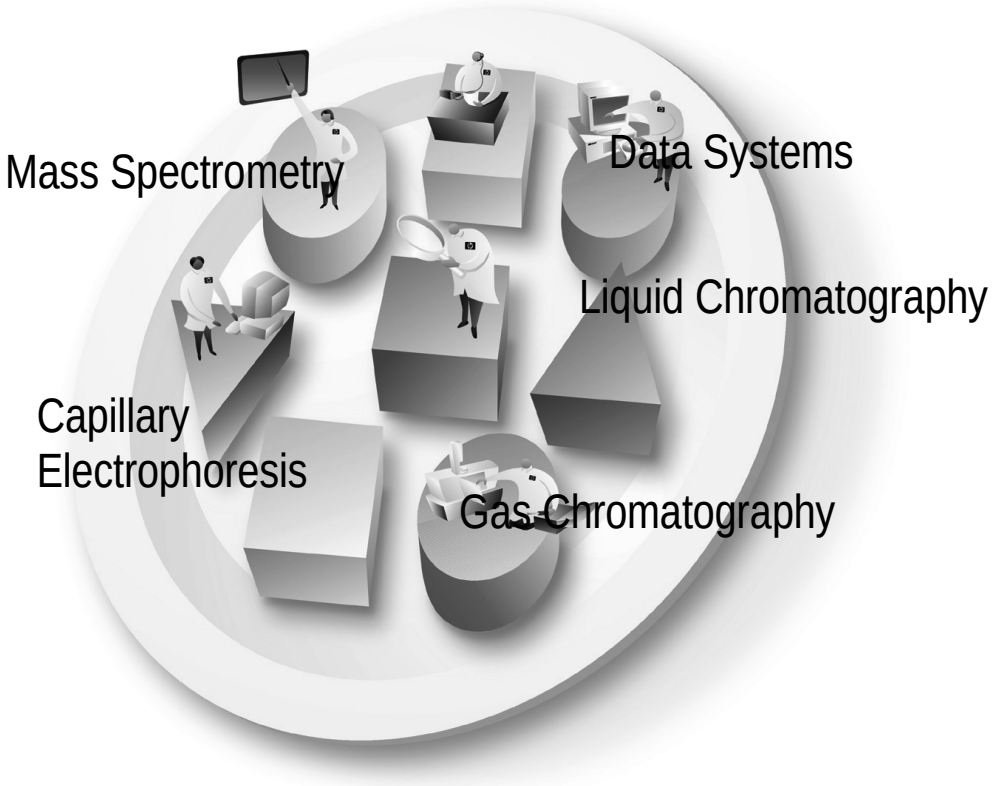
Agilent Technologies
Innovating the HP Way

Agilent 7500
Inductively Coupled Plasma
Mass Spectrometry

Course Number H8974A
ChemStation Revision 01.XX
NT Operating System

Student Manual
Revision 1



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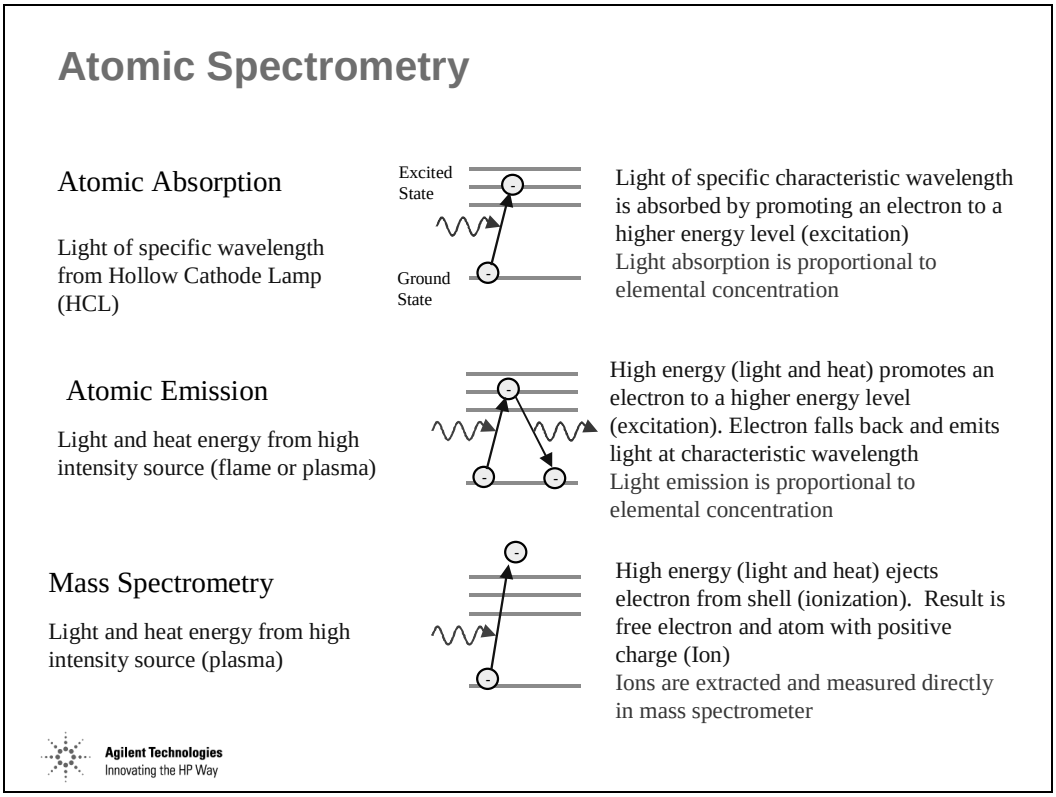
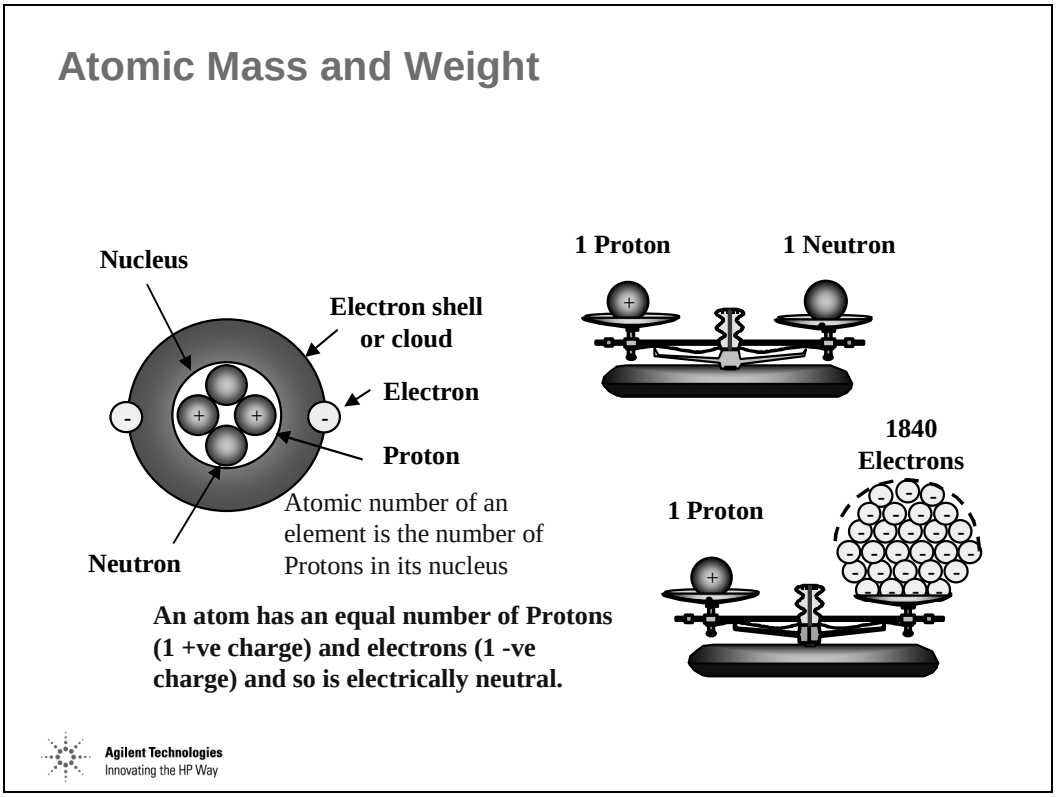


Figure 1

Atomic Mass and Weight



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Isotopes and Isobars

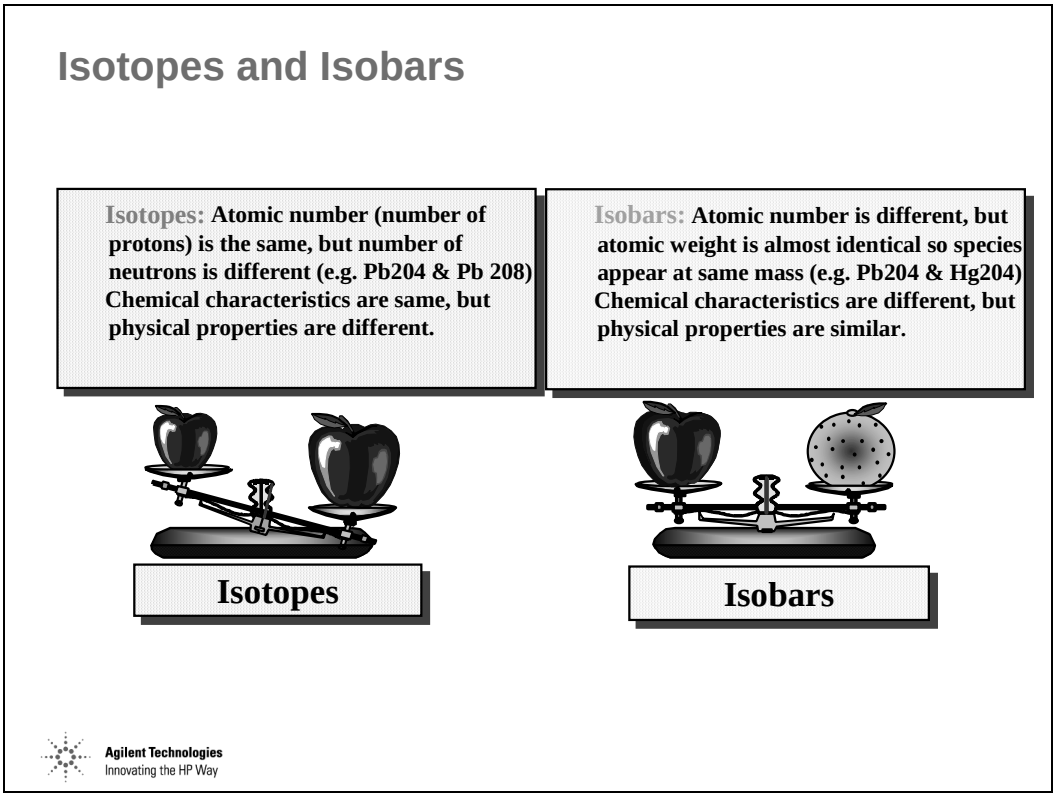
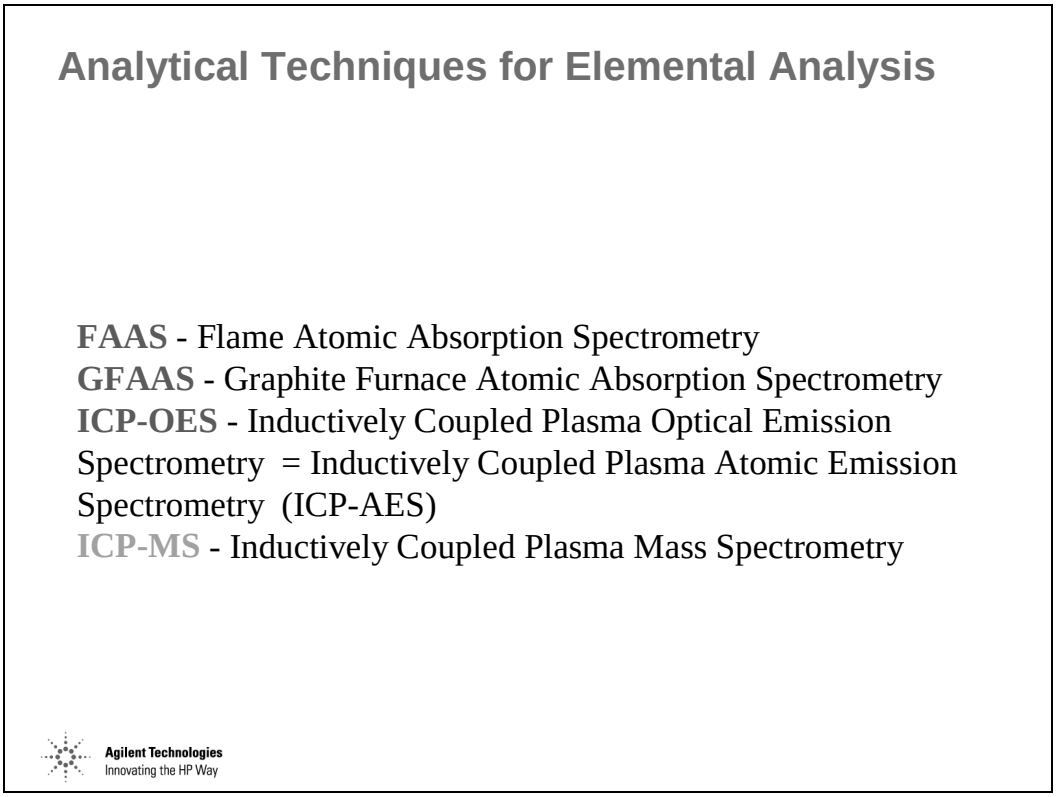


Figure 3

Analytical Techniques for Elemental Analysis



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Elemental Analysis: FAAS

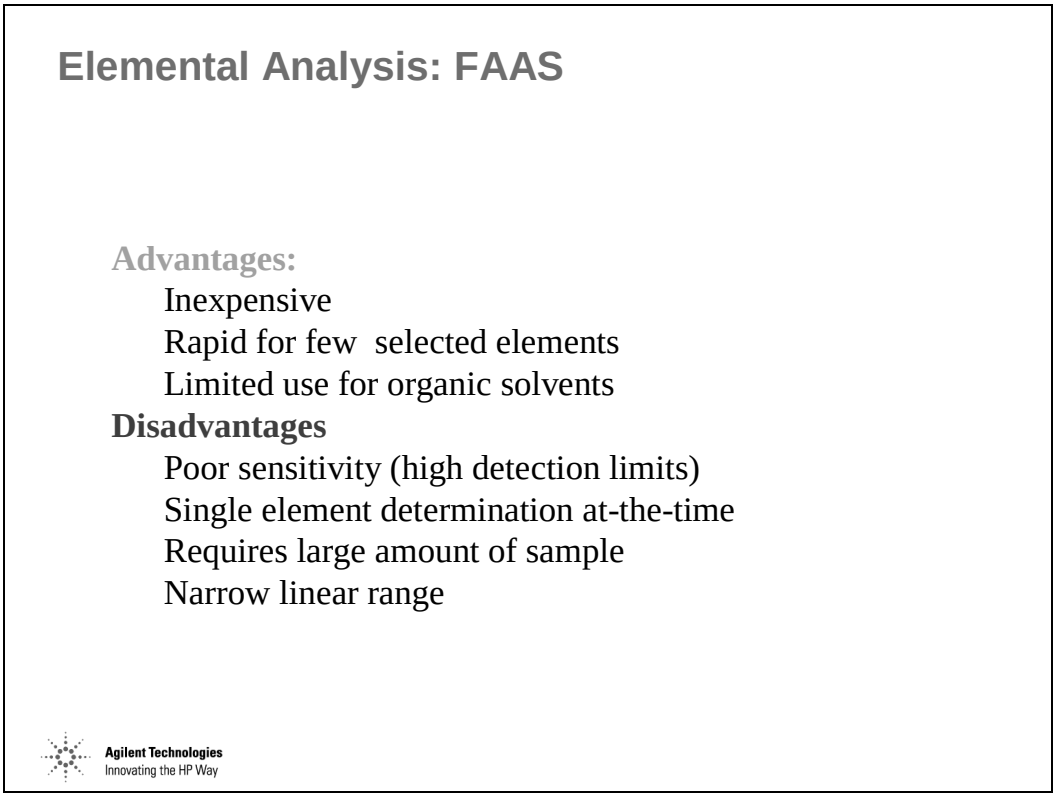


Figure 5

Elemental Analysis: GFAAS

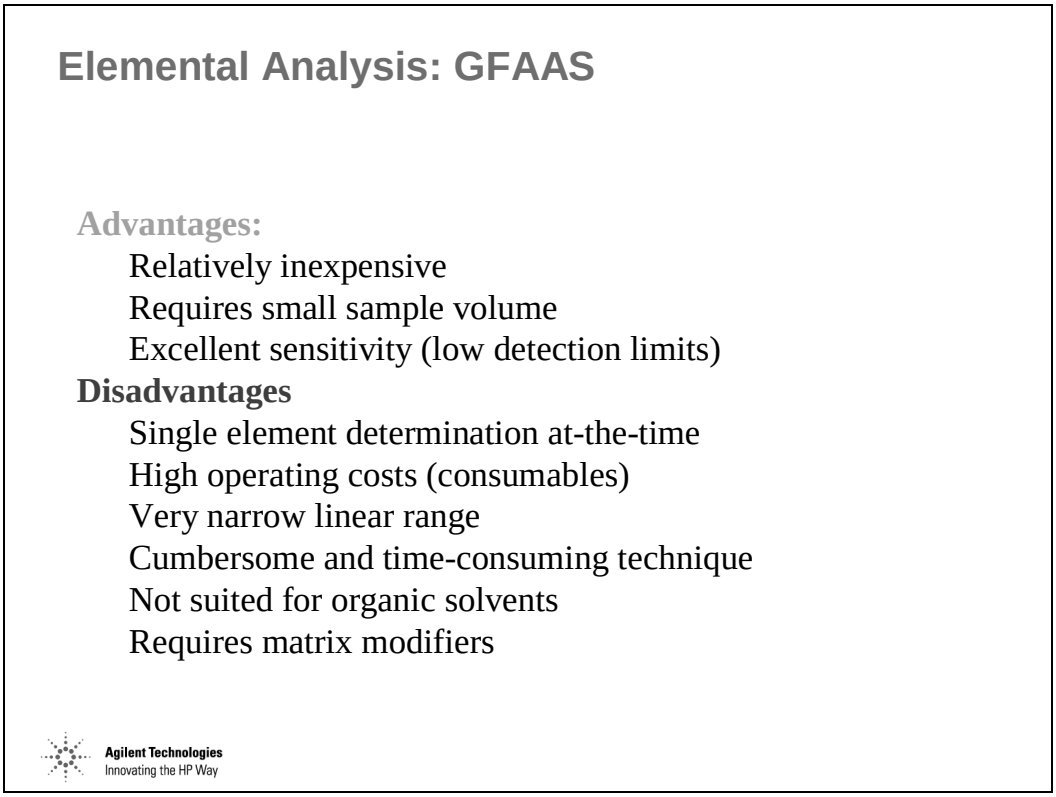


Figure 6

Elemental Analysis: ICP-OES

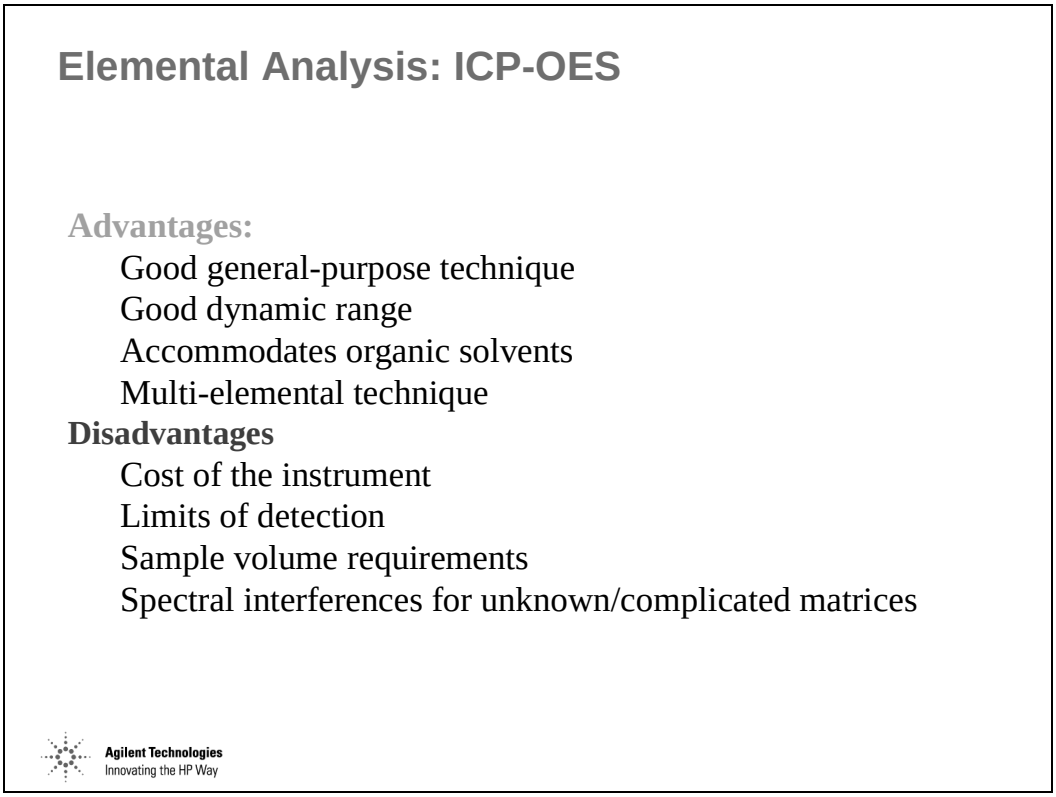


Figure 7

Elemental Analysis: ICP-MS

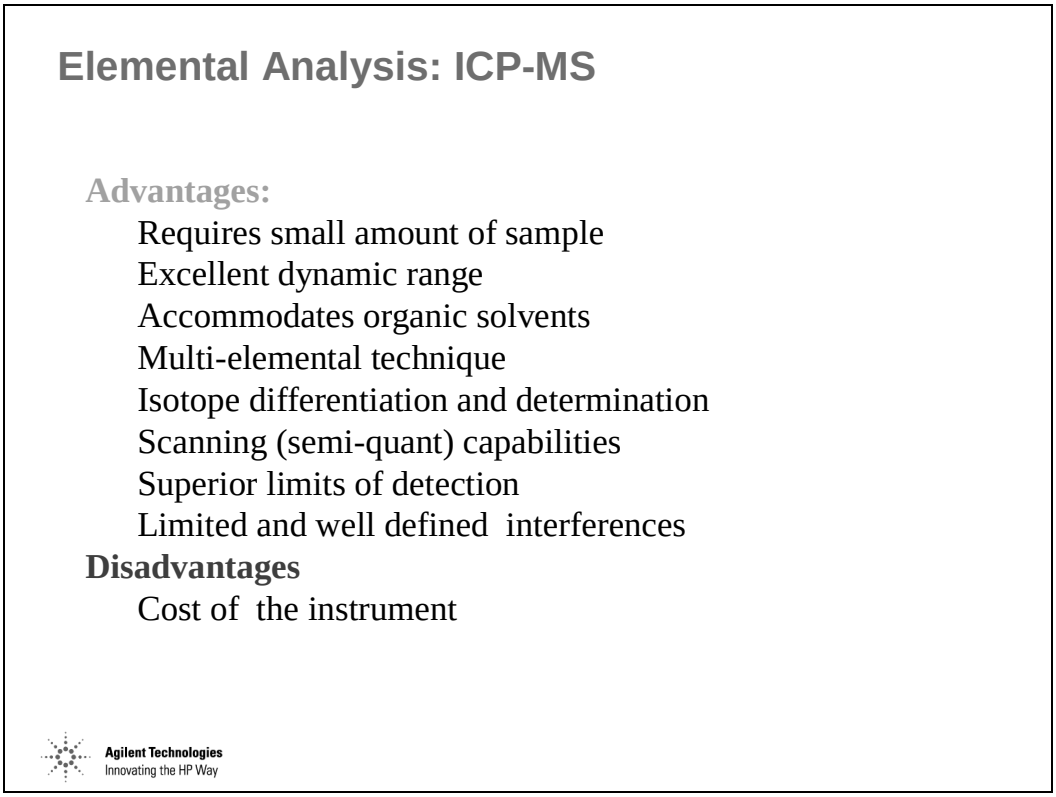


Figure 8

Comparison of Elemental Techniques

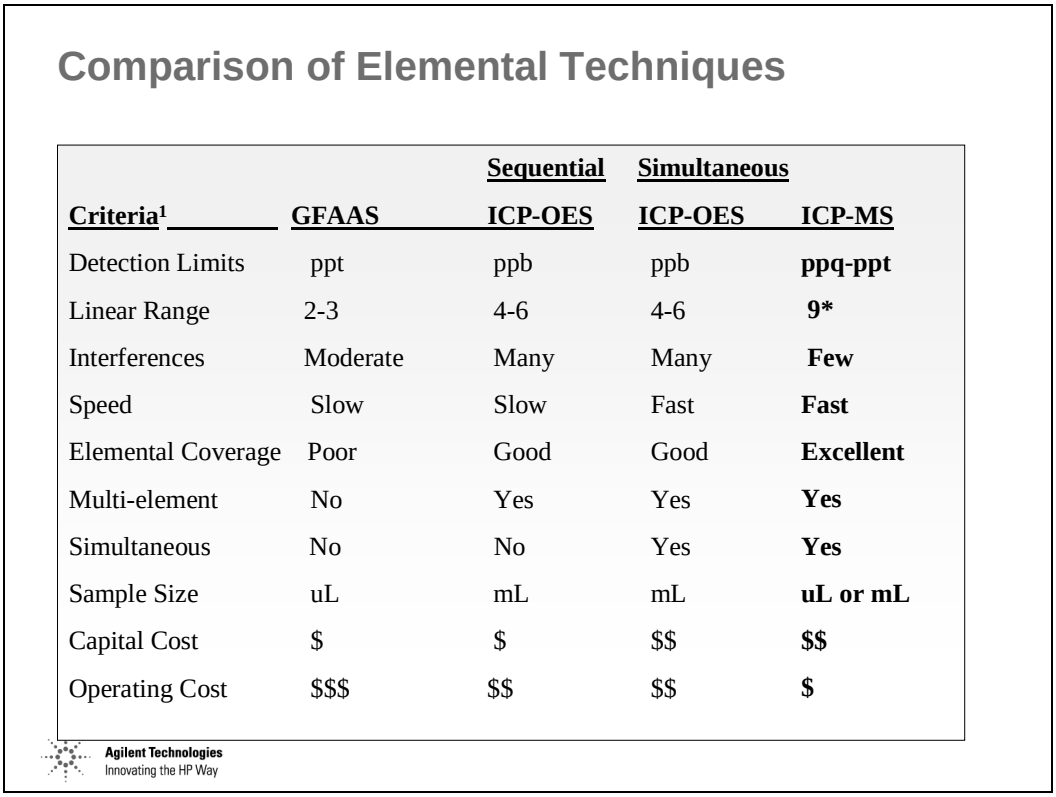


Figure 9

Graphical Comparison of Elemental Techniques

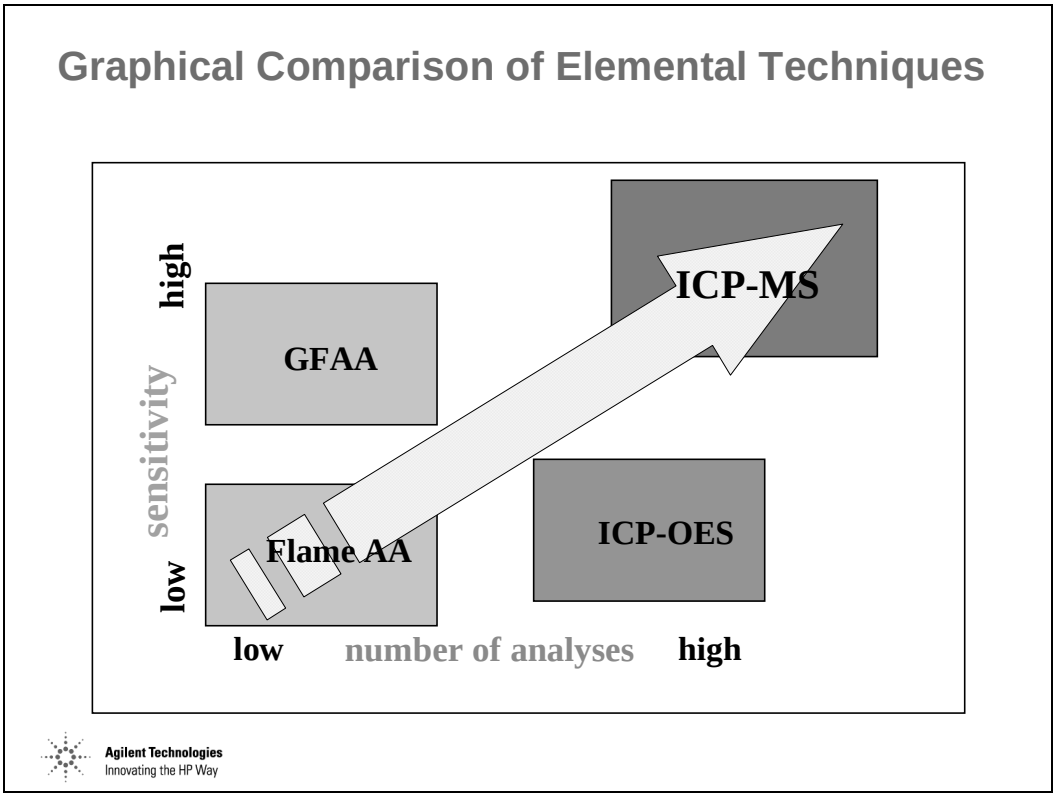
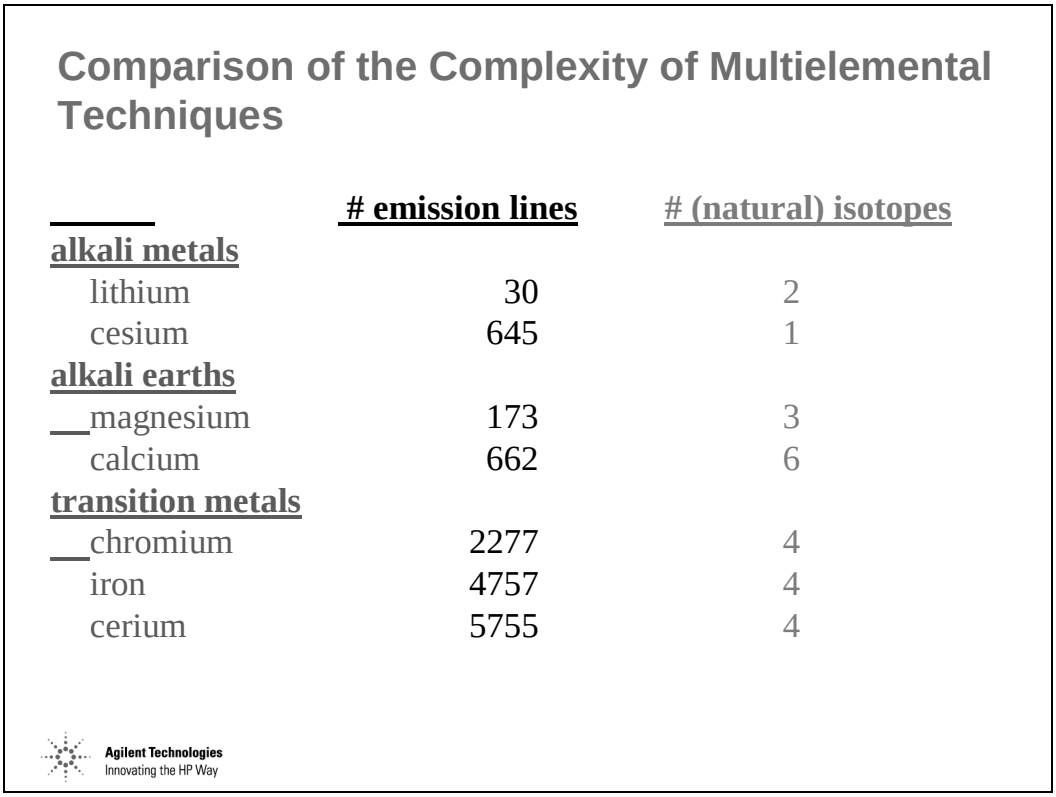


Figure 10

Comparison of the Complexity of Multi-elemental Techniques



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Users/Applications of ICP-MS

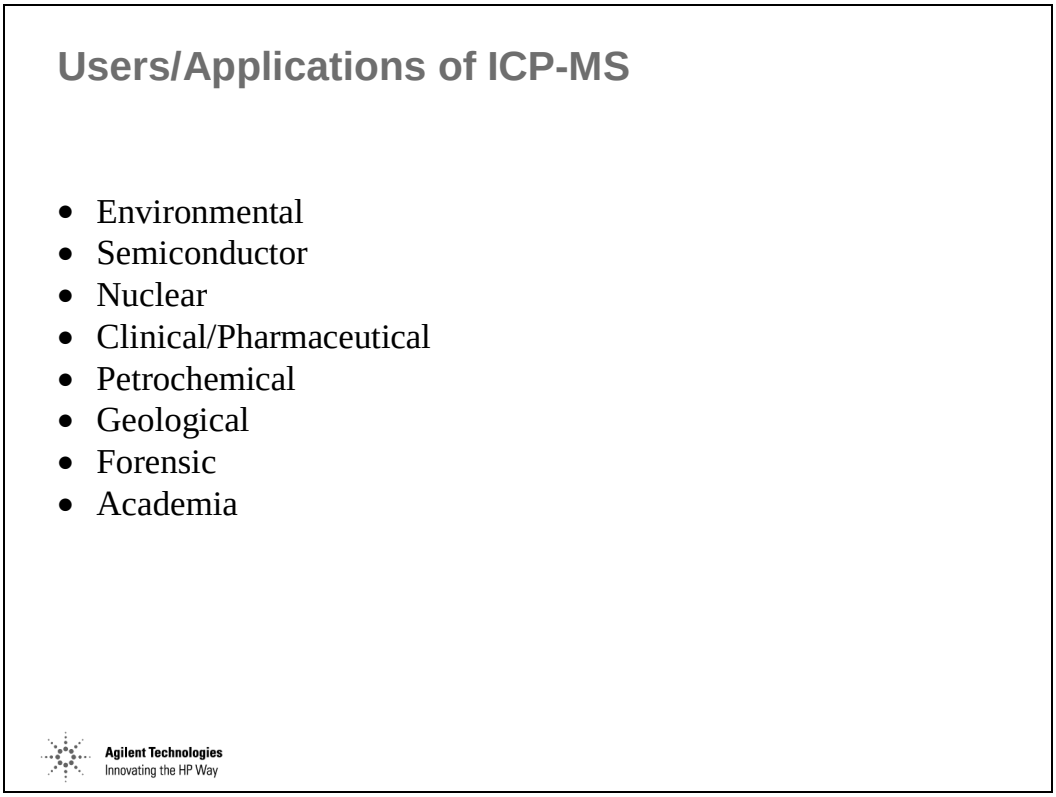

Figure 12

Multi-elemental Analysis of Metals

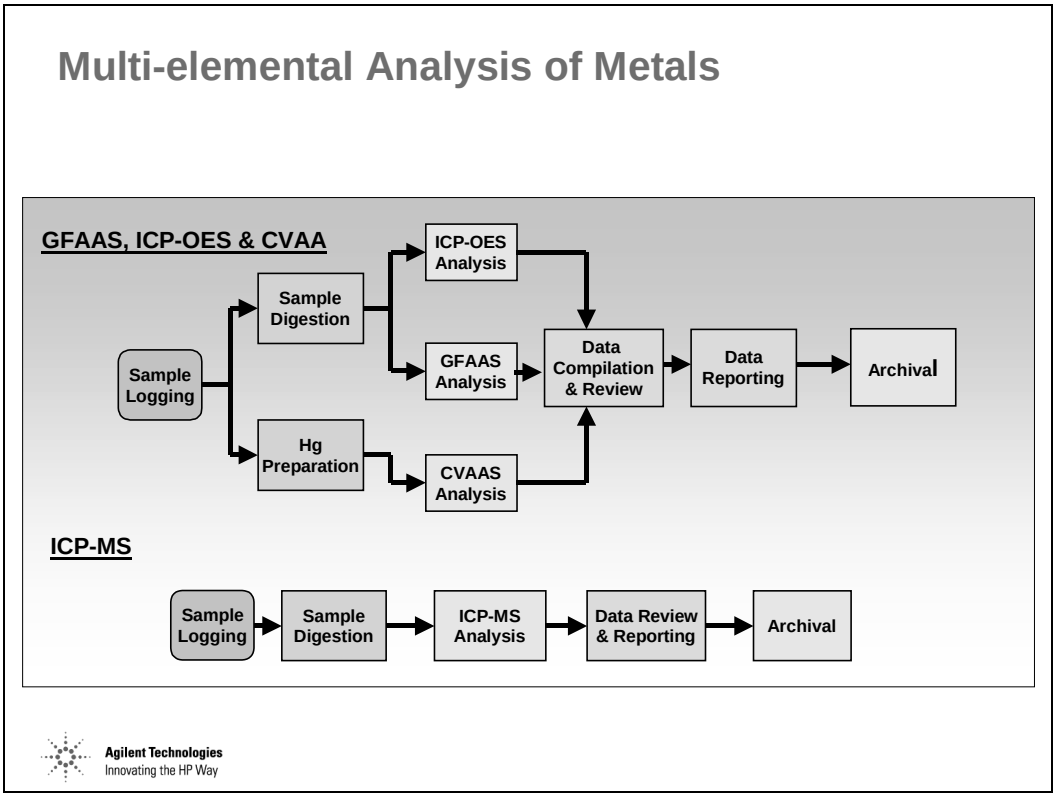

Figure 13

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Introduction: Inductively Coupled Plasma Mass Spectrometry

What is ICP-MS?

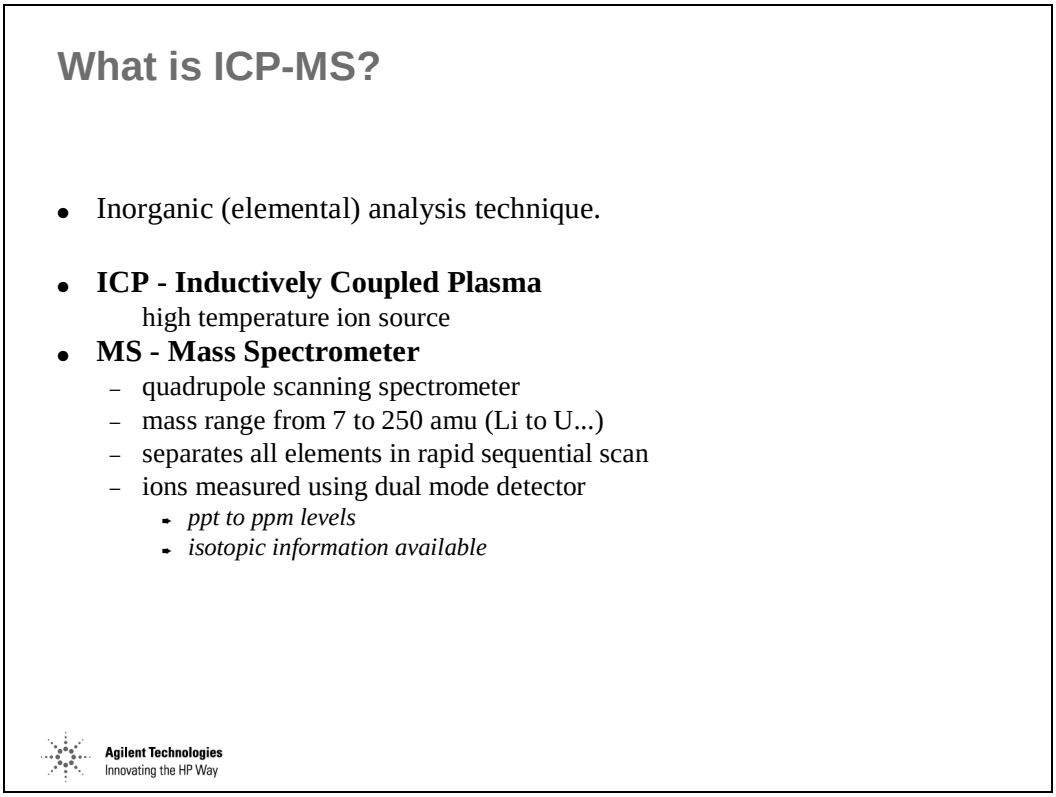
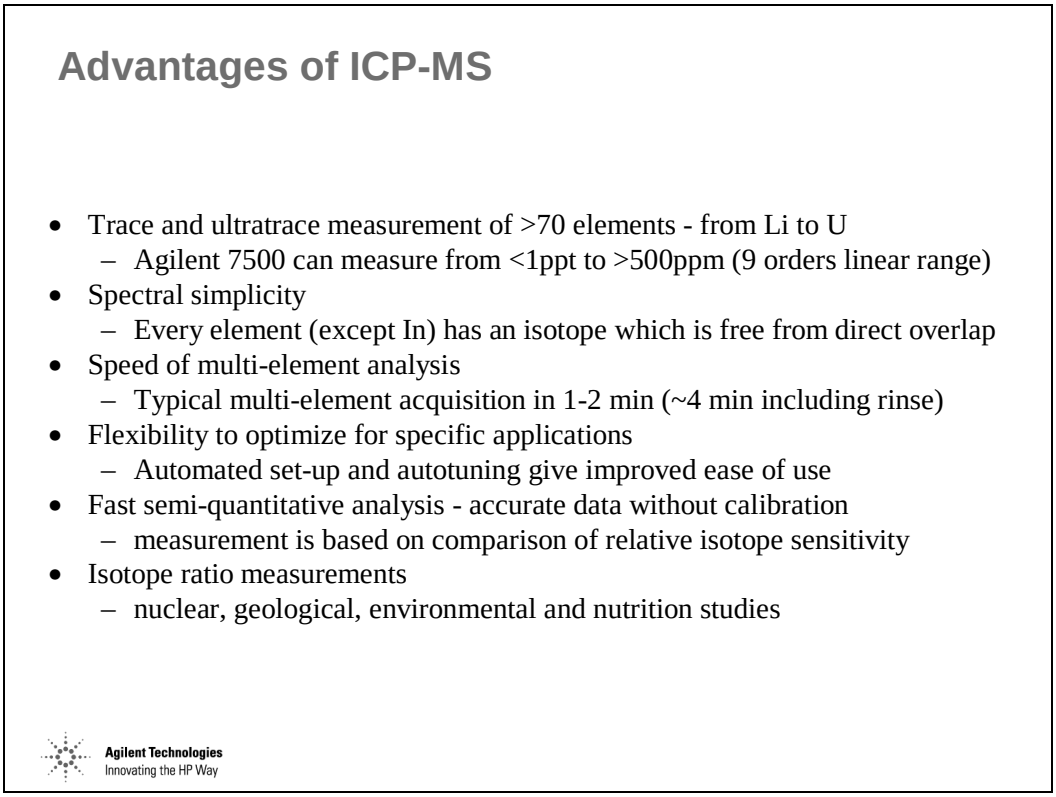


Figure 14

Advantages of ICP-MS



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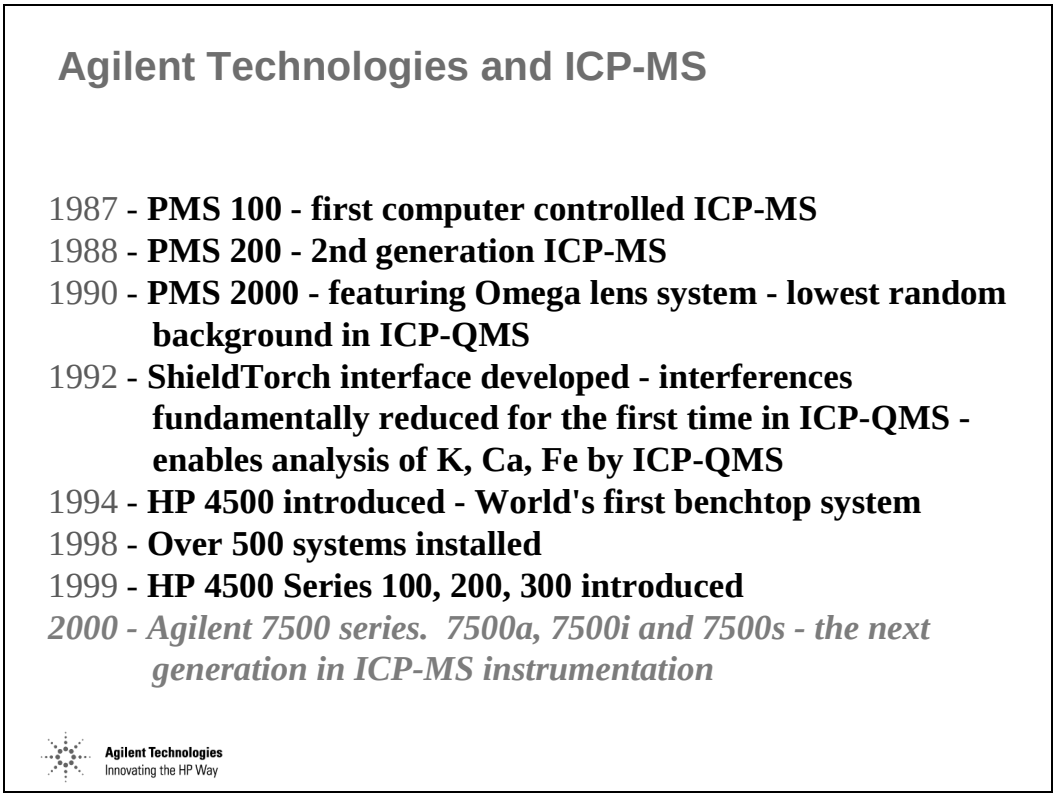
Agilent Technologies and ICP-MS



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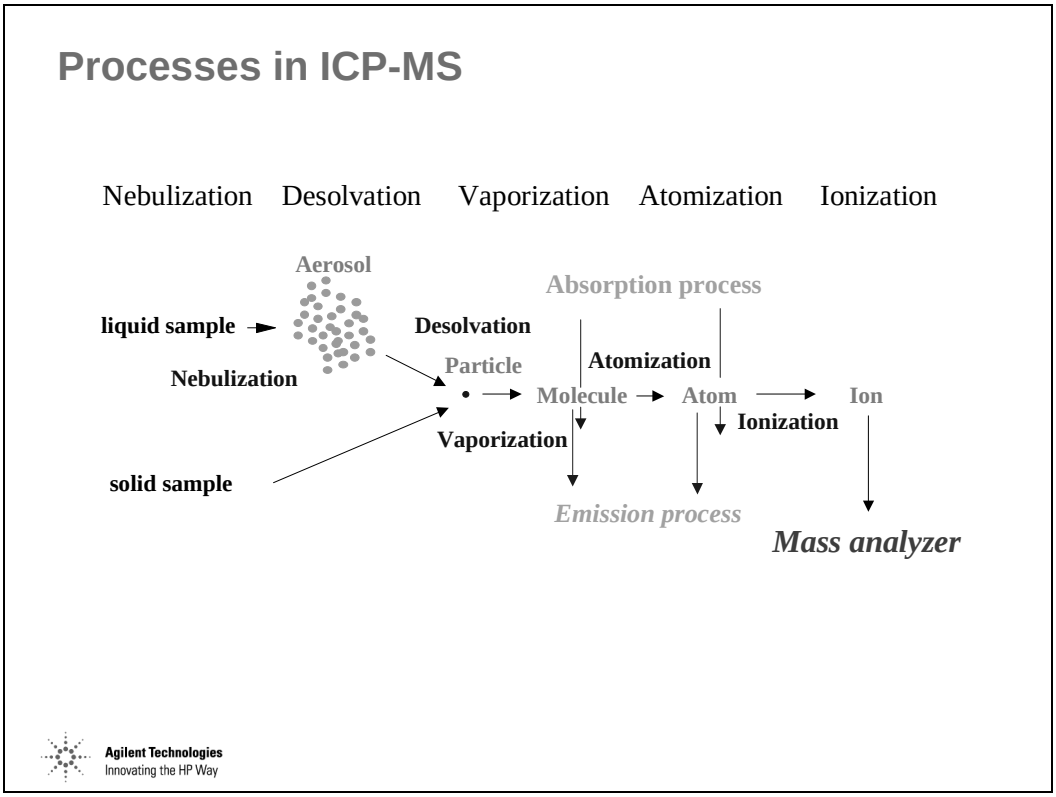
Processes in ICP-MS



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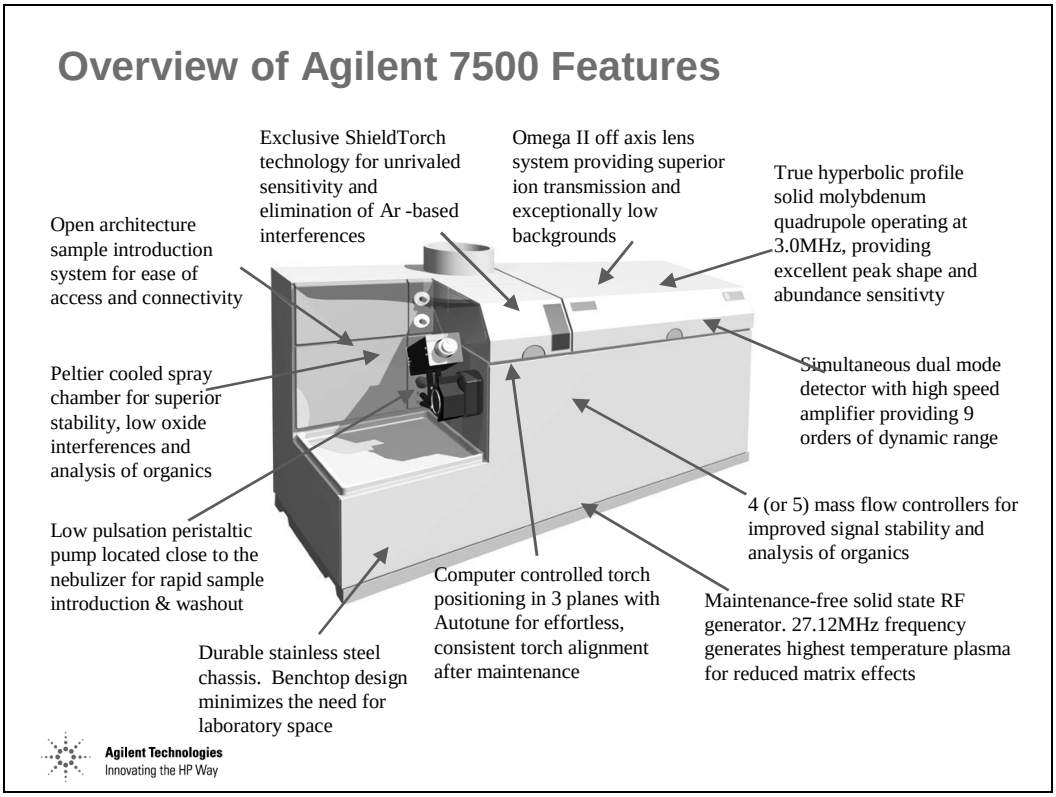
Overview of Agilent 7500 Features



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Schematic Diagram of Agilent 7500a

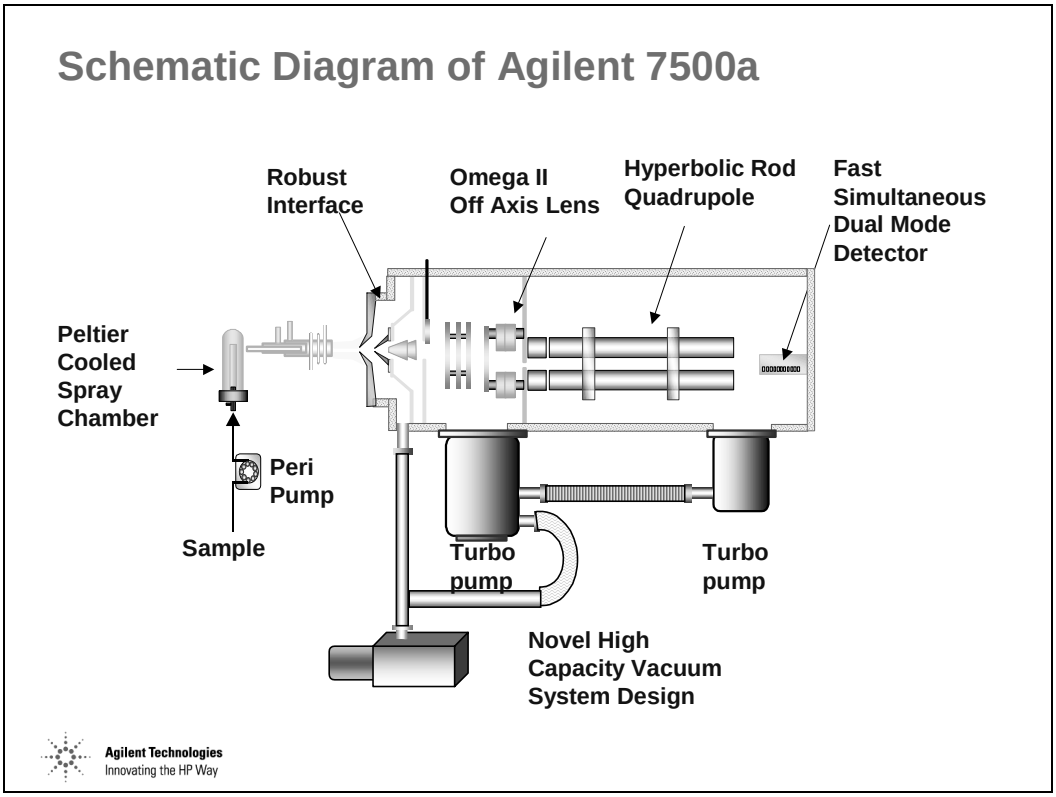

Figure 19

- Sample solution is pumped into the nebulizer. The sample stream is nebulized with argon gas and forms an aerosol of fine droplets.
- The argon gas carries the finest droplets through the turns of the spray chamber and into the plasma where the sample is atomized and ionized.
- Ions are extracted from the atmospheric pressure plasma into the high vacuum region of the mass analyzer via the interface. The interface consists of two water-cooled orifices called cones.
- A three-stage vacuum system provides pressures of 1 Torr between the cones, 10-4 Torr in the lens chamber and 10-6 Torr in the analyzer chamber.
- The ion lens system focuses ions into the analyzer. Light is excluded from the analyzer and detector regions by the Omega lens, which reduces background noise.
- The quadrupole mass filter allows only ions of a specific mass to charge ratio to pass through to the detector at any point in time.

Schematic Diagram of Agilent 7500a

- The EM detector measures the ion signal at each mass and stores it in the MCA. Data is expressed as counts per second, which is directly proportional to the concentration of the element at that mass.

Schematic Diagram of Agilent 7500s

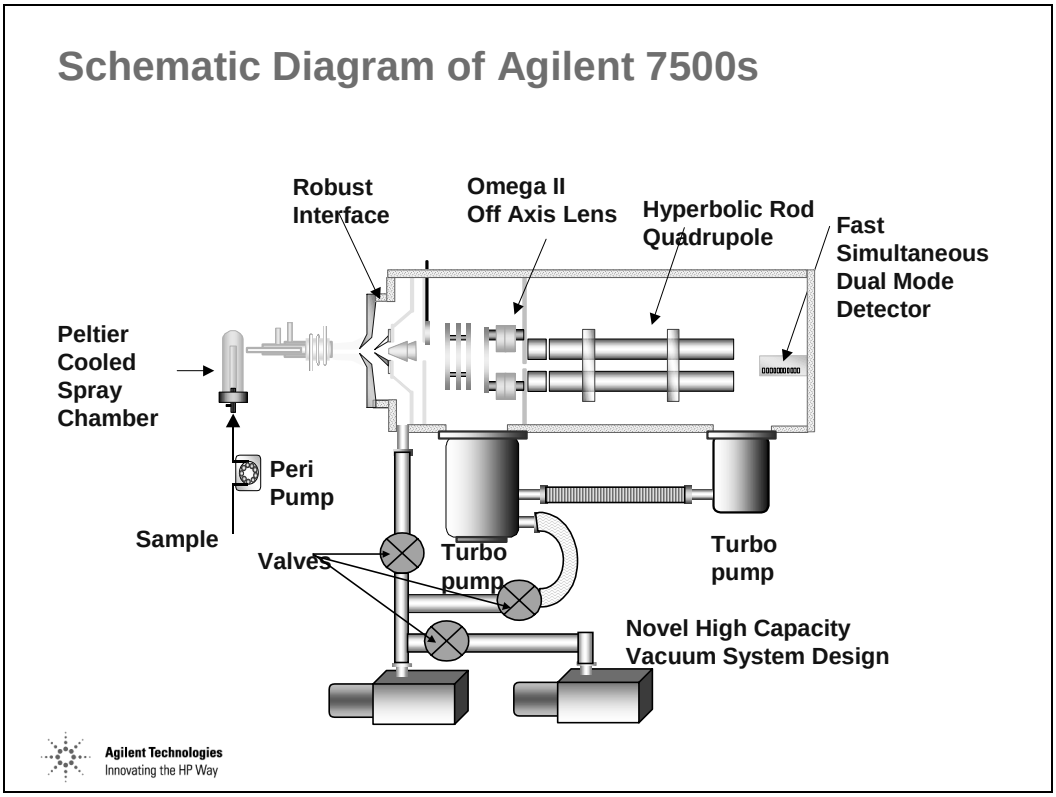

Figure 20

ISIS for Application Flexibility

Figure 21

Sample Introduction

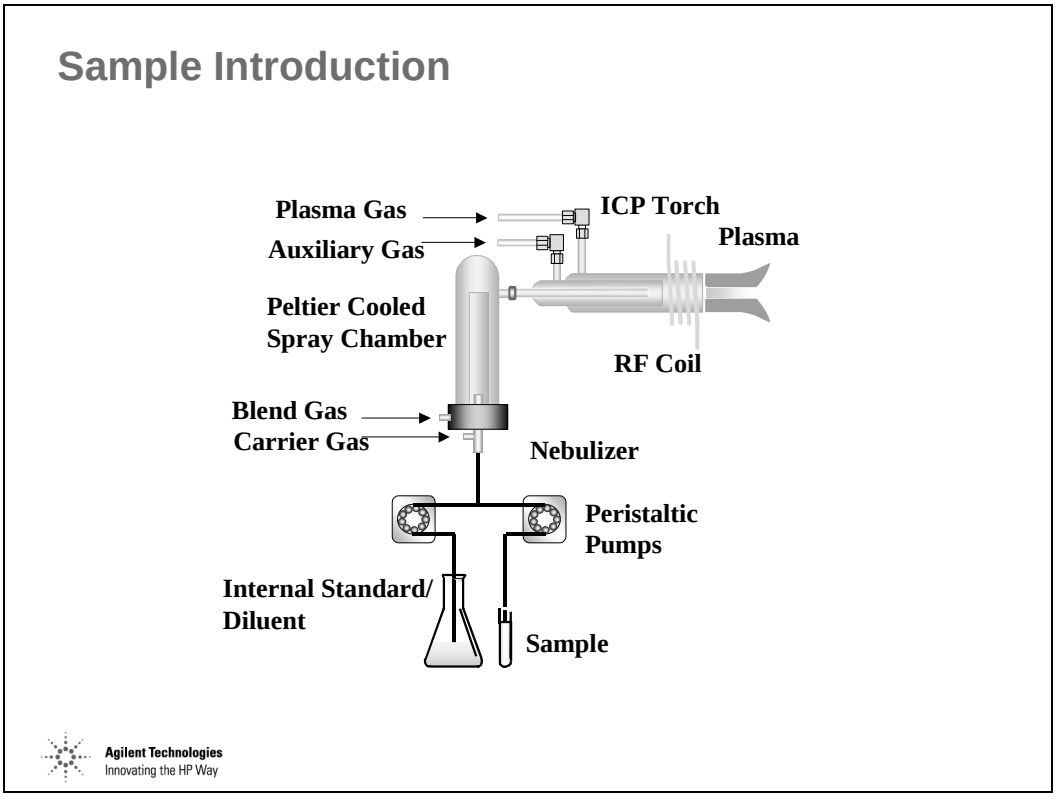

Figure 22

The ease of removal of our torch is a big point:

- 1 minute with Agilent
- 5 minutes with VG
- 10 – 15 minutes with PE

Especially with gloved hands, as in a cleanroom.

We are the only company to offer Pt injector torches. This is in response to demand from Japanese semiconductor users. All other vendors use Al_2O_3 or sapphire, which give high Al background.

Also, we are the only ones to use a polypropylene spray chamber:

- VG use Teflon (poor wetting - bad stability and washout)
- PE use Ryton, which is impure - high Ba, etc. from filler, and also it is not resistant to H_2O_4

Agilent 7500 Sample Introduction

Agilent 7500 Sample Introduction

Externally mounted spray chamber with new Peltier cooling system

New, low-pulsation 3-channel sample introduction pump - close-coupled to spray chamber to reduce uptake time and dead volume

Open sample area protected with sealed polymer tray - easy access to sample intro components and connection of external devices -

- laser ablation
- LC
- GC
- CE

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Figure 23

Autosamplers

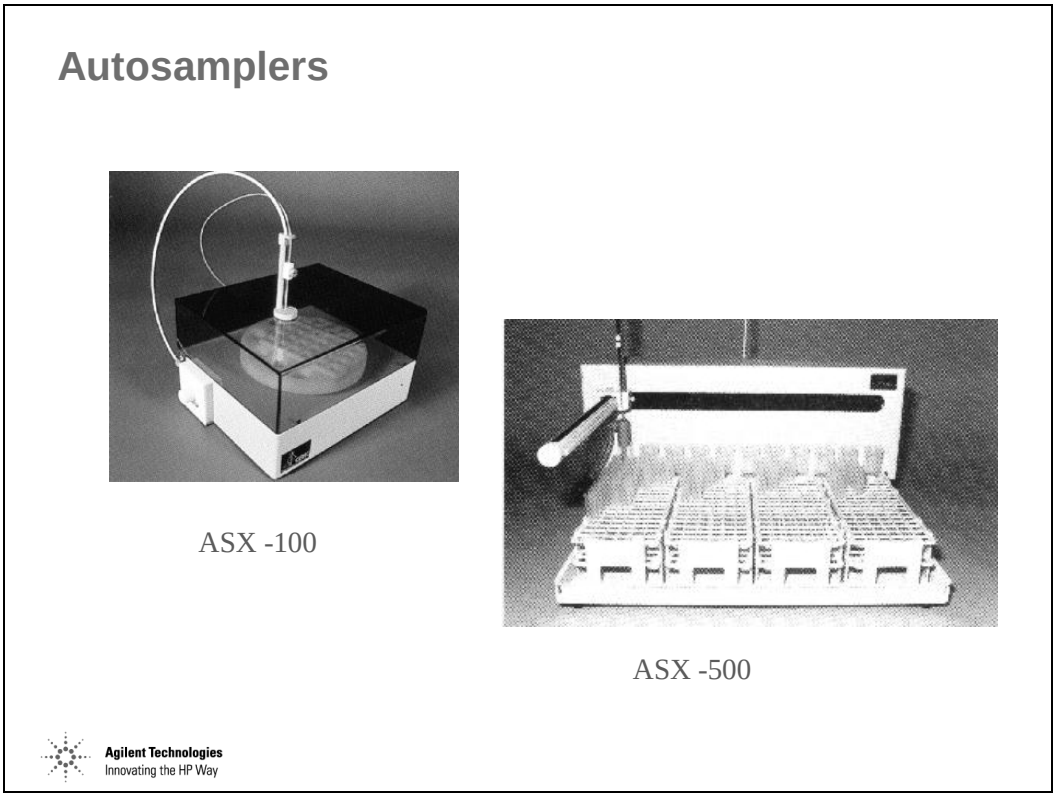


Figure 24

Typical Nebulizer

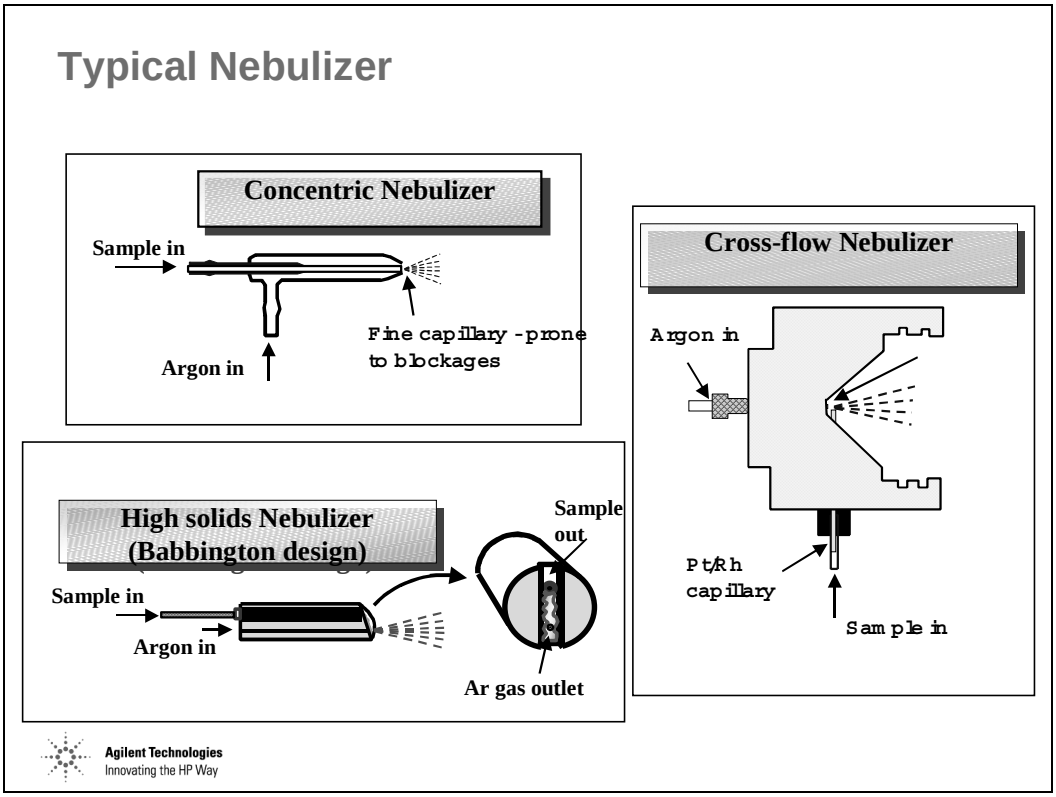


Figure 25

Specialized Sample Introduction Systems

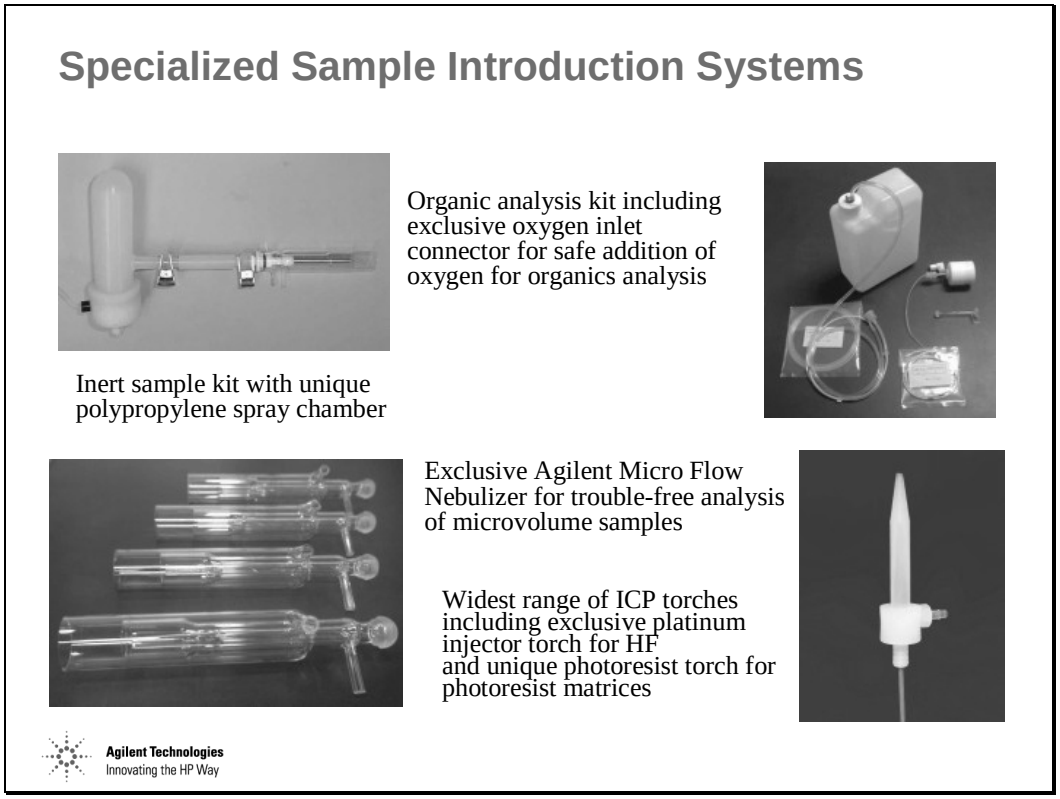


Figure 26

Typical Spray Chamber – Double Pass

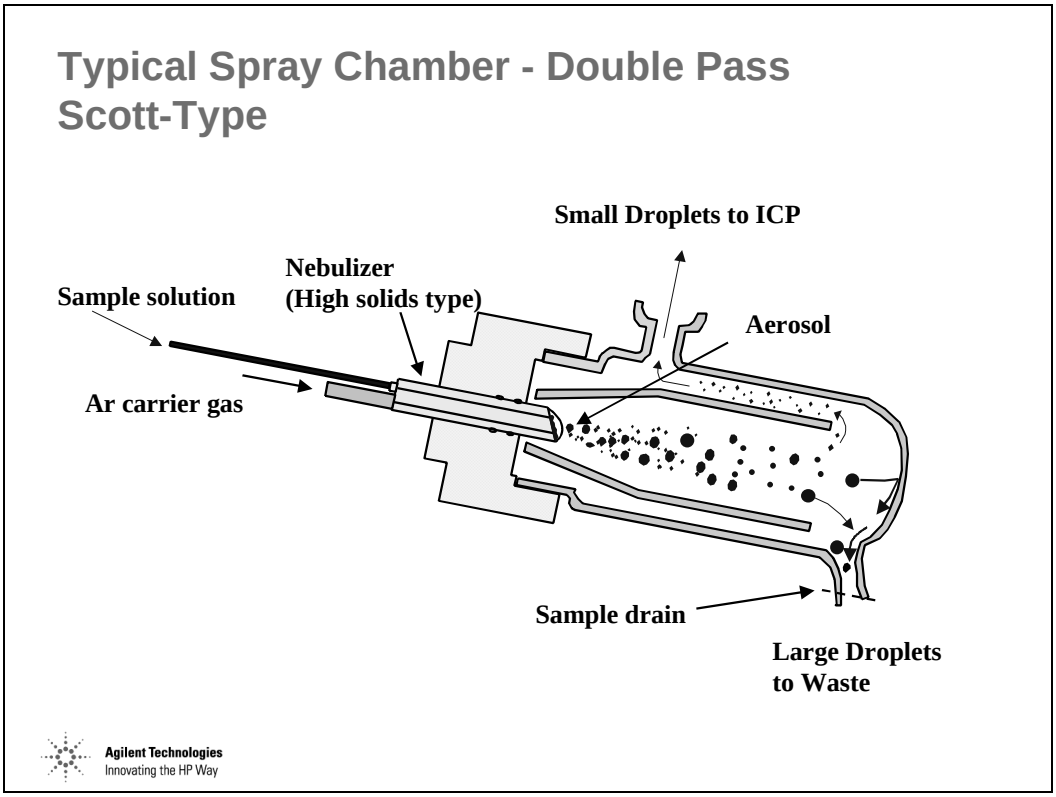


Figure 27

Droplet Distribution With and Without Spray Chamber

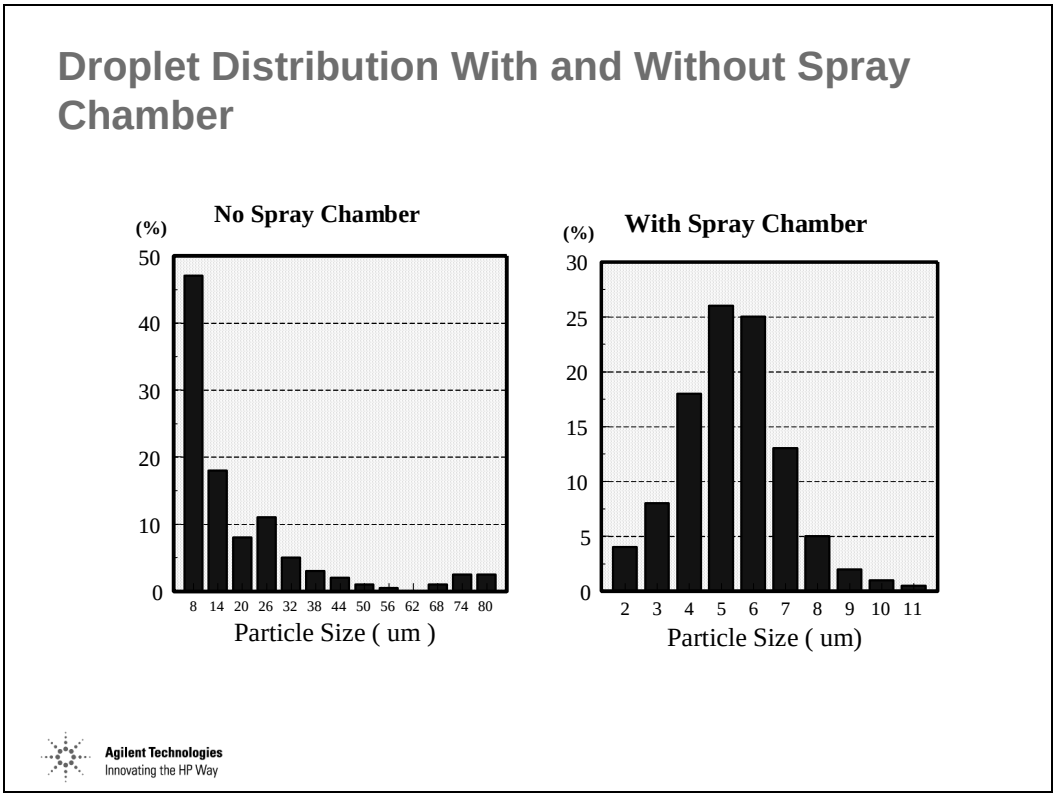
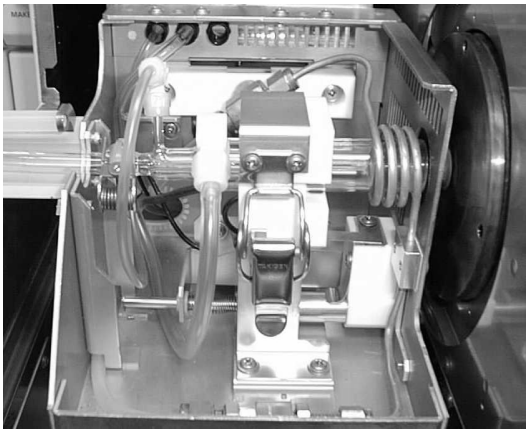


Figure 28

New Design Agilent ICP Torch Box

New Design Agilent ICP Torch Box



New torchbox position control stepper motors (x-, y- and z-adjustment) are fast and precise.

Quick release torch mounting allows for easy torch removal and replacement for cleaning.

Plasma compartment is separated from the main cabinet, and plasma gases vented separately direct to the exhaust duct.

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Figure 29

Inductively Coupled Plasma Mass Spectrometry

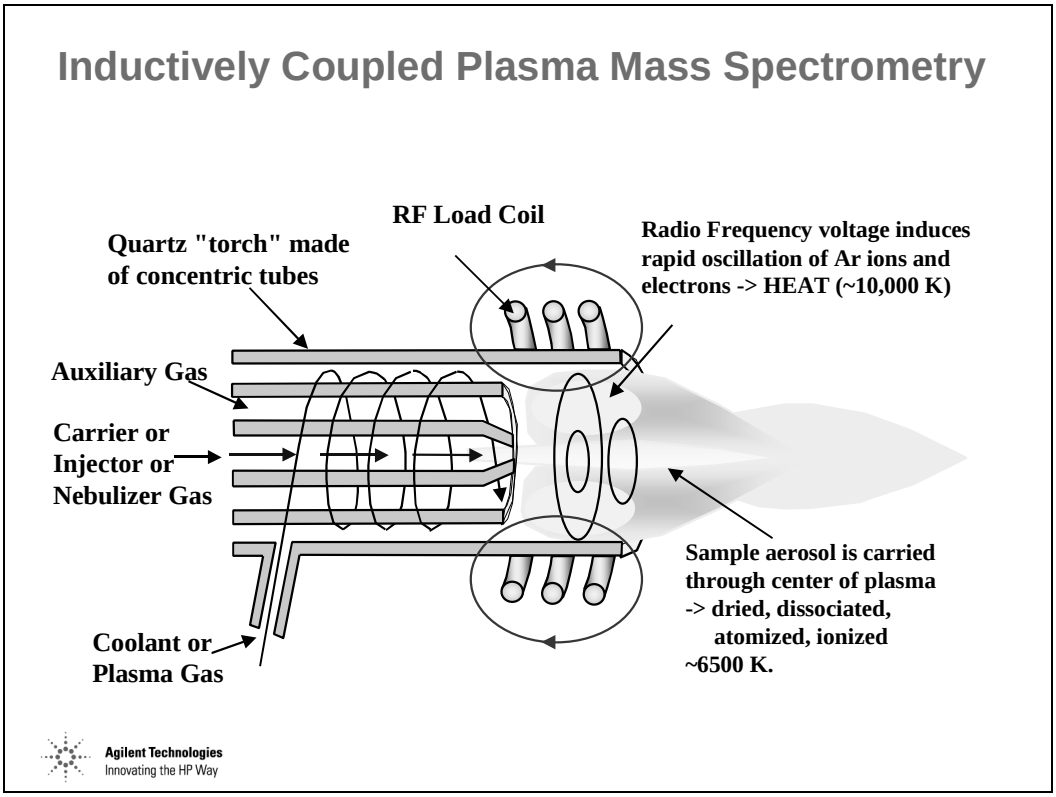


Figure 30

Inductively Coupled Plasma Mass Spectrometry (continued)

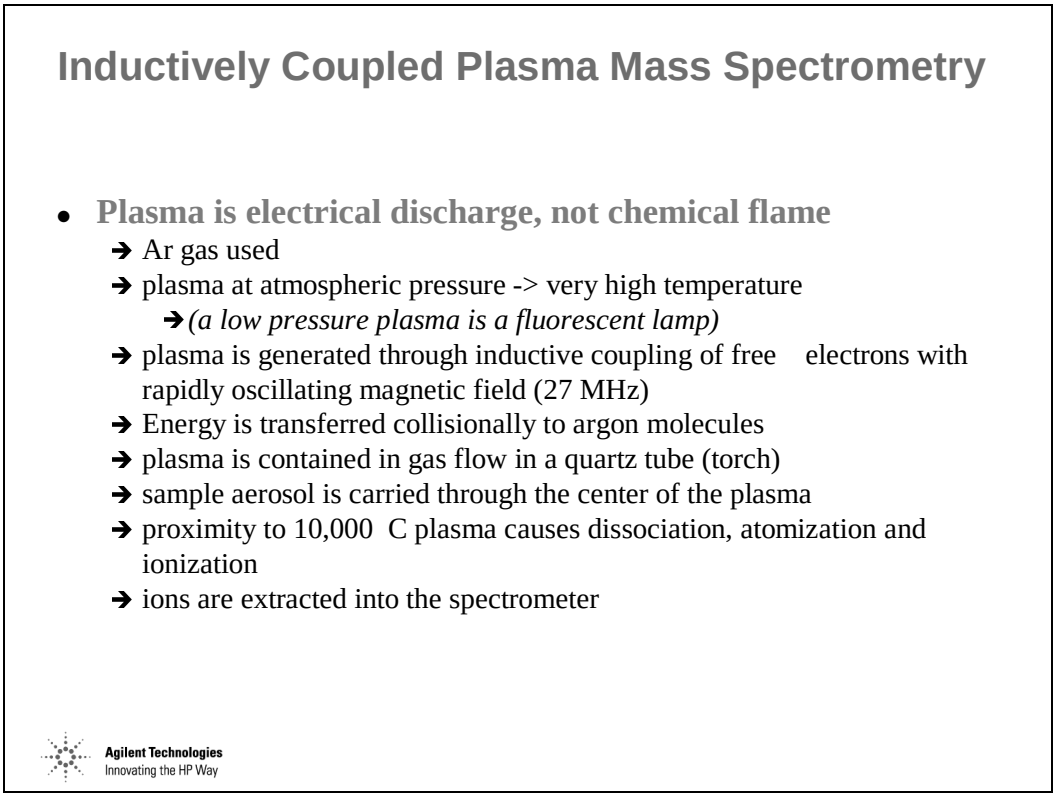


Figure 31

Why Argon?

