate spike. The Sample Type field displays Duplicate Spike of Y as the Sample Type, where Y is the sample batch row number the parent spike appears on.
- **Initial Sample Quantity (mg)**: Specifies the weight of the sample before dilution.
- **Sample Prep Volume (mL)**: Specifies the volume in which the initial sample quantity has been diluted.
- **Aliquot Volume (mL)**: Specifies the volume of an aliquot, when a small amount of the sample (aliquot) is taken and diluted to a final volume.

- **Diluted to Volume (mL):** Specifies the total volume in which an aliquot is diluted.
- **Solids Ratio:** Specifies the correction factor to use if you want the software to convert dry sample weight to the wet sample weight. This value should be entered as a decimal fraction, not as a percentage. Example: For a ratio of 1:2, enter 0.5, not 50%.
- **Wash Override (sec):** Specifies the time in seconds that the autosampler probe is in the wash solution before it moves to the next solution to be analyzed. Any positive value is valid, including zero. Use this function to provide a longer than usual wash cycle for samples where carry-over is a concern.

Items in the Run List dialog box

Use the Run List dialog box to display the sequence of samples prior to running them within a batch. Here you can also set plasma AutoStop options, insert priority samples into a running batch, or append additional samples.

The buttons on the right side of this dialog box are enabled or disabled depending on whether the batch is running (in active analysis) or not. While the batch is running, you can insert a priority sample or append samples to the end of the batch. Note that you can also append new batch lists to a run using the Scheduler.



Run List dialog box

- **AutoStop:** Turns off the plasma automatically following the batch analysis or a QC failure, as specified in the Stop Criteria drop-down list. Here you can also define an automatic wash, which will run after the batch prior to plasma shutdown—click Wash Settings to configure.

Note that the AutoStop controls are not available when running a batch using the Scheduler function, as the Scheduler has its own AutoStop functionality.

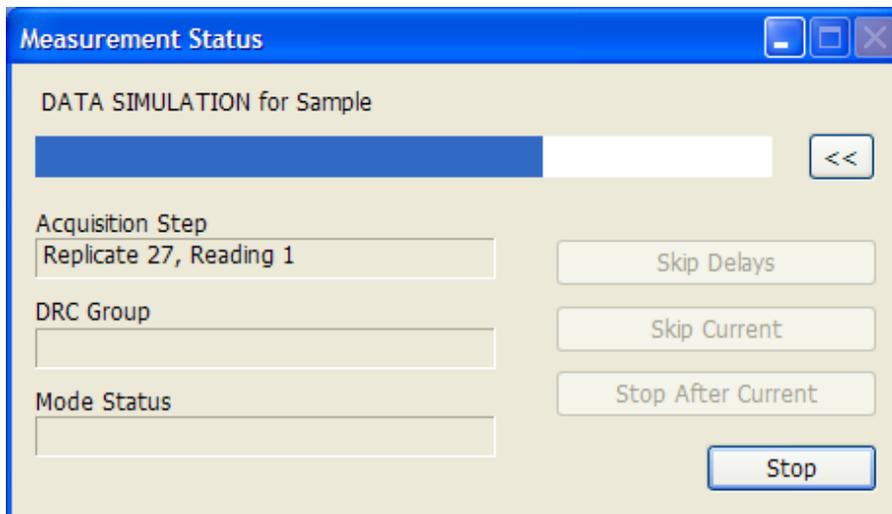
- **Pause After Every Sample check box:** Pauses the analysis after each sample is analyzed. Use this feature when analyzing multiple samples or QC flag samples (QC

dilutions, QC duplicate, QC spike, and QC duplicate spike) without an autosampler. You can use the run list dialog box for manual analysis without an autosampler when you want to add new samples to the batch run as you proceed. The software pauses after each sample; when paused, click Append, add the new samples to the end of the run list, and then click Continue.

- **Status:** Displays the status of the batch; priority and appended samples; and AutoStop and wash functions.
- **Run List table:** Displays the following:
 - ♦ *A/S Loc.:* Location of the sample in the autosampler (if any)
 - ♦ *Sample ID:* An alphanumeric name used to identify each sample
 - ♦ *Batch Index:* The row number of the sample from the Batch tab
 - ♦ *Sample Type:* Identifies the type of sample being used, for example, Blank, Standard, QC Standard
 - ♦ *Method:* Method file used for running the sample
- **Close button:** Allows you to close the Run List dialog box if the batch analysis is not running.
- **Analyze Batch button:** Starts analysis of the samples in the Run List table.
- **Pause button:** Stops the analysis after the analysis of the current sample is complete.
- **Continue button:** Resumes the analysis when the analysis is paused.
- **Priority button:** Opens a dialog box that allows you to insert a priority sample when batch analysis is running.
- **Append button:** Opens a dialog box that allows you to append samples to the end of the Run List table when batch analysis is running.
- **Printable View button:** Displays the contents of the run list in an Internet browser, so that you can print the run list from there.

Measurement Status Dialog Box

The Measurement Status dialog box allows you to terminate scanning on a single sample, to terminate all measurements after the current sample, or to immediately stop all measurements and cancel the determination.



Measurement Status dialog box

This dialog box includes a status indicator that is continuously updated to indicate the progress of the current determination. This is especially helpful if you are performing measurements with large numbers of readings or multiple replicates.

Items in the Measurement Status dialog box

- **Skip Delays (Skip the Sample Flush, Read Delay, and Wash times):** Proceeds directly to data acquisition without performing the defined delays (Flush, Read, Rinse). Available only when performing manual analyses where one or more delays are defined and the same solution is used repeatedly.
- **Skip Current (Skip Scanning of Current Sample):** Stops the measurement of the current sample and proceeds to the next sample listed in the Samples data table. No calculations are performed for the sample that is skipped.
- **Stop after Current (Stop Scanning After Current Sample):** Completes the measurement of the current sample, then terminates the determination. The data associated with all blank, standard or sample solutions that were measured will be listed in the dataset. Any calculations performed, for example the calibration curve, are available for review.
- **Stop (Stop Scanning):** Terminates the determination by immediately canceling all scanning for the current and all remaining samples. The data associated with any blank, standard, or sample solutions that have already been measured will be listed in the dataset. Any calculations performed, for example the calibration curve, will still be available for review.

The software saves partial scans, in the event a scan is cancelled before all readings and replicates are completed. The partial data saved to a Dataset file will depend of the Number of Replicates and Readings per Replicate method parameters. The partial dataset file generated will be made consistent with the method parameters, (the raw data readings acquired will match the method parameters). Data saved during a canceled scan will be displayed in red in the Dataset window. The generation of partial dataset files is applicable to all methods.

For methods with only one replicate, all readings received from the system controller up to the point of cancellation will be saved in the dataset file. The method saved to

the dataset file along with the raw data will have its Reading per Replicate parameter truncated to match the actual number of readings.

For methods with more than one replicate only the readings for completed replicates will be saved in the Dataset file. Partial replicate readings will not be saved. The method saved to the Dataset file will have its Number of Replicates parameter truncated to match the actual number of completed replicates.

4

Tuning and Optimization

Each method includes tuning and optimization files that specify the hardware settings under which determinations will occur.

Topics in this section include:

- ▶ “The SmartTune™ Function” on page 85
- ▶ “Custom Tuning” on page 93
- ▶ “Understanding Deadtime Corrections” on page 94
- ▶ “Tuning Window Software Reference” on page 96
- ▶ “Optimization Window Software Reference” on page 98

Tuning and Optimizing your Instrument

Generally, you should tune and optimize the instrument using the SmartTune function. However, **Advanced Users** can use the Tuning and Optimization windows to perform high-precision or custom calibrations.

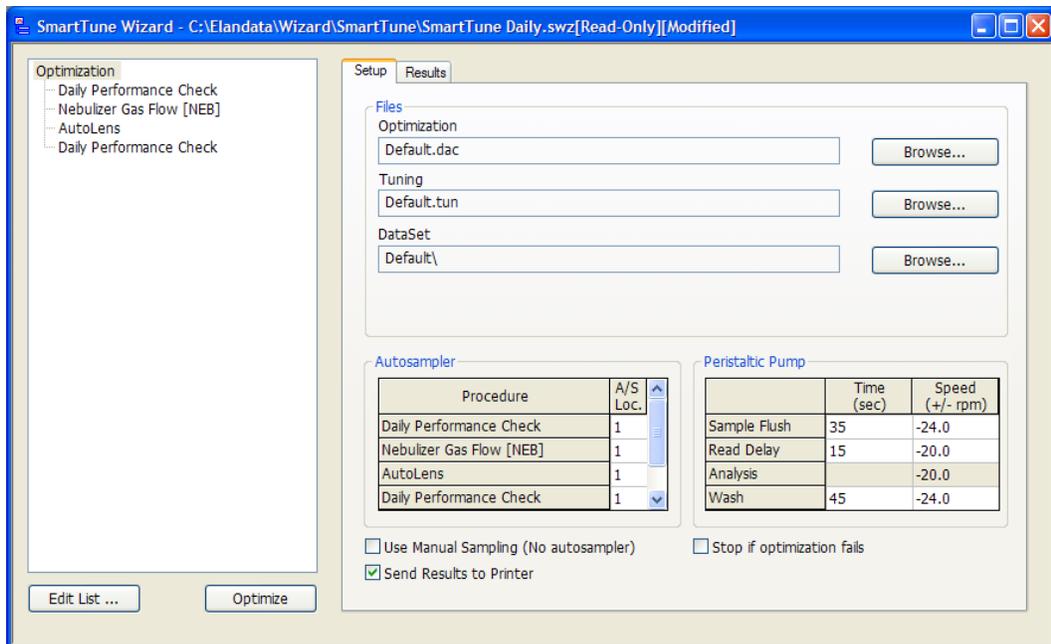
The SmartTune™ Function

The SmartTune function tunes and optimizes the instrument by running a series of procedures you select. The resulting values are saved in the optimization file. All optimization procedures have default settings and methods that can be modified as required. If you modify a default method file, you should save it with a new name, and revise any affected SmartTune files accordingly.

Understanding the SmartTune™ Optimization Process

The SmartTune function optimizes the instrument automatically by executing a series of selectable methods. You use the main SmartTune window to select which procedures to run in sequence and to fine-tune the procedures. You select which method file to use, along with the start, step, and end values for each procedure.

You can select up to two retries for each optimization procedure, and change the start, step, and end values to extend the optimization range in the event that an optimum setting is not achieved on the previous pass. The software automatically selects the same method and criteria for the retries as those used on the previous pass.



Main SmartTune window

The SmartTune™ Default Files

The SmartTune function comes with three default files to cover regular optimization tasks—*SmartTune Daily*, *SmartTune Monthly*, and *SmartTune Full*. You can run these files as they come, or modify and add to them to meet your specific needs.

Daily Optimization Process

The daily optimization process targets the sample introduction system, torch, and cones. Perform this process daily, as long as the instrument has not been modified or had heavy use since the last optimization. If performance is not adequate after this procedure, check the hardware of the sample introduction system, torch, and cones, and clean or replace as needed. If this fails to produce adequate performance, run a monthly or full optimization.

Monthly Optimization Process

This process builds on the daily optimization process, adding Detector Voltages and Dual Detector optimizations. Run a monthly optimization process on a regular—approximately monthly—basis, or whenever you want to verify that the detector voltages are optimized.

Full Optimization Process

This process builds on the monthly optimization process, adding a Mass Calibration and Resolution adjustment. Perform this process only when the state of the instrument is unknown, after a major subsystem has been serviced, or when all else fails to explain poor performance.

When to Perform Optimization Procedures

Note: When run, a Mass Calibration and Resolution should come first in a complex optimization, but it is not normally a daily procedure. Run it daily only if you are using certain EPA methods, such as US EPA method 200.8 or 6020a.

Optimization Procedures: ELAN® 6000/ 6100/ 9000 Instruments

Procedure	When to Perform
X-Y Adjustment	Daily; whenever you clean or replace the cones; or after any maintenance procedures in the torch chamber.
Nebulizer Gas Flow	Daily.
AutoLens™ Calibration	Daily. This procedure is required when the AutoLens option is used in your method. Also, perform an AutoLens Calibration when sample matrices are significantly different to achieve the best performance.
Detector Voltages Optimization	Monthly.
Deadtime Correction	This procedure is required only when the detector is replaced, in which case you should do it after the detector optimization.
Dual Detector Calibration	Perform a Dual Detector Calibration when you require extended dynamic range (above two million counts per second) in a quantitative analysis. A detector calibration is always necessary if you have selected Dual Mode in the Method window Processing tab. You must calibrate for each analyte you want to quantitate. A minimum of two masses is required for cross-calibration.
Lens Voltage Optimization	Perform this procedure only when you require maximum sensitivity for reading a single element.

Standard Mode Optimization Procedures: ELAN® 6100 DRC™ / DRCPlus/ DRC II/ DRC-e Instruments

Procedure	When to Perform
Tuning and Mass Calibration	When the sensitivity cannot be recovered through optimization or when there are changes made to the quadrupole power source electronics.
X-Y Adjustment	After you clean or replace the cones, and after any maintenance procedures in the torch chamber.
Detector Voltages Optimization	When sensitivity cannot be recovered through other cleaning or optimization methods or when the detector is replaced.
Deadtime Correction	Only when a detector has been replaced, and after the new detector has been optimized.
Dual Detector Calibration	When you have selected Dual Mode in the method, and require extended dynamic range (above 2 million counts per second) in a quantitative analysis. You must calibrate for each analyte you want to quantitate. A minimum of two masses is required for cross-calibration.
Optimizing Nebulizer Gas Flow	Daily.
Optimizing Makeup Gas Flow	Daily, if the Makeup Gas Option has been installed.

Standard Mode Optimization Procedures: ELAN® 6100 DRC™ / DRCPlus/ DRC II/ DRC-e Instruments

Procedure	When to Perform
AutoLens™ Calibration	Daily. Required when the AutoLens function is used in your method. Perform an AutoLens Calibration when sample matrices are significantly different.
Optimizing Cell Path Voltage	When the daily performance check does not meet specifications.
Optimizing Cell Rod Offset [Std]	When the daily performance check does not meet specifications.

DRC Mode Optimization Procedures: ELAN® 6100 DRC™ / DRCPlus/ DRC II/ DRC-e Instruments

Procedure	When to Perform
Estimating DRC Mode Detection Limits	When measured detection limits do not meet requirements.
Optimizing Cell Gas Flow	When measured detection limits do not meet requirements.
Optimizing DRC Mode Nebulizer or Makeup Gas (DRC II only) Flow	When measured detection limits do not meet requirements.
Lens Voltage Optimization	Perform this procedure only when you require maximum sensitivity for reading a single element.
Optimizing DRC Mode Cell Rod Offset (CRO)	When measured detection limits do not meet requirements.
Optimizing DRC Mode Quadrupole Rod Offset (QRO)	When measured detection limits do not meet requirements.
Optimizing DRC Mode Cell Path Voltage (CPV)	When measured detection limits do not meet requirements.

SmartTune™ Software Reference

This section describes the SmartTune software.

Main Optimization parameters

You must configure the following overall settings before running an optimization. Click *Optimization* in the list, and then click the Setup tab to access these settings:

- **Optimization list:** The left side of the SmartTune window shows a list of optimization procedures to be processed in sequence. Click Edit List to add procedures. You can change the optimization sequence by dragging and dropping entries in the list. You can also click an entry in the list to show the details for that procedure. Or right-click a procedure in the list, and then click:
 - ♦ *Delete* to remove a procedure from the list.
 - ♦ *Quick Optimize* to run the selected procedure only.
- **Files group:** These fields let you specify the target Optimization, Tuning, and Dataset files to store your optimization data. Use the default files displayed, or browse to select different files.
- **Autosampler:** These settings specify autosampler locations for each procedure:

- ♦ **Procedure** displays read-only entries that are updated when entries in the optimization procedure list are added, deleted, or dragged and dropped
- ♦ **A/S Location** lists the autosampler tray positions for the solution to be used for each optimization. This entry is ignored if a manual analysis with no autosampler is being performed
- **Peristaltic Pump:** These settings provide peristaltic pump settings derived from the default Global Pump Settings. Change these to override the default settings when running a SmartTune:
 - ♦ *Sample Flush Time:* Specifies the time in seconds during which the sample tubing is flushed with sample solution. Type a value between 0 and 999 999.
 - ♦ *Sample Flush Speed:* Specifies the pump speed in rpm during the flush cycle. Any value between ± 48 is valid.
 - ♦ *Read Delay Time:* Specifies the time in seconds between the end of the flush cycle and the beginning of data acquisition. Type a value between 0 and 999 999.
 - ♦ *Read Delay Speed:* Specifies the pump rate in rpm used during the read delay cycle. Any value between ± 48 is valid. A negative (-) value indicates counter-clockwise rotation of the pump head and a positive (+) value indicates clockwise rotation.
 - ♦ *Analysis Speed:* Read only. Displays the pump rate in rpm used during the determination. A negative (-) value indicates counter-clockwise rotation of the pump head and a positive (+) value indicates clockwise rotation.
 - ♦ *Wash Time:* Specifies the time in seconds during which the sample tubing is rinsed with wash solution following completion of data acquisition. Type a value between 0 and 999 999.
 - ♦ *Wash Speed:* Specifies the pump speed in rpm used during the wash cycle. Any value between ± 48 is valid. A negative (-) value indicates counter-clockwise rotation of the pump head and a positive (+) value indicates clockwise rotation. During a wash cycle, you can use a more rapid pump rate to quickly wash sample solution from the sample tubing.
- **Use Manual Sampling (No Autosampler):** Enable this check box if you do not use an autosampler. Note that, if using manual sampling, you will be prompted to aspirate each optimization solution in turn—*Read* and *Flush* delays will not apply.
- **Send Results to Printer:** Enable this check box if you want to automatically print the result reports following optimization.
- **Stop if optimization fails:** Enable this check box if you want the SmartTune process to stop immediately following any unsuccessful optimization.
- **Edit List:** Accesses the optimization procedure selection dialog box.
- **Optimize:** Starts the SmartTune optimization.

SmartTune™ Procedures

Note: Generally, you should accept the default parameters for each optimization procedure. Proceed with the following steps only if you wish to customize the optimization.

- **AC Rod Offset:** *Service mode only. Available on ELAN® 9000 series instruments only.* Use to optimize the AC Rod Offset.
- **AutoLens Calibration:** Use to optimize AutoLens parameters to adjust the lens scanning system for maximum efficiency measuring the isotopes of interest. The AutoLens function compensates for matrix suppression and space charge effects in the ion optics. It also allows you to achieve optimum sensitivity for each isotope in your determinations.
- **Auxiliary Gas Flow:** Use to optimize the Auxiliary Gas Flow. *Available on DRC™ series instruments. Available on ELAN 9000 series instruments only if an MMFC (optional Multi-Channel Mass Flow Controller) is present.*
- **Axial Field Voltage:** *Service mode only. Available on DRC series instruments only.* The Axial Field (AFT) voltage does not require frequent optimization because it has a very broad optimization peak. However, if you suspect that the AFT voltage requires optimization, the following procedure may be used. The AFT voltage optimization value is dependent on the lens voltage, cell path voltage, and the cell rod offset, therefore the AFT voltage should be optimized following the optimization of these parameters. If the value changes by greater than 100 V, you may want to reiterate the optimization of the lens voltage, cell path voltage, the cell rod offset, and finally re-optimize the AFT voltage.
- **Cell Path Voltage Std [CPV]:** *Available on DRC series instruments only.* Use this procedure to set up the DRC Cell Path Voltage for Standard mode. The Dynamic Reaction Cell acts like a long AC-only section, and as such exhibits such properties as mass dependent focusing, and multiple maxima for analyte versus voltage profiles. In addition, to reduce complexity of optimization, the potential (DC-Offset) on the short AC-only prefilter, and the potential on the plate lenses at the entrance and exit of the Cell are linked. Similar mass-dependence, and multiple optima are seen when optimizing the cell path voltage, and cell RF voltage. Optimization for these parameters can no longer consist of a single mathematical criteria, but must take into account mass bias (the relative balance of low, mid, and high mass intensity) and also the continuum background, which is influenced by ion path voltages. The ultimate measure of the instrument's power is its ability to achieve extremely low detection limits. The most important factor contributing to the detection limit measurement is the chemical background signal. In many instances, the measurement is governed by the instrument's continuum background. When optimizing, try to trade off signal intensity for reduced background in almost every instance. An increase in background from 1 cps to 2 cps typically requires a four-fold increase in analyte sensitivity to maintain the same detection power.
- **Cell Path Voltage [CPV]—DRC Mode:** *Available on DRC series instruments only.* While optimizing the CPV for DRC Mode, your aim is to select a value that results in minimum background while maintaining maximum analyte signal.
- **Cell Rod Offset [CRO]:** *Available on DRC series instruments only.* Use this procedure to set up the DRC rod offset voltage for standard mode. The Dynamic Reaction Cell acts like a long AC-only section, and as such exhibits such properties as mass dependent focusing, and multiple maxima for analyte versus voltage profiles. In

addition, to reduce complexity of optimization, the potential (DC-Offset) on the short AC-only prefilter, and the potential on the plate lenses at the entrance and exit of the Cell are linked. Similar mass-dependence, and multiple optima are seen when optimizing the cell path voltage, and cell RF voltage. Optimization for these parameters can no longer consist of a single mathematical criteria, but must take into account mass bias (the relative balance of low, mid, and high mass intensity) and also the continuum background, which is influenced by ion path voltages. The ultimate measure of the instrument's power is its ability to achieve extremely low detection limits. The most important factor contributing to the detection limit measurement is the chemical background signal. In many instances, the measurement is governed by the instrument's continuum background. When optimizing, try to trade off signal intensity for reduced background in almost every instance. An increase in background from 1 cps to 2 cps typically requires a four-fold increase in analyte sensitivity to maintain the same detection power.

- **Cell Rod Offset Std [CRO]—DRC Mode:** *Available on DRC series instruments only.* When optimizing the CRO in DRC Mode, your aim is to select a value that results in minimum background noise while maintaining the maximum analyte signal.
- **Daily Performance Check:** Use this procedure to set up a daily performance check, and to validate that background count, sensitivities, and oxides are all within the desired ranges.

Note: Some systems may not be able to meet the default performance values indicated in the SmartTune files. These default criteria reflect the factory specifications to which your instrument is certified when manufactured. Laboratory conditions and normal instrument use can affect performance over time, as can modifications to instrument operating parameters, sample introduction systems, and other hardware. Consequently, these criteria may no longer be achievable following initial performance verification. In this event, you can still obtain excellent analytical results in most cases by employing the appropriate QC protocols.

- **Detector Voltages Optimization:** This process optimizes the voltages for both the pulse and analog stages to improve detector performance.
- **Discriminator Threshold:** *Service mode only.* A bracket with two capacitors connected in parallel sits on the ion detector high voltage power supply board to reduce the ripple noise on the pulse stage positive high voltage. This bracket has EMI fingers for grounding purposes. By reducing the ripple, the instrument can operate at a lower discriminator level and a lower multiplier gain, thereby extending the life of the detector. The factory setting for the discriminator threshold is printed on the data sheet that is shipped with the instrument. The optimum discriminator threshold is set so the instrument can distinguish between real pulses and electronic noise. If, after a period of time, the noise increases, optimize the discriminator. When you have finished, optimize the detector voltages.
- **Dual Detector Calibration:** Dual detector calibration extends the dynamic range of the detector by normalizing the analog stage to the pulse stage. The calibration must contain each analyte you want to quantitate using extended dynamic range. Perform a dual detector calibration only as required. Before doing this procedure, you must calibrate the detector voltages.
- **ICP RF Power:** *Available on DRC series instruments only.* Use this procedure to optimize the ICP RF power only when required. You will seldom need to perform this procedure. The ICP RF power is set to a value of between 1200 and 1500 watts,

depending on the sample introduction system used and the nature of the sample matrix.

- **Lens Voltage:** Use this procedure to optimize the lens voltage parameters. Generally, you will use the AutoLens functions—use this procedure only when you require maximum sensitivity for reading a single element.
- **Mass Calibration and Resolution:** Use this procedure to set up the mass calibration and resolution optimization parameters. You can alter the Peak Search Window (amu) and custom Resolution DAC in the Tuning window. The SmartTune function performs the calibration based on the definitions in the tuning file. Note that Mass calibration and resolution is not normally performed daily—you should perform this process daily only if you are using certain EPA methods, such as US EPA method 200.8 or 6020a.
- **Makeup Gas Flow [MGF]:** *Available on DRC series instruments only.* This option is available only if the Makeup Gas function is installed and activated within the software. Use this procedure to set up a makeup gas optimization to achieve optimum sensitivity while also meeting the oxide ratio criterion.
- **Makeup Gas Flow [MGF]—DRC Mode:** *Available on DRC series instruments only.* This option is available only if the Makeup Gas function is installed and activated within the software. Use this procedure to set up a makeup gas optimization to achieve optimum sensitivity while also meeting the oxide ratio criterion.
- **Nebulizer Gas Flow [NEB]:** Use this procedure to optimize the nebulizer gas flow. The nebulizer gas flow rate is a key operating parameter. An excessive flow rate cools the plasma and can decrease ionization efficiency while increasing molecular ion formation. Decreasing the flow reduces the analyte introduction rate and warms the plasma, reducing the analyte signal and molecular species, and increasing the number of doubly-charged ions.
- **Nebulizer Gas Flow [NEB]—DRC Mode:** *Available on DRC series instruments only.* Use this procedure to optimize the nebulizer gas flow in DRC Mode. When optimizing nebulizer gas flow in DRC Mode, aim for a value that results in minimum background while maintaining maximum analyte signal.
- **Nebulizer Gas Flow [NEB]—Standard Mode:** *Available on DRC series instruments only.* Use this procedure to optimize the nebulizer gas flow in Standard Mode.
- **Plasma Gas Flow:** Use this procedure to set up the plasma gas flow optimization parameters. *Available on DRC series instruments. Available on ELAN 9000 series instruments only if an MMFC (optional Multi-Channel Mass Flow Controller) is present.*
- **Quadrupole Rod Offset [QRO]—Standard Mode:** *Available on DRC series instruments only.* Use this procedure to optimize the quadrupole rod offset in standard mode.
- **Quadrupole Rod Offset [QRO]—DRC Mode:** *Available on DRC series instruments only.* To obtain sufficient transport through the quadrupole mass filter, the DRC Mode QRO must be made more negative than the DRC Mode CRO. This is because the ions are collisionally damped within the DRC when it is closed and pressurized. At all useful cell gas flows, the ions are nearly thermalized and have a potential energy nearly the same as the cell rod offset. In most cases, the DRC Mode QRO value can be set without optimization according to the relationship: **DRC Mode QRO = DRC Mode**

CRO -5.5. While optimizing the DRC Mode QRO, your aim is to select a value that results in minimum background while maintaining maximum analyte signal.

- **Secondary Gas Flow:** *Available on non-DRC series instruments only.* This option is available only if the Secondary Gas function is installed and activated within the software, and only if an MMFC (optional Multi-Channel Mass Flow Controller) is present. Use this tab to set up the secondary gas optimization parameters.

Procedure Settings

Most of the optimization procedures available through the SmartTune function share common settings. These are listed here.

SmartTune Common Controls

Control	Function
Method	Displays the method file used with this optimization procedure. Use the default method displayed, or click Browse to select a different file.
Criteria	These options define the criteria against which the instrument optimizes for this function. Typically, you will click to choose one analyte for Intensity optimization or one analyte Formula; the formula option allows you to optimize on a relationship between two signals. Other criteria are listed with the individual procedures.
Range	These settings define the range the instrument will measure. During optimization, the system moves through a series of values, with data acquired at each value. You control the start and end flow values, and the step size.
Ramp	Select the Ramp check box to specify that the software should conduct an optimization, but should return to the original value when completed. Use this option when you want to review the data before making any parameter changes, or want to select a value that does not result in the highest possible signal.

Custom Tuning

Important! Generally, you should tune and optimize the instrument using the SmartTune function. However, **Advanced Users** can use the Tuning and Optimization windows to perform high-precision or custom calibrations.

The Tuning file manages the instrument's quadrupole mass filtering performance. The tuning functions permit automated parameter setting for mass calibration and resolution. You should tune the instrument on a monthly basis, or whenever there are changes to the instrument's electronics, or you need to modify resolution for one or more elements.

Note: The instrument must run for at least 30 minutes with the plasma on before you perform tuning.

Using the Tuning Controls

The Tuning controls are used to perform a mass calibration or to adjust resolution of the mass spectral peaks. The tuning procedure is quick to perform and is good for fine-tuning the spectrometer for optimum performance. This procedure should be done on a monthly basis.

The results from each set of tuning adjustments are initially stored in the file default.tun. You can elect to save the results in a separate file with a name that you specify. Each analytical method used to acquire data contains a Tuning file.

What is a DAC?

The software tuning and optimization controls include several entries and controls using the acronym DAC. A DAC is a digital-to-analog converter channel connected to a specific hardware subsystem. An electronically controlled hardware component is adjusted by varying the setting of its related DAC.

What Happens During Tuning?

Tuning adjustments affect the DAC settings for the quadrupole subsystem. The quadrupole systems act as a mass filter; tuning affects the timing of ions through this filter, and the shape of the resulting mass spectral peaks. Use the tuning controls to perform the following operations:

- A mass calibration to adjust the instrument's electronics and ensure the accuracy of the mass spectrometer
- A resolution check and adjustment to ensure that the resolution at each mass of interest is within the defined range

When running either operation, keep the Interactive Graphics window open to view the results.

Mass Calibration

When a mass calibration is performed, the Interactive Graphics window displays a series of graphs corresponding to the individual elements measured during the calibration. During calibration, the instrument performs a determination on a test solution, typically a solution covering a broad mass range. The instrument determines the maximum intensity of each isotope in the solution and its atomic mass relative to its intensity—the measured mass of the isotope.

During this measurement, the system scans for a peak within a predefined scan width region centered around the exact, or known, mass for that isotope. The instrument can then compensate for the differences between the apparent and exact mass.

Resolution Check or Adjustment

Resolution is measured as the peak width at 10% peak height. The hardware is preset to scan the entire mass range at 0.7 amu resolution. This setting provides the best balance between peak separation and signal-to-noise ratio for most applications. The resolution can be adjusted on an individual mass basis, for example to correct for spectral interferences. Again, a test solution covering a broad mass range is typically employed. However, when adjusting resolution, you may want to use the analytes included in your analysis method.

The system scans the specified analytes within a predefined scan width region centered around the known mass for each analyte isotope, then measures the peak width at 10% peak height. This value should normally be approximately 0.7 amu. Resolution should be within ± 0.10 amu of the expected resolution or an adjustment should be made.