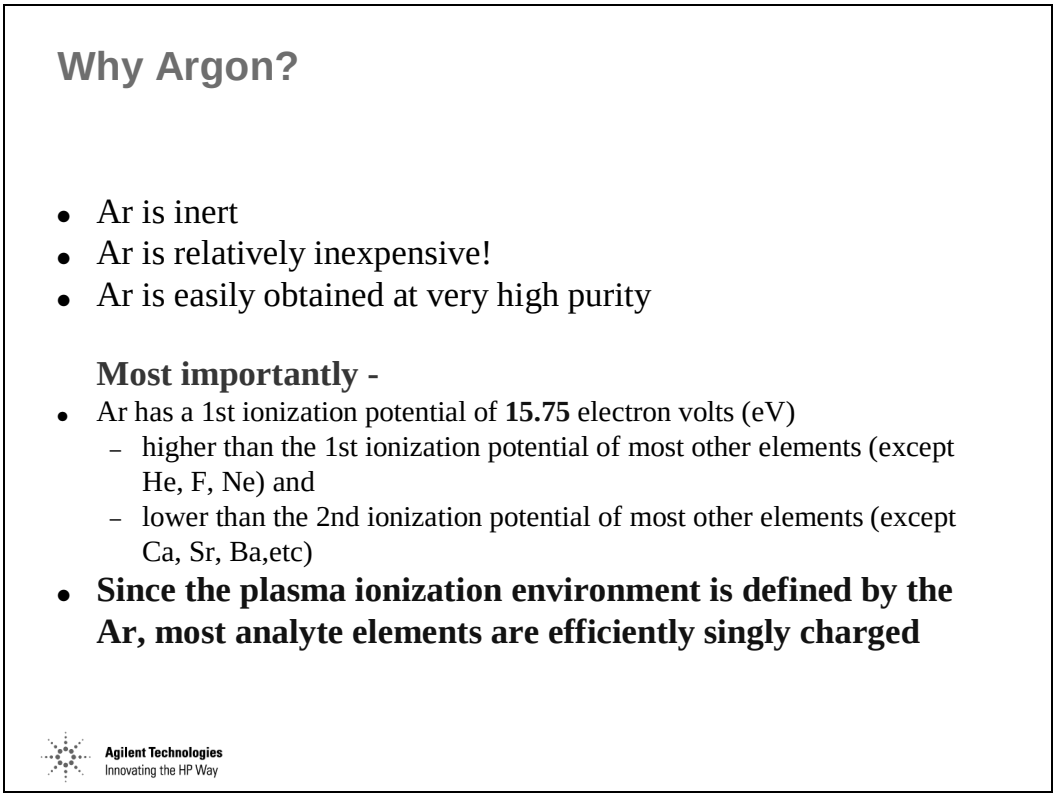


Figure 32

Distribution of Ions in the Plasma

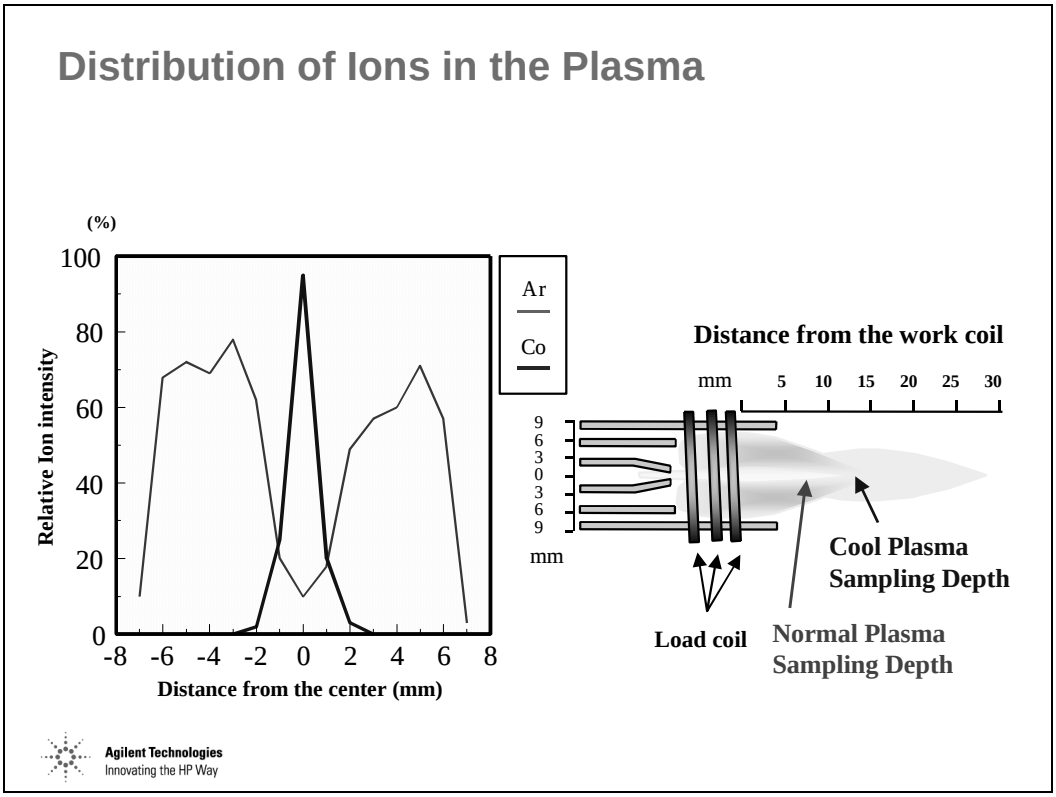


Figure 33

Sample Ionization in the Plasma

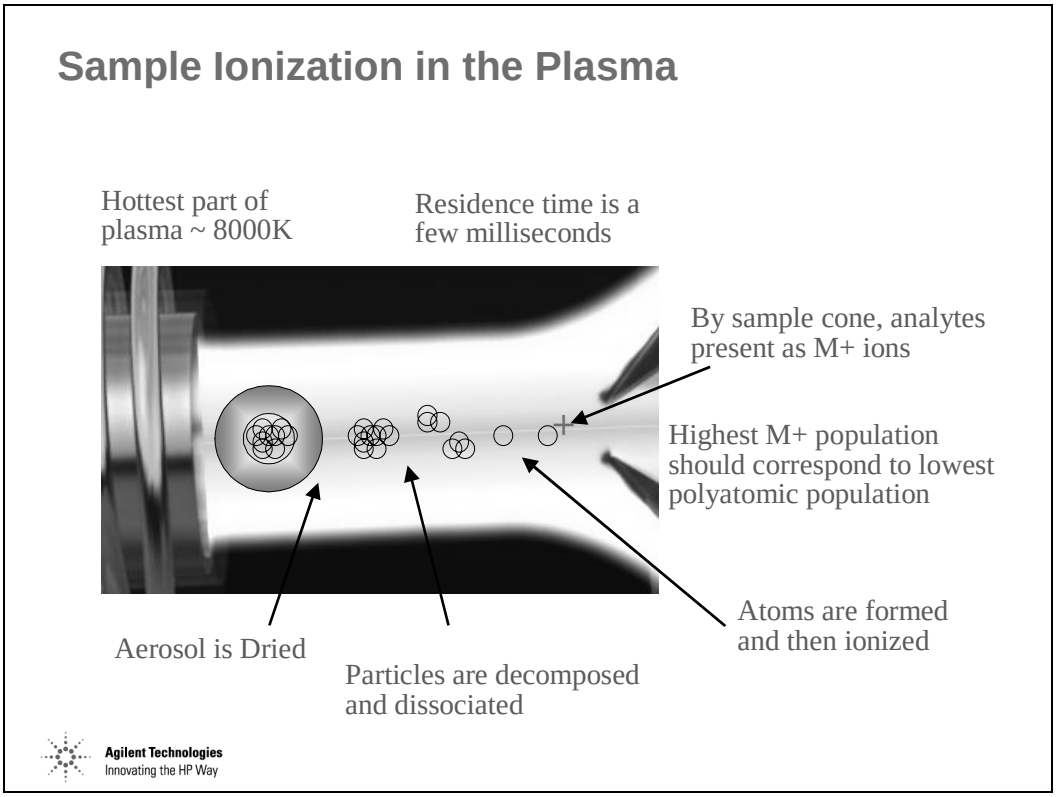
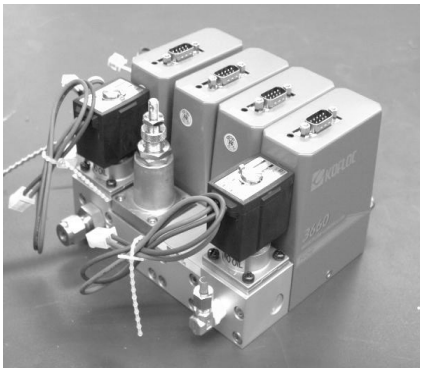


Figure 34

Full Mass Control of All Gas Flows

Full Mass Control of All Gas Flows



Nebulizer gas flow is an important parameter to tune for optimizing signal - separate control of nebulizer gas and total injector flow (by varying make-up gas) is essential for optimum performance

Mass flow control (MFC) has the benefits of
- superior stability - better short and long term signal precision
- more reproducible set-up and optimization
- electronic control via the PC

- 4500 Series - 2 MFCs - nebulizer and blend (make-up)
  - blend gas is required for optimum ShieldTorch analysis, or for organics analysis
- 7500a, 7500i - 4 MFCs - plasma, auxiliary, nebulizer, blend
- 7500s - 5 MFCs - plasma, auxiliary, nebulizer, blend, option

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Figure 35

Interface

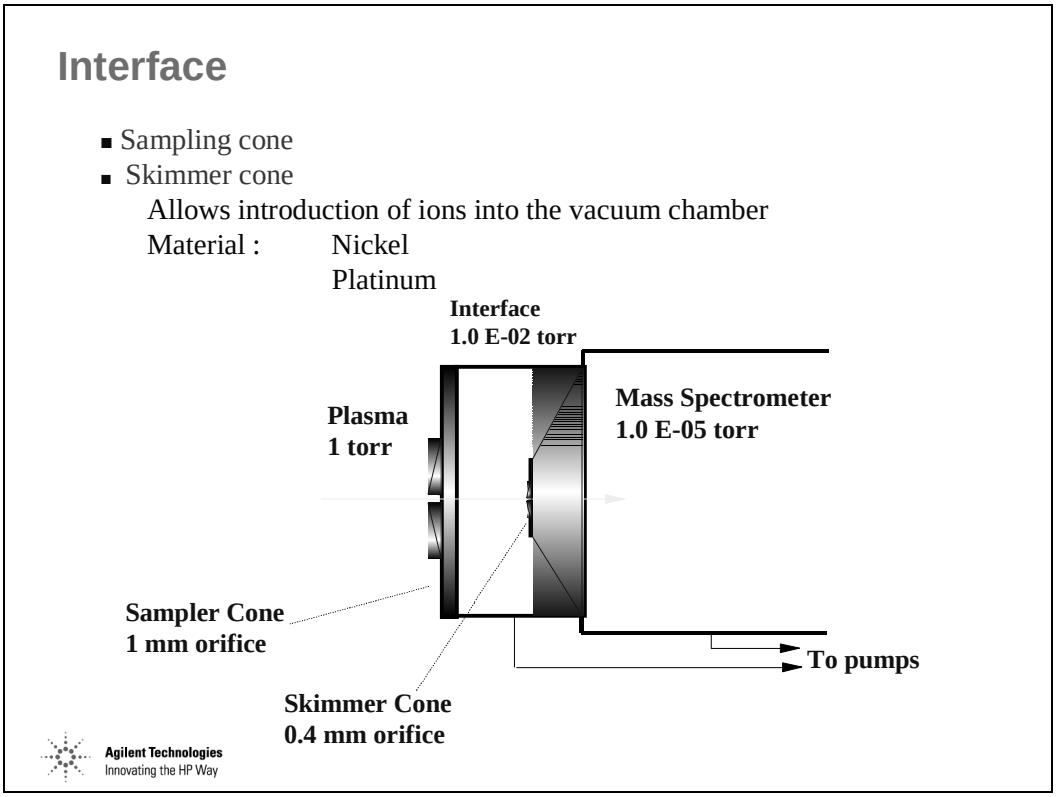

Figure 36

Agilent 7500 Ion Lens System

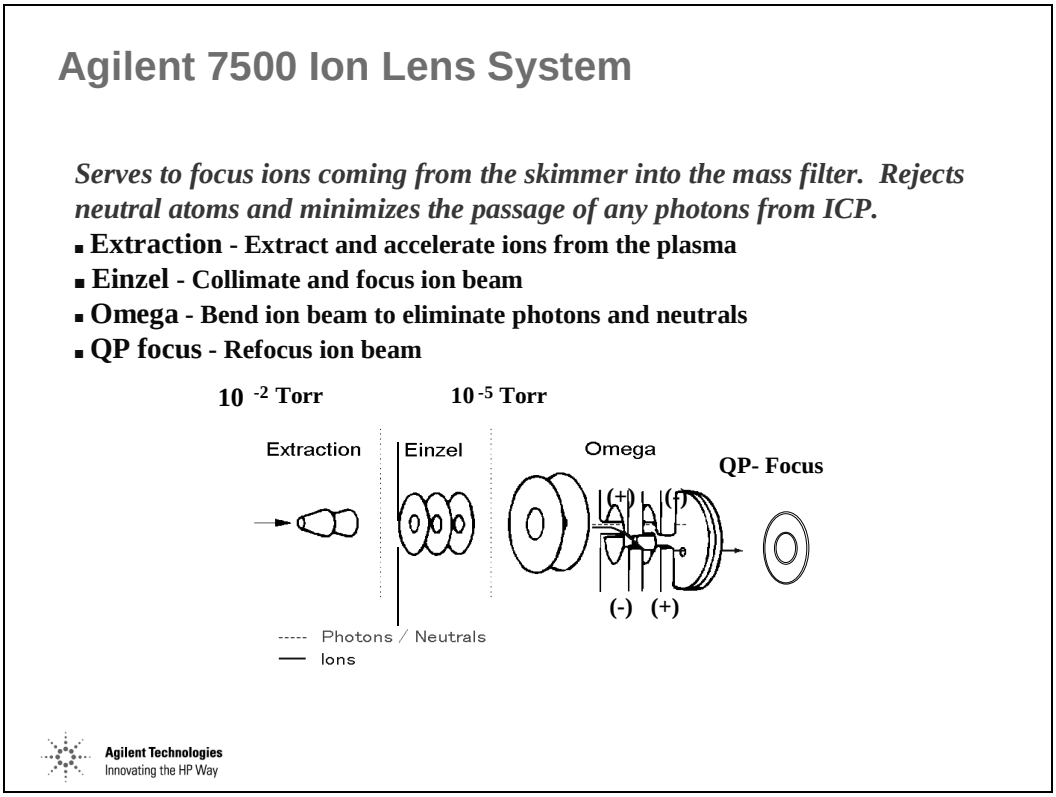

Figure 37

Distribution of Ions and Electrons Around the Interface

Distribution of Ions and Electrons Around the Interface

Neutral Plasma
- equal numbers of electrons and positive ions at high temp

Cooler Interface
- does not support ion stability
- neutral Ar sheath forms acting as a condensor preventing the plasma from grounding on the cones

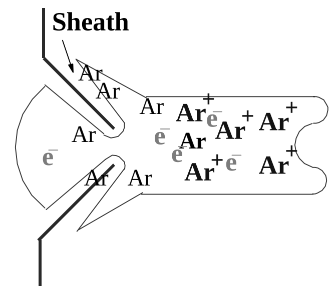

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Figure 38

Ion Energy Distribution in the Interface

Ion Energy Distribution in the Interface

- Ion lenses are optimized for a particular range of ion energies (potential + kinetic). Low mass ions have lower kinetic energy.
- Cooling the plasma increases the thickness of the sheath, increasing the plasma potential and the energy of the ions.
  - Shifts the energy distribution profile to the right - increasing low mass sensitivity.

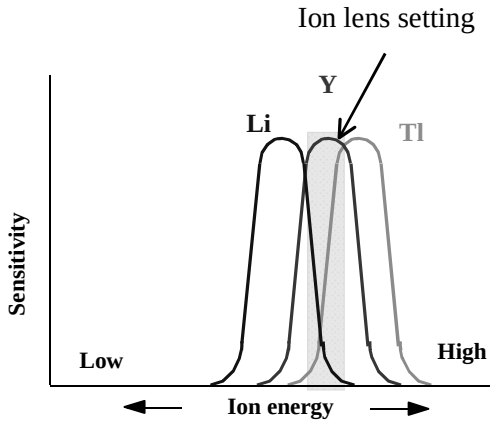

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Figure 39

The Electrostatic Lenses

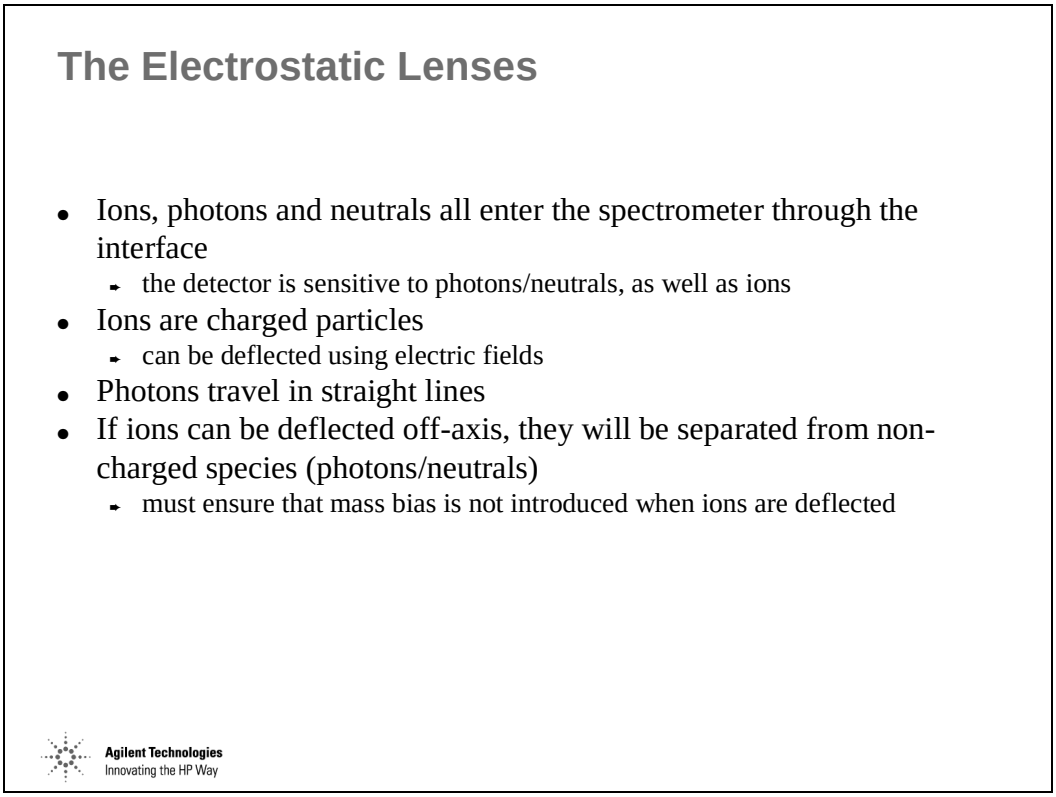


Figure 40

Why “Off-Axis”?

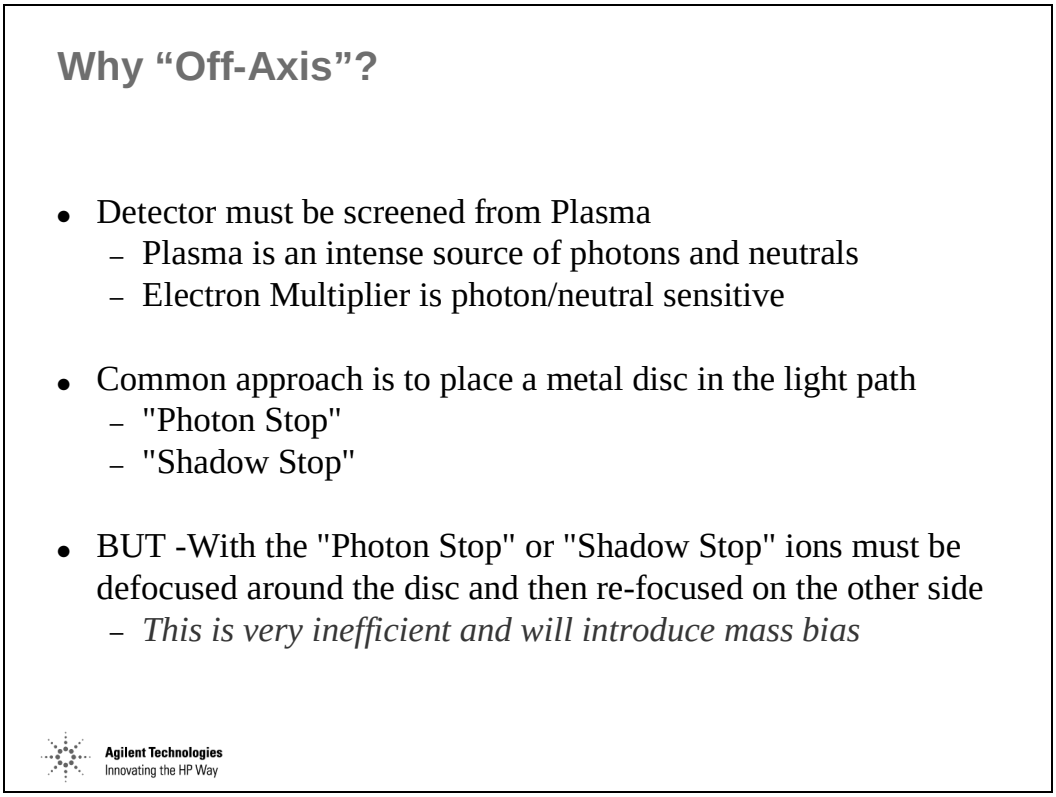


Figure 41

Low Transmission Photon Stop System

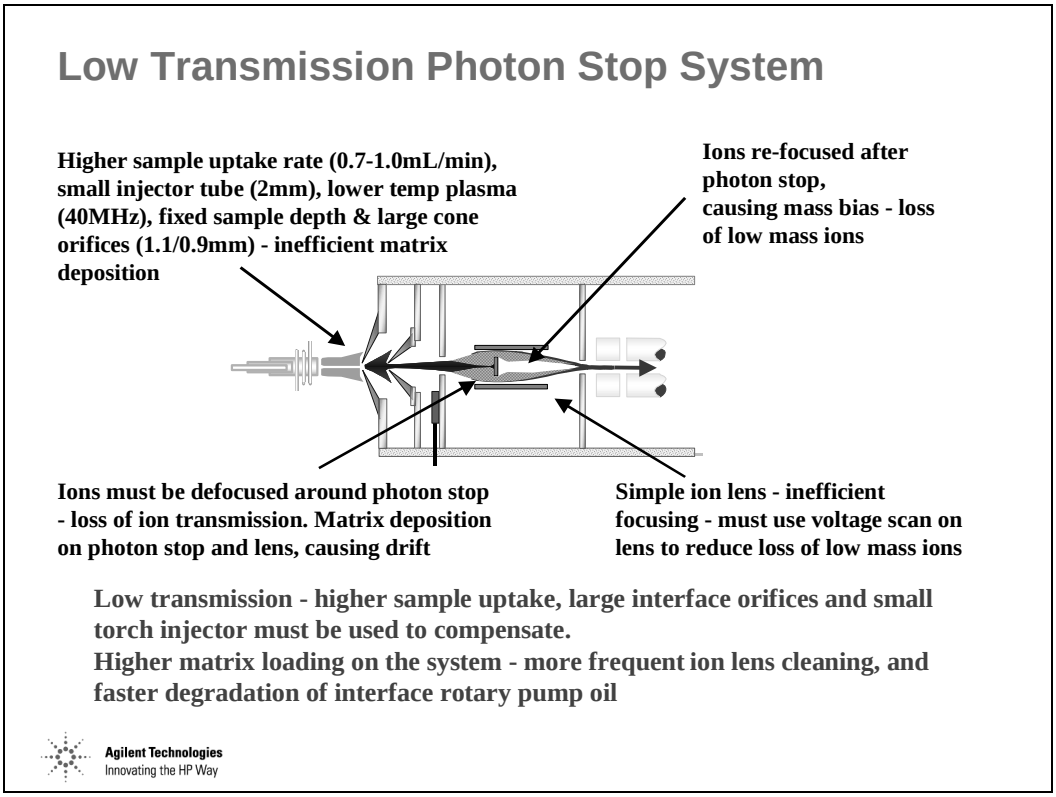


Figure 42

Agilent High Transmission Off-Axis System

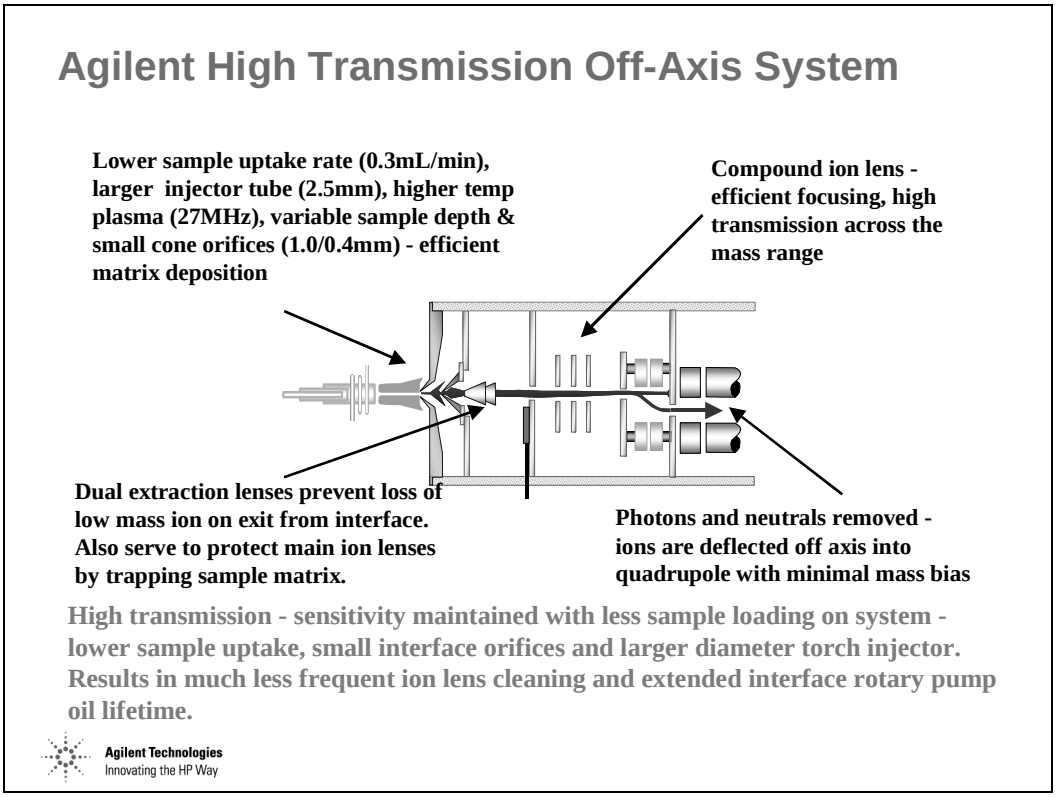


Figure 43

Ion Focusing – New Omega II Lens

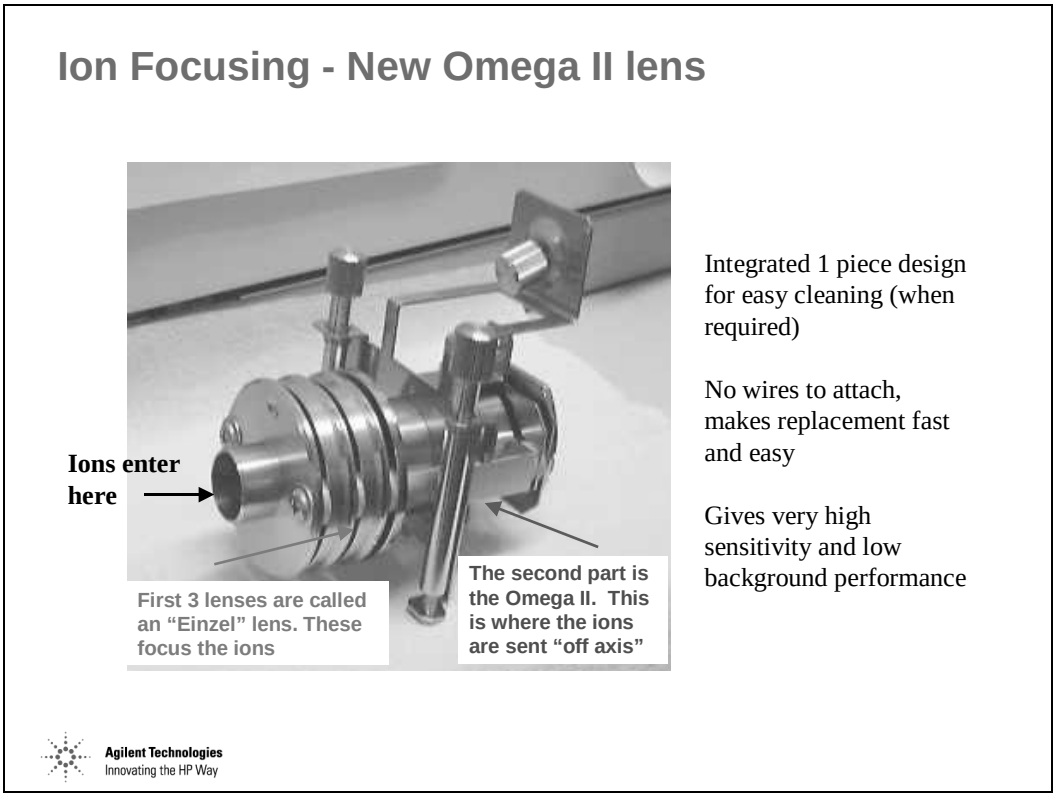


Figure 44

Flat Response Curve – High Sensitivity at All Masses

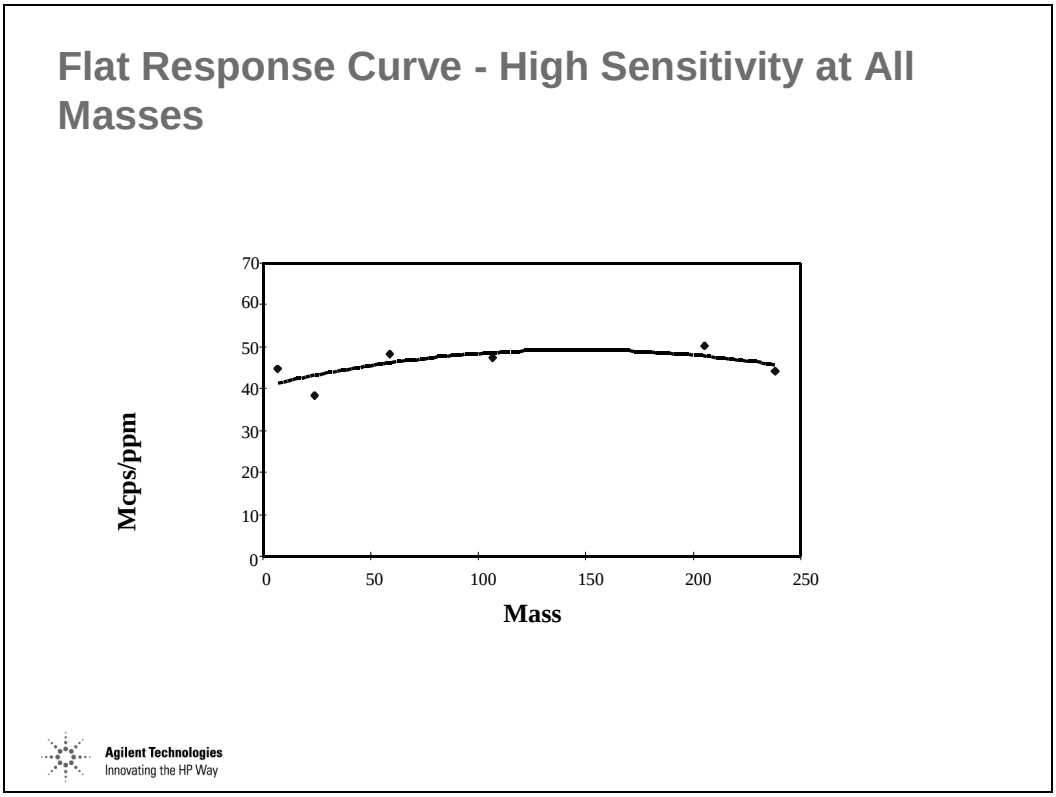
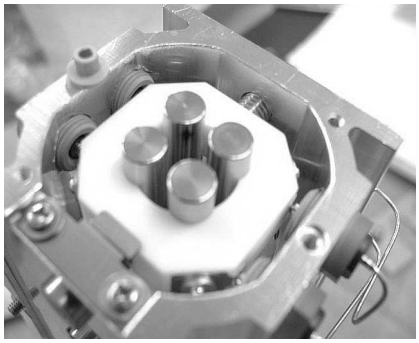


Figure 45

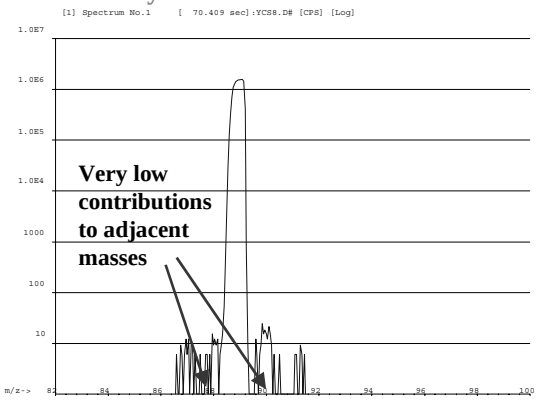
Photon stop systems suffer from significant mass bias against low masses due to space charge effects.

Agilent 7500 Quadrupole

Agilent 7500 Quadrupole



TRUE hyperbolic rods - precision ground from solid Molybdenum.
Novel digitally synthesized 3.0MHz RF generator - produce excellent transmission, peak shape and abundance sensitivity



Log scale plot of 1ppm Y solution showing excellent peak shape and abundance sensitivity
- note no tailing at low or high mass

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Figure 46

Resolution and Abundance Sensitivity

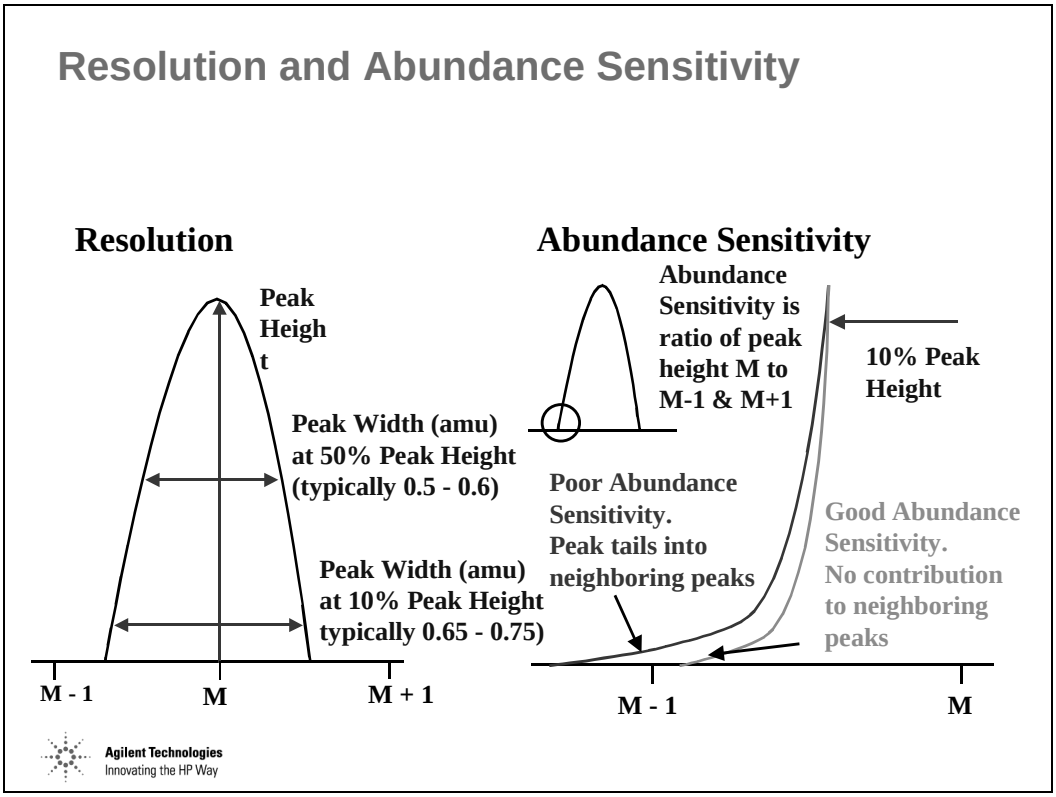
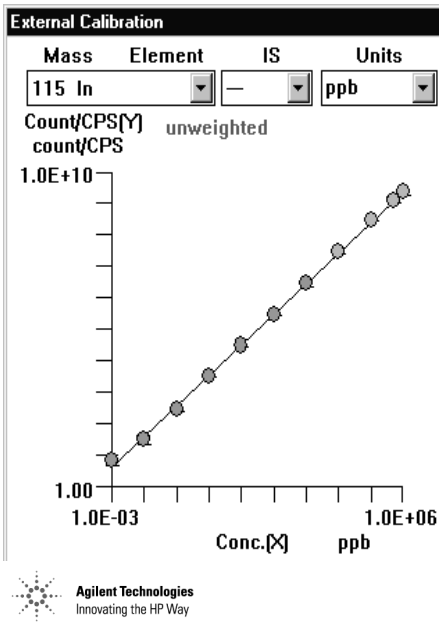
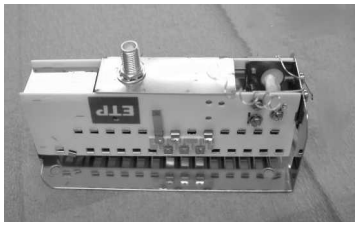


Figure 47

NEW Simultaneous Dual Mode Detector & High Speed Log Amplifier – True 9 Order Dynamic Range

NEW Simultaneous Dual Mode Detector & High Speed Log Amplifier - True 9 Order Dynamic Range





New true simultaneous detector - with extended 9 order dynamic range - largest in ICP-MS!

Agilent's unique new detection circuit means acquisition speed is not compromised when analyzing in analog mode

Pulse counting mode - min dwell time - 100usec
Analog mode - min dwell time - 100usec!

Transient signals such as those from a laser ablation pulse or chromatography can be measured over a wide dynamic range

Figure 48

The Detector

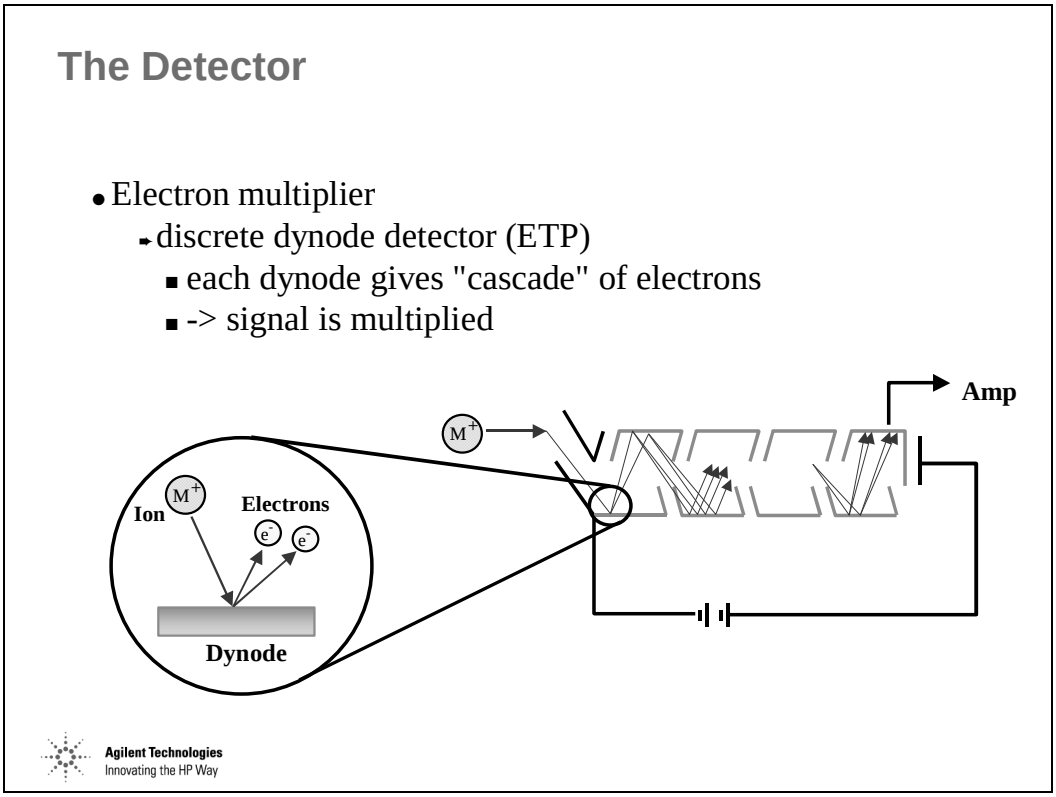


Figure 49

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Interferences in ICP-MS

Interferences in ICP-MS

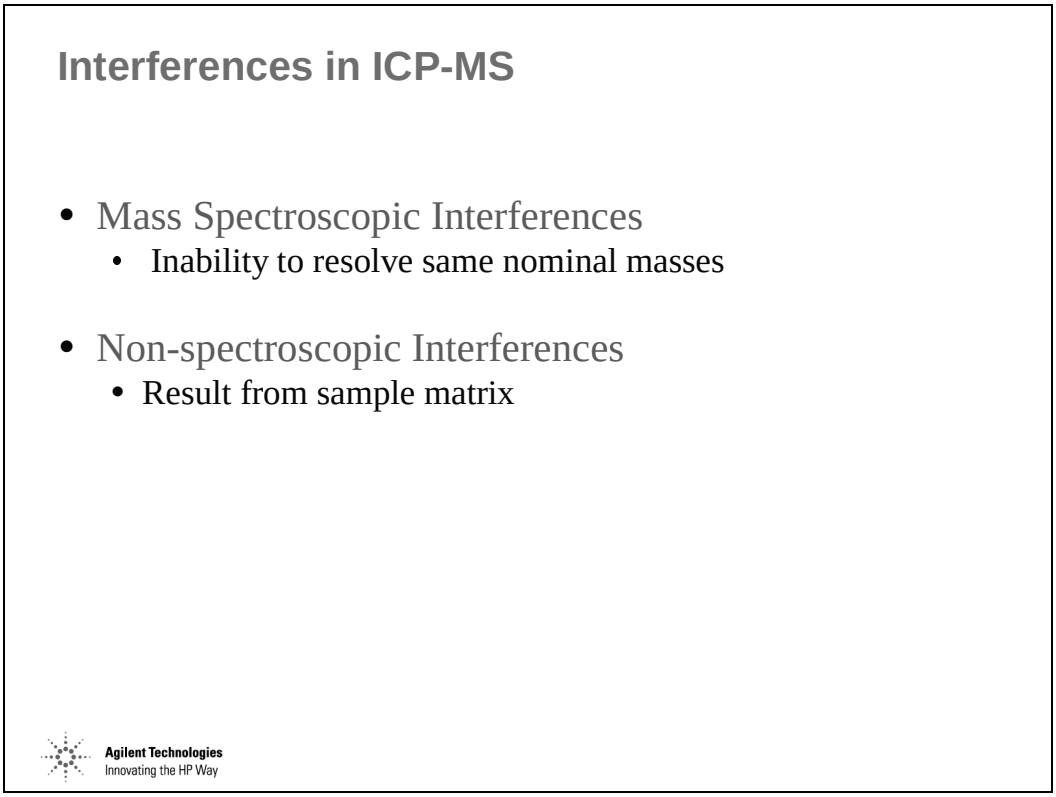

Figure 50

Mass Spectroscopic Interferences

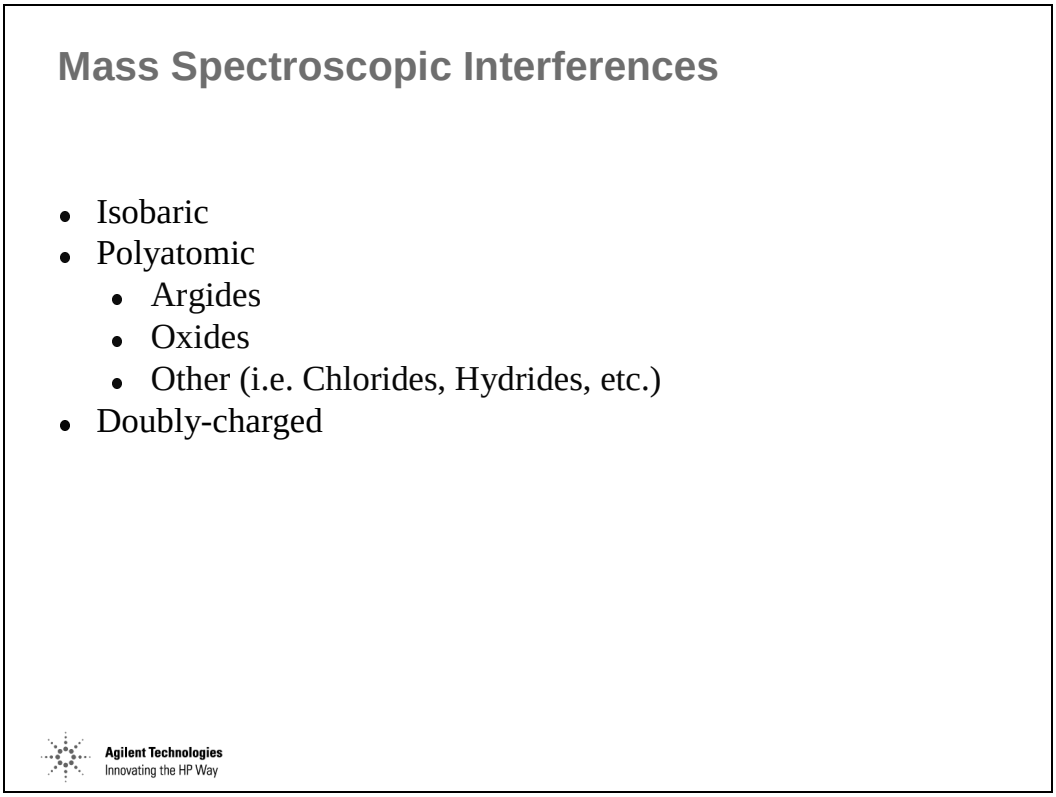

Figure 51

Isobaric Interferences

Isobaric Interferences

Isotopes	*AMU*	*% Abundance*
V	50	0.25
Ti	50	5.4
Cr	50	4.35
Zr	96	2.8
Ru	96	16.68
Mo	96	5.52
Ba	138	71.7
La	138	0.09
Ce	138	0.25

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Figure 52

Polyatomic Interferences

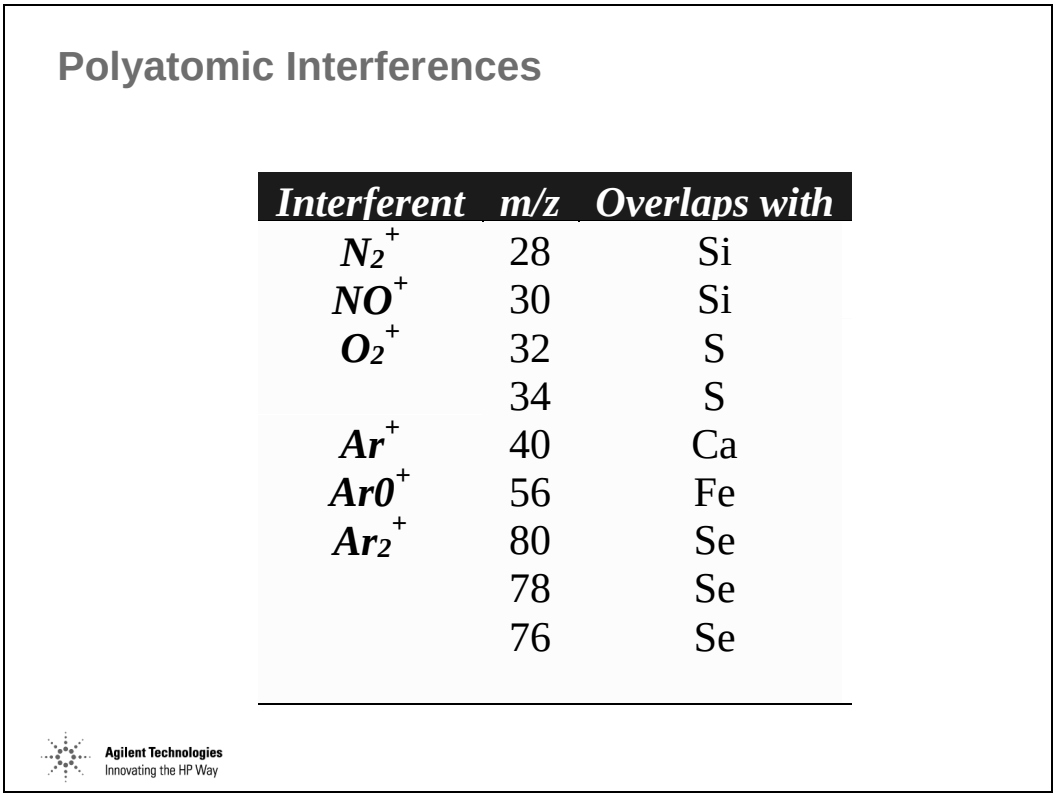


Figure 53

Mass Spectroscopic Interferences

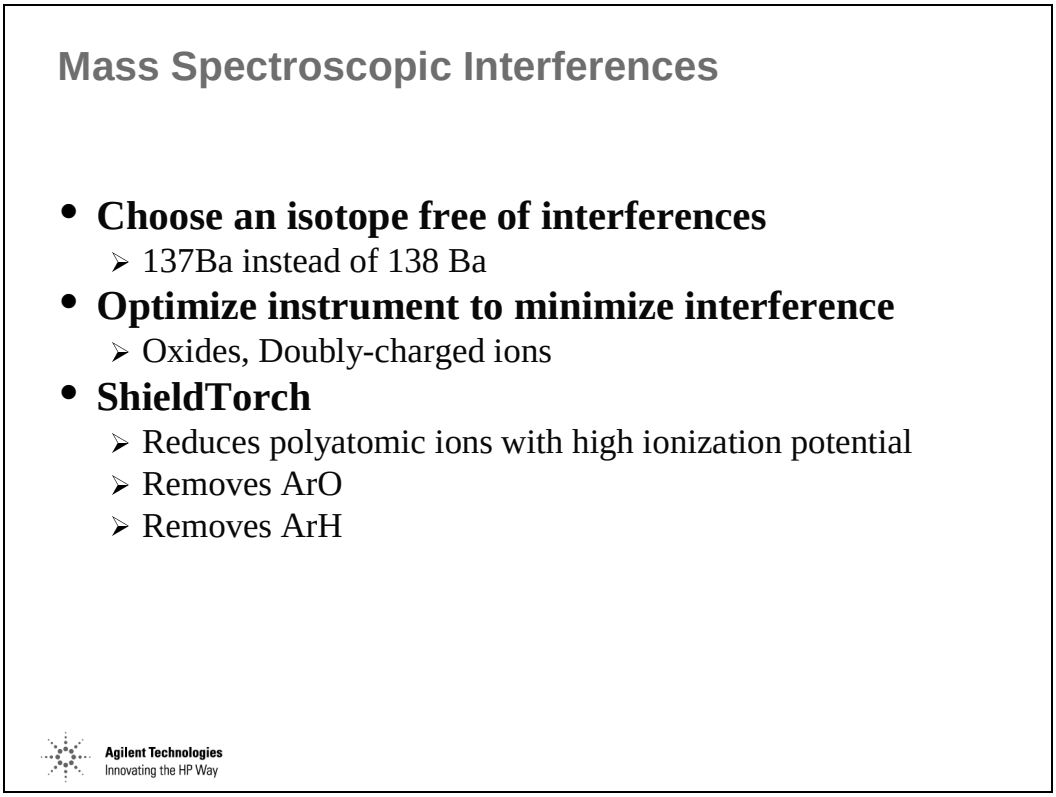


Figure 54

Optimizing to Minimize Interference Formation in the Plasma [1]

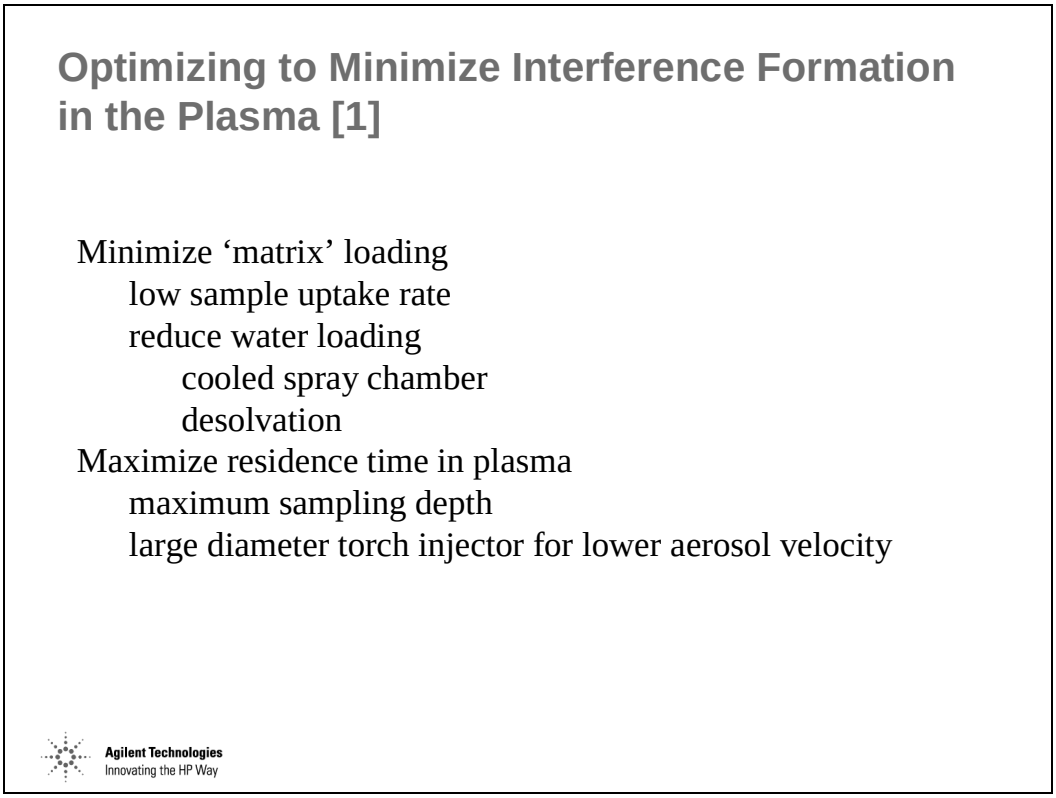


Figure 55

Optimizing to Minimize Interference Formation in the Plasma [2]

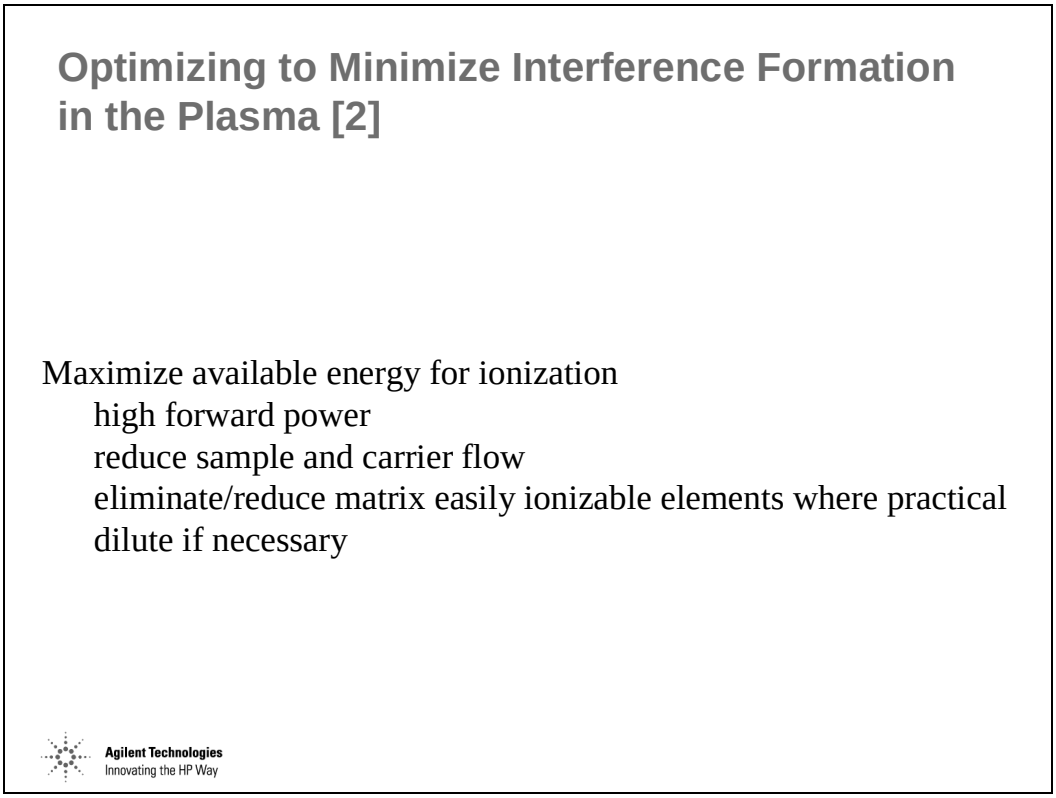


Figure 56

Optimizing to Minimize Interference Formation in the Plasma [3]

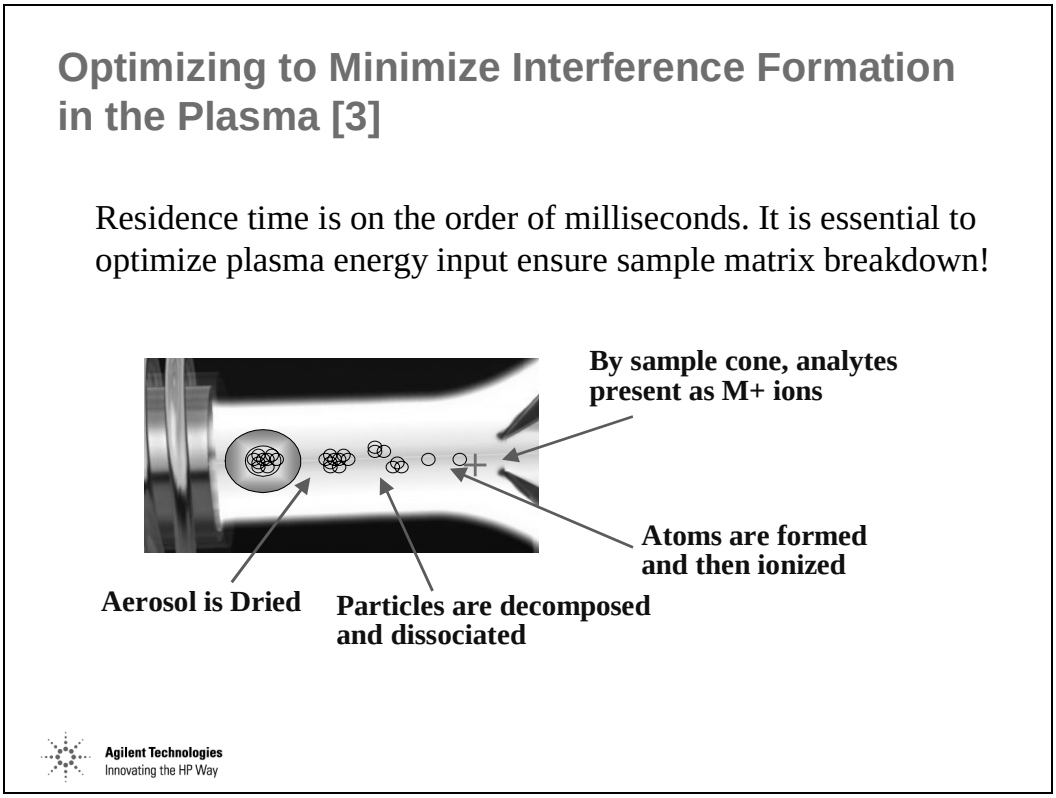


Figure 57

Effect of Plasma Temperature on Degree of Ionization

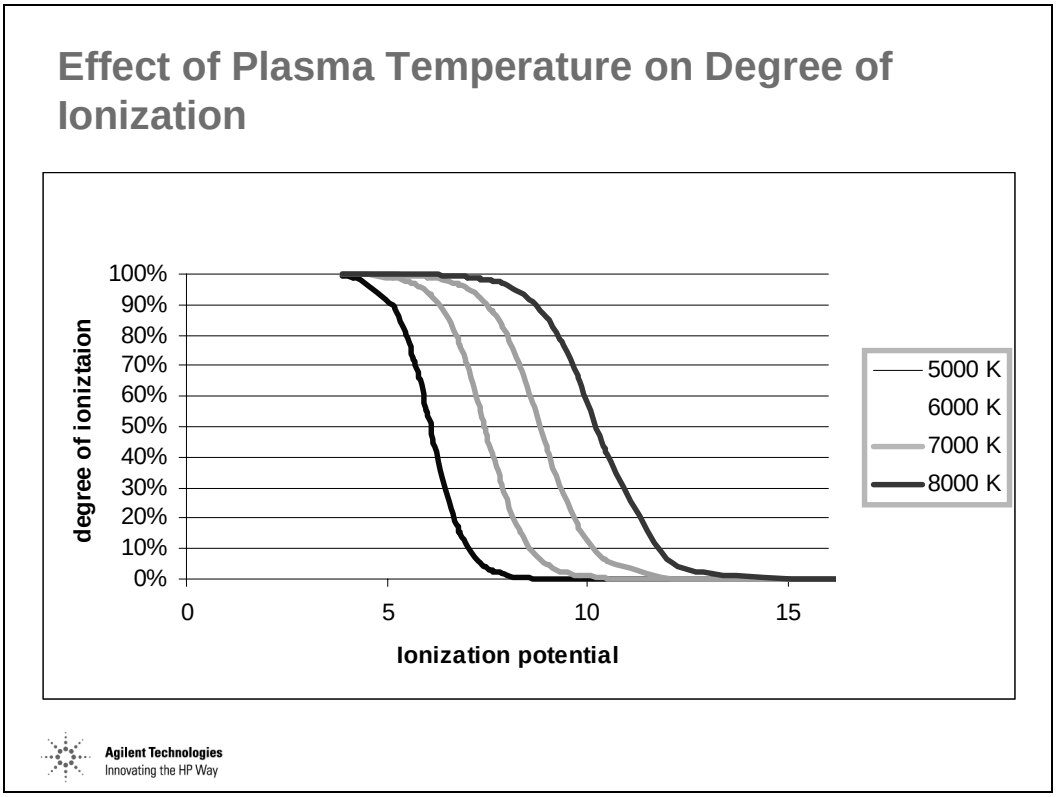


Figure 58

Efficient Aerosol Decomposition

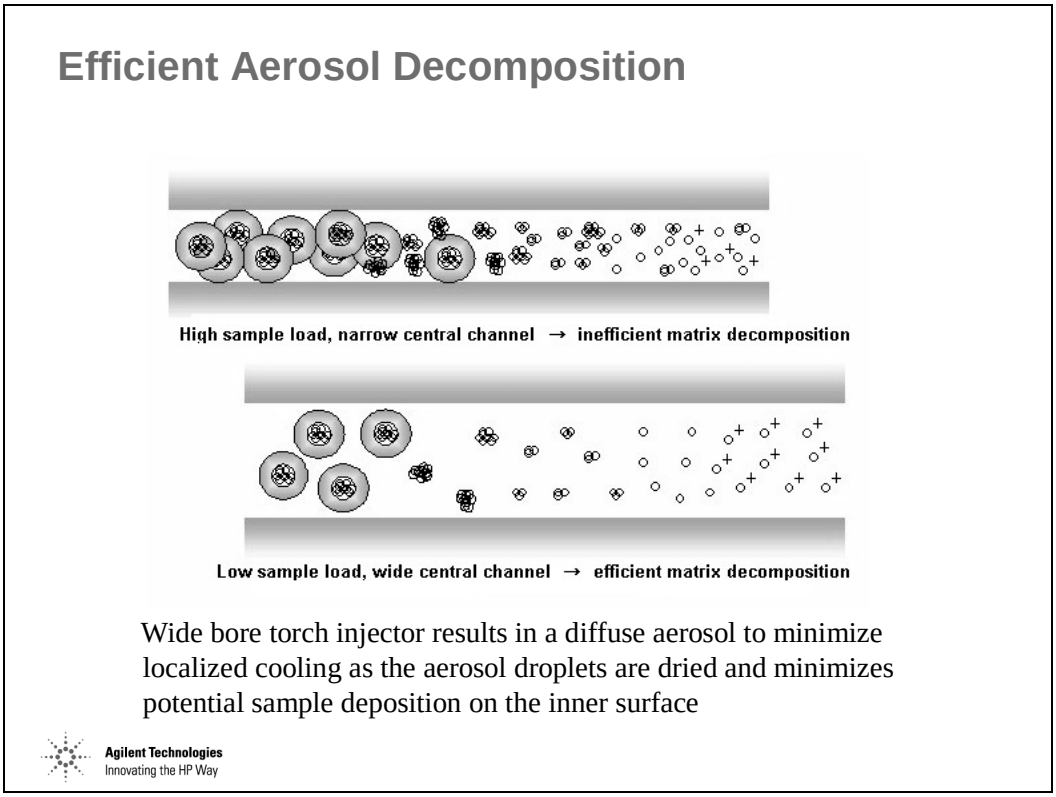


Figure 59

Oxides and Doubly Charged Ions

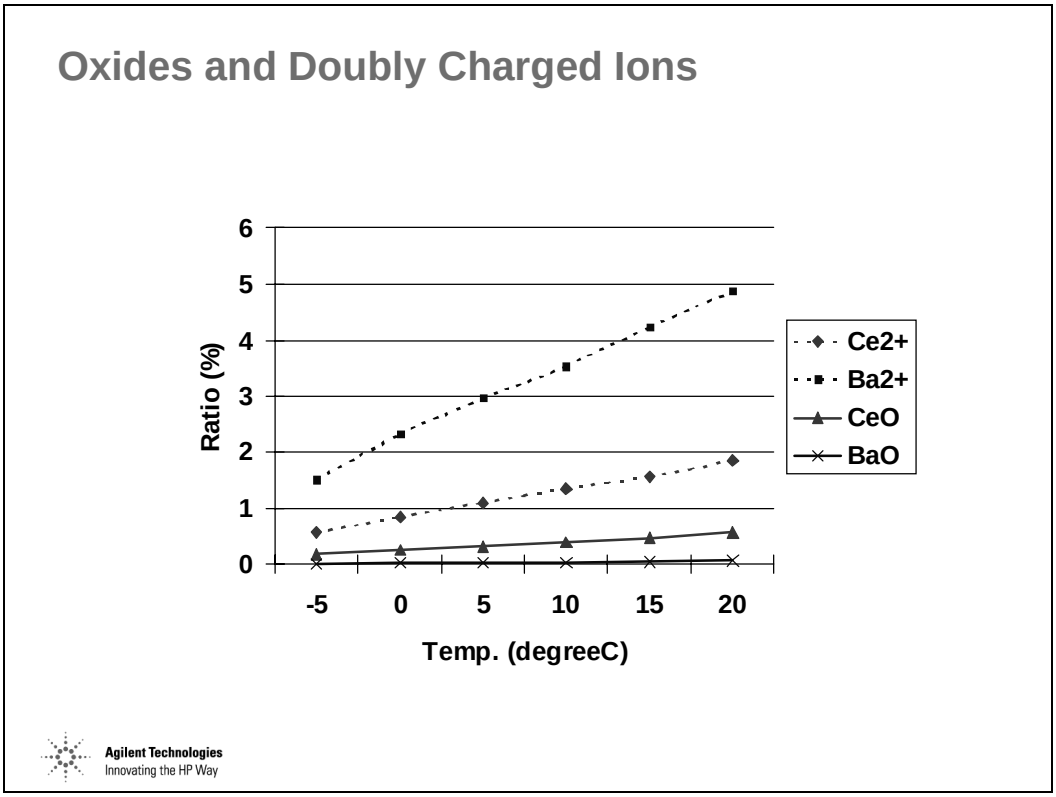


Figure 60

Dealing with Mass Spectroscopic Interferences

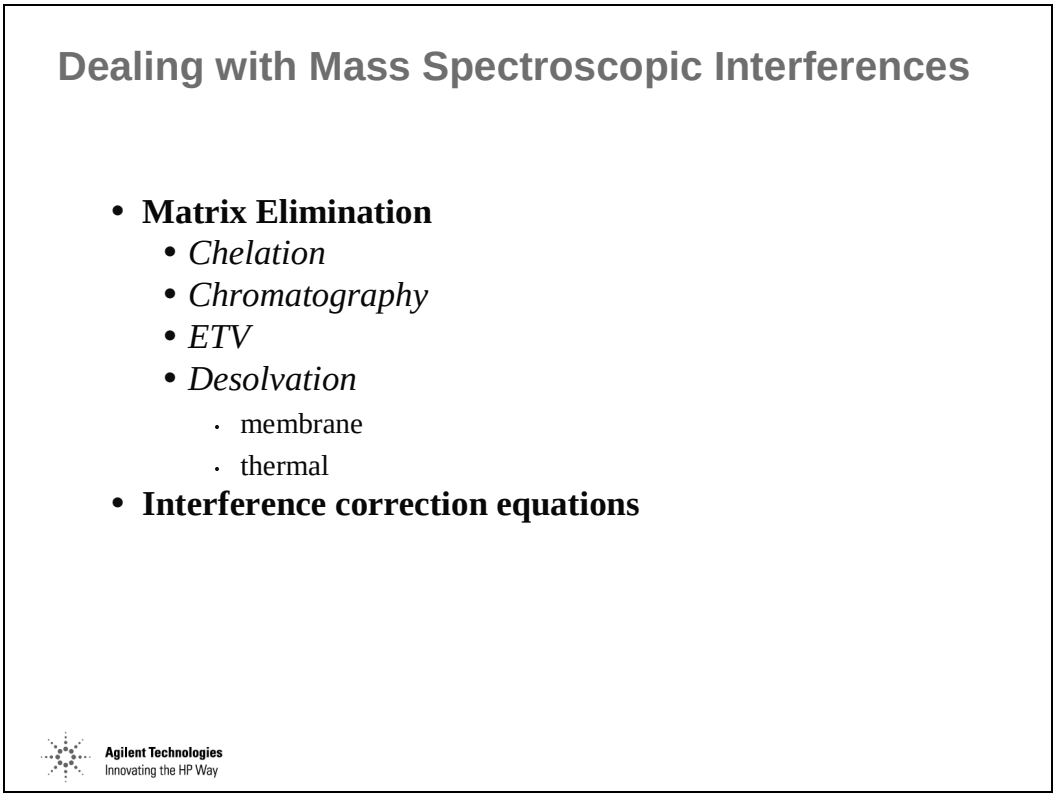


Figure 61

Interference Equations

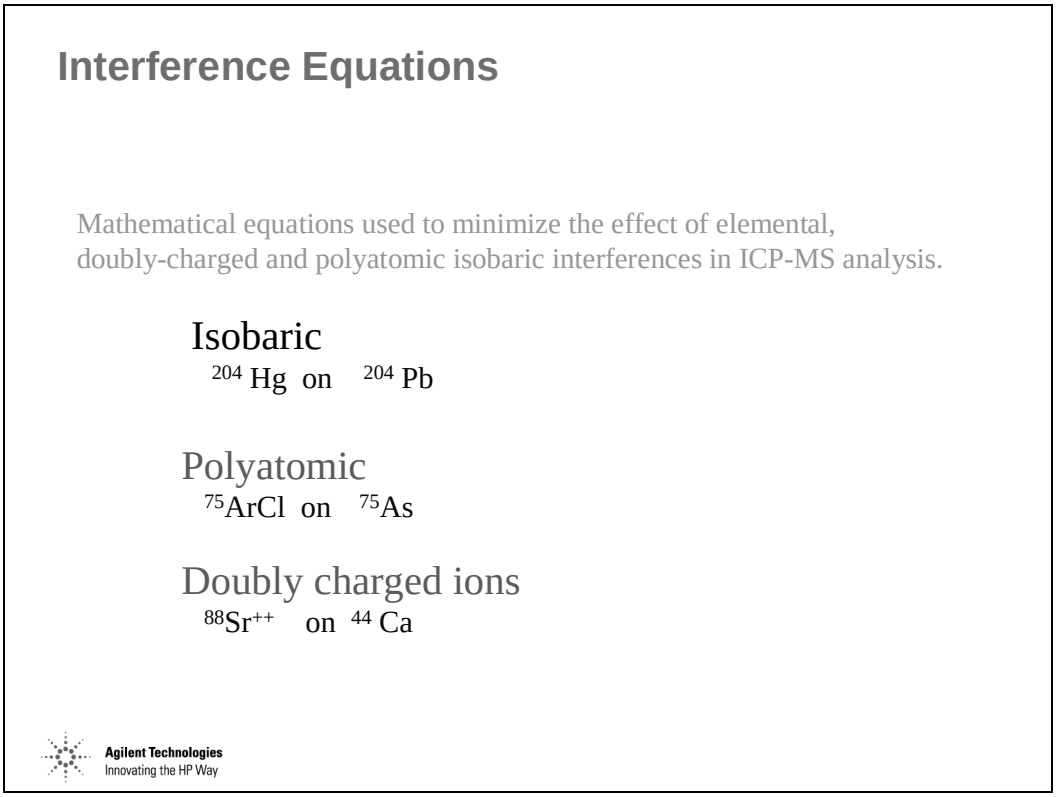
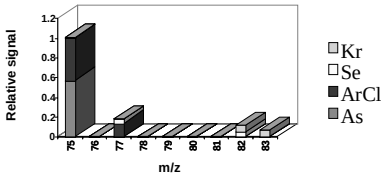


Figure 62

As Interference Correction

As interference Correction



$^{75}As = {}^{75}M - \{ {}^{77}ArCl ({}^{35}Cl \text{ abundance} / {}^{37}Cl \text{ abundance}) \}$
$^{75}As = {}^{75}M - \{ {}^{77}ArCl (3.127) \}$ (1)

But there is Se at m/z 77...

$^{77}ArCl = {}^{77}M - \{ {}^{82}Se ({}^{77}Se \text{ abundance} / {}^{82}Se \text{ abundance}) \}$
$^{77}ArCl = {}^{77}M - \{ {}^{82}Se (0.874) \}$ (2)

So equation 1 and 2 becomes:

$^{75}As = {}^{75}M - \{[{}^{77}M - \{ {}^{82}Se (0.874)\}] (3.127)\}$

$^{75}As = {}^{75}M - {}^{77}M(3.127) + {}^{82}Se(2.733)$ (3)

But, there is Krypton at 82…

$^{82}Se = {}^{82}M - \{ {}^{83}Kr ({}^{82}Kr \text{ abundance} / \text{abundance } {}^{83}Kr) \}$
$^{82}Se = {}^{82}M - \{ {}^{83}Kr (1.009) \}$ (4)

So equation 3 and 4 becomes:

$^{75}As = {}^{75}M - {}^{77}M(3.127) + \{[{}^{82}M - \{{}^{83}Kr (1.009)\}](2.733)\}$

$^{75}As = {}^{75}M - {}^{77}M(3.127) + {}^{82}M(2.733) - {}^{83}M(2.757)$

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Figure 63

Interference Correction Equations - Agilent 7500

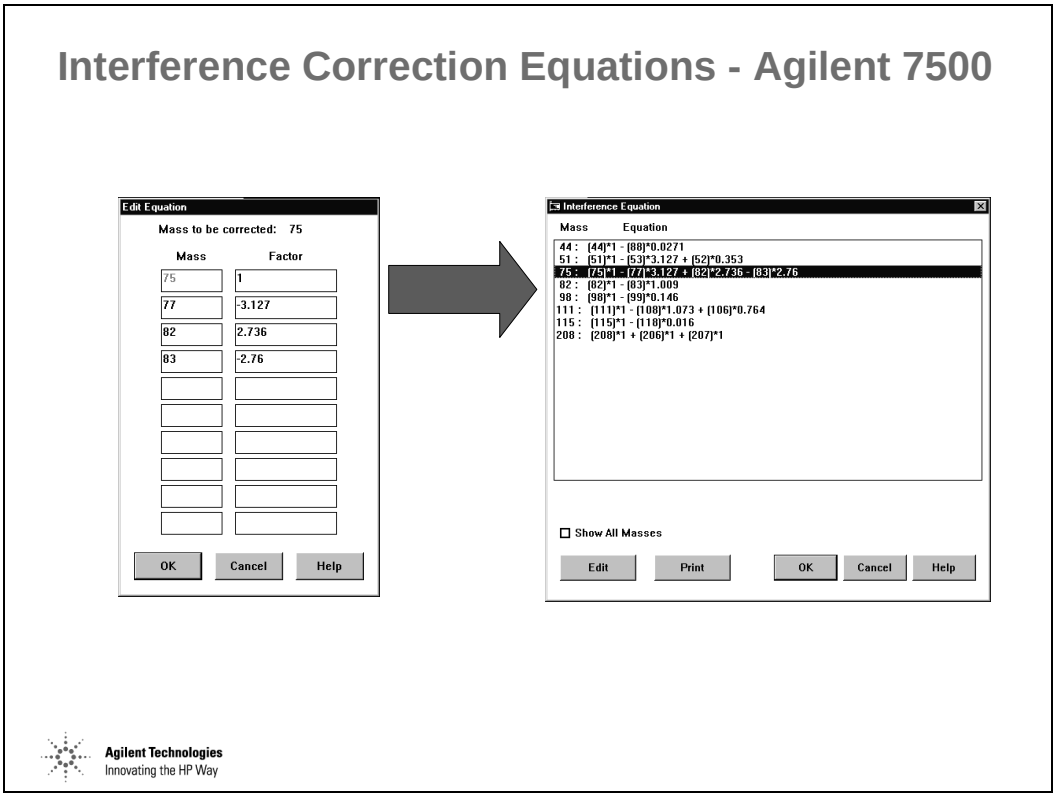

Figure 64

Interference equations are edited from Top >> Methods >> Edit Interference Equation… or from Edit Entire Method.

Equations must be simplified and terms combined before entering them into the Edit Interference Equation dialog box.

The actual values are stored within the method folder as ‘correct.icp’, a text file which can be directly edited if desired.

Non-Spectroscopic Interferences

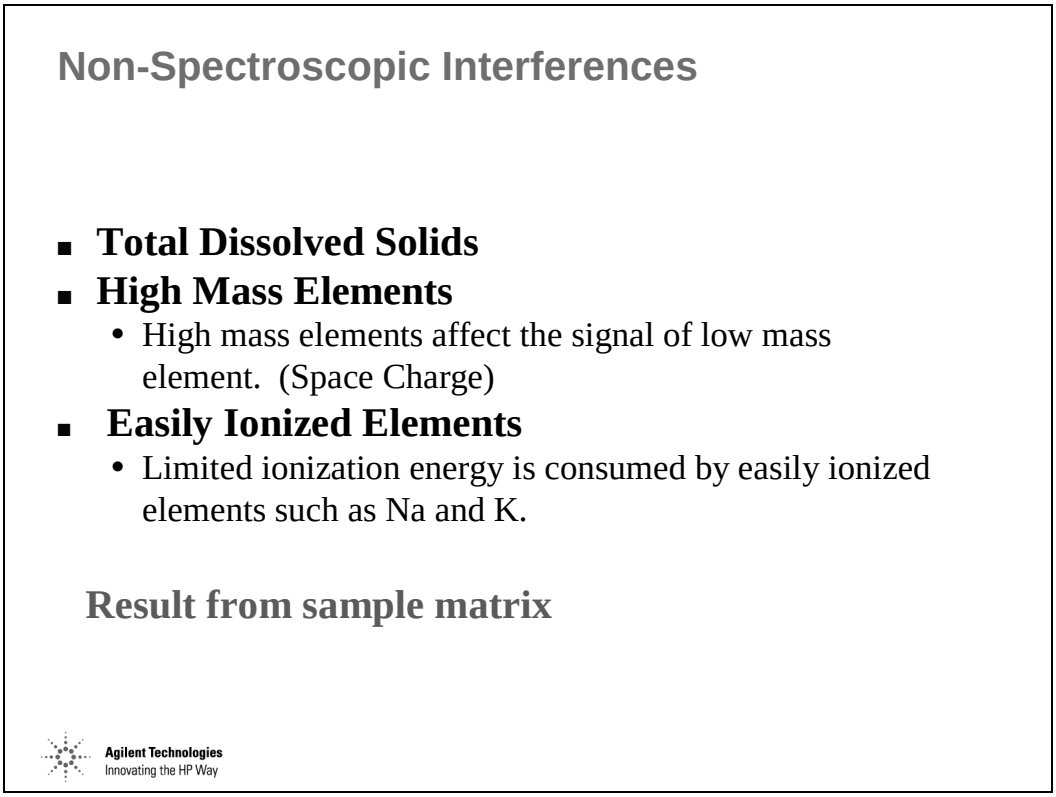

Figure 65

Effect of High Dissolved Solids

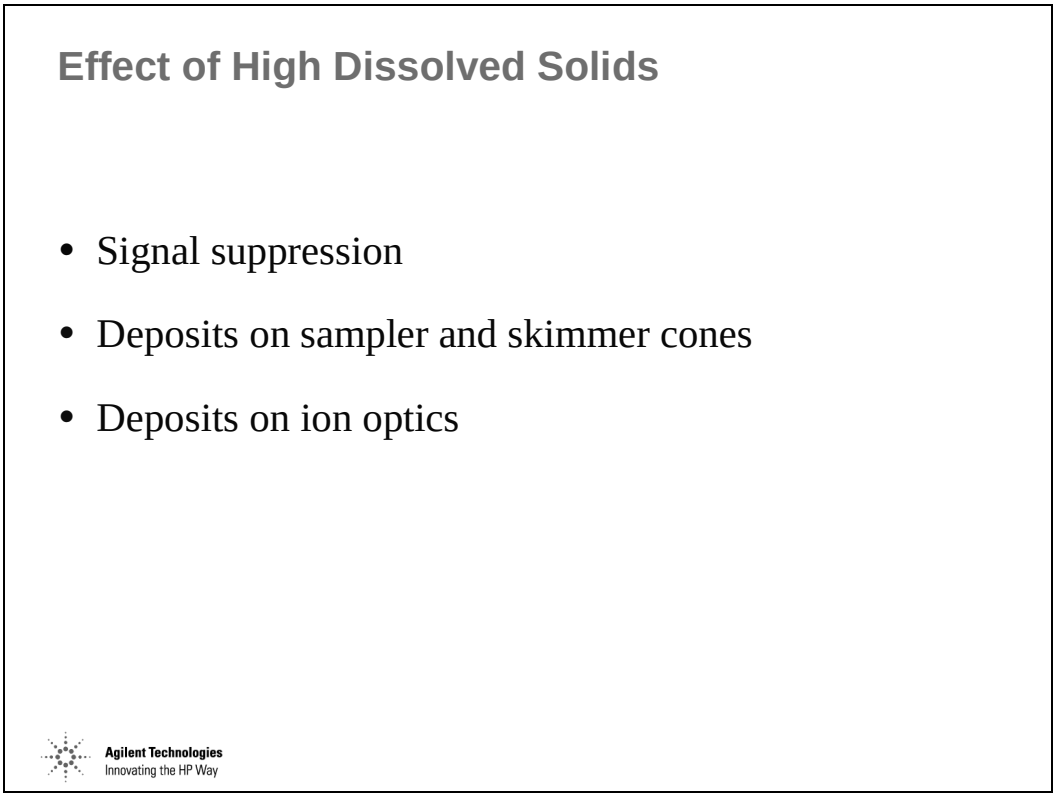

Figure 66

First Ionization Potential

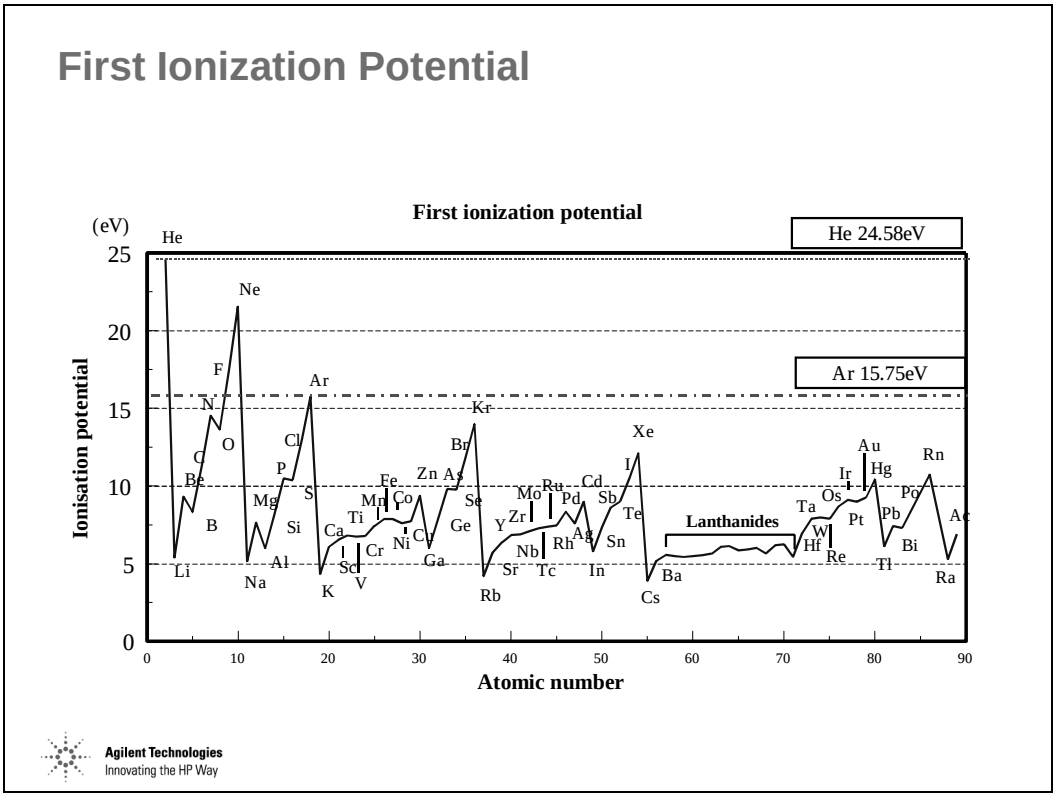

Figure 67

Ionization Efficiency

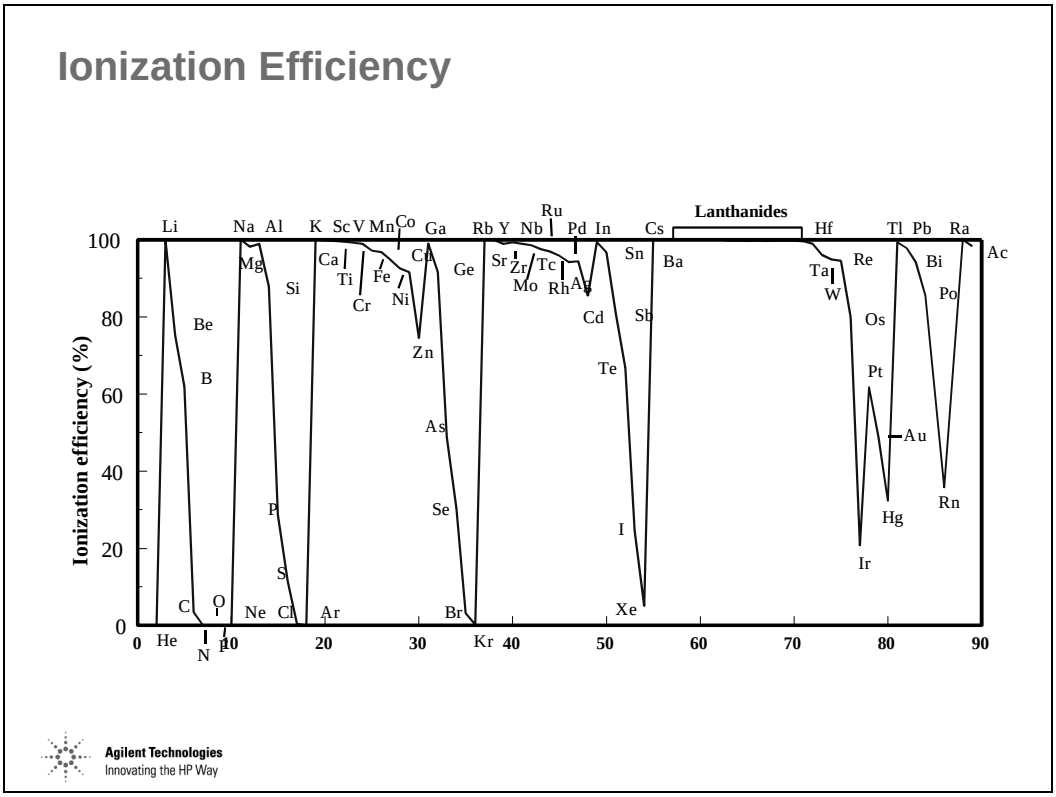

Figure 68

Signal Suppression

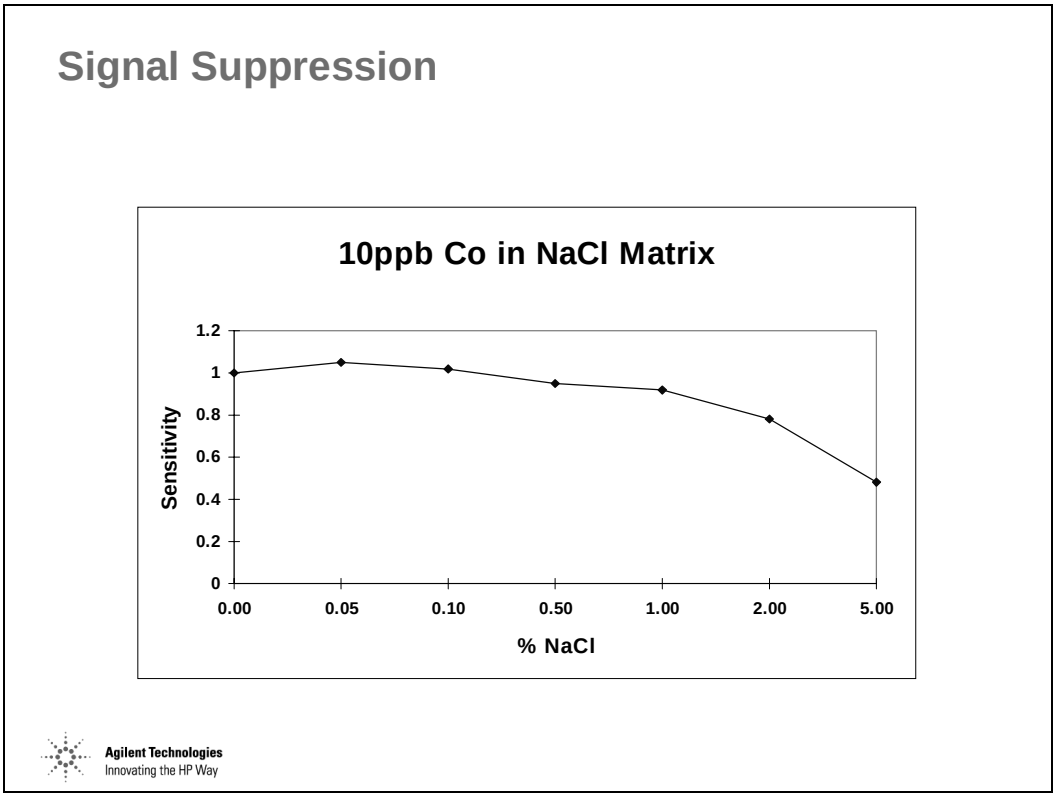

Figure 69

Matrix Effects – On Low Mass Analyte

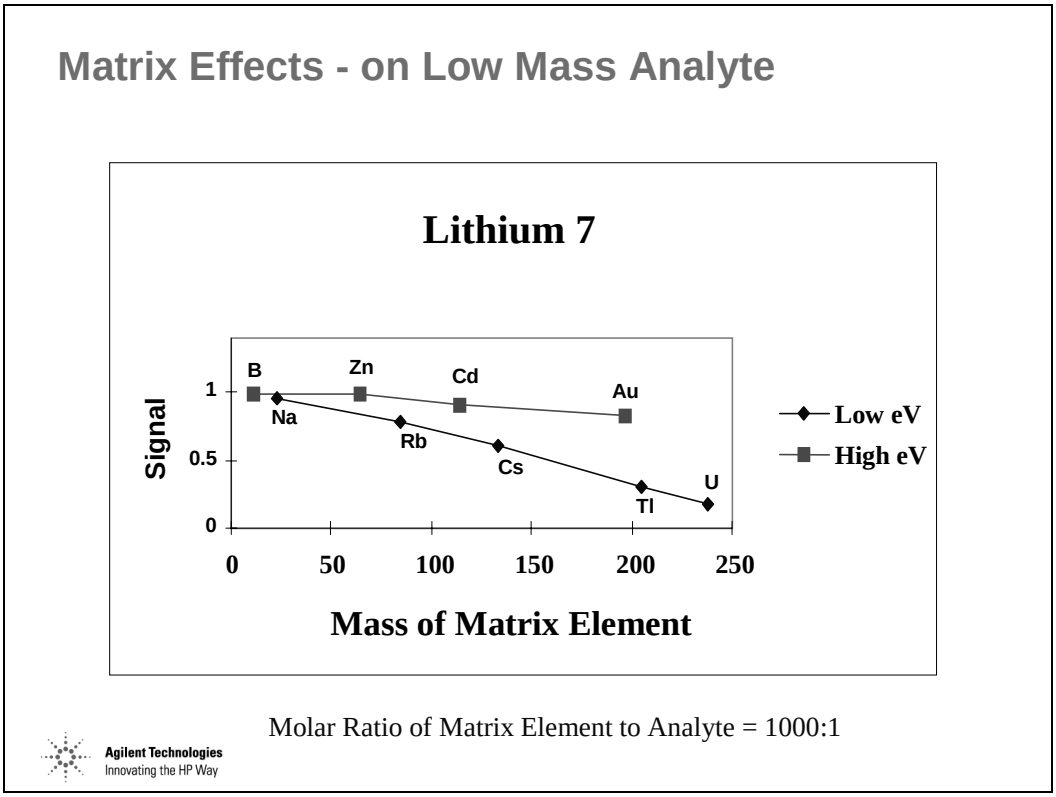

Figure 70

Matrix Effects – On Medium Mass Analyte

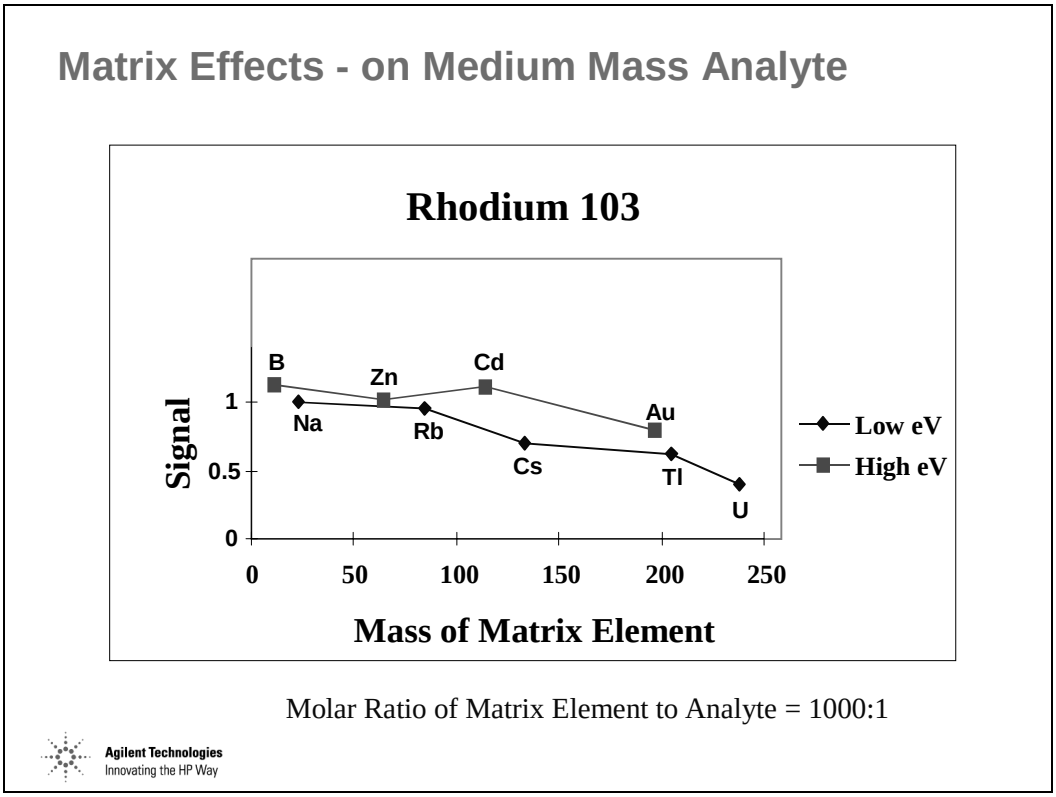

Figure 71

Matrix Effects – On High Mass Analyte

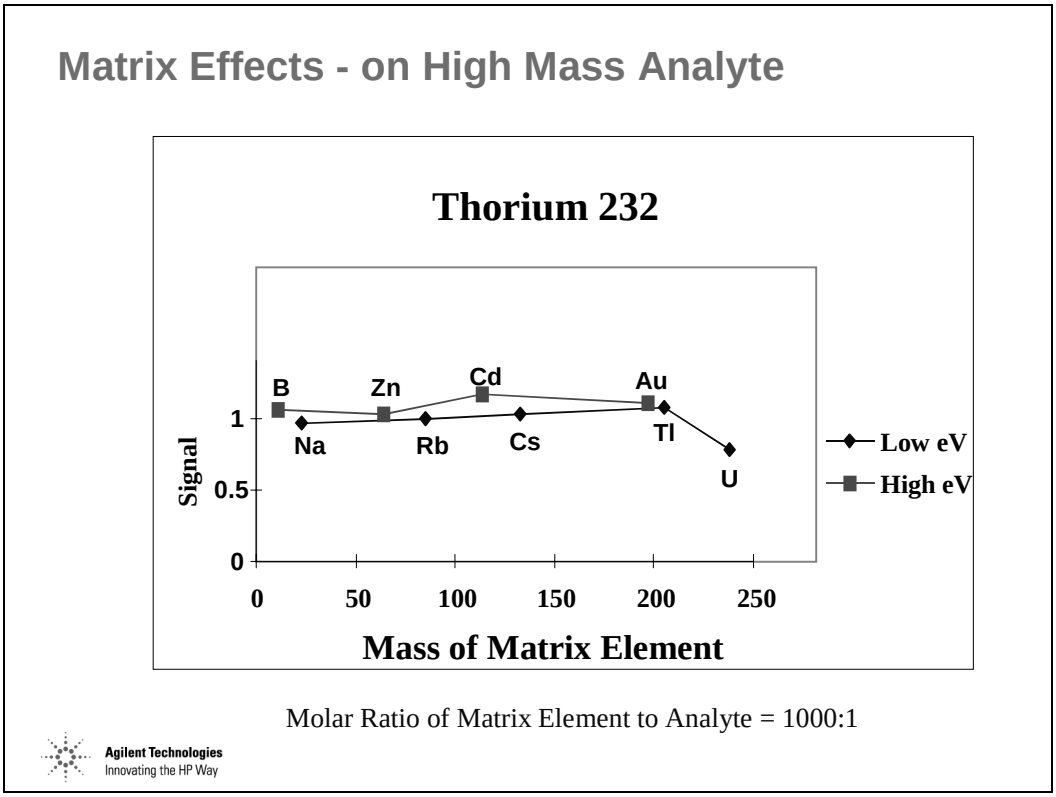

Figure 72

Space Charge Interface and Lens Region

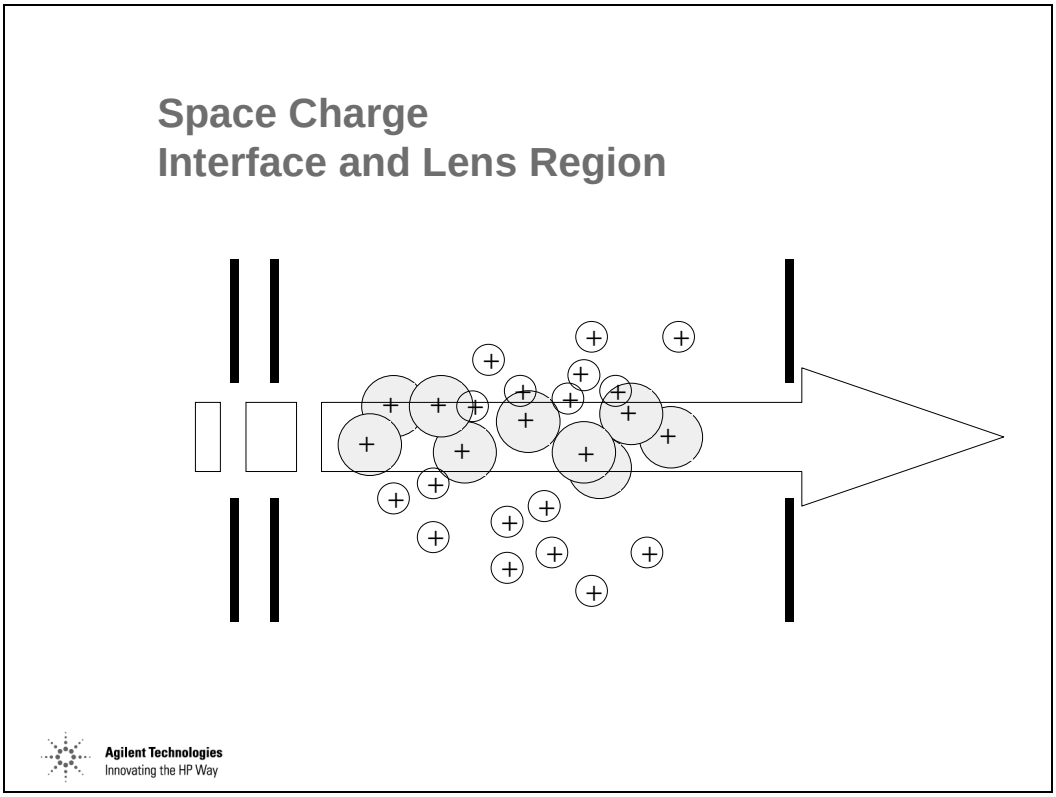

Figure 73

After Extraction Lenses, Ion beam is predominantly positive charged.

Strong repulsive forces exist within the ion beam which affect low mass ions much more than high mass ions tending to disperse the low mass portion of the ion beam. Uncontrolled, space charge results in loss of low mass sensitivity, especially in the presence of high mass matrix. Complex, multi-element ion optics can compensate for this effect.

Ionization Suppression Plasma Region

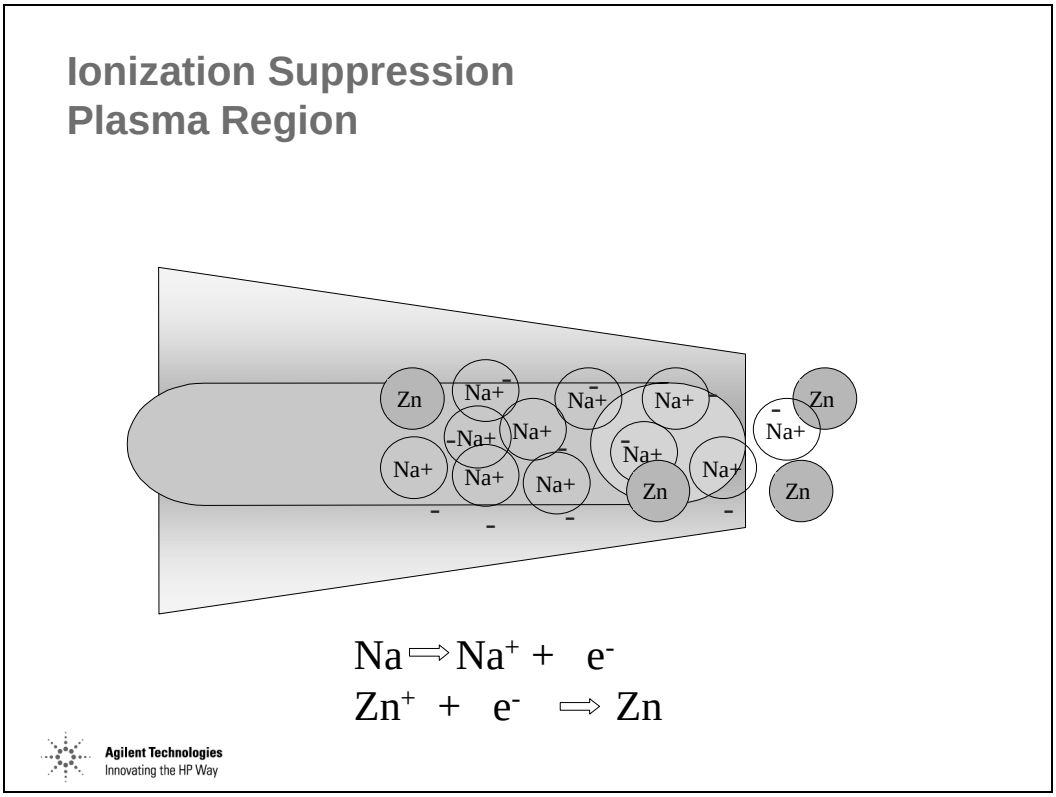

Figure 74

What Can Be Done About Matrix Effects

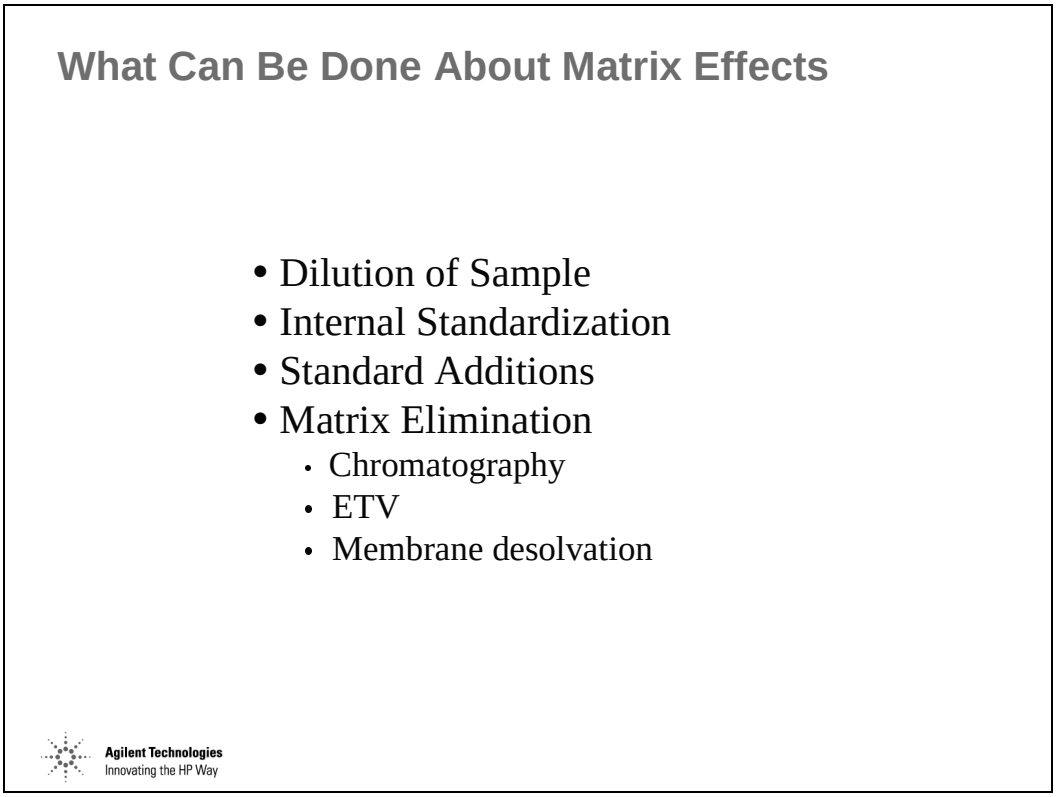

Figure 75

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Tuning the Agilent 7500

Why Tune the ICP-MS?

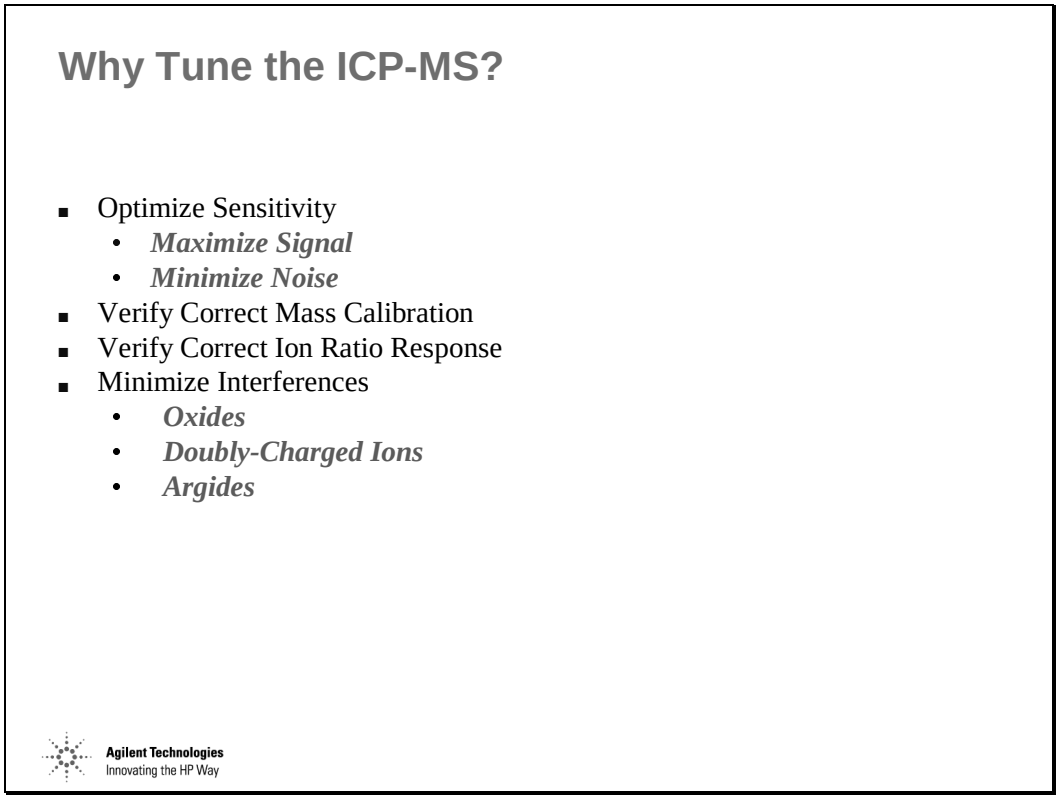


Figure 76

Tuning Procedure Overview

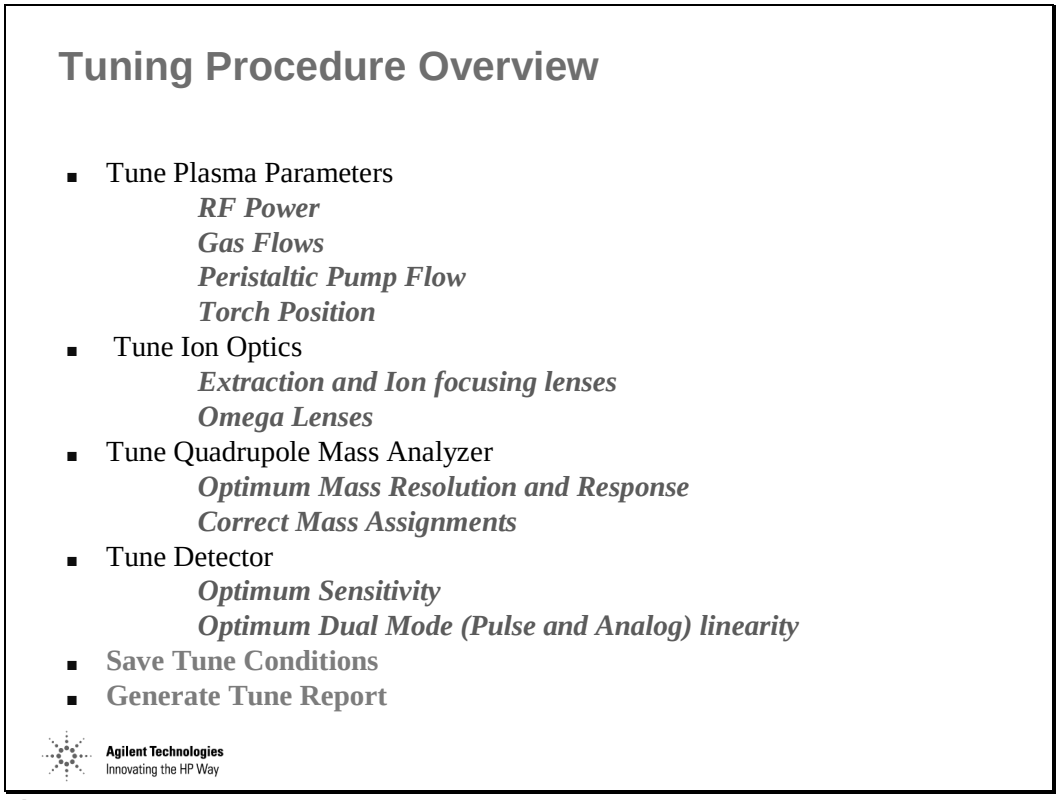


Figure 77

Agilent 7500 ICP-MS Manual Tune Checklist [1]

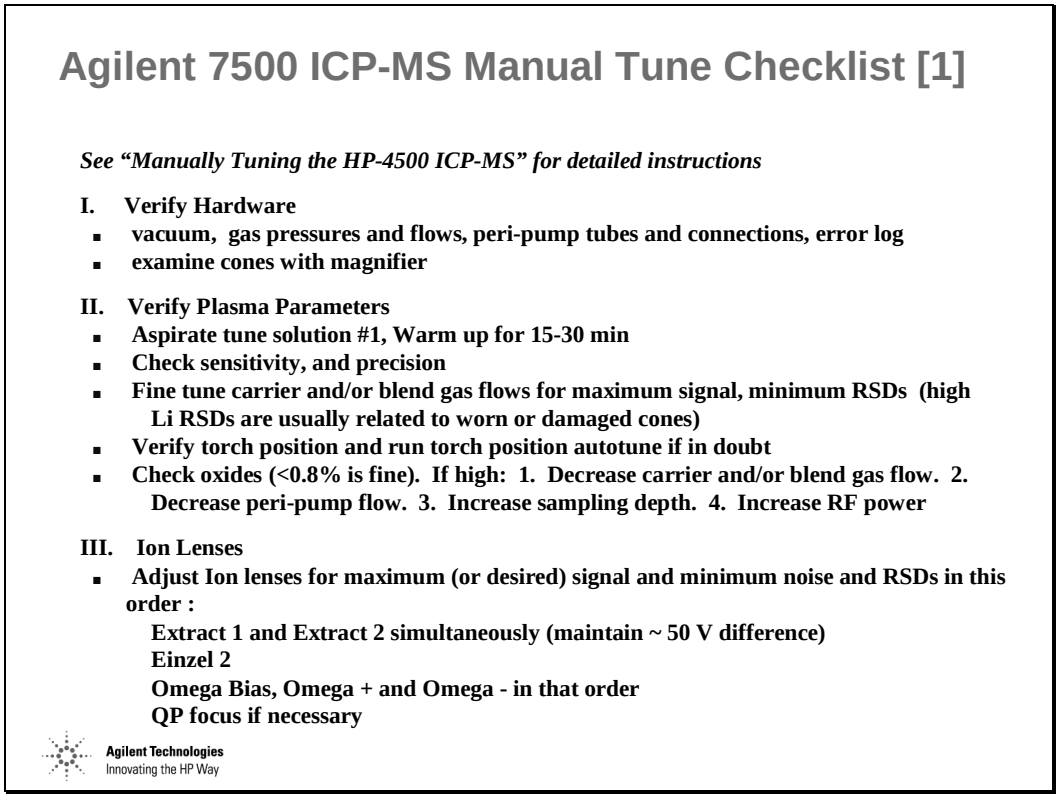


Figure 78

Agilent 7500 ICP-MS Manual Tune Checklist [2]

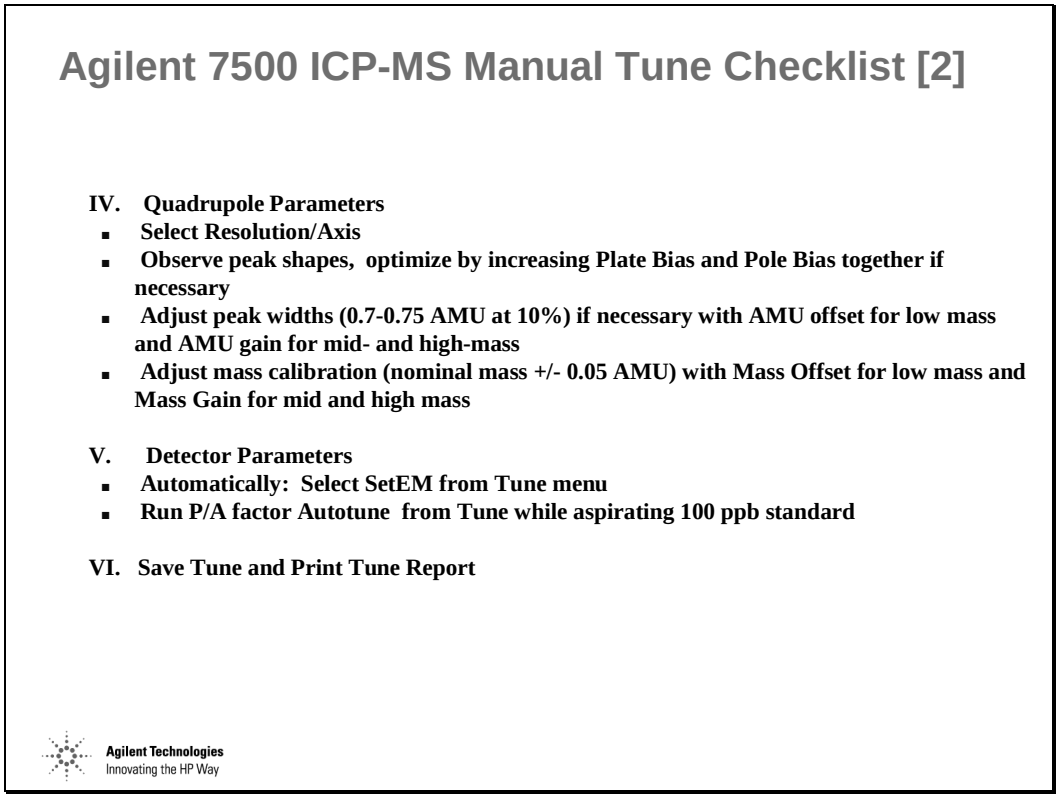


Figure 79

Autotune Screen

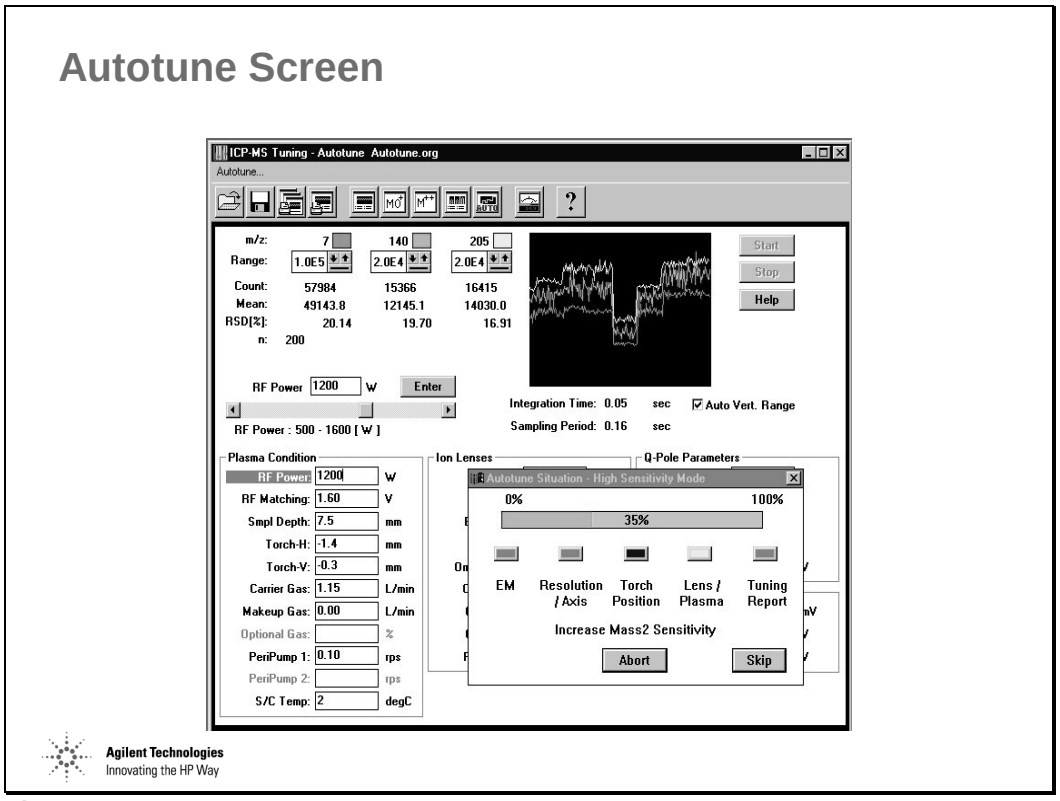


Figure 80

Full Autotune should normally only be used when manually tuning the instrument is unsuccessful. Most adjustments can be made more easily and quickly manually. Exceptions are Torch Position, SetEM, Axis and Resolution, and PA factor setting.

Setting realistic tune targets will increase the probability of a successful autotune and speed up the process.

Setting appropriate and relatively narrow parameter ranges will result in faster and more consistent autotunes

Autotuning of ICP Torch Position and New Target Tune

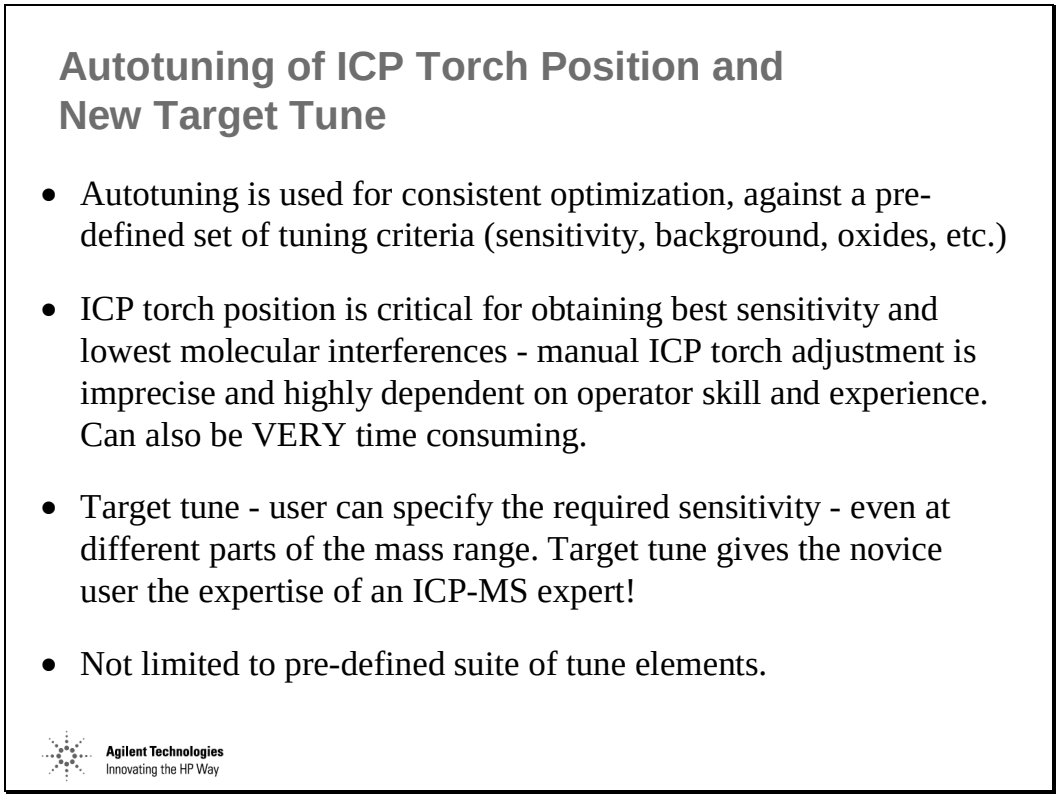


Figure 81

Features of Autotune (1)

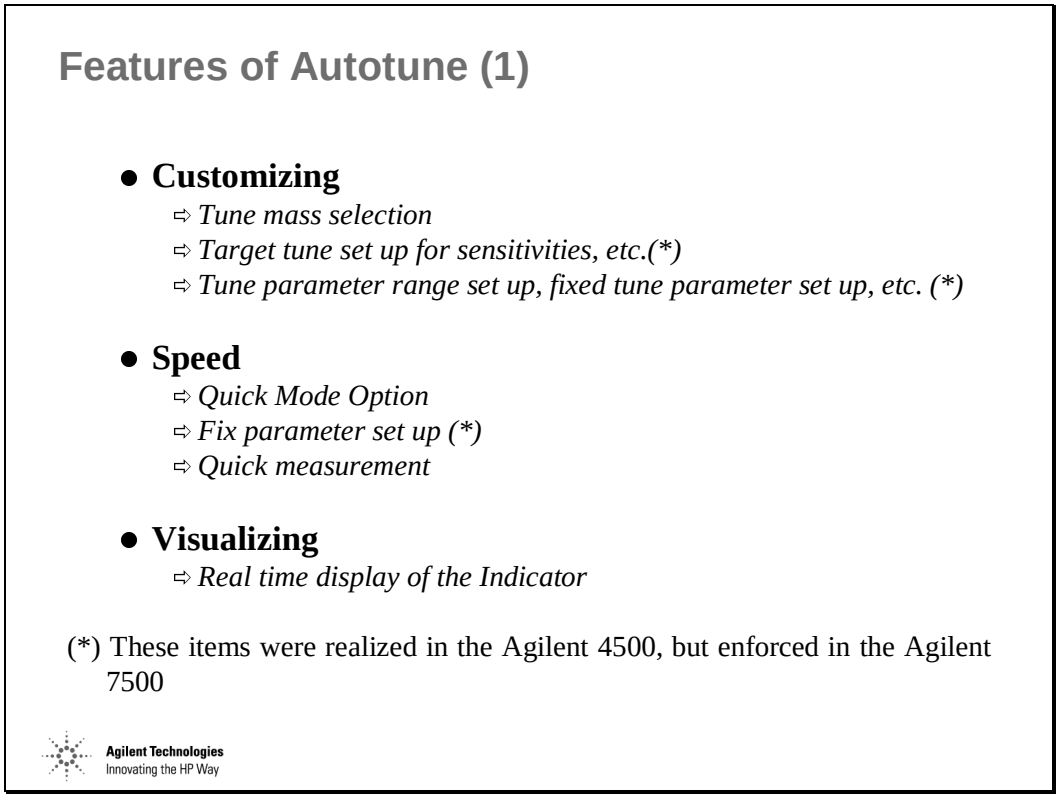


Figure 82

Features of Autotune (2)

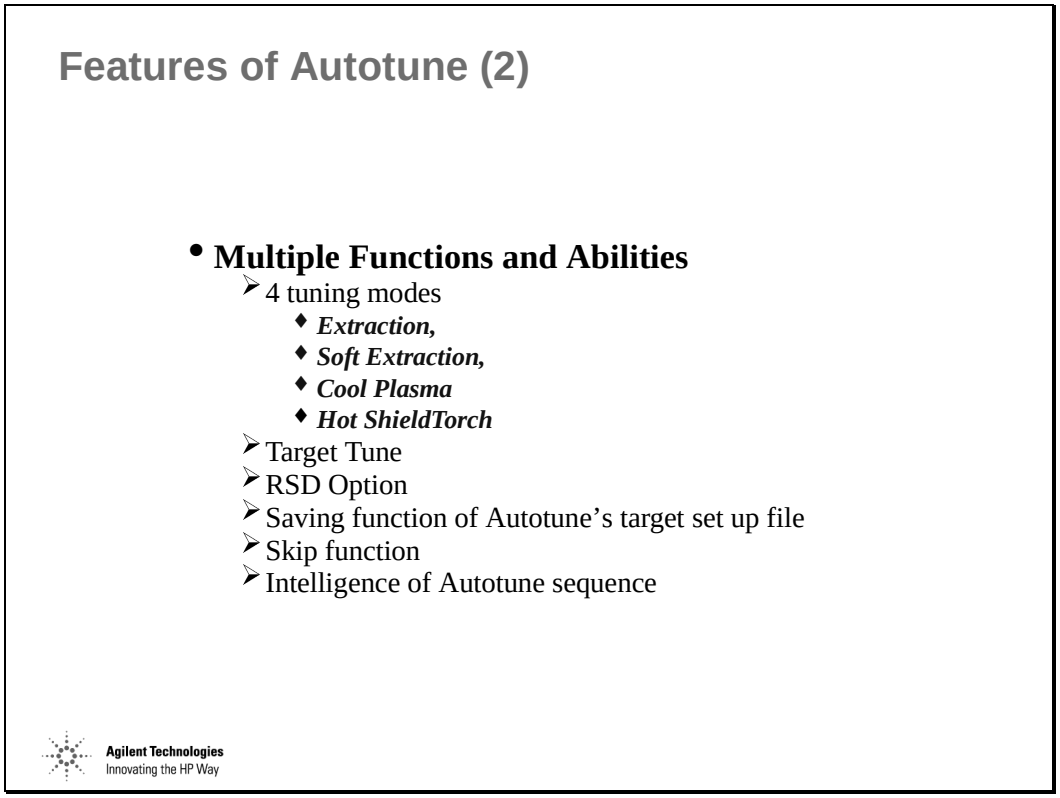


Figure 83

Choosing the Autotune Mode

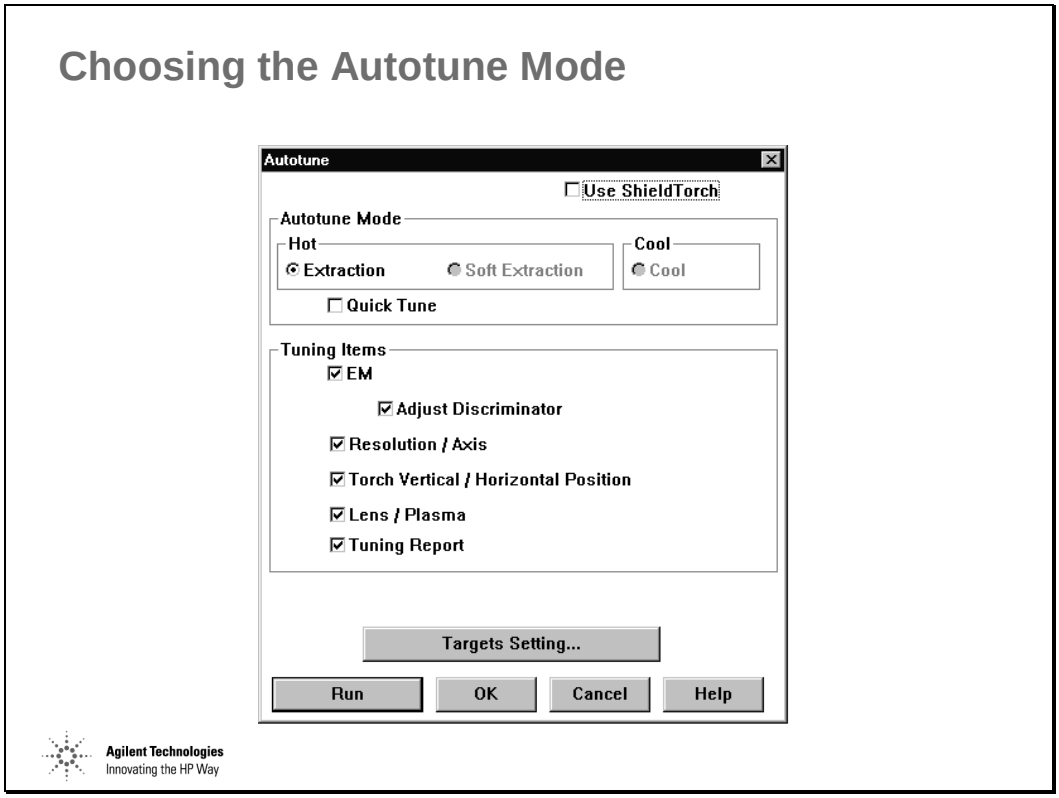


Figure 84

Basics of the Soft Extraction Mode

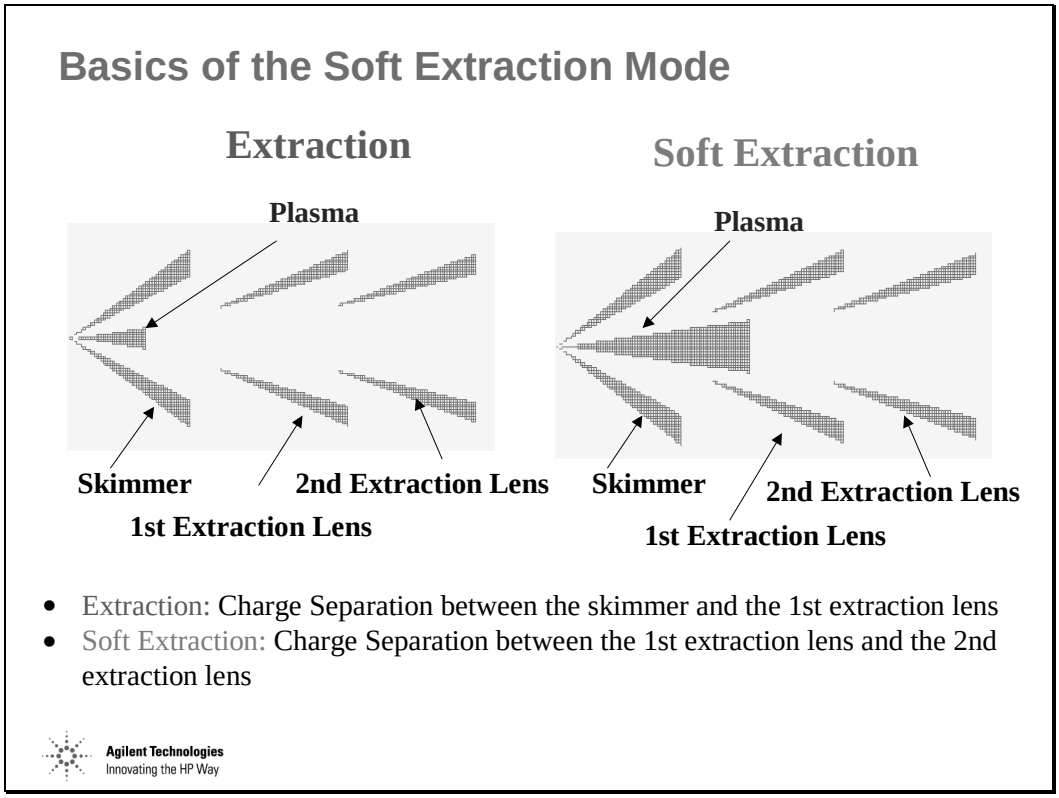


Figure 85

Comparison of Extraction Modes Settings

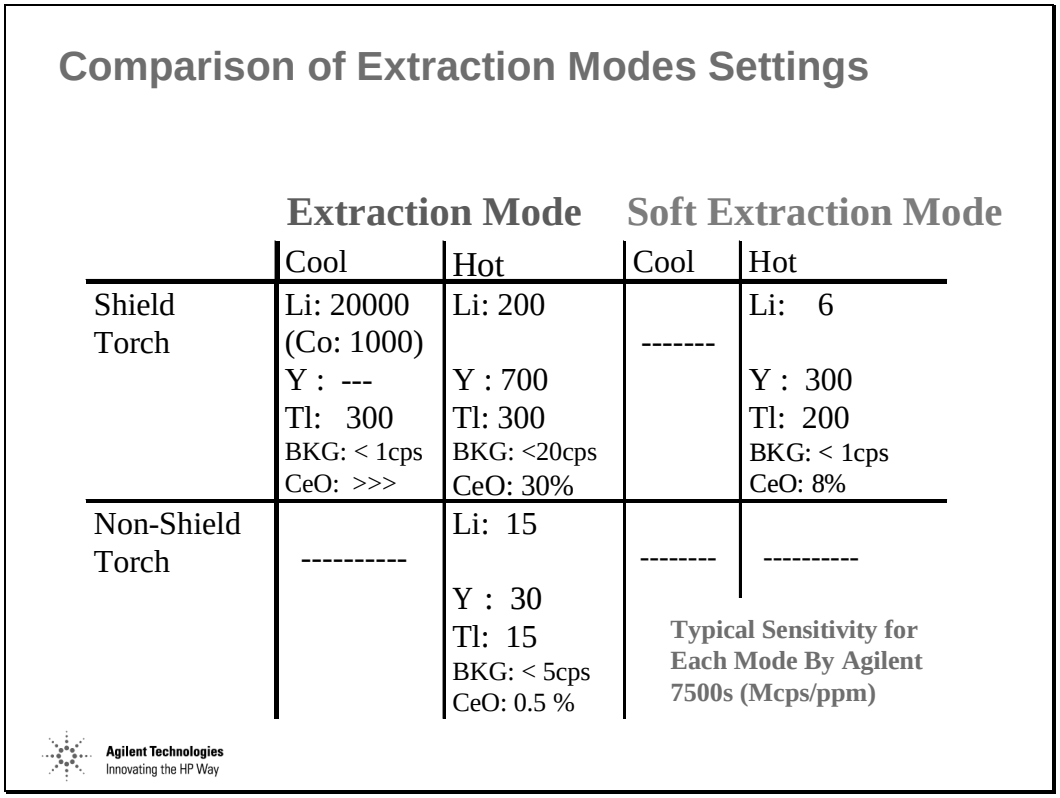


Figure 86

Autotune - Target Setting

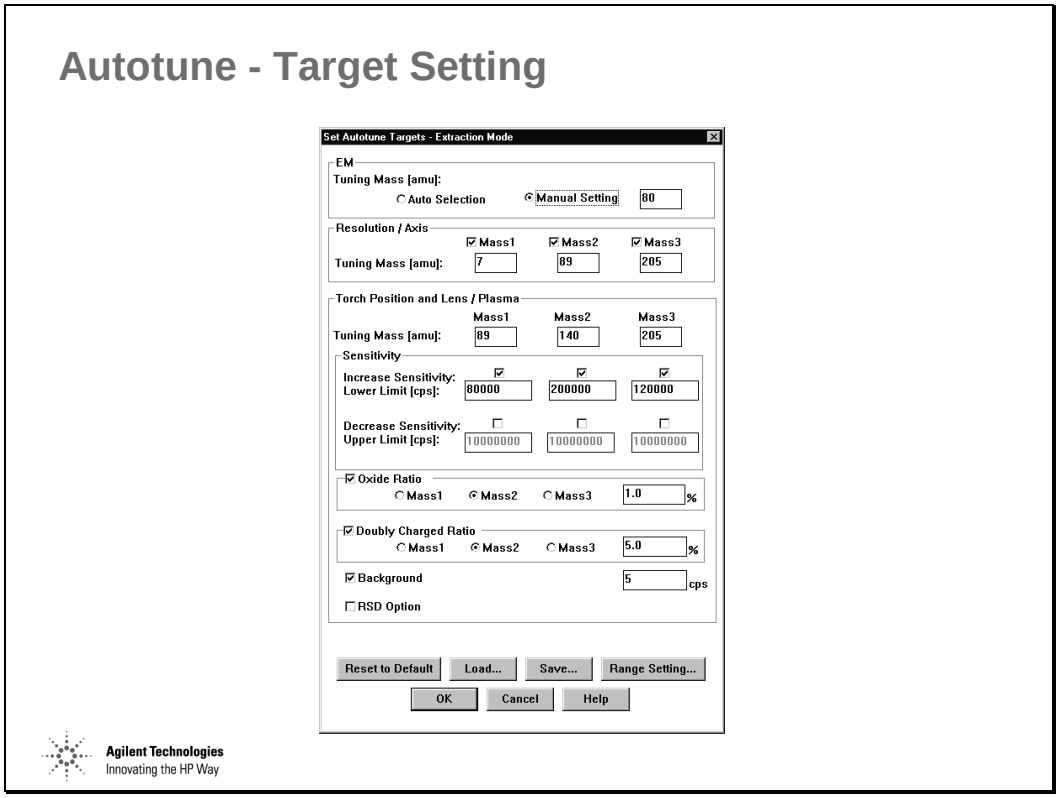


Figure 87

Target Setting - Range Setting

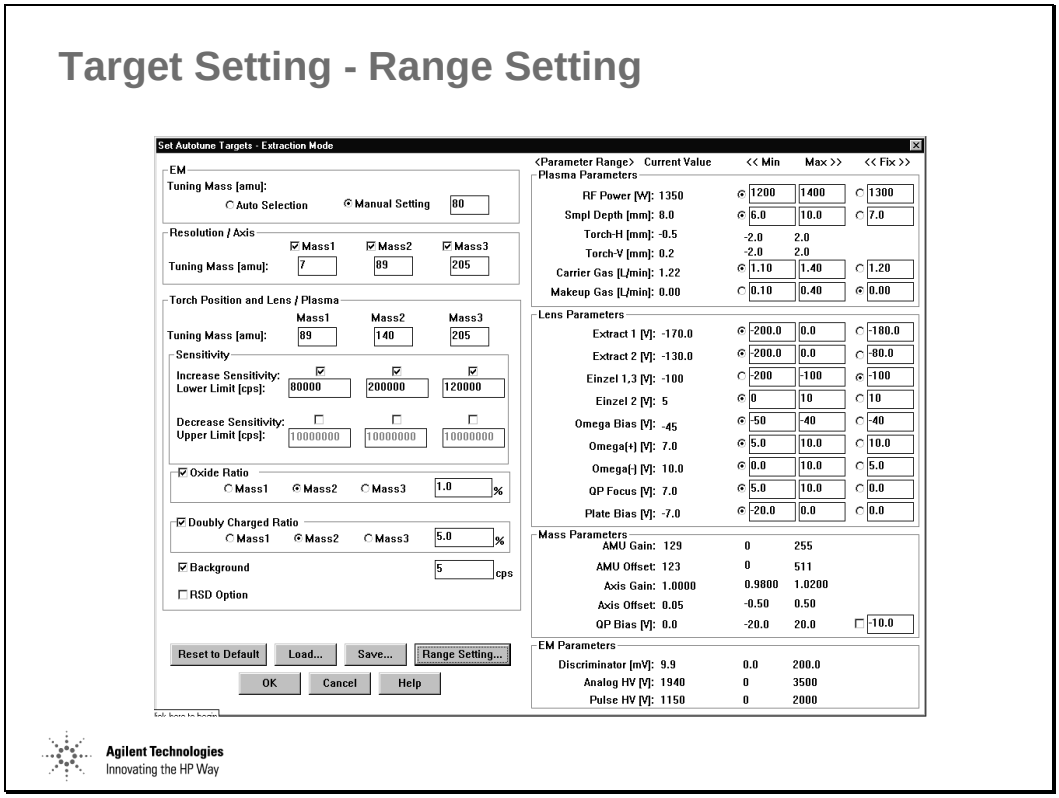


Figure 88

Sensitivity Tuning

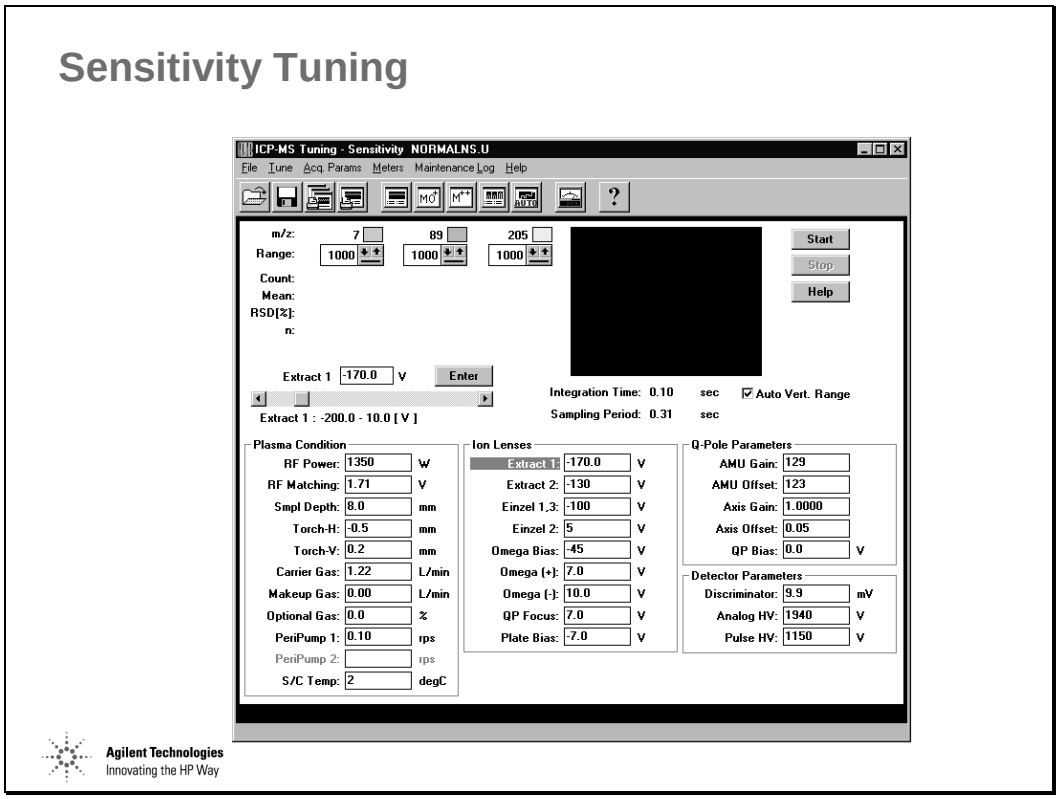


Figure 89

Peak Shape and Resolution

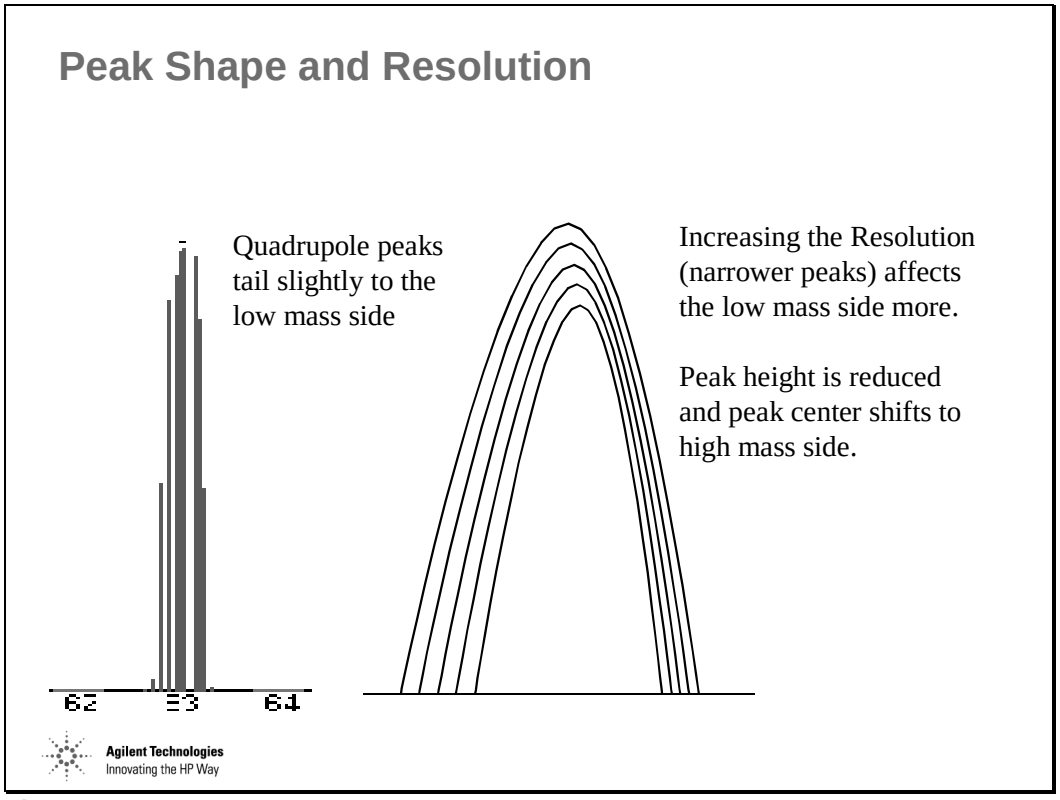


Figure 90

Abundance Sensitivity

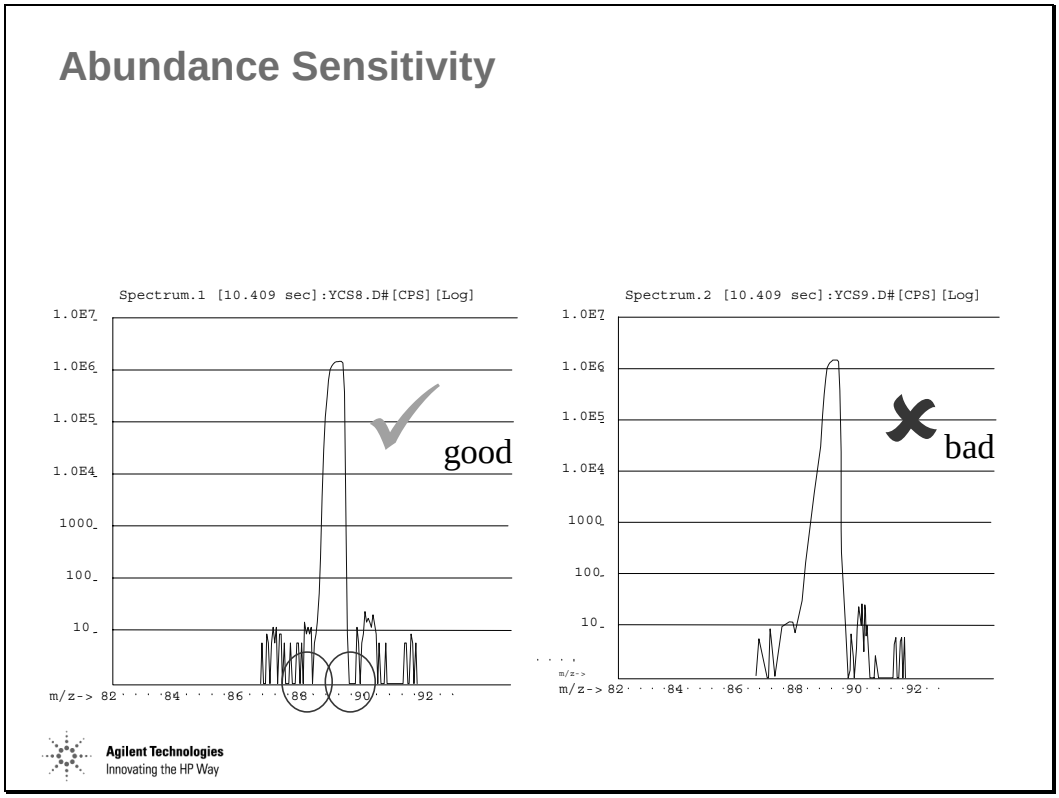


Figure 91

Quadrupole Mass Filter - Scan Line

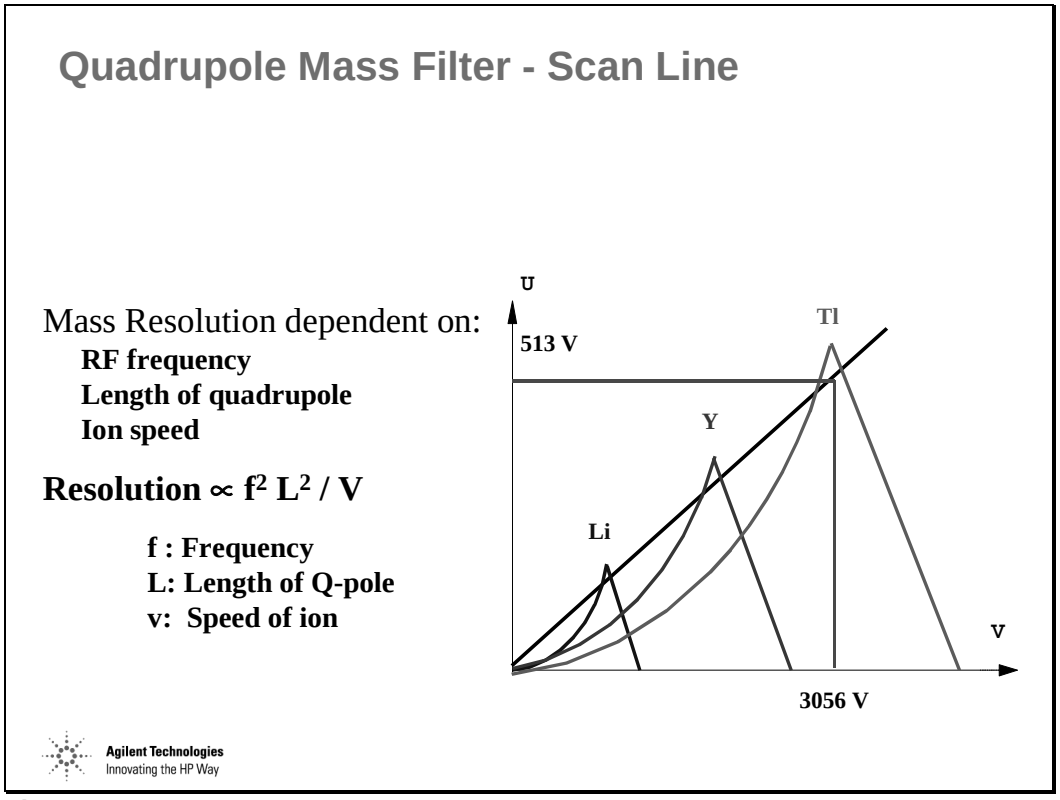
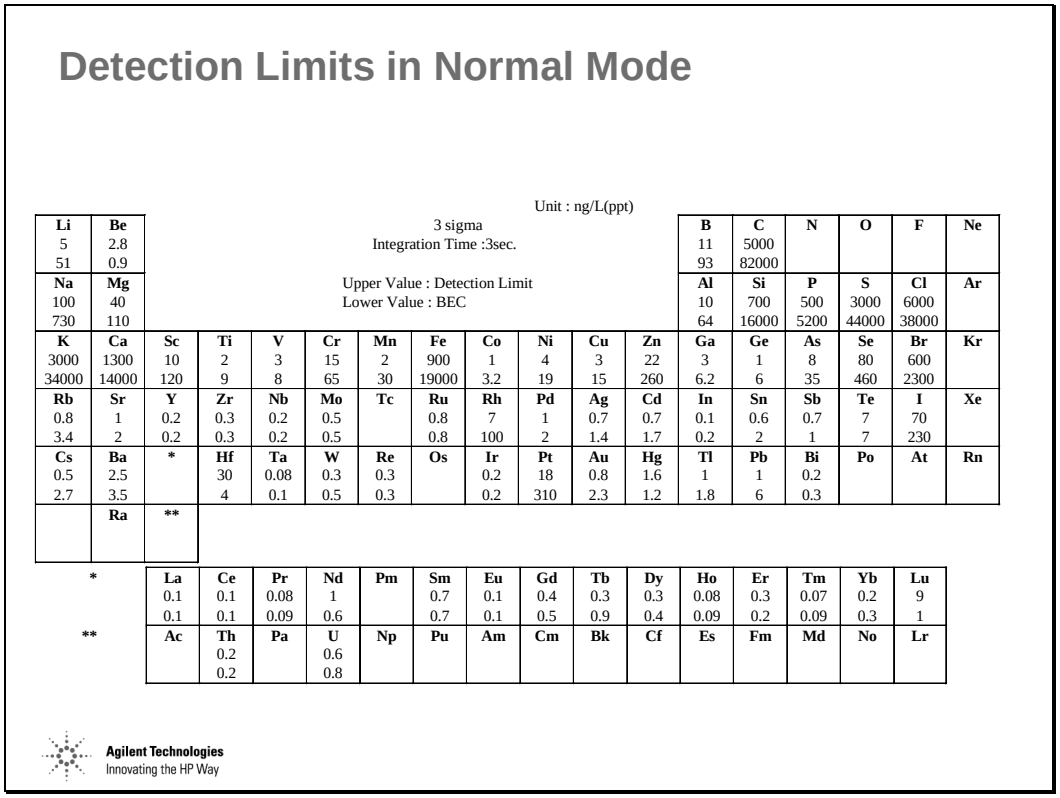


Figure 92

Detection Limits in Normal Mode

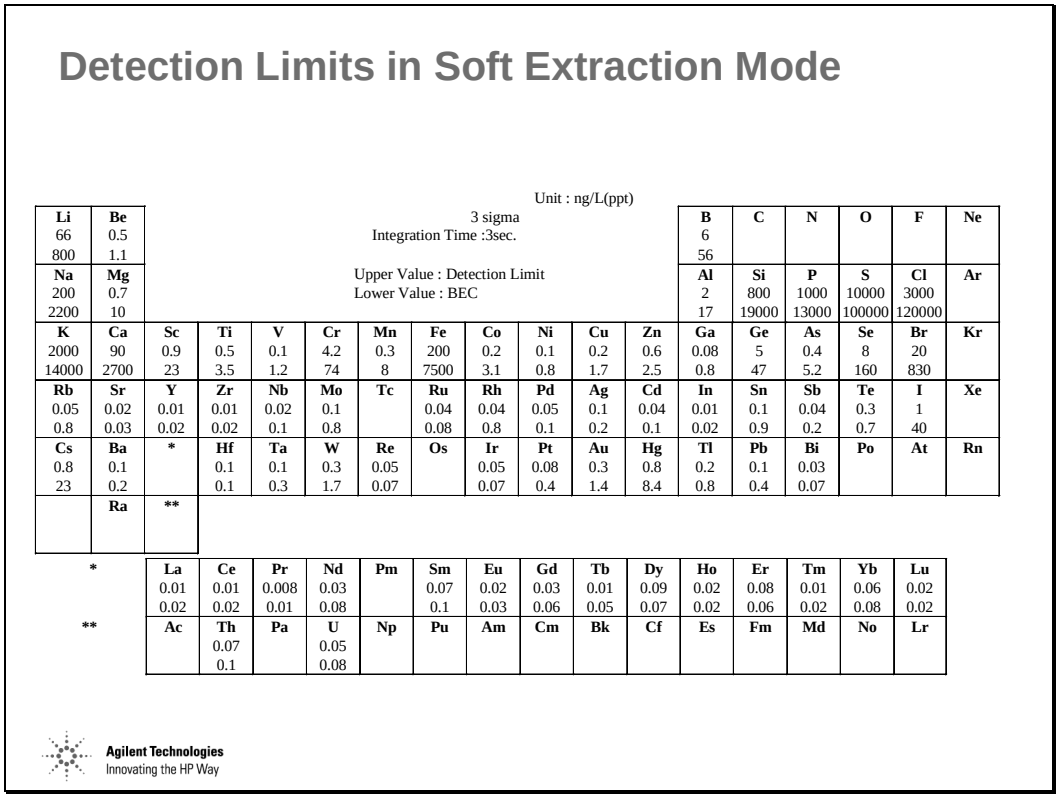


Li 5 51	**Be** 2.8 0.9											**B** 11 93	**C** 5000 82000	**N**	**O**	**F**	**Ne**
Na 100 730	**Mg** 40 110											**Al** 10 64	**Si** 700 16000	**P** 500 5200	**S** 3000 44000	**Cl** 6000 38000	**Ar**
K 3000 34000	**Ca** 1300 14000	**Sc** 10 120	**Ti** 2 9	**V** 3 8	**Cr** 15 65	**Mn** 2 30	**Fe** 900 19000	**Co** 1 3.2	**Ni** 4 19	**Cu** 3 15	**Zn** 22 260	**Ga** 3 6.2	**Ge** 1 6	**As** 8 35	**Se** 80 460	**Br** 600 2300	**Kr**
Rb 0.8 3.4	**Sr** 1 2	**Y** 0.2 0.2	**Zr** 0.3 0.3	**Nb** 0.2 0.2	**Mo** 0.5 0.5	**Tc**	**Ru** 0.8 0.8	**Rh** 7 100	**Pd** 1 2	**Ag** 0.7 1.4	**Cd** 0.7 1.7	**In** 0.1 0.2	**Sn** 0.6 2	**Sb** 0.7 1	**Te** 7 7	**I** 70 230	**Xe**
Cs 0.5 2.7	**Ba** 2.5 3.5	*	**Hf** 30 4	**Ta** 0.08 0.1	**W** 0.3 0.5	**Re** 0.3 0.3	**Os**	**Ir** 0.2 0.2	**Pt** 18 310	**Au** 0.8 2.3	**Hg** 1.6 1.2	**Tl** 1 1.8	**Pb** 1 6	**Bi** 0.2 0.3	**Po**	**At**	**Rn**
	Ra	**															

*	**La** 0.1 0.1	**Ce** 0.1 0.1	**Pr** 0.08 0.09	**Nd** 1 0.6	**Pm**	**Sm** 0.7 0.7	**Eu** 0.1 0.1	**Gd** 0.4 0.5	**Tb** 0.3 0.9	**Dy** 0.3 0.4	**Ho** 0.08 0.09	**Er** 0.3 0.2	**Tm** 0.07 0.09	**Yb** 0.2 0.3	**Lu** 9 1
**	**Ac**	**Th** 0.2 0.2	**Pa**	**U** 0.6 0.8	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

Figure 93

Detection Limits in Soft Extraction Mode

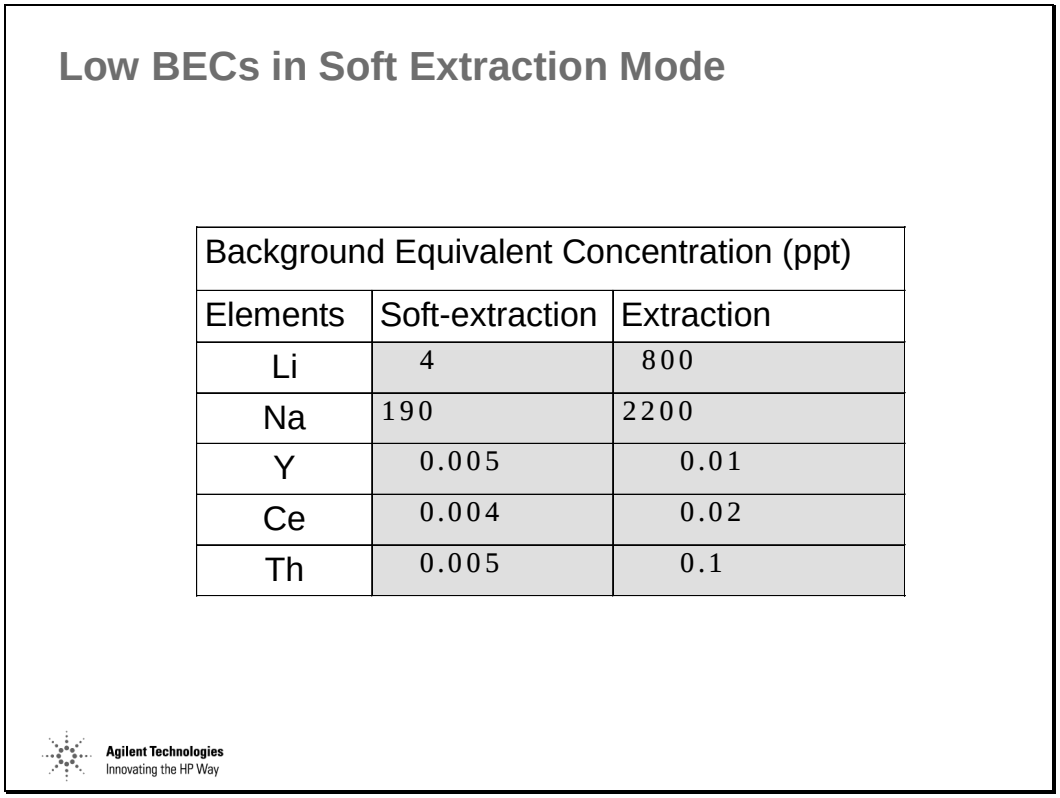


Li 66 800	**Be** 0.5 1.1											**B** 6 56	**C**	**N**	**O**	**F**	**Ne**
Na 200 2200	**Mg** 0.7 10											**Al** 2 17	**Si** 800 19000	**P** 1000 13000	**S** 10000 100000	**Cl** 3000 120000	**Ar**
K 2000 14000	**Ca** 90 2700	**Sc** 0.9 23	**Ti** 0.5 3.5	**V** 0.1 1.2	**Cr** 4.2 74	**Mn** 0.3 8	**Fe** 200 7500	**Co** 0.2 3.1	**Ni** 0.1 0.8	**Cu** 0.2 1.7	**Zn** 0.6 2.5	**Ga** 0.08 0.8	**Ge** 5 47	**As** 0.4 5.2	**Se** 8 160	**Br** 20 830	**Kr**
Rb 0.05 0.8	**Sr** 0.02 0.03	**Y** 0.01 0.02	**Zr** 0.01 0.02	**Nb** 0.02 0.1	**Mo** 0.1 0.8	**Tc**	**Ru** 0.04 0.08	**Rh** 0.04 0.8	**Pd** 0.05 0.1	**Ag** 0.1 0.2	**Cd** 0.04 0.1	**In** 0.01 0.02	**Sn** 0.1 0.9	**Sb** 0.04 0.2	**Te** 0.3 0.7	**I** 1 40	**Xe**
Cs 0.8 23	**Ba** 0.1 0.2	*	**Hf** 0.1 0.1	**Ta** 0.1 0.3	**W** 0.3 1.7	**Re** 0.05 0.07	**Os**	**Ir** 0.05 0.07	**Pt** 0.08 0.4	**Au** 0.3 1.4	**Hg** 0.8 8.4	**Tl** 0.2 0.8	**Pb** 0.1 0.4	**Bi** 0.03 0.07	**Po**	**At**	**Rn**
	Ra	**															

*	**La** 0.01 0.02	**Ce** 0.01 0.02	**Pr** 0.008 0.01	**Nd** 0.03 0.08	**Pm**	**Sm** 0.07 0.1	**Eu** 0.02 0.03	**Gd** 0.03 0.06	**Tb** 0.01 0.05	**Dy** 0.09 0.07	**Ho** 0.02 0.02	**Er** 0.08 0.06	**Tm** 0.01 0.02	**Yb** 0.06 0.08	**Lu** 0.02 0.02
**	**Ac**	**Th** 0.07 0.1	**Pa**	**U** 0.05 0.08	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

Figure 94

Low BECs in Soft Extraction Mode



Background Equivalent Concentration (ppt)		
Elements	Soft-extraction	Extraction
Li	4	800
Na	190	2200
Y	0.005	0.01
Ce	0.004	0.02
Th	0.005	0.1