Understanding Deadtime Corrections

Deadtime correction is a mathematical equation that is used to correct for erroneous readings at high count rates (pulse counting) caused by the finite width of the detector output pulses. At these high count rates ($> 1,000,000$ cps approximately) there is a finite probability that two pulses will arrive at the detector output simultaneously. The deadtime correction function corrects for this anomaly.

Deadtime Calculation

Characteristic of all ion detection systems, deadtime (τ) is the amount of time required for the detector to process the signal from an incident ion. Following an ion strike, the detector is unable to record another strike for a short period of time—this *deadtime* is typically 50 - 60 ns. If two ions arrive at the detector within t seconds of each other, the second ion is not counted. At low count rates of less than $1e5$ cps, only @0.5% ions arrive during this period, and the count rate measured by the detector is 0.5% less than the count rate impinging upon the detector. At higher count rates, however, the effect is more significant and follows the relation:

$$R_{\text{true}} = R_0 / (1 - R_0\tau)$$

where:

R_{true} is the ion count rate arriving at the detector.

R_0 is the ion count rate measured by the detector.

τ is the deadtime.

When the deadtime of the system has been measured, the above equation can be applied to correct for it. The software uses the deadtime correction to compensate for counting loss at high ion arrival rates. When measuring using signals above $2e5$ cps, you must ensure that the deadtime correction is set accurately.

Tuning Window Software Reference

This section describes the Tuning Window software.



Tuning window

Items on the Tuning Window

- Tune Mass Spec:** Initiates a mass calibration and peak width measurement. Results from a resolution measurement are displayed numerically in the Peak Width (amu) column of the data table on this window, and graphically in individual isotope graphs in the Interactive graphics window. Typically, this measurement takes only a few minutes to complete.
- Peak Width Only:** Specifies that the Mass Calibration DAC value will not be adjusted based on the measured mass. This is used to adjust the Resolution DAC value independently of the Mass Calibration DAC value.

Note: Because changes made exclusively to the resolution DAC affect the mass calibration, you should always adjust the resolution and mass calibration in tandem.
- Peak Search Window (amu):** Specifies the width of the search window in which the software will look for a peak to identify with a specific isotope being measured. The value entered defines a window in atomic mass units centered around the known mass for each isotope used in the calibration. You can reduce the value to avoid accidentally calibrating on an interfering peak. If you need to use a value that is above 1 amu to find the peak, you should perform a hardware optimization, because some performance irregularity is affecting the instrument's mass discrimination functionality. For example: If you are calibrating for Mg (24), with a known mass of 23.985 amu, and have set the Peak Scan Width to 1 amu, then the search range extends from 23.485 amu to 24.485 amu.
- Resolution DAC:** Adjusts the digital-to-analog converter setting, which controls the peak width. The text following the field identifies which analyte in the data table is currently selected. To make a change to the DAC value for a specific isotope, click in the Resolution DAC value cell for that isotope and type the new value. To verify the effect of the change on the peak width, you must perform the resolution measurement again. The new results are displayed in the Peak Width (amu) field.

- **Analyte:** Lists the name of an element being included in the calibration measurement. To enter a new element, type the abbreviated symbol for the element, or right-click the mouse and select an element from the Periodic Table dialog box that appears.
- **Mass (amu):** Identifies which isotope of the element shown in the Analyte entry will be used during the calibration. Normally, you use the isotope with the highest natural abundance. To enter a mass value, type the exact known mass for the isotope of interest. If you are not certain of the mass, right-click the Analyte entry. In the Periodic Table dialog box that appears, click the element of interest. Its isotope list displays. You can click the isotope of interest, then click *OK* to return to the Tuning window. The mass value is automatically inserted.
- **Measured Mass (amu):** Lists the atomic mass for the isotope at the point of maximum intensity—the apparent, or measured, mass after a measurement is completed. When the Tuning window is first opened, this field is empty. Because the exact, or actual, mass is known, the instrument can then compensate for the differences in all future determinations and calculations.

If desired, you can use the Resolution DAC Value entry to adjust the Measured Mass result so that it is closer to the actual mass value. When you make an adjustment in the Resolution DAC Value entry, you should always rerun the mass calibration procedure to verify its effect on the Measured Mass value.

- **Mass Calibration DAC Value:** Makes adjustments to the mass discrimination functionality in order to correct for differences between the measured and known mass values. To make a change to the Resolution DAC Value for a specific isotope, click in the Resolution DAC Value cell for that isotope and type the new value. To verify the effect of the change on the calibration, you must perform the mass calibration again. The new results are displayed in the Measured Mass (amu) field.
- **Resolution DAC Value:** Lists the current setting for the Resolution DAC and permits you to modify the value. To adjust the DAC setting, click in the Resolution DAC Value cell for the desired analyte and type the new DAC value. You may also use the DAC field which appears above the data table.

To adjust resolution, make changes to the DAC as follows:

- ♦ To increase resolution (narrow the peak width), increase the DAC setting
- ♦ To decrease resolution (broaden peak width), decrease the DAC setting
- **Measured Peak Width (amu):** Lists the peak width at 10% of peak height after a measurement is completed. When the Tuning window is first opened, this field is empty. If desired, you can use the Resolution DAC field to adjust the peak width. When you make an adjustment in the DAC entry, you should always rerun the resolution adjustment procedure to verify its effect on the peak width value.
- **Custom Resolution:** Marks an analyte that has a different resolution. This entry does not affect the actual spectrometer controls and is used only as a reminder for the operator.

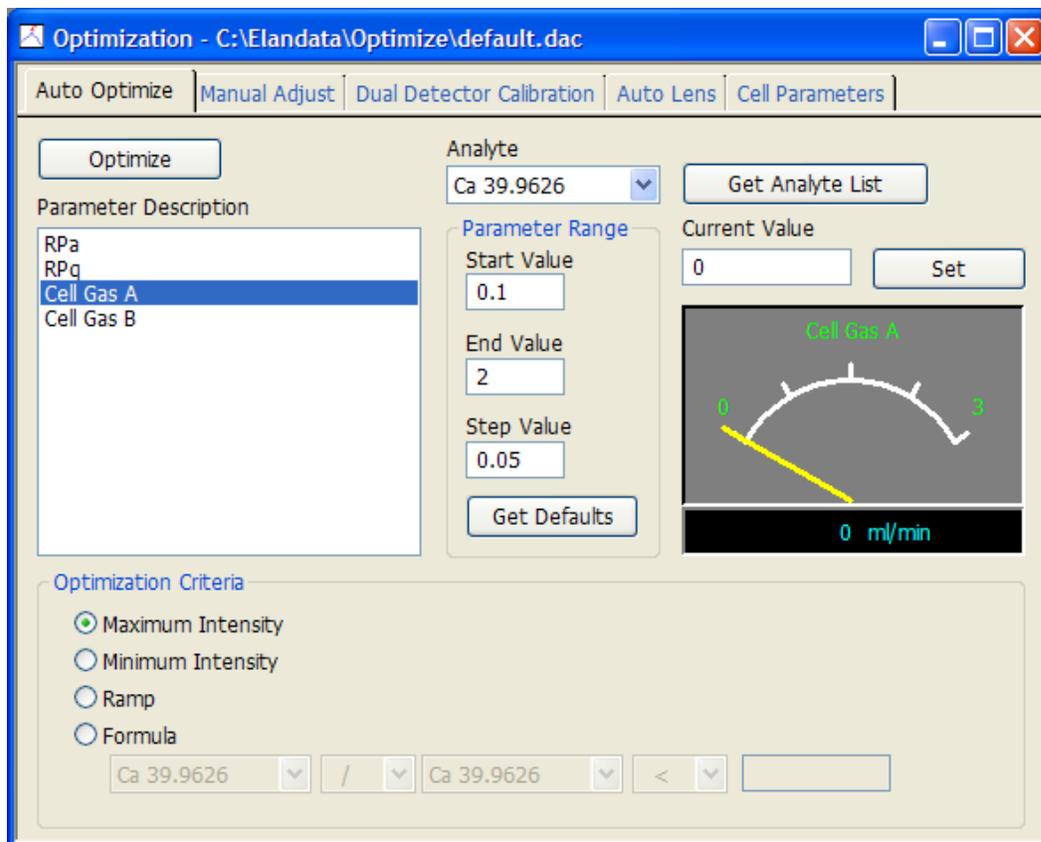
Optimization Window Software Reference

Use the Optimization window to fine-tune the hardware subsystems in the torch/quadrupole assembly. Here you can adjust control parameters for the digital-to-analog converters (DACs) associated with these functions. When opened, this window displays the last file accessed. The Optimization window has several tabs:

- **Auto Optimize tab:** Use this tab to control advanced optimization routines for cell gases and RPa/RPq. *DRC Series instruments only.*
- **Manual Adjust tab:** Use this tab to manually adjust the DAC values, so you can make DAC adjustments without having to perform the full optimization procedure.
- **Dual Detector Calibration tab:** Use this tab to view the performance of each detector element (pulse and analog) and the crossover points between the two detector systems.
- **AutoLens tab:** Use this tab to view the ion lens scan to maximize ion throughput at all masses.
- **Cell Parameters tab:** Use this tab to view advanced optimization routines for cell gases and RPa/RPq. *DRC series instruments only.*

Auto Optimize tab

DRC series instruments only. **Advanced users only** can use this tab to perform advanced optimization routines for cell gases and RPa/RPq. Generally, you should optimize these settings using the DRC Method Development function. Use the Auto Optimize tab only when you need to examine the process more closely.



Optimization window Auto Optimize tab

Items on the Auto Optimize tab

- **Optimize:** Initiates automated optimization of the subsystem currently selected in the Parameter Description field. The automated routine will proceed using the specifications currently listed on this tab and in the analytical method that is currently open in the Method window.
- **Get Analyte List:** Retrieves the list of analytes specified in the current method. The complete list of analytes specified on the Timing tab of the Method window are retrieved
- **Current Value:** Lists the active value of the hardware parameter specified in the Parameter Description field. This current value is the number which will be used whenever a determination is run using the active Optimization file. To change the default value, click in the field, delete the existing value, type a new number, and click **Set**. The valid range of entries depends on the specific subsystem selected. The system prompts you with a warning message if a value you enter falls outside the allowable range. Any change you make in the Current Value entry will be used for all subsequent determinations.

- **Description:** Displays a description of the Optimization file. Read-only. File descriptions are entered when you save a new file.
- **Analyte:** Specifies the element on which you want to optimize. To select an element, select the desired isotope from the drop-down list. If no isotopes are listed in the drop-down list, click Get Analyte List to retrieve the list of available isotopes.
- **Spike Concentration (ppb):** Use this entry to specify the concentration in ppb of the standard solution or spike when performing an automated RPq optimization. All analytes in this solution must have the same concentration.
- **Start Value:** Specifies the start value for system optimization. The value applies to the currently selected parameter in the Parameter Description field. During optimization, the software ramps the Resolution DAC Value between the Start Value and the End Value, increasing in successive measurements by the Step Size parameter. The intensity for the selected analyte is then plotted in the Interactive graphics window as a function of the parameter value to determine the optimum setting.
- **End Value:** Specifies the final value for system optimization. The value applies to the currently selected parameter in the Parameter Description field. During optimization, the software ramps the DAC value between the Start Value and the End Value, increasing in successive increments by the Step Size parameter. The intensity for the selected analyte is then plotted as a function of the parameter value to determine the optimum setting.
- **Step Value:** Specifies the amount the Start Value will be increased during successive measurements of a system optimization procedure. The value applies to the currently selected parameter in the Parameter Description field. During optimization, the software ramps the DAC value between the Start Value and the End Value, increasing in successive measurements by the Step Value. The intensity for the selected analyte is then plotted as a function of the parameter value to determine the optimum setting.
- **Maximum Intensity:** Specifies that the software should calculate the parameter value which creates the highest signal intensity during an optimization, then insert that value into the Current Value entry.
- **Minimum Intensity:** Specifies that the software should calculate the parameter value that creates the lowest usable signal intensity during an optimization, and then insert that value into the Current Value entry.
- **Ramp:** Specifies that the software should conduct an optimization, but should return to the original value when completed. This option is selected when you want to review the data before making the parameter change, or want to select a value which does not result in the highest possible signal.
- **Formula:** Allows you to optimize on a relationship (formula) between two signals. The most common relationship is signal-to-noise ratio. This involves placing the analyte of interest in the first window under the Formula option. Then select an operation (+, -, × or /). Select the second analyte and determine the relationship of either greater than, less than or max (<, >, or max). In the final field insert a value. For example: CeO 156/Ce 140 < 0.03 (Formula used to optimize the oxide ratio.)
- **Parameter Description:** Lists the available hardware subsystems, which can be optimized using the electronic optimization protocol. To select an option, click the desired parameter. The following parameters are available for optimization:

- ♦ **RPa**: Adjusts the DC voltage applied to the reaction cell quadrupole.
- ♦ **RPq**: Adjusts the RF voltage applied to the reaction cell quadrupole.
- ♦ **Cell Gas A**: Adjusts the flow rate of the first reaction cell gas. If Cell Gas A and B are <0.1, the instrument is in Standard Mode.
- ♦ **Cell Gas B**: Adjusts the flow rate of the second reaction cell gas. This parameter is only available if cell gas B option is installed. If Cell Gas A and B are <0.1, the instrument is in Standard Mode.

Manual Adjust tab

This tab displays the active optimization parameters for the current optimization file in the data table. Use this tab to make fine adjustments to the hardware subsystems without having to perform a full optimization routine.

These settings are intended for **trained service representatives and experienced users only**. If you are unfamiliar with these settings, use the SmartTune™ functions instead.

DRC series instruments only: The data table is split in order to differentiate between standard and DRC mode. The parameters specific to DRC mode are grouped together and highlighted in yellow. Parameters specific to standard mode are grouped together and remain white. Reaction cell parameters are blue.

	Current Value	Description	Step Value	Settling Time (sec.)	Minimum Value	Maximum Value
1	0.9	Nebulizer Gas Flow [NEB]	0.02	10	0	1.5
2	1.2	Auxiliary Gas Flow	0.025	10	0.6	2
3	15	Plasma Gas Flow	0.5	10	10	20
4	6	Lens Voltage	0.25	0	-24	20
5	1100	ICP RF Power	50	15	500	1600
6	-1850	Analog Stage Voltage	-100	2	-3000	0
7	950	Pulse Stage Voltage	50	2	0	2500
8	0	Quadrupole Rod Offset Std [QRO]	0.5	1	-17.9	17.9
9	-10	Cell Rod Offset Std [CRO]	1	1	-40	10
10	70	Discriminator Threshold	5	0	0	1000
11	-15	Cell Path Voltage Std [CPV]	1	1	-60	20
12	0	RPa	0.005	0	0	0.24
13	0.25	RPq	0.05	0	0.05	0.9
14	0	Cell Gas A	0.05	10	0	3
15	0	Cell Gas B	0.05	10	0	3
16	0	DRC Mode NEB	0.01	10	0	1.5
17	-6	DRC Mode QRO	0.5	1	-17.9	17.9

Optimization window Manual Adjust tab

Items on the Manual Adjust tab

- **DAC:** Lists the DAC which is currently selected in the data table along with an entry showing the current value assigned to the DAC.
- **Analyte:** Displays the analyte currently selected in the Auto Optimize tab. Read-only.
- **Display Mode:** Select *Basic View* to display only the commonly used DAC parameters in the Manual Adjust tab. These are the parameters that are optimized more routinely. Select *Advanced View* to display all of the DAC parameters in the Manual Adjust tab. The basic view and advanced view settings also control the parameter list in the Parameter Description field on the Auto Optimize tab. When Service Mode is enabled, the service DAC parameters are displayed in addition to the basic or advanced parameters.
- **Current Value:** Lists the current value assigned to the DAC. To change the value, click in the desired cell, delete the old entry and type a new value. The acceptable range for entries is listed in the Minimum Value and Maximum Value entries.
- **Description:** Lists a description of the hardware subsystem associated with the DAC. The software is shipped with descriptive information already filled in.
- **Step Value:** Defines the default Step Value that will be used in an automated optimization.
- **Settling Time (sec.):** Shows the amount of time in seconds that the instrument waits after a parameter value has incremented before making the analyte measurement. This time allows the analyte signal to stabilize.
- **Minimum Value/Maximum Value:** Displays the acceptable parameter range for each DAC. The DAC Resolution value may not be set outside the limits defined by these numbers.

Dual Detector Calibration tab

Use this tab to view the dual detector settings, to ensure that the two stages of the detector provide a linear response over the entire dynamic range of the system. You should generally perform a dual detector calibration using the SmartTune™ function. Use the Dual Detector Calibration tab only to view current dual detector calibration settings, or to reprocess a calibration using previously acquired data.

Optimization - C:\Elandata\Optimize\default.dac

Auto Optimize | Manual Adjust | **Dual Detector Calibration** | Auto Lens | Cell Parameters

Get Analyte List | Clear Calibration | Calibrate From Dataset

Dataset Pathname: Default\
 Sample Filename: C:\Elandata\Dataset\Default\Dual Detector Calibration.011
 Date: 2006/12/21 2:40:54 PM
 Points Acquired: 65

	Analyte	Mass	#Points	Coefficient	Gain	N(max)	Conversion Factor
1	N	14.0031	65	1	978020	1.2801e+007	9.99924
2	H3O	19.0183	65	1	977993	1.28013e+007	9.99897
3	O2	32.994	65	1	977919	1.28023e+007	9.99821
4	ArO	55.9573	65	1	977797	1.28039e+007	9.99696
5	Ar2	79.9248	65	1	977669	1.28056e+007	9.99565
6							
7							
8							

Optimization window Dual Detector Calibration tab

Items on the Dual Detector Calibration tab

- **Get Analyte List:** Copies the list of analytes that are included in the active method. Before a calibration can proceed, analytes must be listed in the dual detector calibration data table, and a method which measures the listed analytes must be loaded in the Method window. If you have the proper analytical method loaded, you can copy the list of analytes in the Dual Detector Calibration data table by clicking the Get Analyte List button.
- **Clear Calibration:** Clears the current dual detector calibration data before a new calibration is created by collecting new data or using Calibrate From Dataset.
- **Calibrate From Dataset:** Reads dual detector calibration information from previously acquired data, as long as two data files corresponding to a dual detector calibration are selected. When data is acquired, the dual detector calibration information is stored along with other operating parameters in the dataset. This information can be used to calibrate the system for current analytical determinations.

Any valid dataset data can be used, regardless of the original method type, as long as the data was acquired using both detectors.

- **Points Acquired:** Specifies the number of unique voltages measured during the dual detector calibration procedure.

Detector Parameters in the Table

- **Analyte:** Specifies the analytes that will be used in the dual detector calibration. The analytes listed here should match the list of analytes that are being determined in the method. To automatically list all the analytes in the active method, click the Get Analyte List button at the top of the Dual Detector Calibration tab. When you require extended dynamic range (above 2 million counts per second) in a quantitative analysis, you need to calibrate for each analyte you want to measure.
- **Mass:** Specifies the exact mass at which the dual detector calibration will be performed for the analyte listed in the same row of the Dual Detector Calibration data table. Populate the Analyte and Mass fields by clicking Get Analyte List. This gets the analyte and mass from the method. To add an analyte, add it to the Method window Timing tab and then and then click Get Analyte List.
- **#Points:** Lists the number of crossover data points included in the dual detector calibration curve. This entry is read-only. When the software calibrates the dual detector system, response curves are generated for both the pulse and analog stages of the detector. These two response curves are integrated to yield a single curve which will serve as the detector response curve for analytical determinations. For accurate dual detector calibration, the system should have as many common data points (that is, crossover points) as possible. These are data points at which the system acquired both analog and pulse count data during the calibration sequence.
- **Coefficient:** Lists the correlation coefficient for the composite response curve that the software creates during dual detector calibration. This correlation coefficient is generated during the linear regression of the data points and is a measure of the quality of the final calibration curve. This entry is read-only. A poor correlation coefficient is an indication that the two response curves had very different slopes prior to their integration. In this event, it is recommended that you recalibrate the system before proceeding with analytical determinations.
- **Gain:** Lists the gain factor that will be used for the analyte in the same row of the Dual Detector Calibration data table. This entry is read-only. The gain value is used to determine how the software translates an analog current signal into usable pulse count data during measurements.
- **N(max):** This read-only entry is the dynamic range of the detector using the extended dynamic mode (dual mode), in counts per second. Signal intensities above the N(max) value are considered to be in shutdown. Shutdown is denoted by S.
- **Conversion Factor:** Indicates the ratio of the analog signal to pulse signal. It is the slope of the line on the dual detector calibration graphs. These values are plotted in the Detector Response Function. This entry is read-only.

AutoLens tab

Use this tab to view the lens scanning system to ensure maximum efficiency measuring the isotopes of interest. The AutoLens™ function is used to compensate for matrix suppression and space charge effects in the ion optics. It also allows you to achieve optimum sensitivity for each isotope in your determinations. You should generally optimize the AutoLens using the SmartTune™ function. Use the AutoLens tab only to view current AutoLens calibration settings, or to reprocess a calibration using previously acquired data.

	Analyte	Mass	#Points	Dac Value	Max Intensity
1	Be	9.0122	57	9	1126.59
2	Co	58.9332	57	9	7369.64
3	In	114.904	57	9	14374.4
4					

Optimization window AutoLens tab

Items on the AutoLens tab

- **Get Analyte List:** Copies the list of analytes that are included in the active method. Before a calibration can proceed, analytes must be listed in the lens scanning data table, and a method that measures the listed analytes must be loaded in the Method window. If you have the proper analytical method loaded, you can copy the list of analytes in the Lens Scanning data table by clicking the Get Analyte List button.
- **Clear Calibration:** Clears current AutoLens calibration data before creating a new calibration or before loading calibration data from previously acquired data.
- **Calibrate From Dataset:** Reads AutoLens calibration information from previously acquired data as long as at least one data file corresponding to an AutoLens calibration is selected. When data is acquired, the lens scanning information is stored along with other operating parameters in the dataset. This information can be used to calibrate the system for current analytical determinations. Any valid dataset data can be used, regardless of the original method type, as long as the data was acquired with an AutoLens calibration. To use the Calibrate From Dataset command, first clear existing

calibration data using the Clear Calibration button. Select the desired entry in the Dataset window, then on the AutoLens tab click Calibrate From Dataset.

- **Points Acquired:** Specifies the number of unique voltage values that were measured during the lens scanning procedure. This value is determined by the Start Value, End Value and Step Size parameters. The Points Acquired value is the total DAC range (End Value - Start Value) divided by the Step Value +1.
- **Slope:** Specifies the voltage/mass on the lens voltage versus mass graph.
- **Intercept:** Specifies the offset on the lens voltage versus mass graph, when the mass is zero.

Parameters in the AutoLens Table

- **Analyte:** Specifies the analytes that will be used in the lens scanning calibration. The analytes listed here should match the list of analytes that are being determined in the method. To automatically list all the analytes in the active method, click the Get Analyte List button at the top of the AutoLens tab.
- **Mass:** Specifies the exact mass at which the AutoLens calibration will be performed for the analyte listed in the same row of the Lens Scanning data table. You can populate the Analyte and Mass fields by clicking Get Analyte List. This gets the analyte and mass from the method. To add an analyte, add it to the Method Timing window and then and then click Get Analyte List on the AutoLens tab of the Optimization window.
- **Points:** Indicates the number of measurements taken during AutoLens calibration. This entry is read-only.
- **DAC Value:** Lists the DAC Value that will be used for the lens during determinations. This value represents the DAC setting that yielded the highest signal intensity during the lens scanning calibration procedure. This entry is read-only.
- **Max Intensity:** Lists the maximum intensity value obtained for the listed analyte during the Autolens calibration. This entry is read-only.

Cell Parameters tab

DRC Series instruments only. This tab displays the active cell gas parameters for the current optimization file in the data table. Entries on this tab are sorted in parallel with the entries on the Method window Timing tab—when the order of the analytes on the Timing tab changes, the order of the analytes on the Cell Parameters tab changes.

Note: In version 3.0 or higher of the software, reaction cell parameters are stored directly in the Method file to simplify the transferability of methods. As a result, for most applications, the Default.dac file can be selected in the Method timing table. During data acquisition, the reaction cell parameters in the Method window Timing tab are used. The reaction cell parameters in the Optimization window are no longer used during data acquisition, except for optimization. During optimization, the cell parameters corresponding to the analyte in the Auto Optimize tab are applied.

	Analyte	Begin Mass (amu)	End Mass (amu)	Cell Gas A (ml/min)	Cell Gas B (ml/min)	RPa	RPq
1	K	38.9637		0	0	0	0.25
2	Ca	39.9626		1.05	0	0	0.25
3	Fe	55.9349		0	0	0	0.25
4	Co	58.9332		0	0	0	0.25

Optimization window Cell Parameters tab

Items on the Cell Parameters tab

- Get Defaults:** Loads the default reaction cell parameters in the data table. Highlight the desired row in the table, and then click this button to reset parameters for Cell Gas A, Cell Gas B (if installed), RPa (Rejection Parameter a), and RPq (Rejection Parameter q). The elemental library keeps the default values for the gas flows and rejection parameters for each element. The file (elan.elm), in ASCII format, can be edited.

Cell Parameters in the Table

- Analyte, Begin Mass (amu), and End Mass (amu):** A location where optimized values are stored for cell parameters. They are read-only parameters whose values are determined in the Timing tab of the Method window. The Begin Mass setting specifies the exact mass to be scanned. The End Mass setting specifies the end mass of a scan range when using data only methods. To populate a row with the default cell parameter values, highlight the row and then click Get Defaults.
- Cell Gas A (ml/min):** Specifies the flow rate in ml/min at which Cell Gas A flows into the reaction cell. The flow rate is controlled by a mass flow controller.

- **Cell Gas B (ml/min):** Specifies the flow rate in ml/min at which Cell Gas B flows into the reaction cell. This parameter is available only if Cell Gas B is installed.
- **RPa (Rejection Parameter a):** Specifies the DC voltage that is applied to the reaction cell quadrupole for all methods. In normal operation, this entry is automatically filled by the software when you type the atomic symbol and/or isotope number in the Analyte column. To enter information in this column, click the desired cell and type the exact voltage at which the measurement should occur.
- **RPq (Rejection Parameter q):** Specifies the RF voltage that is applied to the reaction cell quadrupole for all methods. In normal operation, this entry is automatically filled by the software when you type the atomic symbol and/or isotope number in the Analyte column. To enter information in this column, click the desired cell and type the exact voltage at which the measurement should occur.

5

Sampling System Options

In addition to pneumatic nebulization, the software incorporates control parameters for different sample preparation and delivery options.

Topics in this section include:

- ▶ “Using a FIAS™ Sampling System” on page 109
- ▶ “Using an HGA-600MS Sampling System” on page 113

Using a FIAS™ Sampling System

Flow injection analysis differs from conventional ICP-MS solution sampling with a nebulizer in that small, discrete volumes of sample are introduced into the ICP-MS in a timed sequence. When analyzing samples via FI-ICP-MS, you can use any method type.

Before proceeding with an analysis on the FIAS system, you should carefully review your analytical requirements. To define an effective FI-ICP-MS analysis, you must be familiar with the chemical characteristics of your sample analytes and the matrix. These chemical properties will determine the optimal FIAS program to use.

FIAS™ Program Example

Go through the following example for a better understanding of how the FIAS programs function:

- **Pre-Sample step:** We entered 10 seconds for the duration and a speed of 120 rpm for pump 1 and 60 rpm for pump 2. Pump 1 delivers the sample from the autosampler to the injection valve for loading the sample loop. Pump 2 directs the carrier solution through the bypass to the system.
- **Step 1 (Load):** We used a 10-second duration for pump 1 at 120 rpm and pump 2 at 60 rpm, and set the FIA valve to position 1. This acts as a loop-filling step for additional replicates.
- **Step 2 (Sample Injection and Read):** We set pump 2 to 120 rpm and the FIA valve to position 2 to deliver the sample to the instrument at approximately 6 mL/min. The duration is set to 20 seconds. This value corresponds to the estimated replicate time on

the Method window Timing tab. This should not exceed the total time for the signal peak to appear, maximize, and return to baseline. Step 2 also contains the read—note the **X** in the Read column.

- **Post-Run step:** We set the pumping time to continuous operation (“-”) and set both pump speeds to 60 rpm. An appropriate post-run A/S location must be entered, or it will remain at the last sample tube position. If the post-run step is wash, enter “0” for the wash station.

Method Window FIAS Tab

Use the FIAS tab to set FIAS program parameters, including pumping time, pump speed, FIA valve position, and autosampler location.

Step Number	Read	Duration	Pump 1	Pump 2	Valve	A/S Loc.	Switch 2	Switch 3	Switch 4
1	-	10	120	60	1				
2	X	10	120	60	1				
3	X	20	0	120	2				
4			0	0	1				
5			0	0	1				
6			0	0	1				
7			0	0	1				
8			0	0	1				
9			0	0	1				
10	-	<->	60	60	1				

Method window Devices>FIAS tab

Items on the Method Window FIAS Tab

- **Repeat Steps:** Allows a continuous set of program steps (for example, 1 through 3) to be repeated an additional number of times. Note that these repeats are in addition to the number of times the steps will be repeated automatically as a result of programming multiple replicates in the parameter set. For example, a value of zero (0) times entered here means that the program steps will be executed once and repeated zero times, unless multiple replicates have been specified.
- **Step Number:** Defines the sequence in which the FIAS program parameters will be executed. The pre-sample step is used before each sample. For example, it can be used to set up the FIAS program by pumping sample from the autosampler to the sample loop. This step will not be repeated for multiple replicates of an individual sample. The post-run step defines the stand-by status of the FIAS accessory at the end of an analysis of samples. To return the autosampler to the wash position after an analysis set the A/S position to “0” in the post-run step; otherwise it will stay in the last sample position.
- **Read:** The step that includes the Read defines when the system will begin to acquire data from the FIAS injection. The instrument begins its read cycle at the beginning of this step. To select the step in which the Read occurs, click in the Read column of the

appropriate step, press any key and press Enter. Only one Read may be included in any FIAS program. Therefore a Read cannot be specified in a repeated step. The instrument will read for as long a time as is specified in the active method, whether this is a shorter or longer time than specified in the FIAS program.

- **Duration:** Specifies the length of time for a step in the FIAS program. One or both pumps may be utilized in any single program step. The acceptable range is 0 - 99 seconds. A value of “-” specifies continuous operation.
- **Pump 1 / Pump 2:** Defines the rotation rate in rpm at which the FIAS pumps will operate. A positive entry (default) indicates clockwise rotation of the pump, while a negative entry specifies counterclockwise rotation. The acceptable range is -10 to -120, 0, and 10 to 120. The actual flow rate depends on the inner diameter of the tubing used and the speed of rotation of the pump. You should calibrate this rate every day.
- **Valve:** This is the position of the FIAS valve. Use *Position 1* for filling the sampling valve, and *Position 2* to inject the sample into the ICP-MS.
- **A/S (Autosampler) Location:** In this column you will enter the rack location to which the autosampler probe should move before the corresponding row or “step” is executed. This location is the “start point” of sampling and is available to all rows including the Pre-sample and Post-run steps. An autosampler must be used in conjunction with the FIAS sampling device. There are three ways to specify the autosampler location in this column:
 - ♦ As an absolute number, such as 10 (indicates an actual rack location)
 - ♦ As a relative number, such as +5 or -5 (indicates a location relative to a reference A/S location)
 - ♦ As a blank entry (the reference A/S location).

No pre-run error checking on the validity of the A/S location entered is done by the software. If an incorrect A/S location is entered, the error message “*Autosampler position is out of range*” appears during the run and the FIAS program is aborted. Any partial data collected will not be saved to the dataset. Erroneous A/S location entries will only be flagged during a run, in which case the FIAS program will be aborted. The Reference A/S Location will depend on the context in which the FIAS program is executed:

- ♦ If the FIAS program is being applied to a manual or batch sample analysis, the Reference A/S Location is the A/S Loc. entry in the Details dialog box on the Sample window Manual tab or Batch tab
- ♦ If the FIAS program is being applied to a Blank or Standard, the Reference A/S Location is the net resultant location specified by the A/S Loc. entry in the Method window Sampling tab
- ♦ If the FIAS program is being applied to a QC Standard, the Reference A/S Location is the A/S Loc. entry in the Method window QC/Autosampler tab

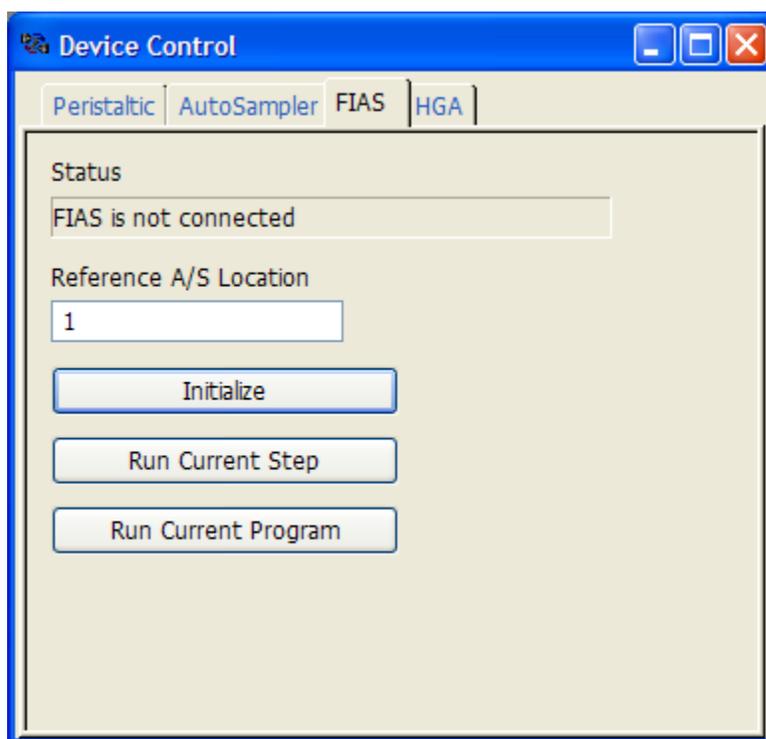
Based on these rules, a net A/S location is calculated for each step of the FIAS program. The A/S probe is moved to the net A/S location prior to the execution of the corresponding FIAS step. If the net A/S location is the same for two consecutive FIAS steps, the A/S probe is not moved between the FIAS steps. You can also specify the Reference A/S Location in the Reference Autosampler Location field in the FIAS tab of the Device Control window. When *Run Current Step* or *Run Current Program* are selected, this A/S location is used as the Reference Location for blank or relative autosampler location entries on the Method window Devices/FIAS tab. You must fill

in this field prior to selecting *Run Current Step/Program* or an error message will appear.

- **Switches (2, 3, 4):** Activates switch closures 2, 3 and 4 on the back of the FIAS device at the beginning of the program step in which the action is programmed. Remotes are programmed by setting the cursor to the desired remote position, and then pressing any keyboard character, followed by Enter.

Device Control FIAS Tab

Use this tab to establish communication with and manually run the FIAS program without making measurements. Note that these controls cannot execute a Read command, even if the FIAS step contains the Read.



Device Control FIAS tab

Items on the Device Control Window FIAS Tab

- **Status:** Indicates the status of communication and the current step in the FIAS program.
- **Reference A/S (Auto Sampler) Location:** Displays the autosampler location. This location is used as the Reference Location for blank or relative autosampler location entries in the FIAS tab. If you do not enter a location prior to selecting *Run Current Step/Program*, an error message appears.
- **Initialize:** Initializes communication with the FIAS device. A message appears in the Status field.

- **Run Current Step:** The software performs the step where the cursor is located. There must be an entry in the Reference A/S Location field to run this step.
- **Run Current Program:** Performs the FIAS program in the active method. This will not execute a Read command. There must be an entry in the Reference A/S Location field to run this program.

Using an HGA-600MS Sampling System

The HGA-600MS employs an *Electrothermal Vaporization* (ETV) analysis system, which differs from conventional ICP-MS solution sampling with a nebulizer in that small, discrete volumes of sample are introduced into a tube-shaped graphite sampling cell that is electrically heated in a timed sequence. As the heating sequence proceeds, solvent, volatile matrix components, and finally the analyte and any residual matrix components are vaporized. Under computer control, vaporized elements are swept away in a stream of inert carrier gas and either vented or transported to the plasma source of the ICP-MS for analysis. When analyzing samples via ETV-ICP-MS, you can use any method type.

Designing Your ETV Application

Before proceeding with an analysis using the HGA-600MS, you should carefully review your analytical requirements. To define an effective ETV-ICP-MS analysis, you must be familiar with the chemical characteristics of your sample analytes and the surrounding matrix. These chemical properties determine:

- The optimal temperature program to use for vaporization, including final temperature and rates of heating (ramp rates).
- The need for matrix modifiers or alternate purge gases.

While developing your method, ensure that the sample dries slowly and evenly, without spattering; otherwise analytical precision may be adversely affected. You may find it helpful to view the droplet during the drying stage of your HGA program. Swing the movable light shield out of the way and look into the graphite tube while pressing the tube illuminator button.



WARNING! Potentially harmful UV radiation is emitted from the graphite tube during the vaporization step in the HGA program. Always move the light shield back into place immediately after the sealing probe begins to close. When the sealing probe is in position, UV hazard is imminent. Do NOT look directly at the graphite tube during vaporization.

Note: For more information about the **HGA-600MS**, refer to the manual supplied with the sampler.

Method Window HGA Tabs

Electrothermal vaporization analyses are defined by entries in two tabs in the software:

- **HGA 1:** Defines specific sampling parameters to be used during the analysis.
- **HGA 2:** Controls furnace heating and gas flow parameters (upper pane of window). Controls the sequence of events to be followed by the autosampler during the analysis (lower pane of window).

HGA 1 tab

Use the HGA 1 tab to set up the autosampler and timing parameters of the HGA program.

The screenshot shows the 'Quantitative Analysis Method' window with the 'Sampling' tab selected. The window title is 'C:\Elandata\Method\Daily Performance.mth[Read-Only][Modified]'. The 'Description' field contains 'High purity acid analysis'. The 'Sample Volume (uL)' is set to 20, 'Injection Temperature' is 20, and 'Injection Speed' is 100. 'Read Delay (sec)' is 0.5 and 'Closure Delay (sec)' is -5. There are two modifier sections: 'Modifier #1' with 'Description' 'Pd NO3 10mg/l', 'Volume (uL)' 10, and 'Location' 40; and 'Modifier #2' with 'Description', 'Volume (uL)' 0, and 'Location' 0. The bottom status bar shows 'FIAS \ HGA 1 \ HGA 2'.

Method window Devices>HGA1 tab

ITEMS ON THE HGA 1 TAB

- **Description:** Type a description for this HGA process.
- **Sample Volume (µL):** Specifies the volume of sample to be injected into the furnace by the autosampler. Type a value from 1 to 99 µl.
- **Read Delay (sec):** Defines the time between the initiation of the Read cycle and the start of data acquisition. The delay compensates for transport time of the analyte from the graphite furnace to the torch. Setting an adequate delay avoids excessive baseline data collection.
- **Injection Temperature:** Specifies the temperature in °C of the graphite furnace at the time of the sample injection. When analyzing organic samples, it is useful to inject the samples into a warmed tube to compensate for surface tension differences that cause the samples to flow more freely inside the tube.
- **Closure Delay (sec):** Defines the time between the sealing of the graphite furnace by the sealing probe and the initiation of the Read cycle. The value set must be less than the hold time of the step before the Read. This value is negative (for example, -2 sec).

This means the sealing probe closes 2 seconds before the heating begins in the Read step.

- **Injection Speed:** Specifies the speed at which samples are injected into the sample cell (graphite tube). Type the percentage of maximum speed from 40 to 100%. When injecting viscous samples 40 to 60% is recommended.
- **Mod #1 (#2) Description:** Type a description for up to two chemical modifiers being used in the analysis routine. Modifiers can be injected into the graphite furnace along with the sample to change the chemical characteristics of the sample or to react with sample components. When using no modifiers, leave this field blank.
- **Mod #1 (#2) Volume (μL):** Defines the volume of modifier to be injected by the autosampler. When using no modifiers, enter a value of zero (0).
- **Mod #1 (#2) Location:** Specifies the location of the matrix modifier vials #1 and #2 in the autosampler. When using no modifiers, leave this field blank.

RAMP HEATING

You must specify a Ramp Time to control the rate of heating for a step in the temperature program. Three ramp rates are available for use in temperature programming, each differing in their relative rate of heating and the manner in which the system controls the heating process. These ramp rates are:

- *Normal Ramp Heating*—Normal ramp heating provides a relatively slow rate of heating for vaporization. Select it by typing a Ramp Time of one second or longer in a program step. During normal ramp heating, the temperature of the graphite tube is controlled by the voltage applied to the tube. This mode is used primarily for drying and charring.
- *Fast Ramp Heating*—Fast ramp heating provides a rate of heating governed by: the initial temperature (final temperature of the preceding program step); the final temperature in the current (vaporization) step; and the numerical entry (in the format 0.X) in seconds for the ramp time. Select it by typing 0.1 to 0.9 (seconds) for the Ramp Time. The leading zero distinguishes fast ramp from normal ramp heating. Heating of the graphite tube to the preselected isothermal temperature is controlled by the voltage measured across the tube as in normal ramp heating. When fast ramp heating is selected, the graphite tube is heated under voltage control at a rate calculated to achieve a theoretical temperature of 3000 °C within the preselected ramp time. However, as soon as the pre-selected isothermal temperature is reached, as measured by the optical temperature sensor, heating of the graphite tube is terminated and the tube is maintained at this temperature for the duration of the hold time. The optical temperature sensor is mounted on the left-hand window assembly of the furnace. When the optical temperature sensor is employed for control of tube heating, calibration of the sensor is performed automatically. Calibration is valid for further determinations using the same program. The system recalibrates automatically if the vaporization temperature is changed, or if the furnace assembly has been opened.
- *Maximum Power Heating*—Maximum power heating provides the highest rate of heating to the preselected isothermal temperature. Select it by type zero (0) for the Ramp Time. Maximum power heating is controlled via the optical temperature sensor. When the preselected isothermal temperature is reached, normal voltage control of tube heating is resumed. As in Fast Ramp heating, the system automatically calibrates the optical temperature sensor before the first measurement in which it is required, and recalibrates if the vaporization temperature is changed, or if the furnace assembly has been opened.

HGA 2 tab

Use this tab to set up the HGA program parameters. Use the upper pane of the HGA 2 tab to define the temperature program and flow of purge gases through the graphite furnace. Effective drying, thermal pre-treatment, and vaporization are crucial to the success of an HGA analysis.

Program Step	Cell Temp	Ramp Time	Hold Time	Internal Flow	Gas Type Norm	Gas Type Alt	Gas To Vent	Gas To ICP	Read
1	110	30.0	30	300	X		X		
2	400	15.0	15	300	X		X		
3	2400	0.0	6	0	X			X	X
4	2600	1.0	5	0	X			X	
5	20	1.0	15	0	X			X	
6	0	1.0	1	0					
7	0	1.0	1	0					
8	0	1.0	1	0					

Pipet Seq	Mod #1	Mod #2	Sample	Start Step	End Step	Wash	Sequence Repeat Start	Sequence Repeat End	Number of Repeats
3				1	2	0	0	0	0
4				0	0	0	2	3	2
5				0	0	0	0	0	0
6				0	0	0	0	0	0
7				0	0	0	0	0	0
8				0	0	0	0	0	0
9				0	0	0	0	0	0
10				0	0	0	0	0	0

Method window Devices>HGA2 tab

ITEMS ON THE HGA 2 TAB (UPPER PANE)

- Program Step:** Defines the sequence in which the HGA program steps are executed. A temperature program may contain one or more steps. A typical program contains four discrete operations: sample drying, thermal pretreatment, sample vaporization, and system cool-down.
- Cell Temp:** Specifies the final temperature in °C which you want the cell (the graphite furnace) to reach during the current program step.

Note: The term *cell* when used in relation to the HGA-600MS, refers to the graphite tube furnace in its function as a sampling cell.
- Ramp Time:** Defines the time period in seconds in which the HGA-600MS heats the cell from the final temperature of the prior HGA program step (ambient for step 1) to the Cell Temperature set in the current step of the HGA program:
 - A setting of 0 designates maximum power heating.
 - A setting of 0.1 - 0.9 specifies fast ramp heating.
 - A setting of 1.0 specifies normal ramp heating.
- Hold Time:** At the end of each heating period, it is normal to specify a period of isothermal heating at the specified Cell Temperature. This length of time for this isothermal hold is specified by the Hold Time. Values entered are in seconds.
- Internal Flow:** Specifies the flow rate for the internal carrier gas in mL/min.

- **Gas Type (Norm/Alt):** Specifies whether the normal carrier (argon) or an alternate gas is to flow through the cell during the current program step.
- **Gas To Vent/ICP:** Specifies the destination of gases flowing through the graphite tube. Read-only. This parameter is automatically determined by the status of the Read parameter. When a Read instruction is specified, the parameter indicates that the gas flowing through the graphite tube is diverted to the ICP. For all other program steps, the parameter will indicate that the internal gas is directed to vent.
- **Read:** Specifying a Read begins the data acquisition process at the instrument. Setting the Read parameter On (an **x** appears) causes the sampling valve to switch the purge/carrier gas flows so that ICP carrier gas is used to transport analytes to the plasma. Then, according to the Closure Delay, the furnace sealing probe closes, and after the Read Delay, your system begins acquiring data.

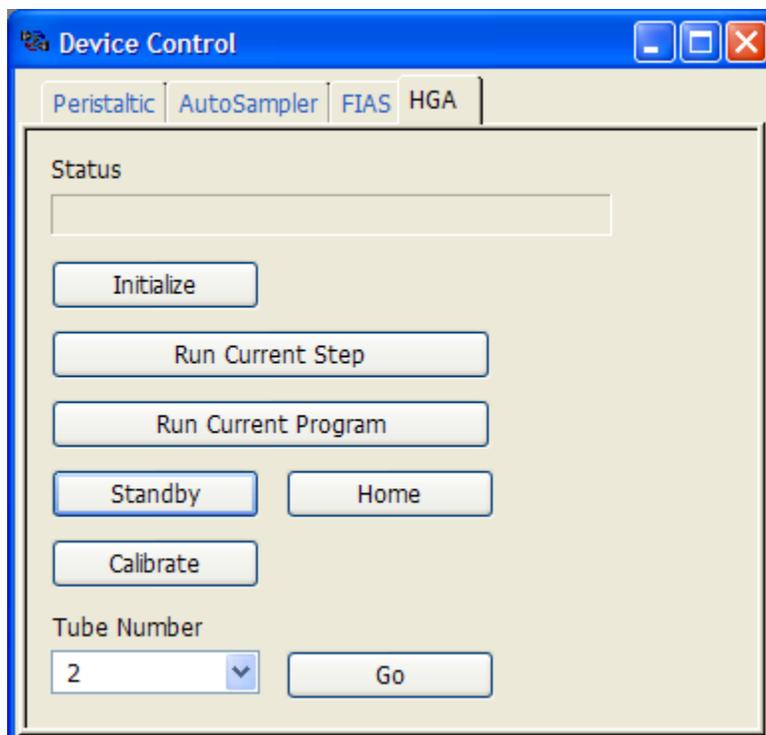
ITEMS ON THE HGA 2 TAB (LOWER PANE)

The Pipette Sequence section controls the entire HGA-600MS system. It is used to integrate the cell temperature/time program entered in the Furnace Program section, with specific actions of the autosampler, including multiple additions of sample or the use of chemical modifier solutions. The following list describes the parameters set in this section:

- **Pipette Seq:** Pipette Sequence steps define the order of actions to be executed by the autosampler and graphite furnace. During any single Pipette Sequence step, you can specify one action from the available options: *Pipette Solution*, *Activate Furnace*, *Wash*, and *Repeat Sequence*.
- **Mod #1 / Mod #2 / Sample:** Specifies which solutions (*Sample*, *Modifier 1*, *Modifier 2*) are to be injected into the cell during the current Pipette Sequence step. You may select a single solution or any combination of solutions to be injected during a program step.
- **Start Step / End Step:** Defines which furnace program steps, shown in the upper pane, should be activated in the current Pipette Sequence step. You must specify a Start and End step number. Entering an asterisk (*) for the End Step causes the temperature program to execute from the step specified in the Start Step column to the last step in the temperature program.
- **Wash:** Specifies the number of times the autosampler tip will be cleaned with a wash solution.
- **Sequence Repeat:** Defines which steps in the Pipette Sequence program will be repeated, if any. Permits multiple additions of sample or other similar procedures. For example, this function allows thermal pre-concentration of your sample in the furnace prior to vaporization. You must specify a Start and End sequence to define the sequence to be repeated, as well as the number of times the cycle should be repeated (*Number of Repeats*).

Device Control HGA Tab

Use this tab to establish communications with and manually run the HGA program without making measurements. Note that these controls cannot execute a Read command, even if the HGA step contains the Read.



Device Control HGA tab

Items on the Device Control HGA Tab

- **Status:** Displays HGA error messages along with furnace temperatures and elapsed time during an ETV analysis.
- **Initialize:** Initializes (establishes communication) between the computer and the HGA-600MS and the AS-60.
- **Run Current Step:** Executes the Furnace Program Step that has the cursor in it. In the example shown on the HGA 2 (upper pane), Step 5 would be executed.
Note: Even though the program step may call for a Read, no data will be acquired.
- **Run Current Program:** Runs the complete furnace program from beginning to end. No data will be acquired.
- **Standby/Home:** Puts the AS-60 in Standby mode and releases control of the pipetting arm. This feature is used to align the sampling capillary tip after initialization. Click Home when alignment is complete to restore automated control of the pipetting arm.

- **Calibrate:** Performs a temperature calibration of the optical sensor for Max Power and Fast Ramp heating modes. If the Furnace program does not use one of these heating modes, no condition will be performed.
- **Tube Number/Go:** Momentarily sends the autosampler capillary tip to the tube. Also used to manually wash the sampling capillary tip.



6

Quality Control

This section describes the instrument's *Quality Control* (QC) functions for quantitative measurements.

Topics in this section include:

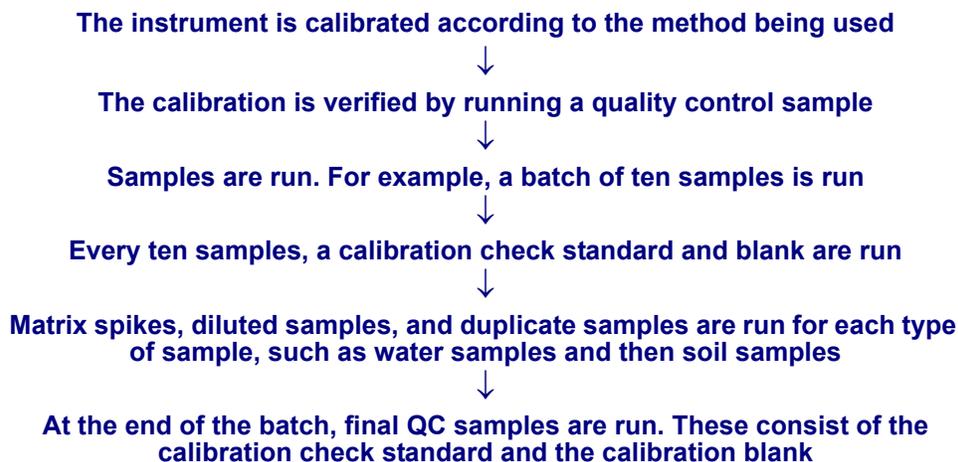
- ▶ “Quality Control Overview” on page 121
- ▶ “Instrument Actions and Quality Control Functions” on page 122
- ▶ “Quality Control Software” on page 124

Quality Control Overview

The software incorporates a series of sophisticated routines for monitoring your data integrity during unattended operation. Quality control software routines are not invoked during a manual analysis; they are used only during an automated batch analysis.

Quality Control Workflow

This is the workflow that the instrument typically follows when running a QC analysis:



Instrument Actions and Quality Control Functions

Instrument Action	Quality Control Function	Quality Control Action
Calibrate instrument according to method being used	<p>Calibration results (for example, correlation coefficient) checked against limits set up in method</p> <p>For example, Correlation Coefficient >0.995</p>	<p>Upon failure of checked limit (for example, correlation coefficient is < 0.995), the message entered by the user is printed and the specified actions are taken</p> <p>For example, recalibrate</p>
The calibration is verified by running a quality control sample. The software names it "QC Std N"	<p>The results of the QC analysis are compared to the true value and acceptance limits entered in the QC/ QC Standards tab of the Method window. Percent recoveries as compared to the true value are printed in the QC Calculated Values section of the report</p> <p>For example, true value = 50 ppb * 10%</p>	<p>Upon failure (For example, Analysis shows measured values not within limits), the message entered by the user in the Message column of actions section is printed (for example, "QC standard is out of limits") and the specified actions are carried out</p> <p>For example, recalibrate and rerun</p>
Samples are run. For example, a batch of 10 samples are run	<p>Samples are checked against sample limits. For example, sample result between detection limit and upper linear range</p> <p>Internal Standard recoveries are monitored and checked against limits. For example, Internal Standard Percent Recoveries must be between 60-120% of that in the blank for the selected method</p>	<p>Upon failure of any limit checked, either upper or lower sample concentration limits or internal standard limits the action selected in the QC tab for that limit is carried out and the message entered by the user is printed on the QC Out of Limits summary in the report</p> <p>For example, rerun, and/or recalibrate</p>

Instrument Actions and Quality Control Functions

Instrument Action	Quality Control Function	Quality Control Action
At a frequency of every 10 samples a calibration check standard and blank are analyzed	<p>The results for the check standard and check blank are compared against the limits</p> <p>For example, calibration check standard limits are *10% of the true value. Blank limits are set at 3 times the instrument detection limit</p>	<p>The appropriate message is printed upon failure of either or both calibration check and/or blank checks and the appropriate action is carried out</p> <p>For example, the calibration check is out of limits and the recalibrate action is carried out</p>
Matrix spikes, dilutions and duplicates are performed on one out of every ten samples, diluted samples and duplicates	<p>The spiked sample results or dilution or duplicate results are compared to an aliquot of the unspiked sample and the spike recovery is calculated. The spike recoveries are compared to the limits set in the Spike tab</p> <p>For example, spike recovery limits are required to be within * 30% of the spiked value</p>	<p>If the spike recoveries are not within the stated limits, the message “Spike recovery is out of limits” or other user-entered message is printed and the designated action is carried out</p> <p>For example, rerun original sample and spiked sample</p>
At the end of the batch, final QC samples consisting of the calibration check standard and the calibration blank are run	<p>The results for the check standard and check blank are compared against the limits. Internal Standard recoveries are monitored and checked against limits</p> <p>For example, Internal Standard Percent Recoveries must be between 60-120% of that in the blank for the selected method</p>	<p>The appropriate message is printed upon failure of either or both calibration check and/or blank checks and the appropriate action is carried out</p> <p>For example, the calibration check is out of limits rerun action is carried out</p>

Basic QC Settings

You can set up the software to automatically perform a variety of QC functions. In order to take advantage of these functions, you must first configure several areas of the software:

- The QC checking algorithms are active only during a batch analysis. The sample batch file, which controls the autosampler for samples, must be configured correctly.
- The QC Checking Enable check box on the Method window Timing tab must be selected.
- All true values and limits must be entered into the various screens in the software for which QC checking is desired. It is important to note that the QC checks are embedded in the individual methods, and not stored in a separate file. This means that for each different set of QC standards or limits, a new method must be created.
- The report options file must have the QC functions and the desired fields selected in order for you to actually see the results from the QC checking calculations.

QC Software Conventions

The software employs several conventions which pertain to the QC functions:

- When a control label has a star in parentheses (*) in it, this indicates that options are available through a drop-down menu that is activated by right-clicking.
- The fill down command for columns with the (*) option will work for that column only. You cannot fill down multiple columns.
- The Calibration and Blank information in the Method window must be completed for the standards that are used to calibrate the instrument, as well as the Autosampler tab which gives the location for the calibration blank and standards only. The calibration, blank and standard locations are not entered in the Batch tab of the Sample window.
- For flagged QC samples (QC spike, QC duplicate, QC dilution, and so forth), a detailed name or description may be entered in the Description column of the Sample window Batch tab. Also, if dilution factors are entered using the Aliquot and Diluted to Volume columns on the Sample window Batch tab, the dilution factors for the reference sample and the flagged QC sample must be the same.

Quality Control Software

The software incorporates a comprehensive series of quality control functions as part of the method. These functions are available only when using a Quantitative Analysis method and only when the Enable QC Checking check box has been selected on the Method window Timing tab. When this option is selected, the QC tab becomes active. The QC tab contains a series of additional sub-tabs with the following functions:

- **Calibration Standards tab:** Used to monitor calibration curve statistics, including the slopes, intercepts and correlation coefficients of the calibration curves for each of the analytes in your method. The slope of the calibration curve is one measure of the system's sensitivity, and by monitoring it over time, you can measure when the system's overall sensitivity has degraded significantly. Intercepts can be monitored so that the zero point in the calibration curve is never too far from the original value obtained. The correlation coefficient can be monitored to assure those calibration standard data are well correlated to the calibration algorithm chosen.
- **QC Standards tab:** Used to set concentration limits for the QC standards to measure if the system continues to provide accurate answers for solutions of known concentrations.
- **QC Measurement Frequency tab:** Used to specify the frequency with which QC measurements is made.
- **QC Standard Internal Standards tab:** Used to set up the parameters for measuring an internal standard element within the QC standards. This feature enables the setup of limits on the Internal Standard Intensity drift for QC standards.
- **Calibration Standards tab:** Used when calibration standards are measuring how well the system is performing. The standard deviation of the blank or RSD of the standards can both be monitored. If either the standard deviation or RSD of the standards is too high, then the system may not provide sufficient precision for your determinations.

This may indicate a problem with the sample introduction system or other hardware components.

- **Sample Internal Standards tab:** Used to set up the measurement of the internal standard element that can be monitored for drift of the sample. This feature enables the setup of limits on the Internal Standard Intensity drift for samples.
- **Sample tab:** While samples are being measured, the following parameters can be monitored: sample concentration, sample standard deviation and sample RSD. Sample concentrations can be monitored to determine when the results are below or above a pre-defined measurement limit. As a result of this monitoring, certain actions can be automatically executed when a sample is out of range. Monitoring the sample standard deviation is especially useful for estimating a detection limit on samples with no concentrations. Sample RSDs can be monitored to see if the instrument system is providing satisfactory precision, a measure of the performance of the sample introduction system and other hardware components.
- **Spike tab:** Used to set spike recovery limits for a determination. Spike recovery is performed by spiking samples with a known concentration of an analyte, then measuring how accurately the system determines this spike concentration.
- **Dilution tab:** Used to monitor dilution measurements on sample solutions. The percent difference between a sample and a dilution of that sample can be measured during determinations. You can then set a maximum allowable percent difference and have out-of-range samples identified.
- **Duplicate tab:** Used to measure the relative percent difference between two aliquots of the same sample solution.
- **Spike Tables tab:** Used to set up spiking tables. A spike table contains the spike concentrations. Spike concentrations are set up in up to 20 tables for use during the QC measurements.
- **QC Action Controls tab:** Used to specify how often Action 1 is to be done before preceding to Action 2 and how often Action 2 is to be done before the analysis is stopped or continued (user controlled).
- **Autosampler tab:** Used to identify the location in the autosampler for each of the QC standards.

Common Information and Controls

The following information settings and controls are found on multiple QC tabs. Details about settings specific to a particular tab can be found later in this section.