Figure 95

Pulse/Analog (P/A) Tuning

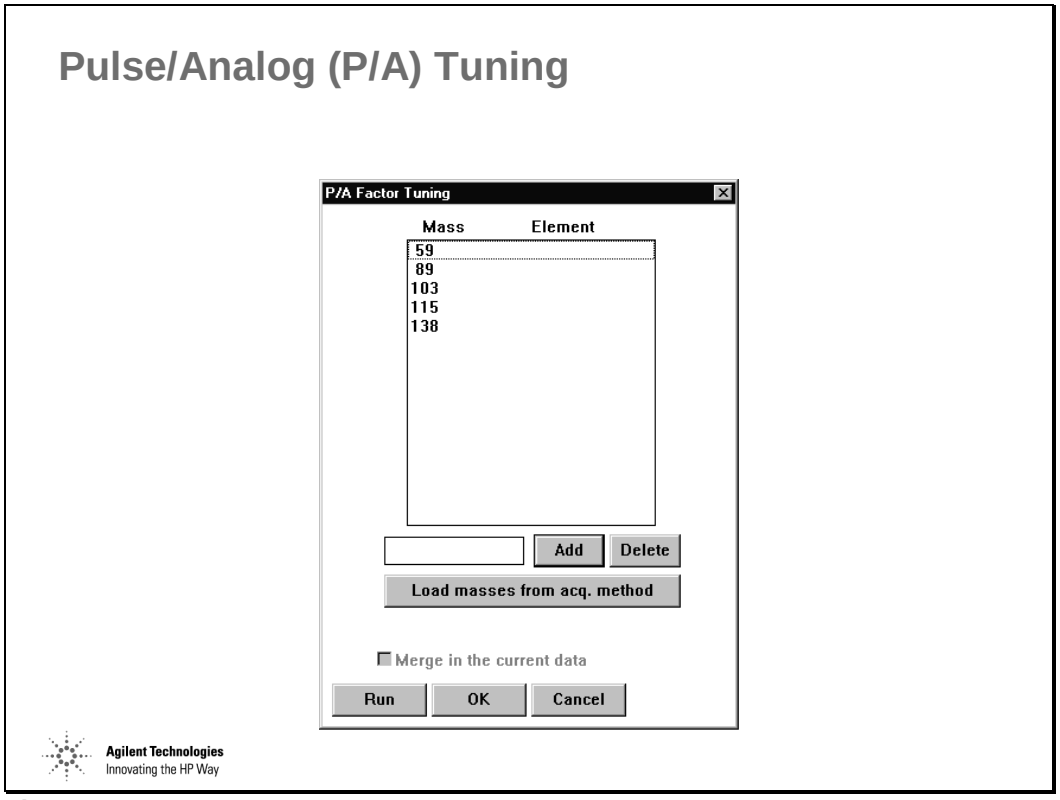


Figure 96

Agilent Technologies

Innovating the HP Way

Maintenance of the Agilent 7500

Maintenance Schedule

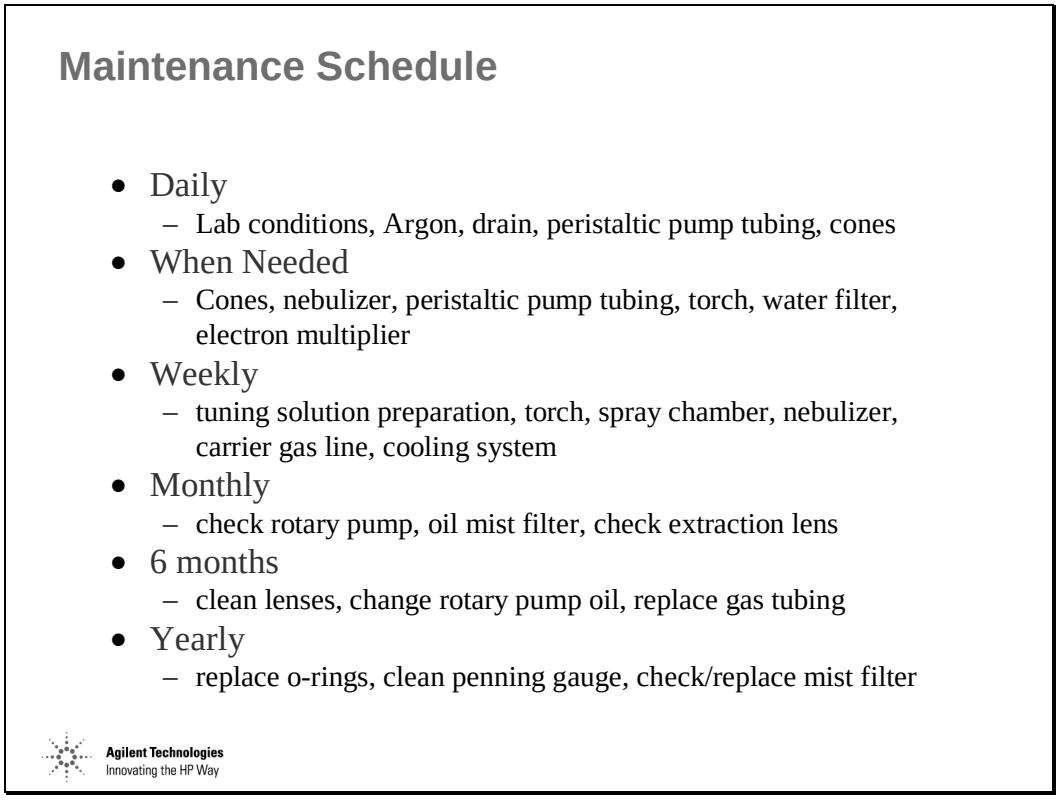


Figure 97

Running Time Maintenance Screen

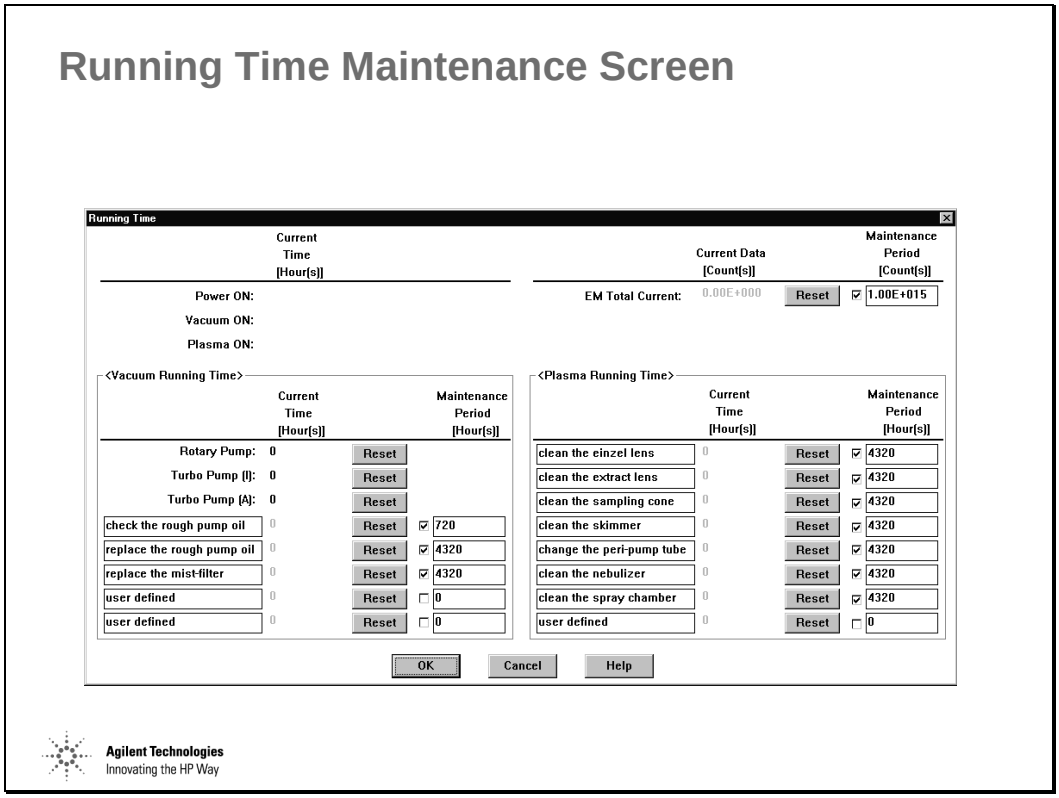
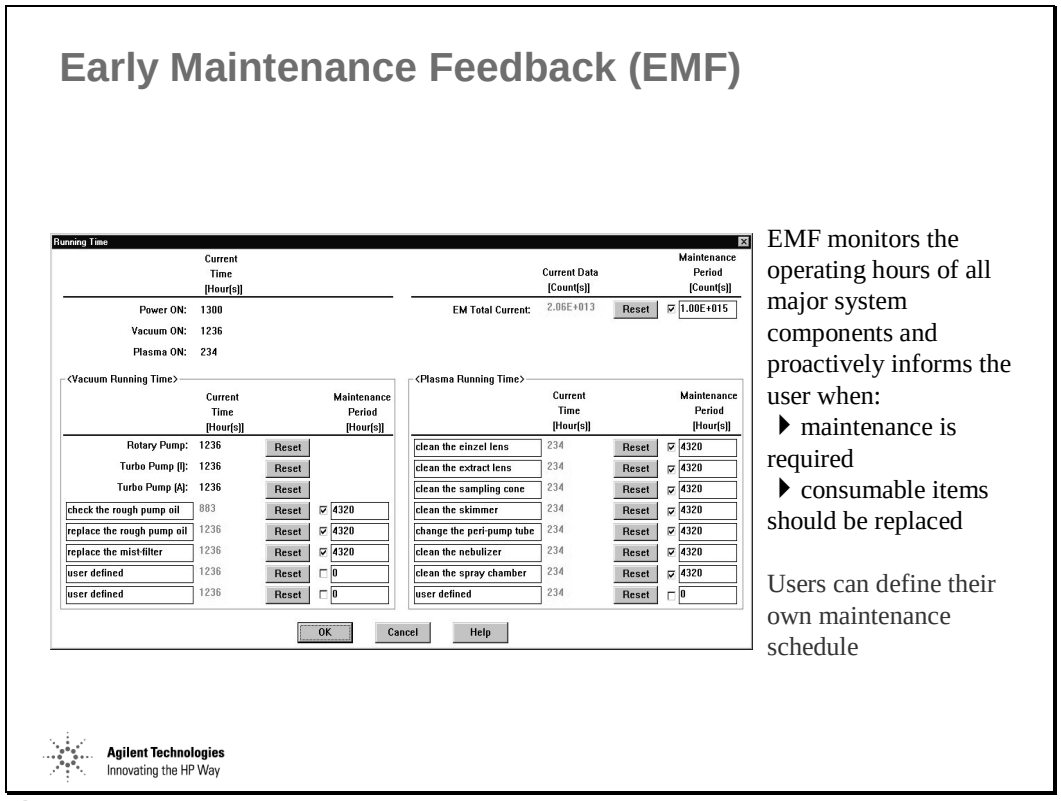


Figure 98

Early Maintenance Feedback (EMF)



EMF monitors the operating hours of all major system components and proactively informs the user when:

- maintenance is required
- consumable items should be replaced

Users can define their own maintenance schedule

Figure 99

Normal Maintenance of the Sample Introduction System

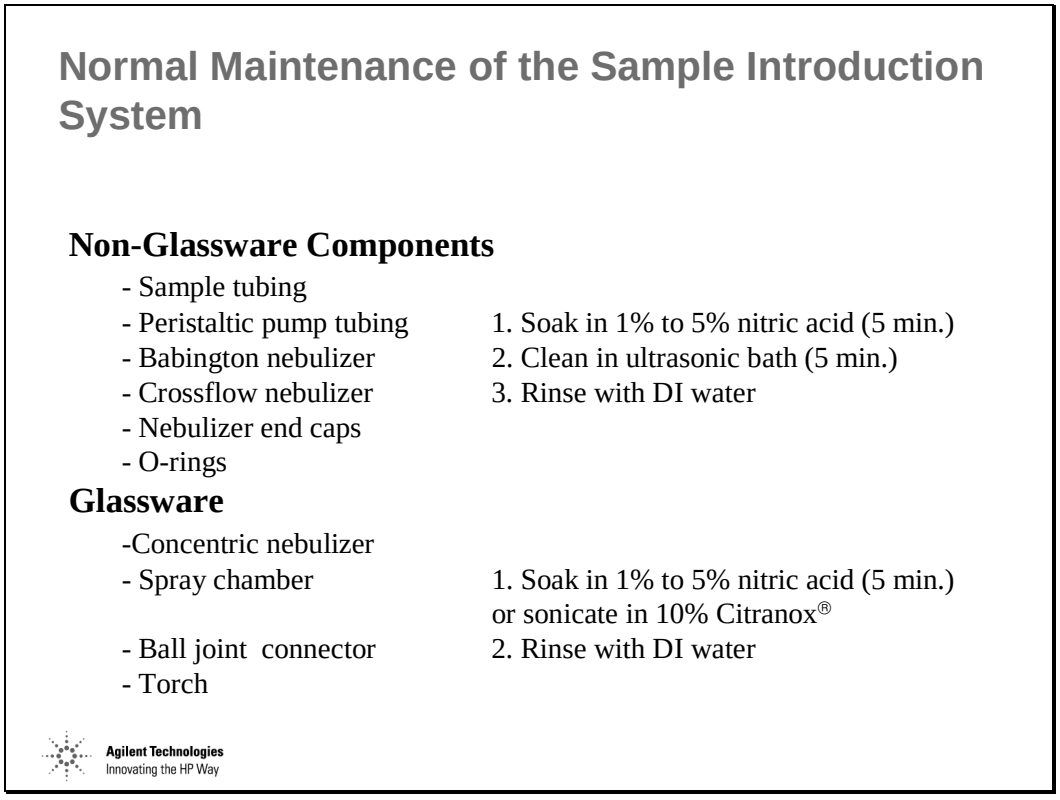


Figure 100

Overnight Cleaning of the Sample Introduction System

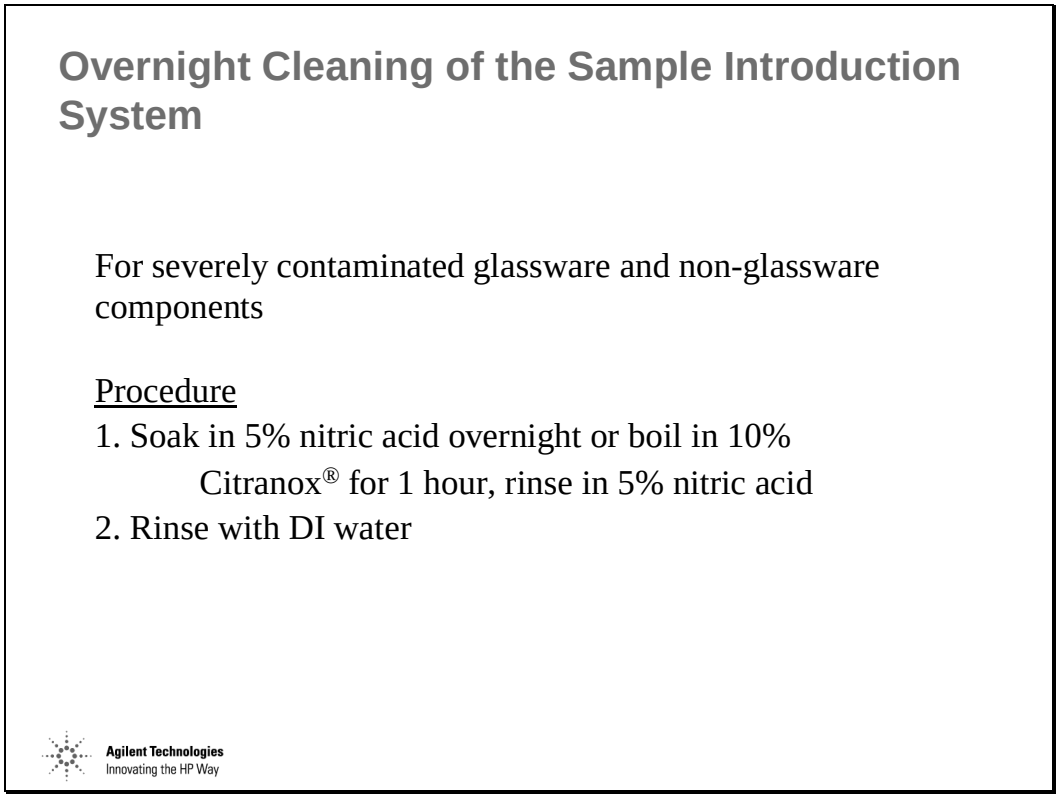


Figure 101

Sample Introduction Maintenance

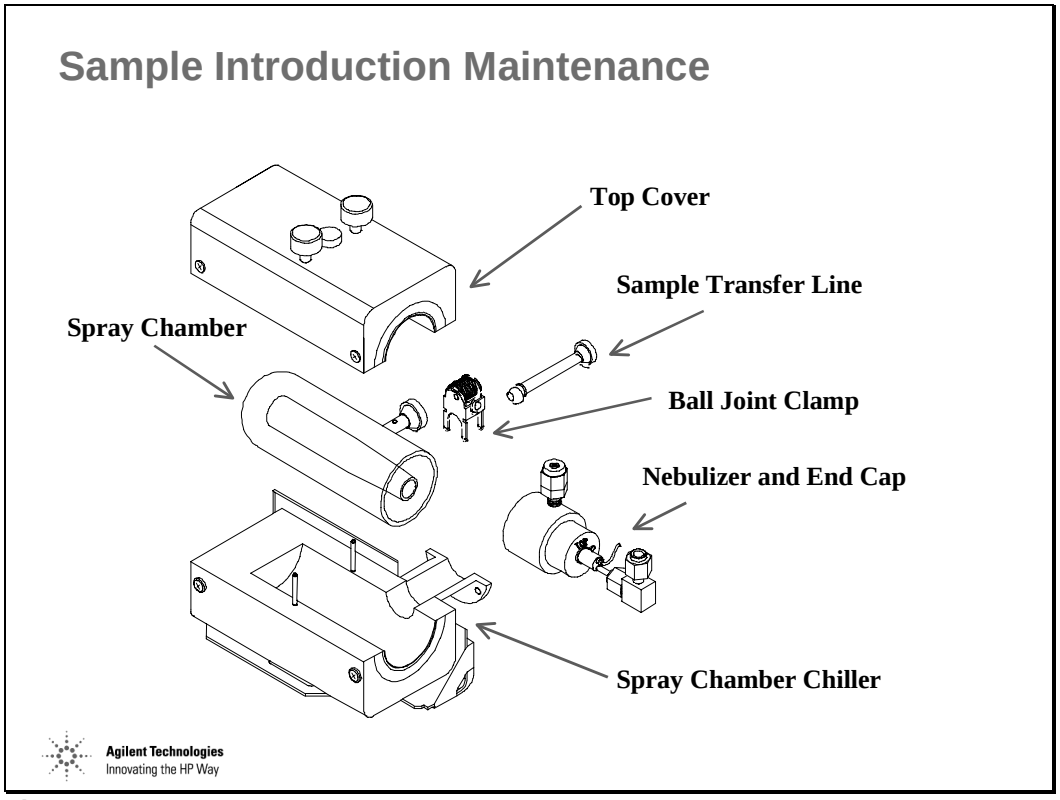


Figure 102

Nebulizer Connections

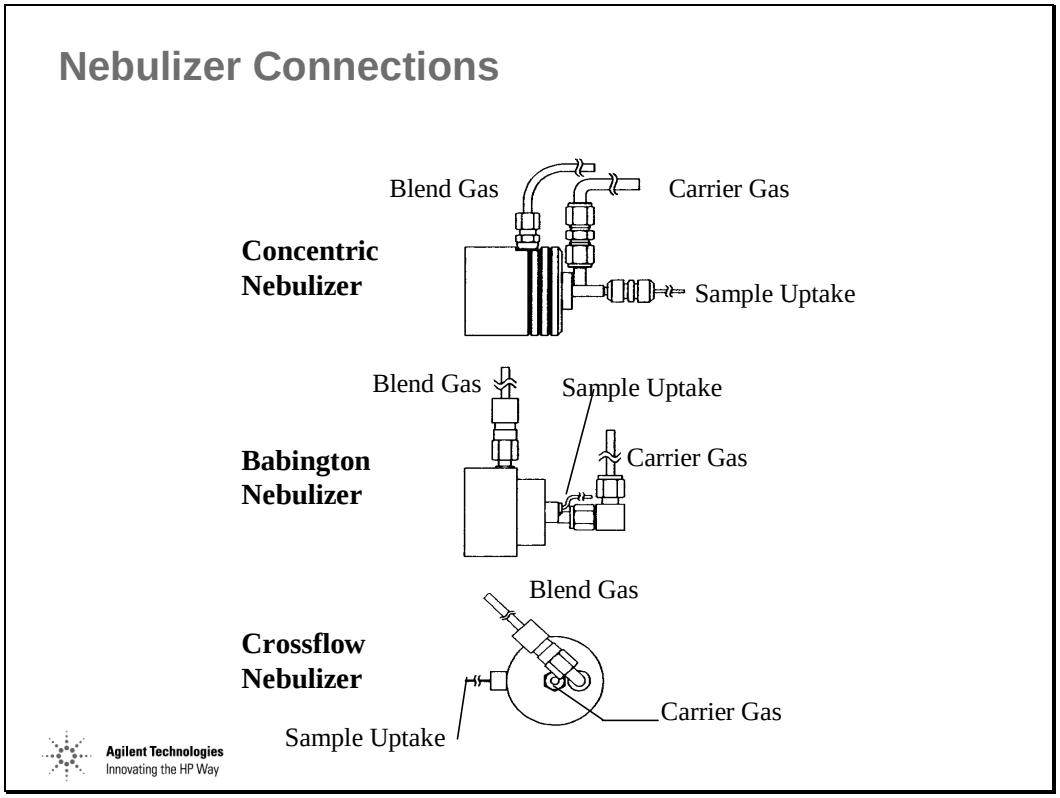


Figure 103

Maintenance of a Babington Nebulizer

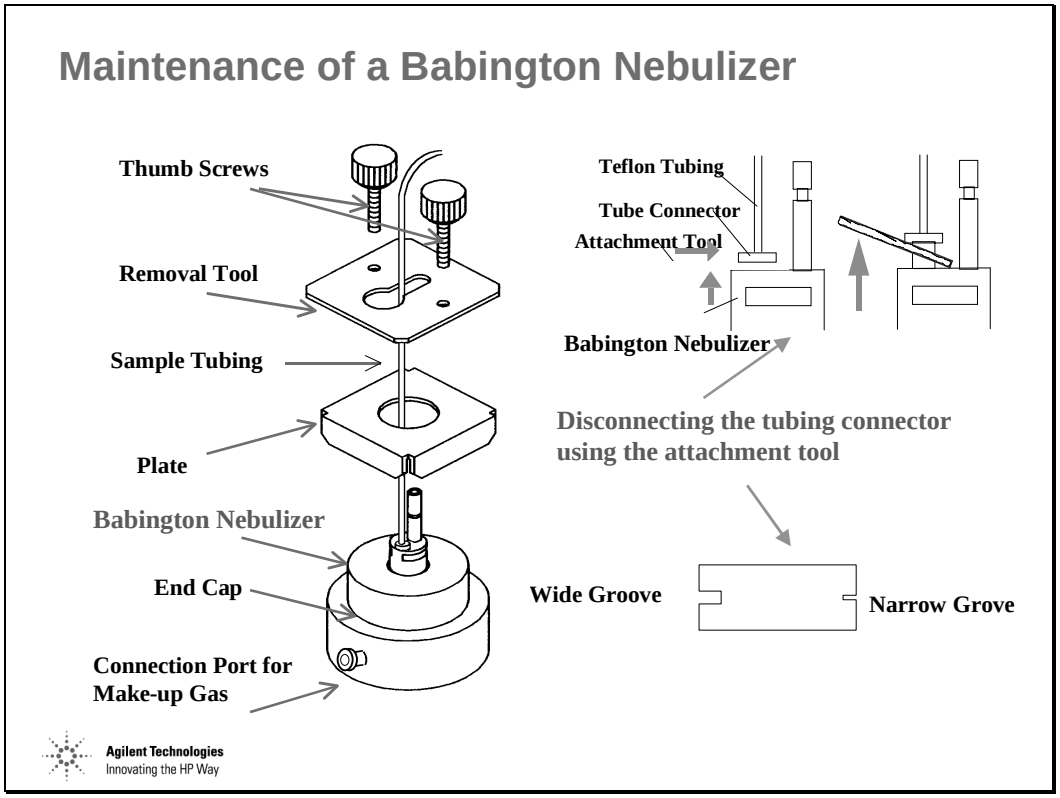


Figure 104

Torch Maintenance

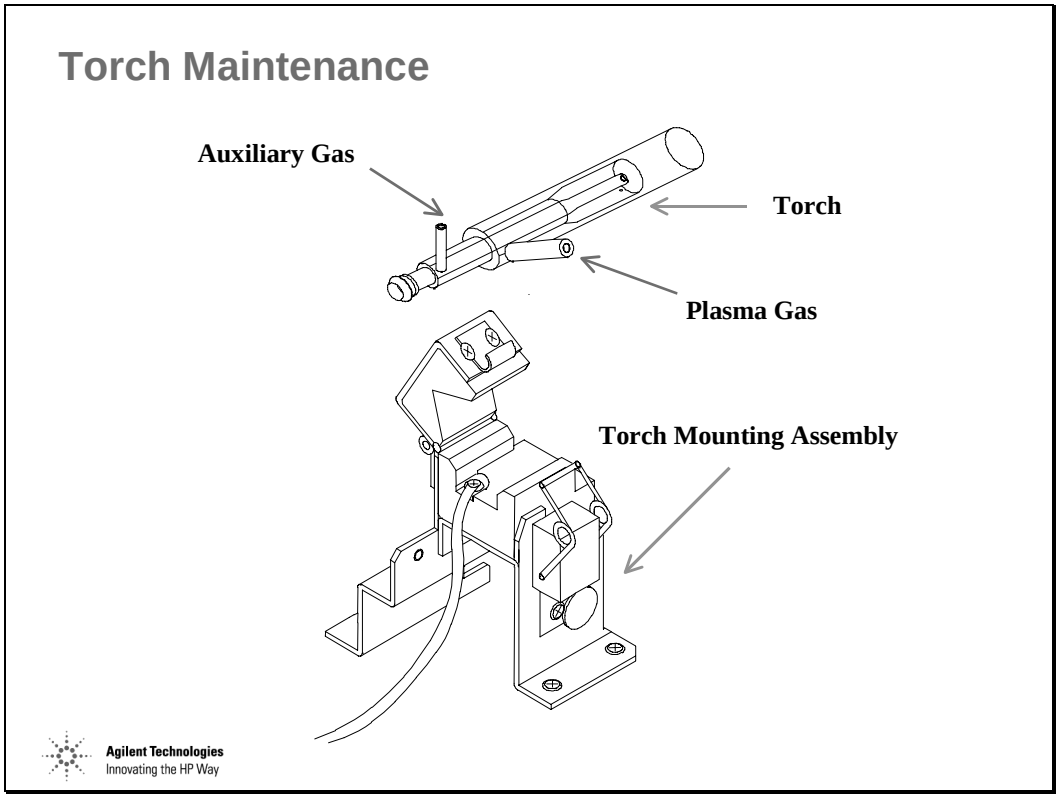


Figure 105

Interface Maintenance

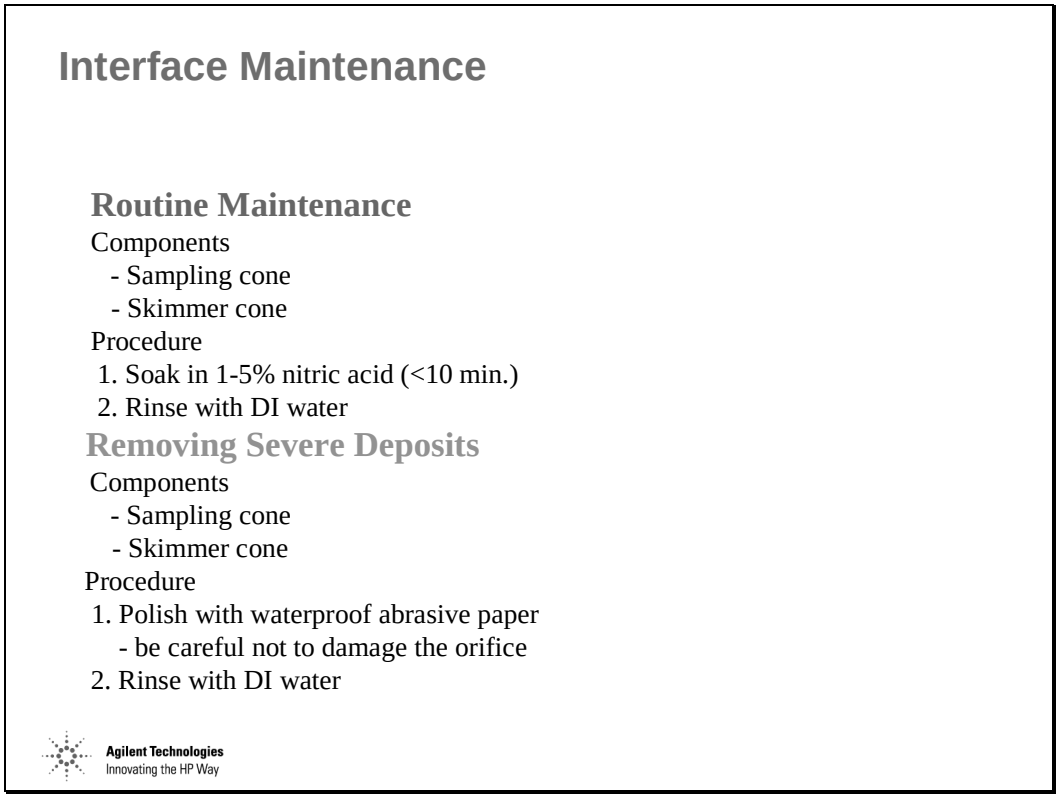


Figure 106

Maintenance of the Cones

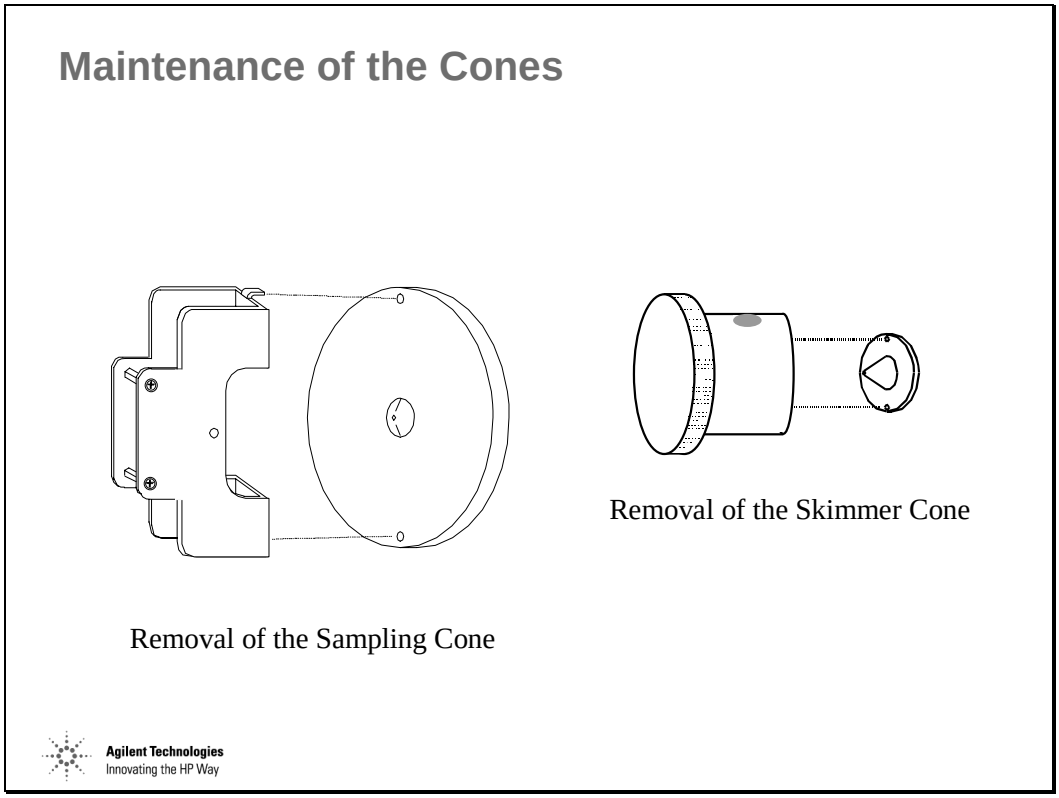


Figure 107

Extraction Lenses Maintenance

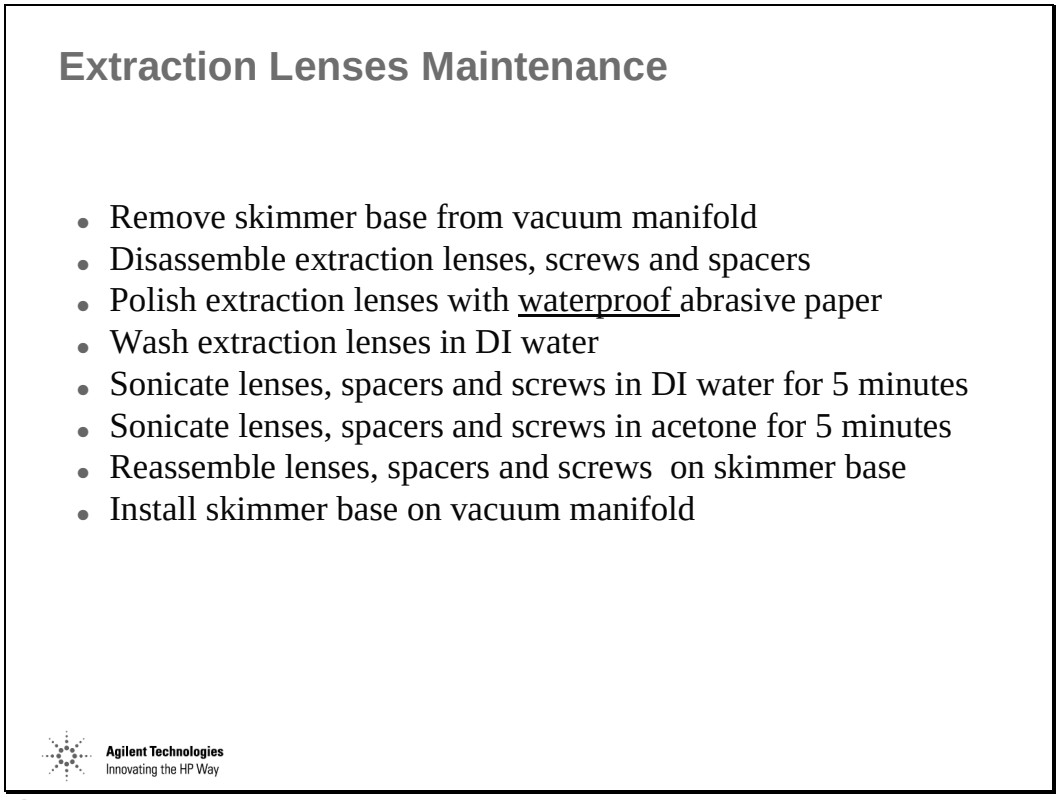


Figure 108

Extraction Lenses

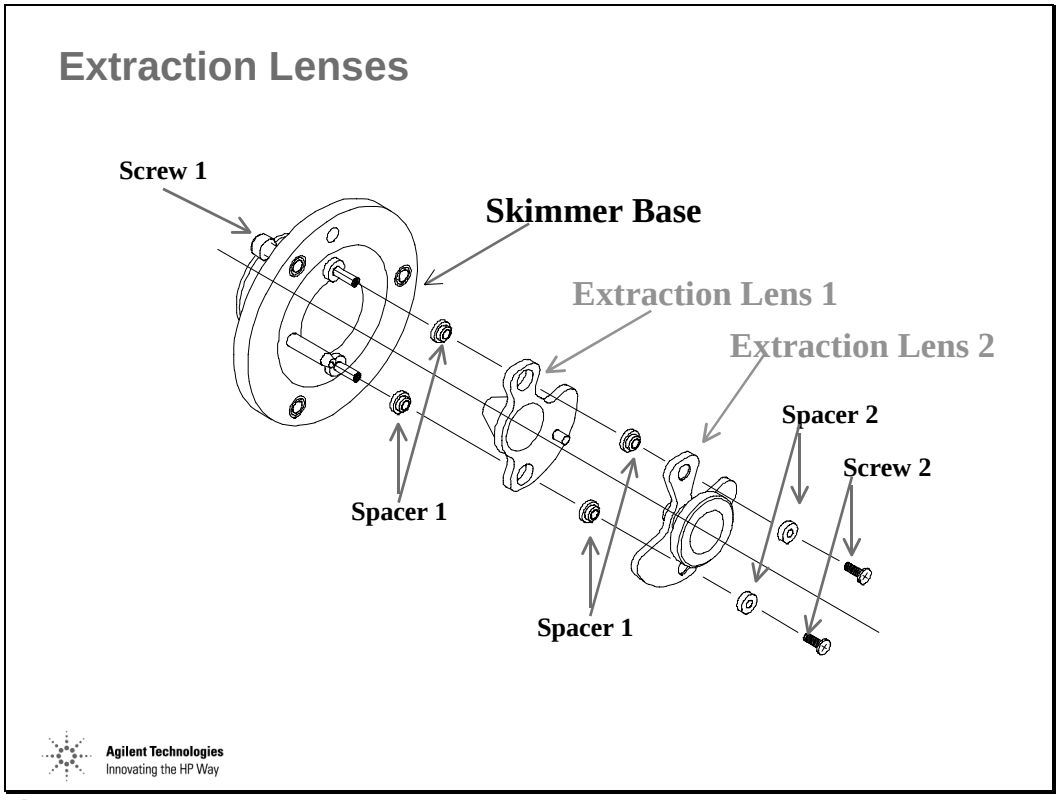


Figure 109

Cleaning of the Einzel Lens and Omega Lens Assembly

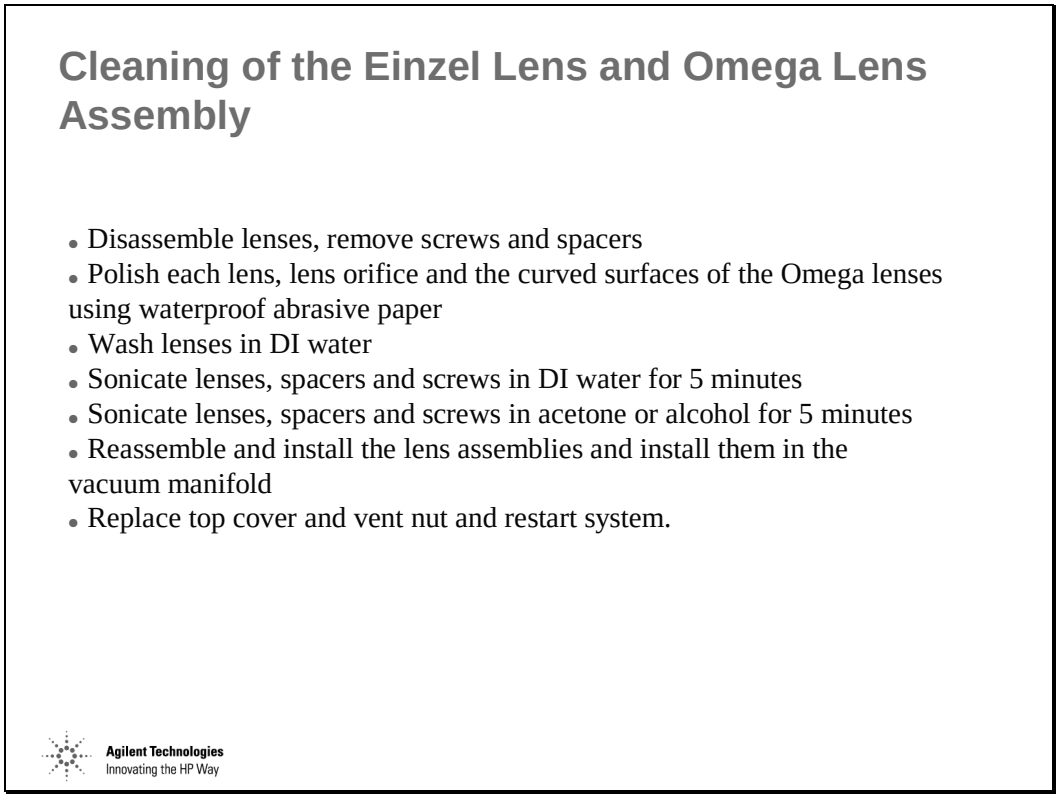


Figure 110

Instrument Shutdown

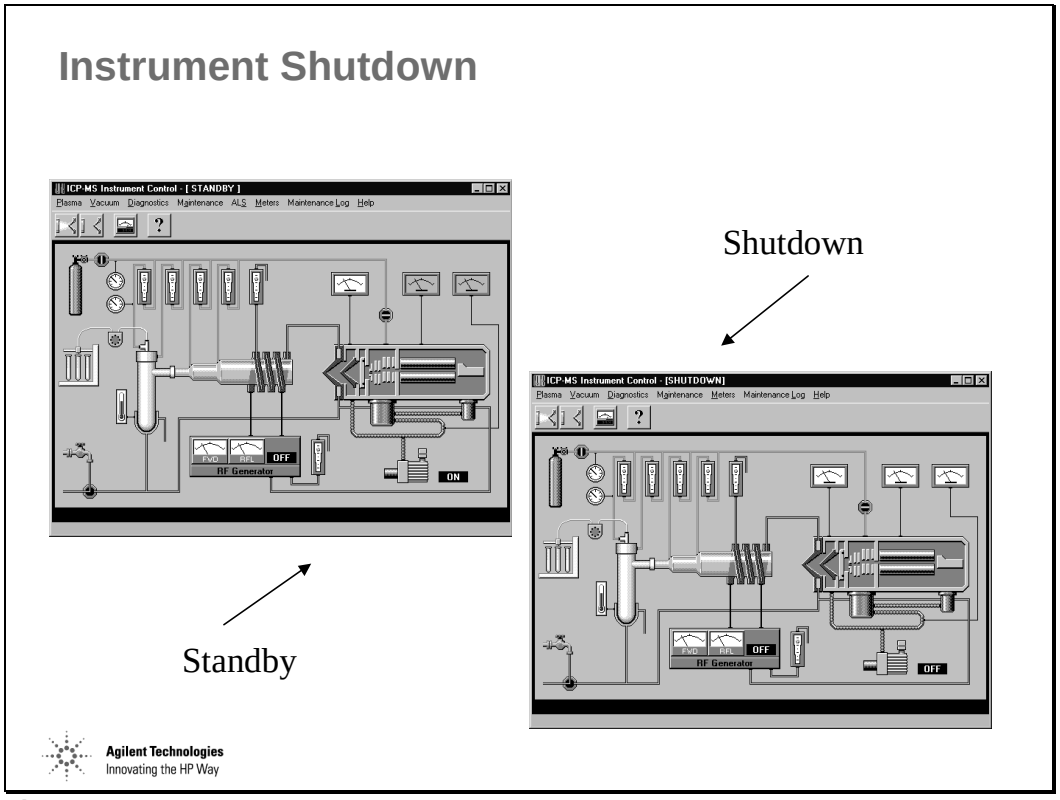


Figure 111

Removal of the Einzel Lens - Omega Lens Assembly

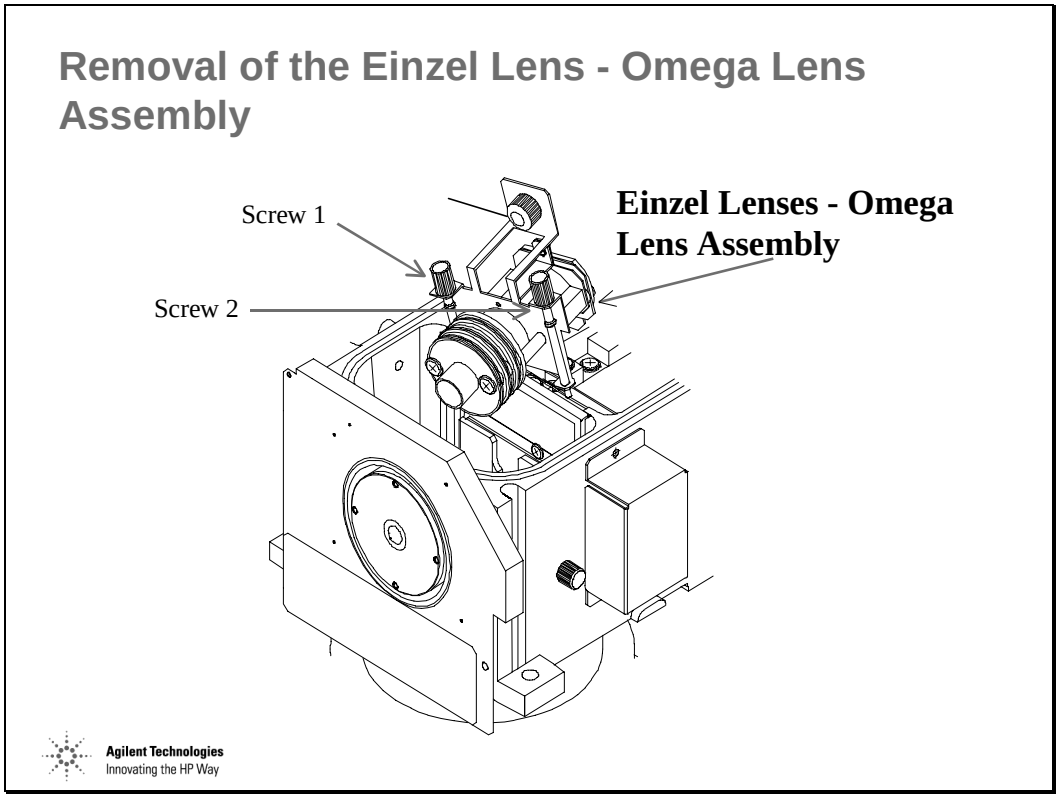


Figure 112

Expanded View of Einzel Lens - Omega Lens Assembly

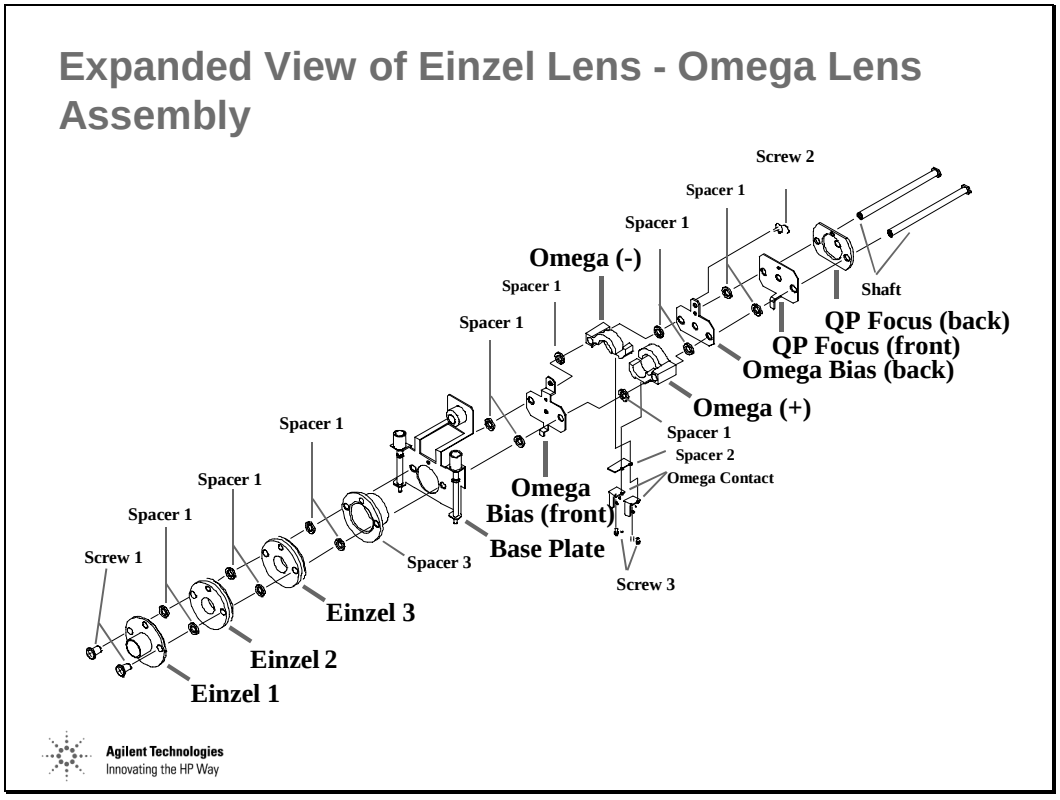


Figure 113

Plate Bias Lens

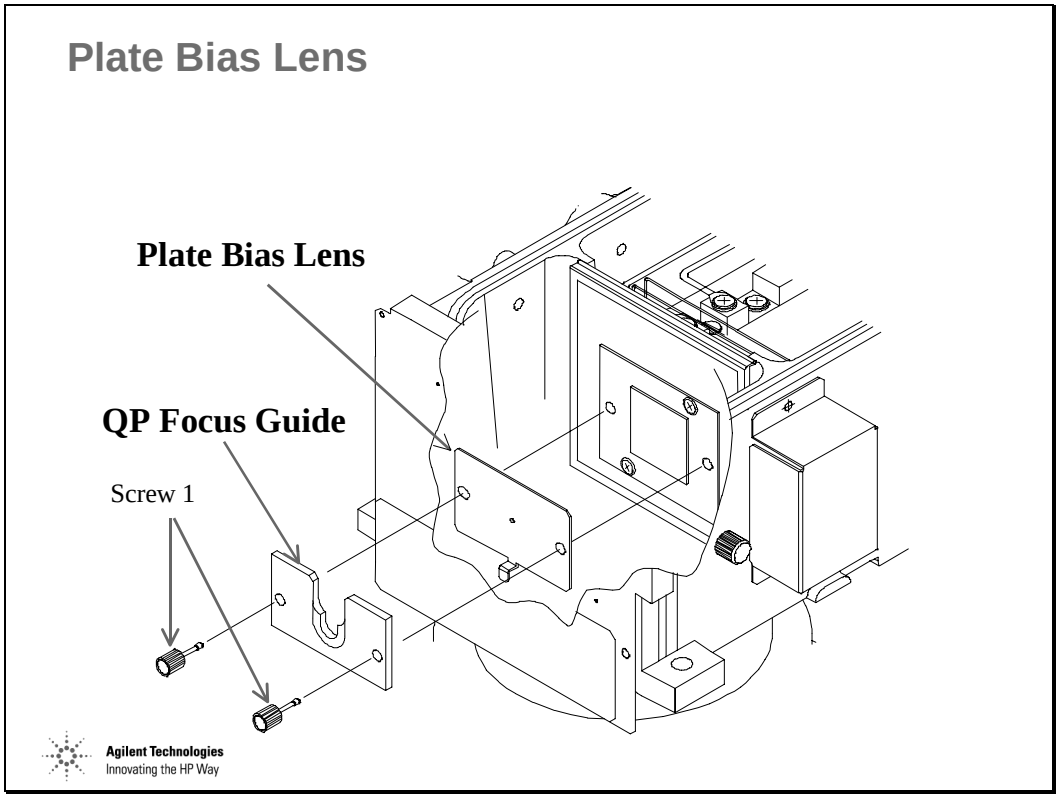


Figure 114

Penning Gauge

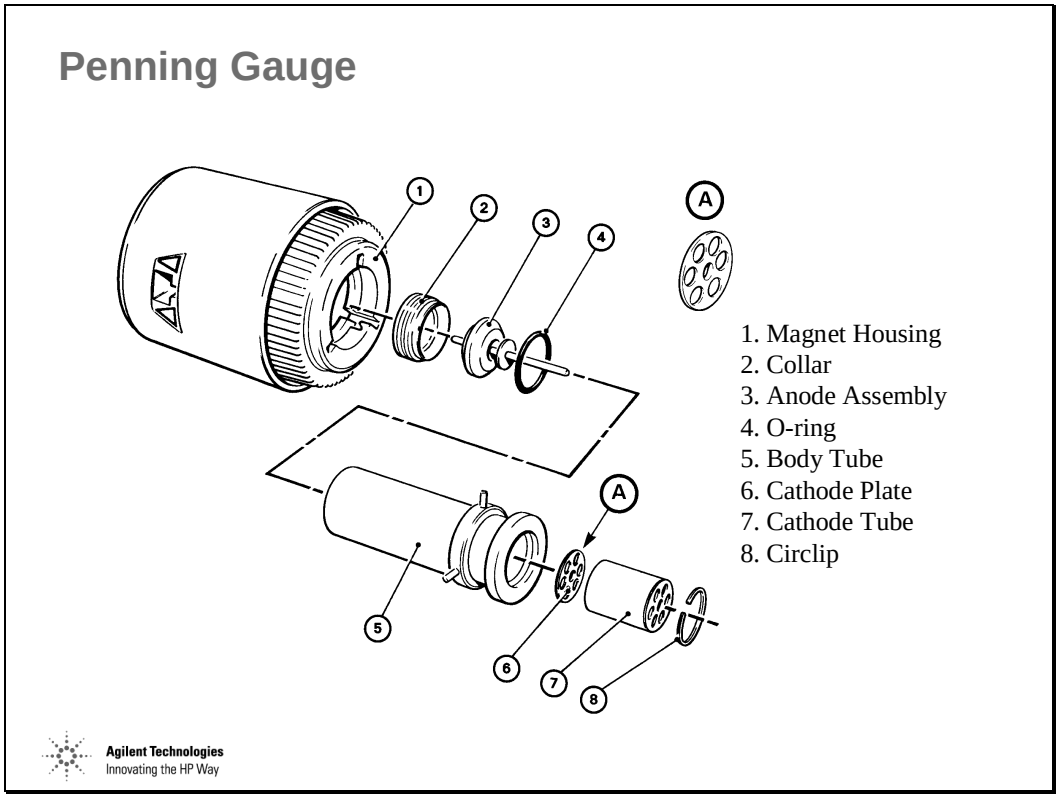


Figure 115

Rotary Pump Maintenance

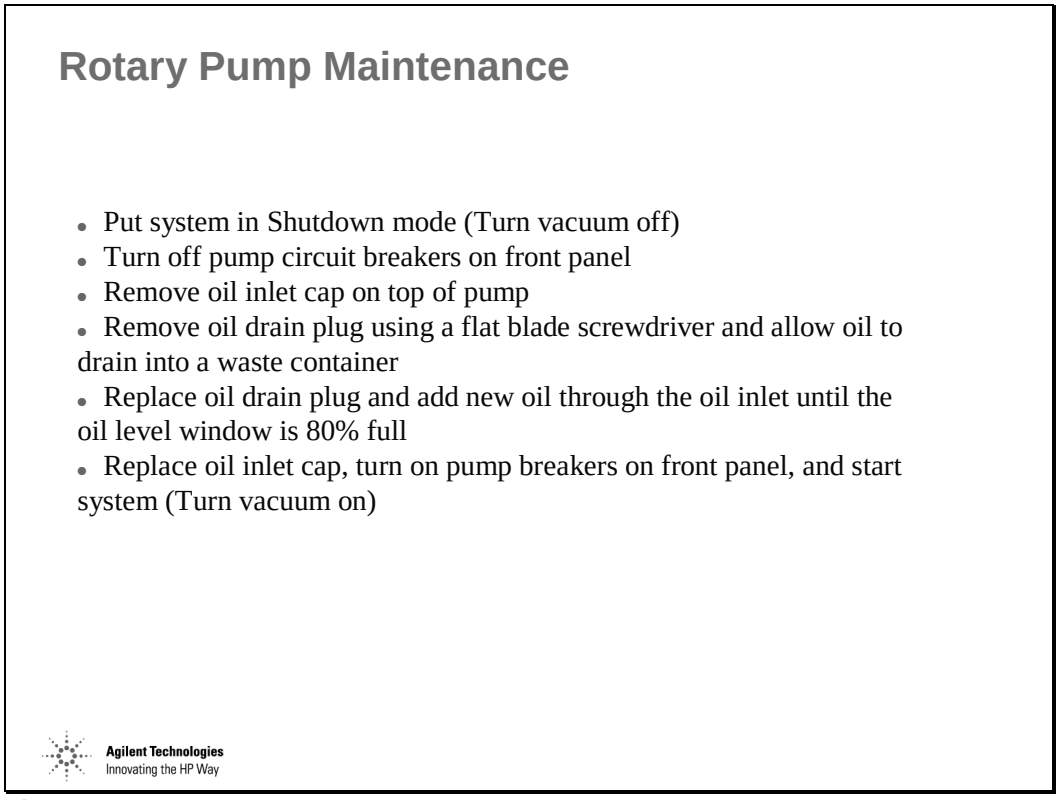


Figure 116

Changing Rotary Pump Oil

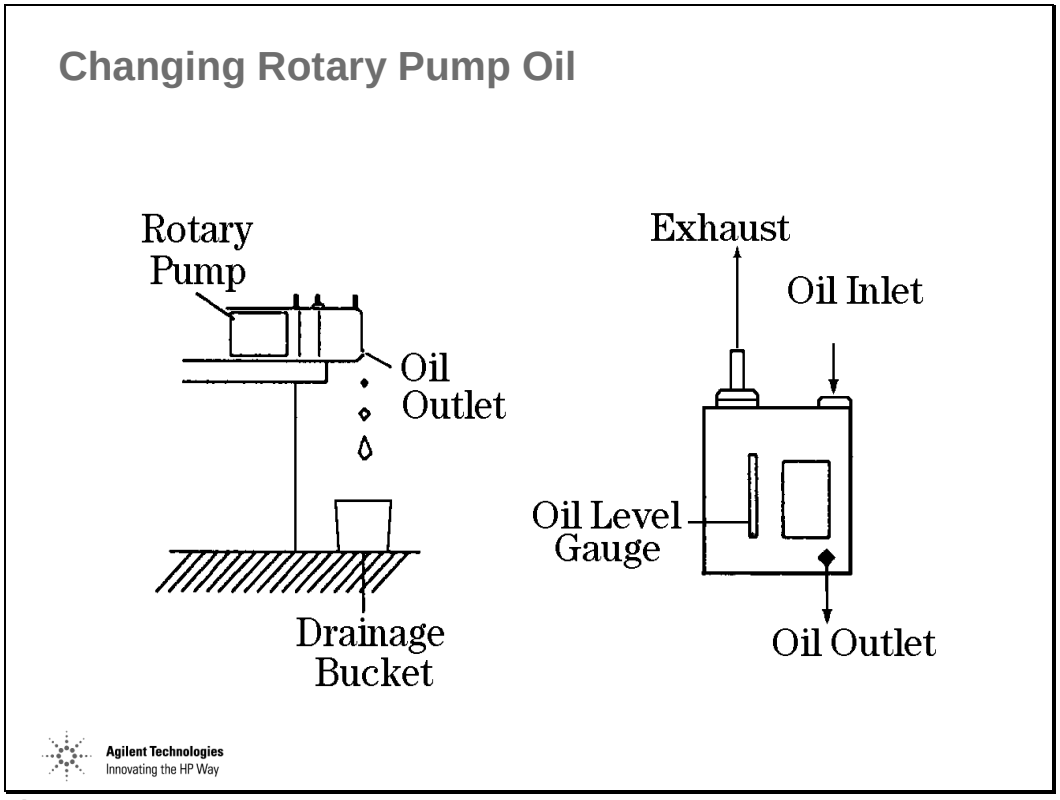


Figure 117

Maintenance Logbook Setting

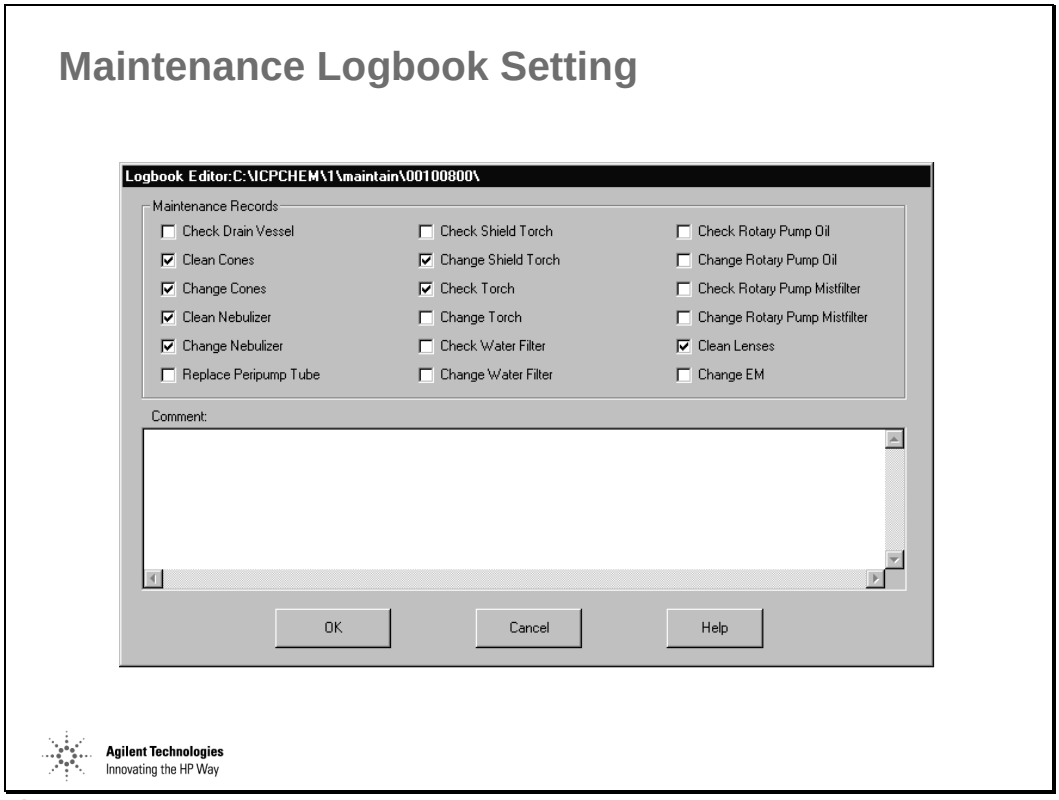


Figure 118

Maintenance Logbook

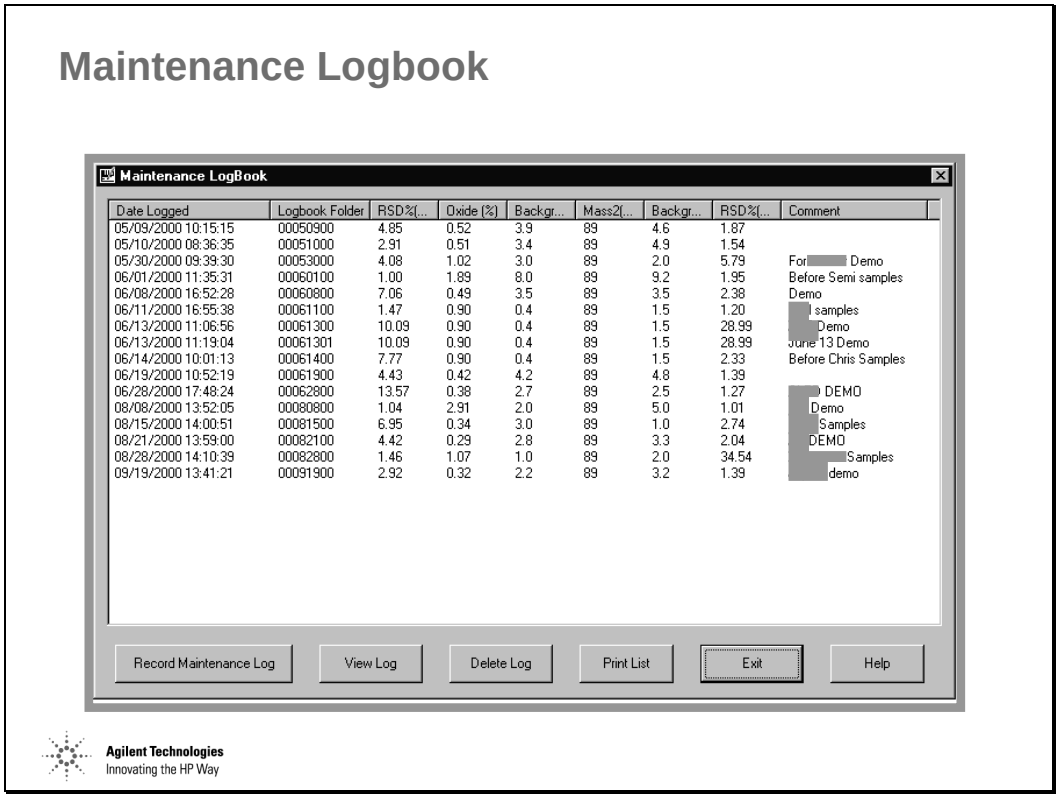


Figure 119

Sample Introduction Maintenance

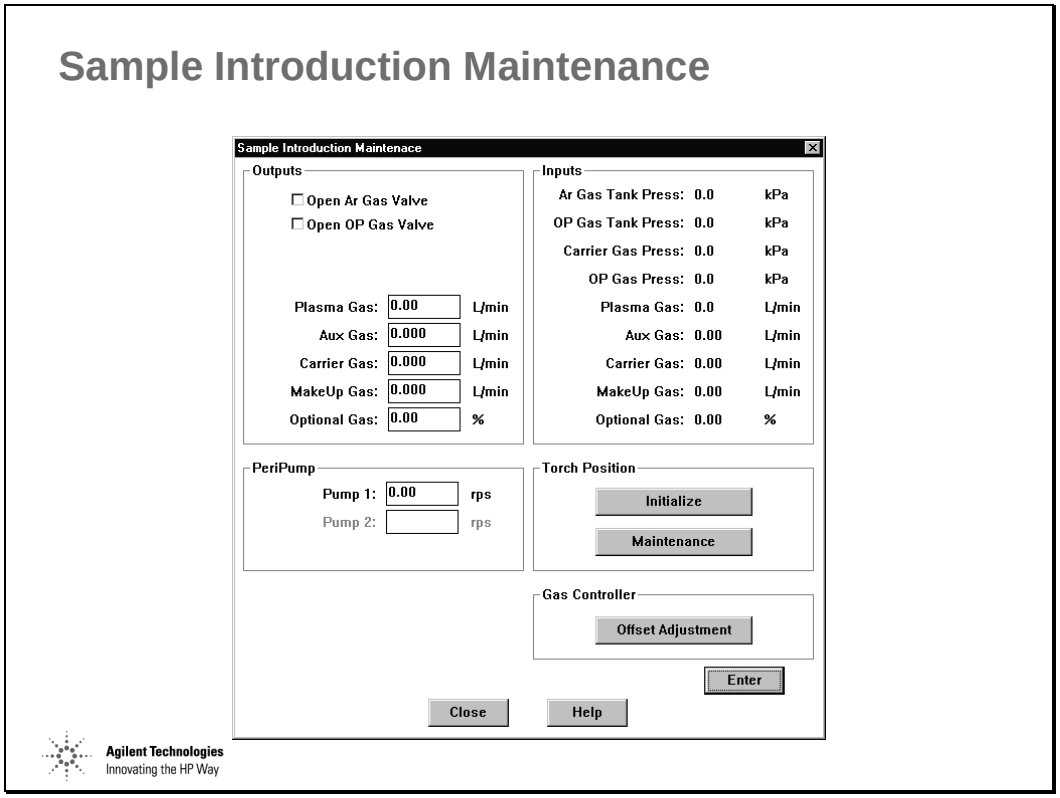


Figure 120

Air Filters Maintenance

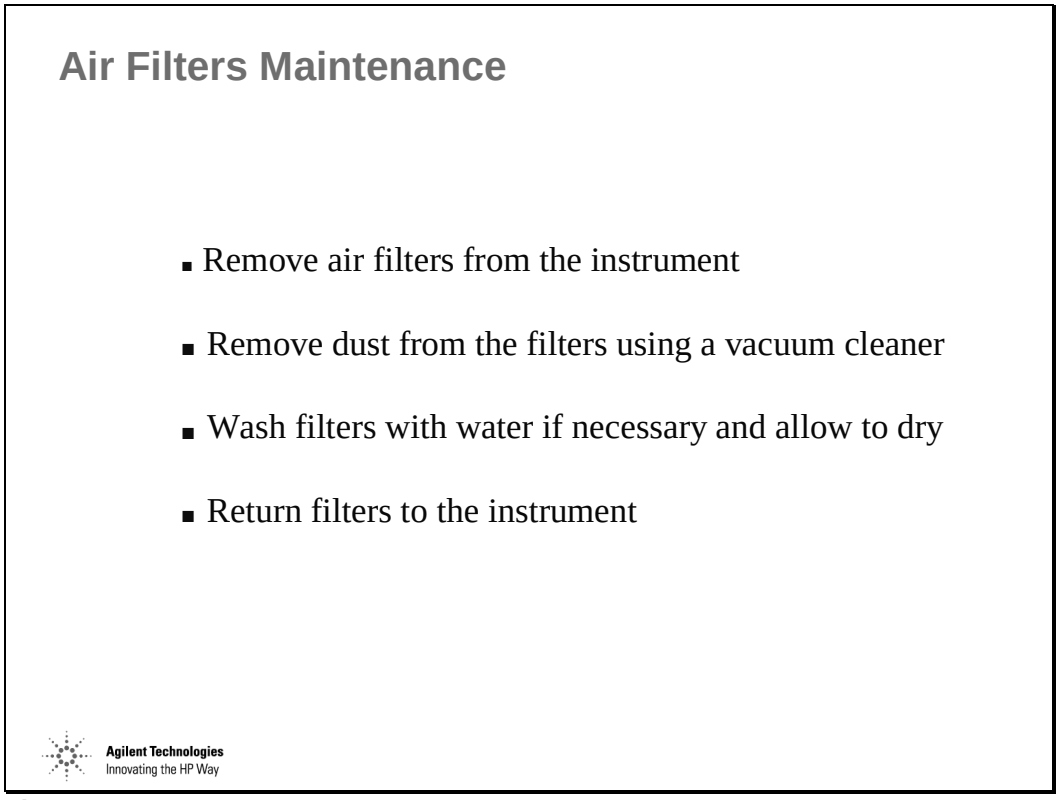


Figure 121

Instrument Start-up

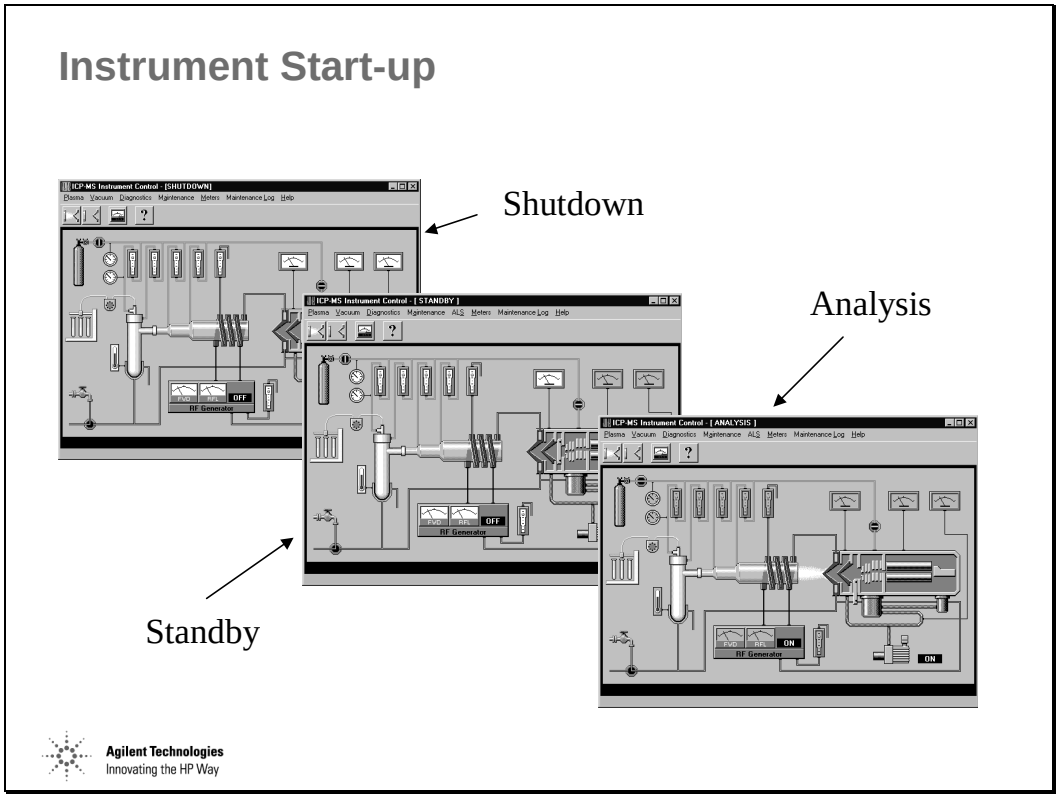


Figure 122

Agilent Technologies

Innovating the HP Way

Internal Standardization in ICP-MS

The Role of Internal Standards

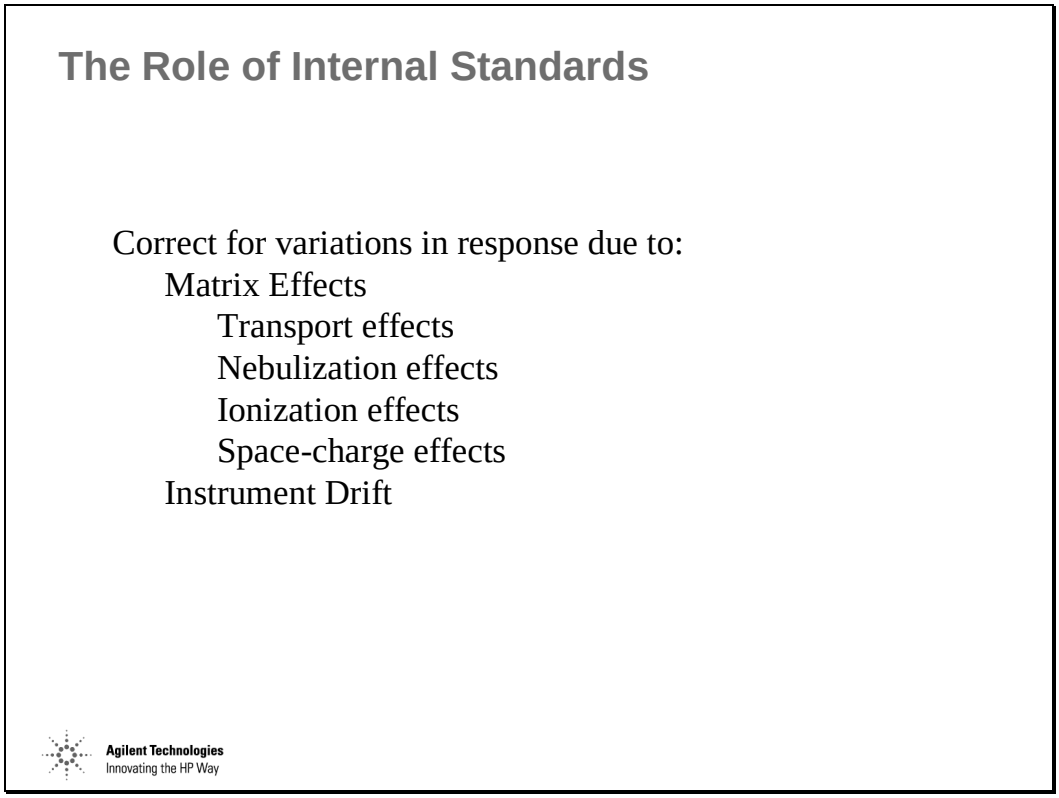


Figure 123

How the Internal Standards Work - 1

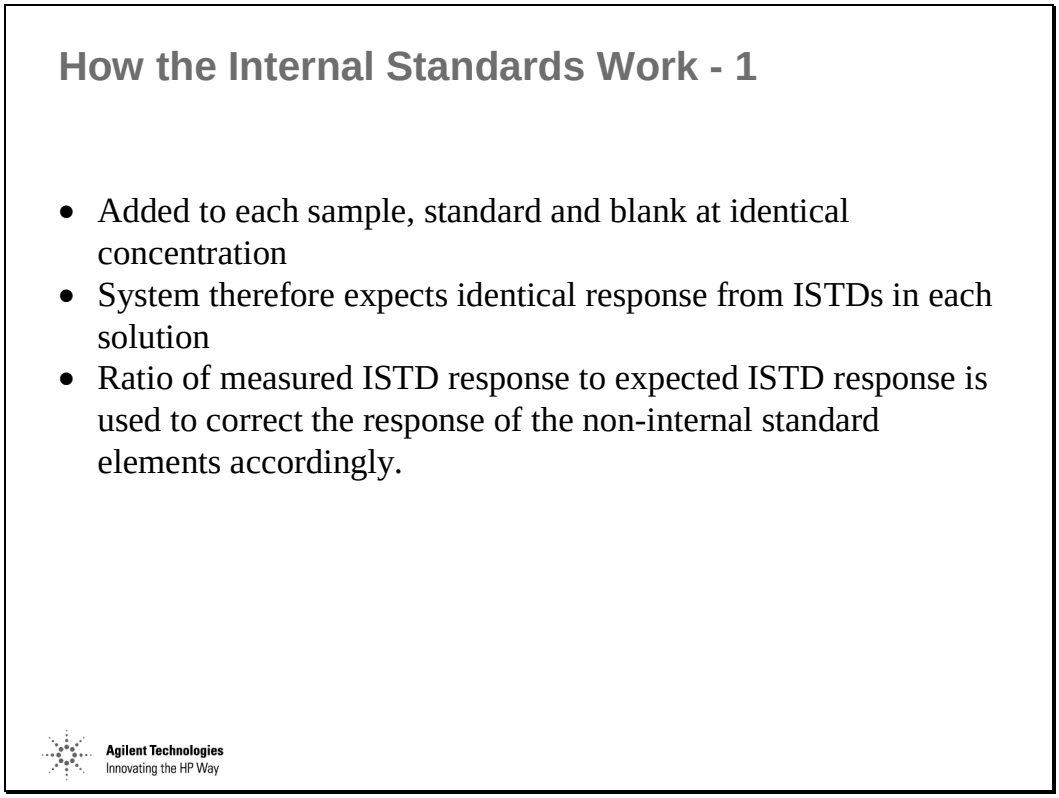


Figure 124

How the Internal Standards Work - 2

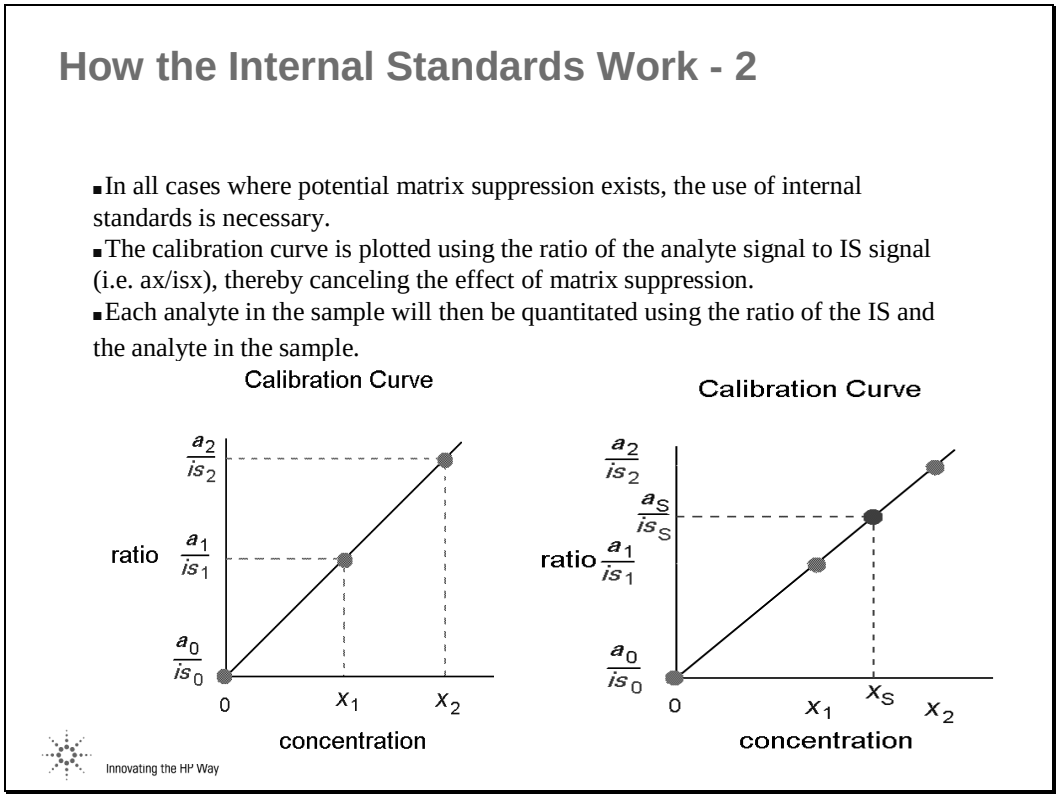


Figure 125

Choice of the Internal Standard

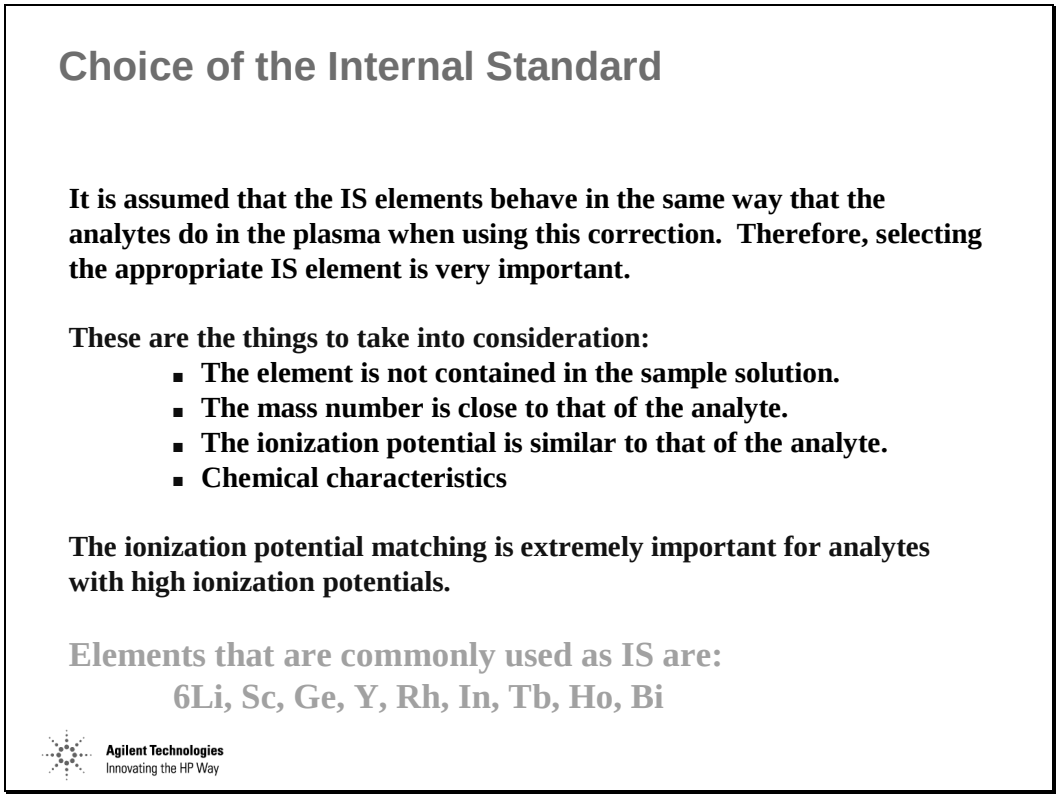


Figure 126

Concentration of Internal Standards

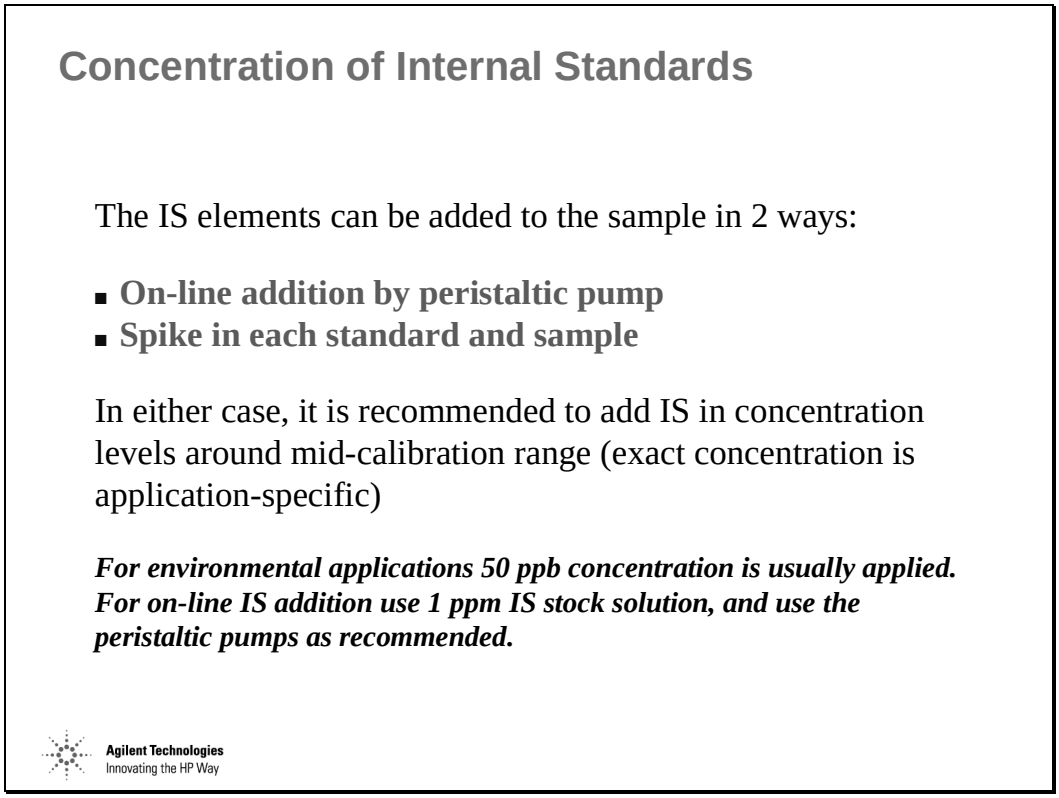
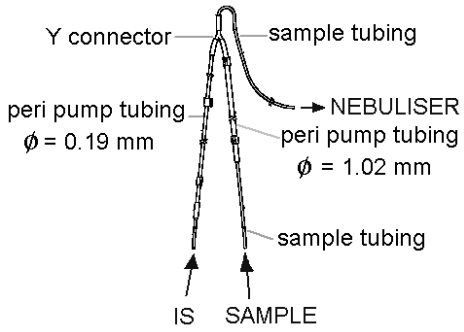


Figure 127

On-line Addition of Internal Standards

On-line Addition of Internal Standards



- **On-line Addition**

The IS solution is introduced by a narrow tubing (f = 0.19 mm), and is mixed with the sample at the Y connector. The dilution factor of the IS by the sample is about 1/20. Therefore, a 1 ppm solution in 5 % HNO3 would yield approximately 50 ppb in the sample. At least 5 % HNO3 is needed to avoid absorption of elements to the tubing, as absorption is more severe using narrow tubing.