Control	Description
Analyte	Specifies the element that the instrument will determine in each measurement. Read-only. To add or delete an analyte, go to the Method window Timing tab
Mass (amu)	Specifies the mass at which the element will be measured. Read-only. The system sets the mass based on the analyte specified. To change the mass, go to the Method window Timing tab
Action 1 (*) / Action 2 (*)	<p>Specifies what action the system should take if the corresponding measurement is out of limits. Action 1 is executed first, and is repeated as often as indicated on the QC Action Controls tab if results are beyond the specified limits. Action 2 is then performed, and is also executed as often as indicated if results are beyond the specified limits. If the results are still out of limits, the analysis is either continued or stopped, depending on the QC Action Control settings</p> <p>When a measurement is out of limits, the text is entered in the Message to Print column for all the elements out of limits. Select one of the following from the drop-down list. Note that some tabs will have a sub-set of the options listed here:</p> <ul style="list-style-type: none"> • Continue: The out-of-limits message is printed, and the analysis continues. This is the default action. • Stop: The out-of-limits message is printed, and the analysis stops • Wash for X and Recalibrate: The out-of-limits message is printed. The autosampler probe returns to the wash position for X seconds. Then, all elements are recalibrated by analyzing from the blank solution again • Wash for X, Recalibrate and Rerun Current: The autosampler probe returns to the wash position for X seconds. For X enter any positive number. If zero is entered, a wash is not done and only a recalibration and rerun of the current standard will occur. The failed QC standard is recalibrated and rerun • Wash for X, Recalibrate and Rerun Samples: The autosampler probe returns to the wash position for X seconds. For X enter any positive number. If zero is entered, a wash is not done and only a recalibration and rerun of the samples occurs. All the elements are recalibrated. Recalibration is performed by analyzing from the Blank solution again. For the Rerun Samples portion of this action, the analysis resumes with the first sample between the last passed QC and the failed QC. For example, if you ran a blank, Standard 1, Standard 2, QC1, samples 1 through 10, QC1 again, samples 11 through 20 and QC1. If this QC1 now fails the instrument recalibrates and resumes at sample 11 • Wash for X and Continue: The autosampler probe returns to the wash position for X seconds. For X enter any positive number. If zero is entered, a wash is not done and the analysis continues. For the Continued portion of this action, the analysis continues with the next determined solution type

Control	Description
	<ul style="list-style-type: none"> • Wash for X and Rerun Current: The autosampler probe returns to the wash position for X seconds. For X enter any positive number. If zero is entered, a wash is not done and only a rerun of the current blank or standard occurs. For the Rerun Current portion of this action, the failed QC is rerun • Wash for X and Rerun from Original: The autosampler probe returns to the wash position for X seconds. For X, enter any positive number. If zero is entered, a wash is not done and only a rerun of the original sample occurs. For the Rerun from Original portion of this action, the analysis starts with the original sample • Wash for X, and Continue from Sample: The autosampler probe returns to the wash position for X seconds. For X, enter any positive number. If zero is entered, a wash is not done and only a rerun of the current blank or standard occurs. The analysis continues with the sample specified. Select a sample from where the analysis should resume
Action 1 Data / Action 2 Data	Displays any variable associated with Action 1 or Action 2, such as the number of seconds specified to wash and recalibrate
Message To Print	Type a message to be printed in the summary section of the report to warn that the element on that line is out of limits. The message can be up to 78 characters in length. For example, "Slope not within set limits"
QC Action Criteria (*)	<p>Specifies the conditions required for an action to be taken. You can specify how many or which elements in your QC standards must be out of limits before an action is taken. For each element, right-click and select one of the following options from the drop-down list:</p> <ul style="list-style-type: none"> • Must Act: The action designated for that QC standard will be carried out if that one element is out of limits • Do Not Act: The action designated for the QC standard will not be carried out regardless of whether it is out of limits. Any message specified in the Message To Print column is printed to allow you to monitor the element • Act if X Elements Out: The action designated for that QC standard will be carried out only if a specified number of elements are out of limits. Any number from 1 to the total number of elements can be specified (but this number must be the same for all elements for which you specify this option)
QC Action Priority (*)	<p>Specify the relative priority of each analyte. The value entered can be from 0 to 500. A value of zero, indicating a DO NOT ACT priority, is used if the analyte is to be monitored for information purposes only. Values from 1 to 500 indicate a MUST ACT priority. A value of 1 has the highest priority and its actions are performed if that analyte is out of limits. If no value is entered, the analyte is assigned the default priority. The default sequence of values starts from 1</p> <p>The QC Action Priority column is used to tell the software the priority of checking for the individual isotopes in the checking routine. Only the action for the element out of limits with the highest priority (lowest number) is carried out to avoid multiple actions. In the event that multiple isotopes have the same level of priority, action is taken only if all are out of limits</p>

Calibration Tab

Use this tab to monitor calibration curve statistics, including the slopes, intercepts, and correlation coefficients of the calibration curves for each of the analytes in your method. The slope of the calibration curve is one measure of the system's sensitivity, and by monitoring it over time, you can measure when the system's overall sensitivity has degraded significantly. Intercepts can be monitored so that the zero point in the calibration curve is never too far from the original value obtained. The correlation coefficient can be monitored to assure that calibration standard data are well correlated to the calibration algorithm chosen.

	Analyte	Mass (amu)	Slope Lower	Slope Upper	Intercept Lower	Intercept Upper	Corr. Coef. (min.)
1	Mg	23.985					
2	In	114.904					
3	U	238.05					
4	CeO	155.9					
5	Ba++	68.9525					
6							
7							

	Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)	Action 2 Data	Message To Print
1	Slope	Continue		Continue		
2	Intercept	Continue		Continue		
3	Corr. Coef.	Continue		Continue		

Calibration tab

Items on the Calibration Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- **Slope Lower:** Enter the lower slope limit for each analyte (except the internal standards). The lower and upper slope limits determines the out of limit conditions. Any positive or negative value is valid. Either an upper or lower slope value can be entered for limit checking to be performed for that analyte.
- **Slope Upper:** Enter the upper slope limit for each analyte (except the internal standards). The upper and lower slope limits determines the out of limit conditions. Any positive or negative value is valid. Either an upper or lower slope value can be entered for limit checking to be performed for that analyte.
- **Intercept Lower:** Enter the lower intercept limit for each analyte (except the internal standards). The lower and upper intercept limit determines the out of limit conditions. Any positive or negative value is valid. Either an upper or lower intercept can be entered for limit checking to be performed for that analyte.
- **Intercept Upper:** Enter the upper intercept limit for each analyte (except the internal standards). The upper and lower intercept limit determines the out of limit conditions.

Any positive or negative value is valid. Either an upper or lower intercept can be entered for limit checking to be performed for that analyte.

- **Corr. Coef. (min):** This limit determines the minimum acceptable correlation coefficient for each analyte except the internal standards. A value of 0.0000 to 1.0000 is valid. If no value is entered, limit checking will not be performed for that analyte.
- **Measurement:** Lists the types of measurement available, such as slope, intercept, and correlation coefficient. Read-only. To make changes, go to the Method window Timing tab.

QC Standards Tab

Use this tab to set concentration limits for the QC standards to determine if the system continues to provide accurate answers for solutions of known concentrations.

Analyte	Mass (amu)	QC Action Criteria (*)	QC Std 1 (Conc.)	QC Std 1 Lower (Conc. or %) (*)	QC Std 1 Upper (Conc. or %) (*)	QC Std 1 Conc RSD
1 Mg	23.985	Must Act				
2 In	114.904	Must Act				
3 U	238.05	Must Act				
4 CeO	155.9	Must Act				
5 Ba++	68.9525	Must Act				
6 Bkgd	220	Must Act				
7 Bkgd	8.5	Must Act				

Measurement	Solution ID	Action 1 (*)	Action 1 Data	Action 2 (*)
1 QC Std 1		Continue		Continue
2 QC Std 2		Continue		Continue
3 QC Std 3		Continue		Continue
4 QC Std 4		Continue		Continue
5 QC Std 5		Continue		Continue
6 QC Std 6		Continue		Continue
7 QC Std 7		Continue		Continue

QC Stds tab

Items on the QC Standards Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- **QC Std 1 (Conc.) to QC Std 50 (Conc.):** For each QC standard used (up to 50) enter a concentration value for each analyte. Zero or any positive value is valid.
- **QC Std 1 Lower to QC Std 50 Lower:** The upper and lower concentration limits for each analyte determine the out-of-limit parameters. These limits can be expressed as a percent or as a concentration value. To access the dialog box, right-click in a cell in the QC Std Lower (Conc. or %) column. Select Absolute Concentration Value, Absolute Percent Value, or Relative Percent Value option from the dialog box that appears. Type the lower value. If you selected Absolute Concentration Value the lower

value can be a positive or negative value. This number will appear in this column. If you selected Absolute Percent Value, the lower integer value shown in this column will be followed by a %. If you selected Relative Percent Value the lower integer value shown in this column will be shown as a + or - value with a percent. If a value is not entered for a limit, limit checking will not be performed for that limit for that analyte. Up to 50 QC standards are available. QC limit checking will be performed for each QC standard.

- QC Std 1 Upper to QC Std 50 Upper:** The upper and lower concentration limits for each analyte determine the out-of-limits parameters. These limits can be expressed as a percent or as a concentration value. To access the dialog box, right-click in a cell in the QC Std Upper (Conc. or %) column. Select Absolute Concentration Value, Absolute Percent Value, or Relative Value option from the dialog box that appears. Type the upper value. If you selected Absolute Concentration Value the upper value will be a positive value. This number will appear in this column. If you selected Absolute Percent Value, the upper integer value shown in this column will be followed by a %. If you selected Relative Percent Value, the upper integer value shown in this column will be shown as a + or - value. If a value is not entered for a limit, limit checking will not be performed for that limit for that analyte. Up to 50 QC standards are available. QC limit checking will be performed for each QC standard.
- QC Std 1 Conc. RSD to QC Std 50 Conc. RSD:** For each QC standard Concentration RSD used (up to 50) enter a maximum value for each analyte. Any positive value is valid.
- Measurement:** Lists up to 50 QC standards. Read-only.
- Solution ID:** This field allows you to enter specific Solution IDs for QC Standards. You can use the solution ID to identify a reference material instead of using the defaults QC Std 1, QC Std 2, and so forth in the Measurement field.

QC Measurement Frequency Tab

Use this tab to specify the frequency with which QC measurements should be made.

	Measurement	Count As Sample	Initial	Final	After Recalb	Every # Samples	Before A/S Loc.	Before A/S Loc.
1	Calibration							
2	QC Std 1	X			X	5	10	
3	QC Std 2	X	X	X		10	20	
4	QC Std 3	X	X	X		20	30	
5	QC Std 4	X			X	20	40	
6	QC Std 5							
7	QC Std 6							
8	QC Std 7							
9	QC Std 8							
10	QC Std 9							
11	QC Std 10							

QC Measurement Frequency tab

Items on the QC Measurement Frequency Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls” on page 126](#).

- **Measurement:** Lists the calibration and all the QC standards (up to 50 available) that have been entered on previous method tabs. Read-only.
- **Count as Sample:** An **X** entry specifies that the QC standard will be counted as a sample when determining at what point subsequent periodically run QC standards will be run. If it is counted as a sample, all the subsequent measurements that will be made every so many samples will take this into account. Select the box you wish to modify by selecting it with the mouse or by using the cursor keys. Enter an **X** by pressing any letter or number on the keyboard and press Enter. An **X** entry appears in the box. To remove the **X** entry, press the spacebar or use the backspace and press Enter. When a QC standard is run that is designated as a sample the sample count goes up by one. When the sample count reaches the number entered in the Every # Sample column for a particular measurement, the corresponding measurement is performed.
- **Initial:** An **X** entry specifies that the designated QC standard will be run at the beginning of the analysis, directly after the initial calibration is performed. Select the box you wish to modify by selecting it with the mouse or by using the cursor keys. Enter an **X** by pressing any letter or number on the keyboard and press Enter. An **X** entry will appear in the box. To remove the **X** entry, press the spacebar or use the backspace and press Enter.
- **Final:** An **X** entry specifies that the designated QC standard will be run at the end of the analysis, after the last sample is run. Select the box you wish to modify by selecting it with the mouse or by using the cursor keys. Enter an **X** by pressing any letter or number on the keyboard and press Enter. An **X** entry will appear in the box. To remove the **X** entry, press the spacebar or use the backspace and press Enter.
- **After Recalib:** An **X** entry specifies that the designated QC standard will be run immediately after a recalibration. Select the box you wish to modify by selecting it with the mouse or by using the cursor keys. Enter an **X** by pressing any letter or number on the keyboard and press Enter. An **X** entry will appear in the box. To remove the **X** entry, press the spacebar or use the backspace and press Enter.
- **Every # Samples:** Specifies when the QC standards will be run during the analysis by defining how many samples should be run between QC standards. Type a number representing the number of samples to be run between each QC standard.
- **Before A/S Loc.:** Specifies when the QC standards will be run before the selected autosampler position. For example, you can indicate that a QC standard should be run before autosampler position 10. This tab has fifty Before A/S Location columns. This allows you the flexibility of spacing the QC standards as needed and not in a fixed pattern as in the Every # Samples column.

Note: When multiple QC standards are to be run (for example, QC Std 1, QC Std 2, QC Std 3, and QC Std 4 have the Initial Box checked), the QC Standards are run in numerical order: QC Std 1 then QC Std 2 then QC Std 3 and then QC Std 4.

QC Std Internal Standards Tab

Use this tab to set limits for intensity drift of internal standards within the QC standards. For example, Cu can drift to a negative 60% or to a positive 25%.

	Analyte	Mass (amu)	QC Stds Int. Std. Lower (%)	QC Stds Int. Std. Upper (%)
1	Ce	139.905	-10	-10
2	Ba	137.905	-10	-10

	Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)
1	Ce 140 Int Std for QC Std	Wash for X and Continue	60 seconds	Continue
2	Ba 138 Int Std for QC Std	for X, Recalibrate and Rerun Samples	60 seconds	Continue

QC Std Int Stds tab

Items on the QC Standard Internal Standards Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- QC Stds Int Std Lower %:** Right-click to display the Enter Percent Limit Value dialog box. To enter an absolute value, select the Absolute Value option and type a value (for example, 90). To enter a relative value, select the Relative Value option and type a negative value in the Lower box (for example, -10). Only numerical entries are accepted. After the entry is accepted, the default units appear on the QC Stds Int. Std tab as a percentage (%).
- QC Stds Int. Std Upper %:** Right-click to display the Enter Percent Limit Value dialog box. To enter an absolute value, select the Absolute Value option and type a value (for example, 110). To enter a relative value, select the Relative Value option and type a positive value in the Upper box (for example, 10). Only numerical entries are accepted. After the entry is accepted, the default units appear on the QC Stds Int. Std tab as a percentage (%).
- Measurement:** The list shown is based on the number of internal standards. Read-only. To add or change an entry, go to the tab on which it was made.

Calibration Standards Tab

You can run calibration standards to gain information about how well your instrument is performing. The standard deviation of the blank or RSD of the standards can both be monitored. If either the standard deviation or RSD of the standards are too high, then the system may not be providing sufficient precision for your determinations. This may indicate a problem with the sample introduction system or other hardware components.

	Analyte	Mass (amu)	QC Action Criteria (*)	Blank Inten SD	Std 1 Inten RSD	Std 2 Inten RSD	Std 3 Inten RSD	Std 4 Inten RSD
1	Mg	23.985	Must Act					
2	In	114.904	Must Act					
3	U	238.05	Must Act					
4	CeO	155.9	Must Act					
5	Ba++	68.9525	Must Act					
6	Bkgd	220	Must Act					
7	Bknd	8.5	Must Act					

	Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)	A
1	Blank	Continue		Continue	
2	Std 1	Continue		Continue	
3	Std 2	Continue		Continue	
4	Std 3	Continue		Continue	
5	Std 4	Continue		Continue	
6	Std 5	Continue		Continue	
7	Std 6	Continue		Continue	

Calibration Stds tab

Items on the QC Calibration Standards Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- Blank Intensity SD:** For the blank a standard deviation (SD) value for the net intensity can be entered to determine the maximum acceptable value for each analyte. Any positive value is valid. If no value is entered, limit checking will not be performed.
- Std 1 Intensity RSD to Std 30 Intensity RSD:** For each standard (to a maximum of 30 standards) a relative standard deviation (RSD) value for the net intensity can be entered to determine the maximum acceptable value for each analyte. Any positive value is valid. If no value is entered, limit checking will not be performed.
- Measurement:** Lists the blank and up to 30 standards. Read-only.

Sample Internal Standards Tab

Use this tab to set up the measurement of the internal standard element which can be monitored for drift throughout the course of the determinations.

	Analyte	Mass (amu)	Sample Int. Std. Lower (%)	Sample Int. Std. Upper (%)
1	Ce	139.905	-10	10
2	Ba	137.905	-10	10

	Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)
1	Ce 140 Int Std for sample	Wash for X and Continue	60 seconds	Continue
2	Ba 138 Int Std for sample	Wash for X and Continue	60 seconds	Continue

Sample Int Stds tab

Items on the Sample Internal Standards Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- Sample Int. Std Lower %:** Right-click to display the Enter Percent Limit Value dialog box. To enter an absolute value, select the Absolute Value option and type a value (for example, 90). To enter a relative value, select the Relative Value option and type a negative value in the Lower box (for example, -10). Only numerical entries are accepted. After the entry is accepted, the default units displays on the Sample Int. Std tab as %.
- Sample Int. Std Upper %:** Right-click to display the Enter Percent Limit Value dialog box. To enter an absolute value, select the Absolute Value option and type a value (for example, 110). To enter a relative value, select the Relative Value option and type a positive value in the Upper box (for example, 10). Only numerical entries are accepted. After the entry is accepted, the default units appear on the Sample Int. Std tab as a percentage (%).
- Measurement:** The list shown is determined by the internal standard elements specified on the Timing tab. Read-only. To add or change an entry, go to the tab on which it was made.

Sample Tab

You can monitor the following parameters while samples are being measured: sample concentration, sample standard deviation, and sample RSD. Sample concentrations are monitored to determine when the results are outside a pre-defined measurement limit. As a result of this monitoring, certain actions can be automatically executed when a sample is out of range. Monitoring the sample standard deviation is especially useful for estimating a detection limit on samples with no concentrations. Sample RSDs are monitored to determine if the system is providing satisfactory precision, which is a measure of the performance of the sample introduction system and other hardware components.

	Analyte	Mass (amu)	QC Action Priority	Sample Lower (Conc.)	Sample Upper (Conc.)	Sample Conc SD	Sample Conc RSD
1	Mg	23.985	3				
2	In	114.904	0				
3	U	238.05	0				
4	CeO	155.9	0				
5	Ba++	68.9525	0				
6	Bkgd	220	0				
7	Bkgd	8.5	1				

	Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)	Action 2 Data
1	Mg 24 Lower	Wash for X, Recalibrate and Continue	15 seconds	Continue	
2	Mg 24 Upper, S, EEE	Continue		Continue	
3	Mg 24 Std Dev	Continue		Continue	
4	Mg 24 RSD	Continue		Continue	
5	In 115 Lower	Continue		Continue	
6	In 115 Upper, S, EEE	Continue		Continue	
7	In 115 Std Dev	Continue		Continue	

Sample tab

Items on the Sample Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- **Sample Lower (conc.):** For each analyte, enter a sample lower concentration limit. This number will determine the acceptable lower limit for the sample concentration value. Any value entered is valid. The lower limit must be a smaller value than the upper value.
- **Sample Upper (conc.):** For each analyte, enter a sample upper concentration limit. This number will determine the acceptable upper limit for the sample concentration value. If a measurement exceeds the value entered, it will trigger the prescribed action (for example, *Wash for X, Dilute and Rerun Current*).

Any value is valid. The upper limit must be a larger value than the lower limit. If the upper limit is exceeded the software will indicate either **S** for *Shutdown*, or **EEE** for *Elemental Equation Error*.

Note: This option is available only if an autodiluter has been installed.

- **Sample Conc SD:** Type a standard deviation (SD) value for the net intensity. This determines the maximum acceptable value for each analyte. Any positive value is valid. If a value is not entered, limit checking will not be performed.
- **Sample Conc RSD:** Type a relative standard deviation (RSD) value for the net intensity. This determines the maximum acceptable value for each analyte. Any positive value is valid. If a value is not entered, limit checking will not be performed.
- **Measurement:** Each element has four lines, listing the upper concentration, lower concentration, SD and RSD. Read-only. To add or change an entry, go to the tab on which it was made.

Spike Tab

Use this tab to set spike recovery limits for a determination. Spike recovery involves spiking samples with a known concentration of an analyte, then measuring how accurately the system determines this spike concentration.

	Analyte	Mass (amu)	QC Action Priority	Spike % Rec (lower) (*)	Spike % Rec (upper) (*)
1	Mg	23.985	0	70	130
2	In	114.904	0	70	130
3	U	238.05	0	70	130
4	CeO	155.9	0	70	130
5	Ba++	68.9525	0	70	130
6	Bkgd	220	4	70	130
7	Bkgd	8.5	1	70	130

	Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)	Action 2 Data
1	Mg 24 Spike	Wash for X, and Rerun Original	60 seconds	Continue	
2	In 115 Spike	Wash for X, and Rerun Original	60 seconds	Continue	
3	U 238 Spike	Wash for X, and Rerun Original	60 seconds	Continue	
4	CeO 156 Spike	Wash for X, and Rerun Original	60 seconds	Continue	
5	Ba++ 69 Spike	Wash for X, and Rerun Original	60 seconds	Continue	
6	Bkgd 220 Spike	Wash for X, and Rerun Original	60 seconds	Continue	
7	Bkgd 8.5 Spike	Wash for X, and Rerun Original	60 seconds	Continue	

Spike tab

Items on the Spike Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- **Spike % Rec (lower) (*):** To enter a limit, right-click in this box to display the Enter Percent Limit Value dialog box. To enter an absolute value, select the Absolute Value option and type a value (for example, 90). To enter a relative value, select the Relative Value option and type a negative value in the Lower box (for example, -10). Only

numerical entries are accepted. After the entry is accepted, the default units displays on the Spike tab as %.

Note: If the spike recovery calculated for any spiked sample is below the lower limit a corresponding message is printed. To set a limit, type any positive value. Spike % recovery is calculated as:

$$\text{Spike \% Recovery} = [(SS - US) / SA] \times 100$$

where:

US = unspiked sample result

SA = spike added

SS = spiked sample result

If the original sample result is smaller than the detection limits specified in the Spike Table used, zero is used in this equation instead of the original result. This avoids subtracting negative sample results. Specifying the detection limit is optional. If this box is empty, the original sample results are used.

- **Spike % Rec (upper) (*):** To enter a limit, right-click in this box to display the Enter Percent Limit Value dialog box. To enter an absolute value, select the Absolute Value option and type a value (for example, 110). To enter a relative value, select the Relative Value option and type a positive value in the Upper box (for example, 10). Only numerical entries are accepted. After the entry is accepted, the default units appear on the Spike tab as a percentage (%).

Note: If the spike recovery calculated for any spiked sample is above the lower limit a corresponding message is entered. To set a limit, type any positive value. Spike % recovery is calculated as:

$$\text{Spike \% Recovery} = [(SS - US) / SA] \times 100$$

where:

US = unspiked sample result

SA = spike added

SS = spiked sample result

If the original sample result is smaller than the detection limits specified in the Spike Table used, zero is used in this equation instead of the original result. The defining detection limits are optional. If this box is empty, the original sample results are used.

- **Measurement:** Lists the spikes for the elements specified on the Timing tab. This column is read-only—to change an entry or add another measurement to monitor, you must change the entry on the tab on which it was made. You cannot edit entries in this column. If you want to change an entry, or add another measurement to monitor, you must change the entry on the tab on which it was made, and then return.

Dilution Tab

Use this tab to monitor dilution measurements on sample solutions. The percent difference between a sample and a dilution of that sample can be measured during determinations. You can then set a maximum allowable percent difference and have out-of-range samples identified.

Analyte	Mass (amu)	QC Action Priority	% Difference (max)
1 Mg	23.985	1	
2 In	114.904	2	
3 U	238.05	3	
4 CeO	155.9	4	
5 Ba++	68.9525	5	
6 Bkgd	220	6	
7 Bkgd	8.5	7	

Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)	A
1 Mg 24 Dilution	Wash for X, and Rerun Original	60 seconds	Continue	
2 In 115 Dilution	Wash for X, and Rerun Original	60 seconds	Continue	
3 U 238 Dilution	Wash for X, and Rerun Original	60 seconds	Continue	
4 CeO 156 Dilution	Wash for X, and Rerun Original	60 seconds	Continue	
5 Ba++ 69 Dilution	Wash for X, and Rerun Original	60 seconds	Continue	
6 Bkgd 220 Dilution	Wash for X, and Rerun Original	60 seconds	Continue	
7 Bkgd 9 Dilution	Wash for X, and Rerun Original	60 seconds	Continue	

Dilution tab

Items on the Dilution Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- **% Difference (max):** Sets the limit for the percent difference allowable between a sample and its dilution. If the percent difference calculated for any solution identified exceeds the limit a corresponding message is entered. To set a limit, type a number between 0 and 100. The default setting is 10%. A Percent Difference (%Diff) is calculated as follows:

$$\% \text{ Diff.} = [|OS - (DS \times DF)| \div OS] \times 100$$

where:

OS = original undiluted sample result

DS = diluted sample result

DF = dilution factor

OS = original sample result (same name as dilution)

- **Measurement:** Lists dilutions for the elements specified on the Timing tab. This column is read-only—to change an entry or add another measurement to monitor, you must change the entry on the tab on which it was made.

Duplicate Tab

Use this tab to measure the relative percent difference between two aliquots of the same sample solution.

Analyte	Mass (amu)	QC Action Priority	% Rel % Diff (max)
1 Mg	23.985	1	
2 In	114.904	2	
3 U	238.05	3	
4 CeO	155.9	4	
5 Ba++	68.9525	5	
6 Bkgd	220	6	
7 Bkgd	8.5	7	

Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)	Action 2 Data
1 Mg 24 Duplicate	Wash for X, and Rerun Original	60 seconds	Continue	
2 In 115 Duplicate	Wash for X, and Rerun Original	60 seconds	Continue	
3 U 238 Duplicate	Wash for X, and Rerun Original	60 seconds	Continue	
4 CeO 156 Duplicate	Wash for X, and Rerun Original	60 seconds	Continue	
5 Ba++ 69 Duplicate	Wash for X, and Rerun Original	60 seconds	Continue	
6 Bkgd 220 Duplicate	Wash for X, and Rerun Original	60 seconds	Continue	
7 Bkgd 8.5 Duplicate	Wash for X, and Rerun Original	60 seconds	Continue	

Duplicate tab

Items on the Duplicate Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- % Rel % Diff (max):** Sets a limit for the relative percent difference allowable between a sample and its duplicate. If the relative percent difference calculated for any solution identified as a duplication exceeds the limit, a corresponding message is entered. To set a limit, type a number between 0 and 100. A *Relative Percent Difference (%D)* is calculated as follows:

$$\%D = \frac{|o - d|}{\frac{1}{2}(o + d)} \times 100$$

where:

o = original sample result (result of sample with same name as duplicate)

d = duplicate sample result

- Measurement:** Lists duplicates for the elements which were specified on the Timing tab. This column is read-only—to change an entry or add another measurement to monitor, you must change the entry on the tab on which it was made.

Spike Tables Tab

Use this tab to set up spiking tables. Spike concentrations are set up in up to 20 tables for use during the QC measurements.

	Analyte	Mass (amu)	Spike Table 1 (Conc.)	Spike Table 1 Det. Limit (Conc.)	Spike Table 2 (Conc.)	Spike Table 2 Det. Limit (Conc.)	Spike Table 3 (Conc.)	Spike Det. Lin
1	Mg	23.985			50		100	
2	In	114.904			50		100	
3	U	238.05			50		100	
4	CeO	155.9			50		100	
5	Ba++	68.9525			50		100	
6	Bkgd	220			50		100	
7	Bkgd	8.5			50		100	

Spike Tables tab

Items on the Spike Tables Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- **Spike Table 1 (Conc.) to Spike Table 20 (Conc.):** Displays the concentrations for each element in the current spike table. The units are assumed to be those of the standard units, as specified on the Calibration tab.
- **Spike Table 1 Det. Limit (Conc.) to Spike Table 20 Det. Limit (Conc.):** Optional. Specifies the detection limits for the elements in the current spike table. If the original sample result is smaller than the detection limits specified in the Spike Table used, zero is used in this equation instead of the unspiked sample result. The defining detection limits are optional. If this box is empty the original sample results are used. The equation used to perform unspiked recovery is as follows:

$$\text{Spike \% Recovery} = [(SS - US) / SA] \times 100$$

where:

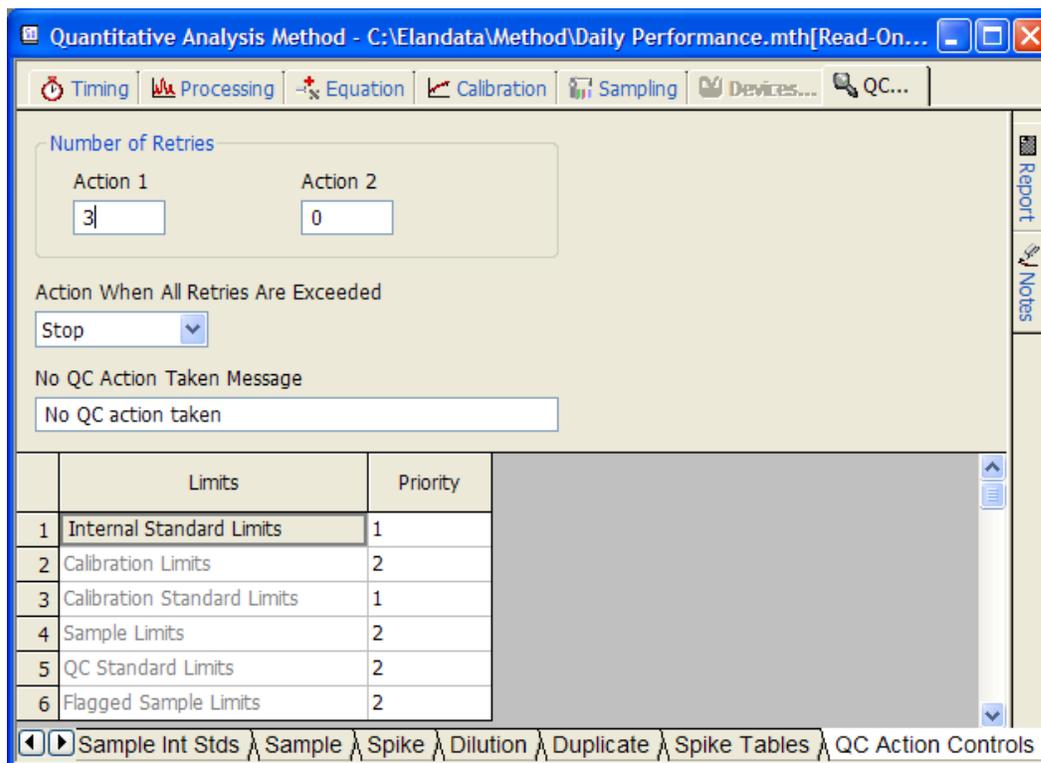
SS = spiked sample result

US = unspiked sample result

SA = spike added

QC Action Controls Tab

Use this tab to specify how actions are taken and how often they are repeated.



QC Action Controls tab

Items on the QC Action Controls Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls”](#) on page 126.