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Figure 128

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Sample Preparation Techniques for ICP-MS

Contamination

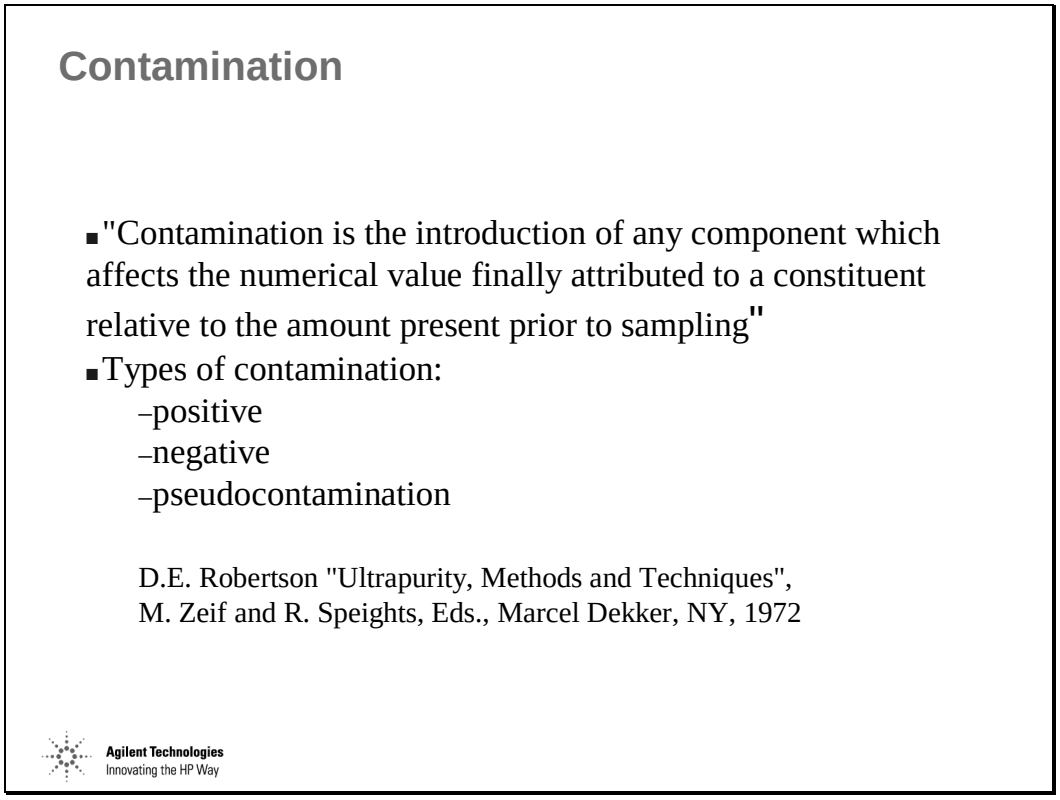

Figure 129

Types of Contamination

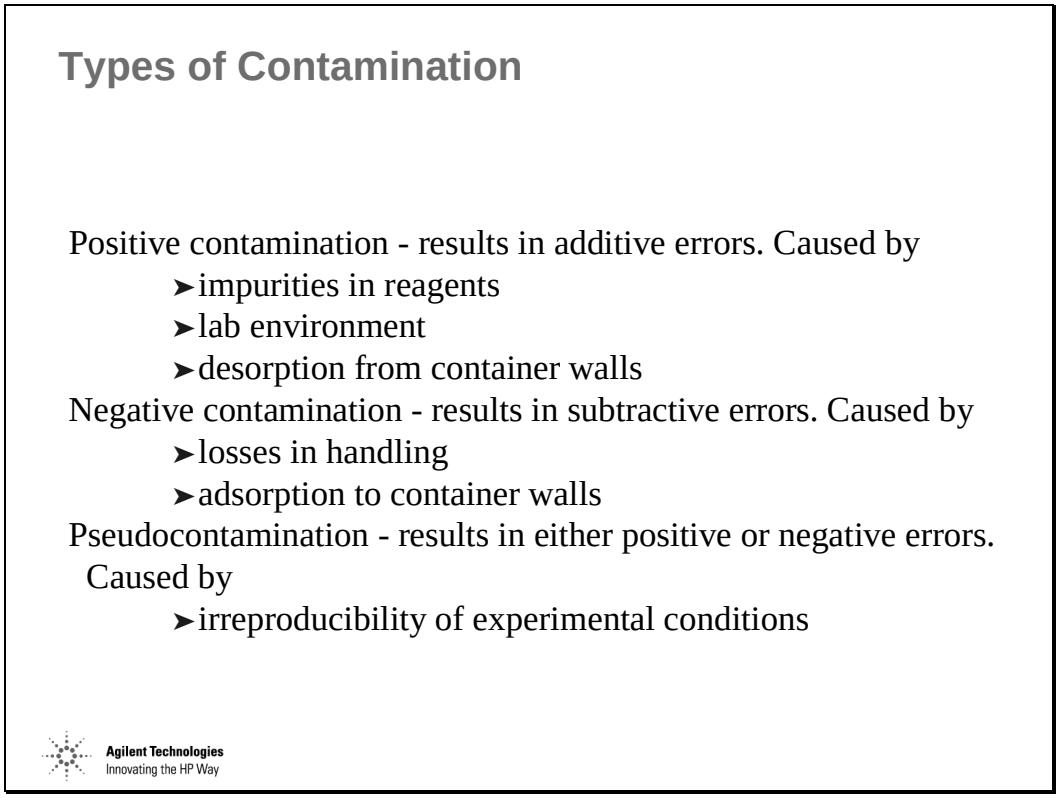

Figure 130

Challenges of Trace Analysis

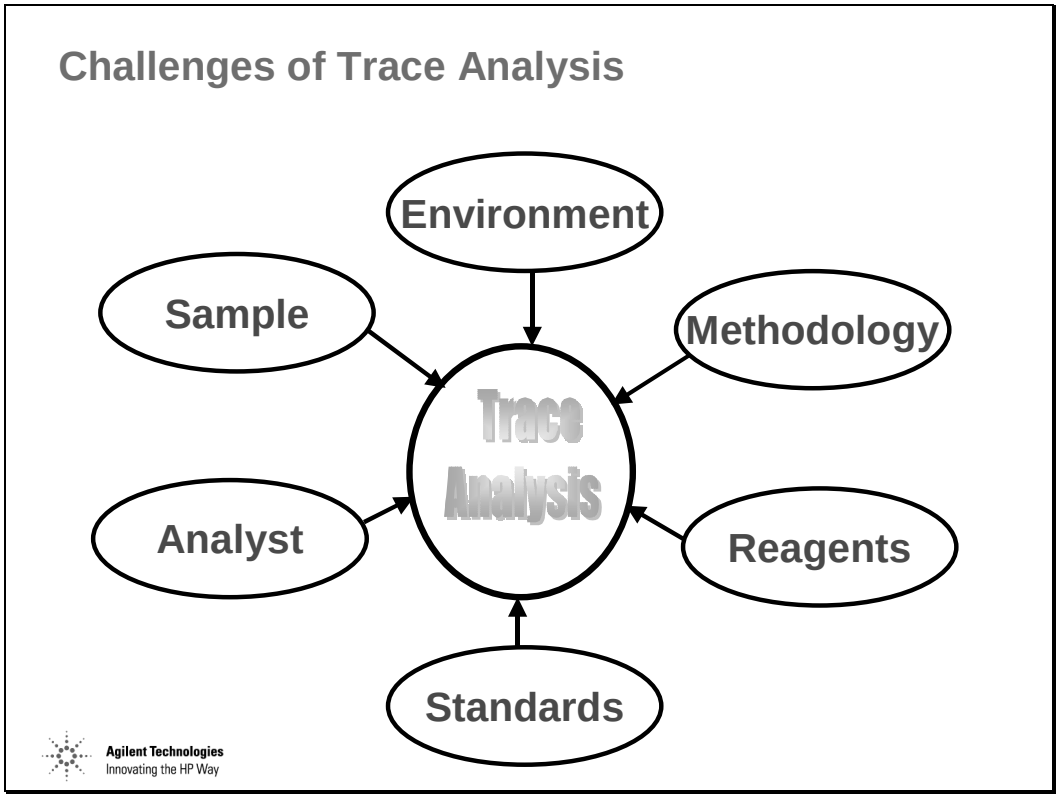

Figure 131

When a Contamination Can Occur

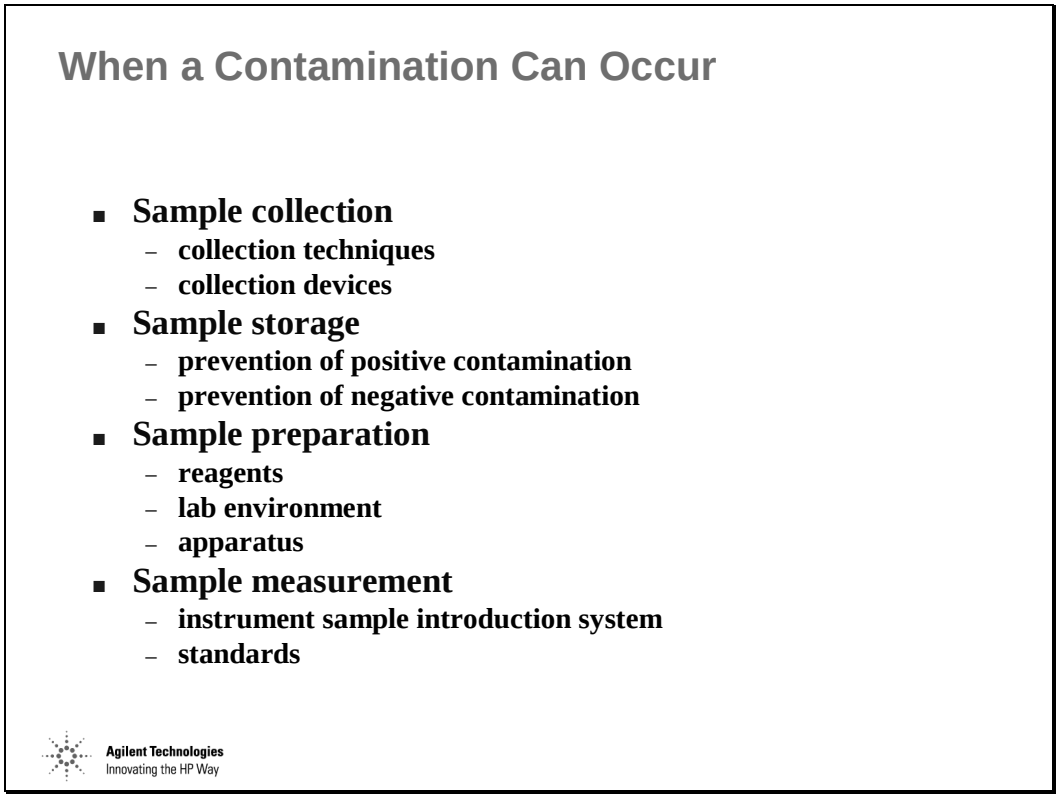

Figure 132

Reagents

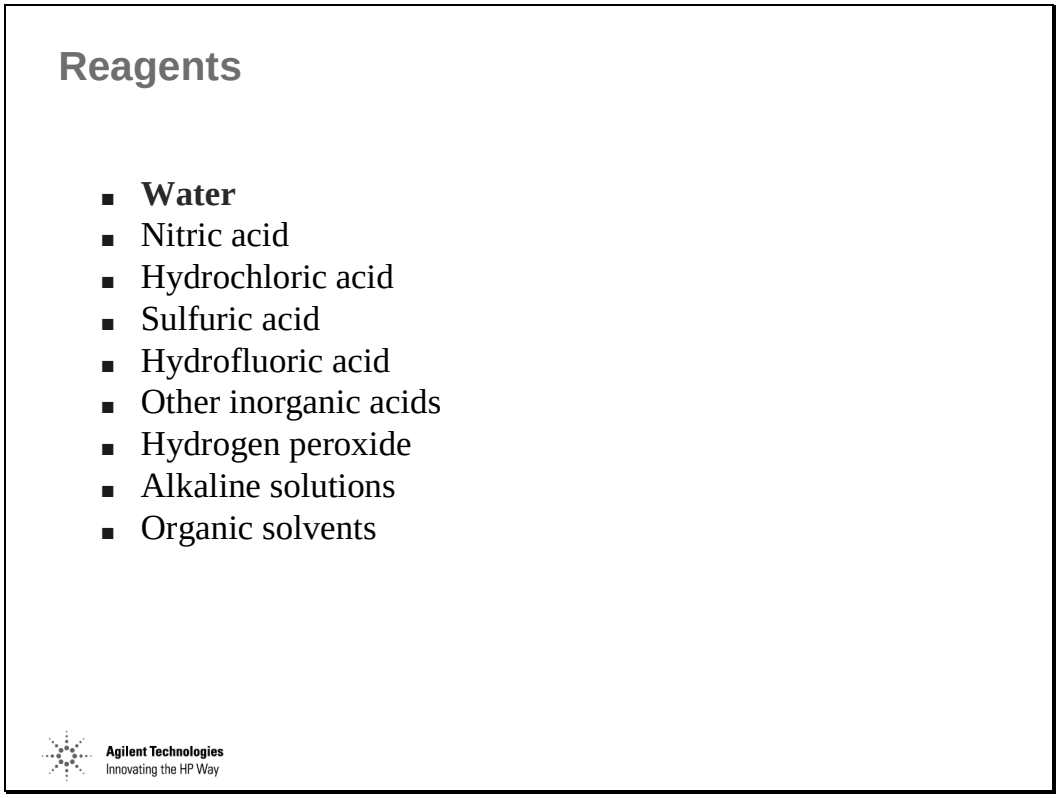

Figure 133

Water - Millipore

Figure 134

Nitric Acid

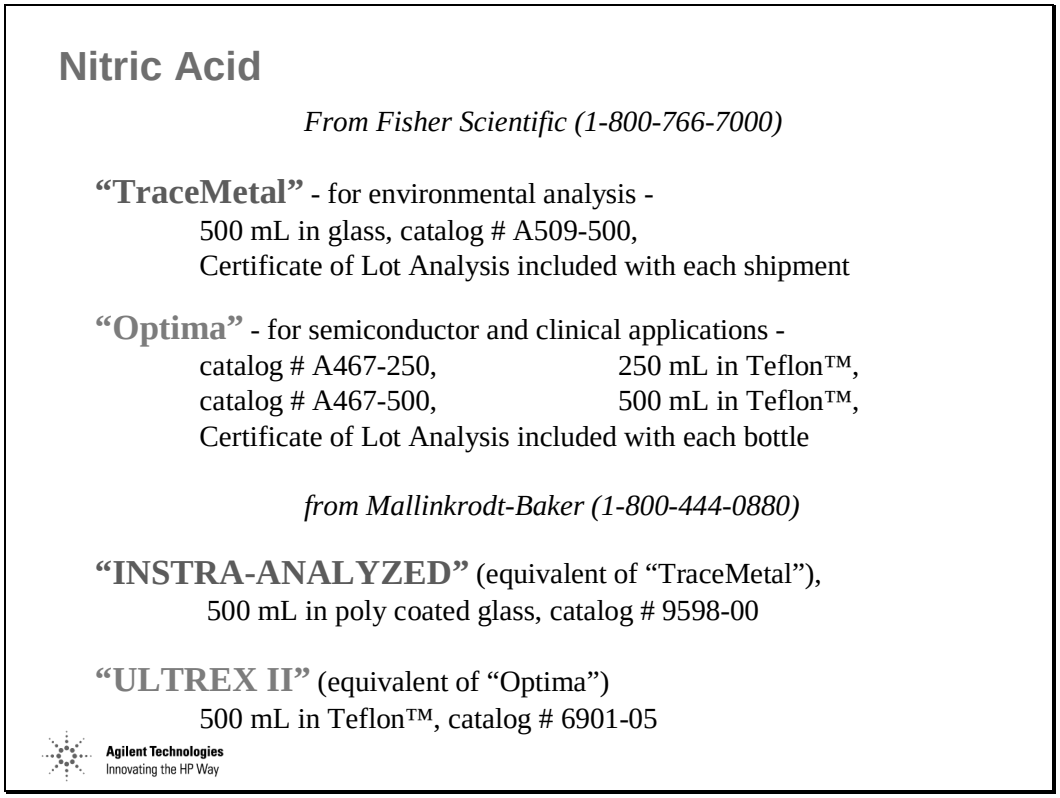

Figure 135

Selected Methods of Sample Preparation

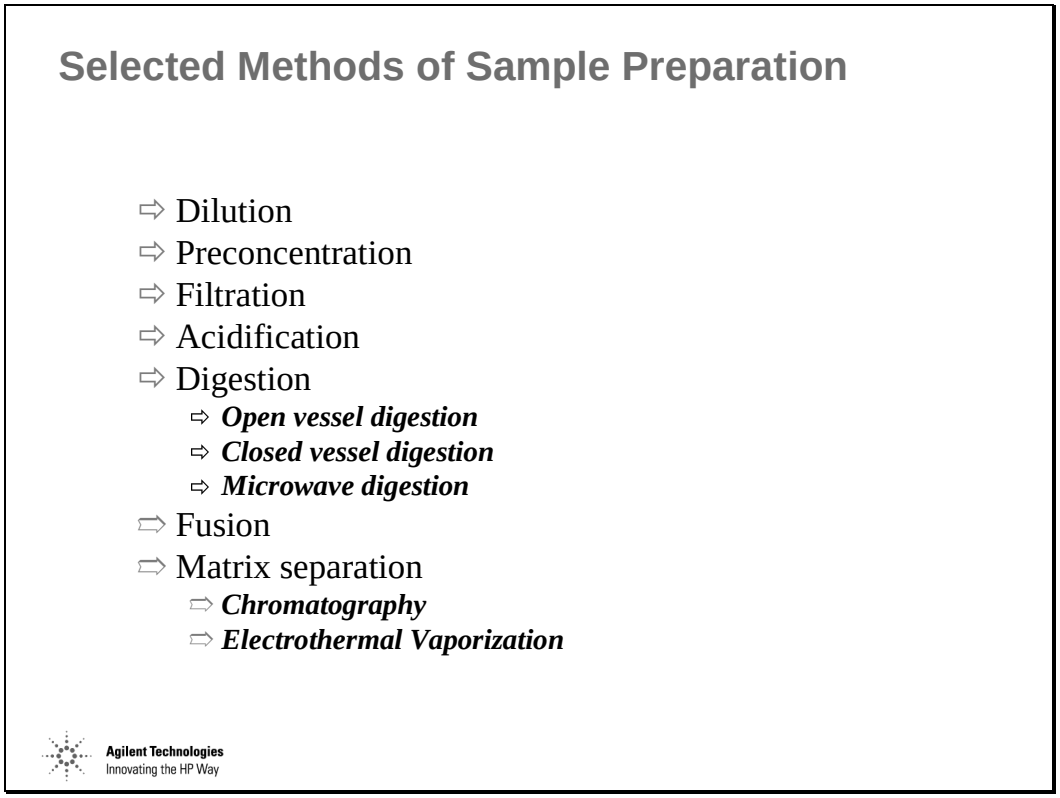

Figure 136

Commonly Used Reagents (1)

Commonly Used Reagents (1)

Nitric Acid (HNO_3)

Used to dissolve a variety of materials such as metals, alloys, biological samples.
Available in very high purity form.
Most preferable acid for ICP-MS work, as polyatomic ions are not increased.

Hydrochloric Acid (HCl)

Used commonly for sample digestion.
Generates Cl derived polyatomic ions.
Can be evaporated to dryness and reconstituted in HNO3.

Hydrofluoric Acid (HF)

Used to dissolve silica-based materials and geological samples.
HF attacks glass, therefore the inert sample introduction system must be used.
Teflon containers are often used.
Extreme health hazard.

Figure 137

Commonly Used Reagents (2)

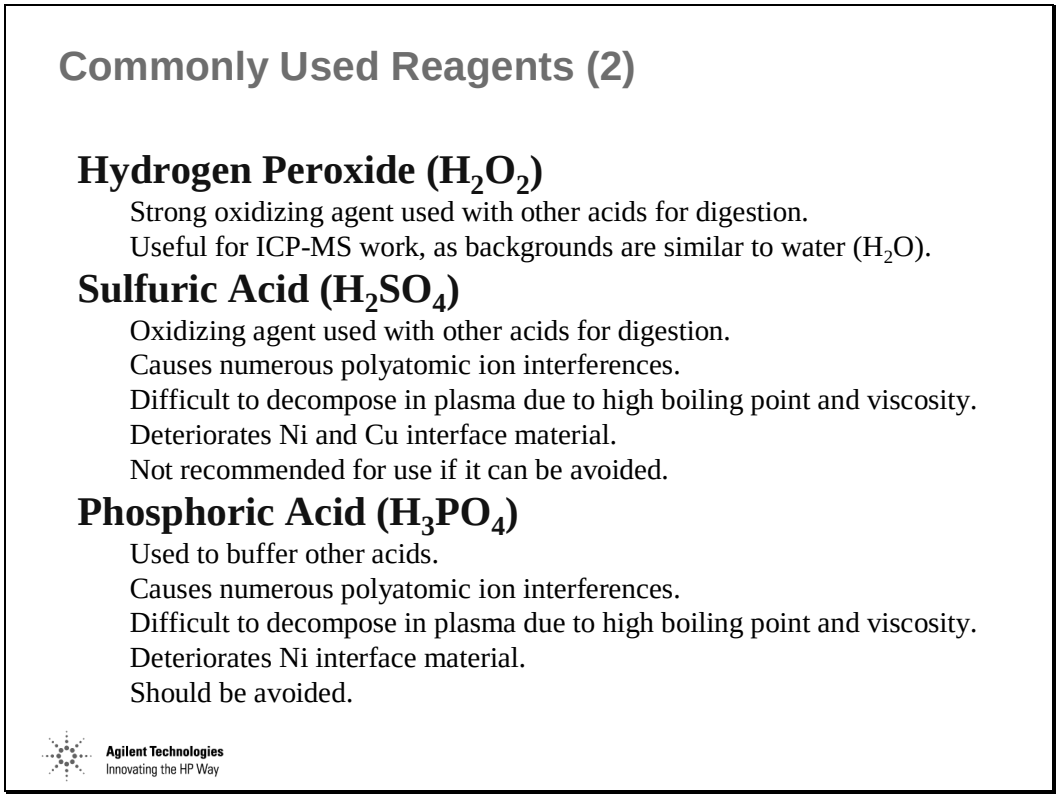

Figure 138

Commonly Used Reagents (3)

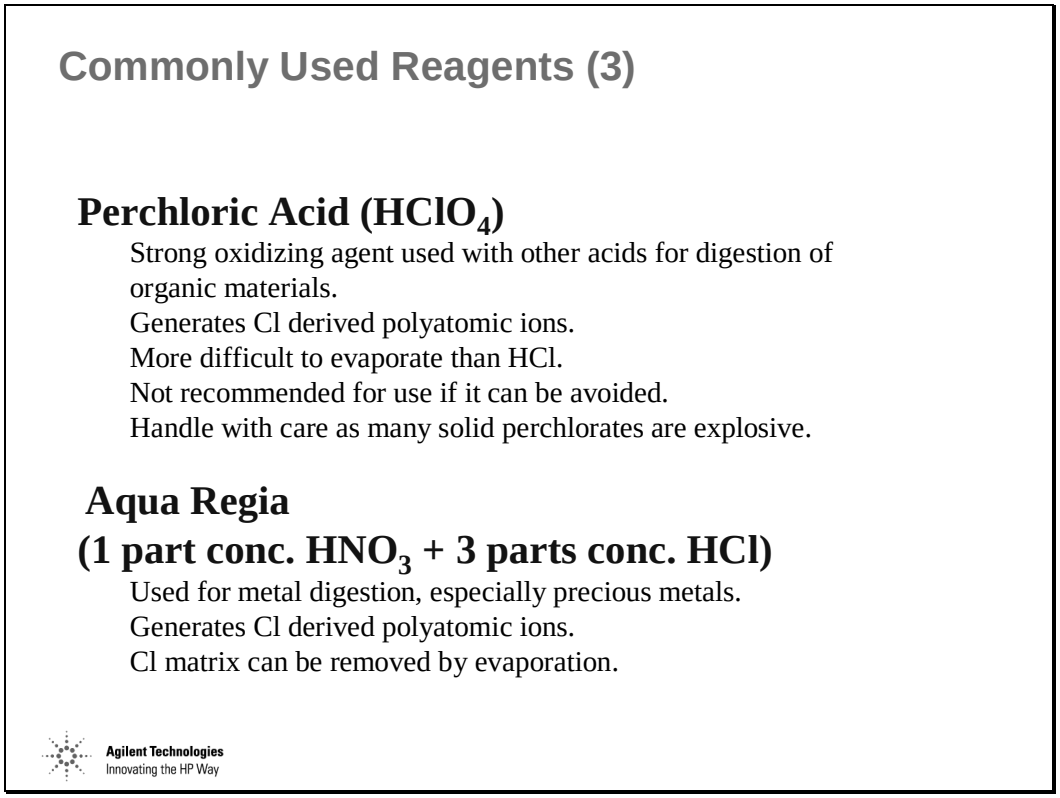

Figure 139

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Semi-quantitative Analysis of Samples

Semi-quantitative Analysis

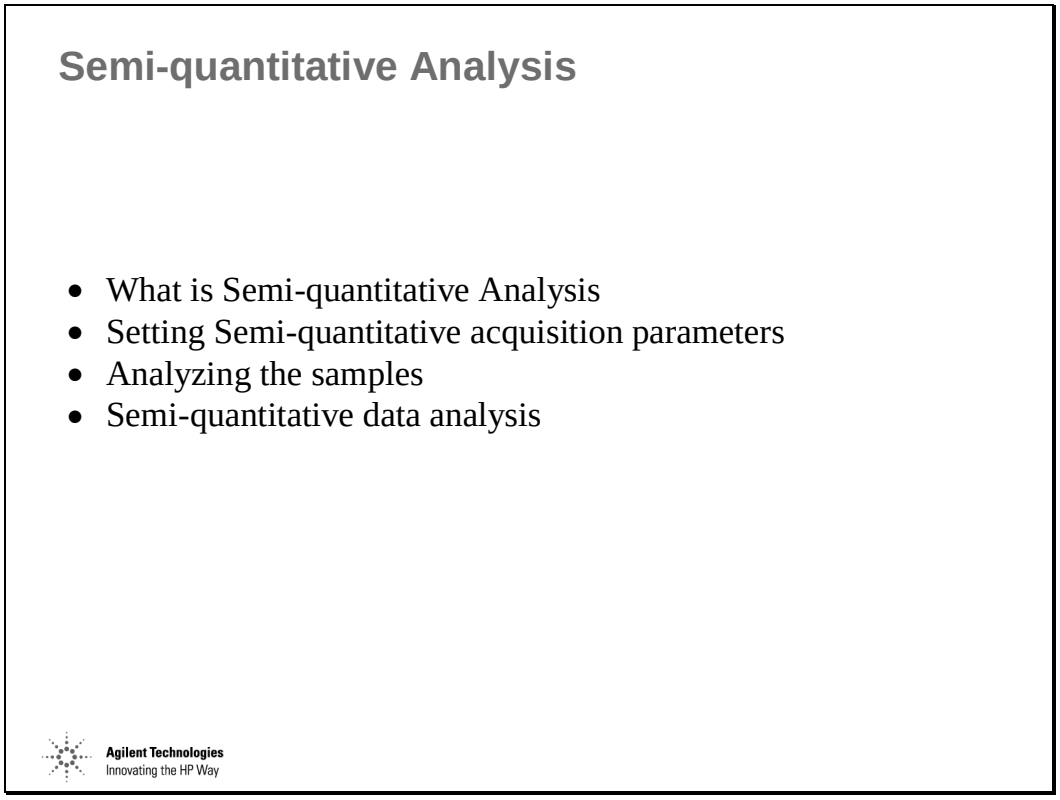

Figure 140

What is Semi-quantitative Analysis?

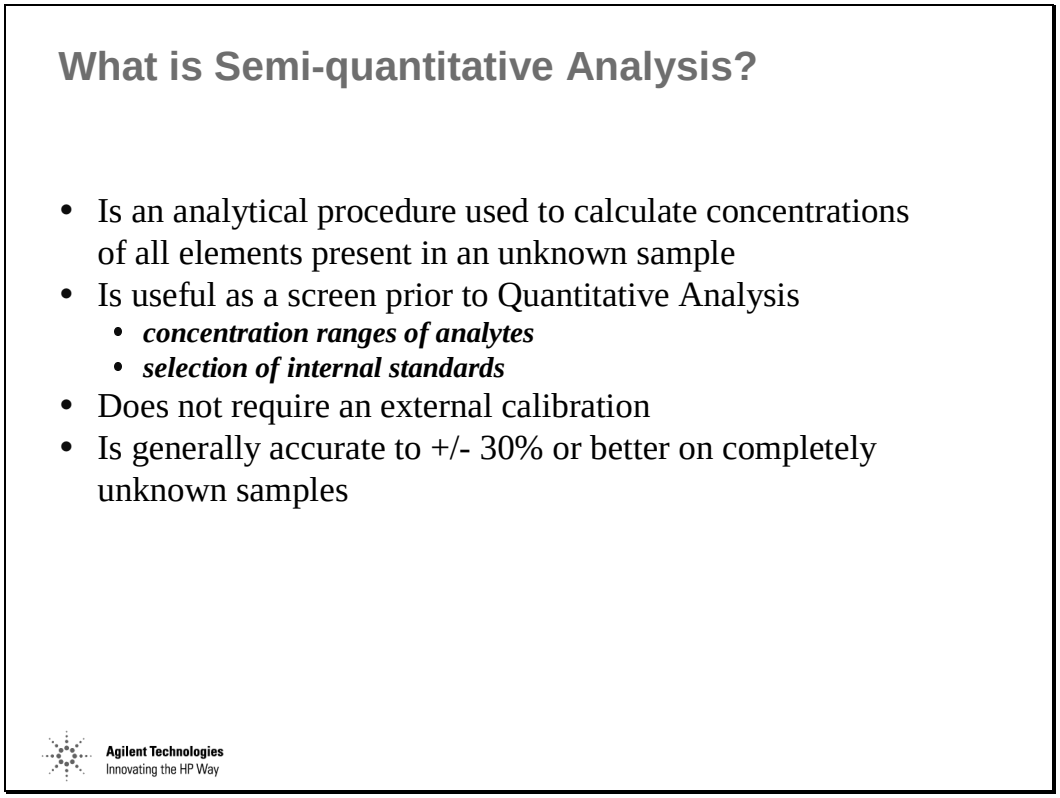

Figure 141

Data Acquisition

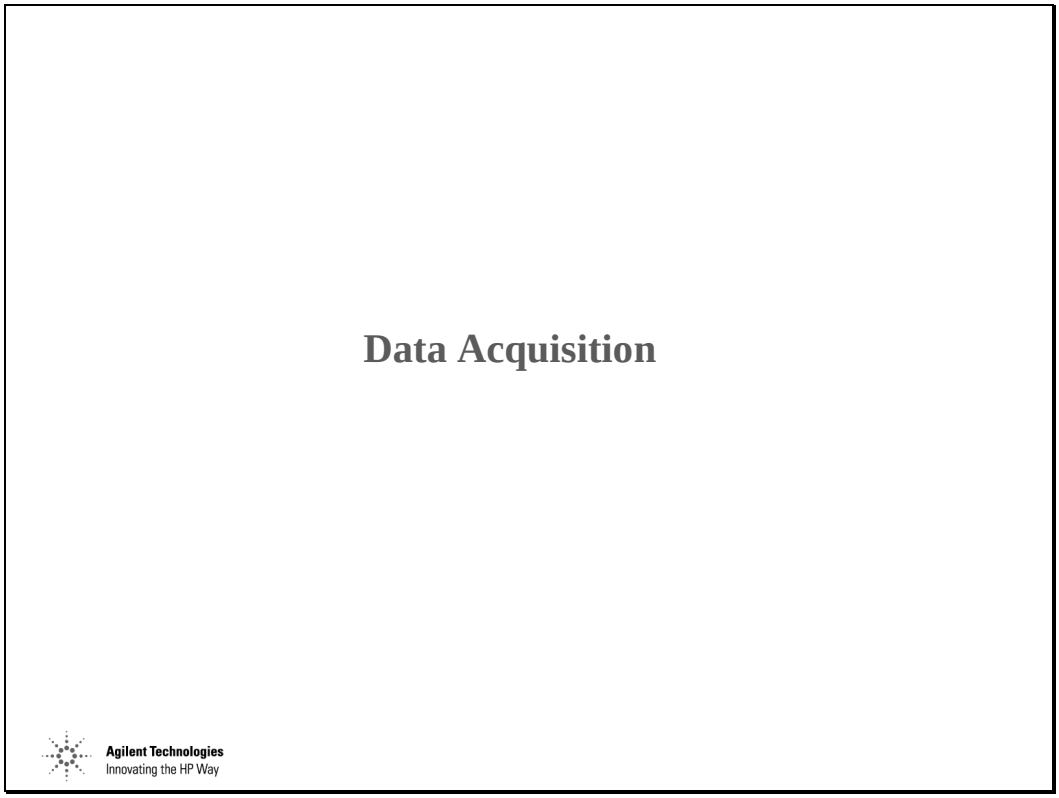

Figure 142

Method Set-up for Semi-quantitative Analysis

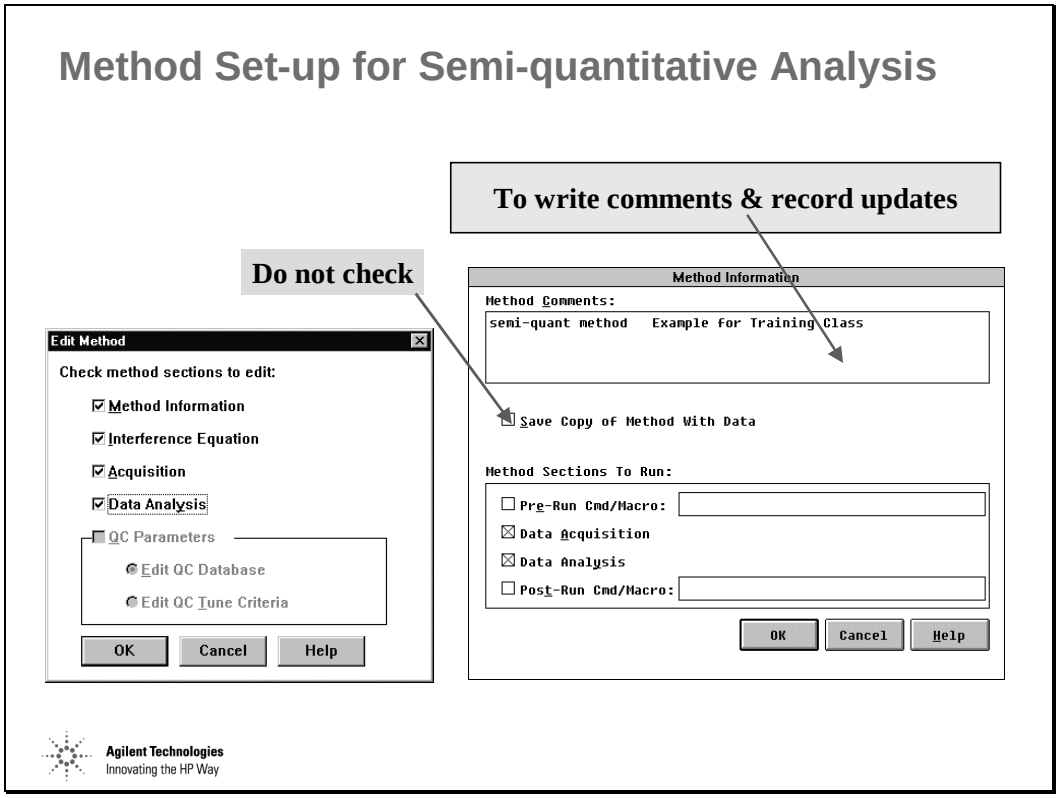

Figure 143

Parameters Selection - Spectrum Acquisition

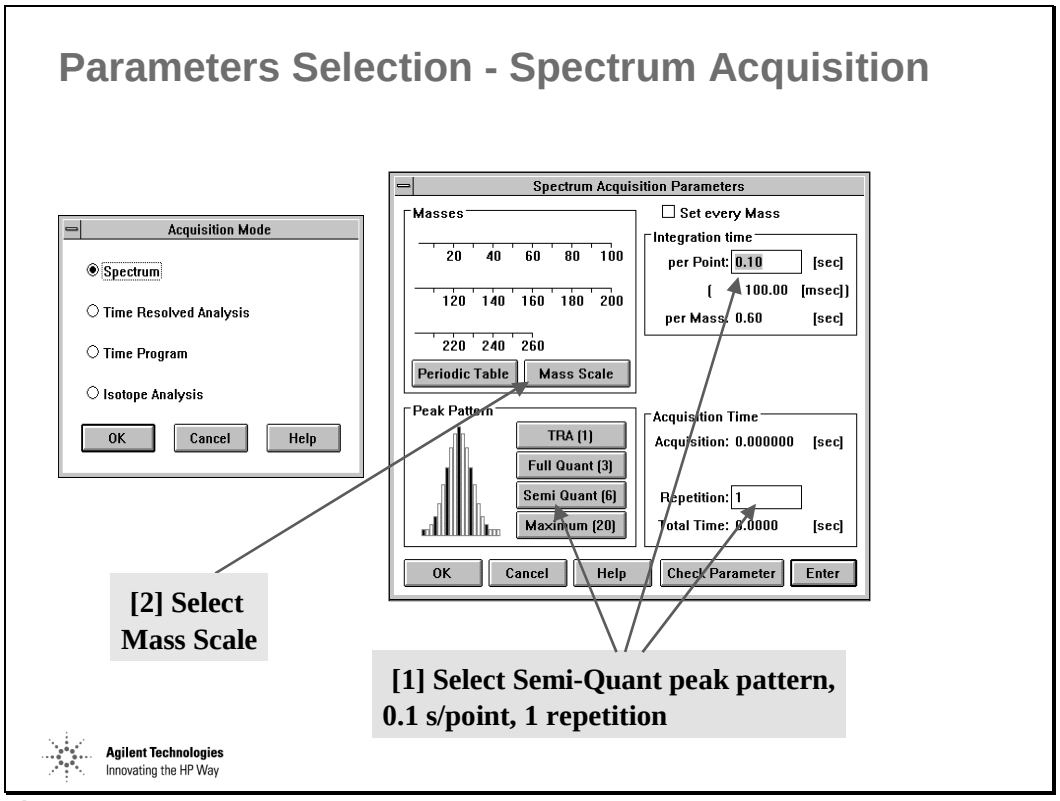

Figure 144

Parameters Selection - Selection of Masses

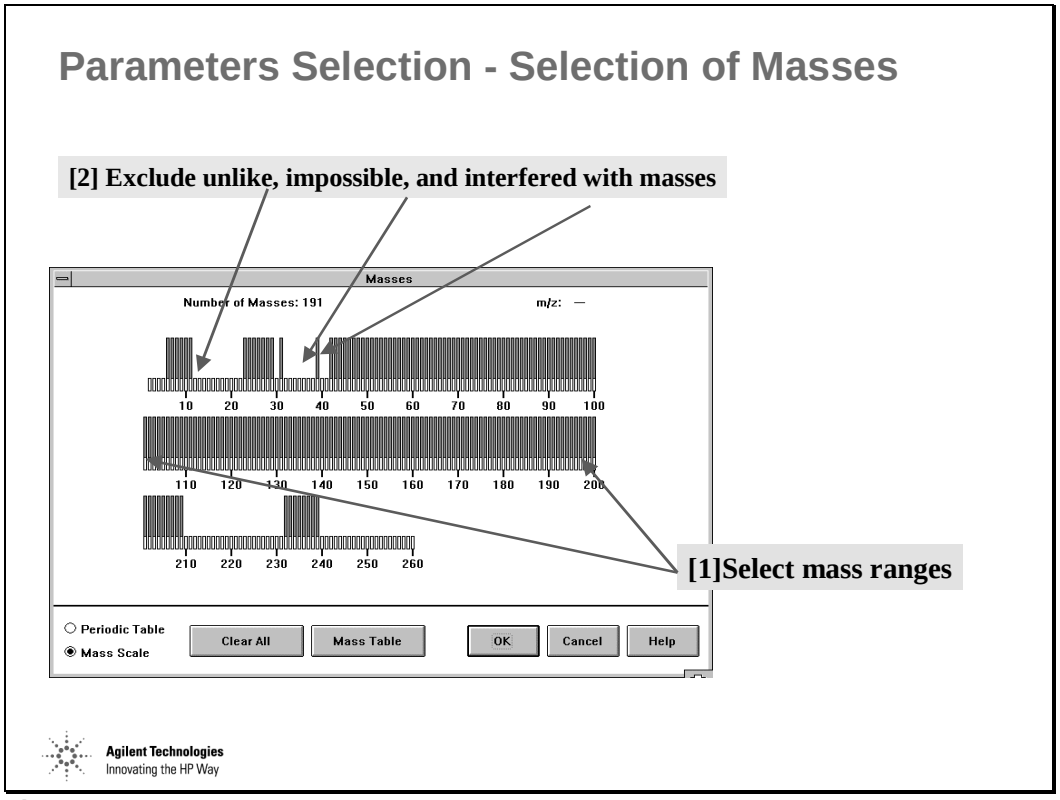

Figure 145

More Acquisition Parameters

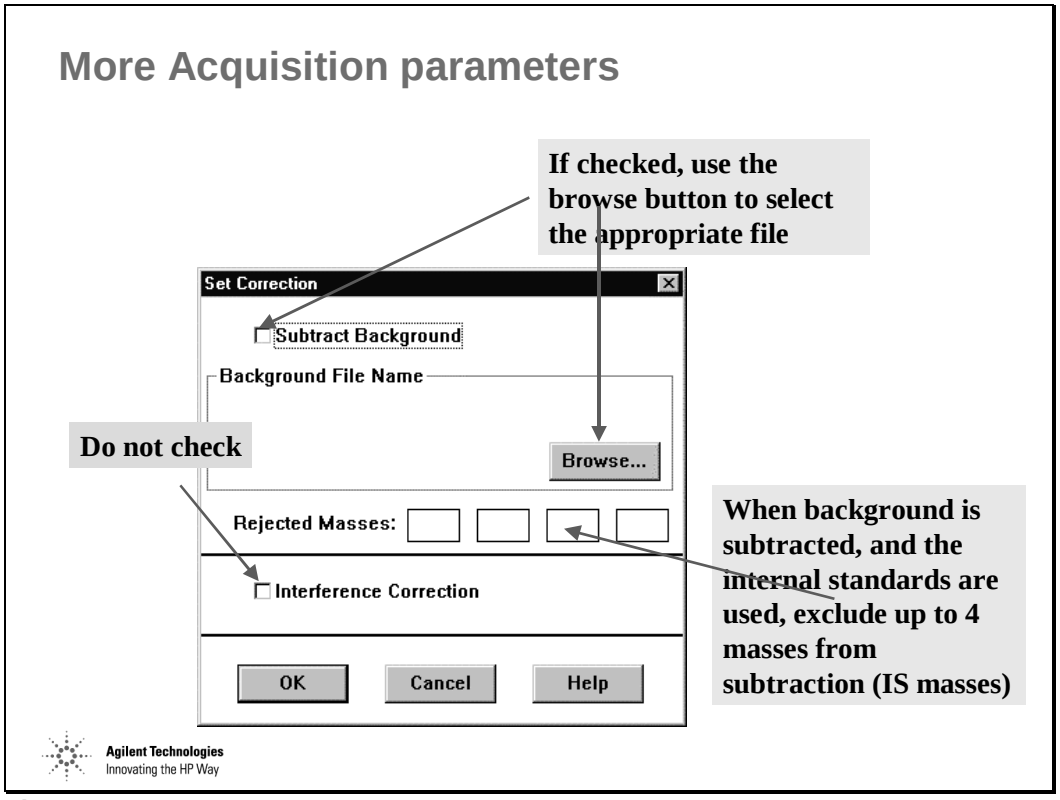

Figure 146

Report Generation

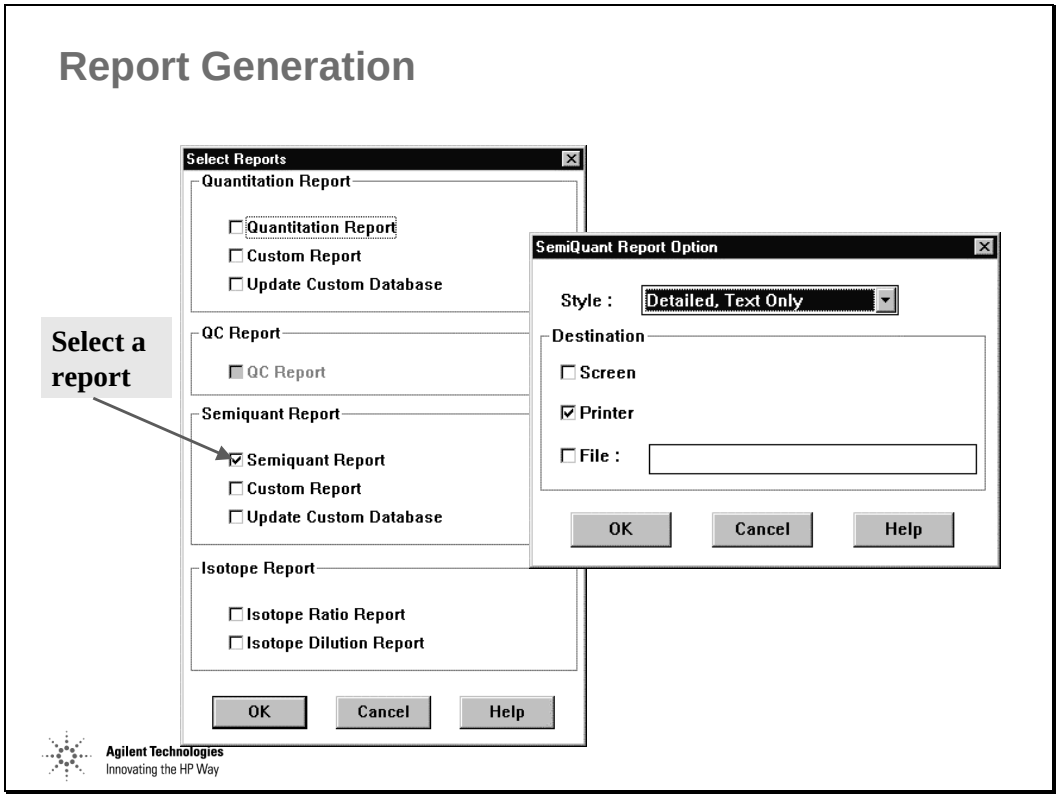

Figure 147

Semi-quant Parameters

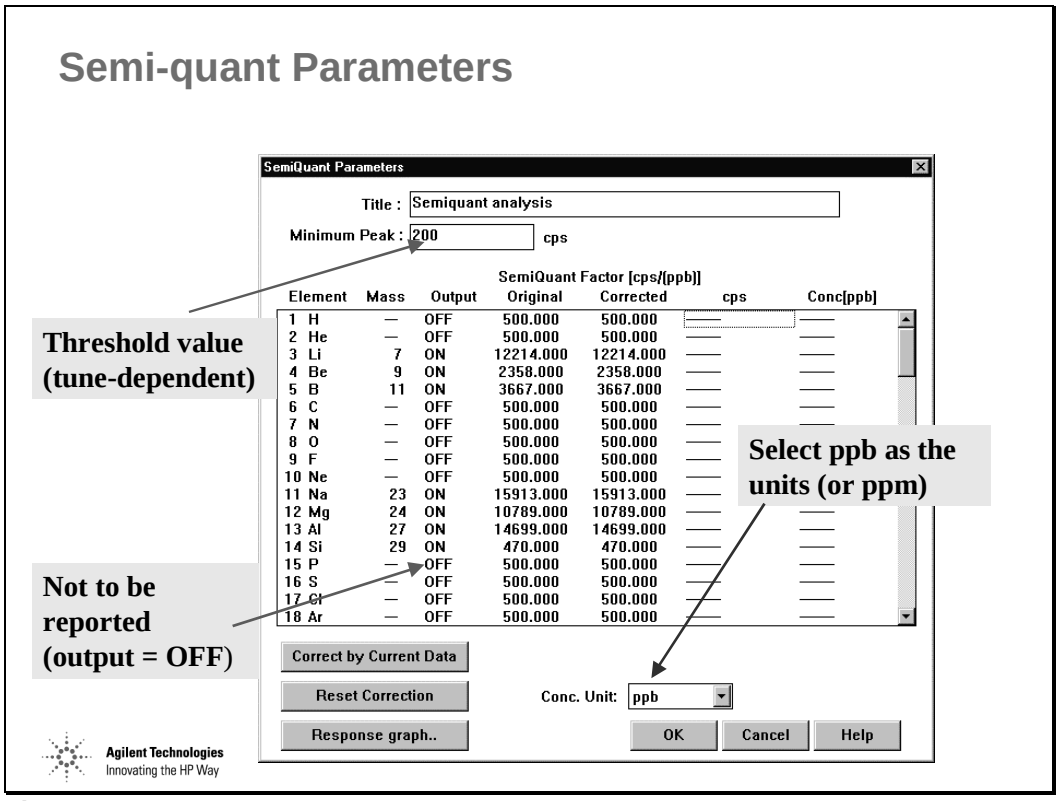

Figure 148

Set the Minimum Peak threshold to reject results based on noise. The default is 50, but remember, typical response in tuning is 20 million cps/ppm which is 20K cps/ppb. Therefore at least 200 cps represents a reporting threshold of approximately tens of ppt, a reasonable value.

Output Mode is either ON, OFF or AUTO. ON - this element will always be reported; OFF - this element will never be reported; AUTO - this element will be reported IF no significant interference is detected. The acceptable level of interference is stored in WIN.INI and can be edited there.

Concentration Units is either user selectable or when set to AUTO, the ChemStation will select the appropriate units based on the estimated concentration. Enter the concentration in ppb (or ug/L) of the elements in the cal standard. Leave the other concentration fields blank.

Semi-quantitative Data Analysis

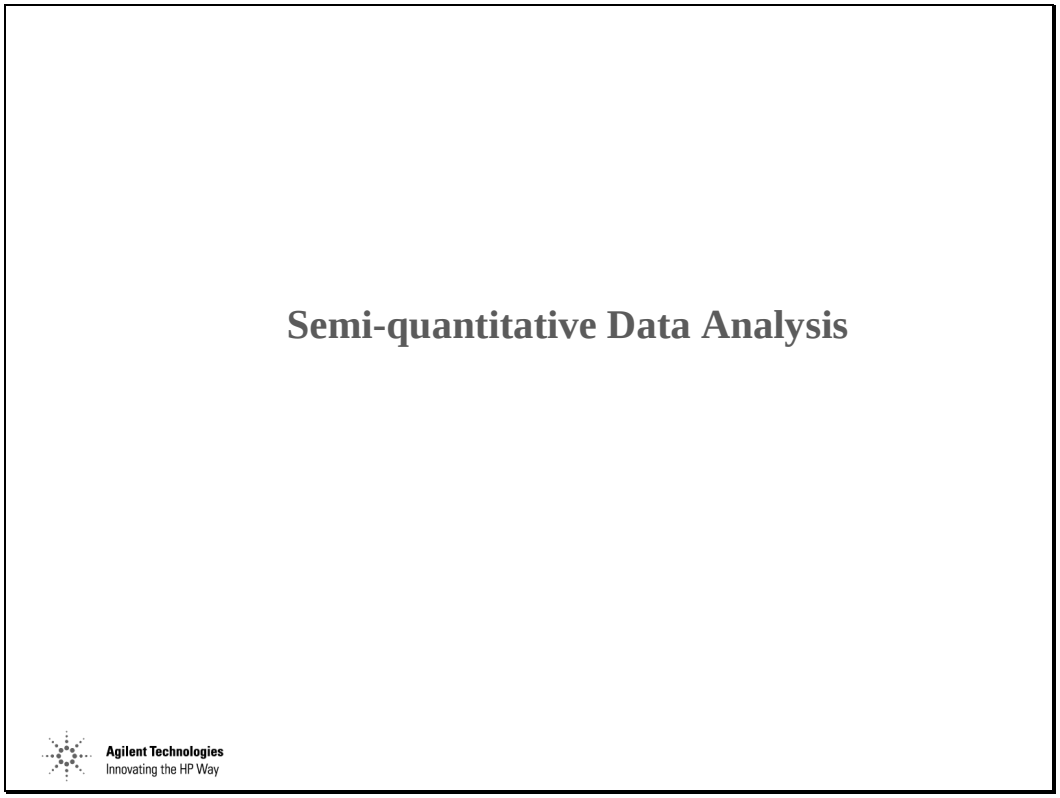

Figure 149

Semiquant analysis can be used to estimate the concentration of any element for which a precise measurement can be made by ICP-MS (> 70 elements).

Typically, semiquantitation is accurate to within +/- 30 percent on completely unknown samples. However, semiquantitation is subject to the same interferences as quantitation. Possible interferences due to oxides, hydrides, argides, dimers and doubly-charged ions are checked and flagged on the report. Interference correction equations can be used to minimize these effects where applicable. The use of internal standards can help correct for matrix differences. Blank subtraction can be used to eliminate contributions from laboratory reagents and sample preparation.

The ChemStation comes configured with default SemiQuant response factors. These factors are based on relative ionization potentials and numbers of isotopes for each element. These factors can be updated to reflect the tune state of the HP-4500 by analyzing a calibration mix. At least 3 elements should be used, though more is better. The ChemStation will then interpolate between analyzed masses to update all SemiQuant response factors.

Editing Parameters

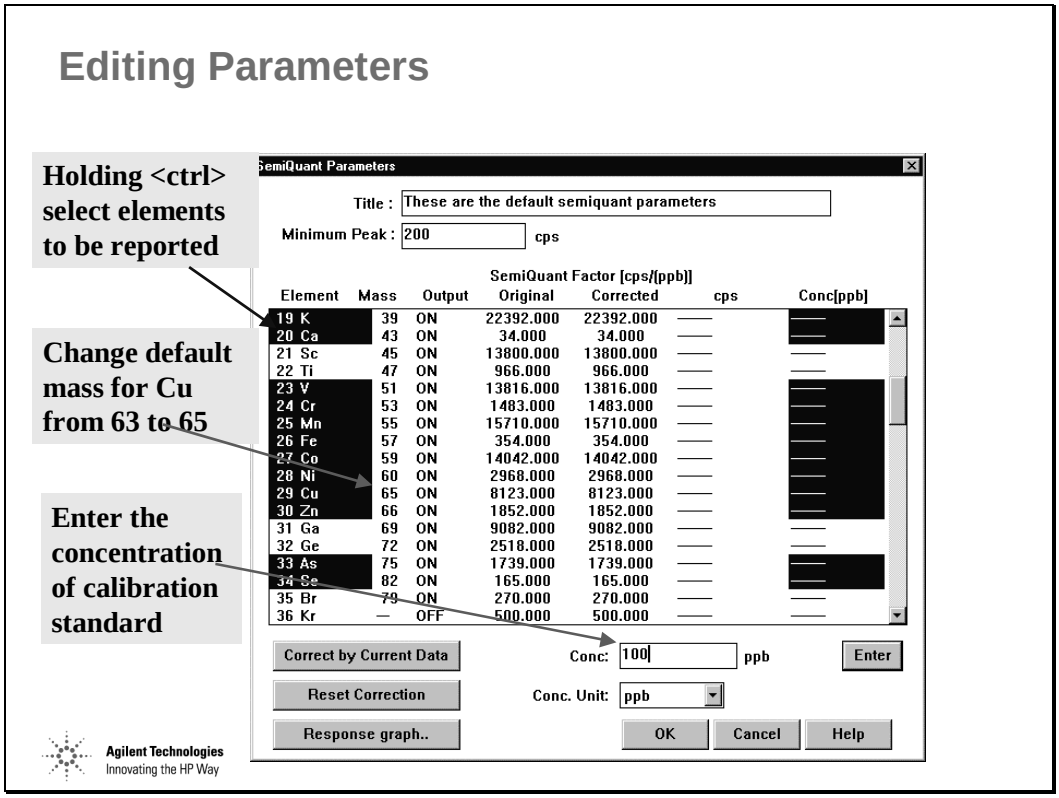

Figure 150

Daily Update of the Semi-Quant Parameters

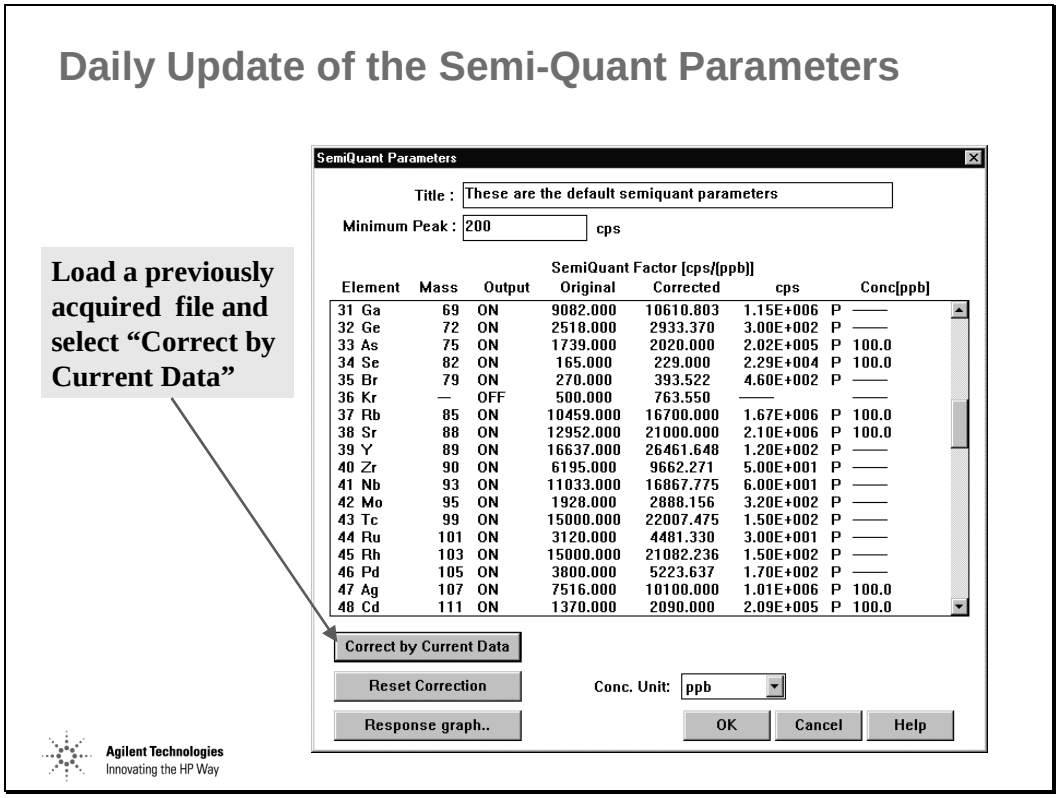

Figure 151

Correct by Current Data recalculates all semi-quant response factors by first dividing the supplied concentrations by the responses for those elements. Other, non-calibrated element response factors are estimated by interpolation.

Internal Standard Correction for Off-line Internal Standard Addition

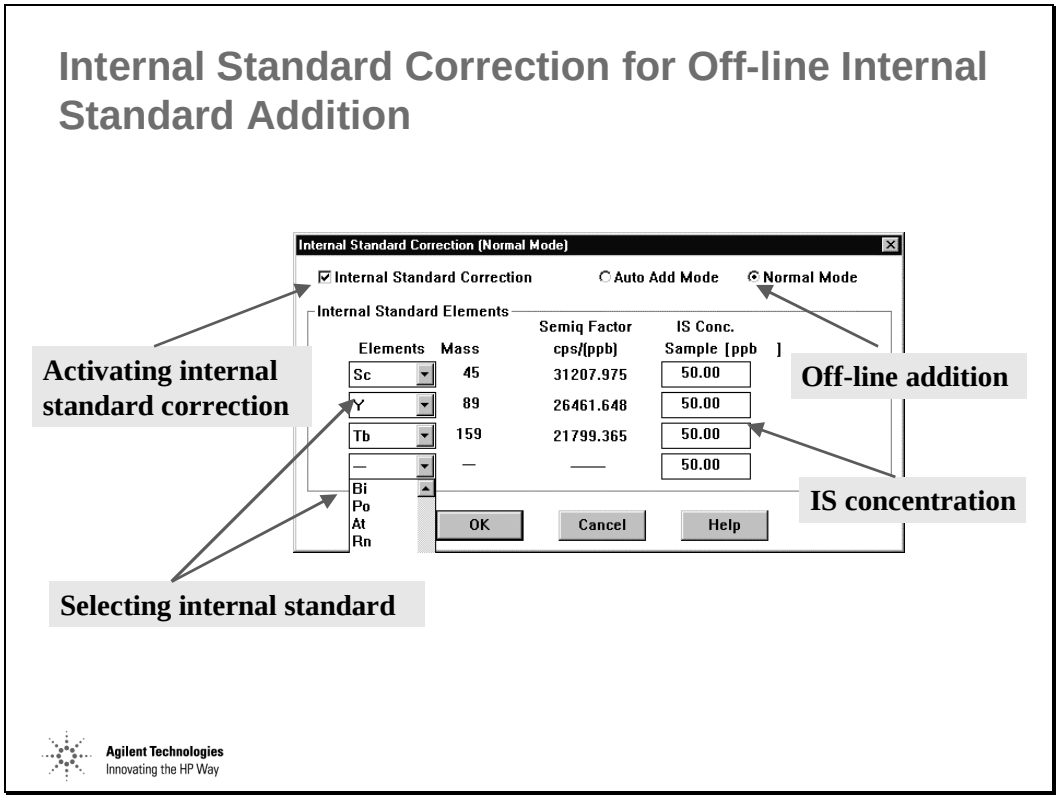

Figure 152

Internal Standardization is recommended since it corrects for changes in instrument sensitivity due to matrix and other effects.

To configure internal standard correction:

Data Analysis >> SemiQuant >> Internal Standard Correction…

Internal standard correction can be applied in two modes:

'Normal Mode' assumes that internal standards are added to the samples only and no ISTD reference data file is required. This can be used for analyses such as Laser Ablation, where a matrix element is used as the internal standard. The ISTD factor is calculated from the supplied ISTD concentration and the ISTD response. Up to four internal standard elements can be selected.

Internal Standard Correction for On-line Internal Standard Addition

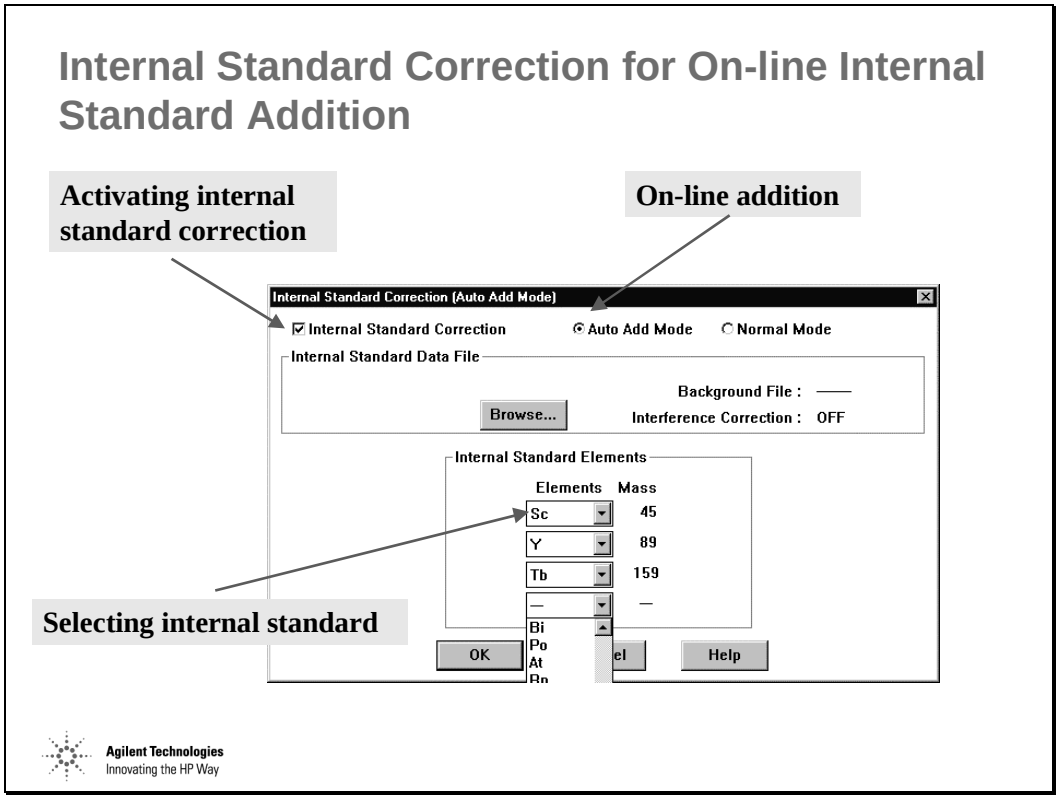

Figure 153

'Auto Add Mode' assumes that the online internal standard addition configuration is used. In this case, the exact concentration of the ISTD elements need not be known since an ISTD reference file used. Only the internal standard masses need be selected. In this case, the only requirement is that the ISTD concentration in all samples be identical to the ISTD reference file.

The ISTD reference file can be either a blank or a calibration standard containing online added internal standards.

Example of Semi-Quant Report [1]

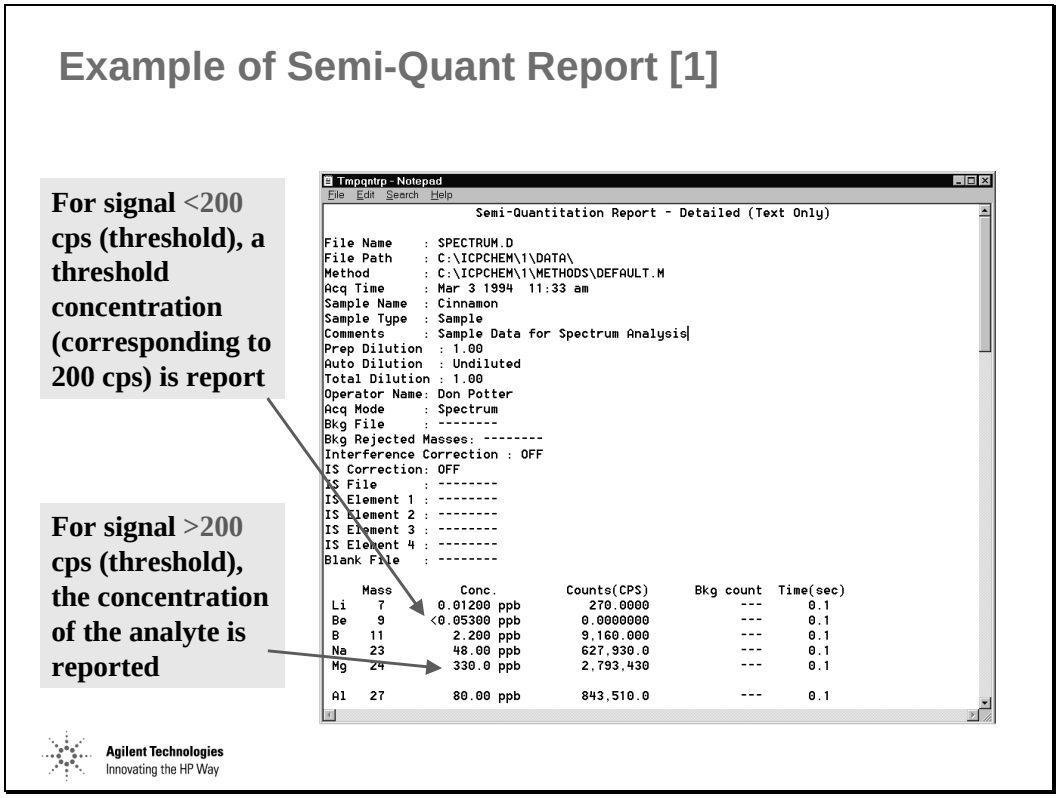

Figure 154

Example of Semi-Quant Report [2]

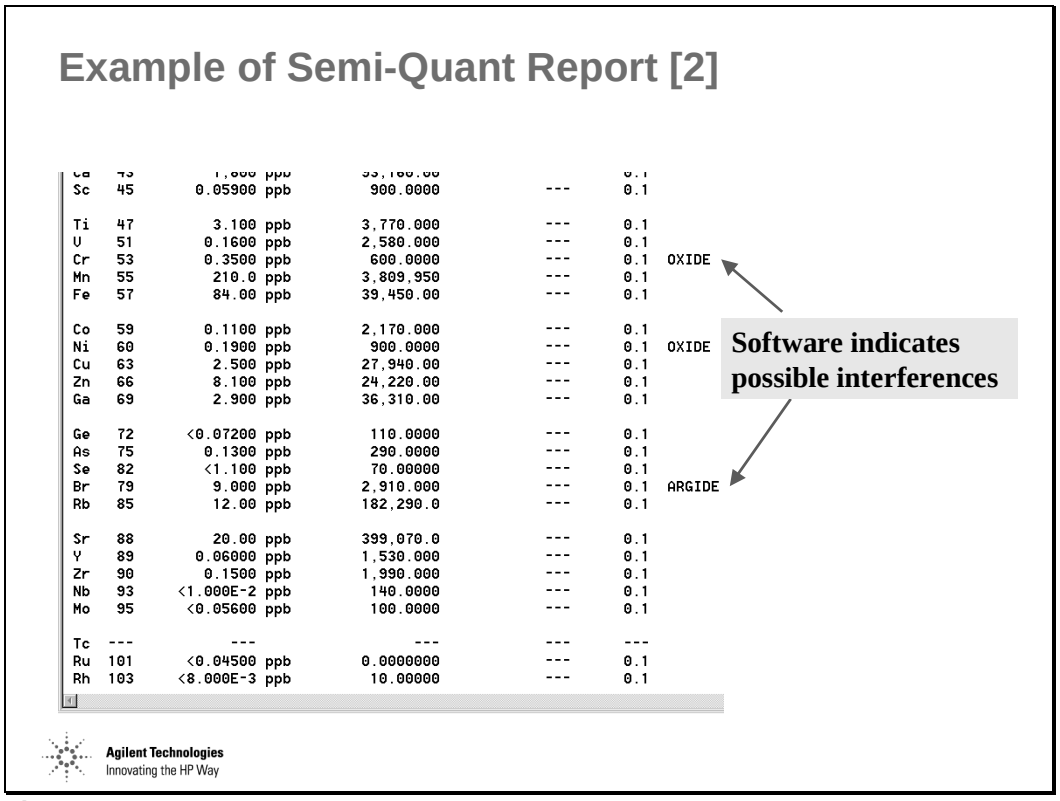

Figure 155

Generating a Semi-quant Report

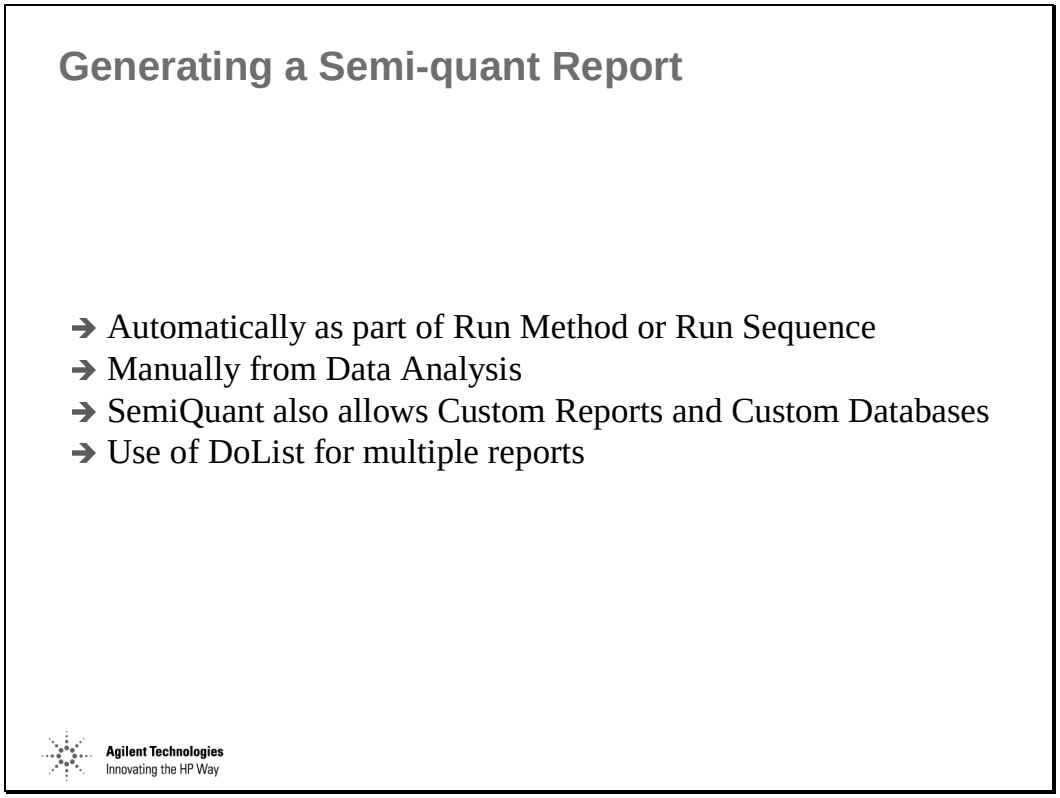

Figure 156

Manual Verification of the Data

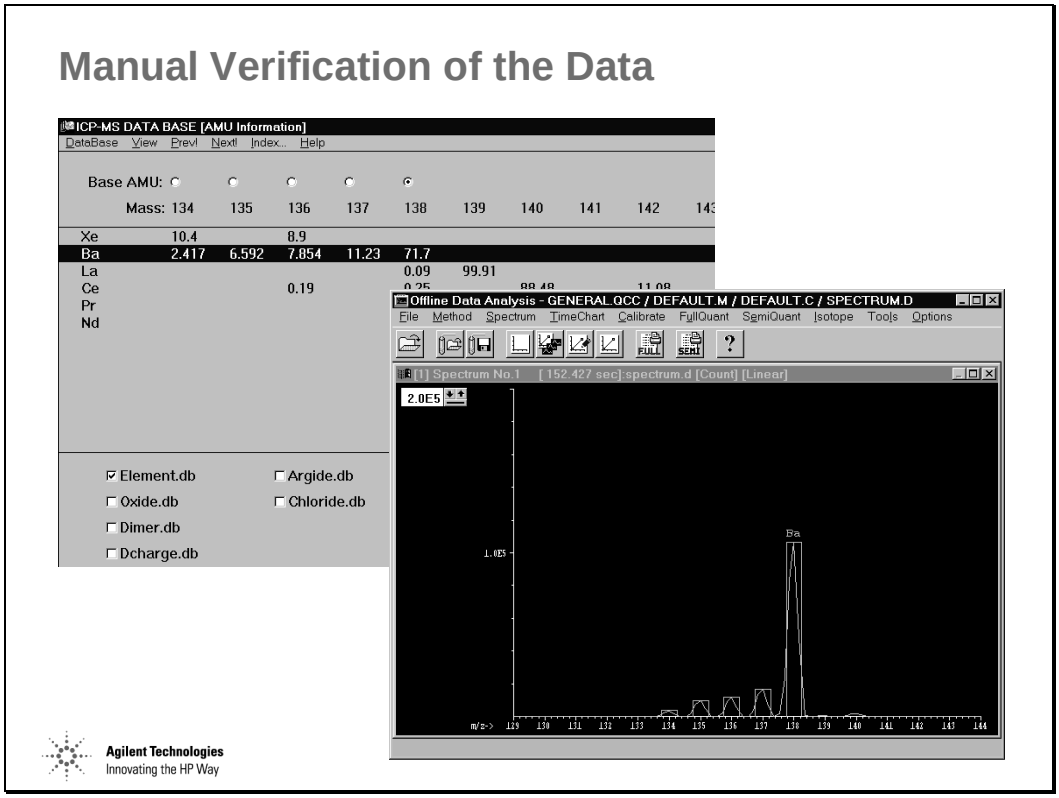

Figure 157

Manual Verification of the Data

Agilent Technologies

Innovating the HP Way

Quantitative Analysis of Samples

What is Quantitative Analysis?

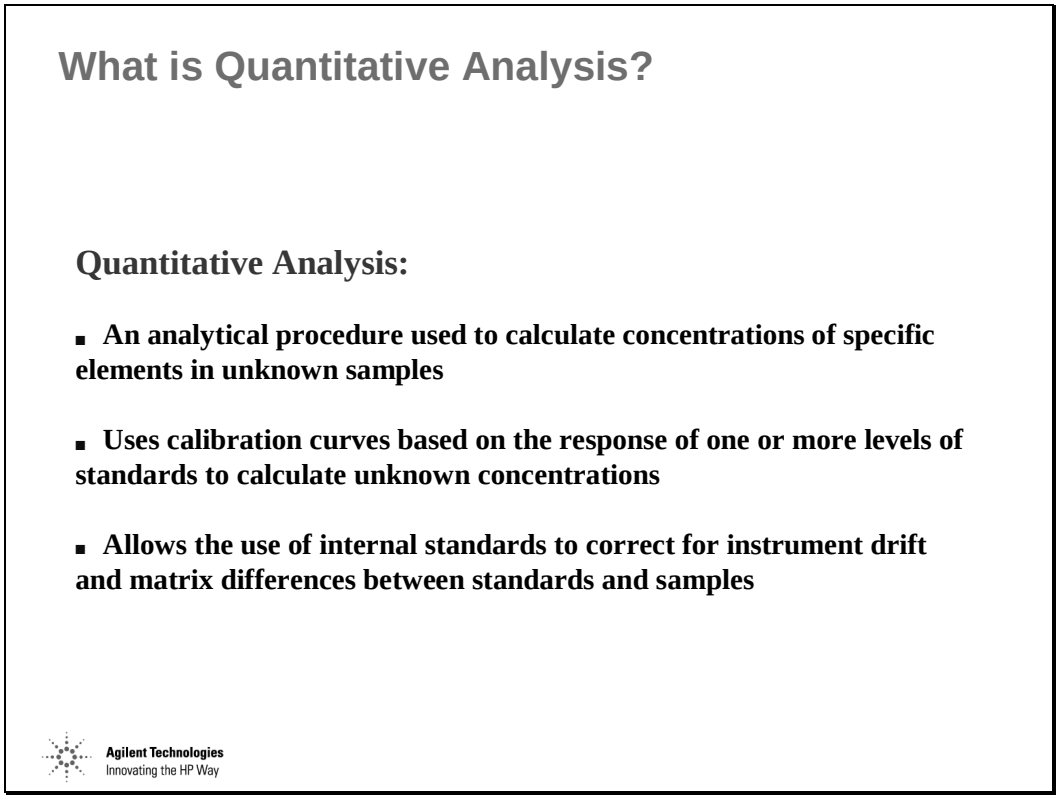

Figure 158

Method Set-up for Quantitative Analysis

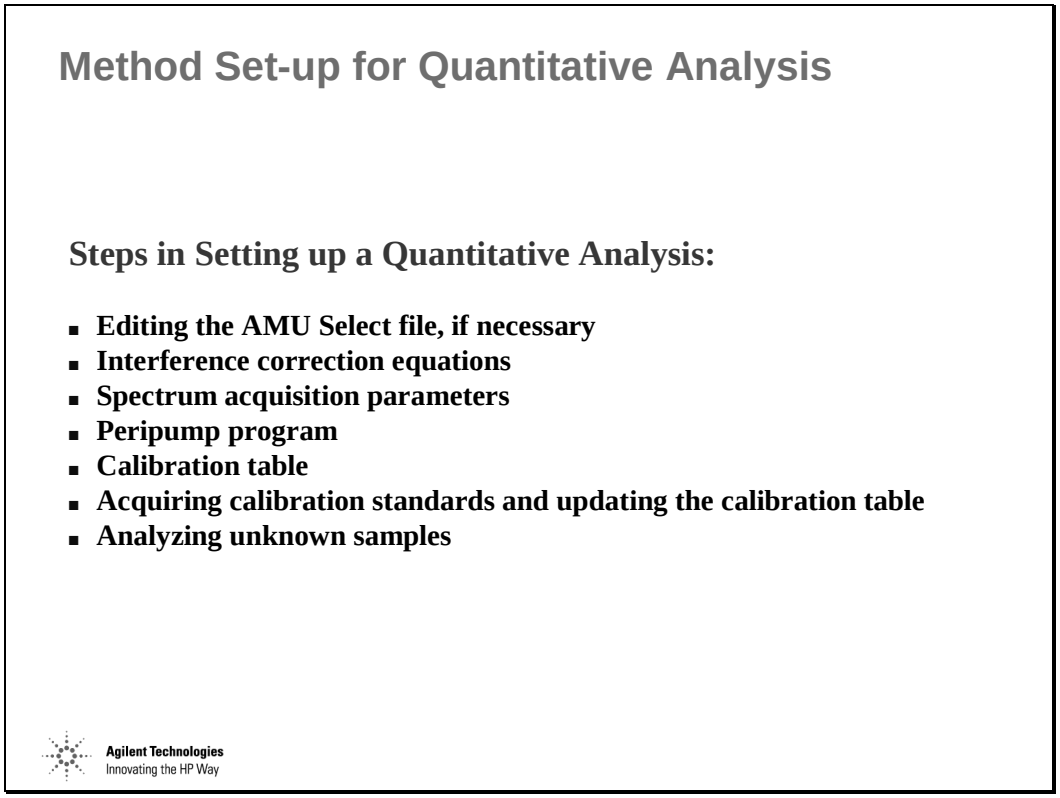

Figure 159

Step One: Editing the AMU Select File

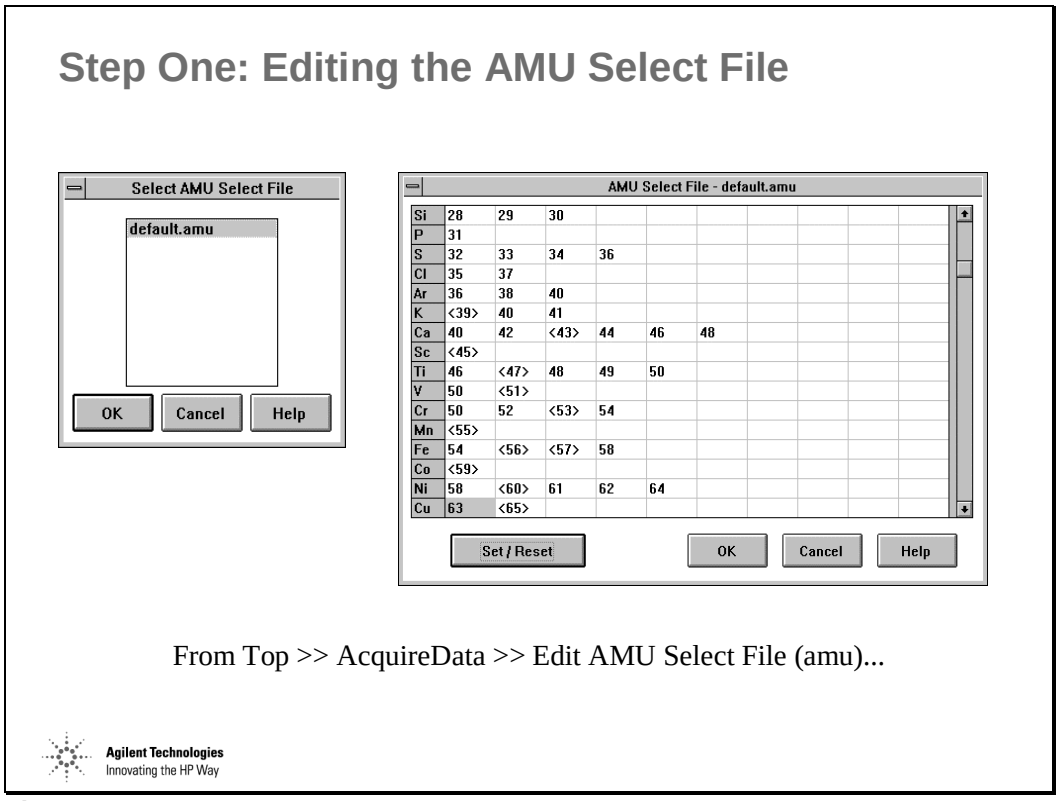

Figure 160

The AMU select file is the database from which default isotopes are selected when elements are selected from the Periodic Table in Edit Entire Method.

Multiple AMU select files can be created for different applications. For example AMU select files can be created which automatically select the EPA specified isotopes when running EPA methods. AMU select files can also be created for specific matrices in order to avoid known isobaric or polyatomic interferences.

The element needs to have at least one isotope selected, in order to be accessible in the method setting. If needed, select isotopes for P, and Si.

Editing a Method for Quantitative Analysis

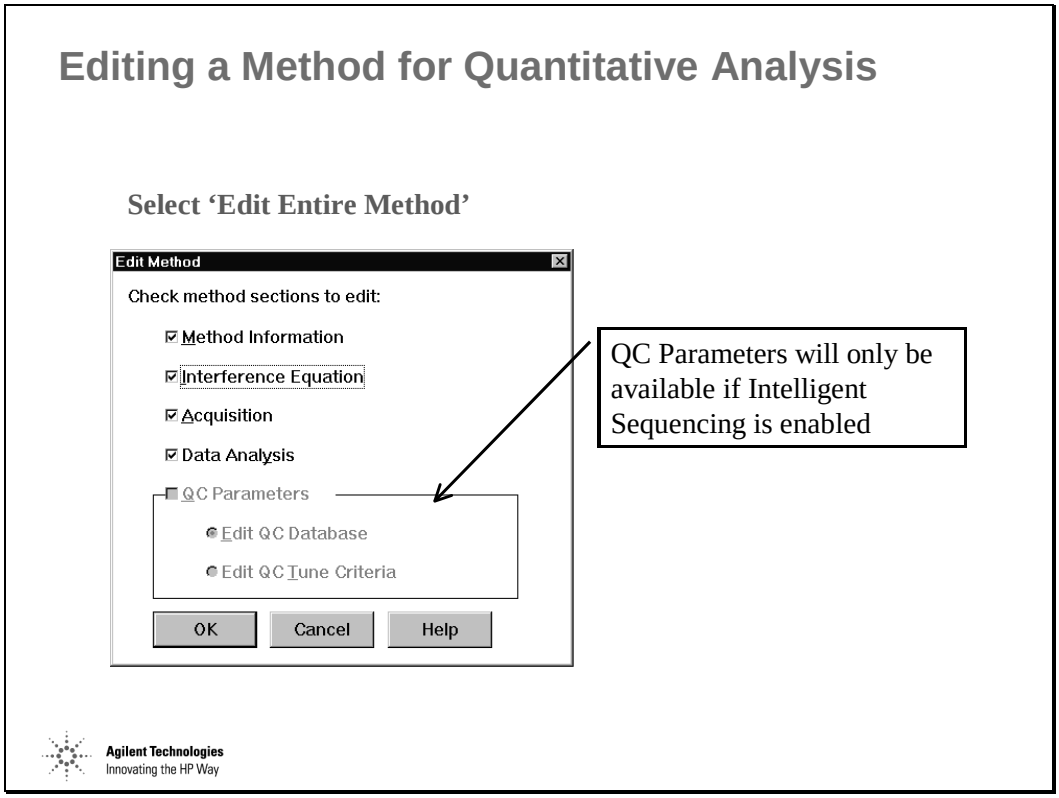

Figure 161

Method Information

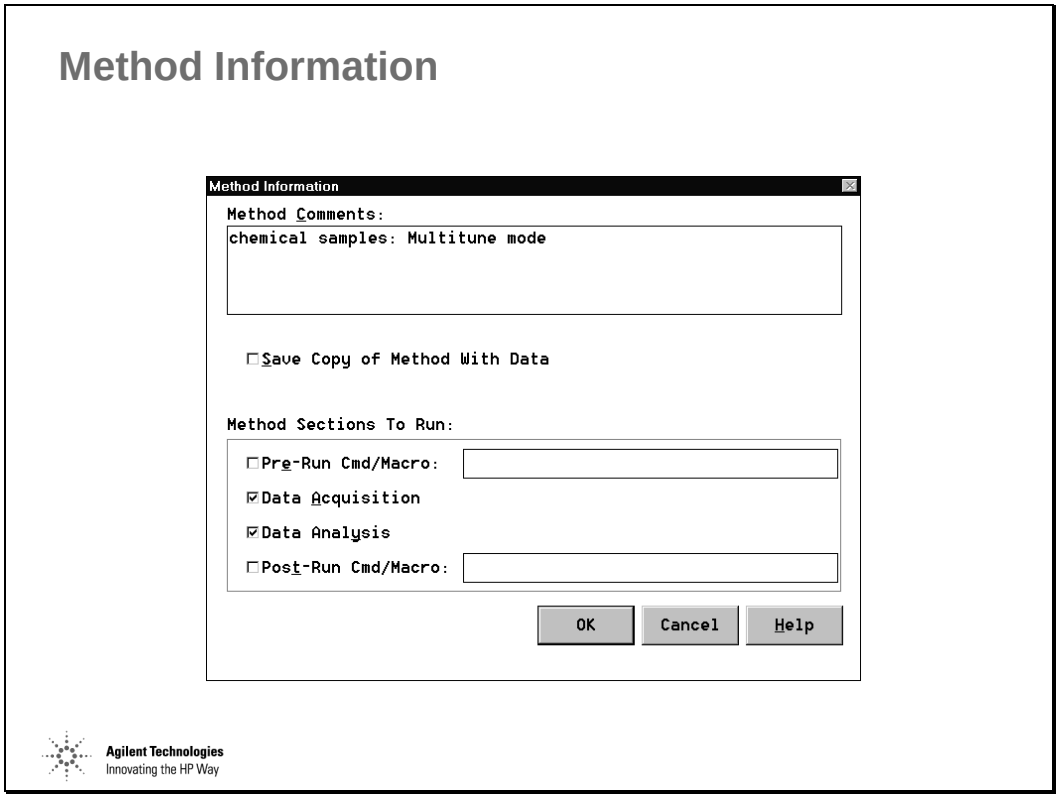

Figure 162

Acquisition Modes

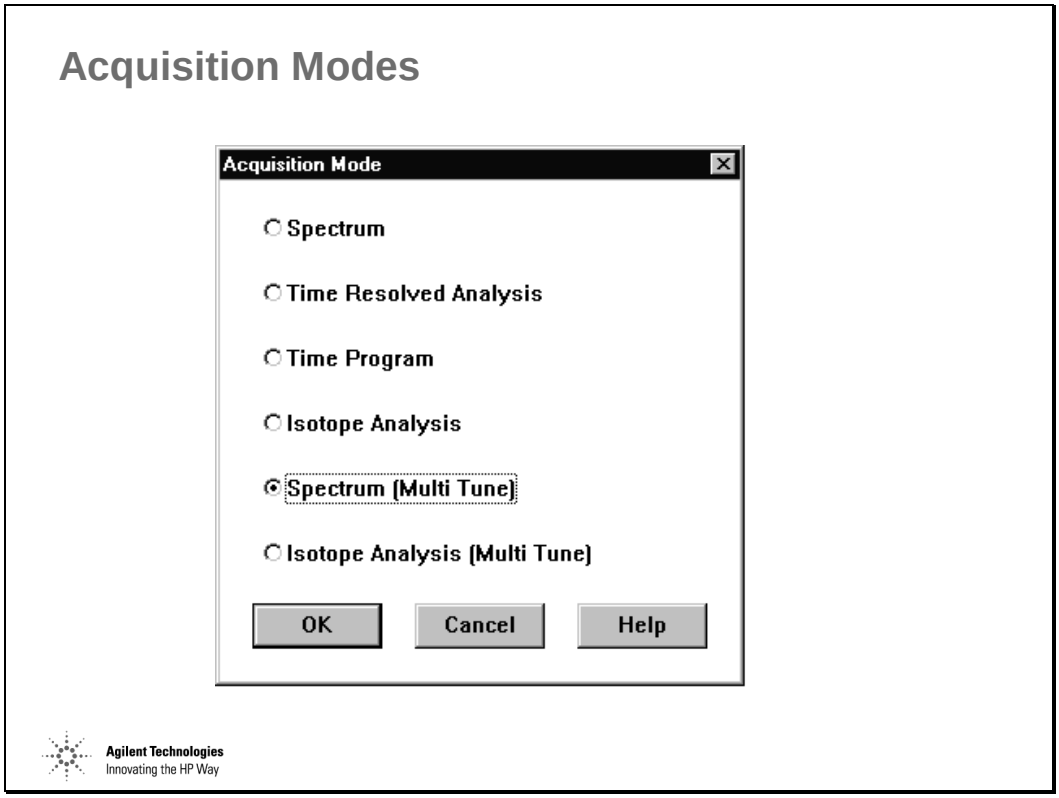

Figure 163

Spectrum mode is the most common acquisition mode for standard applications:

- Quant
- Semiquant

Time Resolved Analysis (TRA) and Time Program (more sophisticated than TRA) are used when a transient signal is measured:

- Electrothermal Vaporization (ETV)
- Laser Ablation (LA)
- Discrete Sampling Analysis (using ISIS)
- Chromatographic analysis (LC, GC, IC, CE)

Isotope Analysis mode is used when additional precision is needed for isotope ratio measurements. It is similar to spectrum mode, but with 10X higher sampling frequency.

Acquisition Modes

Multitune mode is used when during a single acquisition more than one tuning parameters are needed to accomplish the optimum performance.

Acquisition Parameters - Multitune Method

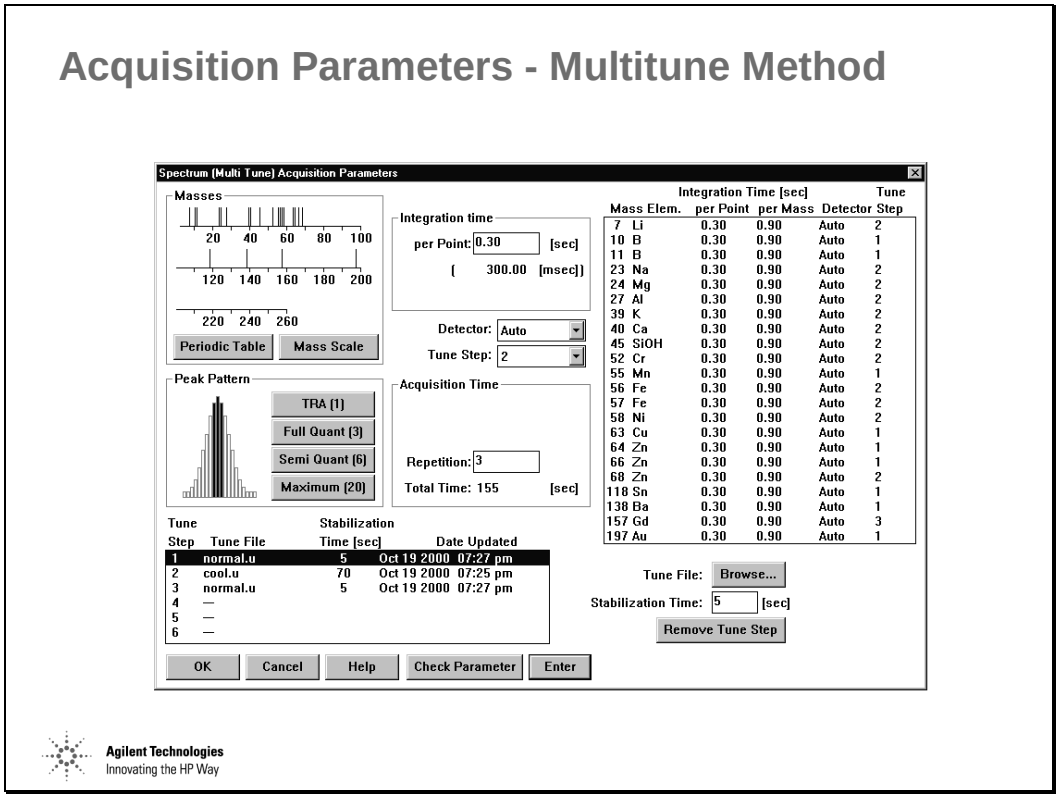

Figure 164

Periodic Table

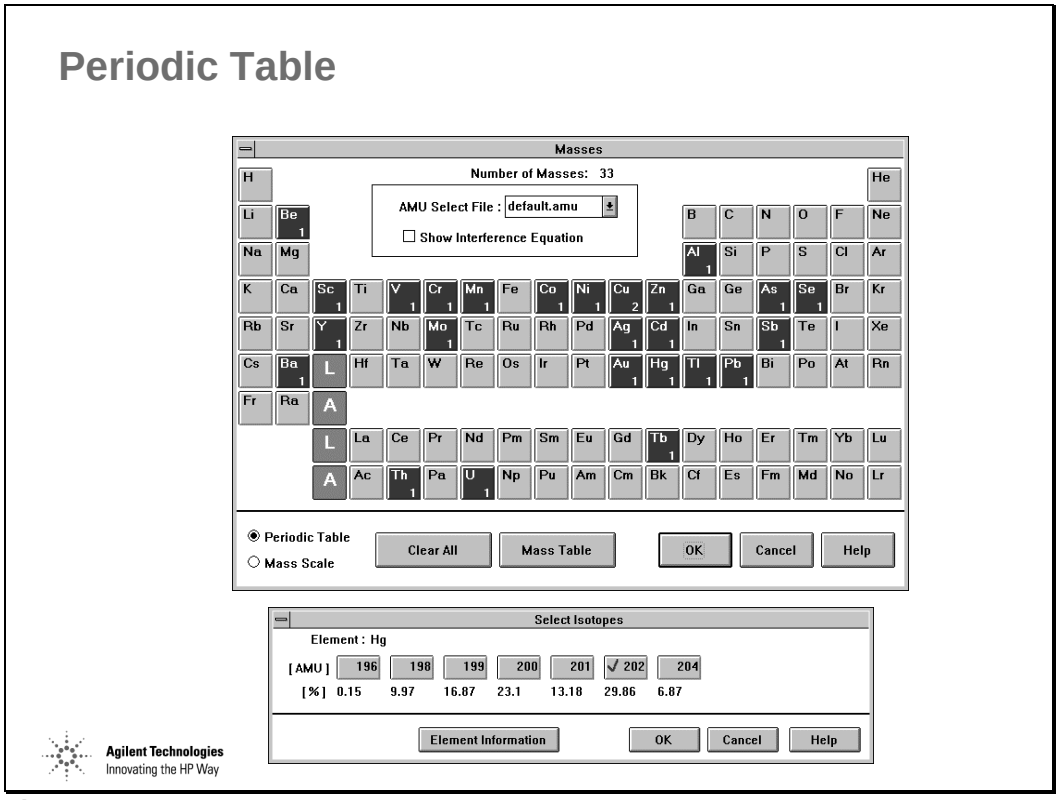

Figure 165

Mass Table

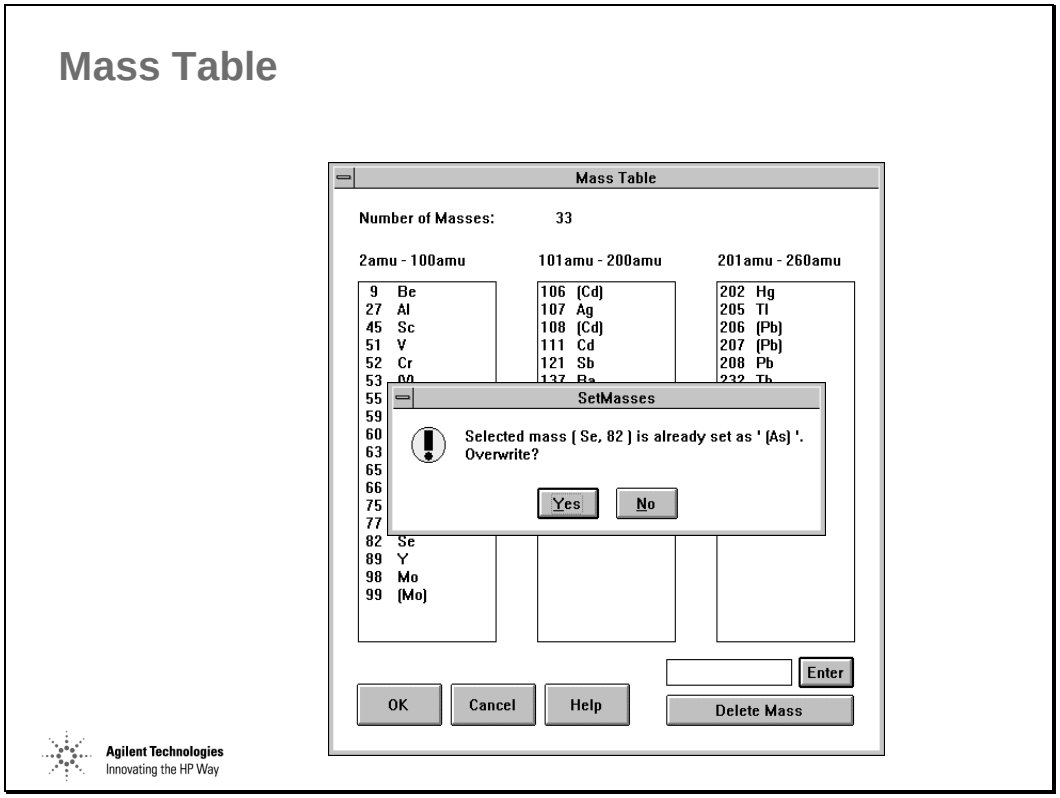

Figure 166

Peristaltic Pump Program

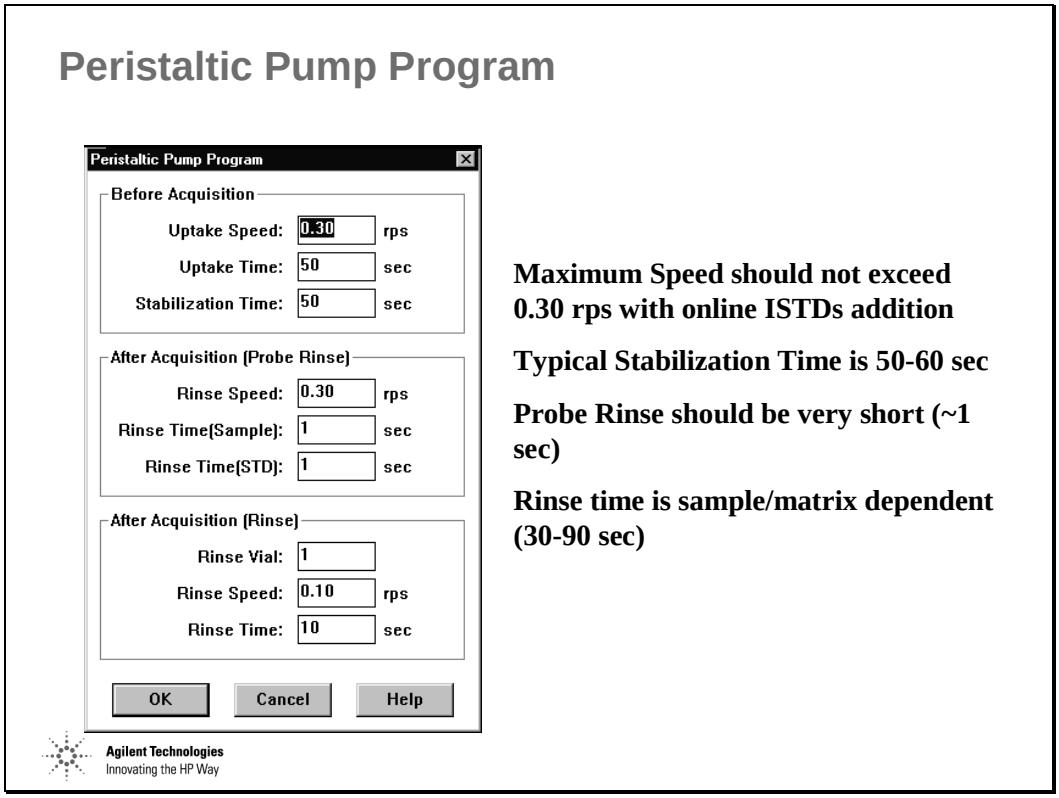

Figure 167

Raw Data Corrections

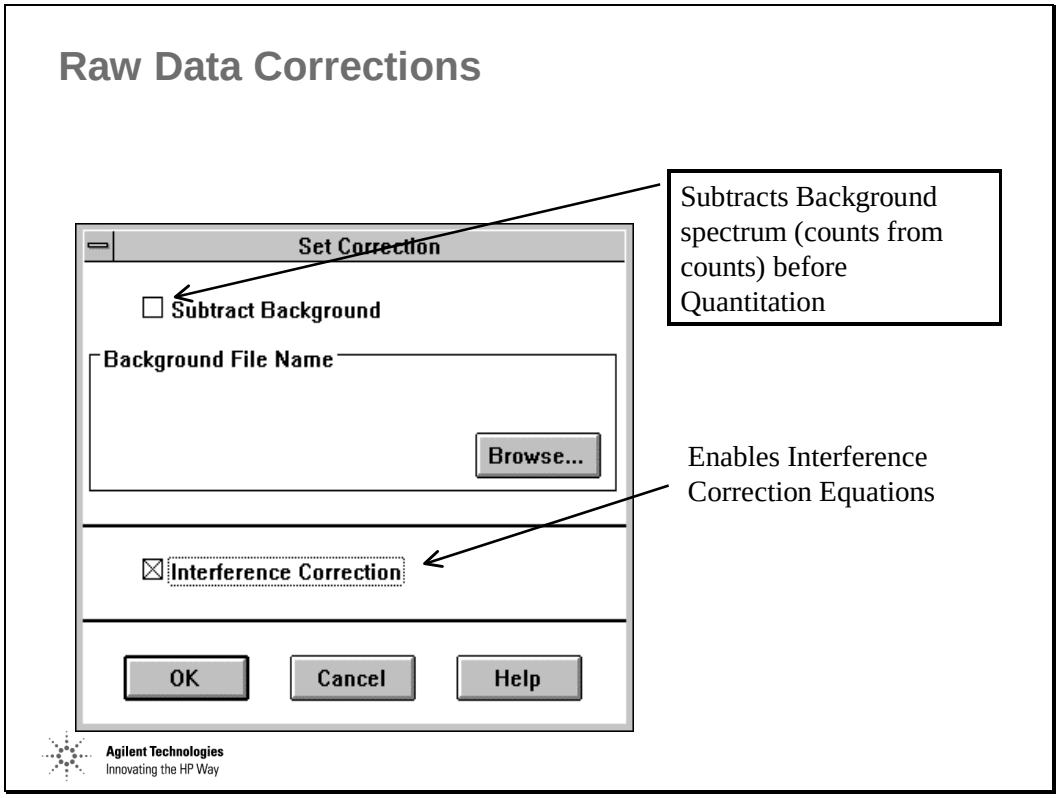

Figure 168

Configure Reports

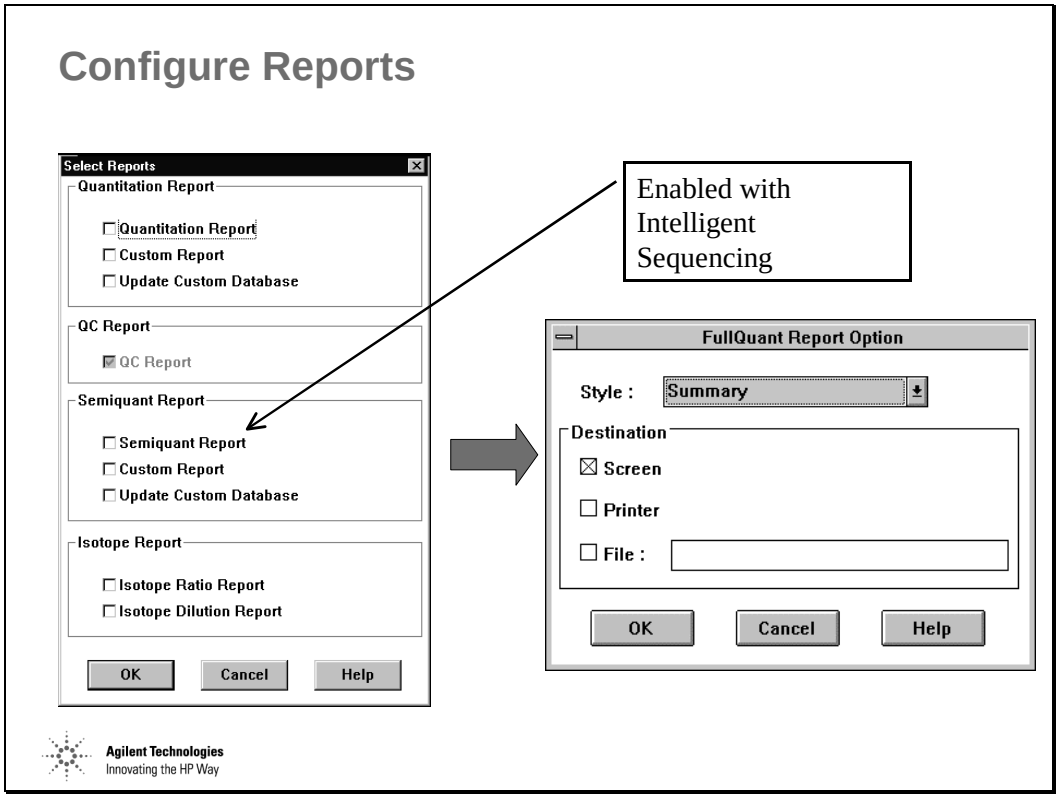

Figure 169

Calibration

Calibration

- Now independent of the method
- Multiple methods can share the same calibration
- Current calibration is displayed on the TOP and Data Analysis title bar

- Link between calibration and method is established when method is saved

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Figure 170

Calibration Table

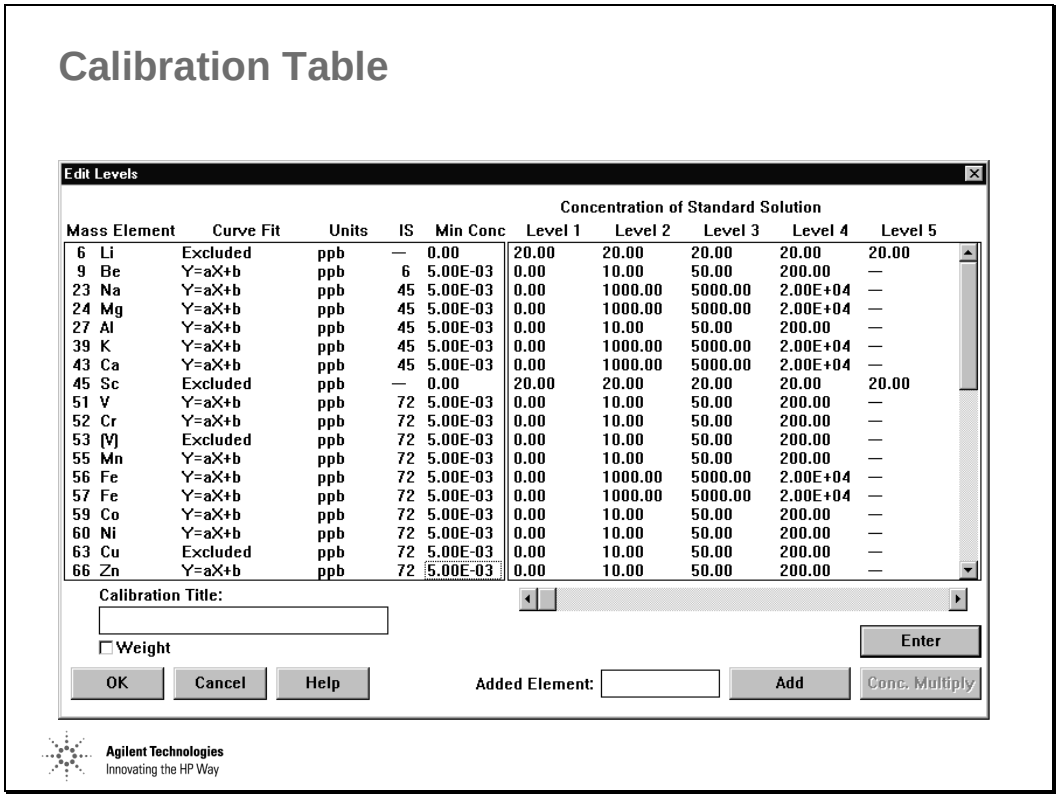

Figure 171

Shortcuts:

- Double click any column selects entire column.
- Fill Across is useful for copying Internal Standard Concentrations to all levels.
- Multiple entries can be selected using <Ctrl> plus left click or Shift plus left click.
- Min. Conc. is the lower reporting limit, to disable it replace it with '---', often the reporting limits are entered here.

Save the Calibration and the Method

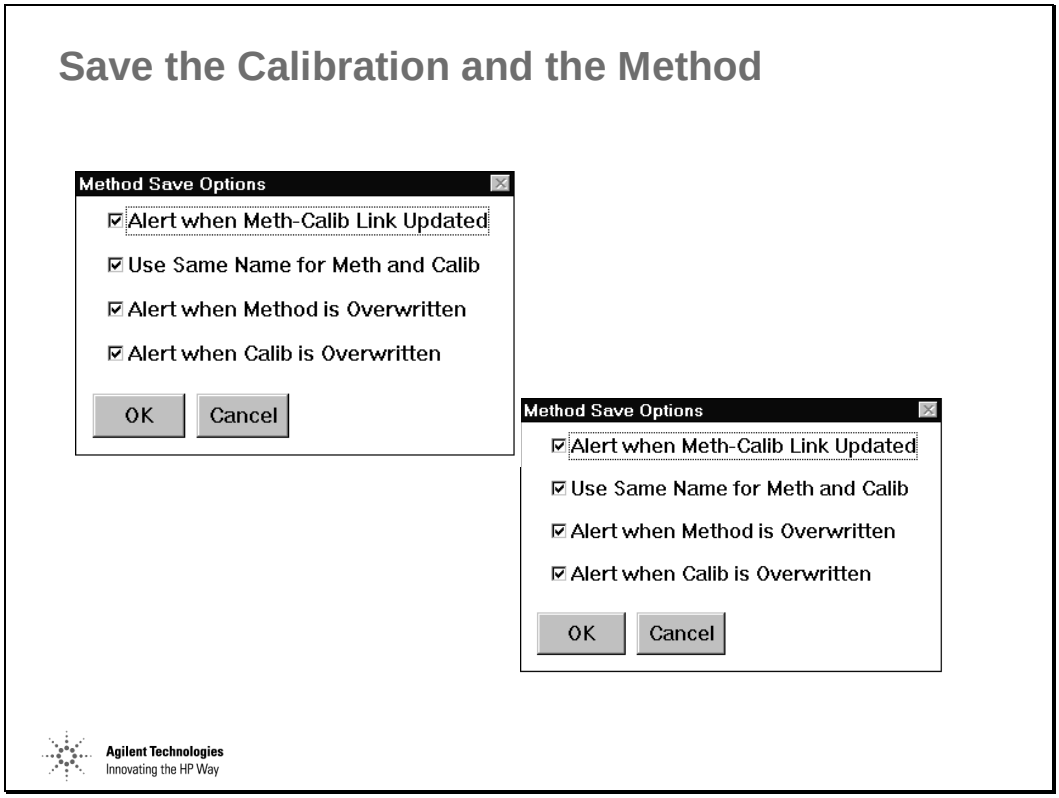

Figure 172

Quantitative Data Analysis

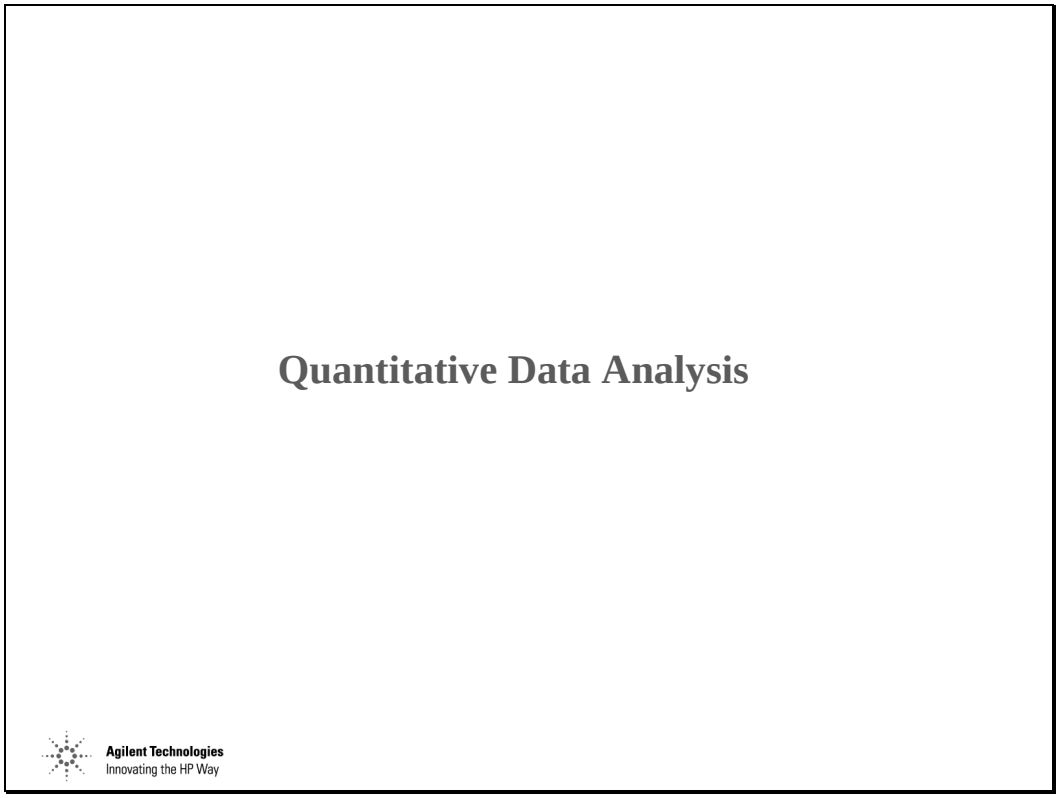

Figure 173

Standard Data Files

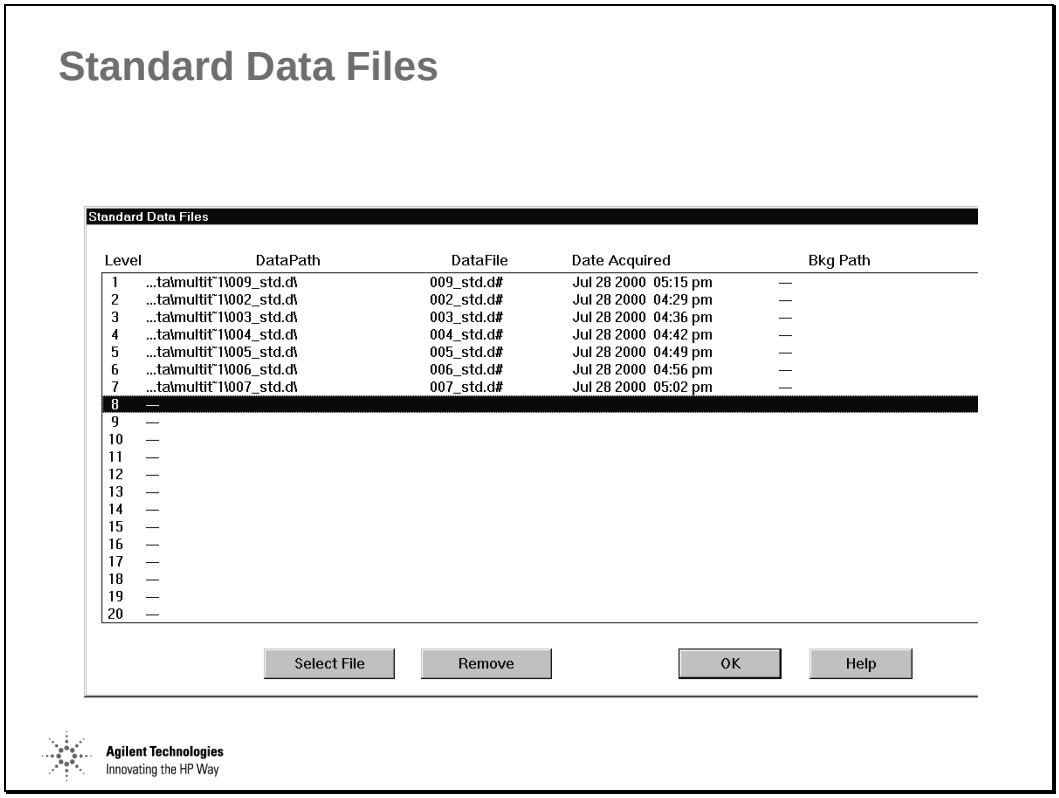

Figure 174

Calibration Curves

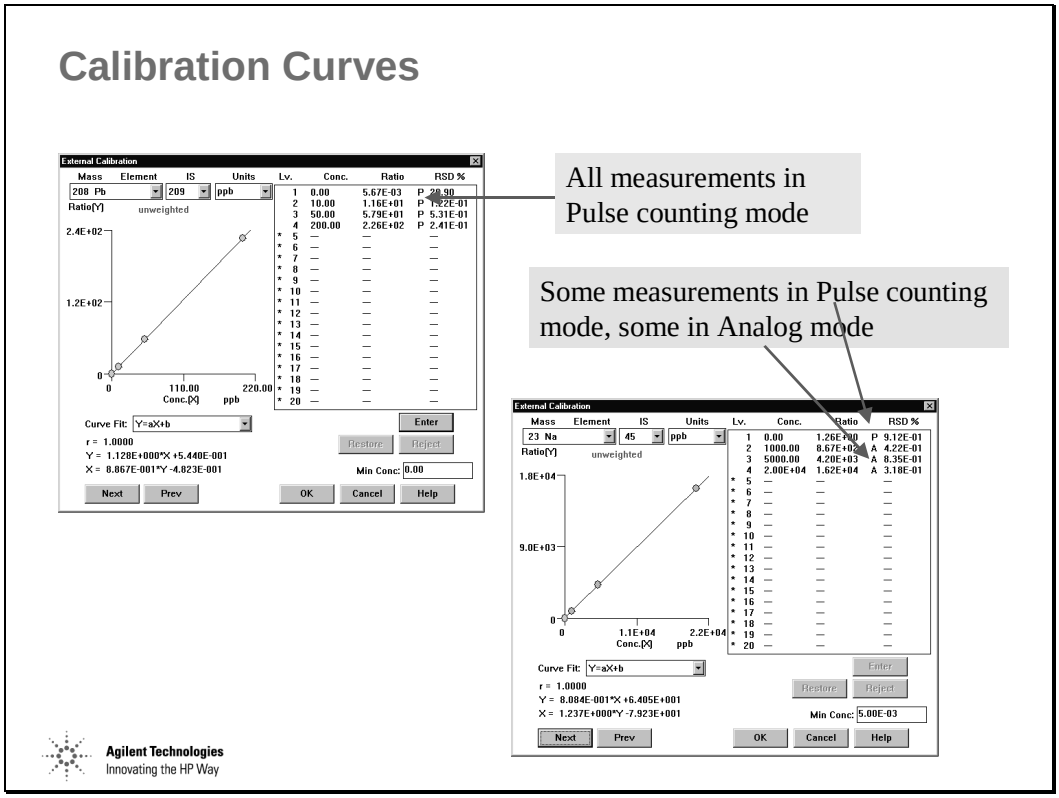

Figure 175

Examples of the Calibration Curves for "Excluded"

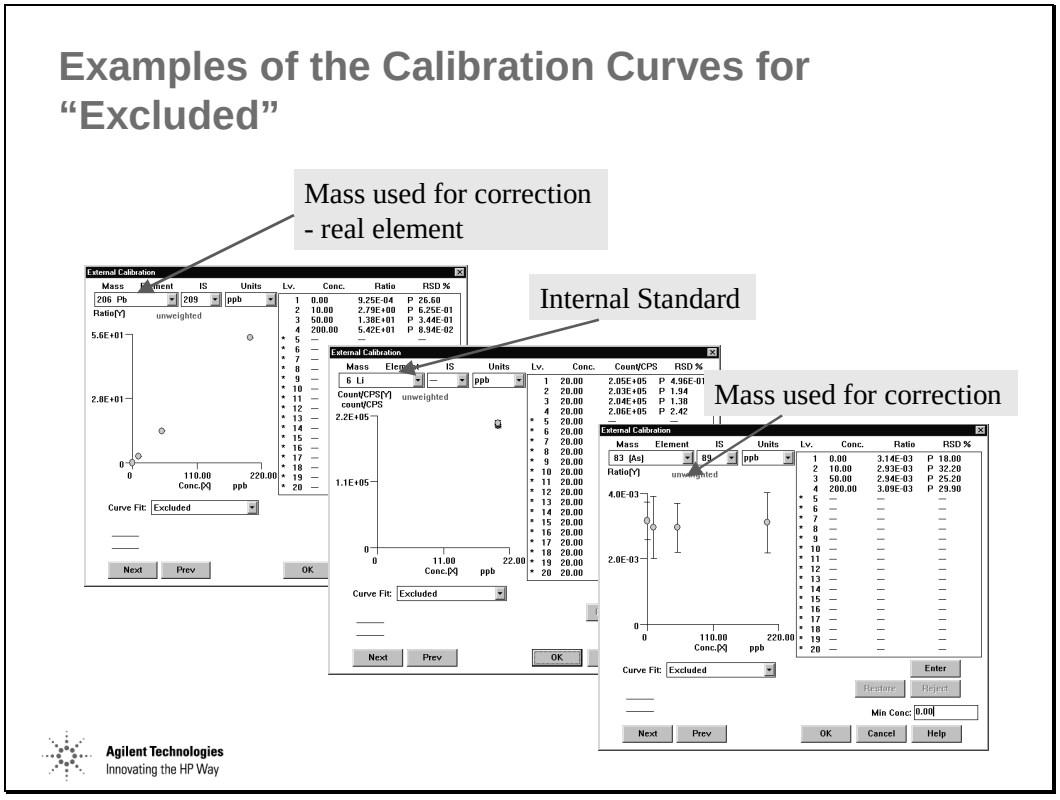

Figure 176

Examples of the Calibration Curves for “Excluded”

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Simple Sequencing (Intelligent Sequencing Disabled)

Sequencing

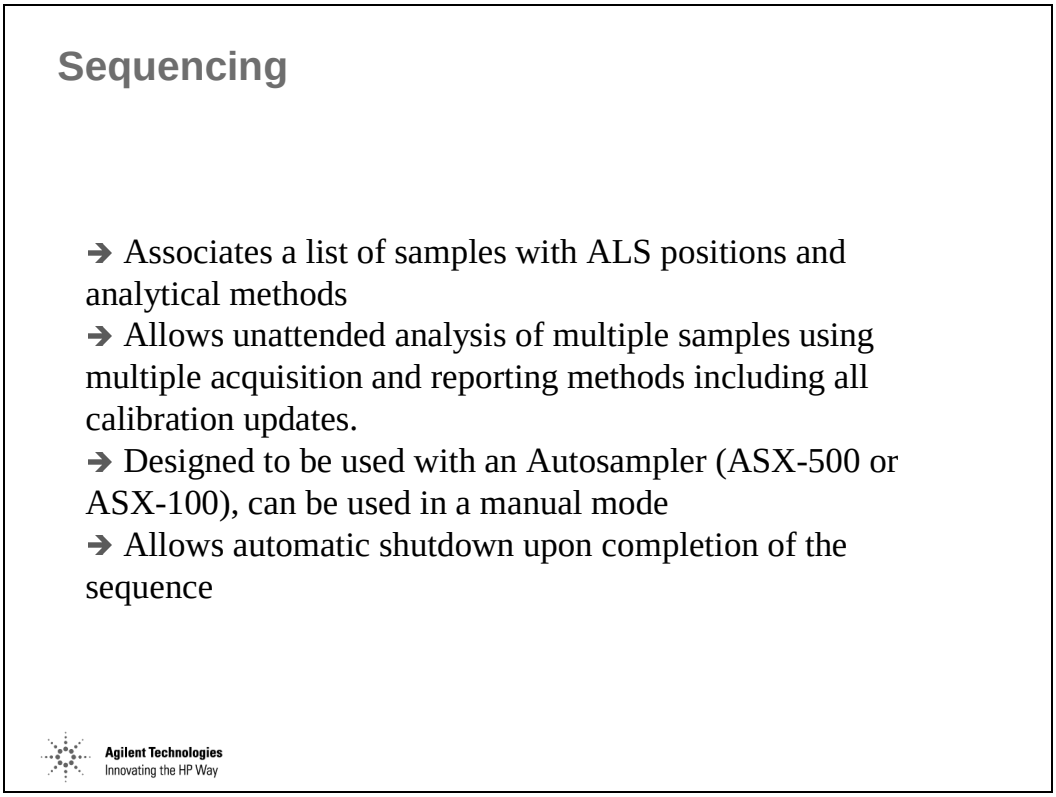

Figure 177

ASX-500 Vial Position Nomenclature

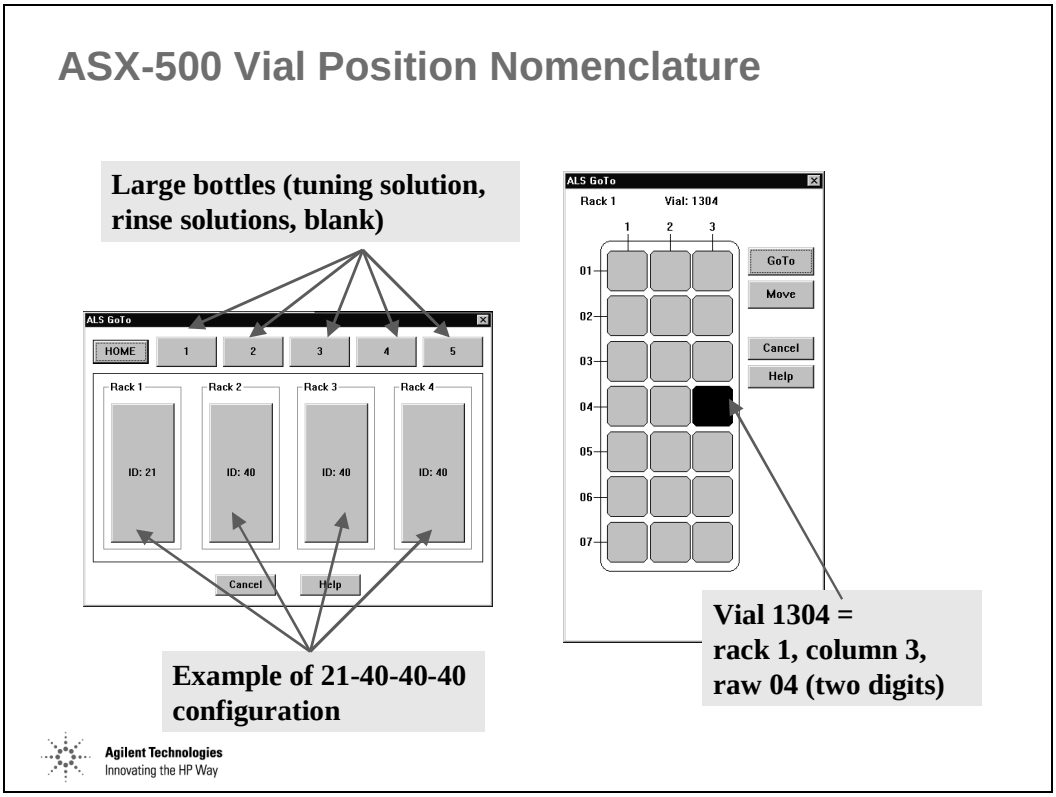

Figure 178

Sequencing

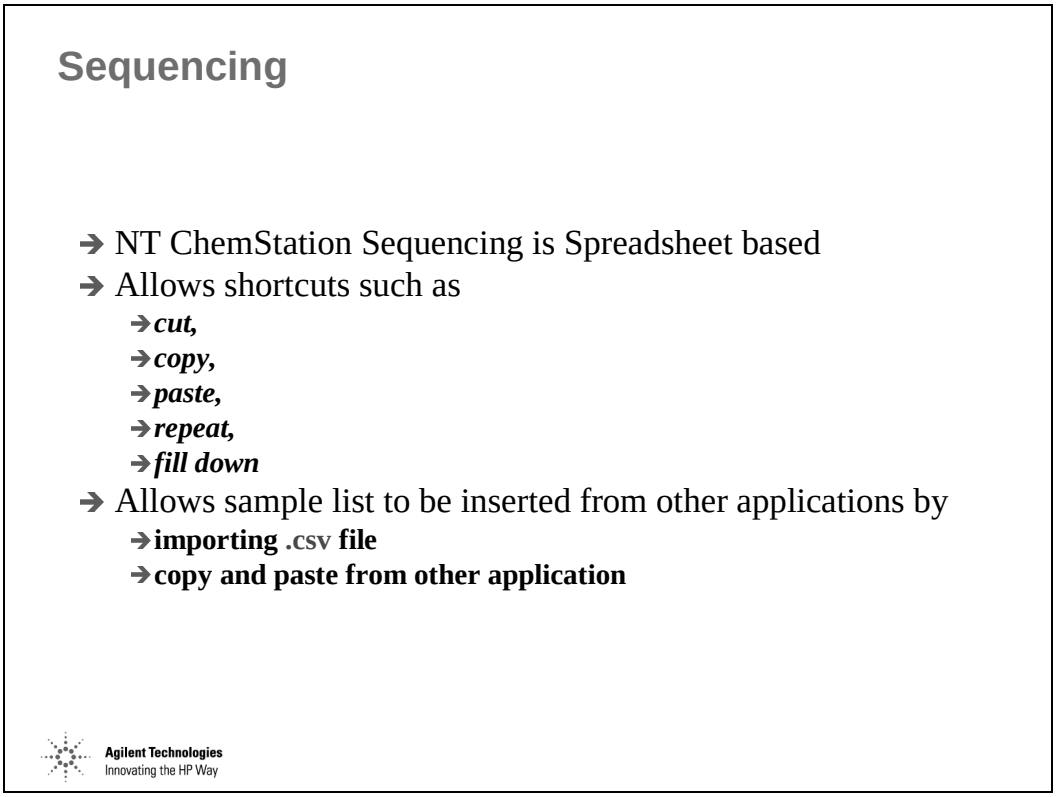

Figure 179

Sample Log Table - Sequence Flow and Periodic Block

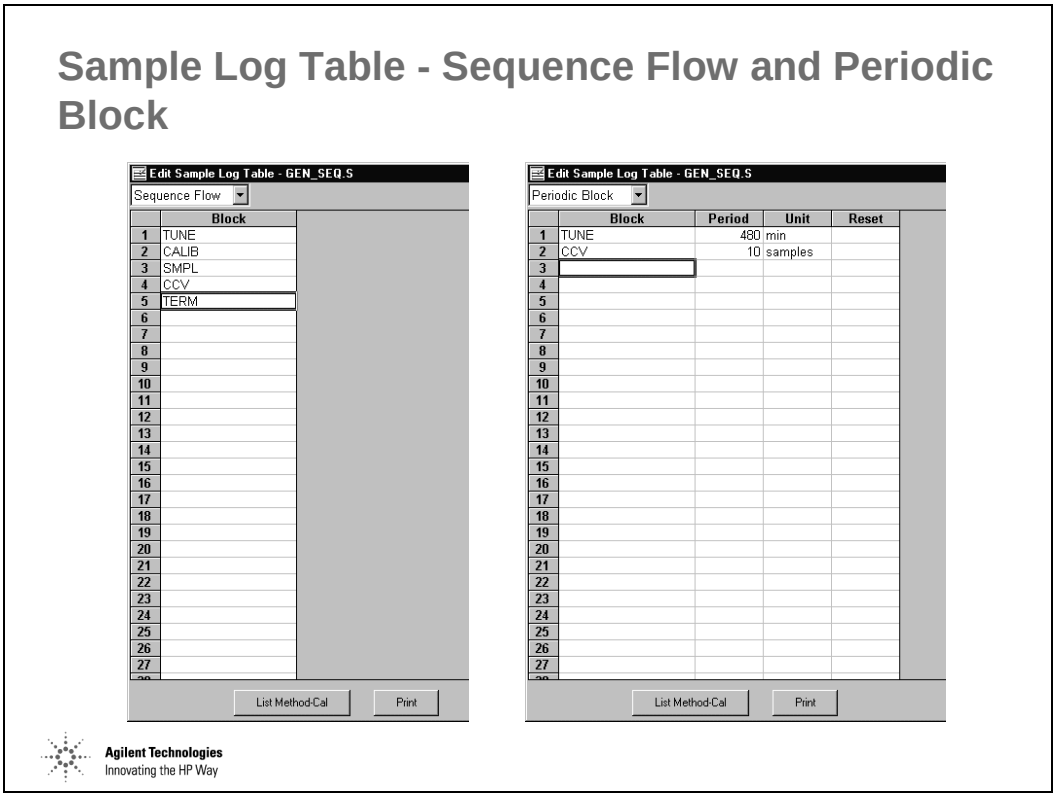

Figure 180

Sequencing is **Modular**, each functional part of the sequence is created as a separate block such as calibration block, sample block etc. This is used more fully by Intelligent Sequencing.

Sample Log Table

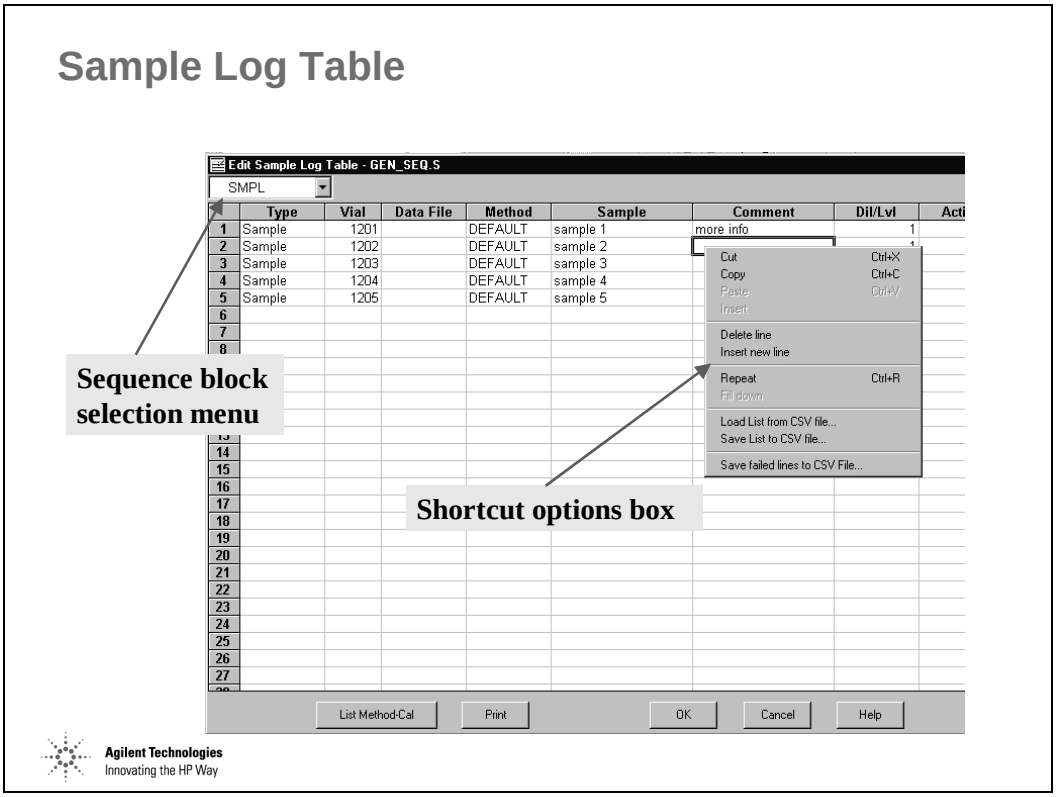

Figure 181

Right Click selects shortcut options box.

Left Click or **Double Click** selects options for Type, Method, Dil/Lvl, Action on Failure (Intelligent Sequencing Only), and Skip.

Vial positions increment correctly by reading ALS rack configuration when using fill down.

Any numeric characters in Sample Name, Data File Name, or Comment Fields will be **increment**ed by using fill down.

To avoid auto-incrementation, use **copy and paste** instead of fill down.

"List Method-Cal" displays the **complete path** for the method on each sequence line with it's associated calibration file.

Special Features - Keywords

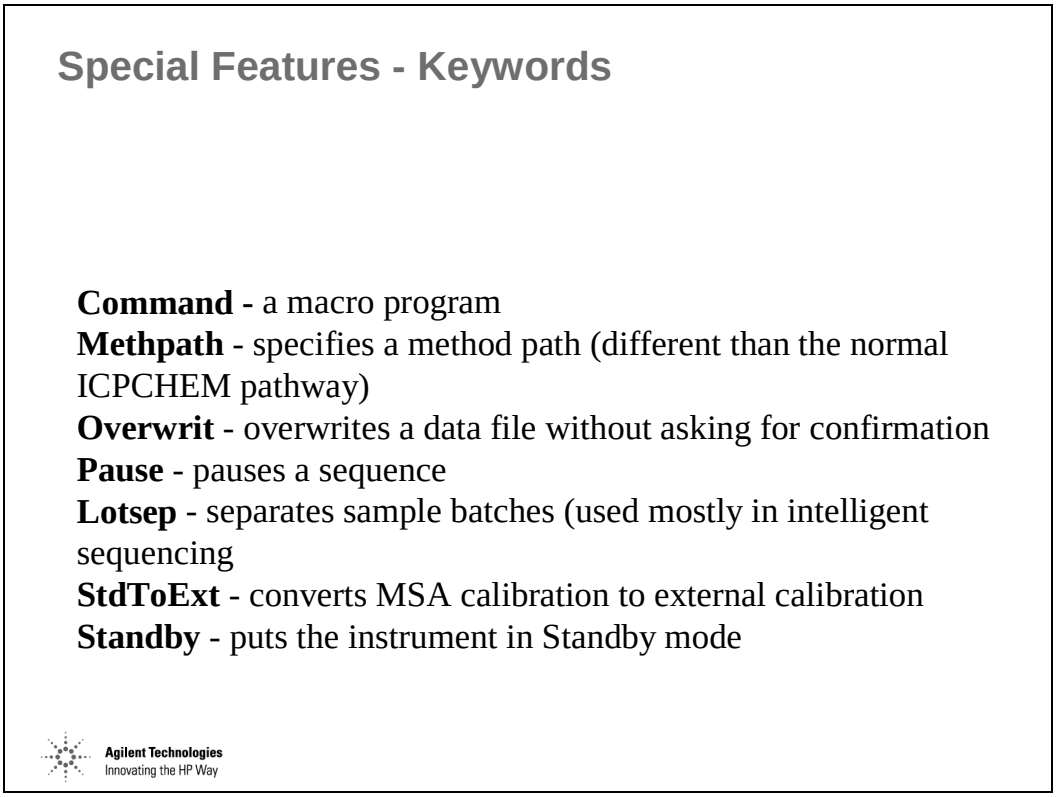

Figure 182

Keywords are enabled by selecting ‘Keyword’ Under ‘Type’ and then selecting the desired keyword in the Method Column.

If Keyword Command is selected, the Command or Runstring is entered in the ‘Sample’ Column.

For Example to incorporate the shutdown macro into a Sample Log Table:

Keyword Command Tune “Macro `shutdown’, go”

Running a Sequence

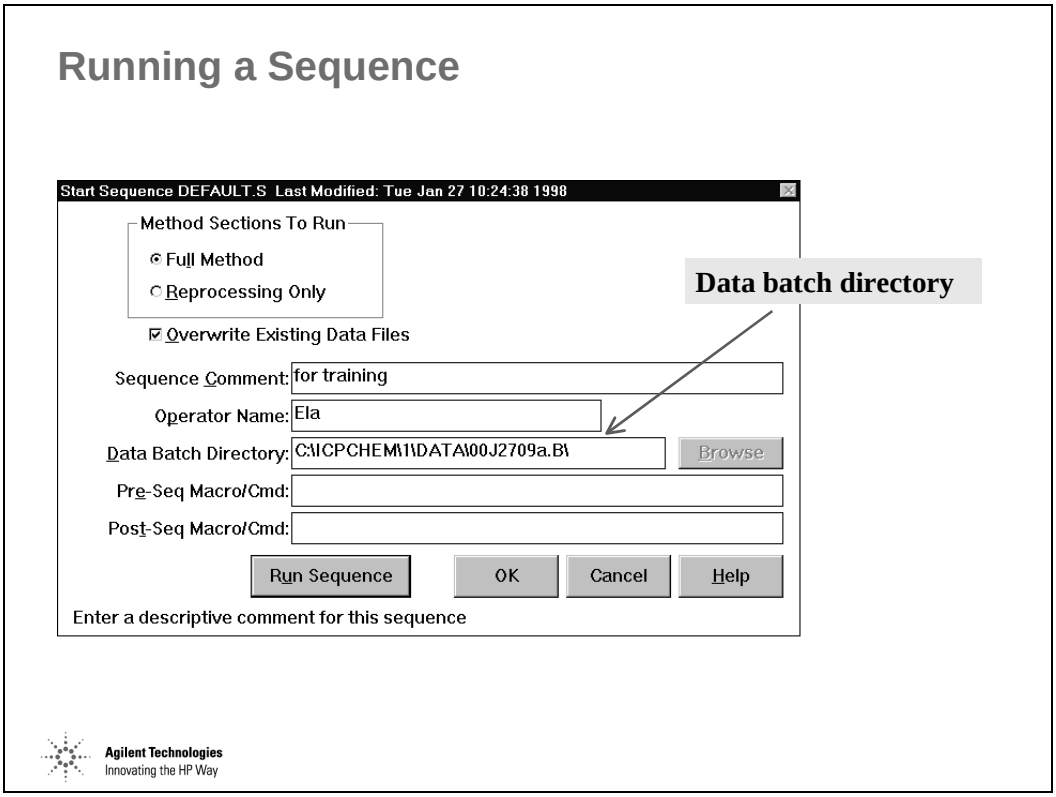

Figure 183

Upon selecting Run Sequence, a data batch directory is automatically created in the form **YYMDDHHx.b,** where:

- YY is 2 digit year
- M is month, A=Jan, B=Feb etc
- DD is day HH is hour (24 hour clock)
- x is a letter from **a** to **z** for the sequence number within a given hour.

This can be appended, deleted, or modified as needed.

Chained Sequence

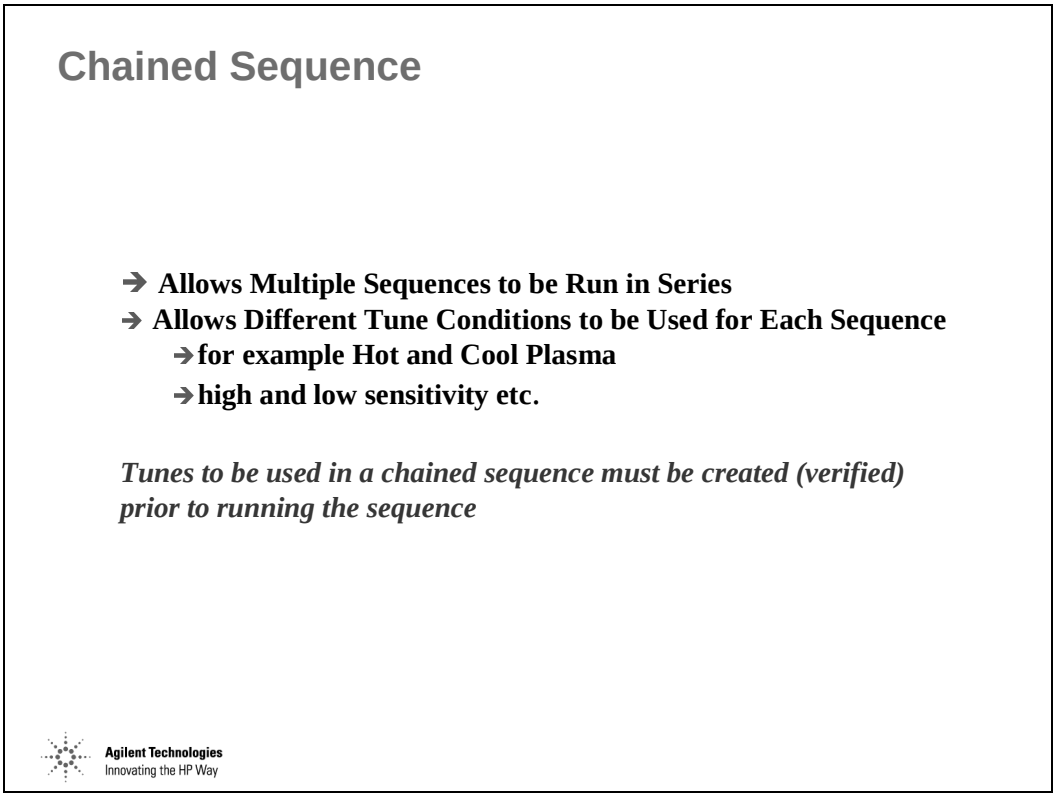

Figure 184

Chained Sequence

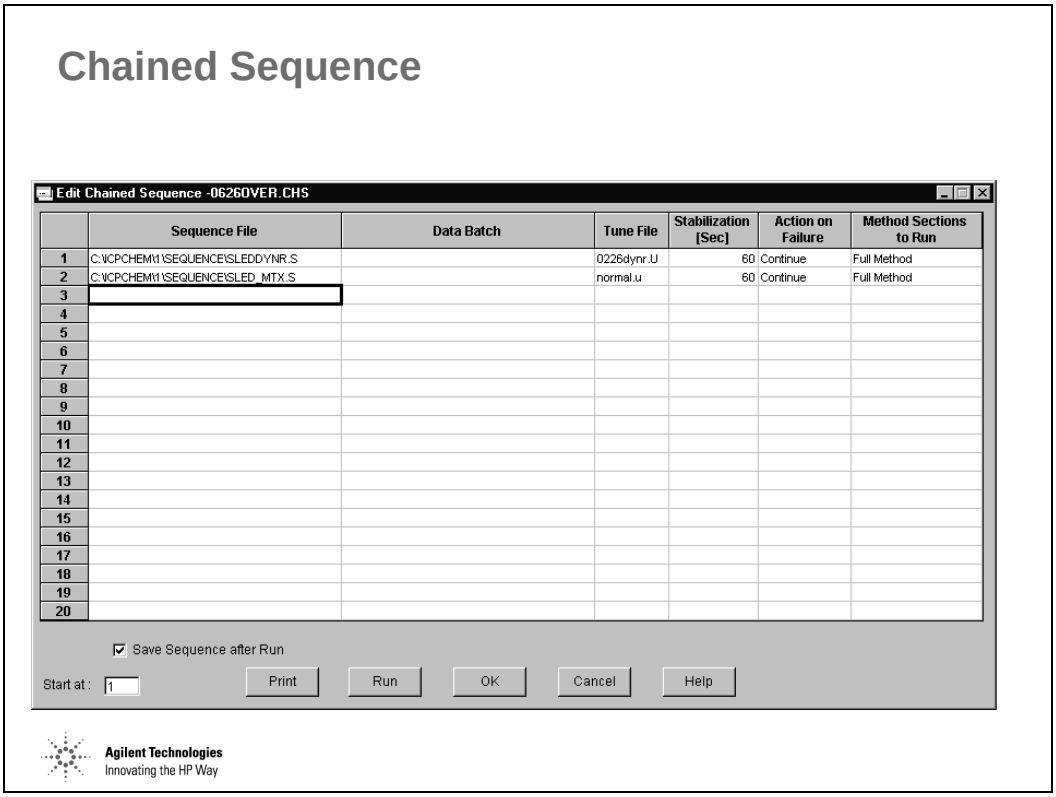

Figure 185

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Method of Standard Additions (MSA)

External Calibration

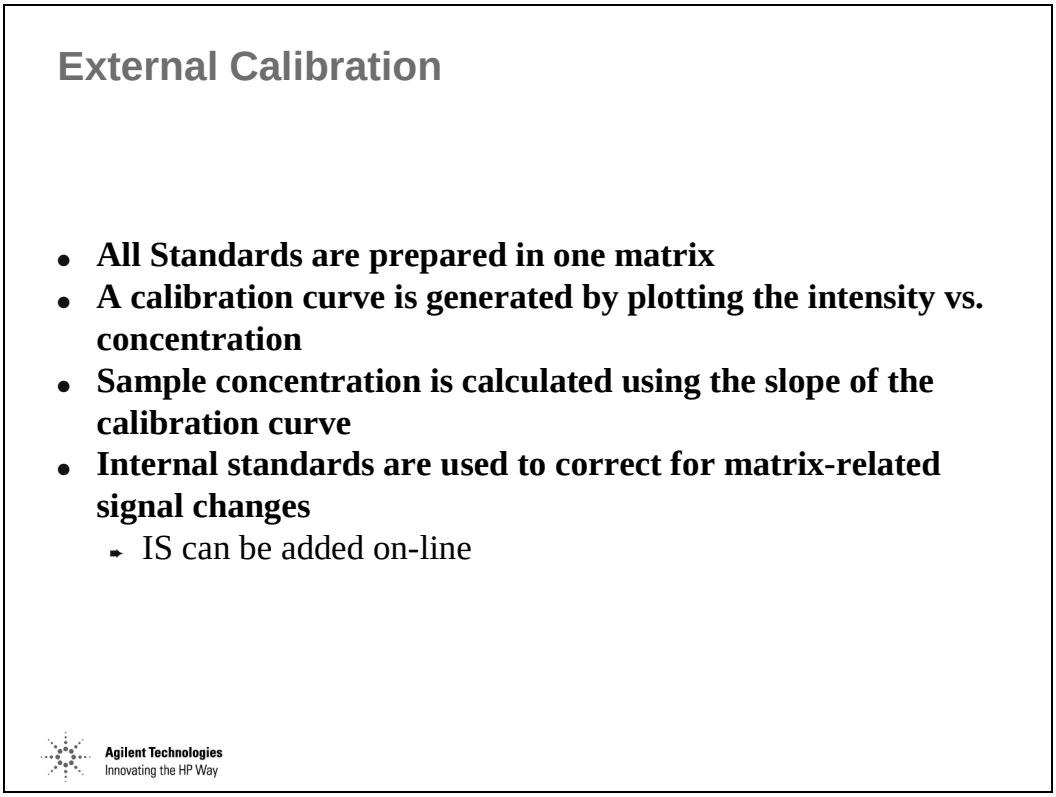

Figure 186

Pros and Cons of External Calibration

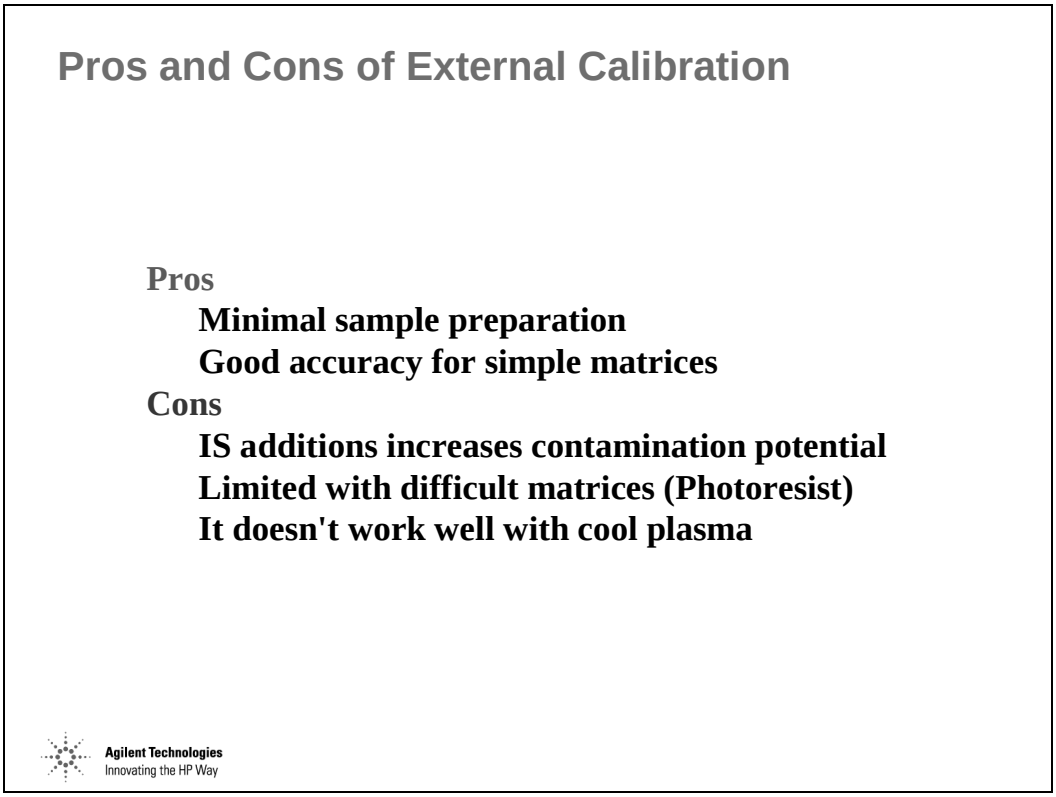

Figure 187

Method of Standard Addition (MSA)