- Number of Retries:** Denotes the number of times each action will be re-tried before proceeding to the next action. Any positive integer value is allowed. For example, if the number of retries for Action 1 is zero then Action 1 will be performed only once. If retries equal 1, then Action 1 would be tried again before proceeding to Action 2. If the condition is not satisfied by this action, then Action 2 will be performed.
- Action When All Retries Are Exceeded:** Determines what happens to the analysis if both actions fail to remedy the QC condition. *Stop* will stop the analysis (the plasma will not turn off). *Continue* will allow the analysis to continue. The QC criteria will continue to be applied to other samples in the analysis.
- Limits Priority Table:** This table shows the priority of the QC Limits in the method. A value of 1 indicates that this limit has the highest priority, if more than one of the QC Limits have been exceeded. In the event that QC Limits are exceeded in one sample, the software will perform only the action with the higher priority. For example, when the sample concentration and the internal standard intensity are both out of limits, the software will perform the corrective action for the Internal Standard because it has a higher priority. We recommend that you not change the priorities that appear in the default Quantitative Analysis Method.

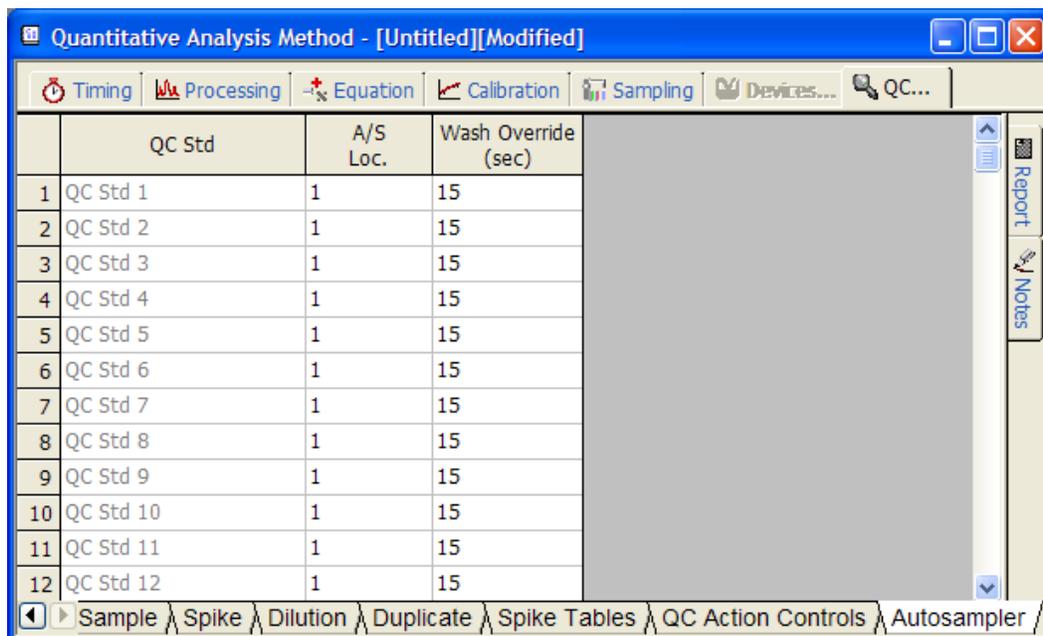
QC Actions		Priority
Calibration Limits:	Correlation Coefficient	1
	Intercept	2
	Slope	3
Sample Limits:	Lower Conc.	2
	Upper Conc.	3
	SD	4
	RSD	5
	Internal Std. Inten.	1
QC Standard Limits:	Conc. and/or RSD	2
	Internal Std. Inten.	1
Flagged Sample Limits:	Flag. Calc.(Spike Rec. %Diff, Rel.%Diff.)	2
	Internal Std. Inten.	1

Note: Four of the six solution limit types in the QC Action Controls tab are further prioritized internally in the software. The priorities within each solution type are shown below. When multiple limit conditions are exceeded within a solution type, the action for the limit with the highest priority will be executed. These internal priorities are non-editable

- **No QC Action Taken Message:** This default message is printed when all QC measurements are found to be within proper limits. If desired, you can type in another message.

Autosampler Tab

Use this tab to identify the location in the autosampler for each of the QC standards.



Autosampler tab

Items on the Autosampler Tab

This section of the software contains the following information and controls. For more information about common QC controls, see [“Common Information and Controls” on page 126](#).

- **QC Std.:** 50 QC standards are listed in this column.
- **A/S Loc.:** Specifies at what autosampler position the QC standard is located. Any positive value is valid. Positions can be reused if it is the same solution. For example, QC Std 1 and QC Std 3 are the same solution.
- **Wash Override (sec):** Specifies the time in seconds that the autosampler probe is in the wash solution before it moves to the next solution to be analyzed. Any positive value is valid, including zero. Use this function to provide a longer than usual wash cycle for samples where carry-over is a concern.



Interference Correction

This section provides information on interferences which can affect your ICP-MS results, how to identify these problems in your data, and procedures for correcting for these defects.

Topics in this section include:

- ▶ “Interferences in ICP-MS” on page 145
- ▶ “Identifying Interference Problems” on page 148

Interferences in ICP-MS

The ICP-MS technique offers numerous analytical benefits. However, during method development, it is necessary to understand the influence of spectral interferences that can affect your final results. An interference is anything that causes the signal from an analyte to be different from the same signal for the same concentration of that analyte in a calibration solution.

As with all other atomic spectrometric analytical techniques, interferences of various types can occur during routine ICP-MS determinations. Interferences associated with sample introduction using a nebulizer/spray chamber are common to atomic absorption, optical emission ICP, and ICP-MS. These are termed transport interferences. In addition, interferences can occur from the presence of other isotopes or elements with the same atomic weight or mass number as an analyte of interest. These are termed *Spectral Interferences*.

Matrix Interferences

Sample introduction effects when using a nebulizer/spray chamber system are common in ICP-MS determinations. These interferences are generally the result of either sample matrix effects that influence aerosol formation or the formation of ions in the plasma (surface tension, viscosity). Complex sample matrices may interfere with focusing ions into the sample and skimmer cone orifices, and focusing and transporting ions through the ion lenses and quadrupole.

Matrix interferences can be identified by:

- Observing the intensity of the argon dimer, (Ar 40)(Ar 40), versus the blank. The argon dimer peak and analyte element signals are usually affected similarly by matrix interferences
- Determining if response is linear with dilution. Response dependence on the absolute concentrations of analyte and matrix is an indicator of a matrix interference
- Analyzing at low and high nebulizer argon flow rates

Note: A sample with an interference and a standard solution will respond differently.

The most commonly observed result of matrix interference is the ion intensity if an analyte element becomes dependent upon the total composition of the sample. Typical signal suppression is observed. For example, a given concentration of selenium will exhibit a signal about 25% lower in a 1000 mg/L NaCl solution than the same concentration of selenium in water. This signal attenuation is mass dependent. Light analytes in a predominantly high mass matrix (e.g. 1000 mg/L U) are more prone to signal attenuation than a heavy analyte in the presence of a light mass matrix (for example, 1000 mg/L Li).

Several methods can be used to compensate for matrix-induced signal suppression. For a well-defined matrix, it is simple to match the composition of the standard solutions with the sample solutions, and thus obtain the desired analytical accuracy. For a matrix of unknown composition, standard addition calibration, in which known concentration standards are added directly to a sample solution, provides a method for compensating for the sensitivity difference between samples and standards.

Spectral Interferences

Spectral interferences are the result of other chemical species (isotopes or ions) which are present at the same atomic mass as the analyte of interest. Spectral interferences generally occur from the sources listed in the following sections.

Isobaric Overlaps

Because most elements have more than one naturally occurring isotope, it is possible for the mass spectrum of an isotope of one element to directly overlap that of an isotope of another element. These interferences are termed isobaric overlaps. All elements, except indium, have at least one isotope free from overlap. Therefore, you can overcome this problem by selecting of isotopes carefully when developing your methods.

Minor overlaps are corrected by measuring the intensity of the interfering element at one of its major isotopes. Then, using published isotope ratios, it is possible to subtract the intensity of the interfering isotope that is contributing to the analyte signal. Using this principle, the software uses built-in calculation routines to automatically correct for known isobaric overlaps when calculating analyte concentrations in samples. In general, you do not need to make any further adjustments to the system, assuming that the default calculations are not modified.

Plasma-Induced Polyatomic Ions

The presence of atmospheric gases or the argon carrier are sources of potential interfering ions as the result of reaction with other analyte or matrix components. These interfering ions occur as polyatomic, molecular ions. The following table lists the most severe of the common overlaps which occur.

Isotope Interferences

Analyte	% Abundance of Isotope	Interfering Ion
S 32+	95.0	(O 16)(O 16)+
K 39+	93.3	(Ar 38)(H)+
Ca 40+	96.9	Ar 40+
Fe 56+	91.7	(Ar 40)(O 16)+
Se 80+	49.6	(Ar 40)(Ar 40)+

Of these, only the overlap of the most abundant isotope of argon with calcium precludes analysis at the desired isotope. In the case of calcium, determinations using the ELAN[®] 6000, 6100, or 9000 are generally performed at Ca44, which is about 2% abundant.

Note: With the interference reduction capabilities of the ELAN[®] DRC[™] series of instruments, the most abundant isotopes for K, Ca, Fe, and Se can be used.

Sulfur detection limits are affected both by poor ionization in the ICP (14%), resulting in low ion intensity, and by the overlap of the primary sulfur ion by diatomic oxygen. Unless the oxygen entering the plasma can be reduced to trace levels, the overlap forces the use of a less abundant sulfur isotope (S34) for determinations.

Matrix Solvent-Induced Polyatomic Ions

The solvent or acid in which the sample is dissolved can also be a source of interfering polyatomic ions. Chlorine from hydrochloric or perchloric acid and sulfur from sulfuric acid all form polyatomic ions with argon and other plasma gases. For organic solvents, carbon and oxygen can form polyatomic ions. The most severe solvent-induced interference is from CO on silicon. All three silicon isotopes are overlapped by carbon species, precluding the determination of silicon in organic matrices. The major solvent-induced overlaps are listed in the following table.

Matrix Solvent-Induced Molecular Ion Overlaps

Analyte	% Abundance of Isotope	Interfering Ion
Si 28+	92.2	(C 12)(O 16)+
Ca 44+	2.0	(C 12)(O 16)(O 16)+
Ti 48+	73.8	(S 32)(O 16)+
V 51+	99.7	(Cl 35)(O 16)+
Zn 64+	48.6	(S 32)(O 16)(O 16)+, (S 32)(S32)+
As 75+	100.0	(Ar 40)(Cl 35)+

Matrix-Induced Polyatomic Ions

Polyatomic ions may also be generated by sample constituents, usually in combination with oxygen. Oxides of some heavier elements can be formed in the plasma/spectrometer interface. Typically, oxides are formed in relatively low concentrations, with even a worst case being only a few percent of the parent isotope. In sufficient concentrations, however, oxide-forming elements can interfere with determinations of analytes at higher masses. One example is the formation of molybdenum oxide which overlaps all the major isotopes of cadmium.

In most cases, these interferences can be compensated by a knowledge of the intensities of the oxide and the parent ion. Then, by measuring the intensity of parent interfering ion, you can subtract the calculated interfering oxide intensity from the analyte intensity.

Dissolved Solids Limitations

In ICP-MS, the physical design of the ICP-mass spectrometer interface limits the concentration of dissolved solids to about 0.25%. At higher concentrations, the sampler cone orifice may become plugged when performing steady-state determinations. While in principle this is a limitation, in practice, the extremely low detection limits of the your instrument more than offset the problem, because you rarely need to run a solution at high enough concentration to cross the dissolved solids limit. In fact, it is routinely necessary to dilute samples 50-100X before introducing them to the spectrometer, in order to not exceed the signal range of the detection system and to not coat the ion optics.

Identifying Interference Problems

Whenever samples of unknown composition are received by an ICP-MS laboratory, the method development/selection process involves a careful, stepwise approach to determining potential interference problems and to defining a solution to these interferences. This approach generally begins by performing a TotalQuant™ analysis on the solution to determine:

- Elements present at measurable concentrations
- The concentration ranges for the elements of interest
- Interfering molecular ions
- Masses at which no elements are present (masses where internal standards could be defined)

This same information could also be determined by performing a full mass scan and manually reviewing the spectral results in the Interactive graphics window. However, the TotalQuant approach provides a fully automated means of gathering both spectral and semi-quantitative data.

Using this information, you can determine which element isotopes to use to best avoid potential interference problems, plus you can determine the best mass ranges for internal standards.

Correcting for Interferences

This section describes various interference correction strategies, and provides relevant examples.

Corrections in Quantitative Analysis, Isotope Ratio and Isotope Dilution

Sample specific matrix effects and spectral interferences require two different approaches for correction. The use of internal standards and standard addition calibration are the primary means of correcting for matrix interferences in sample solutions.

For spectral interferences, your system uses elemental equations to correct for the spectral overlaps that can affect your results. Corrections for isobaric overlaps and many known polyatomic ion overlaps are pre-programmed into the software. The standard equations are automatically listed on the Method window Equation tab. The standard equations correct for known isotope interference, however, they do not correct for interferences due to molecular species.

Using the Equation tab, you can modify the standard equations or construct new equations to suit your specific requirements. In working with the Equation tab, it is important to note that the entries available in a TotalQuant method are different from those available in other analytical techniques. This is because TotalQuant methods perform calculations over a broad mass range. Thus, provisions are made for correcting for both atomic and polyatomic interfering species.

Corrections in TotalQuant™ Analyses

As in Quantitative Analysis, Isotope Ratio or Isotope Dilution, elemental equations are used to correct for sample-specific molecular or polyatomic ion interferences in TotalQuant analyses. The TotalQuant software not only incorporates standard isotopic interference equations, but also uses a polyatomic species table to correct for common polyatomic interferences. However, it is still often necessary to manually alter measurement calculations for certain elements due to sample-specific interferences.

The Equation tab of the Method window in the software permits you to specify the isotope you want to measure, then specify any corrections that are needed to accurately measure the element of interest.

By selecting your isotope carefully, you can minimize the number of corrections necessary. Note that the Equation tab is used to program the isotope to be used for element concentration calculations, and to program corrections for interferences. This is different from the correction protocol in other analytical methods, where you only specify corrections. An elemental equation in a TotalQuant method entered by the user overrides all the heuristics normally associated with that element. As a result, it is normally not necessary to program corrections for polyatomics. However, if your sample solution is an especially complex matrix, polyatomic corrections may also be programmed in the TotalQuant Equation tab.

Interference Correction: Examples

Interference correction in software can be easily and rapidly completed using the Equation tab in the Method window. The following examples demonstrate the use of elemental equations for both Quantitative Analysis/Isotope Ratio/Isotope Dilution measurements and for TotalQuant measurements.

Correcting for Spectral Overlap (Quantitative)

The following example explains how the software uses elemental equations to correct for simple elemental overlap.

The instrument measures the intensity of an isotope at the indicated mass. This measurement represents the total intensity at the mass value, including contributions from both the analytes and any other element or polyatomic species that might occur at that mass. For example, to determine the amount of Zr 94 present in a sample, the system measures signal intensity at mass 93.906. Imagine a sample in which the system measures 100,000 counts at mass 93.906. This measurement includes contributions from Zr 94 and Mo 94.

During the determination, the system measures the intensity of an isotope of the interfering element (Mo) that does not overlap with the analyte. For our example, the instrument can measure the intensity of molybdenum at mass 94.906. In this example, let the intensity at this mass be 5,000 counts.

The software calculates the proportion of the interfering isotope present in the sample based on the intensity of the non-interfering isotope and the ratio of the naturally occurring abundances of the interfering and non-interfering isotopes. For example, the natural

abundance ratio of Mo 94 to Mo 95 is 0.581030. So, if the system measures 5,000 counts for Mo 95, there must be $(0.581030 * 5000)$ counts of Mo 94 present that are interfering with Zr 94.

The software can now calculate the intensity of the analyte by subtracting the intensity of the interfering isotope from the total intensity at the analyte's atomic mass.

In this example, we know that 2,905 (that is, $0.581030 * 5000$) of the counts at mass 94 are due to Mo 94. We also know that the remainder of the counts at mass 94 are likely due to Zr 94. As a result, the elemental equation calculation for this example is:

$$(\text{Zr } 94) = I(94) - [I(95) * (\text{abundance (Mo } 94) / \text{abundance (Mo } 95))]$$

where:

I = intensity of the specified mass

abundance = natural abundance of the isotope

You would make the following entry on the Equation tab to perform this calculation:

0.581030 * Mo 95

Detector Shutdown

The pulse shutdown threshold is two million count per second (cps). When acquiring data in pulse mode and the measured intensity for an analyte is above 2 million cps, then the analyte is in pulse shutdown.

Shutdown values are reported by the letter **S**. To convert the **S** to a cps value reprocess this data with a method that uses a dual detector calibration. For quantitative accuracy you must perform a dual detector calibration for every mass that you want to measure above two million cps. Intensities above two million cps can be viewed or determined using the analog or dual modes of the detector. However, if the analyte intensity exceeds the dynamic range of the detector (typically $1e9$ cps) then the analyte is in analog shutdown. Analog shutdown values are also reported by an **S**. In this case, the true value cannot be determined unless the solution is diluted and reanalyzed.

When acquiring data in pulse mode, analytes whose correction equation has some terms in shutdown will be calculated by substituting the value of $2e6$ for the terms that are in shutdown. The resultant value will be reported in brackets. See the following table as an example.

Analyte	Intensity	Std. Dev	%RSD	Concentration	Conc. Std Dev
V 51	[623000]	9898	N/A	[40] ppb	4.2 ppb

The value under the Intensity column is shown in brackets. This means that an interelement or polyatomic correction has gone into shutdown and an accurate determination of the vanadium intensity was not possible. If the data was acquired in pulse mode, it is possible to accurately determine the analyte's intensity by converting the signal that was in pulse shutdown (**S**) to a cps value. To convert the **S** to a cps value reprocess this data with a method that uses a dual detector calibration.

However, if the data was acquired in analog or dual mode and the intensity/concentration is reported in brackets, this means that the intensity of the correction mass has exceeded the dynamic range of the detector. It will not be possible to accurately determine the analyte or interference signal unless the solution is diluted and reanalyzed. When the analyte intensity can not be accurately determined due to a correction mass being in shutdown, the intensity will be denoted by an **E** on the plot. This **E** point will be included in the regression automatically. The **E** denotes elemental equation error.

Correcting for Polyatomic Species (Quantitative)

Elemental equations can be used to correct for the effect of polyatomic species interference on an analyte isotope. For example, arsenic has a single isotope, As 75, which is overlapped by a peak from (Ar 40)(Cl 35). While this interference is normally quite small, you may want to correct for it in samples with a high chloride concentration. Because chlorine has isotopes at both masses 35 and 37, (Ar 40)(Cl 37) can be measured at mass 77 and this information used to calculate and correct for the interference at mass 75.

The following equations are used:

$$I(\text{As } 75) = I(75) - I(\text{Ar } 40 \text{ Cl } 35)$$

$$I(\text{Ar } 40 \text{ Cl } 35) = I(75) - [\text{abundance}(\text{Cl } 35) / \text{abundance}(\text{Cl } 37)] * I(77)$$

where:

I = intensity of the specified mass

abundance = natural abundance of the isotope

By combining these two equations and rearranging, we get:

$$I(\text{As}75) = I(75) - [\text{abundance}(\text{Cl } 35) / \text{abundance}(\text{Cl}37)] * I(77)$$

Substituting the abundances for the chlorine isotopes yields the following result:

$$I(\text{As}75) = I(75) - [(0.7577 / 0.2423)] * I(77) = I(75) - 3.127 * I(77)$$

As a result, you would enter the following on the Equation tab:

$$- 3.127 * \text{mass } 77$$

Correcting for Spectral Overlap and Polyatomics (Quantitative)

In certain cases, it will be necessary to account for interferences resulting from both spectral overlap and from polyatomics. For example, when determining arsenic concentration in the presence of high chloride concentrations, you can use the (Ar 40)(Cl 37) intensity at mass 77 to calculate a correction for the presence of (Ar 40)(Cl 35) at mass 75. This was demonstrated in the above example. That example, however, assumed that no other isotope other than Ar Cl occurred at mass 77. In actual practice, selenium has an isotope at mass 77 and would therefore display an ion intensity, if present.

To accurately determine the amount of (Ar 40)(Cl 37) present, it would be necessary to perform an additional correction for selenium. The selenium isotope at mass 82 is subject to very few interferences, and can be used to determine the selenium concentration.

The following equations are used:

$$I(\text{As } 75) = I(75) - I(\text{Ar } 40 \text{ Cl } 35)$$

$$I(\text{Ar } 40 \text{ Cl } 35) = I(75) - [\text{abundance}(\text{Cl } 35) / \text{abundance}(\text{Cl } 37)] * I(77)$$

$$I(\text{Se } 77) = (\text{abundance}(\text{Se } 77) / \text{abundance}(\text{Se } 82)) * I(82)$$

where:

I = intensity of the specified mass

abundance = natural abundance of the isotope

By combining these equations and rearranging, we get:

$$I(\text{As } 75) = I(75) - [\text{abundance}(\text{Cl } 35) / \text{abundance}(\text{Cl } 37)] * \{I(77) - [\text{abundance}(\text{Se } 77) / \text{abundance}(\text{Se } 82)] * I(82)\}$$

Substituting the abundances for the chlorine and selenium isotopes yields the following result:

$$I(\text{As } 75) = I(75) - 3.127 * [I(77) - (0.874 * I(82))]$$

As a result, you would enter the following on the Equation tab:

$$- 3.127 * (\text{mass } 77 - (0.874 * \text{mass } 82))$$

Selecting an Isotope for Measurement (TotalQuant™ Methods)

When using elemental equations in TotalQuant methods, the first step is specification of the measurement isotope that you want to use. This can be either the actual isotope (that is, Se 77 to measure selenium at mass 77) or it can be an alternate isotope. For example, the major isotope of sulfur occurs at mass 32. However, this mass is also subject to interference from a plasma-induced molecular ion overlap caused by (O 16)(O 16)+ ions. For more accurate data in the presence of a high oxygen concentration, it can be helpful to identify an alternate isotope, such as S 34, which is subject to fewer interferences.

To specify S 34 as the measurement isotope for sulfur, we first determine the natural abundance (4.21), then calculate its inverse * 100.

$$[(1 / 4.21) * 100] = 23.75$$

You would make the following entry in the Corrections column of the Equation tab:
23.75 * mass 34

Correcting for Spectral Overlap (TotalQuant™ Analyses)

TotalQuant elemental equations retain all of the correction functionality of the elemental equations in other analytical techniques. The primary difference in their use is the requirement to first specify the measurement isotope. After you have specified the isotope to use as the base intensity measurement, you can enter additional corrections as required by your sample.

For example, the major isotope of selenium occurs at mass 80. This mass is also subject to interference from a plasma-induced molecular ion overlap caused by (Ar 40)(Ar 40)+ ions. The argon intensity generally dwarfs the selenium signal, so an alternate isotope is usually selected. For this example, we will select Se 82 which has a relative abundance of 8.73.

First, we set the abundance factor by calculating the inverse of the normal natural abundance, multiplying the quotient by 100.

$$[(1 / 8.73) * 100] = 11.45$$

Next, we set the determination mass to 82. However, the signal at mass 82 is also subject to contribution from Kr 82, so a correction must be programmed.

To correct for Kr 82, we must find a non-interfering Kr signal. Here, we will use Kr 83. Because the ratio of the natural abundance of Kr at mass 82 and mass 83 is nearly identical, the abundance factor is 1.00. And, because we must subtract the contribution from Kr, we will set the factor to -1.00. Thus, our equation for the calculations is:

$$I(\text{Se}) = 11.45 * [I(82) - (\text{abundance}(\text{Kr } 82) / \text{abundance}(\text{Kr } 83)) * I(83)]$$

where:

I = intensity of the specified mass

abundance = natural abundance of the isotope

The entries to be made in the Corrections column of the Equation tab are:

$$11.45 * (\text{mass } 82 - 1.00 * \text{mass } 83)$$

In practice, you would compensate for the Kr overlap by performing a blank subtraction before analyzing the sample. The assumption is that the Kr comes from the argon gas supply, and is the same for samples and blanks.

8

Working with Graphic Data

This section discusses the graphic viewing and manipulation tools.

Topics in this section include:

- ▶ “Understanding Graphic Displays” on page 153
- ▶ “The Graphics Display Toolbar” on page 154
- ▶ “Realtime Graphics Window” on page 155
- ▶ “Interactive Graphics Window” on page 160
- ▶ “Interactive Graphics Options Dialog Boxes” on page 163
- ▶ “Composite Signal and Spectral Options” on page 166
- ▶ “Cell Parameter Optimize Options” on page 166

Understanding Graphic Displays

The software provides extensive displays of signal and spectral data in realtime or post-run. There are three main windows through which you routinely work with graphic data:

- “Realtime Graphics Window”
- “Interactive Graphics Window”
- “Calibration View Window”

While each of these windows is designed to support different requirements, the functions available in each are similar, and all are supported by a set of common controls.

The Graphics Display Toolbar

The graphics windows share a common set of tools for managing the display and appearance of graphical data. When a toolbar button is selected, it appears depressed against a white background. Mouse-over screentips describe each button's function.

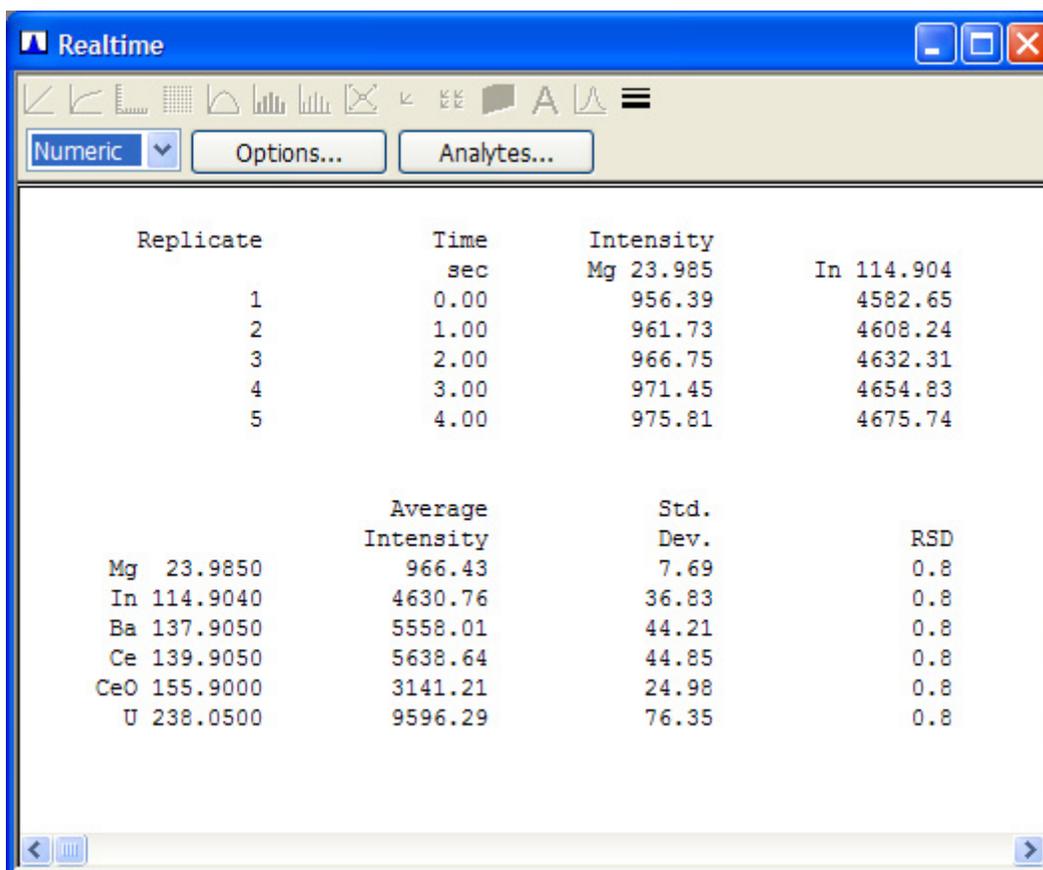


- 
 - **Linear/Logarithmic Display:** Click to toggle between a linear value axis (Y-axis) graph display and a logarithmic value axis graph display.
- 
 - **No Grid/Grid Display:** Click to toggle between a full grid background and no grid, but with tick marks along each axis.
- 
 - **Spectral/Bar/Line Graph Display:** Click to display results in *Spectral Mode*, or as a *Bar or Line Graph*.
- 
 - **Zoom Control:** Click to select the desired zoom level from the drop-down menu. Each time you zoom, a number is assigned to the view, with **0** the full display, **1** the first zoom, **2** the second, and so forth. To switch between zoom levels, click the Zoom Control button, and then click the number associated with the zoom level you want to use. To reset the zoom series, set the display to zoom level **0**, then redraw a different area with the cursor. All remaining zoom levels in the original series are deleted.

To zoom in a graph, drag the cursor to draw a box around the region you want to enlarge. When you release the mouse button, the graph is redrawn with the area inside the box displayed at zoom scale.
- 
 - **Print Single/Multiple Graphs:** Click these buttons to control the output of graphs displayed in the window to a printer attached to the computer. To print a single graph in a one-graph display, click the Print Single button. To print a single graph in a multiple-graph display, click the graph you want to print, then click the Print Single button. To print all the graphs in a multiple-graph display, click the Print Multiple button.
- 
 - **Plot Options:** Click to display the Plot Options dialog box. Here you can control the colors used for axes, labels, and tick marks on graphs displayed in the Interactive Graphics window. You can also specify the display of titles, labels, and scroll bars.
- 
 - **Text Control:** Click to manage type parameters for the labels and titles of graphics displayed in the Interactive Graphics window. To modify text parameters, click the Text Control button, and select *Titles* or *Labels* from the drop-down list; the Font Options dialog box appears. Select the desired font parameters and then click OK. The parameters selected are applied to all graphs displayed in the window.
- 
 - **Autoscale:** Click to automatically scale a displayed graph. The software automatically adjusts the y-axis intensity to maximize the display so that the largest peak is on-scale and shown at its maximum intensity.
- 
 - **Line Width:** Click to select and apply a line width to the displayed graph. Select from *1 pt*, *2 pts*, or *3 pts* wide.

Realtime Graphics Window

Use the Realtime Graphics window for realtime viewing and interpretation of signal, spectral, and numeric displays of data during an acquisition. Here you can adjust the axis range and display parameters, manage the printing of graphics data, specify the colors used, and control the font and type size for title and label text.