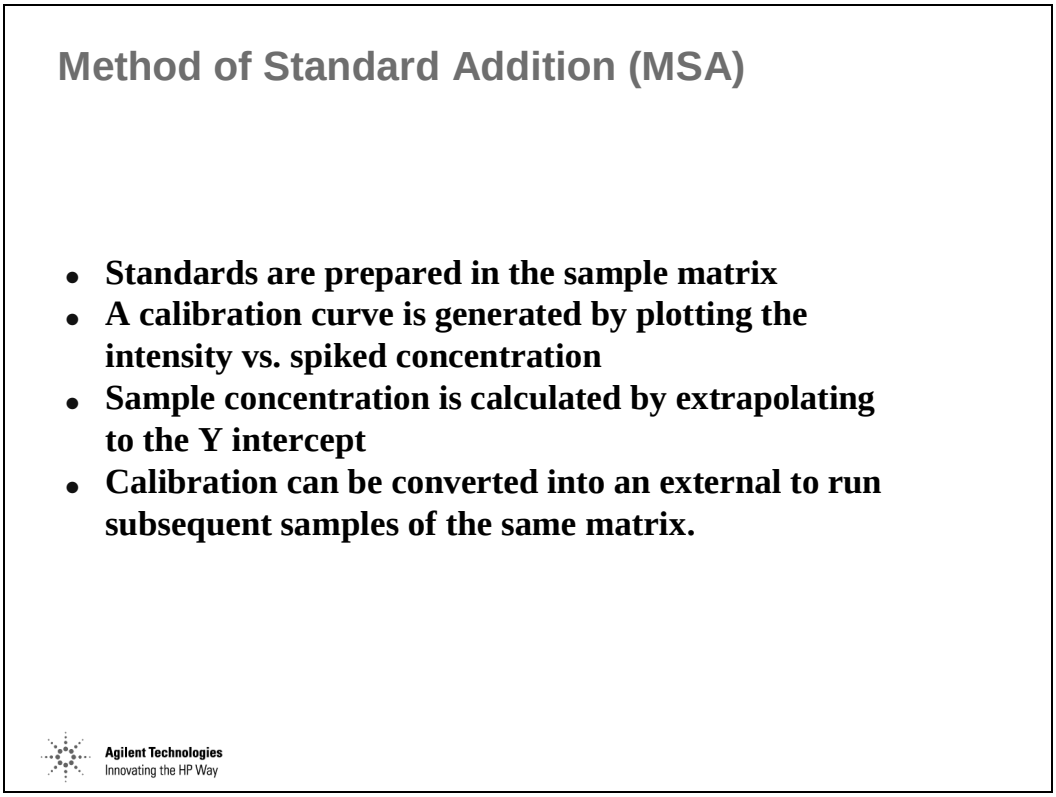

Figure 188

Pros and Cons of Method of Standard Additions

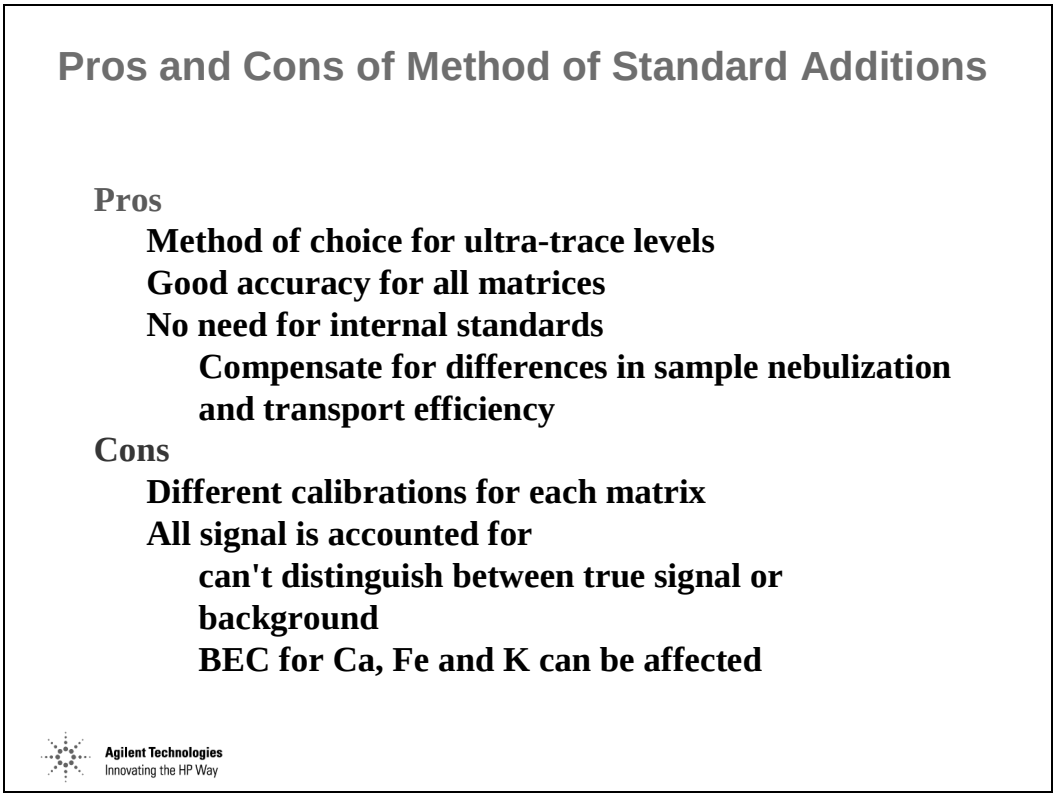

Figure 189

Determination of Uranium in Urine by MSA

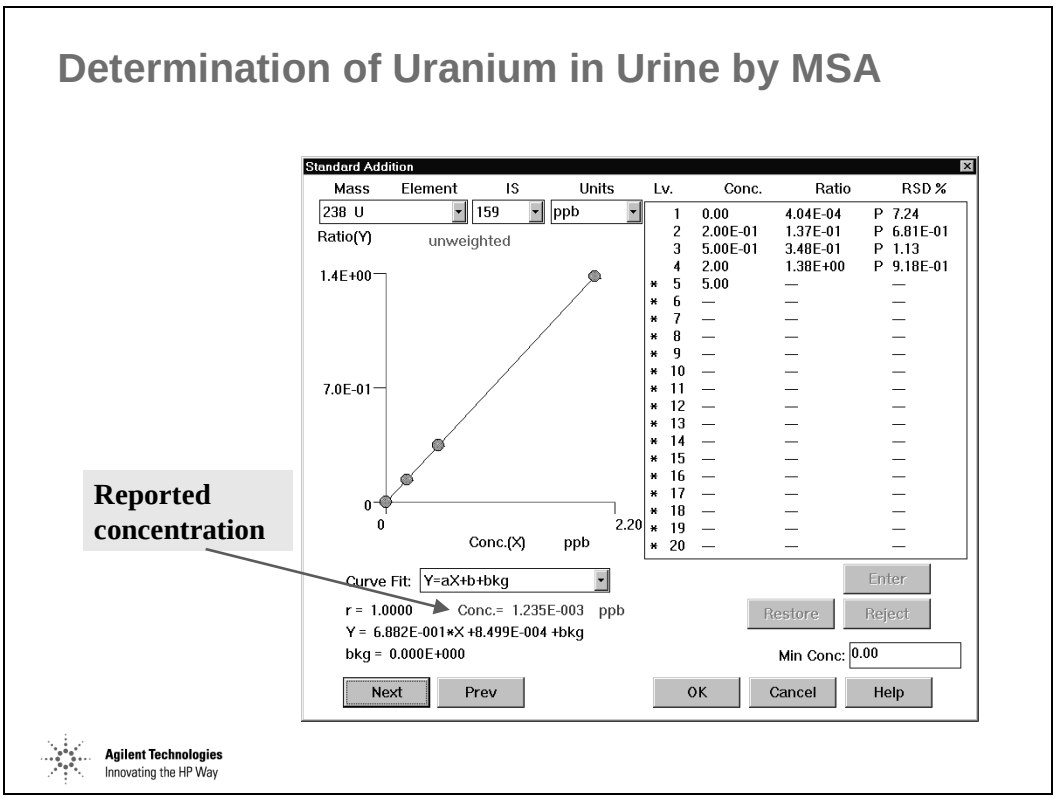

Figure 190

Converting from MSA to External Calibration

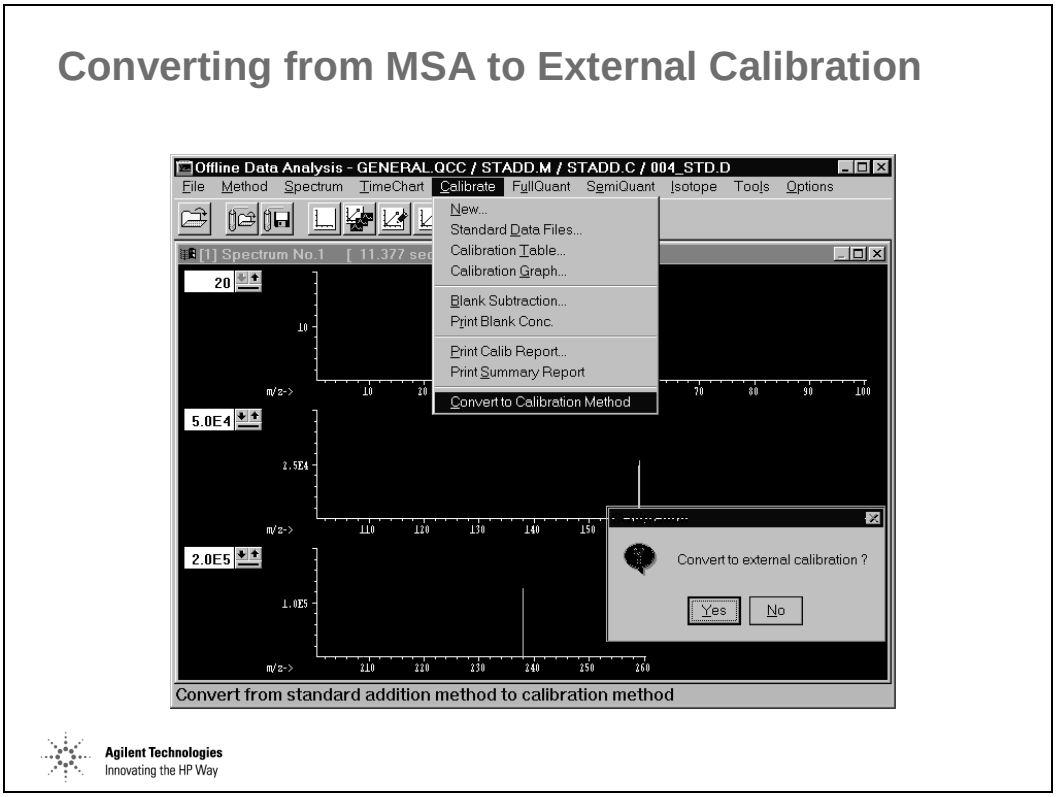

Figure 191

Matrix-matched Uranium in Urine External Calibration

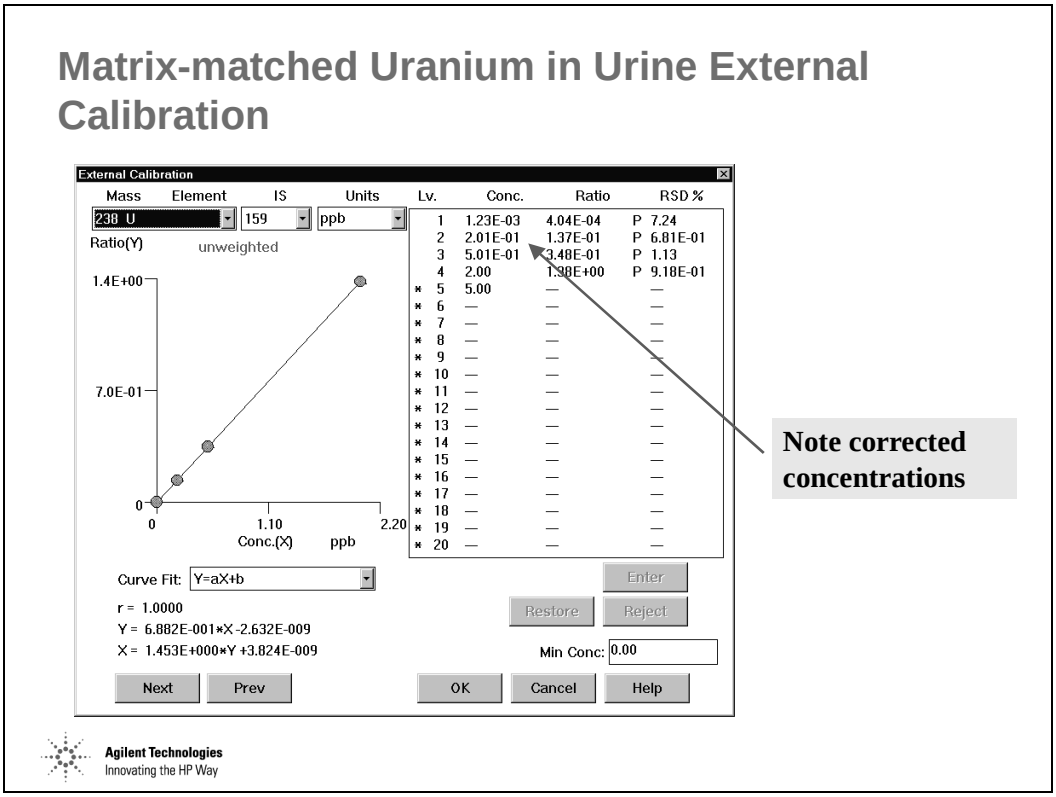

Figure 192

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Off-line Data Analysis and Sequence Reprocessing

Off-line Data Analysis

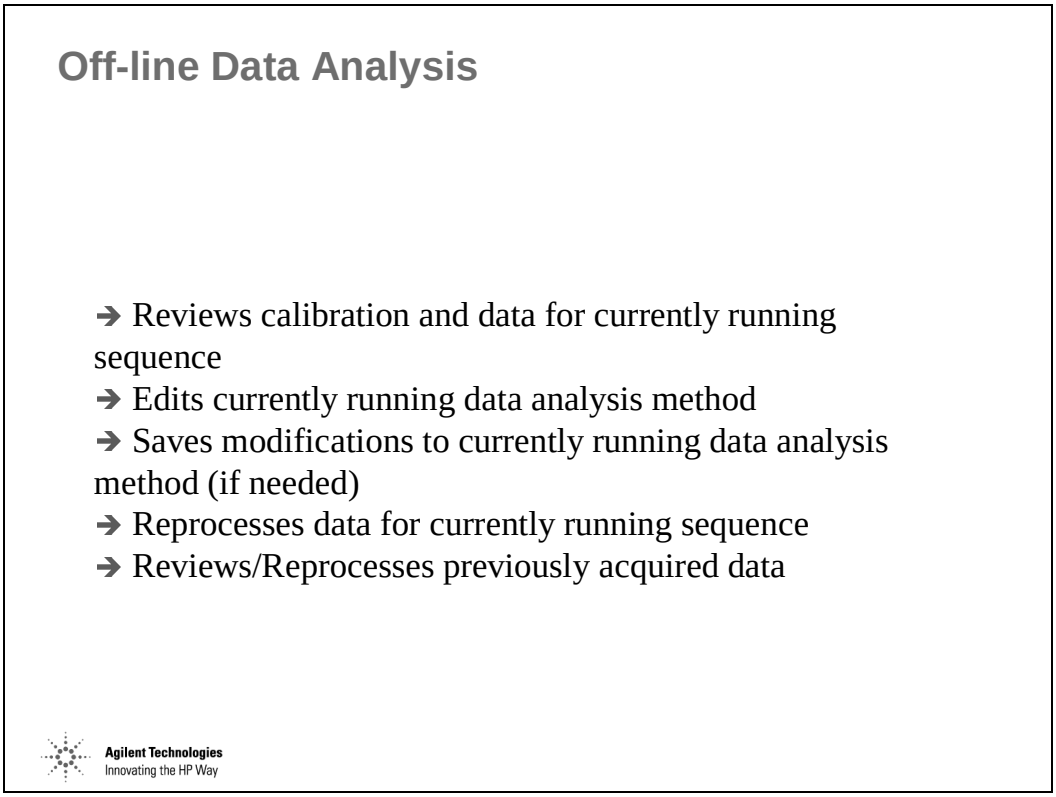


Figure 193

Procedure for Off-line Data Analysis

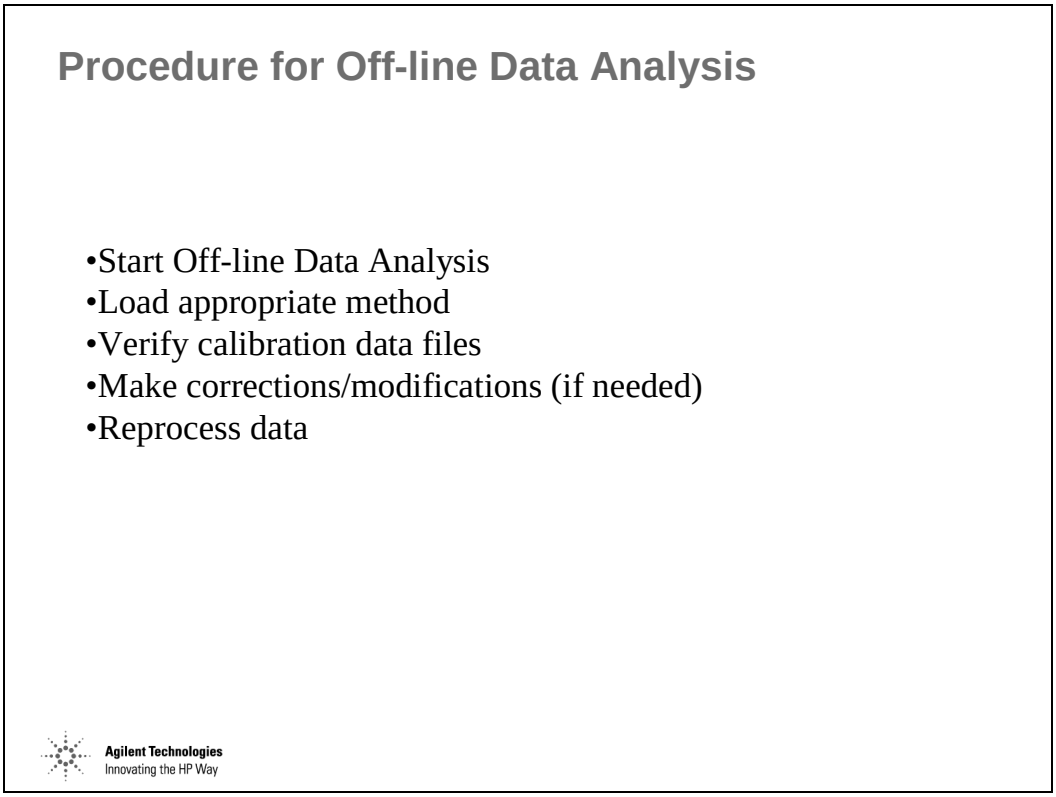
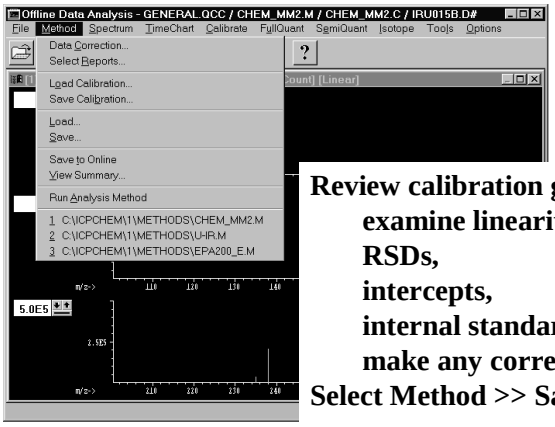


Figure 194

Off-line Calibration Review of Currently Running Method

Off-line Calibration Review of Currently Running Method



Review calibration graphs:
- **examine linearity,**
- **RSDs,**
- **intercepts,**
- **internal standard reproducibility etc.**
- **make any corrections or changes**

Select Method >> Save to Online

This procedure updates currently running method

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Figure 195

Using DoList for Off-line Data Reprocessing

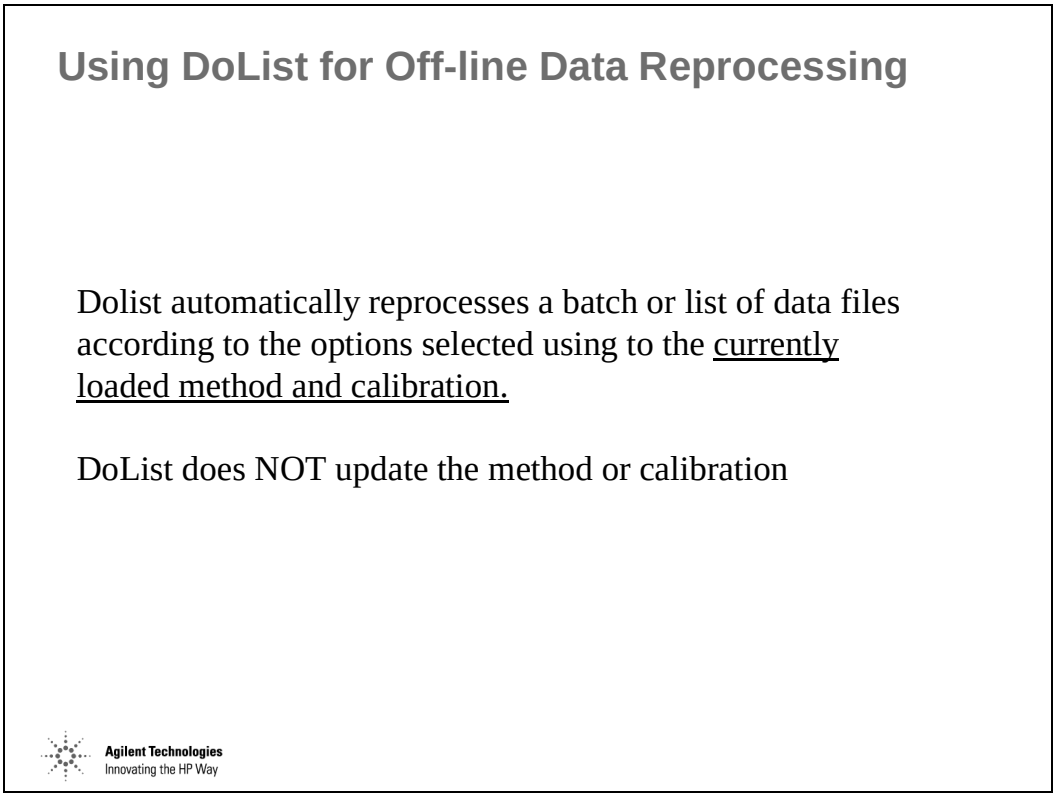

Figure 196

Dolist always uses the currently loaded method, not necessarily the method originally used to acquire the data.

Dolist does not load the method from disk or resave the method to disk when finished. Therefore, it is possible to make temporary changes to the method for reprocessing only (such as different report destination etc.) and not save the changes permanently to the disk.

How to Use DoList

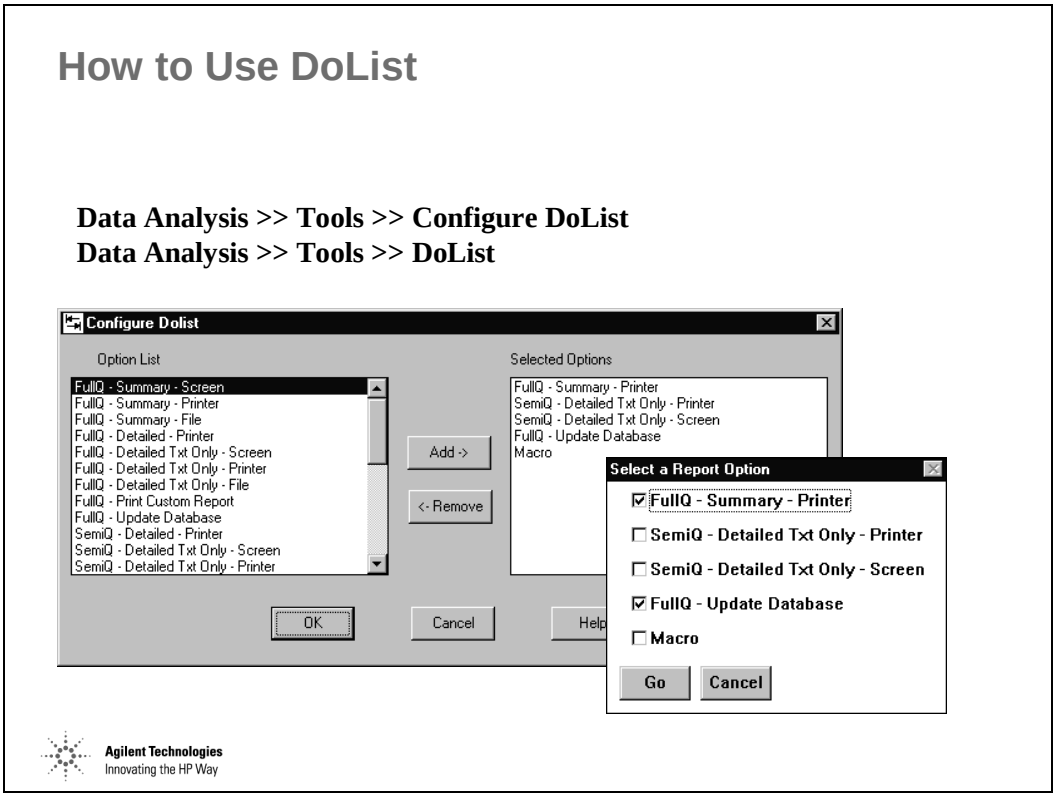

Figure 197

Selecting Files Using DoList

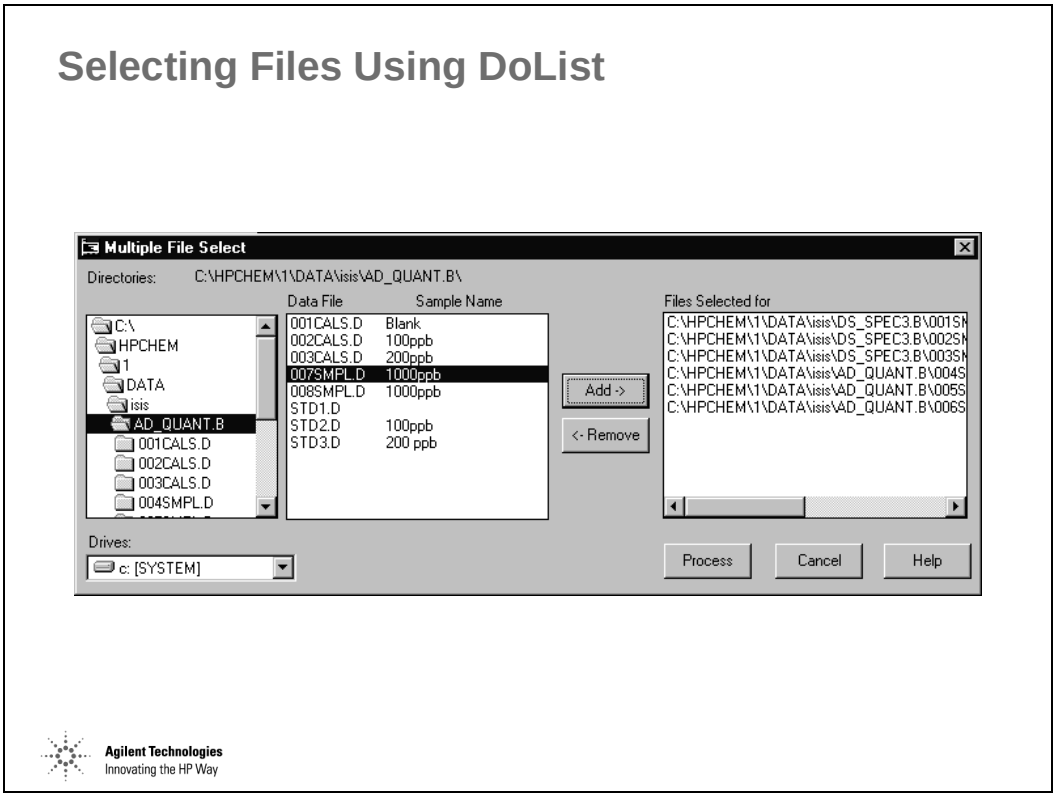

Figure 198

Sequence - Reprocessing Data Batch

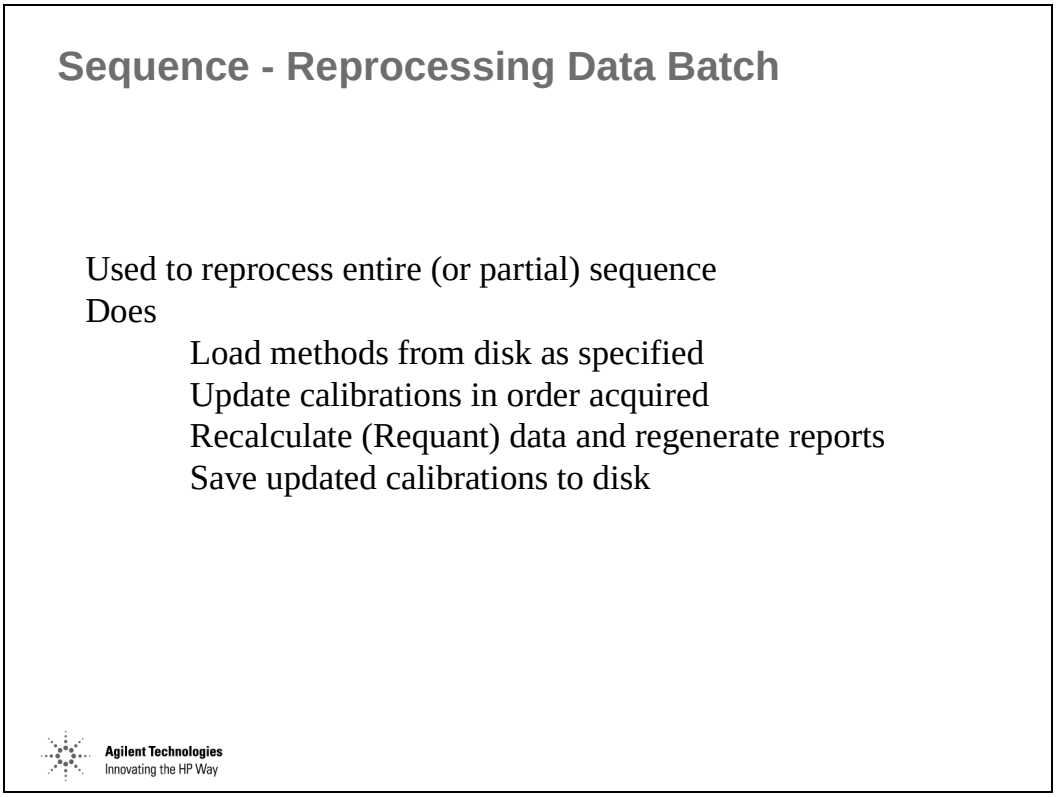

Figure 199

Sequence Reprocessing

Sequence Reprocessing

- ➔ Top Menu>> Sequence >> Reprocess Data Batch
- ➔ Select Data Batch
- ➔ Reprocess Data Batch (click OK)

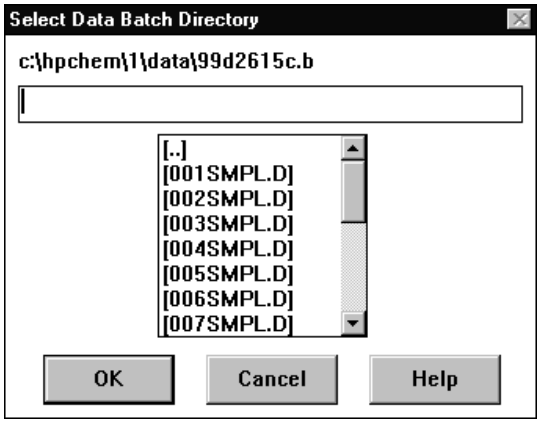

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Figure 200

Reprocess Data Batch uses the sequence stored within the data batch directory for reprocessing. This sequence is created at the time of analysis and is named according to the date and time of acquisition. It is possible to modify the sequence before reprocessing by removing undesired data files. However, care must be taken not o remove necessary files such as calibration files or reference files for sample types such as spikes or duplicates.

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Custom Reports and Databases

What You Will Learn

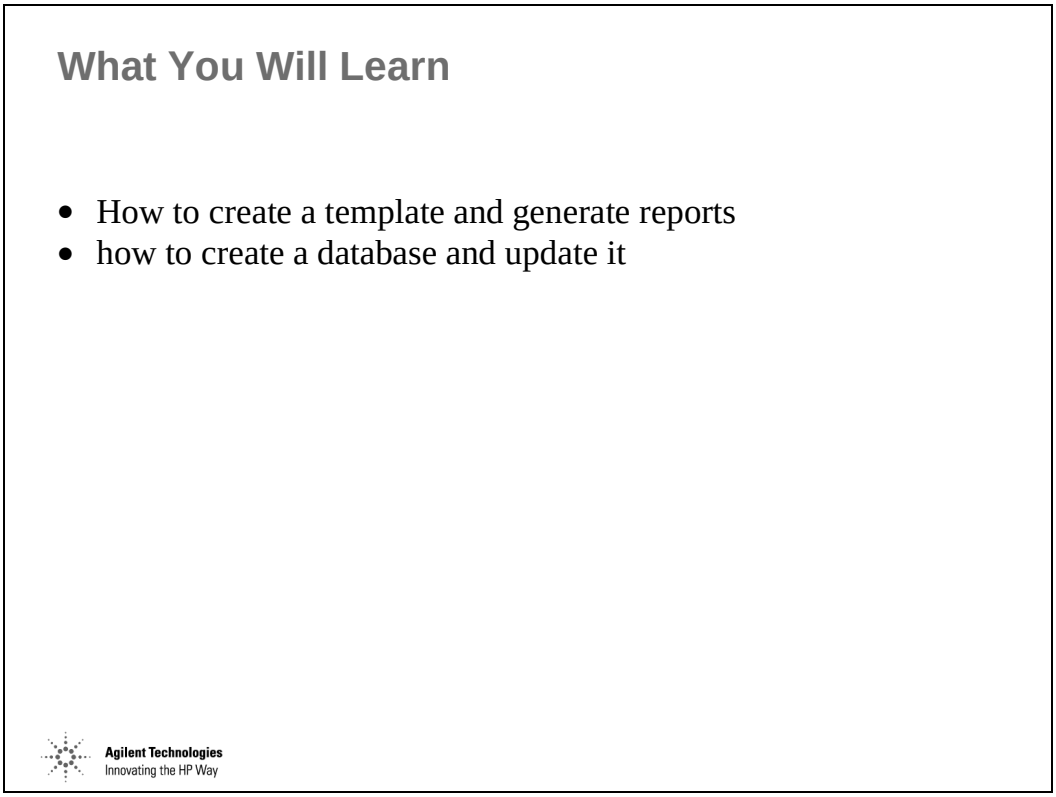


Figure 201

This section will introduce you to the Custom Reports package included in the Agilent 7500 Series ChemStation Software.

Custom Reports is a windows application with three basic functions:

- spreadsheet
- database
- charts

Spreadsheet functions allow to easily design a report template and produce a report for a single sample.

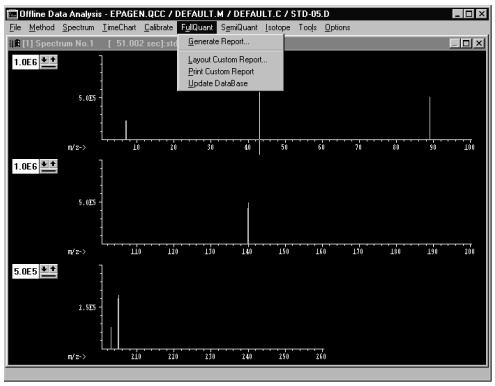
Custom databases contain information from many samples.

Charting of the database is useful for trend analysis and/or monitoring QA/QC samples.

A ChemStation method can have one report template and/or one database assigned for FullQuant analysis and one report template and/or one database assigned for SemiQuant analysis.

Custom Reports and Databases

Custom Reports and Databases



- **Based on Visual Basic runtime program**
- **When installed, creates \icpchem\custrpt directory**
- **Also creates \icpchem\1\rpttmp**
- **Accessible through FullQuant and SemiQuant menus**
- **Custom report templates are *.fqt or *.sqt files**
- **Custom report databases are *.fqd or *.sqd files**

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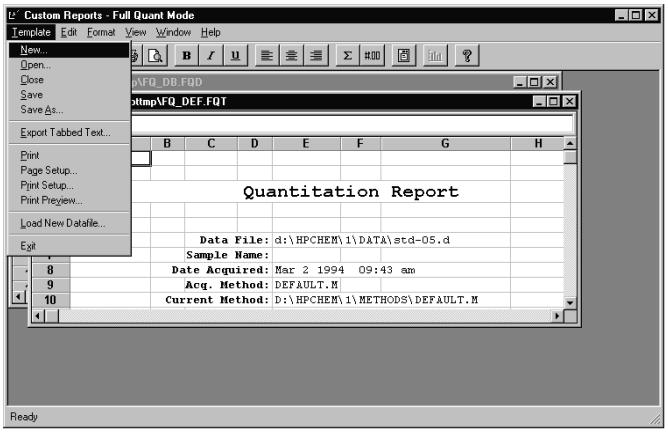
Figure 202

The objective of Custom reports is to provide an interface between the quantitative features of the Agilent 7500 Series ChemStation and the Visual Basic Custom Reports. The link between the two programs is provided through a feature of the Windows environment known as Dynamic Data Exchange (DDE). This link allows easy transfer of information from one program to another.

Creating and Editing a Report Template

Creating and Editing a Report Template



- **Create new report template**
- **Edit the current report template**
- **Specify new report template**

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Figure 203

Selecting the “New …” menu item from the Template menu will bring up the Custom Report / Database Wizard.

Custom Reports - Report Wizard

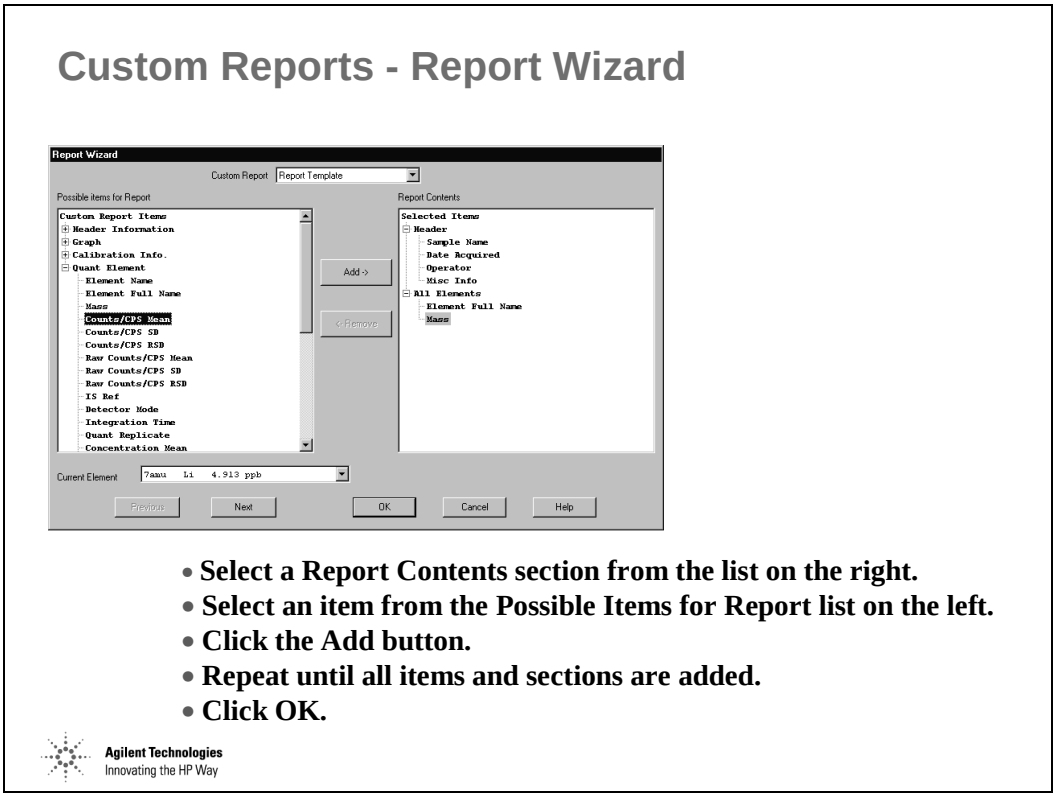


Figure 204

The Report Wizard dialog box is used to build a report template with up to two sections. The header section contains general information about the sample. The All Elements section contains element specific information arranged into tables.

A plus sign next to an item indicates there are sub-items available. Double-click on the plus sign to open the sub-item listing. The plus sign becomes a minus sign. Double-click on the minus sign to close the sub-item listing.

Spectral graphics as well as calibration curves can be added to a custom report template. Graphics can NOT be added to a database.

The Graphic section of the possible report items has two main subsections: Draw Spectrum and Graph of Each Element. Items from the Graphics section can only be added to the Header section of the Report Contents. The items from the Graph of Each Element can be added to either section of the report.

The order of the graphics in the Report Contents listbox of the Report Wizard determines the position in the report for the graphics. The text items are always

drawn together and cannot be interspersed with the graphics through the Report Wizard.

Press the Ctrl key and click the graphics to resize or reposition the graphics.

Custom Reports - Drag and Drop (1)

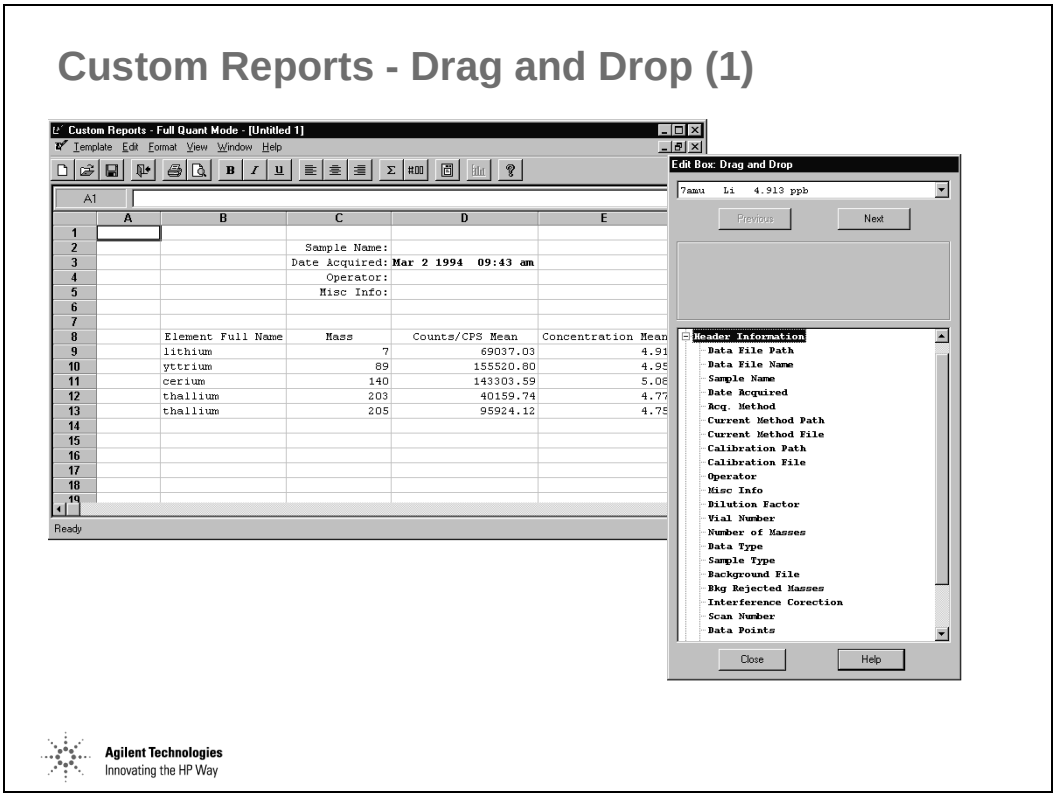


Figure 205

Custom Reports - Drag and Drop (2)

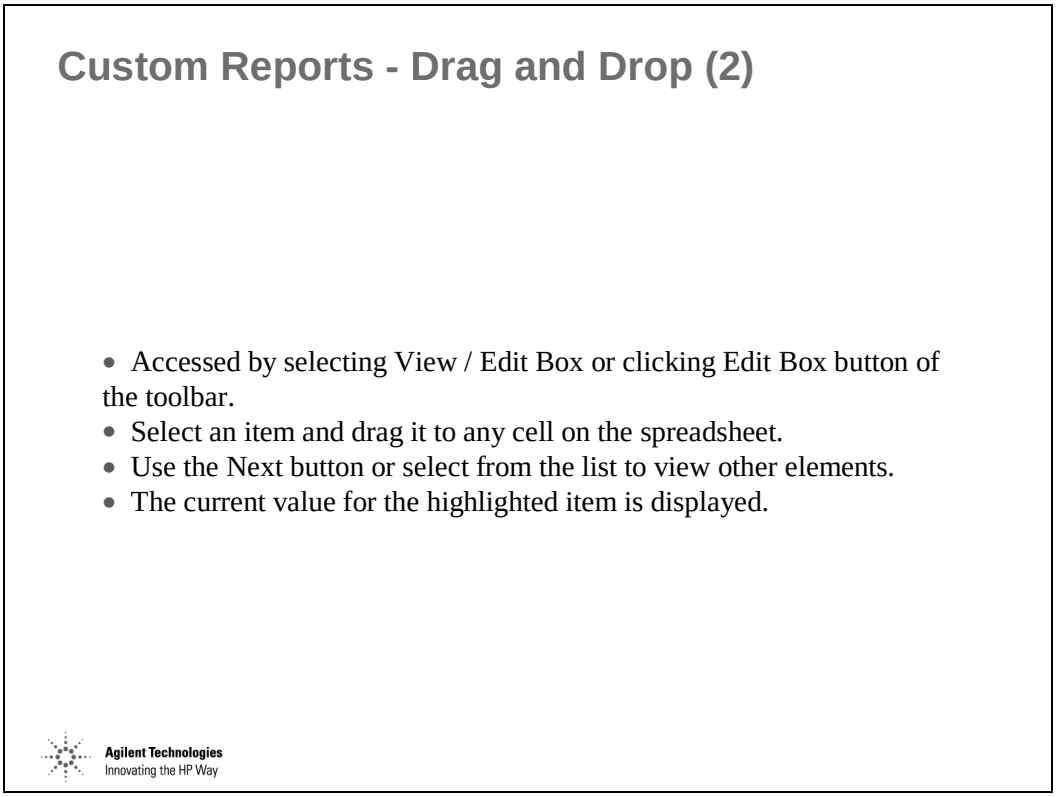
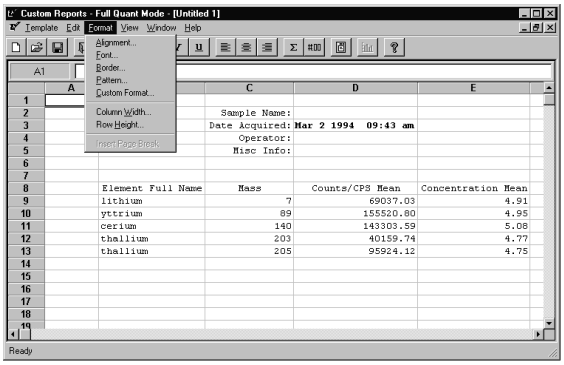


Figure 206

Formatting Custom Reports

Formatting Custom Reports



- **The Report Wizard formats automatically but you can customize the format using the Format menu items.**
- **Highlight the cell(s) you want to format.**
- **Choose a menu item or click a format button on the toolbar.**
- **Repeat as necessary.**
- **Save the template**

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Figure 207

Column width and row height can be controlled form the Format Menu or by using the Mouse.

Other mouse actions:

- select a group of cells
- select a row or column
- select multiple rows or columns
- select multiple, non-contiguous, single cells
- select multiple, non-contiguous, rows and columns
- select multiple, contiguous items

Custom Reports - Printing Set-up

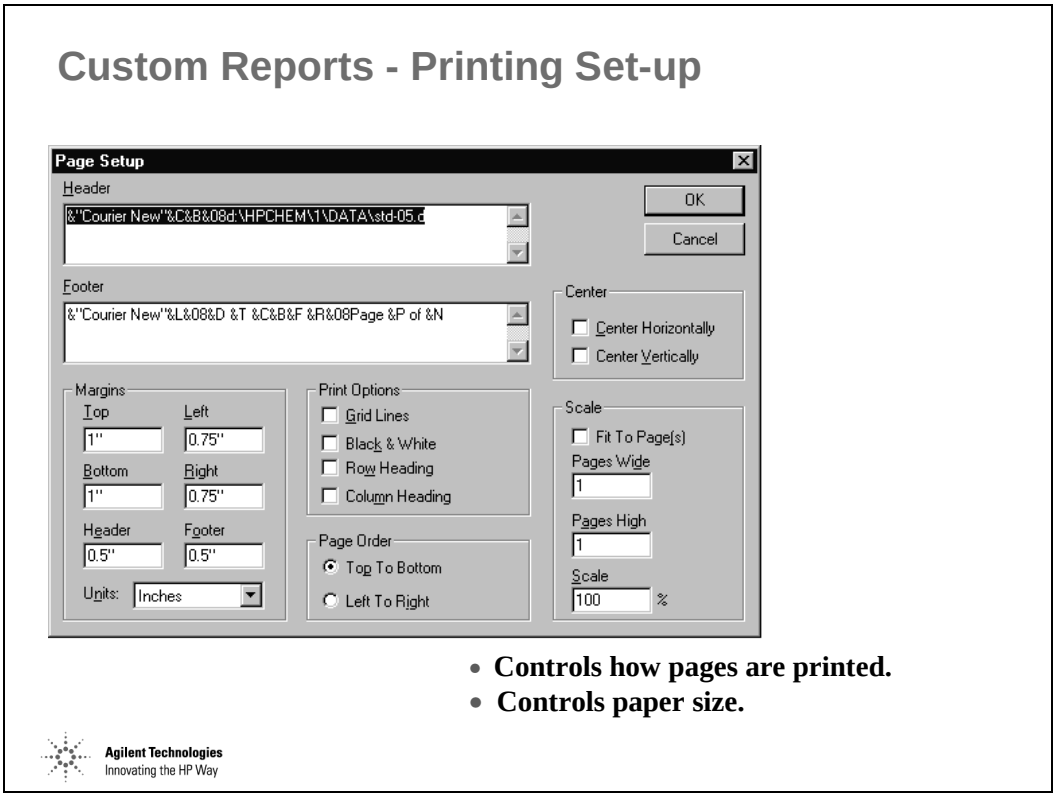

Figure 208

The following “Print Options”are available:

- Grid Lines - lets you print grid lines (otherwise they are visible on the screen only)
- Black &White - prints color in black and white on a color printer

If selected, “fit to Page(s) scales the document to print a document to print on a single or on the number of pages specified in Pages Wide, Page High.

Scale sets the percentage to reduce or enlarge the document when printed.

Custom Reports - Saving the Template

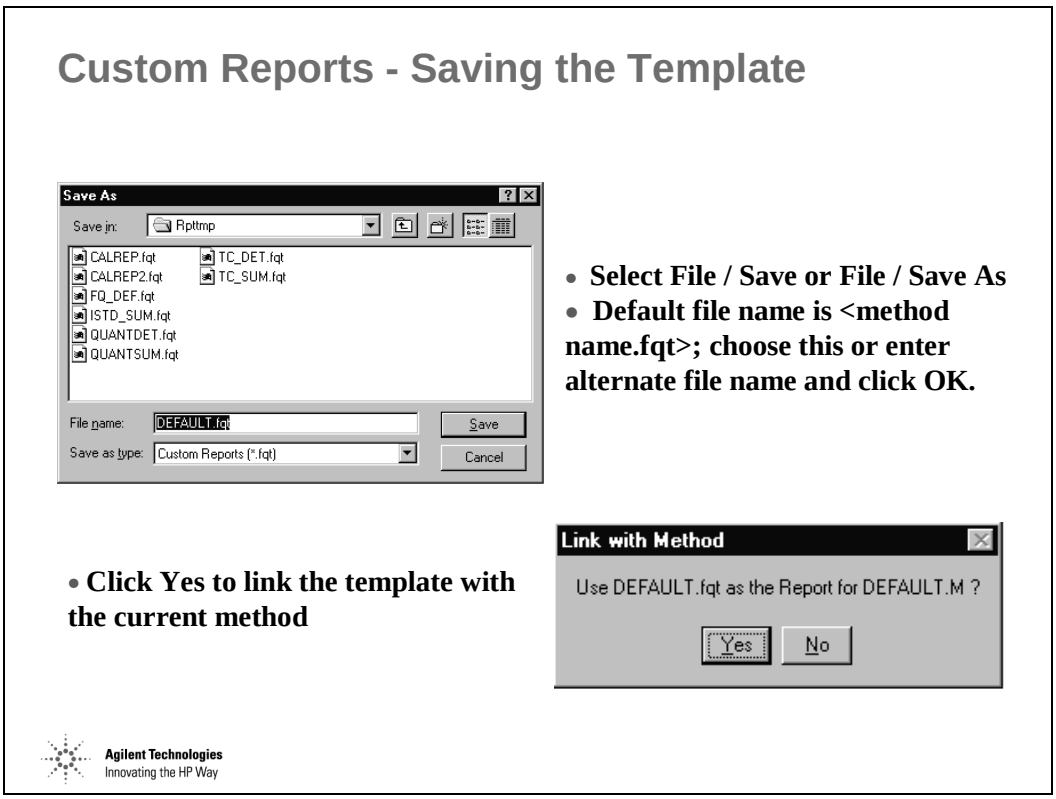

Figure 209

For the report template name, any legal DOS name is OK.

The default file name will have the same prefix as the currently loaded method. Notice that all report templates end with either FQT or SQT extension.

After saving the report template the “Link With Method Dialog Box” will appear.

Printing Custom Reports - Interactively

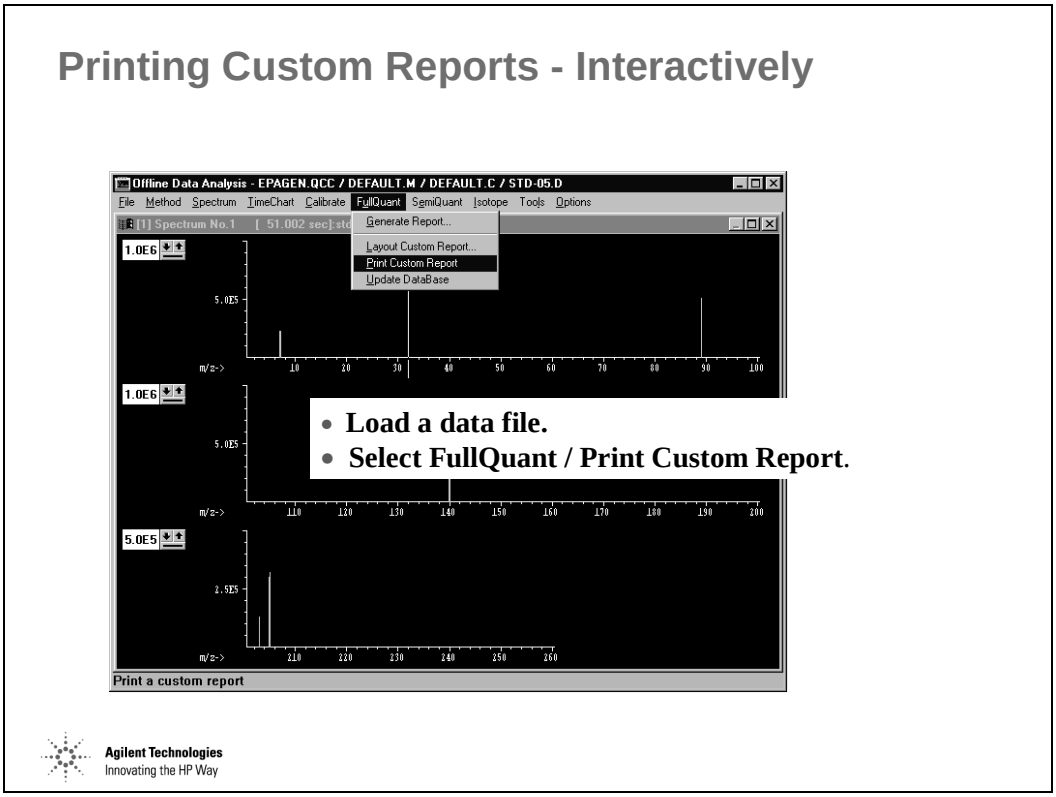

Figure 210

A custom report may be interactively printed at any time using a two step process.

- First, load the data file.
- Second, select FullQuant / Print Custom Report.

Printing Custom Reports - Printing Multiple Files [1]

Printing Custom Reports - Printing Multiple Files [1]

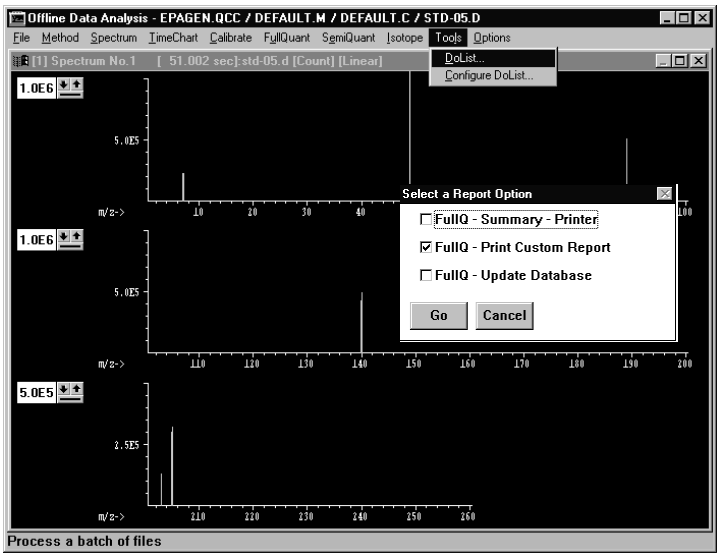

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Figure 211

Printing Custom Reports - Printing Multiple Files [2]

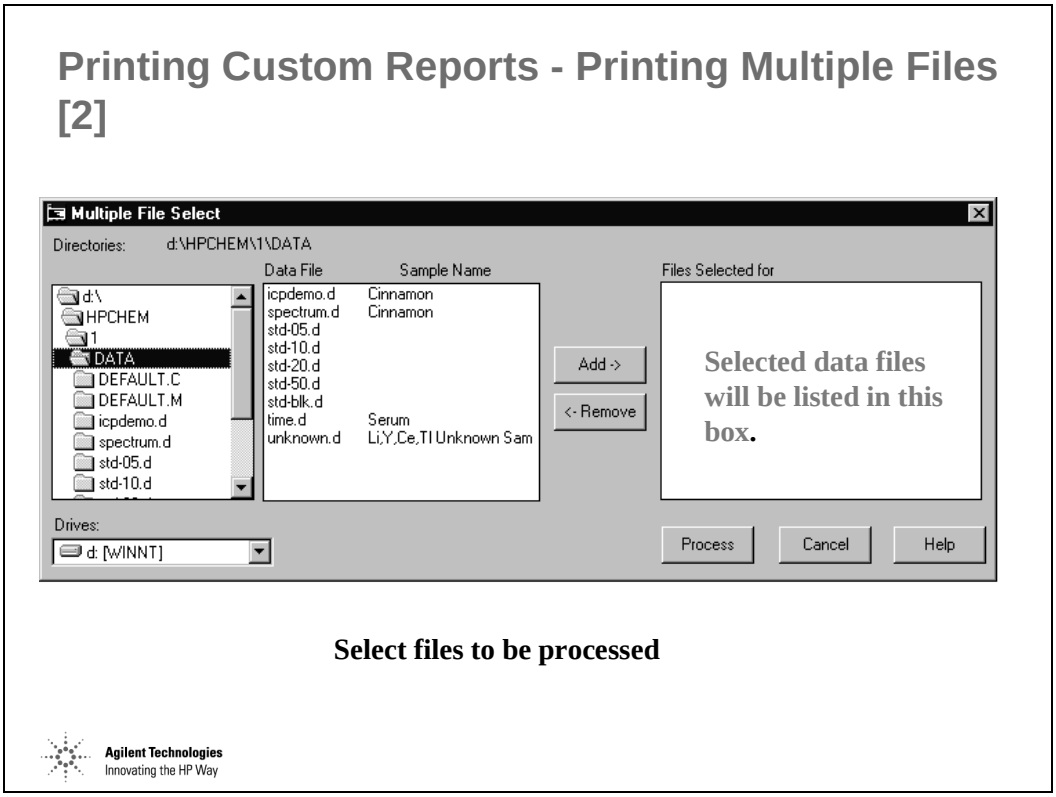

Figure 212

Select files from the Data File listing:

- multiple continuous
- multiple discontinuous
- a single file can be removed from the “Files Selected for Processing” by double clicking on it.

Click Add to insert those names into the “Files Selected for” Section of the panel.

Click the Process button.

Databases

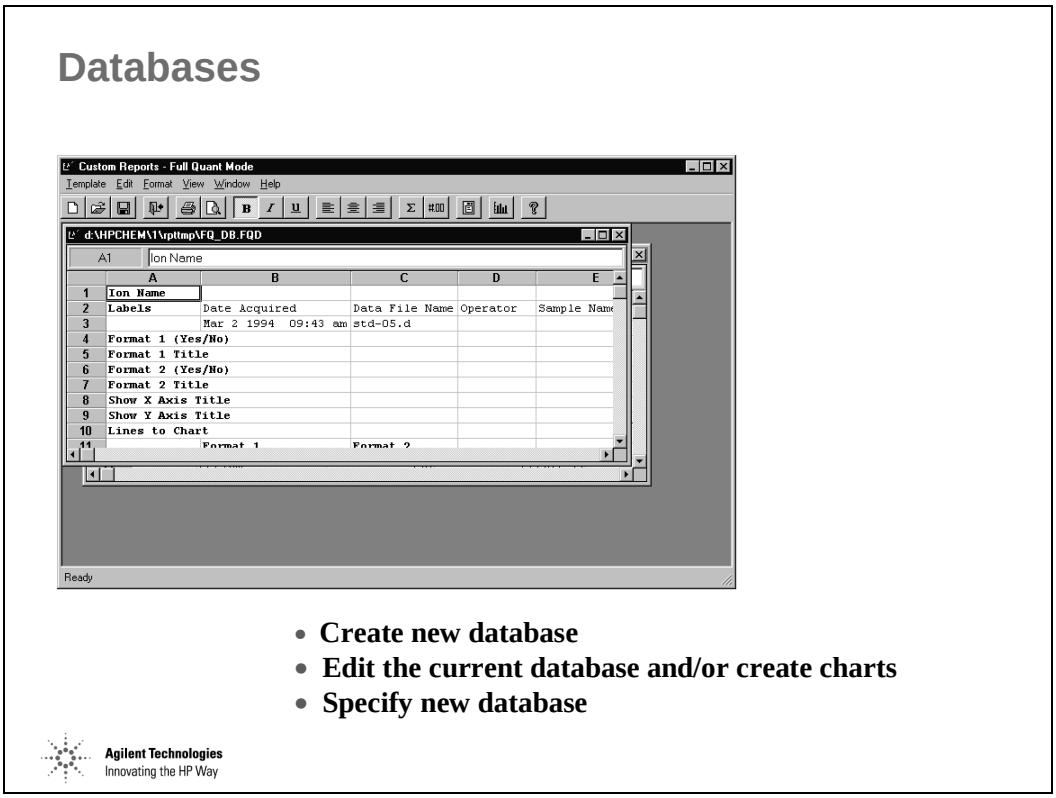

Figure 213

Selecting the “New…” menu item from the Template menu will bring up the Custom Report / Database Wizard.

Database Wizard

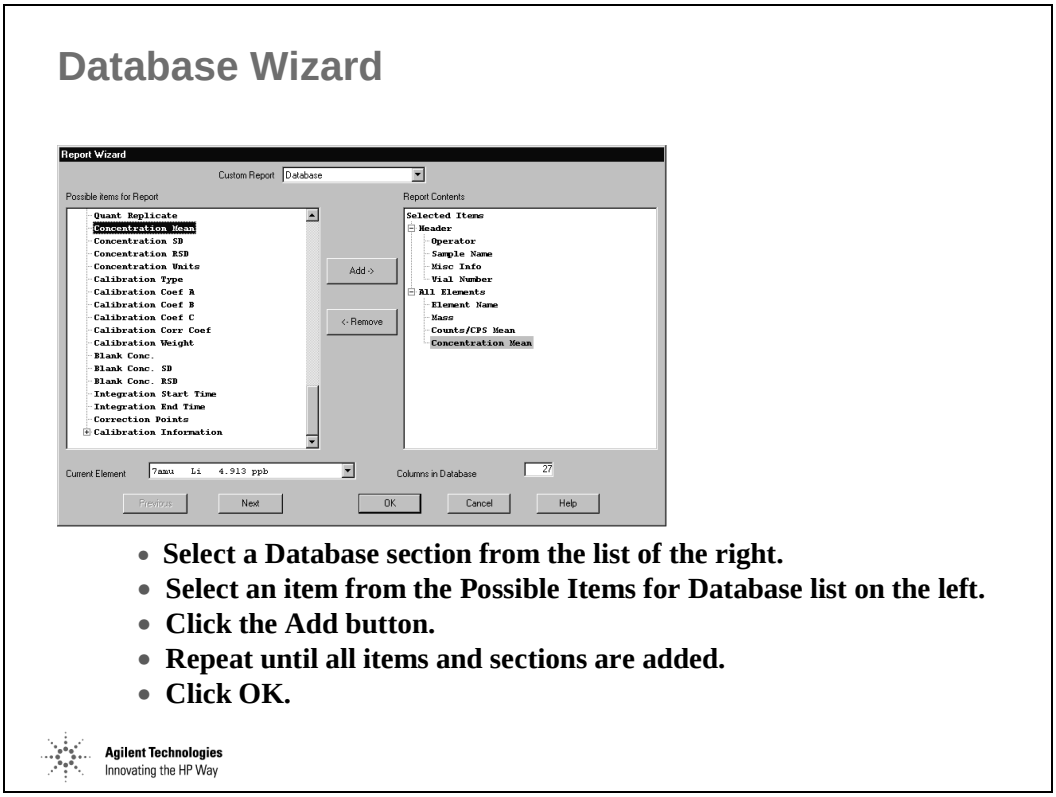

Figure 214

Clicking the Add button will add the selected item to the Database Content list on the right.

Clicking the Remove button will remove the selected item from the Database Content list.

Graphics can NOT be added to a database

Database - Drag and Drop

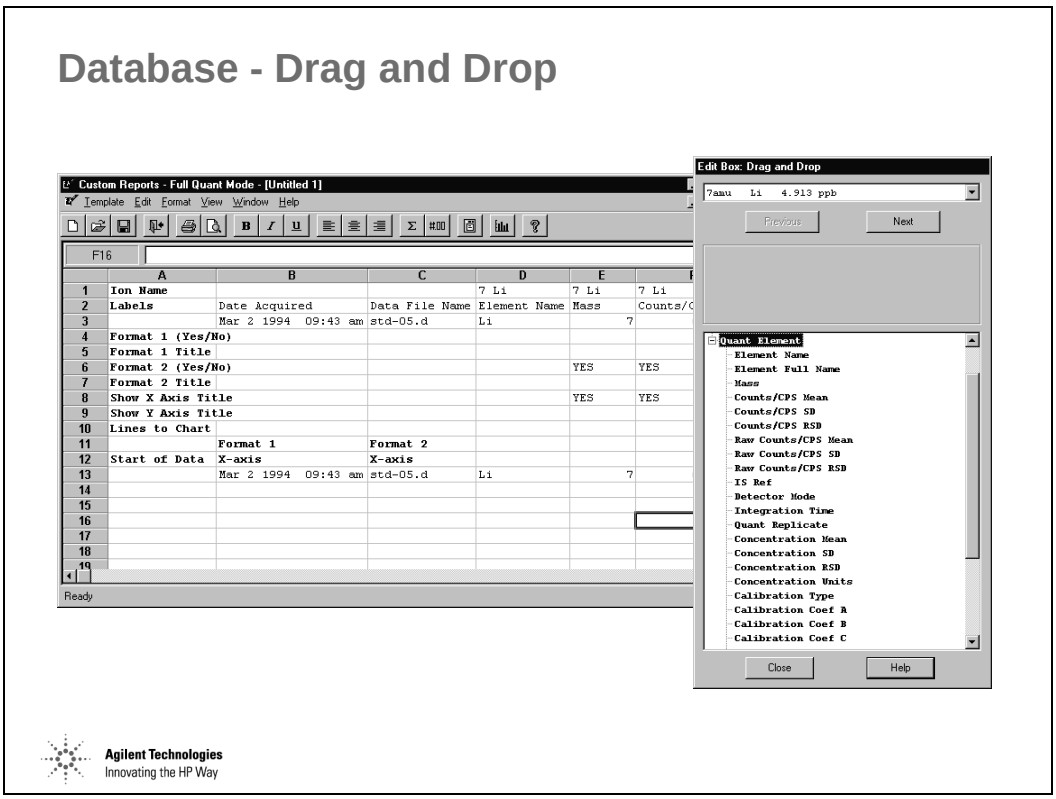

Figure 215

- Accessed by selecting View / Edit Box or clicking Edit Box button of the toolbar.
- Select an item and drag it to any cell in row 3.
- Use the Next button or select from the list to view other elements.
- The current value for the highlighted item is displayed.

Be aware that if you are editing a database, you can only put items from the Edit Box into row 3. This row contains all the information that you want to keep for each data file.

“Next” accesses the next element in the quantitation results. Elements can also be selected by using the element selection box.

Database - Formatting

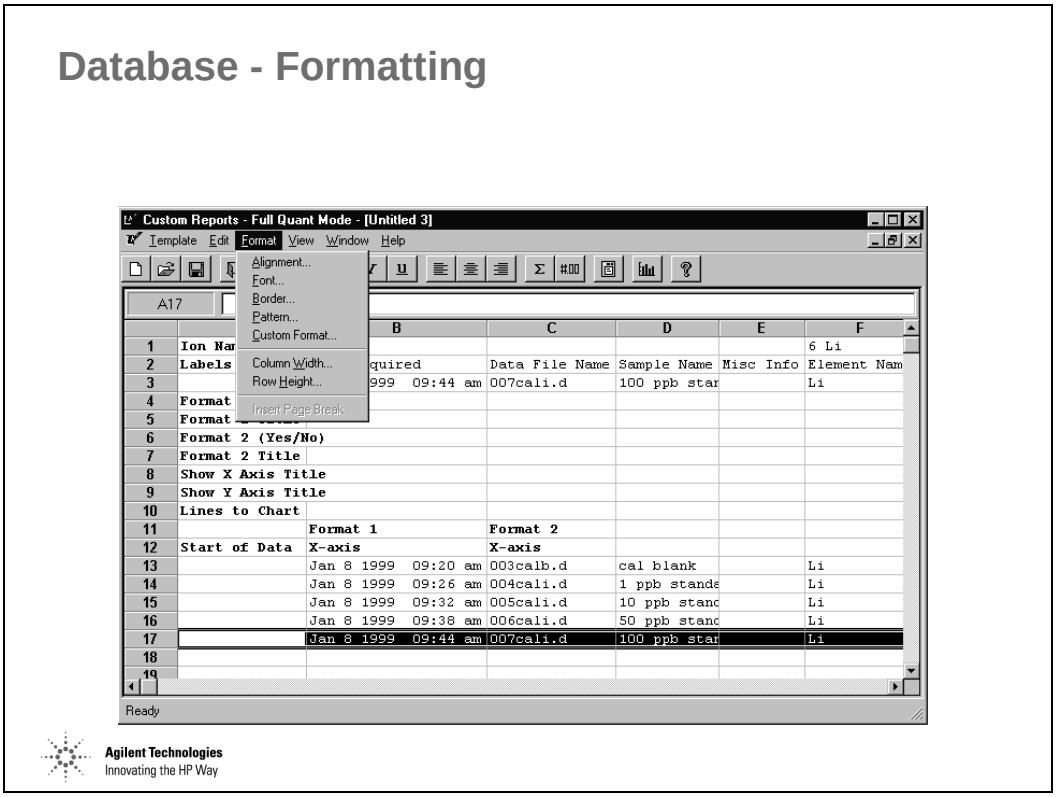

Figure 216

Database - Charts

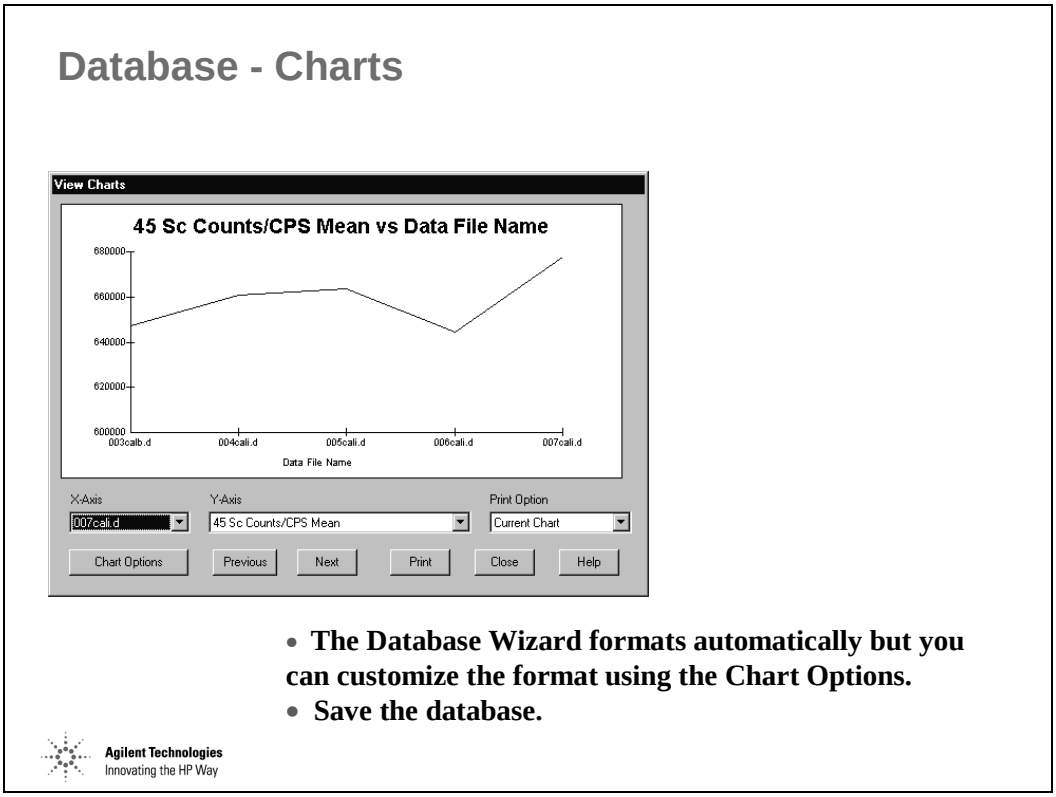

Figure 217

"X-Axis" lets you choose which items to chart on the X-Axis. Column B and C of the database determine the X-Axis items. The default item for Column B is Date Acquired and for Column C is Data File Name.

"Y-Axis" lets you choose which items to chart on the Y-Axis. Only numerical values (such as mass or counts) can be used for the Y-Axis.

The Print Option lets you print the current chart or print all charts in the database.

Global Chart Options

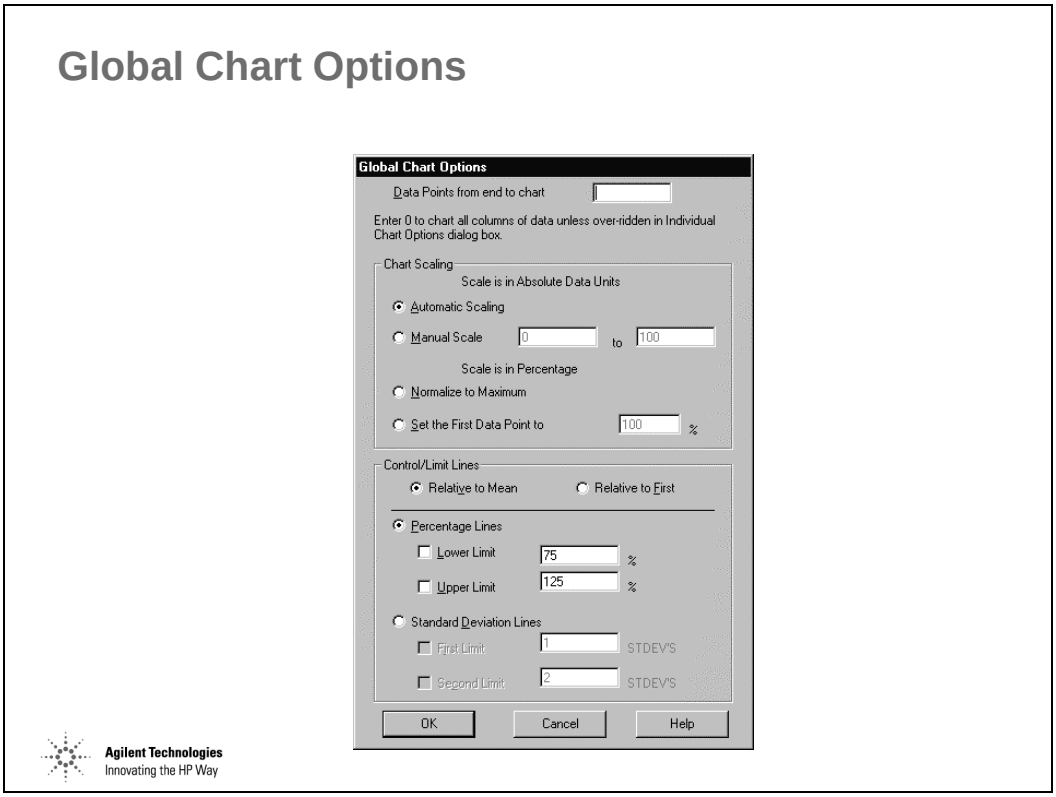

Figure 218

By default, all rows in database are charted. If you enter a number N (other than 0) in the "Data Points from End to Chart" field, then only the last N rows will be charted. This feature is useful when you have added many rows to your database, but are only interested in the last N files. You can override this value for a single chart using the Individual Charts Options dialog box.

Automatic Scaling - The software will automatically choose a range which allows all of the data to be seen. The data is shown in absolute units. The range chosen can be slightly larger than the actual data range.

Manual Scale - The manual scale allows you to control exactly what the scale on the Y axis will be.

Normalize to Maximum - This scale allows you to chart the data as a percentage of the maximum value (set to be 100%).

Set the First Data Point to - This scale allows you to chart all points as a percentage of the first row of data.

You can draw up to four control/limits lines on a chart. These lines can be relative to the Mean or to the first value charted.

You can draw the percentage lines or Standard Deviation lines

Database - Saving

Database - Saving

- **Select File / Save or File / Save As**
- **Default file name is <method name.fqd>; choose this or enter alternate file name and click OK.**

- **Click Yes to link the template with the current method**

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Figure 219

Updating the Database - Interactively

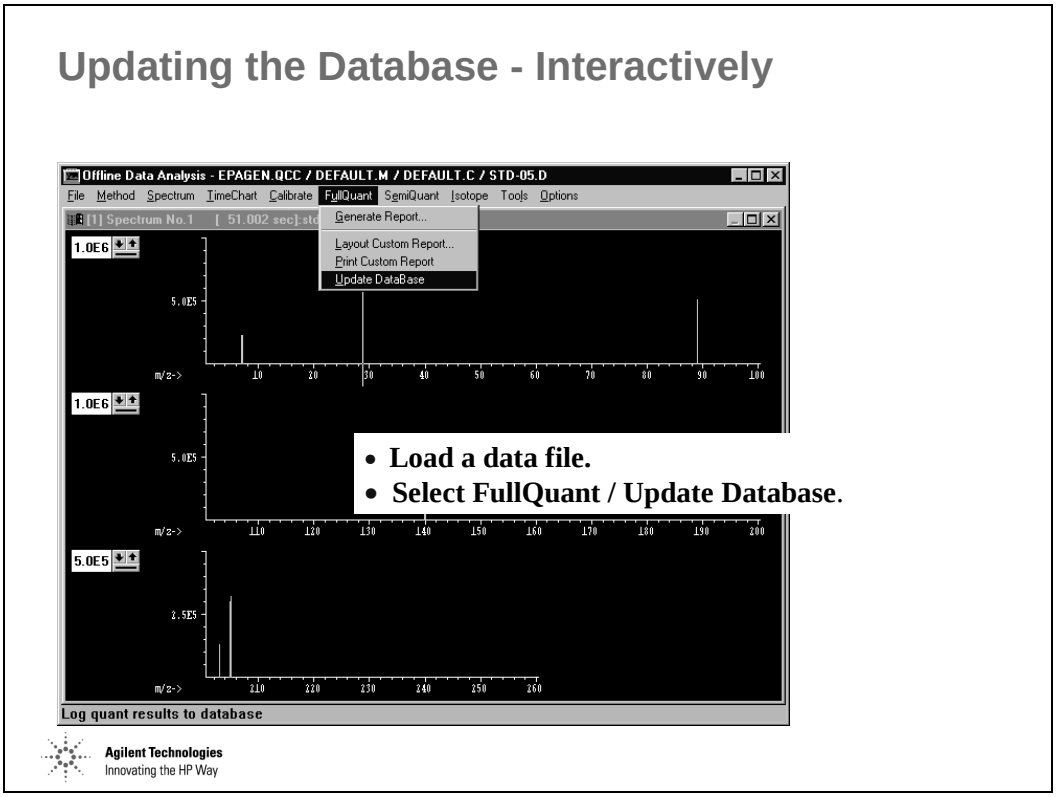


Figure 220

Update the Database - Multiple Files [1]

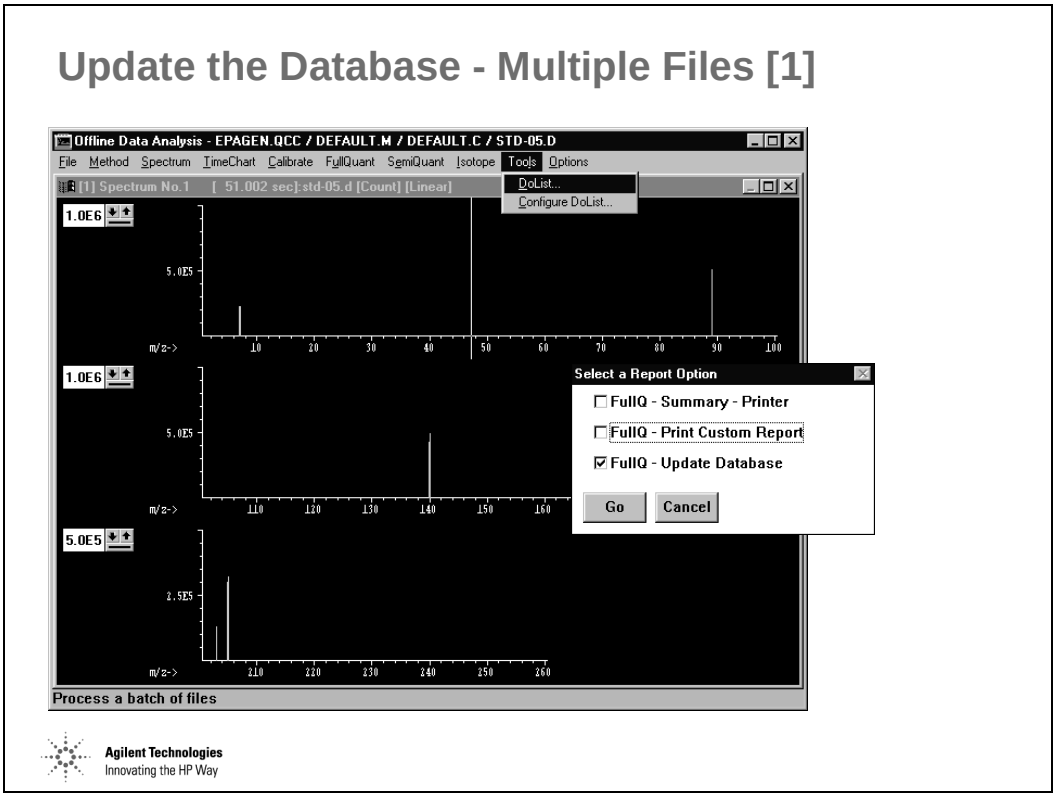
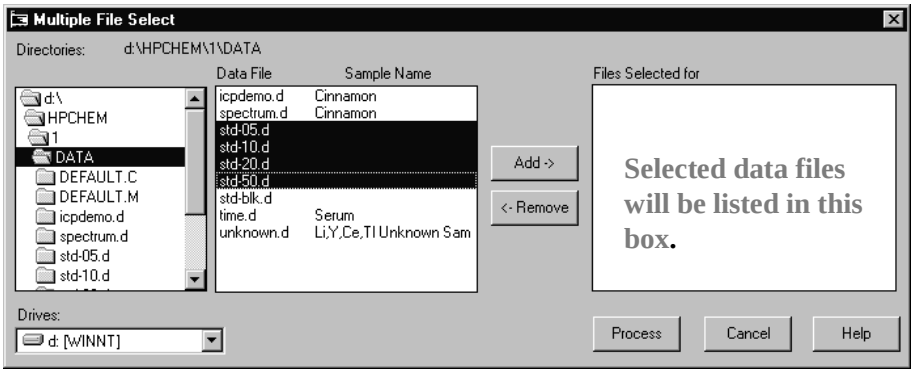


Figure 221

Update the Database - Multiple Files [2]

Update the Database - Multiple Files [2]



- **Select Tools, DoList...**
- **Select FullQ -- Update Database**
- **Select files to be processed**

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Figure 222

Update the Database - Multiple Files [2]

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Isotope Ratio Measurements

Editing a Method for Quantitative Analysis

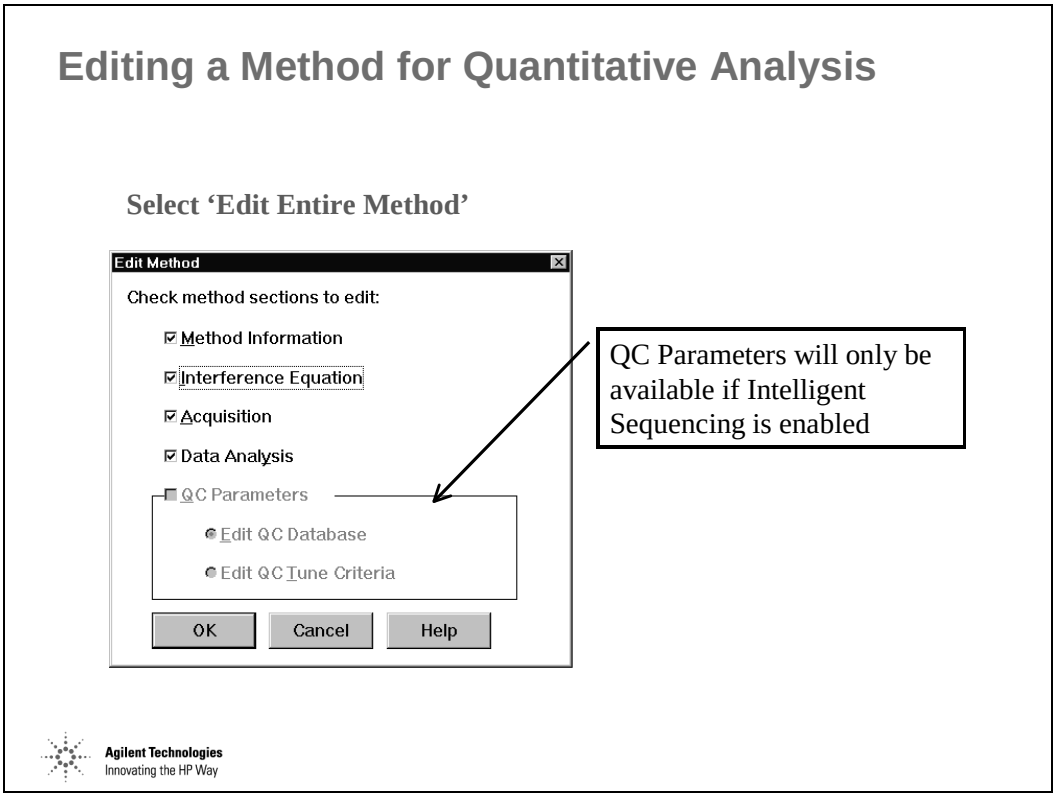

Figure 223

Acquisition Modes

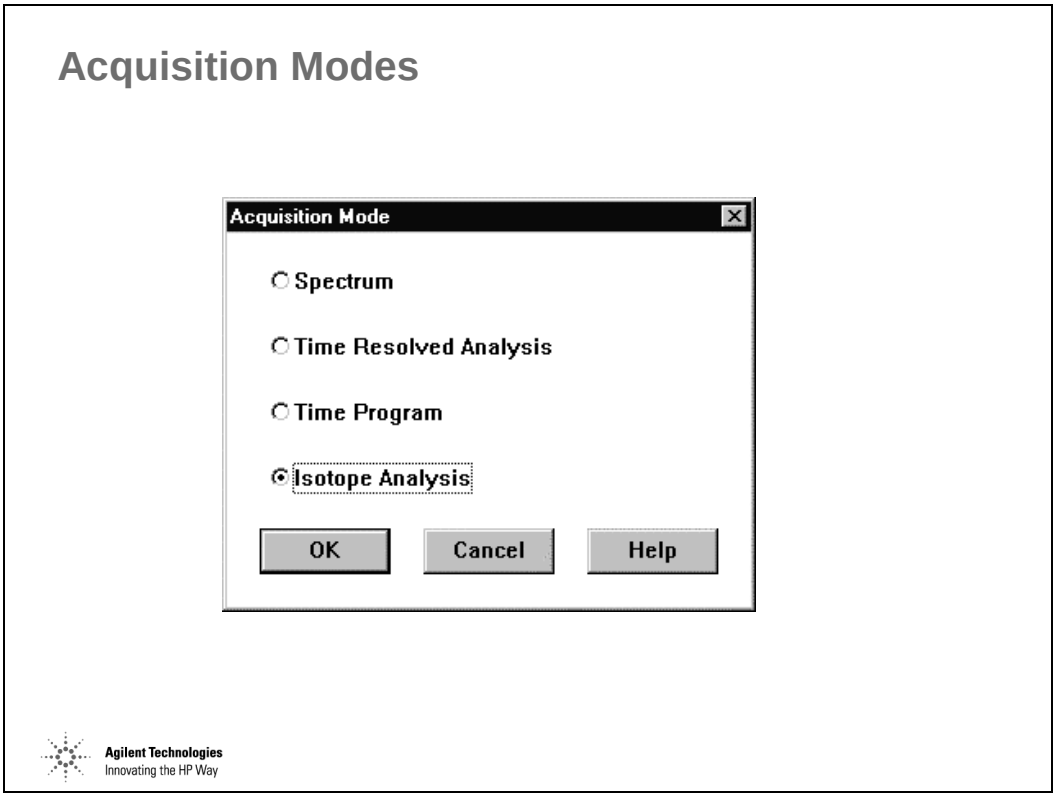

Figure 224

Spectrum mode is the most common acquisition mode for standard applications.