Realtime graphics window

Items in the Realtime Graphics Window

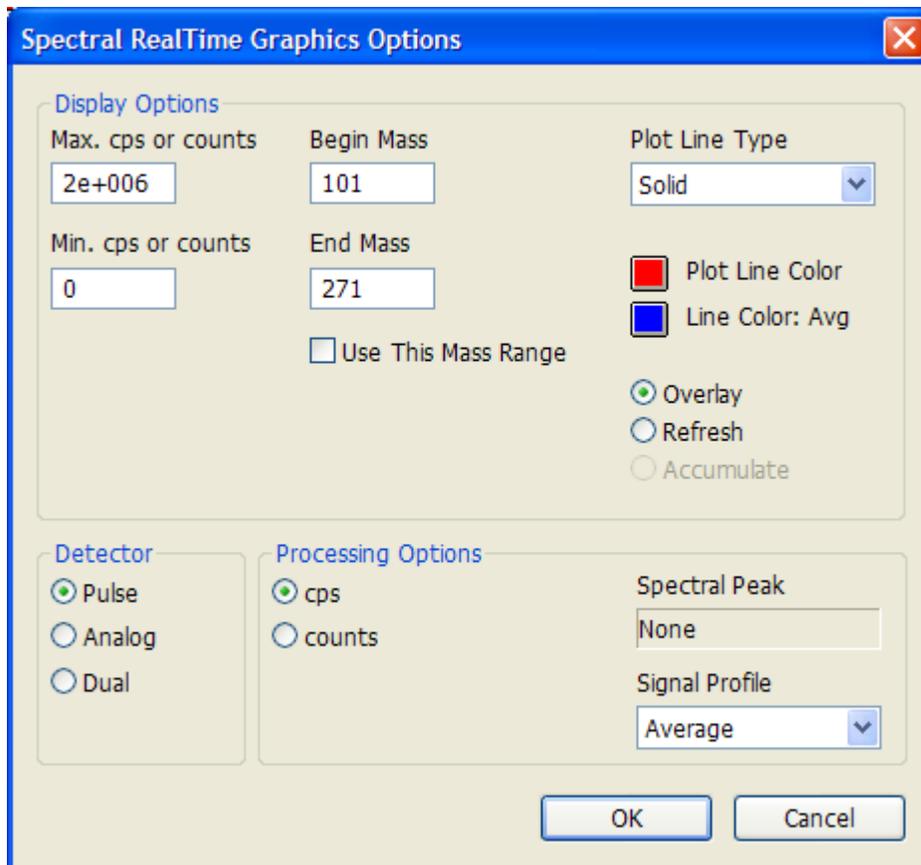
- **Display Type:** Controls the type of data being displayed in the Realtime graphics window. To select the data type to be displayed, click one of the following options from the Display Type drop-down list.
 - ♦ *Signal:* Displays the signal from a data acquisition. This option is available for individual elements/analytes only. The graph displayed has an x-axis listing time in seconds and a y-axis listing signal intensity in counts per second (cps) or total ion counts. A maximum of 6 elements/analytes can be displayed.
 - ♦ *Spectral:* Displays the spectral results for a range of masses/analytes. The graph displayed has an x-axis listing mass range in amu and a y-axis listing signal intensity in cps or total ion counts. A natural abundance spectral fingerprint of a single isotope can be overlaid.
 - ♦ *Numeric:* Displays numerically the elapsed time (in seconds) for the measurement and the raw (uncorrected) analyte intensity.

- **Options:** Displays the options dialog box specific to the Display Type selected. Selecting this button displays the Realtime Graphics Options dialog box which is used to control the display parameters when viewing graphics with the software.
- **Analytes:** Displays the Analyte Display Options dialog box which is used to control the analytes that will be plotted in the graphics window.
- **Natural Abundance Spectral Fingerprint Overlay:** The software allows you to visually determine whether interference is present for an isotope of interest. You can only overlay the natural abundance fingerprint for one element at a time. The natural abundance fingerprint is normalized for the isotope selected as the reference isotope. The name of the reference isotope and its mass value appear beside the histogram. You may print the histogram with the spectral overlay.
Note: This functionality is only available when Spectral is selected as the display type.

Realtime Graphics Options Dialog Boxes

The Realtime Graphics Options dialog boxes allow you to control the display of data on the plot window. Each signal type has a unique set of graphics display options associated with it. The dialog boxes are:

- Signal Realtime Graphics Options
- Spectral Realtime Graphics Options
- Numeric Realtime Graphics Options



Spectral Realtime Graphics Options dialog box

Items in the Realtime Options Dialog Boxes

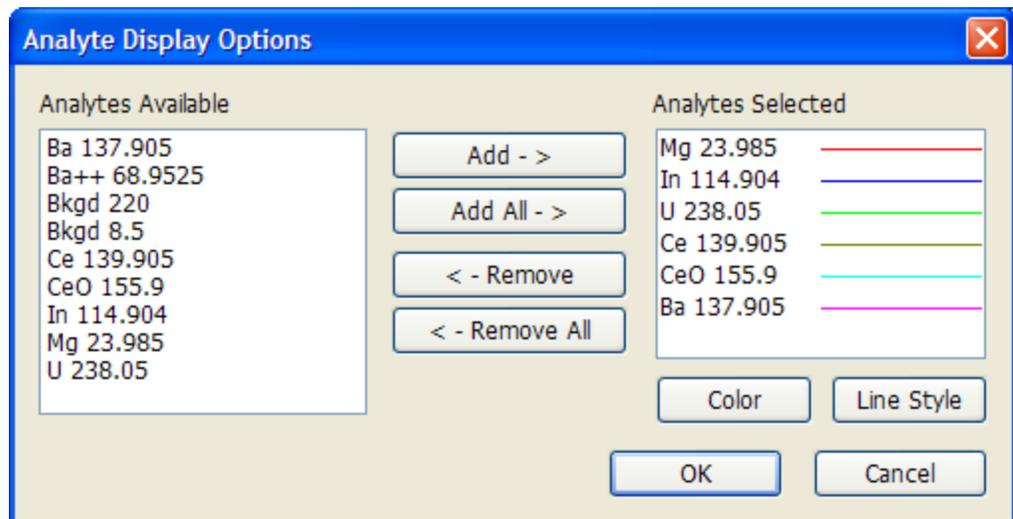
Note that not all options appear in every dialog box.

- **Display Options Group:** Max cps or counts: Sets the maximum y-axis display value for the spectral plot. Entries can be typed out without commas or other character separator (for example, 5000000) or can be typed in scientific notation (for example, 5e+6). The software automatically converts any value not in scientific notation when the dialog box is closed.
 - ♦ *Min cps or counts:* Sets the minimum y-axis display value for the spectral plot. Entries can be typed out without commas or other character separator (for example, 5000000) or can be typed in scientific notation (for example, 5e+6). The software automatically converts any value not in scientific notation when the dialog box is closed.
 - ♦ *Begin Mass:* Sets the beginning mass, in atomic mass units (amu), for the spectral plot. Valid entries are zero or any positive whole number. Decimal entries are automatically converted to a whole number value.
 - ♦ *End Mass:* Sets the ending mass, in amu, for the spectral plot. Valid entries are zero or any positive whole number. Decimal entries are automatically converted to a whole number value.
 - ♦ *Use This Mass Range:* Uses the setting in the Display Options group. If the check box is not selected, the changes made in the dialog box will not take effect.

- ♦ *Plot Line Type*: Sets the line style for display of spectral lines in the Interactive graphics window. Click the drop-down arrow to view the options available, then click the desired option to select a line style.
- ♦ *Line Color (Plot/Avg.)*: Sets the display color for the spectral plot lines, both the individual replicates and the averaged value. Clicking either color block opens the Colors dialog box. To select a color, click the desired color box and click OK. You can exit the Colors dialog box without making a change by clicking Cancel.
- ♦ *Overlay/Refresh/Accumulate*: These options are used to determine how individual replicate measurements are plotted in the Interactive graphics window. Click Overlay to plot all replicates on a single graph, overlaying the results of the successive measurements. Click Refresh to clear the results from one replicate before plotting the next replicate. Note that only the replicates indicated in the Draw Replicates command in the Interactive graphics window will actually be plotted. Click Accumulate to plot a line which represents the total ion counts data from a series of replicates, all accumulated into a single plot. The Accumulate option is only available when the Display Type is Spectral and the Processing Options setting (cps/Counts) is set to counts.
- **Detector Group: Pulse/Analog/Dual**: This set of options is used to set the detector channel generating the signal input to the plot window. Click Pulse to select the pulse detector. Click Analog to select the analog detector. Click Dual to select the dual detector mode using input from both detectors. Dual mode is only active after the detector has been calibrated.
- **Processing Options Group: cps/counts**: This pair of options sets the processing function to display either total counts or counts per second. Click cps for counts per second or click counts to specify total ion counts.
 - ♦ *Spectral Peak*: This entry is used to determine how the data from the individual spectral peaks will be processed before it is displayed on the screen. The drop-down box contains three options: Average, Sum, and Maximum. Click Average to average the values of all the MCA Channels from each peak. Click Sum to add the values of all the MCA Channels to create a total ion count for each peak. Click Maximum to select the MCA channel with the maximum value from each spectral peak. No processing can be performed on the spectral profile when using Spectral Interactive graphics mode.
 - ♦ *Signal Profile*: This entry is used to determine how the signal profile is treated before further calculations are performed. The drop-down box contains three options: average, sum, and maximum. Click Average to average the readings from a profile. Click Sum to add the readings to create a total count for each profile. Click Maximum to select the maximum reading from each profile.
 - ♦ *Isotope Ratio Mode: (DRC II™/DRC-e™ instruments only)* The Isotope Ratio method is a specialized technique that enables measurement of the exact ratio of two isotopes of an element in a sample. This technique is a sensitive indicator of age, reaction or metabolism in nuclear, geochemical or biomedical applications. In addition to providing an accurate ratio of isotope concentration, these measurements are also highly precise.

Analyte Display Options Dialog Box

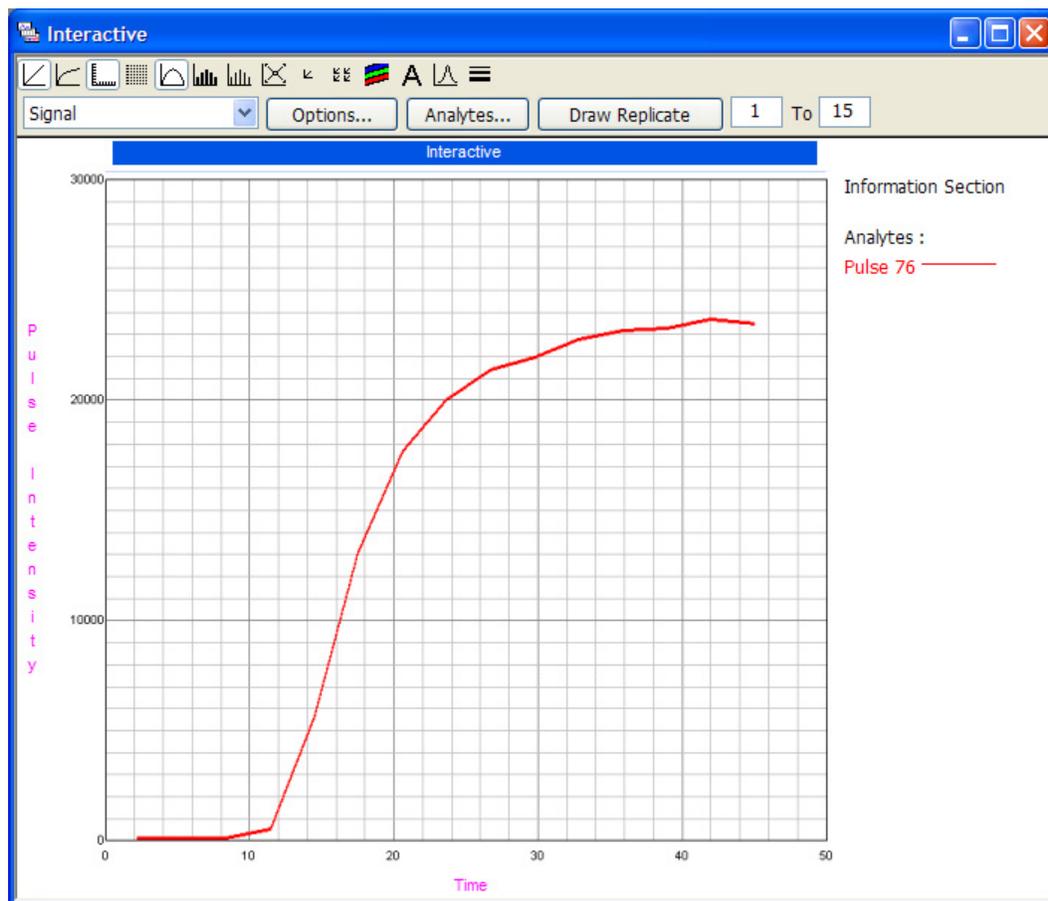
The Analyte Display Options dialog box allows you to select the analytes that will be plotted in the graphics windows.



Analyte Display Options dialog box

Interactive Graphics Window

Use this window for post-acquisition viewing and interpretation of signal and spectral displays. Here you can adjust the axis range and display parameters, manage the printing of graphics data, control the colors used on the display, and to control the font and type size for titles and label text. The Interactive Graphics window is an integral part of tuning and optimization your instrument, and is also useful in post-acquisition analysis of analytical data.



Interactive graphics window

Data Control Commands

- **Display Type:** Controls the type of data being displayed in the Interactive Graphics window. To select the data type to be displayed, click the drop-down arrow alongside the Display Type entry. Select from the following options:
 - ♦ *Signal:* Displays the signal from a data acquisition. This option is available for individual elements/analytes only. The graph displayed has an x-axis listing time in seconds and a y-axis listing signal intensity in counts per second (cps) or total ion counts.
 - ♦ *Spectral:* Displays the spectral results for a range of masses/analytes. The graph displayed has an x-axis listing mass range in amu and a y-axis listing signal intensity in cps or total ion counts. A natural abundance spectral fingerprint of a single isotope can be overlaid.

- ♦ *TQ Spectrum*: Displays a TotalQuant™ spectrum. The graph displayed has an x-axis listing mass range in amu and a y-axis listing intensity in counts per second. To facilitate viewing the full spectrum with the x-axis expanded, a set of four buttons permit you to control x-axis scrolling, as follows:
 - [LEFT FULL]: Moves to the beginning of the mass range included in the scan (lowest masses scanned).
 - [LEFT]: Moves one page down toward the lower mass range included in the scan.
 - [RIGHT]: Moves one page up toward the higher mass range included in the scan.
 - [RIGHT FULL]: Moves to the end of the mass range included in the scan (highest masses scanned).
- ♦ *Composite Signal*: Overlays, adds, subtracts or sets up a ratio for two time-varying signals. It is also useful for blank-subtracted data. This option is available for individual elements/analytes only. The graph displayed has an x-axis listing time in seconds and a y-axis listing signal intensity in counts per second (cps) or total ion counts.
- ♦ *Composite Spectral*: Overlays, adds, subtracts or sets up a ratio for two mass spectrums. It is also useful for blank-subtracted data. The graph displayed has an x-axis listing mass range in amu and a y-axis listing signal intensity in counts per second (cps) total ion counts.
- ♦ *Optimization*: Displays the graph resulting from an optimization scan for one of the digital-to-analog converters controlling the instrument hardware. This option is used in conjunction with the Optimization window during hardware optimization and is automatically displayed as part of the Optimization workspace. The graph displayed has an x-axis listing the range of DAC values to be scanned and a y-axis listing intensity in cps.
- ♦ *Tuning*: Displays the graphs resulting from a mass calibration and/or resolution adjustment performed during instrument tuning. This option is used in conjunction with the Tuning window. When the Tuning workspace is used, the software automatically sets the window up to display individual graphs for up to 6 analytes included in the mass calibration scan. Each graph displayed has an x-axis listing the mass range in amu and a y-axis listing intensity in cps. The individual graphs include a title bar displaying the atomic symbol and the isotope mass for the analyte results being plotted in that graph. When results are plotted, a line is also automatically drawn to indicate the intensity at 10% of maximum peak intensity (the point at which peak width is measured).
- ♦ *Dual Detector*: Use with the Interactive Graphics window as part of the dual detector calibration procedure. Dual detector calibration is used to adjust the response behavior of the pulse and analog stages of the dual detector to provide optimum data integrity when signal intensity varies widely during a run employing both pulse and analog signal detection. By selecting Analytes, the graph can be displayed for any analytes used in the calibration procedure. As part of the dual detector calibration workspace, the system automatically displays graphs for up to 5 analytes. Each graph has an x-axis displaying pulse intensity and a y-axis displaying analog intensity. Detector Response Function graph shows the relationship of the analog to pulse signals across the mass range. Each point represents a mass which has a valid dual detector calibration. The straight lines between points indicate interpolated conversion factors. For an accurate quantitation you must have a measured conversion factor for each isotope of interest. Using the interpolated conversion factor may result in analytical inaccuracies. The detector response functions should have the shape of a $1/x^2$

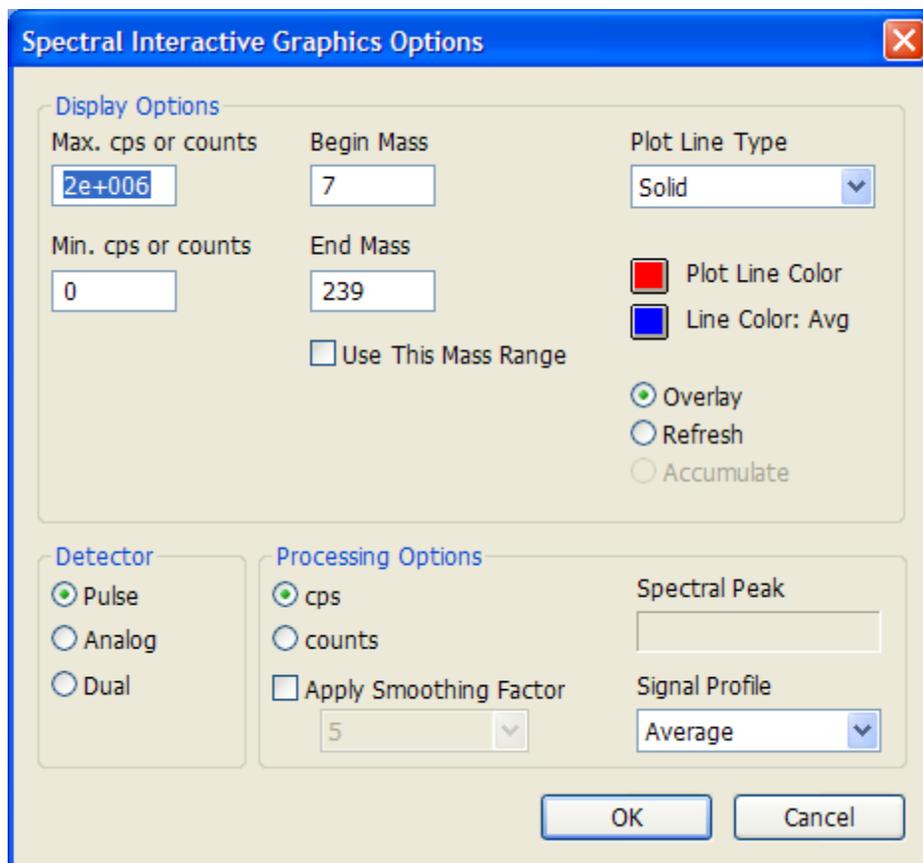
curve. A flattening of the detector response function is an indication that the detector is near the end of its useful life.

- ♦ **AutoLens™ function:** Use with the Interactive Graphics window as part of the AutoLens calibration procedure. Lens scanning is used to adjust the detection systems mass bias to provide optimum signal intensity across the full mass range. By selecting Analytes, the graph can be displayed for up to 5 analytes used during the lens scanning procedure. Each graph has an x-axis displaying lens voltage and a y-axis displaying signal intensity.
 - ♦ **Cell Param Optimize: (DRC series instruments only)** Displays a line graph of the intensities of two solutions as a function of DRC parameter (cell gas flow, RPq) and estimated detection limits, one analyte at a time. The element to be viewed is selected in the Analyte drop-down list box. If no analyte is selected, the first analyte from the list is displayed in the Cell Parameter Optimize plot. The software indicates the gas flow providing the lowest detection limit for each analyte with an x on the graph. Click the x and the optimum gas flow for the selected analyte appears in the Cell Parameters tab of the Optimization window.
 - **Options:** Displays the options dialog box specific to the Display Type selected. Selecting this button displays the Interactive Graphics Options dialog box which is used to control the display parameters when viewing graphics with the software.
 - **Analytes:** Displays the Analyte Display Options dialog box which is used to control the analytes that will be plotted in the graphics window. This button appears for all signal options except Composite Signal, Composite Spectral, and Cell Param Optimize when the Composite button appears in its place.
 - **Composite:** Displays the Composite Signal Graphics Options, Composite Spectral Graphics Options, or Cell Param Optimize Options dialog boxes. Clicking this button displays the dialog box used to control both the analytes that will be plotted in the graphics window and the manner in which the data will be combined for composite display. This button only appears when the signal option for Composite Signal, Composite Spectral, or Cell Param Optimize is selected.
 - **Draw Replicate:** This button and its associated numeric entry boxes are used to control which replicates in a given determination will be plotted in the Interactive graphics window. To set the replicate number, click in the first entry box and type the number of the first replicate you want to plot. Click in the second entry box, after the word “to”, and type in the number of the last replicate you want to plot. To draw the replicate, click the Draw Replicate button.
 - **Natural Abundance Spectral Fingerprint Overlay:** This function allows you to visually determine whether interference is present for an isotope of interest. You can only overlay the natural abundance fingerprint for one element at a time. The natural abundance fingerprint is normalized for the isotope selected as the reference isotope. The name of the reference isotope and its mass value appear beside the histogram. You may print the histogram with the spectral overlay.
- Note:** This functionality is only available when Spectral is selected as the display type.

Interactive Graphics Options Dialog Boxes

Use the Interactive Graphics Options dialog boxes to control the display of data on the plot window. Each signal type has a unique set of graphics display options associated with it. The dialog boxes are:

- Spectral Interactive Graphics Options
- Signal Interactive Graphics Options
- TQ Spectrum Interactive Graphics Options
- Composite Signal Interactive Graphics Options
- Composite Spectral Interactive Graphics Options
- Cell Parameters Optimize Options
- Optimization Interactive Graphics Options
- Tuning Interactive Graphics Options
- AutoLens™ Interactive Graphics Options



Spectral Interactive Graphics Options dialog box

Items in the Interactive Graphics Options Dialog Boxes

All possible options are described in the following topics. However, not all of the options apply to each dialog box.

- **Display Options Group:** Max cps or counts: Sets the maximum y-axis display value for the spectral plot. Entries can be typed out without commas or other character separators (for example, 5000000) or can be typed in scientific notation (for example, 5e+6). The software automatically converts any value not in scientific notation when the dialog box is closed.
 - ♦ *Min cps or counts:* Sets the minimum y-axis display value for the spectral plot. Entries can be typed out without commas or other character separators (for example, 5000000) or can be typed in scientific notation (for example, 5e+6). The software automatically converts any value not in scientific notation when the dialog box is closed.
 - ♦ *Begin Mass:* Sets the beginning mass, in atomic mass units (amu), for the spectral plot. Valid entries are zero or any positive whole number. Decimal entries are automatically converted to whole numbers.
 - ♦ *End Mass:* Sets the ending mass, in amu, for the spectral plot. Valid entries are zero or any positive whole number. Decimal entries are automatically converted to whole numbers.
 - ♦ *Use This Mass Range:* Select this check box to use the setting in the Display Options group. If the check box is not selected, the changes made in the dialog box will not take effect.
 - ♦ *Concentration:* Sets the concentration of the standard solution (in parts per billion) that is used to optimize the reaction cell gas flow. This field is only available when the Display Type is Cell Param Optimize.
 - ♦ *Show Composite Line Only:* Select this check box to display the plot for estimated detection limit in the cell param optimize display only. This setting is not available when the Display Type selected is Overlay.
 - ♦ *Plot Line Type:* Sets the line style for display of spectral lines in the Interactive graphics window. Click the drop-down arrow to display the options available, then click the desired option to select a line style.
 - ♦ *Line Color/Avg. Color:* Sets the display color for the spectral plot lines, both the individual replicates and the averaged value. Clicking either color block opens the Color dialog box. To select a color, click the desired color box and click OK. You can exit the Color dialog box without making a change by clicking Cancel.
 - ♦ *Overlay/Refresh/Accumulate:* Determine how individual replicate measurements are plotted. Click Overlay to plot all replicates on a single graph, overlaying the results of the successive measurements. Click Refresh to clear the results from one replicate before plotting the next replicate. Note that only the replicates indicated in the Draw Replicates command in the Interactive graphics window will actually be plotted. Click Accumulate to plot a line which represents the total ion counts data from a series of replicates, all accumulated into a single plot. The Accumulate option is only available when the Display Type is Spectral and the Processing Options setting (cps/Counts) is set to Counts.
 - ♦ *Calculate/Transform:* Click the Transform button to perform the mathematical equation you have selected. The Transform button is available when the Display Type is Composite Signal or Composite Spectral. Click the Calculate button to

process the data files selected for reaction cell parameters optimization. The Calculate button is only available when the Display Type is Cell Param. Optimize.

- **Detector Group: Pulse/Analog/Dual:** Set the detector channel generating the signal input to the plot window. Click Pulse to select the pulse detector. Click Analog to select the analog detector. Click Dual to select the dual detector mode using input from both detectors. Dual mode is only active after the detector has been calibrated.
- **Processing Options Group: cps/counts:** Set the processing function to display either total counts or counts per second. Click cps for counts per second or click Counts to specify total ion counts.
 - ♦ *Spectral Peak:* Determines how the data from the individual spectral peaks will be processed before it is displayed on the screen. The drop-down box contains three options: average, sum and maximum. Click Average to average the values of all the MCA Channels from each peak. Click Sum to add the values of all the MCA Channels to create a total ion count for each peak. Click Maximum to select the MCA channel with the maximum value from each spectral peak. No processing can be performed on the spectral profile when using Spectral Interactive Graphics mode.
 - ♦ *Apply Smoothing Factor:* This check box is available only in the Interactive graphics window. Use to turn on/off spectral smoothing that can be used to reduce the effects of noise in high sensitivity measurements. You must have multiple readings per replicate to use this option. The smoothing function is a Savitzky-Golay moving average of the readings along the spectral profile. When the check box is selected, the drop-down box alongside is activated. Click the drop-down arrow to display the options for smoothing factor (number of moving average points), based on the number of readings per replicate used for the data acquisition.
 - ♦ *Signal Profile:* Determines how the signal profile is treated before further calculations are performed. The drop-down box contains three options: average, sum, and maximum. Click Average to average the readings from a profile. Click Sum to add the readings to create a total count for each profile. Click Maximum to select the maximum reading from each profile.

Composite Signal and Spectral Options

These dialog boxes are used to overlay, add, subtract, or set up a ratio for two signals or two mass spectra.

Composite Signal Graphics Options dialog box

Cell Parameter Optimize Options

DRC Series instruments only. Use this dialog box to display reaction cell parameter optimization plots.

Cell Parameter Optimize Options dialog box

Using the Cell Parameter Optimize Options dialog box

To optimize reaction cell parameters on a DRC Series instrument, you need to analyze two different solutions—a matrix blank and a spiked matrix blank. In this dialog box, you select the corresponding data files and click Calculate to view the optimization results.

For each analyte, the intensity of both solutions at each time interval is plotted as a function of cell parameter value. The composite line graph represents either the estimated detection limit calculated at each time interval, or the estimated background equivalent concentration calculated at each time interval, as desired.

- **Detection limit option:** The estimated detection limit is calculated at each time interval according to the equation:

$$DetectLimit = \frac{3 \cdot \sqrt{I_{blk}}}{I_{std} - I_{blk}} \cdot Conc_{std}$$

where:

I blk = the measured intensity for a blank solution, for example, deionized water or matrix blank.

I std = the measured intensity for a standard solution, for example, 1 ppb Iron.

Conc std = the concentration of the standard solution or spiked matrix blank.

Note: The unit of the detection limit is the same as that of the standard solution concentration.

- **Background equivalent concentration option:** The background equivalent concentration (BEC) is calculated at each time interval, according to the equation:

$$BEC = I_{blk} / (I_{std} - I_{blk}) \cdot Conc_{std}$$

where:

I blk = the measured intensity for a blank solution, for example, deionized water or matrix blank.

I std = the measured intensity for a standard solution, for example, 1 ppb Iron.

Conc std = the concentration of the standard solution or spiked matrix blank.



Preparing Reports

This section describes the use of the ELAN® Reporter™ function, which provides comprehensive, flexible reporting. Included in this section are details on using the reporting tool to set up a basic report, a description of advanced formatting options, and procedures for producing hardcopy reports or sending measurement data to a file for analysis in another program.

Topics in this section include:

- ▶ “About the Reporter™ Function” on page 169
- ▶ “Using Report Templates” on page 171

About the Reporter™ Function

The Reporter function allows you to create custom reporting options for your determinations. You can define a report with the exact content you need and in a style that best conveys the information content on the page. The editor employs a simple drag-and-drop system to help you create reports. The following are the basic components of a report options template:

- A report option template consists of a series of sections that are placed consecutively on the page or in the file
- Each report section consists of a series of fields that are structured within each section
- All the available determination data can be included in a report. You select the sections and fields that you want to include, then you adjust the default formats, including position on the page, field names and font style and size, according to your individual requirements

Report Windows

The software provides two windows to help you create informative and attractive reports:

- **Report Options:** Use this window to select the sections and fields that will comprise the content of your report, and to adjust the relative positions of each item on the page and the type style used to display the information.
- **Report View:** Use this window when customizing report appearance and for on-screen viewing of report output from a determination. This is a useful tool when designing a report template.

Summary Reports

Summary by Analyte and **Summary by Sample** reports capture the net value, SD, and %RSD for the intensities and concentrations of analytes measured during batch acquisition. The results can be sorted by analyte (*Summary by Analyte*) or by sample (*Summary by Sample*).

There are two ways to generate a summary report: in real time after a batch analysis or during the reprocessing of the data from a batch analysis.

Note: Summary Reports are only available for Quantitative Methods.

Summary Report After a Realtime Batch Analysis

Cross-tab summary reports provide a convenient format for reporting summarized sample ID and concentration data only. You can create a summary report with sample IDs down the left side of the page and the analytes across the top of the page or vice versa. This report format can be used when reprocessing data with the same method only. A cross-tab report displays a concise report of sample runs.

Summary Report After Reprocessing a Batch Analysis

The cross tab summary reports provide a convenient format for reporting summarized sample ID and concentration data only. This report format can be used only when reprocessing data with one method. If you select Reprocess with Original Conditions, the block of data that you highlight for reprocessing in the Dataset window may contain as many sample IDs as you wish, but these sample IDs must all have the same name in the Method column.

Intensity versus Time Reports

The software allows you to automatically generate intensity versus time reports. These reports are sent to file only, and are often used for the manipulation of transient signal data by third party software packages.

The software automatically generates a report output file name for your intensity versus time data by combining the Sample ID name with an .xls extension. The default output file location is the Report Output folder of your computer's elandata folder. The elandata folder location is specified during a new user setup. Although intensity versus time data is not printed by the reporter software, the output file name and the file path are included in other printed reports.

Using Report Templates

Use the Report Options window to design or modify a report template to create print or file output. Here you can specify both the content and appearance of your reports, including location and type. New report options files are linked to the type of method in memory when the file is created.

The software includes several default report templates. These templates describe how the data, reports, and file contents will be printed out. For example, the tuning.rop file provides a printout of the contents of the Tuning file.

Also provided are default templates for tuning, optimization, calibration and the five different method files (Quant, Isotope Method, Isotope Dilution, Data Only, and TotalQuant™ methods). The tuning.rop and optimization.rop templates are method independent, however, as soon as they are modified they will become method dependent.

Intensity vs. Time is a fixed, separated value (csv) format, used to export temporal value to a spreadsheet. The intensity units in the report will be in the units specified by the method.

Modifying the Appearance of Reports

To make report design fast and easy, the software identifies default location and type specifications for each item that you include in a report template. However, you may wish to change these defaults to make the report fit your requirements.

You can customize the following options using the Reporter:

- Report title page
- Headers and footers
- Row and column sizing and spacing
- Font types and styles
- Numerical formats
- Page breaks

Report Options Template Example

The top half of the screen shows the report sections selected to appear in this report. The bottom half of the screen shows the fields selected to appear in the highlighted report section—in this case, the Sample Information section.

The screenshot shows the 'Report Options' dialog box for a report template. The window title is 'Report Options - C:\Elandata\ReportOptions\Quant Comprehensive.rop[Read-Only][Modified]'. The dialog is divided into two main sections: 'Selected Sections' (top) and 'Selected Fields' (bottom). Each section has an 'Available' list on the left, a central control panel with 'Append ->', 'Insert ->', and 'Remove' buttons, and a 'Selected' list on the right.

Selected Sections Table:

	Available Sections	Selected Sections	Section Title	Column Offset	Row Offset	Font (*)	
1	Sample Information	1	Page Header	50	0	Arial\ 16\ B	
2	Replicates	2	Sample Information	Quantitative Analysis - C	200	0	Arial\ 16\ B
3	Mean Values	3	Summary	Summary	50	0	Arial\ 16\ B
4	Standard Deviations	4	Opt. File-Man. Adjust. S	Opt. File-Man. Adjust. S	50	0	Arial\ 16\ B
5	Relative Std. Dev.	5	Opt. File-Auto Lens Sec	Opt. File-Auto Lens Sec	50	0	Arial\ 16\ B
6	Summary	6	Page Footer		50	0	Arial\ 16\ B
7	Calibration	7					

Selected Fields Table:

	Available Fields	Selected Fields	Field Title	Column Offset	Row Offset	Format (*)	Font (*)	
1	Report Title	1	Sample ID	Sample ID:	50	0	Text	Arial\
2	Sample Date/Time	2	Sample Date/Time	Sample Date/Time:	50	0	Date	Arial\ :
3	Acquisition Date/Time&Zo	3	Sample Description	Sample Description:	50	0	Text	Arial\ :
4	Acquisition Date/Time-Sho	4	Solution Type	Solution Type:	50	0	Text	Arial\ :
5	Acquisition Date/Time&Zo	5	Blank File	Blank File:	50	0	Text	Arial\ :
6	Acquisition Date/Time-Int	6	Number of Replicates	Number of Replicates:	50	0	Numeric	Arial\ :
7	Acquisition Date/Time&Zo	7	Peak Processing Mode	Peak Processing Mode:	50	0	Text	Arial\ :
8	Sample ID	8	Signal Profile Processing	Signal Profile Processing	50	0	Text	Arial\ :
9	Batch ID							

Report View Example

In this example, the report contains a footer, header, and four main sections: Sample Information, Replicates, Mean Values, and Standard Deviations.

Header {	Plain Text Report Date/Time: Friday April 12, 2007 17:10:40
Sample Information section title {	Quantitative Analysis - Comprehensive Report
Selected fields in Sample Information section {	Sample ID: Sample 1 Sample Date/Time: Friday April 12, 2007 17:10:40 Sample Description: Solution Type: Sample Blank File: c:\elandata\dataset\apr_12\Blank 019 Number of Replicates: 6 Peak Processing Mode: Average Signal Profile Processing Mode: Average Dual Detector Mode: Dual Dead Time (ns): 65 Sample File: Method File: c:\elandata\Method\Daily.mth Dataset File: c:\elandata\dataset\apr_12\Claire.028 Tuning File: default.tun Optimization File: default.dac Calibration File: c:\elandata\System\apr_12.cal Calibration Type: External Calibration
Section title {	Replicates
Selected fields {	Repeat 1 Analyte Mass Meas. Intensity Net Intensity Concentration Sample Unit
	Mean Values Analyte Mass Meas. Intensity Net Intensity Concentration Sample Unit
	Standard Deviations Analyte Mass Meas. Intensity Net Intensity Concentration Sample Unit
Footer {	Footer Text Page 1

Exporting Report Data

Reports created using a Report Option template are also the basis for the data export facilities. Using the built-in export controls, you can easily create an ASCII file that can be imported into an outside software program for data analysis and reporting. The software provides the ability to include all the information contained in your printed report in either tab delimited or CSV (comma separated variable) formats. Three types of reports can be sent to a serial port: *Sample by Sample*, *Summary by Analyte*, and *Summary by Sample*.

When creating a data file from a report, the following additional options are available to you:

- **File Report Format:** Selects between tab delimited (*Use Delimiter*) or comma separated variable (*Use Separator*) file formats and to specify whether or not to include field titles in the report (*Include Titles*)
- **File Write:** Controls whether the measurement data from each series of measurements will be added to the bottom of the destination file (*Append*), whether the data will overwrite data that already exists in the destination file (*Overwrite*), or whether the data will be new for each sample (*New Per Sample*)
- **Use International Character Set:** Select to send international unicode characters to the file or serial port. When unchecked, ASCII characters are sent. Select this option to send non-ASCII characters, such as Japanese text.

Reported Shutdown Values

Shutdown values are indicated by the letter **S**. If an intensity or concentration is reported in brackets in the Report View window, it means that the interference correction (or elemental equation) was in shutdown. A value of 2e6 for pulse mode or 2e9 for analog mode was substituted into the equation. The resultant calculated intensity or concentration therefore reflects an estimated value for the isotope. This estimated value is denoted by the presence of brackets.

Report Options Controls

Use the following controls in a Report Options template to alter sections and fields:

- **Append:** Include new sections or fields in your report.
- **Insert:** Inserts a section or field in your report.
- **Remove:** Remove a section or field in your report.

Report Options for Sections

- **Available Sections:** Lists all the sections that are available for inclusion in your report.
- **Selected Sections:** This is a read-only field. Shows the sections that are currently selected. To select a section, click the section in the Available Sections column.
- **Section Title:** Automatically fills the Section Title entry; however, you can modify it.
- **Column Offset:** Indents from the left margin in hundredths of an inch. A column offset of 100 is equal to one inch.

- **Row Offset:** Spaces lines for the report in hundredths of an inch. A row offset of 100 is equal to one inch.
- **Font:** Specifies the style of typeface to be used for the section title. Right-click to display the fonts options.

Report Options for Fields

- **Available Fields:** Lists the fields that can be included in your report.
- **Selected Fields:** This is a read-only setting. Shows the fields that are currently selected. To select a field, click the field in the Available Fields column.
- **Field Title:** The software automatically fills the Field Title entry; however, you can modify it.
- **Column Offset:** Indents from the left margin in hundredths of an inch. A column offset of 100 is equal to one inch.
- **Row Offset:** Spaces lines for the report in hundredths of an inch. A row offset of 100 is equal to one inch.
- **Font:** Specifies the style of typeface to be used for the field. Right-click to display the font options.

Selected Fields for Isotope Ratio Methods

This section describes the fields that are available in the Report Options window when the Replicates, Mean Values and Standard Deviation sections are selected for an Isotope Ratio method.

Replicates Section fields

- **Repeat Title:** Indicates replicate number, that is, Replicate 1, Replicate2, and so forth.
- **Reference Mass:** The mass to which other masses of the same element in the method are compared (ratioed).
- **Analyte:** The symbol representing each analyte in the method.
- **Mass:** The mass of each isotope in the method.
- **Measured Intensity:** The intensity measured and corrected for deadtime and elemental equations.
- **Blank Intensity:** The measured intensity of the blank solution corrected for deadtime and elemental equations.
- **Net Intensity:** The blank corrected measured intensities, calculated as follows: Net Intensity = Measured Intensity - Blank Intensity.
- **Correction Factor:** The software automatically calculates a Ratio Correction Factor (RCF) from the results for the reference standard, as follows:

$$\text{RCF} = \frac{\text{Standard Measured Ratio (SMR)}}{\text{Standard Known Ratio}}$$

where:

$$\text{SMR} = \frac{\text{Net Intensity of Isotope in Standard}}{\text{Net Intensity of Reference Isotope in Standard}}$$

Standard Known Ratio is the user entry of the certified ratio for the Standard.

- Ratio Normalized:

$$\text{Ratio Normalized} = \frac{\text{(net intensity of the isotope/net intensity of ref. Isotope)}}{\text{Ratio Correction Factor}}$$

- **Ratio Fraction:**

$$\text{Ratio Fraction} = \frac{\text{Ratio Normalized}}{\text{Sum of all Normalized Ratios in Defined Isotope Group}}$$

Mean Values Section fields

- **Reference Mass:** The mass to which other masses of the same element in the method are compared (ratioed).
- **Analyte:** The symbol for each analyte in the method.
- **Mass:** The mass of each isotope in the method.
- **Measured Intensity Mean:** The arithmetic mean of the replicate measured intensity values.
- **Blank Intensity:** The arithmetic mean of the replicate measured intensity values for the blank solution.
- **Net Intensity Mean:** The arithmetic mean of the replicate net intensity values.
- **Correction Factor Mean:** The arithmetic mean of the replicate “correction factor” values.
- **Ratio Normalized Mean:** The arithmetic mean of the replicate “ratio normalized” values.
- **Ratio Fraction Mean:** The arithmetic mean of the replicate “ratio fraction” values.

Standard Deviation Section fields:

- **Reference Mass:** The mass to which other masses of the same element in the method are compared (ratio).
- **Analyte:** The symbol for each analyte in the method.
- **Mass:** The mass of each isotope in the method.
- **Measured Intensity Std. Dev.:** The standard deviation of the mean intensity of all replicates.
- **Blank Intensity Std. Dev.:** The standard deviation of the mean measured intensity of all replicates for the blank solution.
- **Net Intensity Std. Dev.:** The standard deviation of the mean net intensity of all replicates.

- **Correction Factor Std. Dev.:** The standard deviation of the mean correction factor of all replicates.
- **Ratio Normalized Std. Dev.:** The standard deviation of the “ratio normalized mean” of all replicates.
- **Ratio Fraction Std. Dev.:** The standard deviation of the “ratio fraction mean” of all replicates. The formula for Standard Deviation is as follows:

$$SD(x) = \sqrt{\left(\frac{\sum_{k=0}^{n-1} x_k^2}{n} - \left(\frac{\sum_{k=0}^{n-1} x_k}{n} \right)^2 \right) \left(\frac{n}{n-1} \right)}$$

Standard Deviation formula

where:

- ♦ **n** = the number of replicates for the sample
- ♦ **x** = I_i or N_i or C_i or R_i
- ♦ **li** = the instantiate for analyte i
- ♦ **C_i** = the ratio correction factor for analyte i
- ♦ **N_i** = the net intensity for analyte i (I_i - IO), blank intensity subtracted
- ♦ **IO** = the intensity of the blank
- ♦ **R_i** = the (calculated) corrected (isotope) ratio



Reprocessing Data

This section discusses the use of the data reprocessing tools and describes the typical circumstances under which reprocessing is performed. Reprocessing involves reanalyzing the raw acquired data using either the same or different processing parameters as those used when the data was initially acquired.

Topics in this section include:

- ▶ [“Working with Previously Acquired Data” on page 179](#)
- ▶ [“How a Dataset is Organized” on page 180](#)
- ▶ [“What Happens During Reprocessing” on page 181](#)
- ▶ [“Data and Parameter Considerations During Reprocessing” on page 181](#)
- ▶ [“Determining the Files Needed for Reprocessing” on page 182](#)
- ▶ [“Dataset and Reprocessing Software” on page 183](#)

Working with Previously Acquired Data

You can use the software to reprocess previously acquired analytical data, which can be useful in a number of circumstances:

- If you find, after a determination, that a calibration standard was measured incorrectly, or was made up to a different concentration than you entered in the method, you can reprocess the data using a modified calibration which excludes the standard or which contains the correct concentration entry in the method.
- If analytical results are adversely affected by unexpected interferences, you can modify the method parameters to include additional baseline correction points or modify the elemental equations to correct for the interferences, and then rerun the determination to obtain the effect on the resulting data.

- During method development, you can run one analysis, then alter the method parameters slightly and go through varied scenarios without rerunning the solution each time.
- When performing a determination on a sample for which you only have a limited quantity, you can run the determination once, then fine-tune the measurement without wasting the sample.

Use the Reprocess button in the Dataset window to generate a duplicate report or a new report using a different format. Select Use Original Conditions to generate a duplicate report. If you do not select Use Original Conditions, you may select whether to save the reprocessed results in a new data file (click the Save Reprocessed Data check box).

How a Dataset is Organized

A dataset file is composed of a series of individual data records. Each individual record consists of the raw data from each solution measured during a series of determinations, together with the following relevant information for specifying the conditions under which the data was acquired:

- Method
- Optimization
- Tuning
- Report options
- Calibration
- Configuration

The software stores the data for each sample solution as an individual data file, with the complete series of measurements in the dataset constituting a folder on the hard disk of your computer. If a scan is cancelled, the software saves partial data to a dataset file depending on the Number of Replicates and Readings per Replicate method parameters, and when the scan was cancelled.

For methods with only one replicate, the system saves all readings received up until the point of cancellation. The Readings per Replicate setting of the method saved to the dataset file with the raw data is truncated to match the actual number of readings.

For methods with multiple replicates, only the readings for completed replicates are saved in the dataset file. The Number of Replicates setting of the method saved to the dataset file is truncated to match the actual number of completed replicates.

The software creates the individual file names using the Sample ID entered on the Sample window. If no specific entry exists at acquisition time, the software describes each solution using a default name as follows:

Blank solutions:	BLANK.000, BLANK.001, and so forth
Standards:	STANDARD.001, STANDARD.002, and so forth, or EXTERNAL STANDARD.002 for TotalQuant™ methods
Samples:	SAMPLE.001, SAMPLE.002, and so forth

Use the Dataset window to view the contents of a dataset and reprocess the data contained within.

What Happens During Reprocessing

The software stores the results from each measurement in a dataset file. The raw data stored in this file can be reanalyzed using modified parameters in the same method or by using an entirely different method.

When you reprocess data, your results can be produced as a report in the same fashion as your original report. Reprocessing will use the reporting instructions contained in the method being used. Note that reprocessing does not alter the acquired data—it simply changes the results calculations performed. You can view the original results at any time using the Dataset window—select the Use Original Conditions check box, and then click the Reprocess button.

If you do not select the Use Original Conditions check box, you can then decide whether or not to save the reprocessed results in a new data file, using the Save Reprocessed Data check box.

You can perform data reprocessing in any of several ways:

- Reprocess with original method, optimization, tuning, report options, calibration, and configuration
- Reprocess the data using the same method, but using modified data processing parameters
- Reprocess the data using the same method, but using a different (stored) calibration
- Reprocess the data using a different method-include the standards during the reprocessing
- Reprocess the data using a different method-use a stored calibration and do not reprocess the standards
- Reprocess a TotalQuant™ determination using any of the above combinations and using a different response file
- Reprocess the data using a different dual detector calibration (that is, a different optimization file)

Data and Parameter Considerations During Reprocessing

Properly applied, reprocessing is used to investigate the effect of different data processing parameters on your raw data set, to evaluate the effects of modifications to your calibration, or to see the effects of applying a different calibration.

The reprocessing function is not intended to serve as a substitute for data acquisition under modified acquisition parameters. This means that during data reprocessing, a number of logical considerations should be taken into account in order for the reprocessed results to be of analytical significance.

The usefulness of reprocessed data depends primarily on the parameters under which you collected the original data. You are not allowed to reprocess where it would require the software to fabricate data from conditions, which are not measured. For example, you cannot reprocess data with a method that contains a different number of sweeps or dwell time than the method that was used to acquire the data initially.

Determining the Files Needed for Reprocessing

Depending on the protocol you intend to follow for reprocessing, different files are required. The following table summarizes the file requirements for a variety of commonly performed reprocessing procedures:

To reprocess data using:	The following files are needed:
the same method, but using modified data processing parameters	original method file
the same method, but using a different (stored) calibration	original method file; stored calibration file
a different method—include the standards during the reprocessing	new method file
a different method—use a stored calibration and do not reprocess the standards	new method file; stored calibration file
any of the above combinations for a TotalQuant™ determination plus using a different response file	appropriate files from above, plus the new response file

Dataset and Reprocessing Software

The Dataset window displays the results of a determination. It shows which samples have been run during a measurement and allows you to reprocess acquired data.

	Batch ID	Sample ID	Acquisition Date/Time	Method	Description	Read T
1	SmartTune - Nebu	Nebulizer Gas Flow	2006/11/29 10:54:11 AM	C:\Elandata\Method\Neb Gas C		Sample
2	SmartTune - Dual D	Dual Detector Calibr	2006/12/21 12:05:58 PM	Dual Detector Calibration.mth	Dual Cal. Blank	Sample
3	SmartTune - Dual D	Dual Detector Calibr	2006/12/21 12:05:59 PM	Dual Detector Calibration.mth	Dual Calibration	Sample
4	DRC Method Develc	w (M)	2006/12/21 12:06:17 PM	C:\Elandata\Method\Cell Gas O	w	Sample
5	DRC Method Develc	w (S)	2006/12/21 12:06:23 PM	C:\Elandata\Method\Cell Gas O	w	Sample
6	SmartTune - Dual D	Dual Detector Calibr	2006/12/21 2:40:53 PM	C:\Elandata\Method\Dual Dete	Dual Cal. Blank	Sample
7	SmartTune - Dual D	Dual Detector Calibr	2006/12/21 2:40:54 PM	C:\Elandata\Method\Dual Dete	Dual Calibration	Sample
8	DRC Method Develc	BloodStandard (M)	2006/12/21 2:41:15 PM	C:\Elandata\Method\Dual Dete	Blood -- Standard V	Sample
9	DRC Method Develc	BloodStandard (S)	2006/12/21 2:41:20 PM	C:\Elandata\Method\Dual Dete	Blood -- Standard V	Sample
10	SmartTune - Dual D	Dual Detector Calibr	2006/12/22 10:32:16 AM	C:\Elandata\Method\Dual Dete	Dual Cal. Blank	Sample
11	SmartTune - Dual D	Dual Detector Calibr	2006/12/22 10:32:17 AM	C:\Elandata\Method\Dual Dete	Dual Calibration	Sample
12	DRC Method Develc	Test (M)	2006/12/22 10:32:49 AM	C:\Elandata\Method\DRC Meth	Test	Sample
13	DRC Method Develc	Test (S)	2006/12/22 10:32:54 AM	C:\Elandata\Method\DRC Meth	Test	Sample

Dataset window

Colors Used in this Window

Colors used in the Dataset window indicate the following:

- **Black:** Completed analysis
- **Red:** User-interrupted analysis
- **Blue:** An analysis where autodilution has taken place
- **Green:** Data reprocessed using different conditions than those used at the time of data acquisition

Items in the Dataset Window

The Dataset window contains several controls and a dataset data table.

Note: In previous versions of the software (prior to ELAN 3.2), the dataset included only the method, optimization, and tuning files. If the dataset you are using was created in one of these early versions, only the method, optimization, and tuning files can be loaded from the dataset.

- **Reprocess:** Click to initiate a reprocessing sequence. Before clicking this button, decide whether or not you want to use original conditions in the reprocessing and either select or clear the Use Original Conditions check box. Also, decide whether or

not to save the reprocessed results in a new data file, and either select or clear the Save Reprocessed Data check box.

- **Use Original Conditions:** Used to select whether or not you want to reprocess data with the parameters specified during data acquisition. If this check box is selected when you click Reprocess, all original information is loaded into the workspace from the dataset. If this check box is cleared when you click Reprocess, the conditions specified by the files loaded in the workspace are used.
- **Save Reprocessed Data:** Used to specify whether or not you want to save the reprocessed data in a new data file. If the Use Original Conditions check box is selected, this check box is not available. If this check box is selected when you click Reprocess, a new data file is created for each reprocessed data file.
- **Summary Report: Summary:** Click to specify the summary report type and the destination to which it will be directed.
- **Load:** This option loads one of the following file types from the currently open dataset into the current workspace. Select the file you want to open in the dataset window from the drop-down list, and then click Load.
 - ♦ *Method:* Loads the method (.mth) file used when the data was acquired. This overwrites any current method settings, so save the current method if desired.
 - ♦ *Optimization:* Loads the optimization (.dac) file that was used when the data was acquired. If the dataset file is the result of an optimization, it would contain the resultant values from the optimization. Loading optimization from the dataset can ensure that the dual detector calibration used at the time of data acquisition is also used for reprocessing.
 - ♦ *Tuning:* Loads the tuning (.tun) file used when the data was acquired.
 - ♦ *Calibration:* Loads the calibration file used when the data was acquired. If you the calibration from a specific dataset file, you will load the calibration that includes all calibration standards up to and including that dataset file.
 - ♦ *RSP:* Loads the response (.rsp) file that was used when the data was acquired. When a TotalQuant method is loaded in the workspace, the Elan.rsp file from the current project folder is opened.
 - ♦ *Report Option:* Loads the report options (.rop) file that was used when the data was acquired.
 - ♦ *Configuration:* Loads the configuration parameters that were used when the data was acquired. If you select this option, the System Configuration From Dataset dialog box appears. To apply the displayed parameters in the current session, click Apply. Those settings are then available in the System Configuration dialog box.

Columns in the Dataset table

- **Batch ID:** Specifies the alphanumeric name used to identify the batch of samples. If no Batch ID was used, this field is empty.
- **Sample ID:** Lists the unique alphanumeric name used to identify each sample solution run. Because this is a required field, an entry will always appear in this column.
- **Acquisition Date/Time:** Specifies the exact month, day, year, and time at which the original data was acquired. If the data was acquired on a computer in the same time

zone and daylight savings time bias as where the time is being displayed, the local time is displayed. If the data was acquired in a different time zone than the one where the time is being displayed, the time zone name is also displayed. If the data was acquired using software V 2.4 or earlier, it does not contain time zone information, and the message *Time Zone Unavailable* is displayed. If the data was acquired with a computer and operating system set to a language other than English, the time zone is displayed in that language. The time and date are displayed in the format specified in the regional settings of Windows for the current user.

- **Method:** Lists the name of the method file that was used to acquire the data for the sample/standard/blank listed. The listing includes the complete pathname for the method file; for example, c:\elandata\method\pbtest.mth
- **Description:** Lists any notes or descriptive information entered in the Sample window at the time of determination.
- **Read Type (*):** Describes the original sample type designation for an individual measurement and permits the operator to re-designate the solution as a different type to permit analysis of the effect on a determination. To view the list of available read types, right-click in the appropriate cell of the data table. Select a sample type and click OK. The following options are available:
 - ◆ Blank
 - ◆ Sample
 - ◆ Quant External Standard
 - ◆ Quant Standard Addition
 - ◆ Unspiked
 - ◆ TotalQuant™ External Standard
 - ◆ TotalQuant™ Sample Addition
 - ◆ Isotope Ratio Standard
 - ◆ Isotope Dilution Standard
 - ◆ QC Standard
 - ◆ QC Spike
 - ◆ QC Dilution
 - ◆ QC Duplicate
 - ◆ QC Reagent Blank
 - ◆ QC Duplicate Spike

Selection of the Quant External Standard or Quant Standard Addition option includes arrows that are used to designate which standard number the solution should be used as, because more than one standard may have been used to construct the calibration.

- **Sample File Name:** Lists the name assigned to the individual data record (the individual sample, standard, or blank solution) within the dataset. The file name is created by the software, using the Sample ID from the Sample window when the data was acquired. If no entry was made at acquisition time, the system describes the solution using a default name:

Blank solutions:	BLANK.000, BLANK.001, and so forth
Standards:	STANDARD.001, STANDARD.002, and so forth, or EXTERNAL STANDARD.002 for TotalQuant™ methods
Samples:	SAMPLE.001, SAMPLE.002, and so forth

- **Acquisition Type:** Specifies the instrument configuration used during the data acquisition. The software automatically enters a description for *Dual Calibration Blank*, *Dual Calibration*, and the *AutoLens™* function.
- **Initial Sample Quantity (mg):** Specifies the weight of the sample before dissolution. You must also enter a value for the Sample Prep Volume.
- **Sample Prep Volume (mL):** Lists the volume in which the sample weight has been dissolved. This field will be blank if no entry was made in the Sample window during the determination.
- **Aliquot Volume (mL):** Lists the volume of an aliquot, when a small amount of the sample (aliquot) is taken and diluted to a final volume. This field will be blank if no entry was made in the Sample window during the determination.
- **Diluted to Volume (mL):** Lists the total volume in which an aliquot is diluted when a small amount of the sample (aliquot) is taken and diluted to a final volume. This box will be blank if no entry was made in the Sample window during the determination.
- **Solids Ratio:** Specifies the correction factor to use if you want the software to convert dry sample weight to the wet sample weight. This value must be entered as a decimal fraction, not as a percentage; for example, for a ratio of 1:2, enter 0.5, not 50%. This box will be blank if no entry was made in the Sample window during the determination.
- **Cumulative Autodilution Factor:** This column keeps track of the total autodilution. For example, if a sample has been diluted twice at an autodilution factor of 10 for each, the cumulative autodilution factor is $10 \times 10 = 100$.
- **Technique:** Specifies the analytical technique which was used for the determination (*Quantitative Analysis*, *Isotope Dilution*, *Isotope Ratio*, *Data Only* or *TotalQuant™ method*).

Instrument & Device Control

This section describes the Instrument window, which includes tools for monitoring the instrument performance, turning the system on and off, and for system diagnostics and fault determination. This section also covers use of the Device window which permits external control of sampling devices such as the peristaltic pump, autosampler, HGA-600MS, and FIAS-400MS™.

Topics in this section include:

- ▶ “Monitoring Instrument Performance” on page 187
- ▶ “Monitoring External Devices” on page 195

Monitoring Instrument Performance

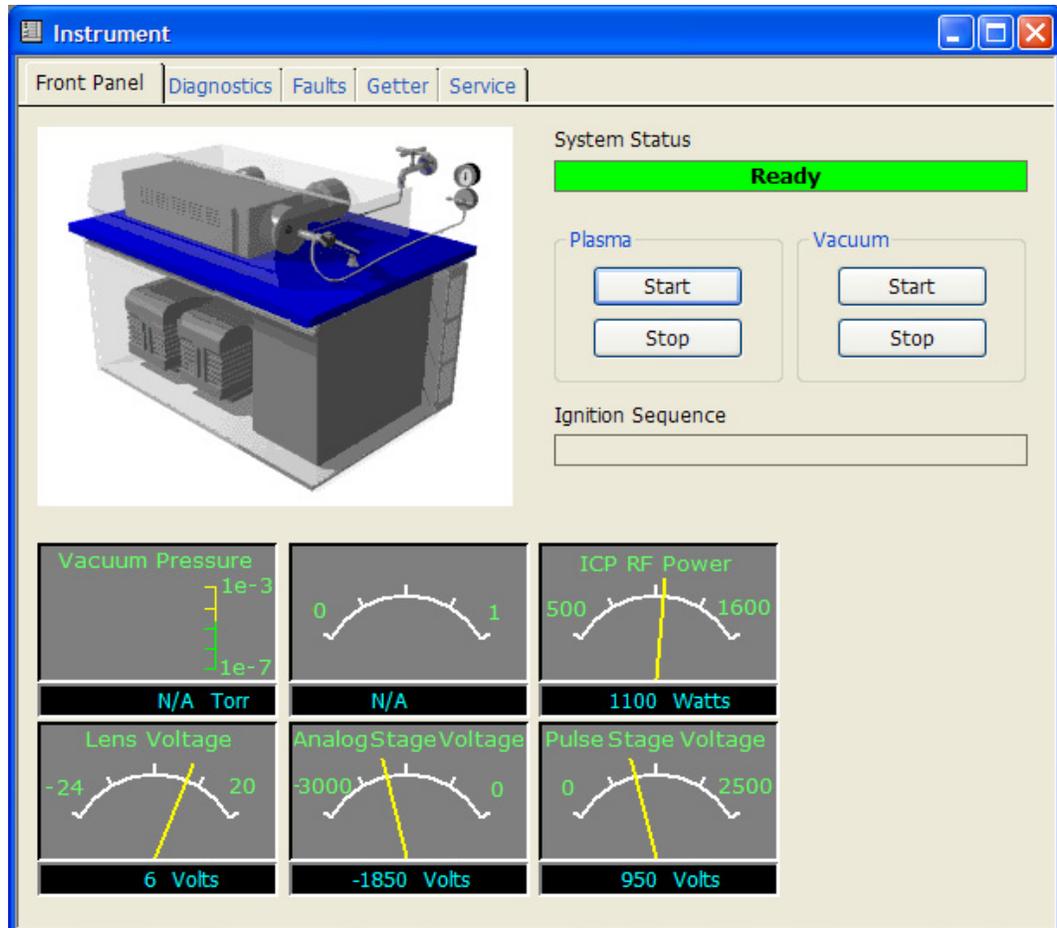
Use the Instrument window to monitor spectrometer performance, to start or stop the system, and to perform instrument diagnostics. Here, the software maintains an automated system of diagnostics monitoring more than 70 test points to check all vital signs of the instrument. This includes a three-dimensional instrument schematic that displays the system status graphically, in addition to a numeric display of operating parameters. The Instrument window contains the following tabs:

- **Front Panel:** Manually controls vacuum and plasma start/stop, to graphically display instrument status, and to display current set points for important instrument hardware parameters.
- **Diagnostics:** Displays the active status and operating conditions for the main instrument hardware subsystems, including the cooling, vacuum, gas and plasma systems.
- **Faults:** Displays current fault messages or to review the faults log maintained by the software.

- **Getter:** (*DRC™ Series only.*) Displays the active status of the getter regeneration and the dynamic reaction cell gate. Enables and disables regeneration.
- **Service:** Displays instrument service controls and messages. This tab is password-protected to restrict access to authorized service personnel or system administrators.

Front Panel Tab

Use the Front Panel tab to view current instrument status, to manually turn the vacuum and plasma systems on or off, to view running vacuum pressure, and to view the set points for the nebulizer flow, ICP power, analog and pulse detector voltages, and lens voltage.



Instrument window Front Panel tab

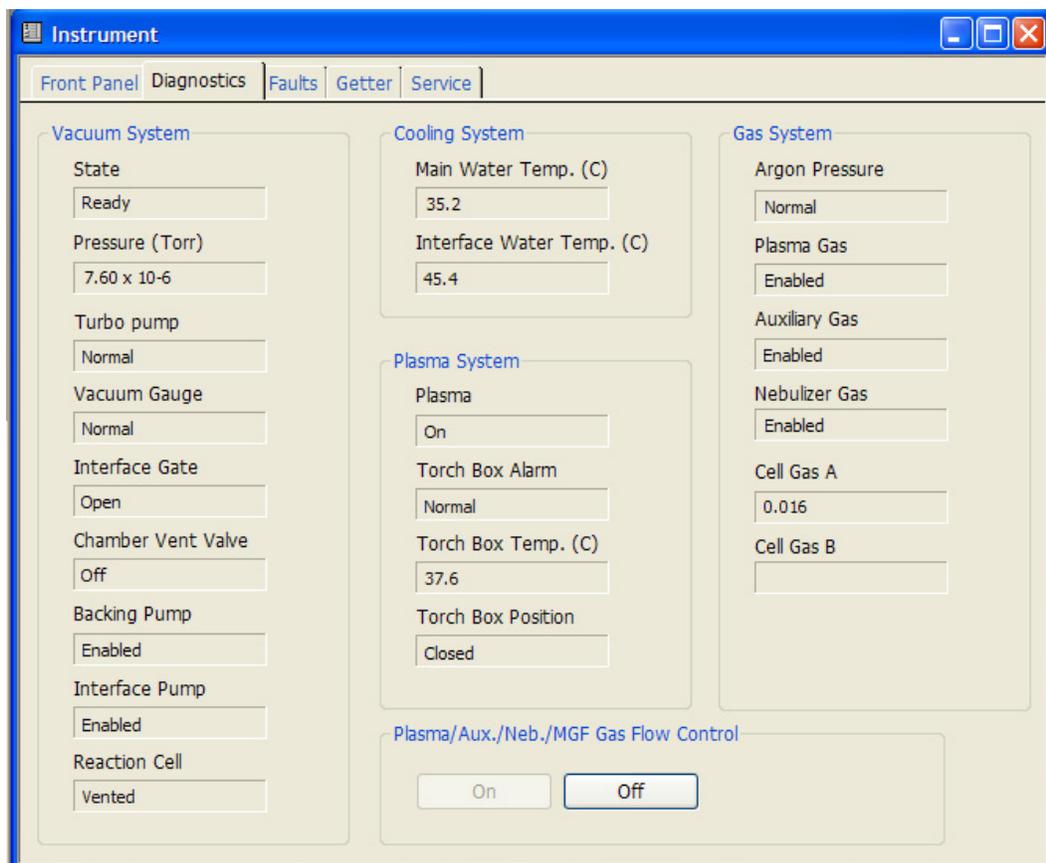
Items on the Front Panel Tab

This tab includes the three-dimensional graphic display of instrument status. It displays a visual representation of the instrument, with major subsystems identified.

- The colors displayed on the instrument graphic indicate the instruments operational status.
 - ♦ **Green:** When the systems are operating properly they are depicted in green
 - ♦ **Yellow:** This indicates that the subsystem is operating but has not reached a ready condition. For example, the vacuum system is yellow when it is pumping down but has not yet reached the running pressure
 - ♦ **Red:** This indicates a fault in the system that is identified. Click the Faults tab to view the error message
- The Front Panel tab also includes a set of indicators which display the following:
 - ♦ Running pressure for the vacuum system
 - ♦ ICP power setpoint
 - ♦ Nebulizer flow setpoint
 - ♦ Lens voltage setpoint
 - ♦ Analog-stage detector setpoint
 - ♦ Pulse-stage detector setpoint
- **System Status:** This read-only box indicates system status. This box must be **green** and read *Ready* before the plasma can be ignited. When a fault condition exists, this box appears **red** and reads *Not Ready* or *Communication Error*. If a communication error occurs, check the IEEE cable connection between the instrument and the computer.
- **Plasma Start/Stop:** Use these buttons to manually start or stop the plasma system. The System Status indicator must be **green** and read *Ready* before you can click Plasma Start. When you click Plasma Start, the Ignition Sequence indicator displays the status of the startup sequence. To shut down the plasma, click Plasma Stop.
- **Vacuum Start/Stop:** Used to manually start the vacuum system to perform measurements or to shut down the vacuum after all determinations are completed. Generally, the vacuum system should be left on unless you expect to not use the instrument for a period of three days or longer. When you shut down the vacuum, the system will take significantly longer to return to the running pressure the next time you want to use the instrument. To start the vacuum, click the Vacuum Start button. To shut down the vacuum, click the Vacuum Stop button.
- **Ignition Sequence:** This displays the status of the startup sequence after you click Plasma Start. The startup takes 90 seconds to complete; this indicator provides continuous feedback during the startup process.

Diagnostics Tab

Use the Diagnostics tab to view the status and operating conditions for checkpoints in the cooling, vacuum, gas, and plasma systems.



Instrument window Diagnostics tab

Items on the Diagnostics tab

All components of the instrument subsystem are monitored on this tab, and their present status is continually updated.

VACUUM SYSTEM GROUP

Contains the current information for the following parameters. Note that any changes in the vacuum system will be apparent because the software updates the information continuously.

- **State:**
 - ♦ *Off* indicates that the vacuum system is off
 - ♦ *Pumping Down* indicates that the vacuum system is pumping down
 - ♦ *Ready* indicates that the vacuum system is ready
 - ♦ *Venting* indicates that the vacuum system has just turned off and that pressure is increasing to atmosphere
- **Pressure:** Indicates the vacuum of the quadrupole chamber in torr. The pressure must fall below the recommended operating pressure before the vacuum state will indicate

that it is ready. A status of **N/A** (not available) indicates that the vacuum gauge is not on.

- **Turbo:** Indicates the status of the turbo pump that pumps down the quadrupole region and interface region of the vacuum chamber. The status shown is that the pump is either Off, Accelerating or at Normal Speed. (ELAN DRC II/DRC-e and ELAN 9000 instruments only.)
- **Analyzer Turbo:** Indicates the status of the smaller rear turbo pump that pumps down the quadrupole region of the vacuum chamber. The status shown is that the pump is either Off, Accelerating or at Normal Speed. (ELAN 6000/6100/DRC/DRC^{plus} instruments only.)
- **Ion Optics Turbo:** Indicates the status of the larger front turbo pump that pumps down the ion optic region of the vacuum chamber. The status shown is that the pump is either Off, Accelerating or at Normal Speed. (ELAN 6000/6100/DRC/DRC^{plus} instruments only.)
- **Vacuum Gauge:** Indicates the status of this gauge. As the system is pumping down the gauge is Off. The gauge will indicate a normal status when the system is at the proper pressure. It is normal for the gauge to be disabled (fault) when either turbo pump is Off or Accelerating.
- **Interface gate:** Indicates the status of this gate valve. When the vacuum chamber is sealed the status of this gate is Closed. This gate is Open when the vacuum chamber is open. The gate valve will open automatically after ICP ignition has occurred. When the ICP goes out, the gate valve will automatically close.
- **Vent valve:** Indicates the status of the valve used to backfill the vacuum chamber with argon. This valve is usually only Open (active) when the vacuum system has been turned off.
- **Backing pump:** This vacuum chamber roughing pump is the backing pump for both turbomolecular pumps. A status of Enabled means that this backing pump and the turbomolecular pumps are operating simultaneously. A status of Disabled means that this backing pump and the turbomolecular pumps are not operating simultaneously.
- **Interface pump:** This is the roughing pump for the interface region. This pump will indicate a status of Enabled when working properly or the status will be Disabled if the pump is not working.
- **Reaction cell:** *DRC Series instruments only.* Indicates whether the reaction cell gate is Open or Closed. The gate must be Open to operate in DRC mode.

COOLING SYSTEM GROUP

Contains the current information for the following parameters. Note that any changes in the cooling system will be apparent because the information on this tab is continuously updated.

- **Water flow state:** Indicates if the coolant flow is through the turbo pump and interface area or just through the turbo pump (available on 6000, 6100, 6100 DRC, and 6100 DRCPlus instruments only).
- **Main water temperature:** Coolant temperature should not be higher than 50°C.
- **Interface water temperature:** Coolant temperature should not be higher than 60°C.

PLASMA/AUX/NEB/MGF GAS FLOW CONTROL

DRC II/DRC-e series instruments only.

- **On button:** Turns on the gas flows for testing purposes when the plasma is not ignited. If you click the On button when the plasma is ignited, a warning message appears.
- **Off button:** Turns off the gas flows and returns gas flow control back to the instrument firmware.

Note: The On and Off buttons appear on the ELAN 6000/6100/9000 interface only if the optional multi-channel mass flow controller kit is installed.

- **Set DC Offset button:** Not available for all instruments. Allows you to set the DC Offset for the Internal MFC only while in Standard mode. This sets the nebulizer gas flow to an optimum value.

PLASMA SYSTEM GROUP

Contains the current information for the following parameters. Note that any changes in the plasma system will be apparent because the information on this tab is continuously updated.

- **Plasma:** Indicates that the plasma system is On or Off.
- **Torch box alarm:** Displays the status of the torch box.
- **Torch box temperature:** A status of Normal or Fault and the actual temperature is displayed for the torch box temperature. A status of Normal appears if the torch box temperature is below 70°C. If the torch box temperature is above 70°C, a status of Fault appears.
- **Torch box position:** Indicates the position of the torch box. If the vacuum chamber has been moved to the left, the torch box position status will be displayed as Open. If the vacuum chamber is all the way to the right, the torch box position status displays as Closed.

GAS SYSTEM GROUP

Contains the current information for the following parameters. Note that any changes in the gas system will be apparent because the information on this tab is continuously updated.

- **Argon pressure:** A normal status indicates that the regulated supply is operating at the recommended pressure. For the correct pressure setting, refer to your *Hardware Guide*. Pressure below 315 kPa (45 psi) will result in a fault status. The instrument will not pump down if the argon pressure is below 315 kPa (45 psi). If the vacuum is below 2.5×10^{-5} torr when the argon pressure falls below 315 kPa (45 psi), the vacuum pumps will not be interrupted.
- **Plasma gas:** Enabled indicates that gas is able to flow through the plasma line. Disabled indicates that gas is not able to flow through the plasma line.
- **Auxiliary gas:** Enabled indicates that gas is able to flow through the auxiliary line. Disabled indicates that gas is not able to flow through the auxiliary line.
- **Nebulizer gas:** Enabled indicates that gas is able to flow through the nebulizer line. Disabled indicates that gas is not able to flow through the nebulizer line.

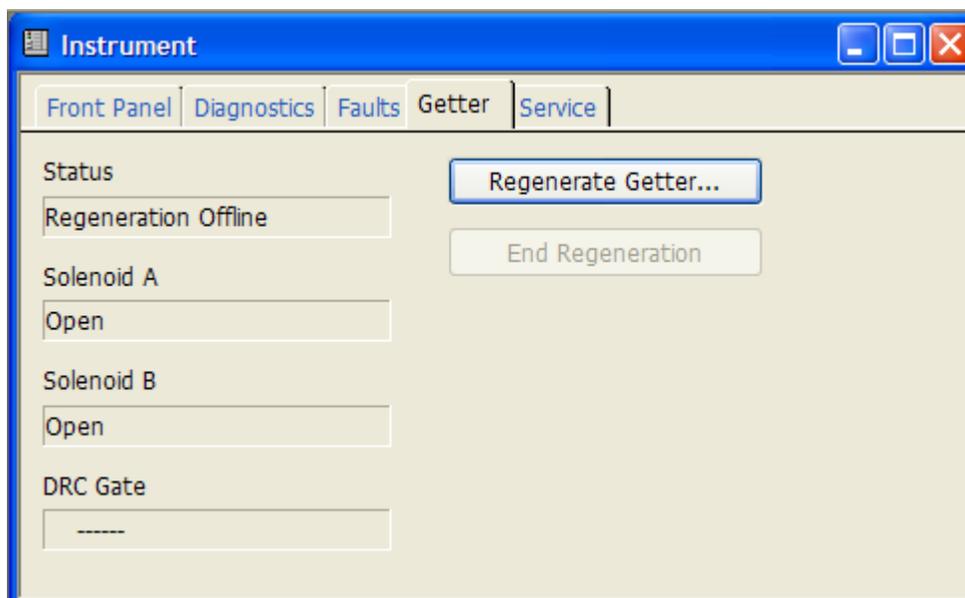
- **Makeup gas:** *Available on DRC II/DRC-e instruments only.* This parameter is only available if a Makeup Gas kit has been installed. It displays the flow of Makeup gas through the line.
- **Oxygen Gas:** *Available on DRC II/DRC-e instruments only.* This parameter is only available if the Oxygen Gas kit has been installed. It displays the flow of Oxygen gas through the line.
- **Cell Gas A:** *Available on DRC II/DRC-e instruments only.* Displays the flow of Cell Gas A through the line.
- **Cell Gas B:** *Available on DRC II/DRC-e instruments only.* Displays the flow of Cell Gas B through the line.

Faults Tab

Use the Faults tab to view current fault messages and the instrument's fault history log. The area of the instrument that has the fault condition is indicated in red on the three-dimensional display on the Front Panel tab. All fault conditions that have occurred since the instrument was installed are recorded in the Faults History. The Faults History assists you in troubleshooting instrument problems.

Getter Tab

DRC Series instruments only. The getter in the DRC gas assembly must be regenerated and cleaned regularly to purge it of impurities. Use the Getter tab to enable and disable getter regeneration, and to view the status of the regeneration and the DRC gate.



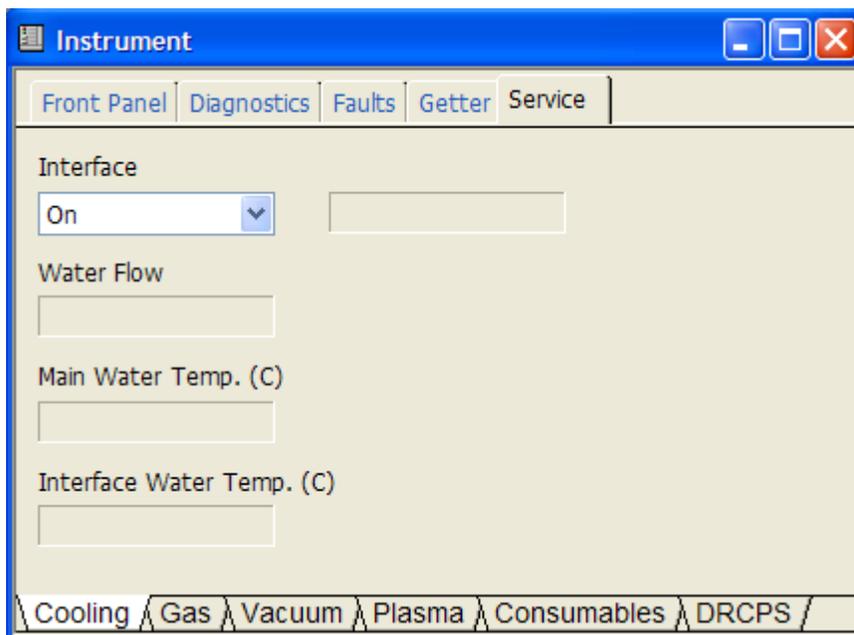
Instrument window Getter tab

Items on the Getter tab

- **Status:** Displays the status of the getter regeneration process, for example Getter Offline or Getter Regenerating.
- **Solenoid A/ Solenoid B:** Displays the status of the solenoids (Open or Closed). The number of solenoids (1 or 2) is dependent on the current configuration.
- **DRC Gate:** Displays the status of the dynamic reaction cell gate (Open or Closed). The DRC gate must be Open during getter regeneration.
- **Regenerate Getter:** Initiates regeneration of the getter. Analysis using DRC mode is not possible during getter regeneration. You are required to connect a source of low pressure inert gas to the channel connected to the getter to begin regeneration.
- **End Regeneration:** Quits getter regeneration.

Service Tab

The service functions are password-protected and available to authorized service personnel only.

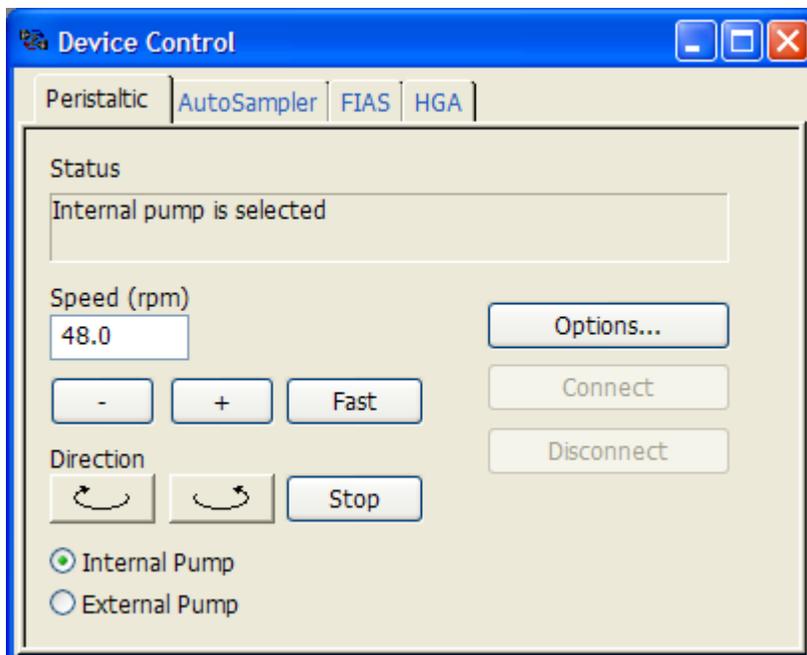


Service window

Monitoring External Devices

During both method development and routine operation, it is periodically necessary to manually control an external sampling device. For example, you may want to test an individual step in an HGA or FIAS™ program to determine if it is correct, to set the peristaltic pump to a high pump speed during a manual analysis to wash out the tubing. The Device window lets you perform these tasks quickly and easily.

Use the Device window to control externally attached sampling devices, including peristaltic pumps, autosamplers, *Heated Graphite Atomization* (HGA) systems, and *Flow Injection* (FIAS™) delivery systems.



Device Control window

Device Control Window Controls

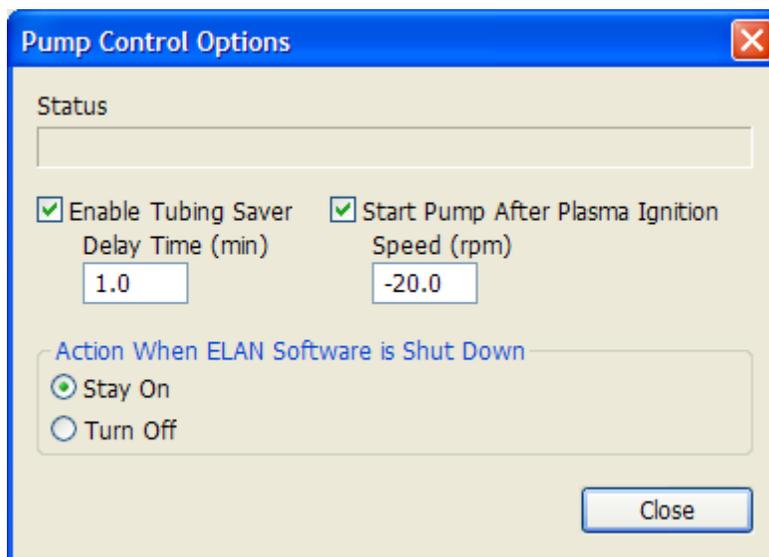
At the top of the Device Control window are three tabs; one for the peristaltic pump, and one for each of the external sampling systems available—HGA or FIAS device. These tabs control communications between these devices and the mass spectrometer.

Peristaltic Tab

Use this tab to control the integrated peristaltic pump (ELAN DRC II, DRC-e, and ELAN 9000 instruments only), and any external peristaltic pumps connected to your instrument.

- **Status:** Indicates the status of pump communications, speed, and the direction of rotation.
- **Speed Controls:** Type to set the pump speed. You can increase (+ button) or decrease (- button) the speed, or type a numeric speed between -48 and 48 in rpm. Click **Fast** to use full speed.
- **Direction:** Click to set the direction of pump rotation—clockwise or counter-clockwise. Click **Stop** to stop the pump rotation.

- **Pump Type:** To indicate which pump the instrument should communicate with, select *Internal Pump* or *External Pump*. If you select *Internal Pump*, the Options button is enabled. Click **Options** to access the Pump Control Options dialog box:

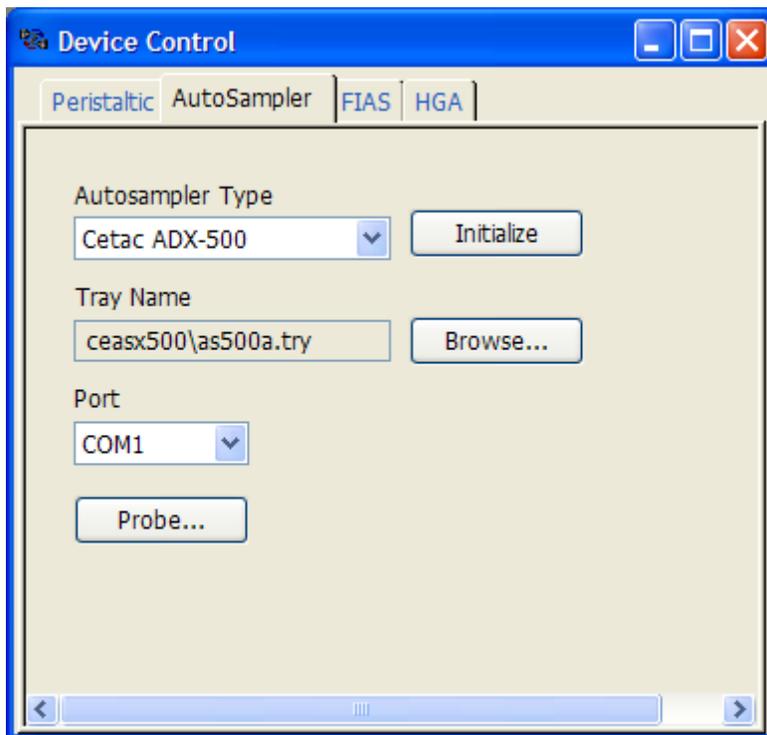


Pump Control Options dialog box

- **Internal Pump Control Options:** With *Internal Pump* selected, click *Options* to access the following controls:
 - ♦ **Status:** This box displays a change in any of the following options.
 - ♦ **Enable Tubing Saver:** To enable the tubing saver option, enable this box and type number of minutes the instrument should wait after the plasma is shut down before activating the tubing saver. The tubing saver feature extends the life of the peristaltic pump tubing by operating the pump at a low speed in alternating clockwise and counterclockwise rotations when the plasma is not on.
 - ♦ **Start pump after plasma ignition:** Enable this check box and type the speed in rpm to turn on the peristaltic pump automatically when the plasma is ignited. The pump goes to the selected speed when the nebulizer gas turns on following plasma ignition.
 - ♦ **Stay On (Action when ELAN software is shut down):** Enable to keep the peristaltic pump running when the software is shut down.
 - ♦ **Turn Off (Action when ELAN software is shut down):** Enable to turn the peristaltic pump off when the software is shut down.
- **Connect:** Click to establish communication between the external pump and the software. When the pump is connected, a message appears in the Status box.
- **Disconnect:** Click to end communication between the external pump and the software.

Autosampler Tab

Use this tab to select the type of autosampler used, the communications port, and the autosampler tray



Autosampler tab

Items on the Autosampler tab

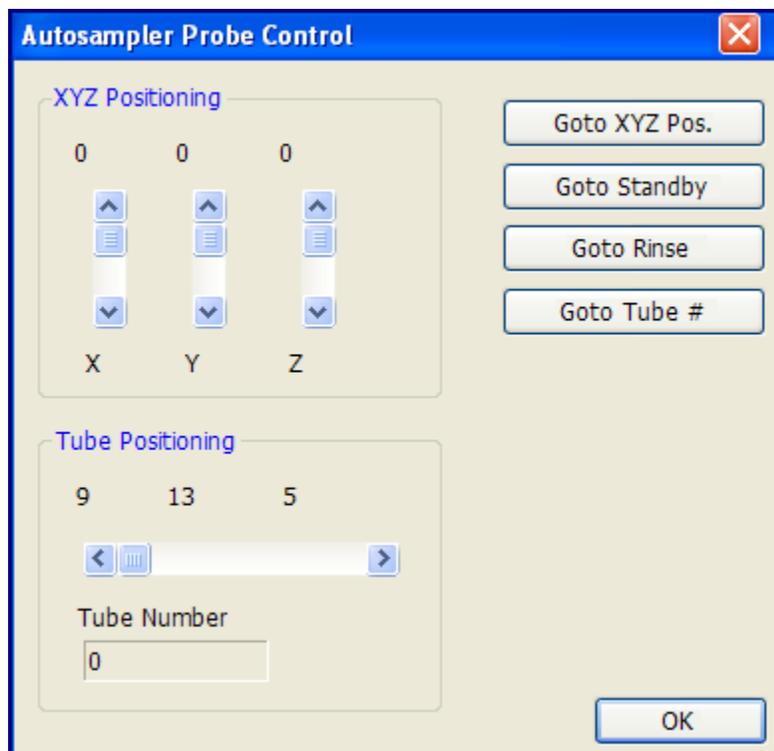
- **Autosampler Type:** In the Autosampler Type drop-down list, select the type of autosampler you are using. If the ADX-500 Auto Diluter is selected, four additional controls become available:
 - ♦ **Dil. Factor:** Enter a dilution factor from 2 to 100, as required. The default dilution factor is 10. A dilution factor of n will lower the measured intensity by a factor of n .
 - ♦ **Dil. To Vol:** Specify the volume, from 2mL to 50 mL, of the diluted samples the autodiluter will create. The default volume is 10mL.
 - ♦ **1st Dil. Pos.:** Specify the position of the first diluted sample to be created. Successive tubes are numbered accordingly.
 - ♦ **Probe Purge Pos.:** This is used when the software is initializing the autodiluter. In order to accurately measure the volumes of liquid involved in each dilution, the dilution probe and associated tubing must be full of diluent before any dilutions are done. To accomplish this, 10 mL of diluent are pumped into the dilution probe as part of the initialization. To contain any excess diluent you can specify the position of the large tube at the back right.
- **Initialize:** Click to begin communication with the autosampler.
- **Tray Name:** Click **Browse** to select the desired Tray Name. To create custom tray files for the Gilson autosampler, click Create and assemble a custom tray from the

standard rack files listed. (The tray files specific to each Cetac autosampler reside in their own autosampler data folder.)

- **Port:** In the Port drop-down list, select the communications port to be used.
- **Probe:** Click to access the Autosampler Probe Control dialog box. Here you can manually control the autosampler probe, or create custom tray files.

Autosampler Probe Control Dialog Box

Use this dialog box to manually control the autosampler probe. It is also useful when you are creating custom tray files.



Autosampler Probe Control dialog box

Items on the Autosampler Probe Control dialog box

- **XYZ Positioning:** Select the autosampler location according to the X-, Y-, and Z-coordinates. Then click **Goto XYZ Pos.** This is most useful when creating a custom tray file.
- **Goto Standby:** Changes the probe or loads a new tray.
- **Goto Rinse:** Moves the autosampler probe to the Wash solution.
- **Goto Tube #:** Use the Tube Positioning scroll bar to select the X-, Y-, and Z-coordinates (from the tray file) for the tube location. The corresponding tube number appears below the scroll bar. Then click **Goto Tube #**.

FIAS™ Tab

Use this tab to establish communication with and manually run the FIAS program without making measurements. Note that these controls cannot execute a Read command, even if the FIAS step contains the Read.

- **Status:** Indicates the status of communication and the current step in the FIAS program.
- **Reference A/S (Auto Sampler) Location:** Displays an autosampler location. This location is used as the Reference Location for blank or relative autosampler location entries in the FIAS tab. If a location is not entered prior to selecting *Run Current Step/Program*, an error message is displayed.
- **Initialize:** Initializes communication with the FIAS device. A message appears in the Status box.
- **Run Current Step:** Runs the step. The software performs the step where the cursor is located. There must be an entry in the Reference A/S Location box to run this step.
- **Run Current Program:** Performs the FIAS program in the active method. This will not execute a Read command. There must be an entry in the Reference A/S Location box to run this program.

HGA Tab

Use this tab to establish communications with and manually run the HGA program without making measurements. Note that these controls cannot execute a Read command, even if the HGA step contains the Read.

- **Status:** Displays the status of the HGA. Read-only.
- **Initialize:** Initializes communication with the HGA. A message appears in the Status box.
- **Run Current Step:** Runs the step you click on the HGA tab of the Method window, then click this button. The software performs the step where the cursor is located. There must be an entry in the Reference A/S Location to run this step.
- **Run Current Program:** Performs the HGA program in the active method. This will not execute a Read command. There must be an entry in the Reference A/S Location to run this program.
- **Standby/Home:** Puts the AS-60 in Standby mode and releases control of the pipetting arm. This feature is used to align the sampling capillary tip after initialization. Click Home when alignment is complete to restore automated control of the pipetting arm.
- **Calibrate:** Performs a temperature calibration of the optical sensor for Max Power and Fast Ramp heating modes. If the Furnace program does not use one of these heating modes, no condition will be performed.
- **Tube Number/Go:** Specifies the tube number that the autosampler will go to. Select Wash to manually wash the sampling capillary tip.



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