- Quant
- Semiquant

Time Resolved Analysis (TRA) and Time Program (more sophisticated than TRA) are used when a transient signal is measured.

- Electrothermal Vaporization (ETV)
- Laser Ablation (LA)
- Discrete Sampling Analysis (using ISIS)
- Chromatographic analysis (LC, GC, IC, CE)

Isotope Analysis mode is used when additional precision is needed for isotope ratio measurements. It is similar to spectrum mode, but with 10X higher sampling frequency.

Acquisition Modes

Multitune mode is used when during a single acquisition more than one tuning parameters are needed to accomplish the optimum performance.

Acquisition Parameters for Isotopic Ratio Measurements

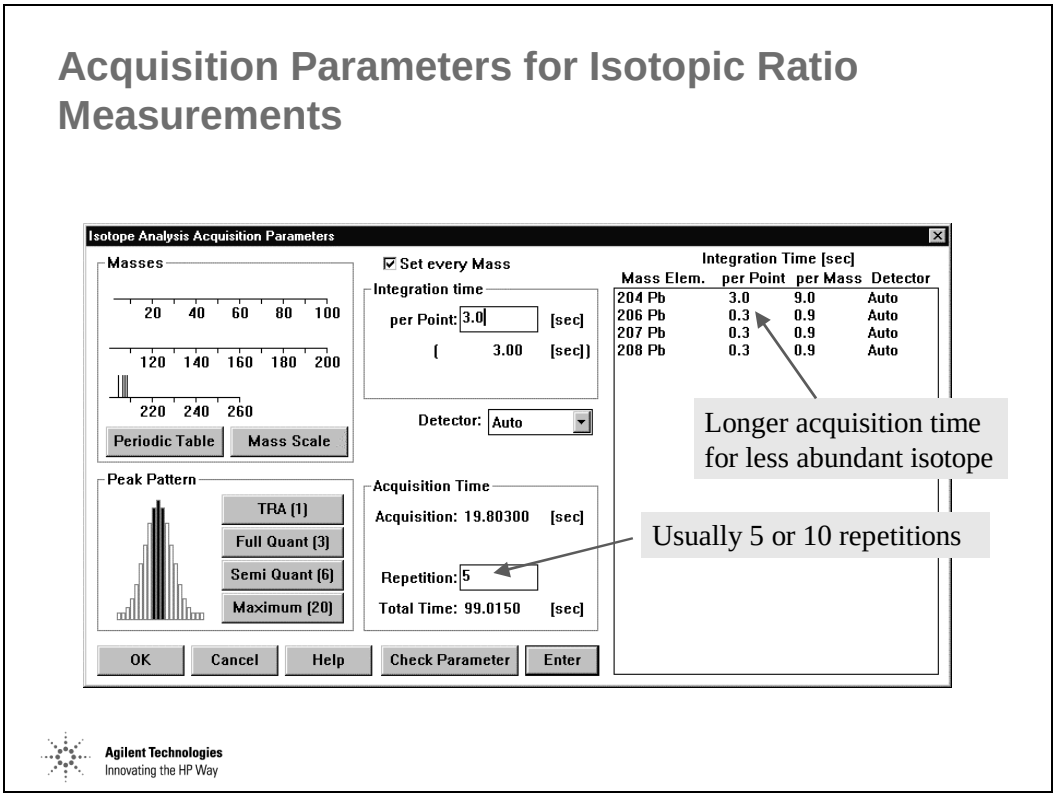

Figure 225

Report Selection

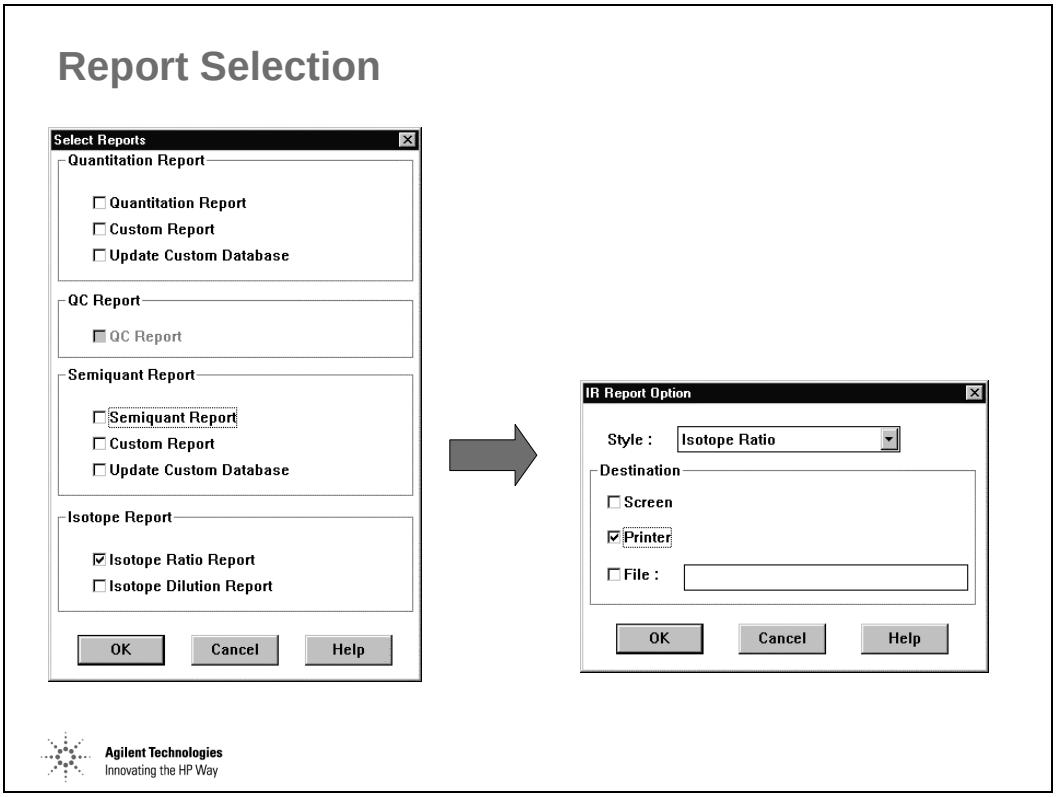

Figure 226

Setting Parameters for Isotopic Ratios

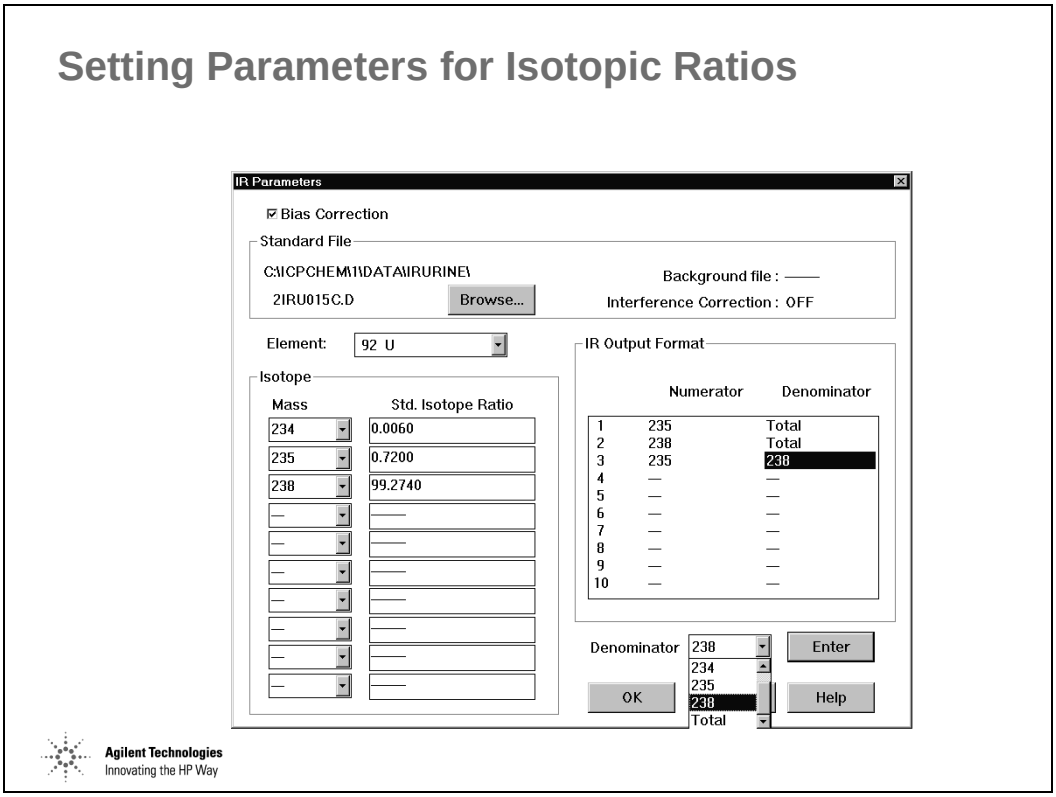

Figure 227

Example of the Isotopic Ratio Report

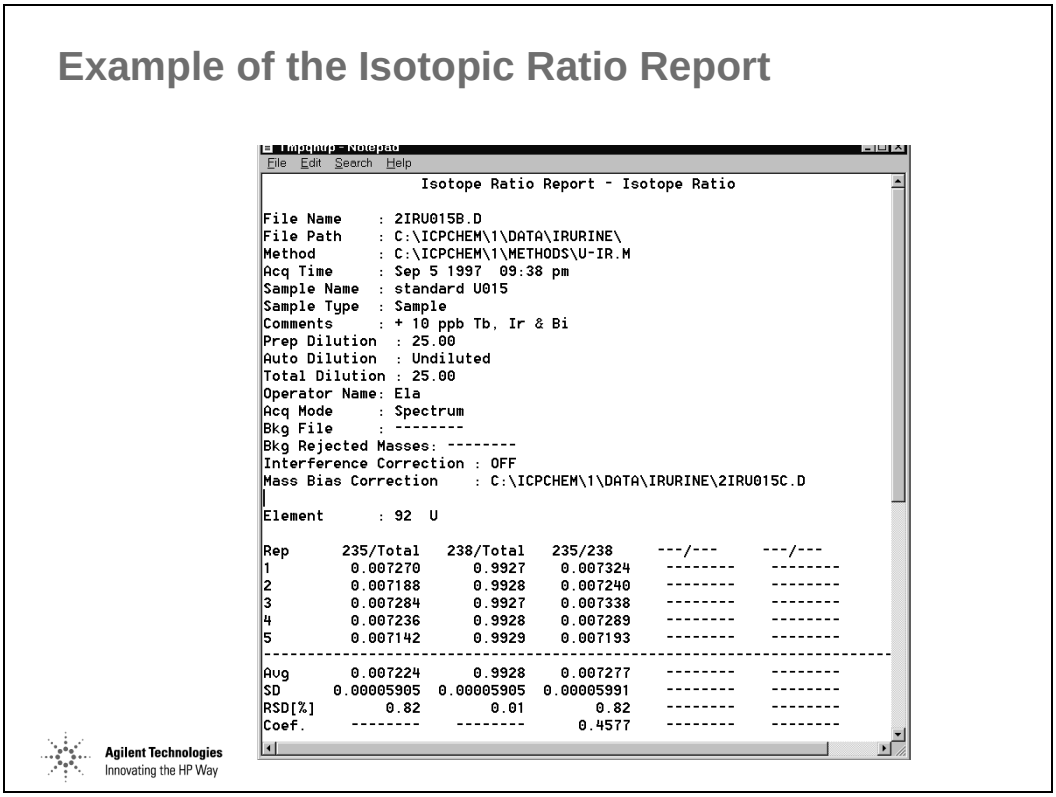

Figure 228

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Agilent ICP-MS ChemStation and Windows Overview

The Windows Interface

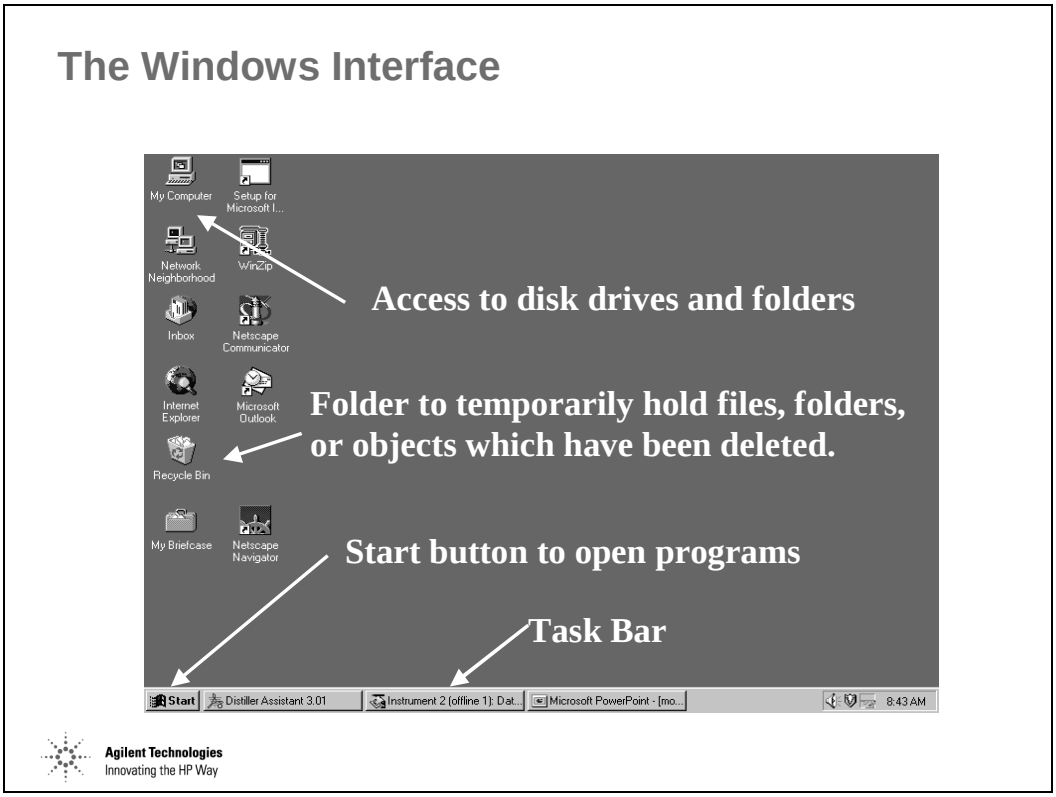

Figure 229

Windows Menus

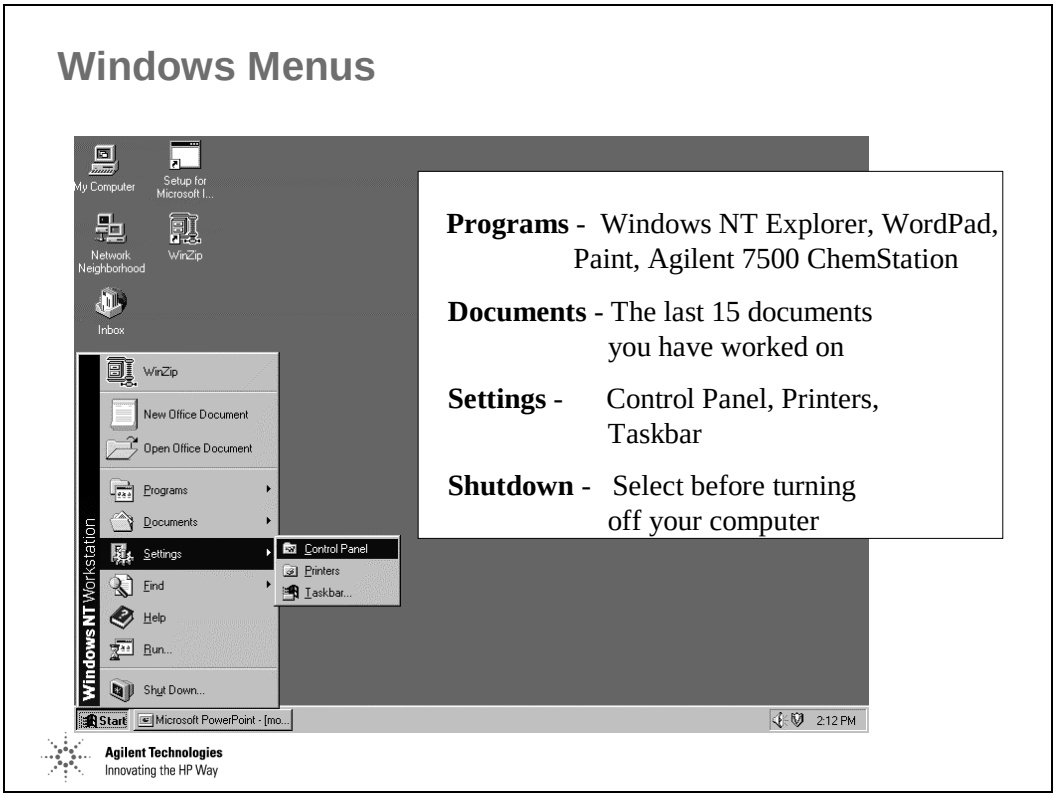

Figure 230

Useful Windows Tips

Useful Windows Tips

- Add Programs to the first-level menu instead of cascading through menus.
- Create Shortcuts by dragging a document to the desktop with a right-click of the mouse button.
- Change the desktop properties with a right-click of the mouse button.
- Use Ctrl-Alt-Del to end a task that is not responding.

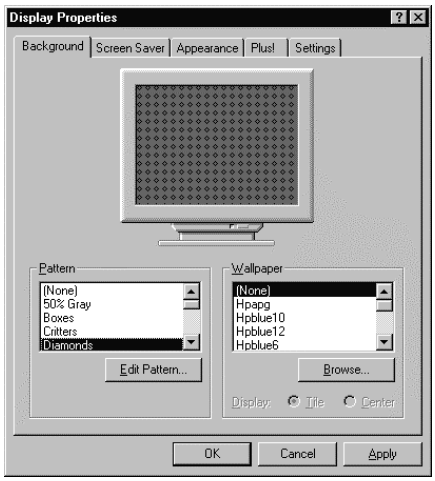

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Figure 231

Maintaining the Computer System

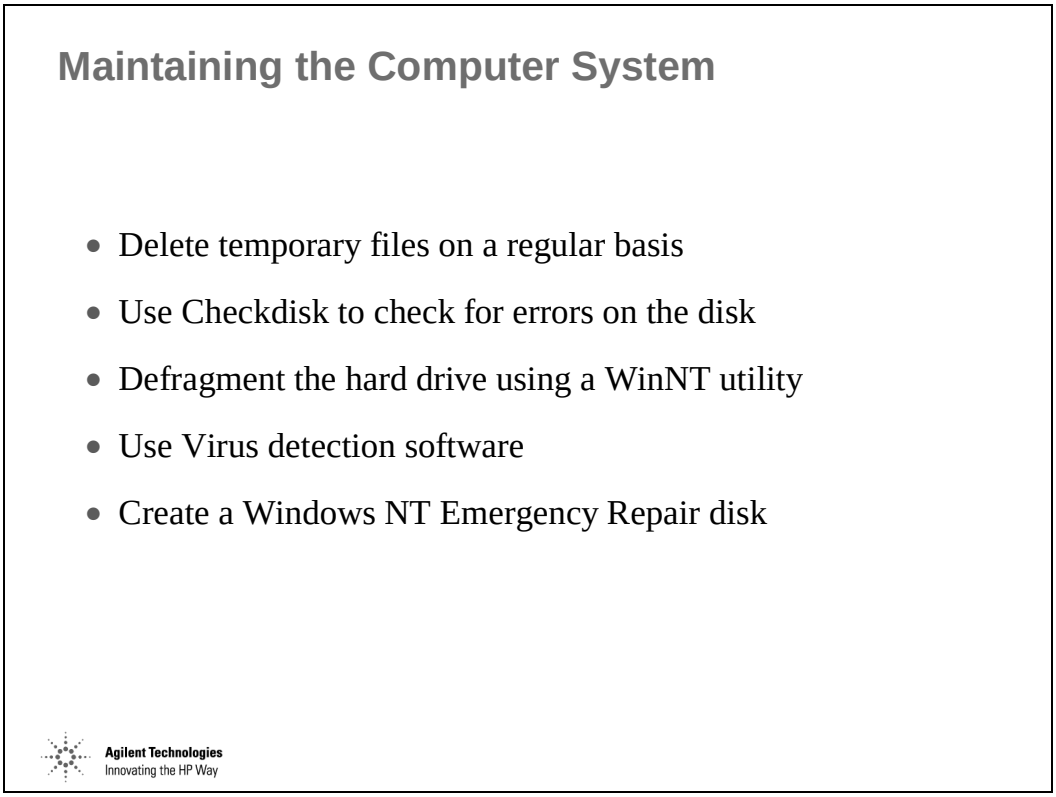
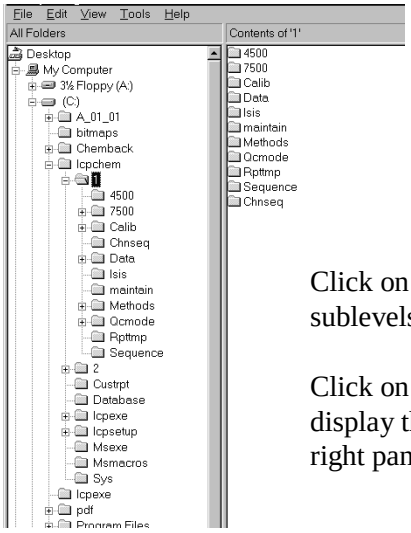


Figure 232

Windows NT Explorer - Enhanced File Management

Windows NT Explorer - Enhanced File Management



Click on + sign to open sublevels in the left pane.

Click on the item to display the contents in the right pane as folders.

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Figure 233

Directory Structure of the Agilent ChemStation

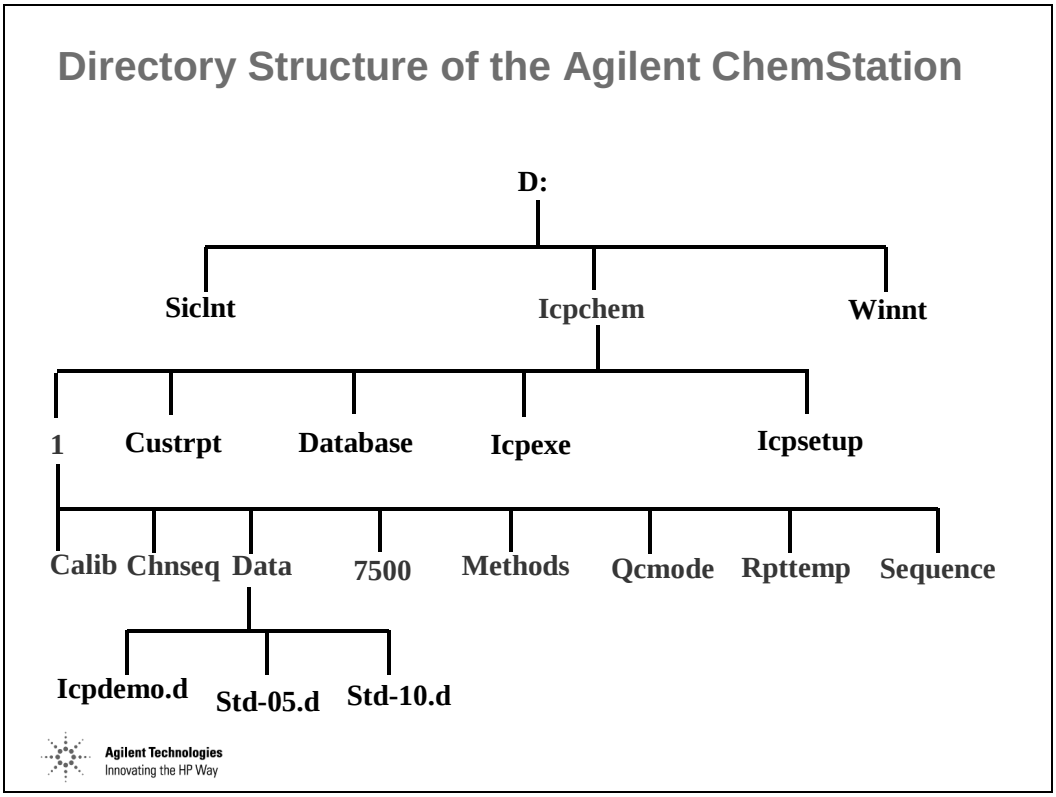

Figure 234

File Naming

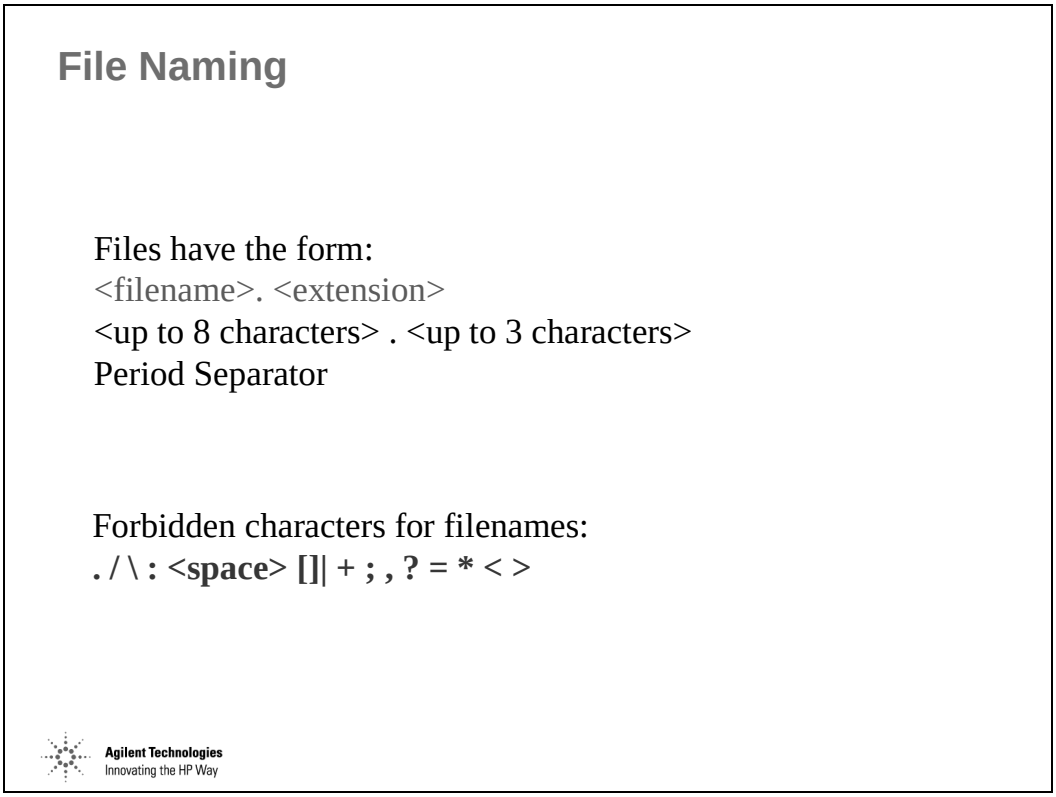

Figure 235

ChemStation File Extensions

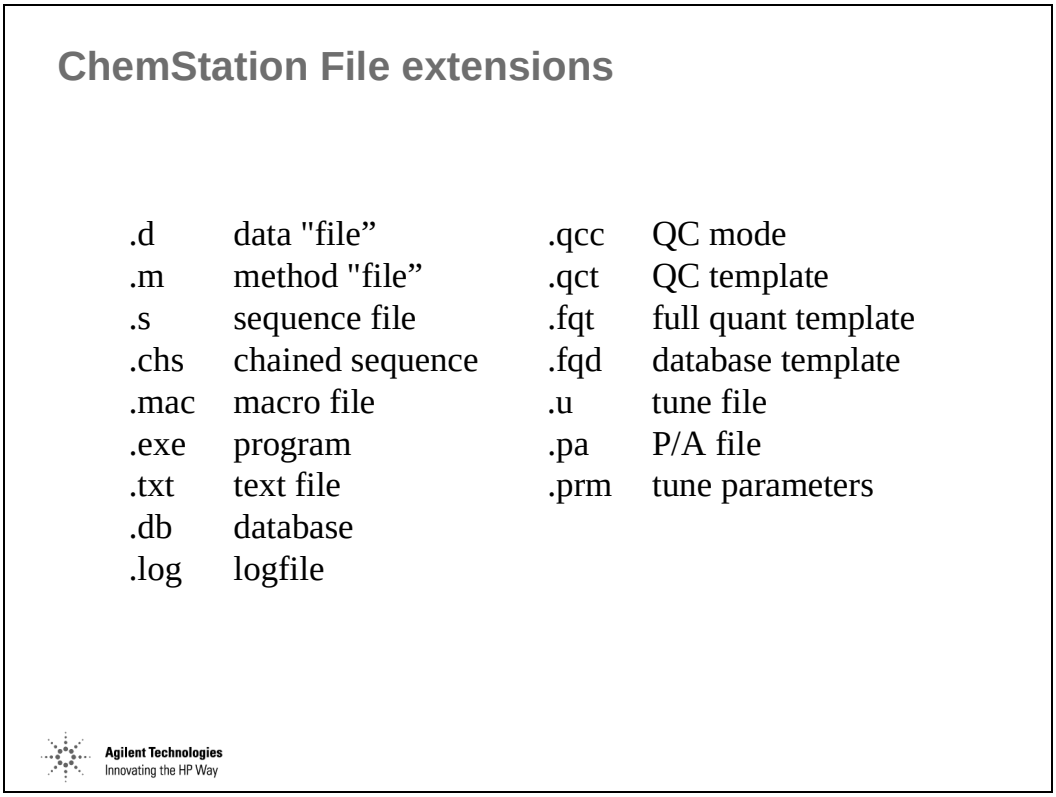

Figure 236

ChemStation File Extensions

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An Overview of ICP-MS Environmental Applications

Optimizing Agilent 7500 for Environmental Samples Analysis

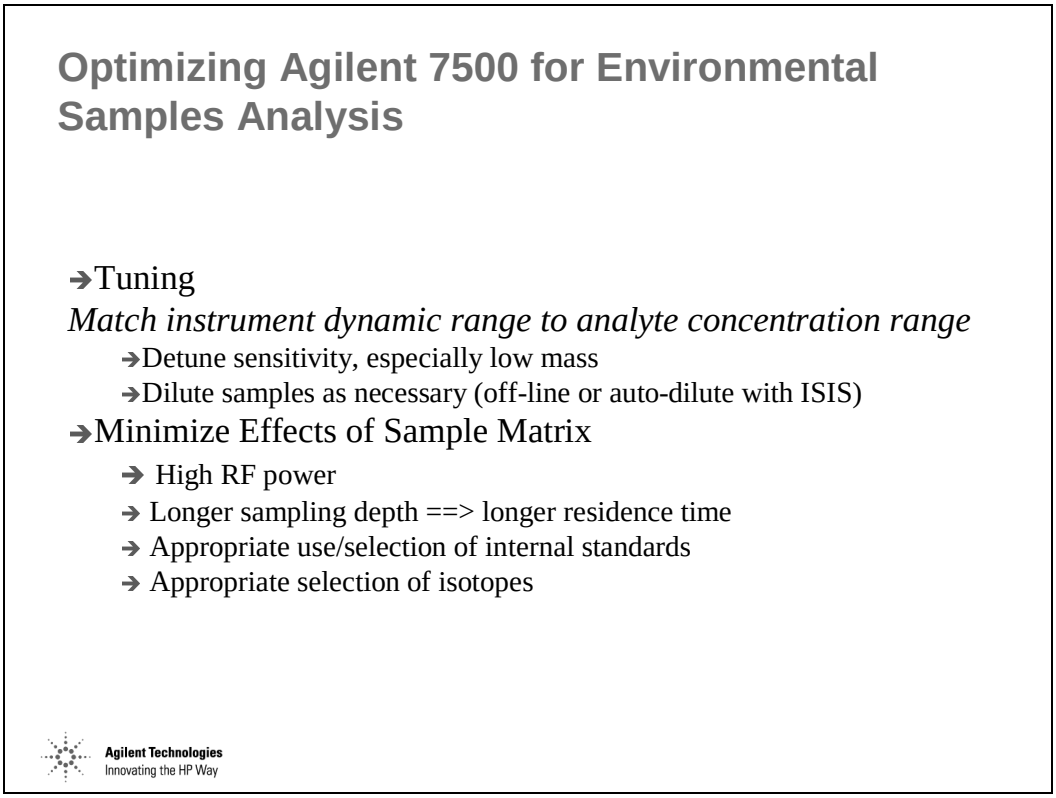


Figure 237

Environmental Tuning

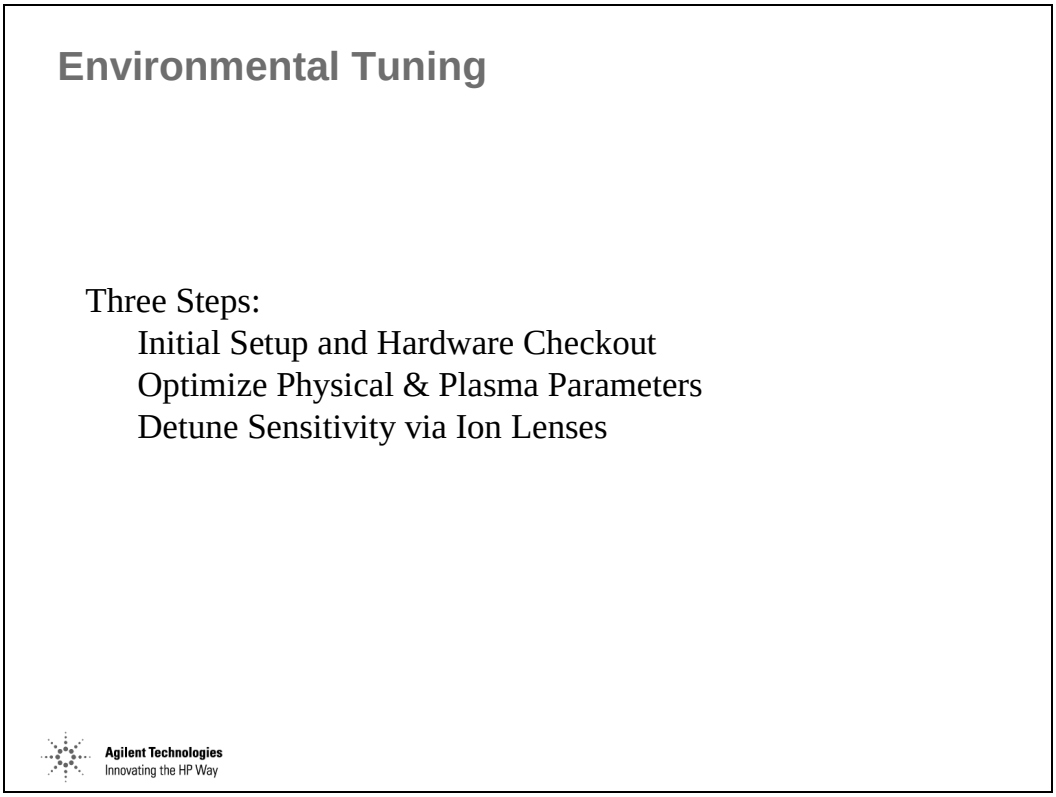


Figure 238

Initial setup/hardware checkout

When any maintenance is executed, it is important to verify that the instrument can meet specifications for sensitivity, precision, mass calibration, oxides and all other parameters. This will verify that the hardware is operating correctly.

Physical/Plasma Parameters

Since typical environmental samples can contain relatively high matrix, it is important to make tuning adjustments that improve the decomposition of the matrix, such as increasing the plasma temperature or increasing the residence time of the sample in the plasma.

Detune Sensitivity via ion lenses

Typical compositions of environmental samples include higher concentrations of low mass elements such as Na, K, Ca and Mg, and lower concentrations of mid and high mass elements such as Se and Hg.

Environmental Tuning

To analyze all the elements at the same time, detuning the low mass only can be an effective technique. However, care must be taken in this process if analysis of Be is required.

Tips

Conditioning of the interface is recommended to improve signal stability, after cleaning the cones or extraction lenses. For conditioning, run tap water through the system for 1/2 hour during tune before finalizing tune conditions and prior to calibration and sample analysis.

Three Goals of Environmental Tuning

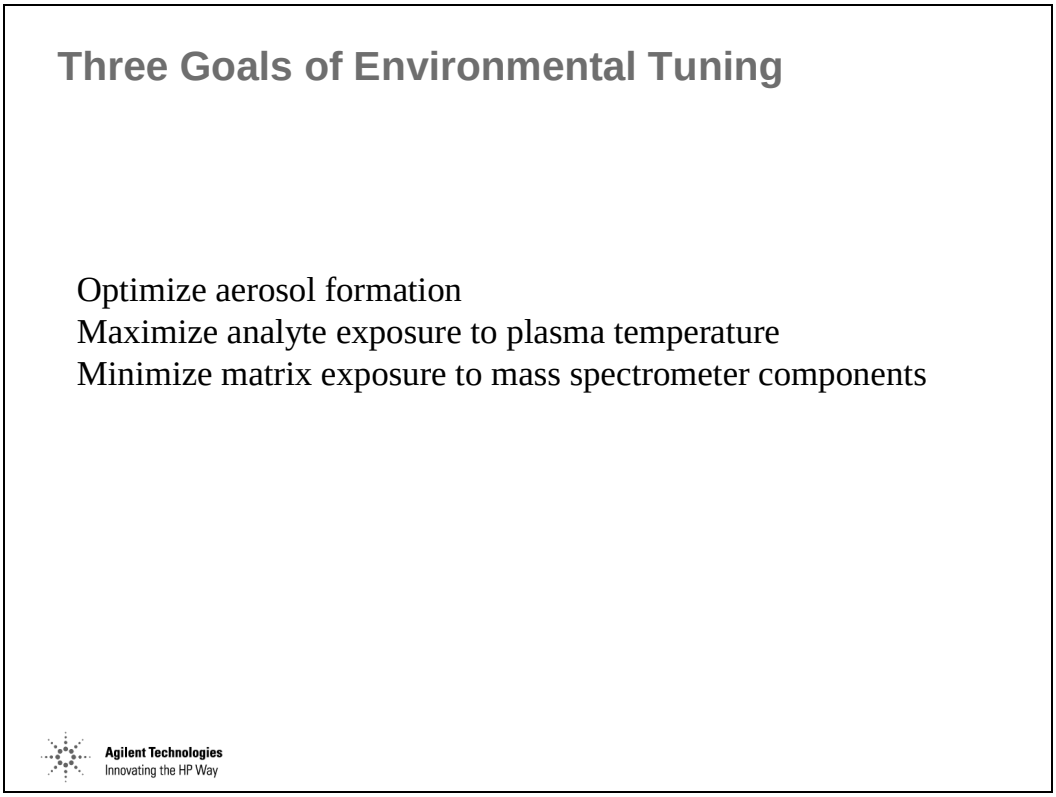


Figure 239

Increasing sampling depth increases the sample residence time in the plasma. The effect is to allow more time for decomposition (atomization and ionization) of the analyte elements. Each nebulizer has optimal values for carrier gas flow rate and sample flow rate. In general, higher carrier gas flow rates create higher carrier gas pressures thereby generating finer droplets, which lead to better instrument sensitivity. However, excessive carrier gas flows cool the plasma, decreasing the sensitivity and increasing the ratios of oxides and doubly-charged ions significantly. Excessively high carrier gas flows cool the plasma which increases low mass (e.g. Li) sensitivity and noise to a non-acceptable level. Lithium signal should not exceed Yttrium signal in a well tuned system.

Oxides are almost completely controlled by the interaction of four parameters, spray chamber temperature, sample depth, carrier gas flow and peri-pump flow. Since we have chosen to maximize sample depth for other reasons and spray chamber temp should normally be set to 2 C. we must control oxides with carrier gas flow and peri-pump flow. The goal here is to maximize the efficiency of the particular nebulizer being used (smallest droplet size and size distribution), without increasing either flow to the point of over-cooling the plasma.

Three Goals of Environmental Tuning

Decreasing the negative voltage on the two extract lenses decreases the number of ions drawn into the mass analyzer. This decreases the sensitivity of the instrument. It also decreases the ion load on the rest of the mass analyzer which minimizes the need to clean the other lenses and components. It is important that the correct voltage gradient between the two lenses be maintained. As such, Ext1 should be set and then Ext2 fine tuned to give the best results. If large changes in Ext1 voltage have little to no effect on sensitivity, this is an indication that the extract lenses need to be cleaned.

Tuning Flow Chart

Tuning Flow Chart

See Appendix 4

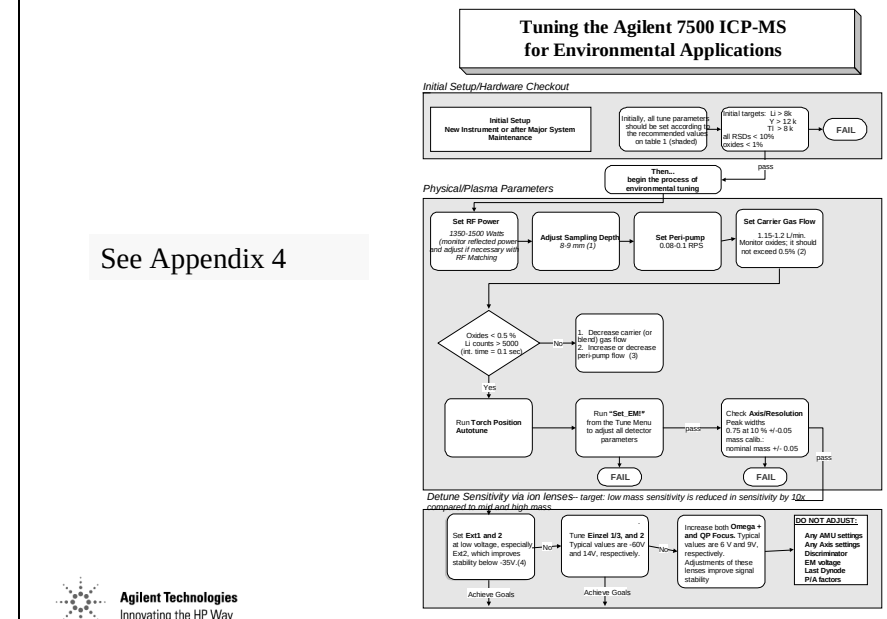


Figure 240

Recommendations on Interference Equations

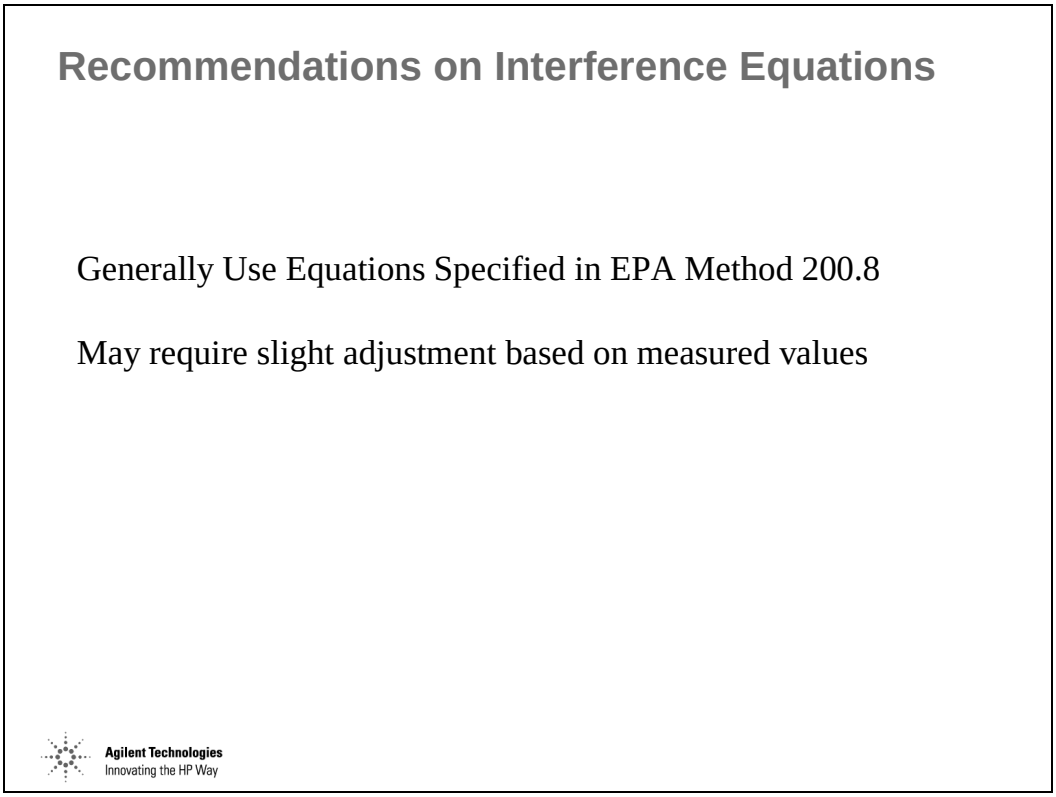


Figure 241

Arsenic

Since there are lots of polyatomic ions are generated around the mass, it is very difficult to apply universal equation.

When the contribution of 82Kr is considered, the equation should be changed as follows:

$$As(75) = (1.000)(75C) - (3.127)(77C) + (2.736)(82C) - (2.760)(83C)$$

However, an unknown peak sometimes appears at mass 83. BrH is also generated at mass 82. As a result, the contribution of Kr is overcorrected, and As might show a negative result.

Selenium

Generally, the use of 82 rather than 77 or 78 is recommended. 77 is interfered with by $^{40}Ar^{37}Cl$, and 78 is interfered with by $^{38}Ar^{40}Ar$ dimer. The 82 isotope needs to be corrected for the possible presence of ^{82}Kr in the Argon gas supply using the following equation.

$$Se(82) = M(82) - 11.6/11.5 * Kr(83)$$

$$= M(82) - 1.0087 * Kr(83)$$

However, as described the above, the unknown peak might appear at mass 83, thereby a portion of the signal at mass 83 is used practically. An example is as follows:

$$Se(82) = M(82) - 0.6 * Kr(83)$$

The monitoring of mass 77 and 78 is also recommended just in case.

More Interference Corrections

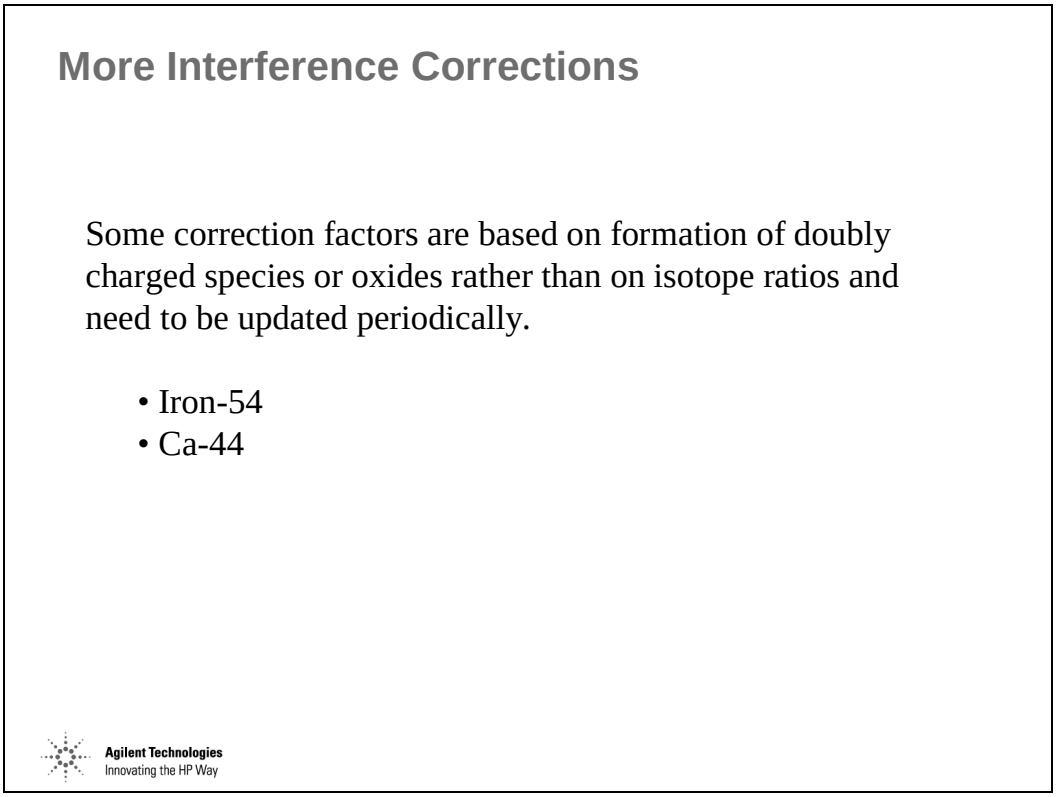


Figure 242

Vanadium

The interference correction might not be useful. Because it is almost redundant (1% NaCl gives about 1ppb ClO equivalent) and can lead to problems when high Cr is present.

Iron

The use of 54 rather than 56 or 57 is recommended. Since mass 54 is interfered with ArN, the concentration of HNO_3 should be the same. If the concentration of HNO_3 cannot be controlled, the following equation would be useful:

Fe(54) = M(54) - ratio of 54/15 * M(15)

In this case, a blank solution must be analyzed at first, and mass 15 and 54 should be measured. The ratio of 54/15 will be calculated, and this ratio will be entered into the equation.

CaN is unlikely to give an interference at 200 ppm Ca carbonate.

Calcium

Ca is normally included at very high concentration; therefore, there is no interference on it.

However, when the mixed standard solution which contains the same concentration of Ca and Sr, the apparent Ca^{44} will be almost double if the system was calibrated in the absence of Sr. The same problem occurs with Ca^{43}. In this case, the following equation is useful:

$$\textit{Ca(44) = M(44) - ratio of } Sr^{2+}/Sr^{+} \textit{ * M(88)}$$

Sr solution must be analyzed at first to get the ratio of Sr^{2+}/Sr^{+}.

Calibration Standards

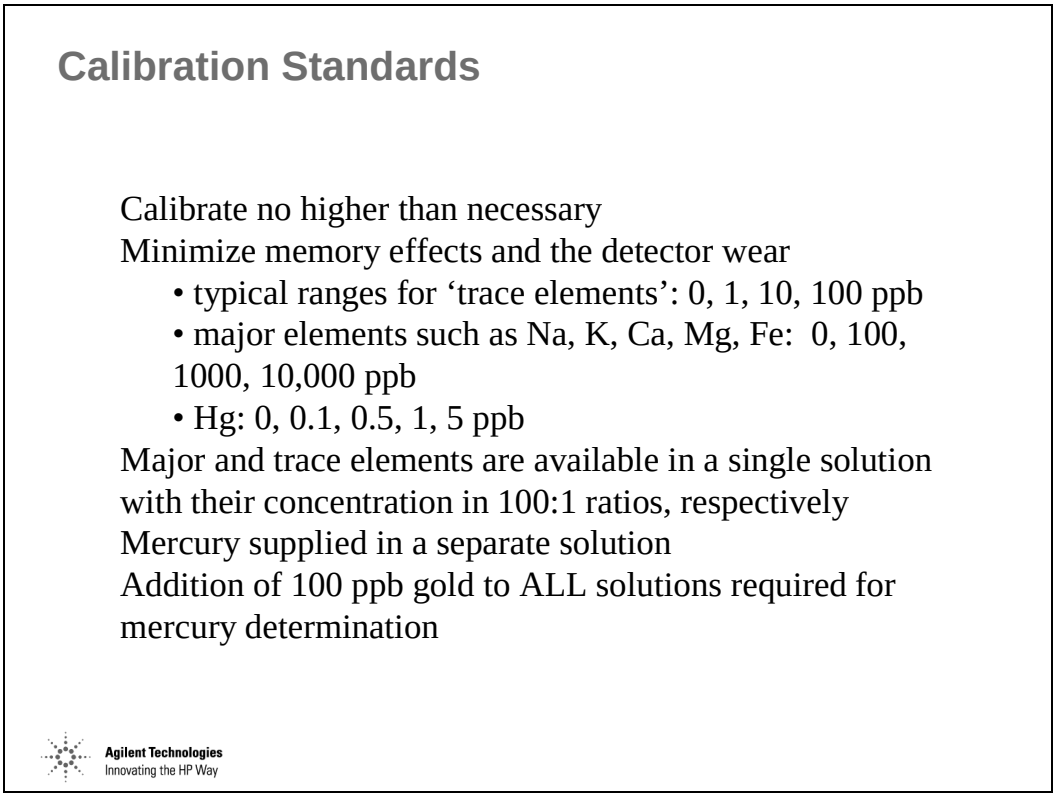


Figure 243

Linear Range Determination

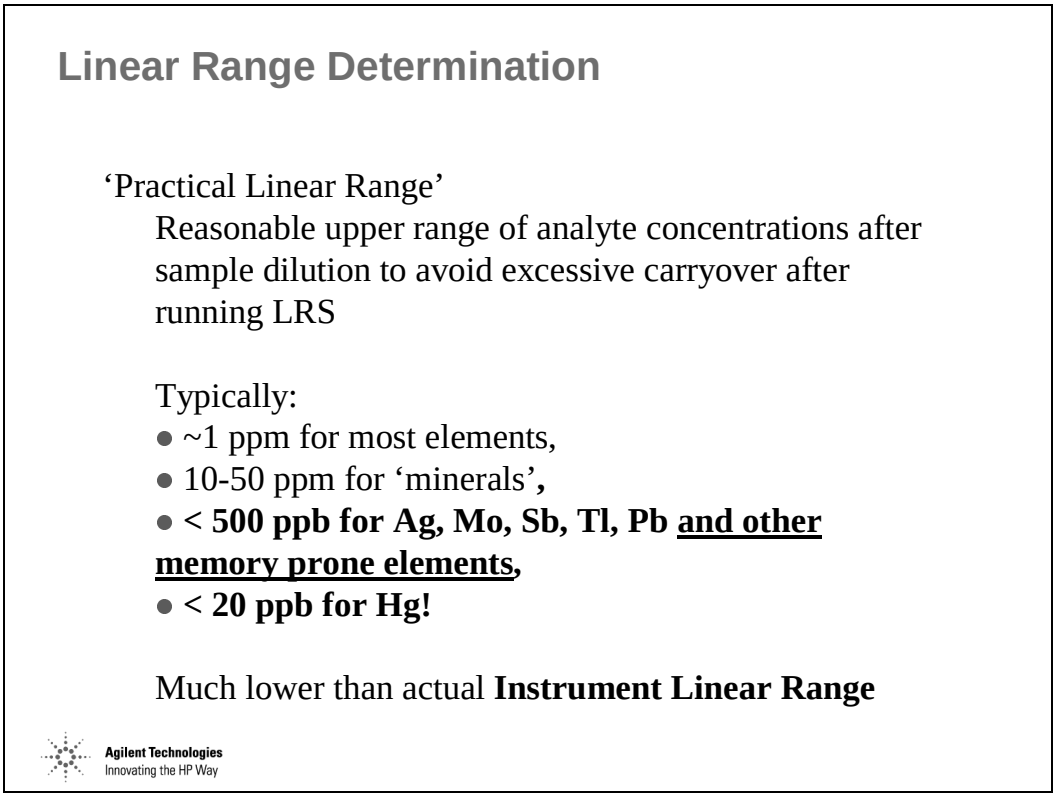


Figure 244

Interference Check Samples

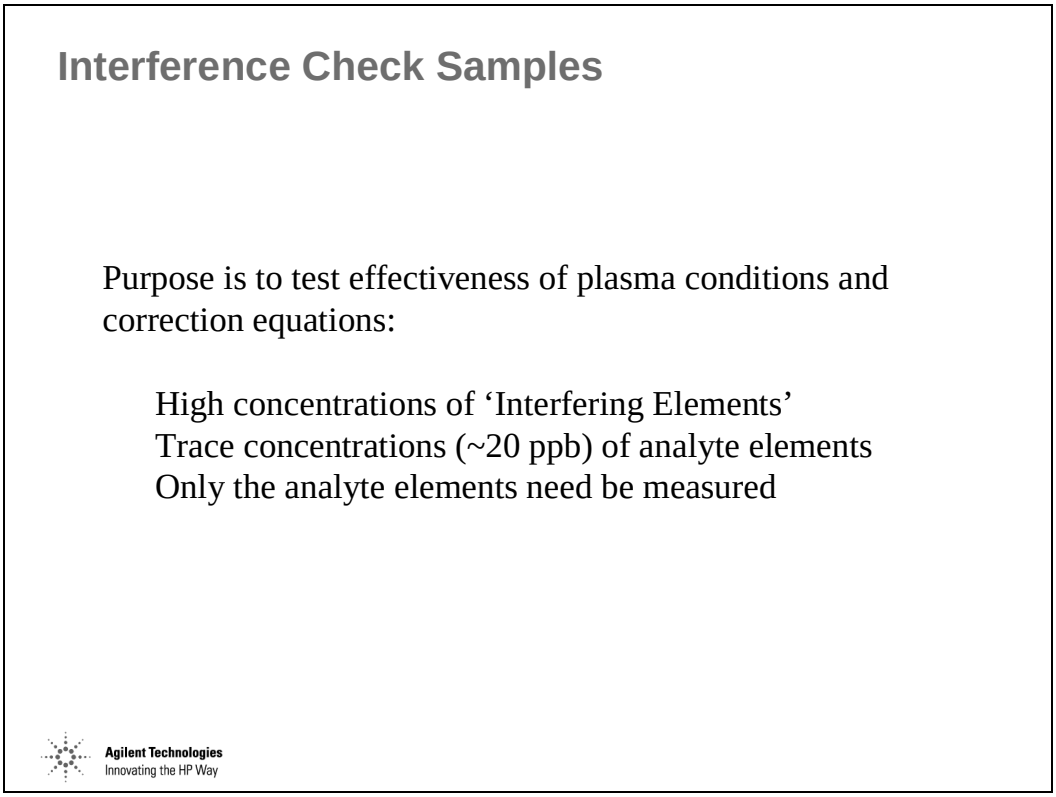


Figure 245

Troubleshooting Environmental Applications [1]

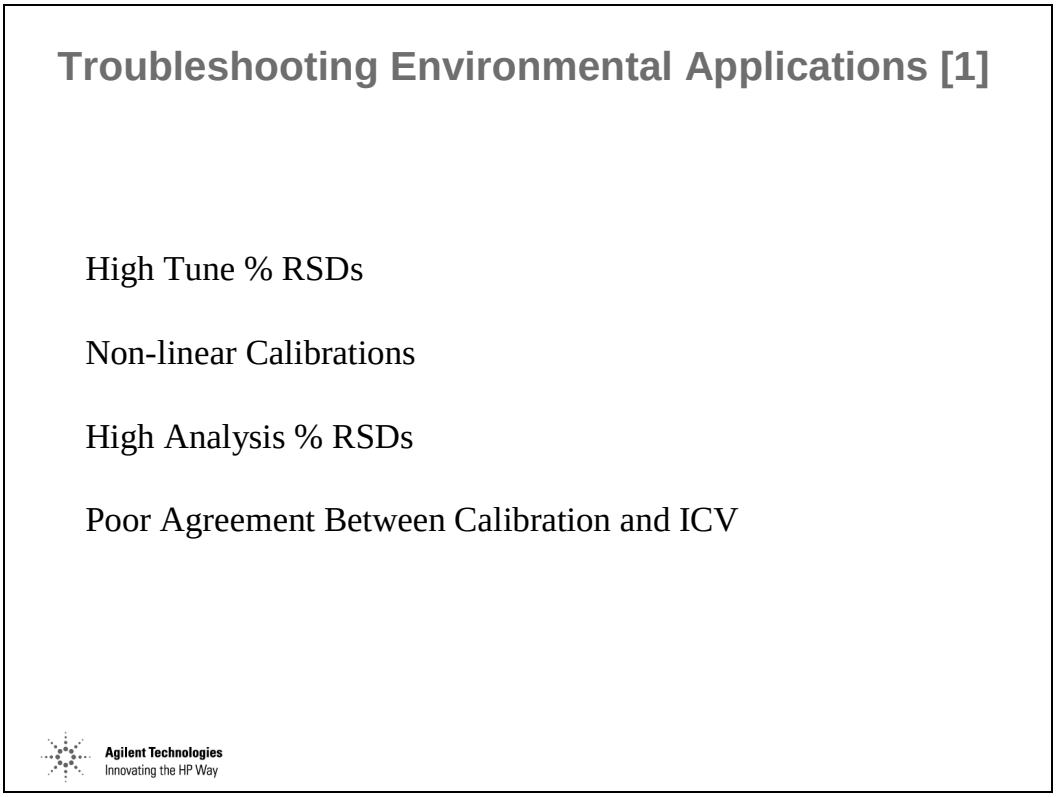


Figure 246

High RSDs During Tune

Incorrectly tuned plasma parameters such as carrier gas or blend gas flow, peri-pump speed or sample depth.

Dirty cones

Worn peri-pump tubing. Incorrect shoe pressure on peri-pump. Should be *just* tight enough to insure a smooth flow of sample (aspirate a bubble and watch its progress through the line).

Non-Linear Calibrations

ICP-MS is a linear technique. Pulse mode calibrations should always be linear, if not, suspect standard preparation errors or possible incompatibilities among elements in multi-element standards.

Non-linearity between pulse and analog mode indicates incorrectly set P/A factors or possible worn out detector.

High %RSDs During Analysis

Troubleshooting Environmental Applications [1]

Insufficient uptake, rinse-out or stabilization time. Use 'Edit Average File' > 'Tabulate' to examine individual replicates for upward or downward trends.

Insufficient signal counts.

May be also be caused by worn peri-pump tubing or bubbles in either the sample uptake or internal standard uptake tubing. Check the connections at the ISTD addition "Y" and replace the peri-pump tubing.

Troubleshooting Environmental Applications [2]

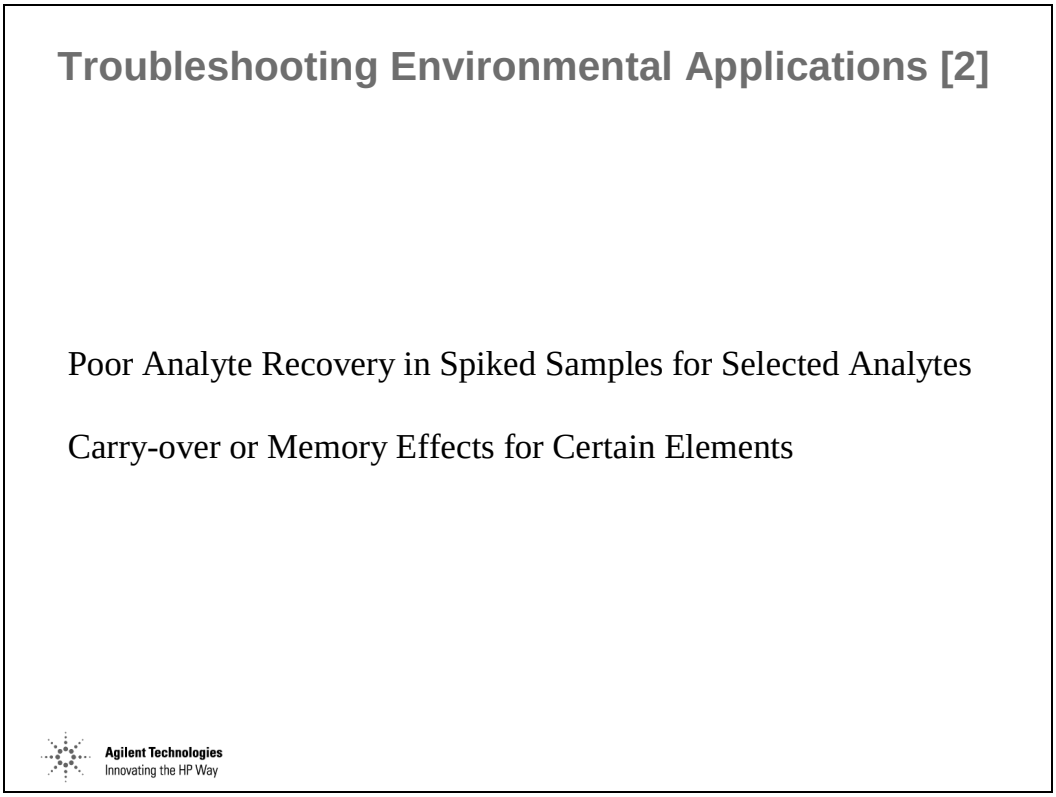


Figure 247

Poor recovery for selected analytes in spikes.

Several conditions can cause poor recovery of certain analytes in spiked samples. Ag is especially insoluble in the presence of even trace levels of Cl^-, therefore the use of HCl should be avoided whenever possible. Several elements (Zn, As, Se, Cd) have relatively high first ionization potentials and may not be as effectively ionized in samples with high concentrations of easily-ionizable elements such as Na and K. Diluting the sample if possible, or selecting an alternative internal standard with a higher ionization potential may help. Possible alternative internal standards include Ge, Te, and Au.

Carryover or memory interference.

Several elements are prone to memory effects for various reasons. Ag, Mo and Tl tend to stick to surfaces in the sample introduction system and slowly rinse into subsequent samples. Keeping the sample introduction system (sample tubing, peri pump tubing, nebulizer, spray chamber, torch and cones) clean will help minimize carry-over. Also, rinsing between samples with relatively high acid concentration rinse blanks (ca. 5% HNO_3) will help. If

possible, avoid introducing samples or standards with concentrations of these elements above a few hundred ppb. Use of the Babington nebulizer should also reduce carryover of these elements. Li, when analyzed for extended periods of time or in very high concentrations tends to accumulate on the back sides of the interface cones. Cleaning the cones will usually reduce Li background and carryover. Volatile elements, or elements with volatile hydrides such as Hg and Sb can also carryover due to off-gassing from droplets on the spray chamber walls. Steps to reduce the volatility of these species are helpful.

Troubleshooting Environmental Applications [3]

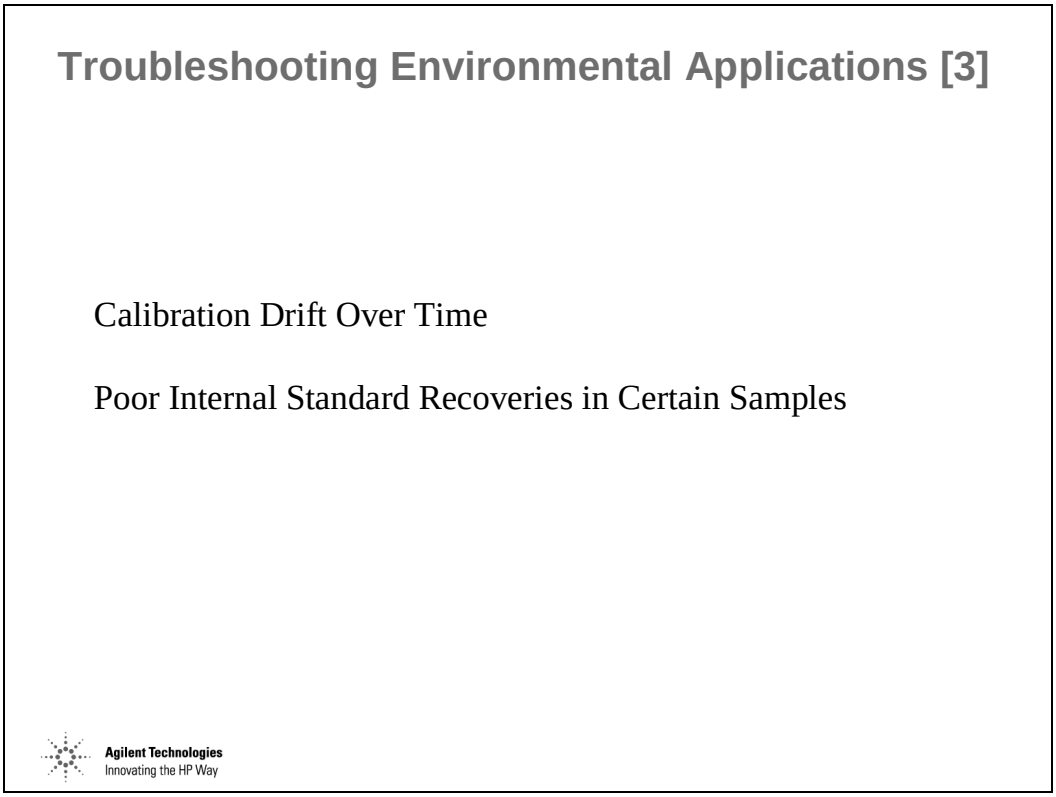


Figure 248

Calibration Drift over time.

Insure that the instrument is adequately warmed up before initial calibration (warm-up, while scanning in tune for 15 minutes).

Insure that laboratory temperature does not vary by more than 3 degrees C. per hour.

Check cones for signs of sample deposits which may be affecting the size and shape of the cone orifices. Clean if necessary.

Check peri-pump tubing for signs of excessive wear or flattening.

Run SetEM. An electron multiplier which is near the end of its useful life may be changing in response over short periods of time. If running SetEM significantly changes the EM voltage from day to day, the EM should be replaced.

Poor internal standard recoveries in samples.

Troubleshooting Environmental Applications [3]

Reduction in internal standard signal is usually caused by high matrix concentration in samples (especially Na, and K). Dilute the samples. It may also be desirable to tune the instrument with a matrix matched tune solution containing appropriate levels of the matrix elements to minimize the effect of any matrix induced suppression of ionization.

Troubleshooting Environmental Applications [4]

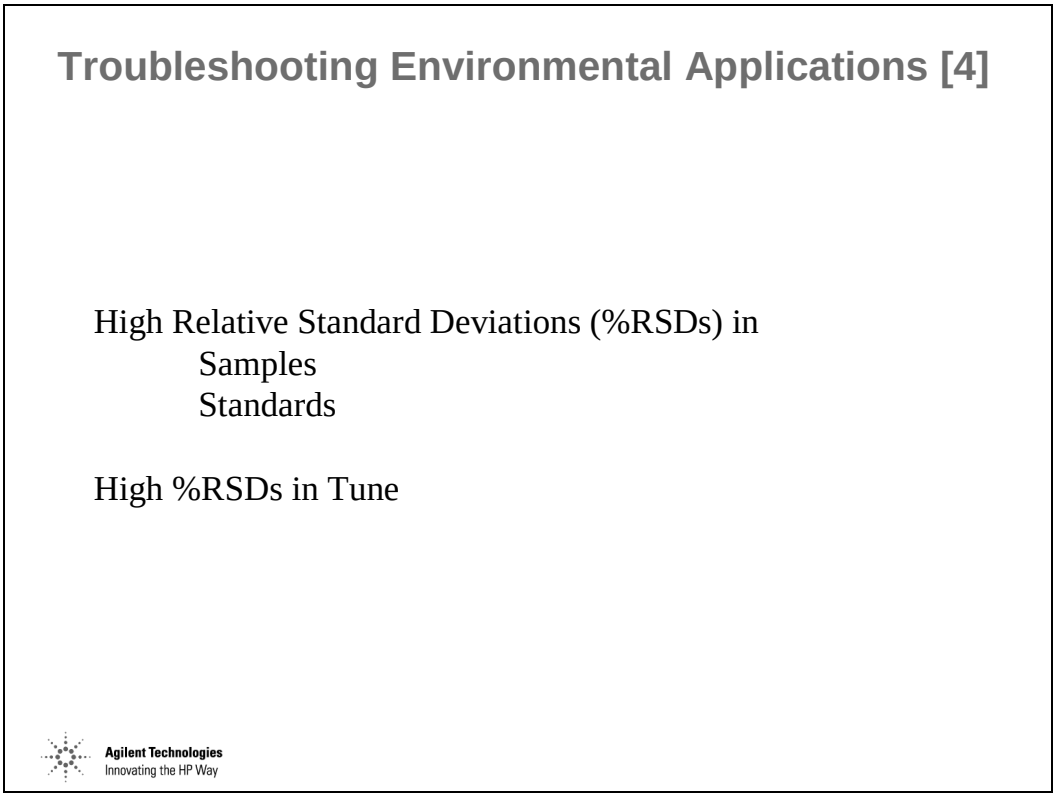


Figure 249

High relative standard deviations (RSDs) for analyte or internal standard elements during sample analysis.

Usually caused by insufficient sample uptake or stabilization time. May be also be caused by worn peri-pump tubing or bubbles in either the sample uptake or internal standard uptake tubing. Check the connections at the ISTD addition "Y" and replace the peri-pump tubing. Shoe pressure on the peri-pump should be *just* tight enough to insure a smooth flow of sample (aspirate a bubble and watch its progress through the line).

High RSDs during tune.

Incorrectly tuned plasma parameters such as carrier gas or blend gas flow, peri-pump speed or sample depth.

Dirty cones.Worn peri-pump tubing.

Incorrect shoe pressure on peri-pump. Should be *just* tight enough to insure a smooth flow of sample (aspirate a bubble and watch its progress through the line).

Troubleshooting Environmental Applications [4]

Omega lens settings can also affect tune precision as can parameters which affect mass peak shape such as plate and pole bias.

Agilent Technologies

Innovating the HP Way

Semiconductor Applications of ICP-MS and Advantages of Agilent 7500s System

Chemicals and Materials Used in Semiconductor Industry

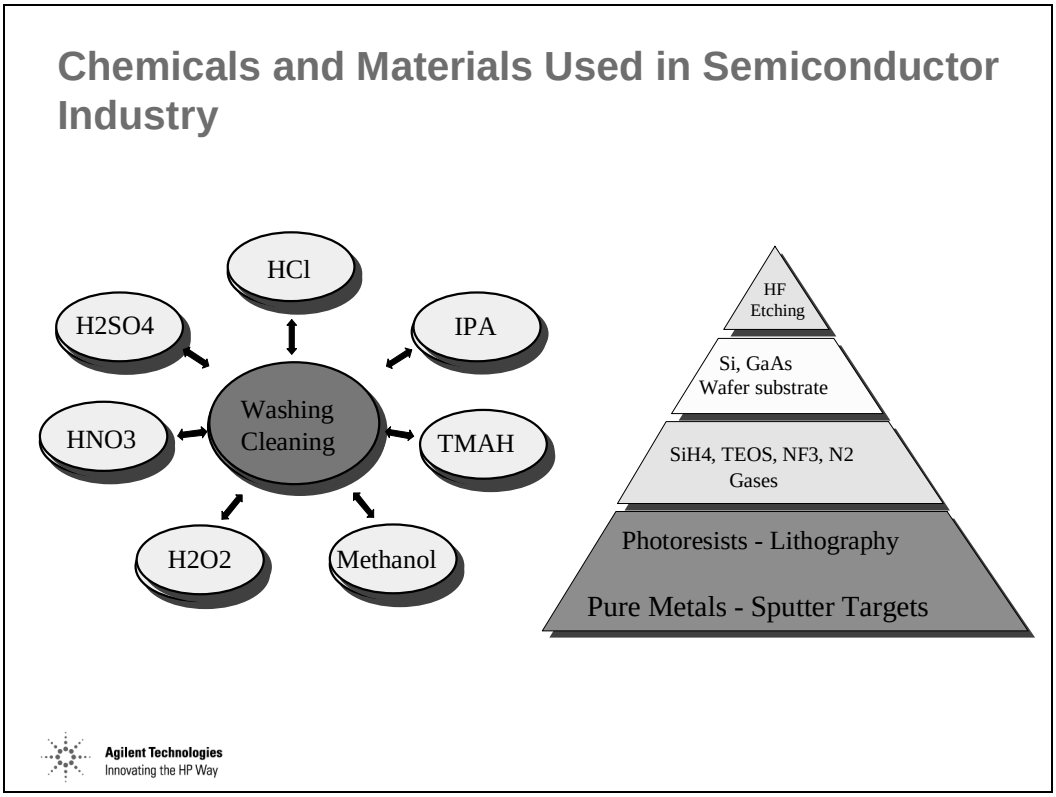


Figure 250

BPSG = boron phosphorus silicon glass used for doping.

TEOS = tetra ethoxy silane (used for depositing SiO_2 layers.

TMAH = tetra methyl ammonium hydroxide.

Multielement analysis and ultra low detection limits have made ICP-MS the technique of choice for the determination of metallic impurities in the industry.

Metals Analysis in the Semiconductor Industry - Customer Groups and Requirements

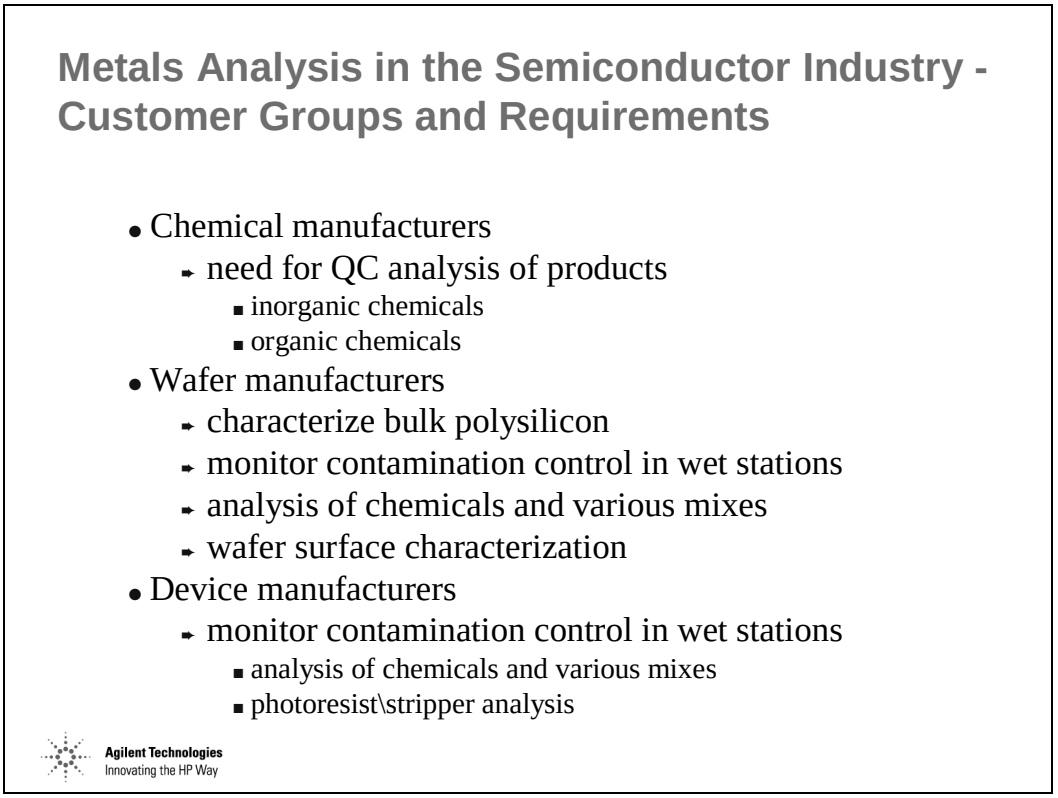


Figure 251

ShieldTorch Interface

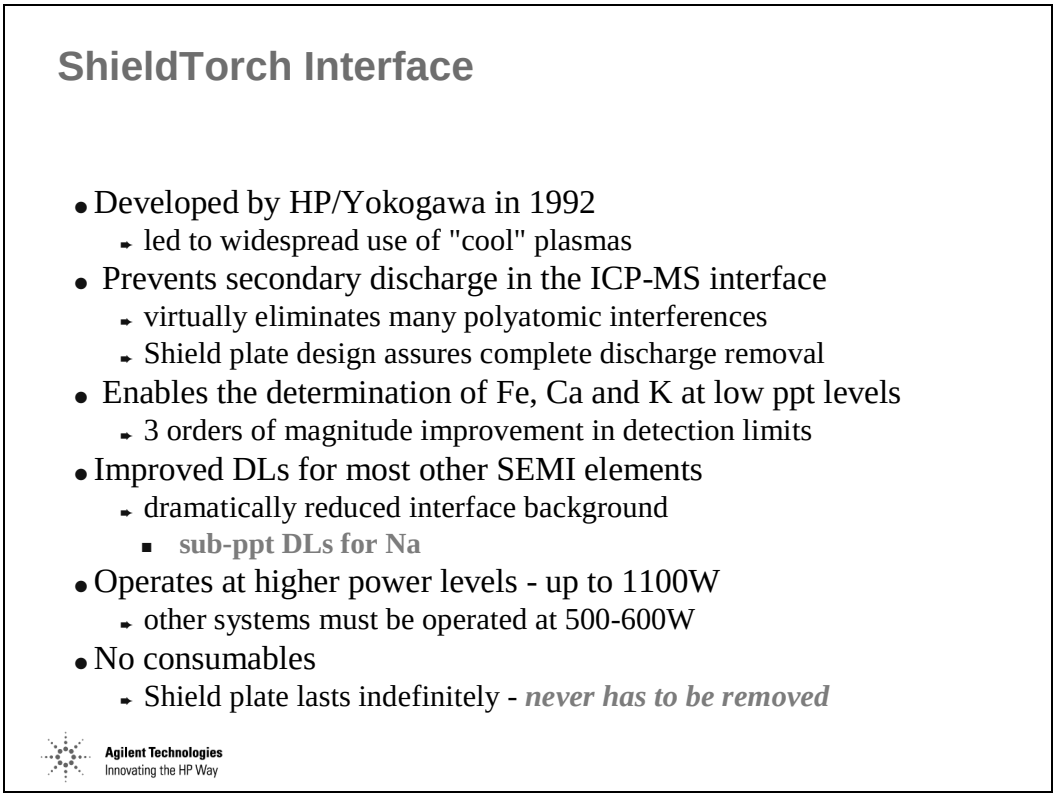


Figure 252

The Agilent 7500 has no loss in sensitivity when switching to cool plasma - Other instruments lose up to 95% of their sensitivity for all Transition metals.

Other Instruments have to run at 600W to reduce ArO - Agilent 7500 can run at 1100W, which means higher sensitivity, lower oxides, and lower matrix effects, and also analyze As, Se.

ShieldTorch Interface

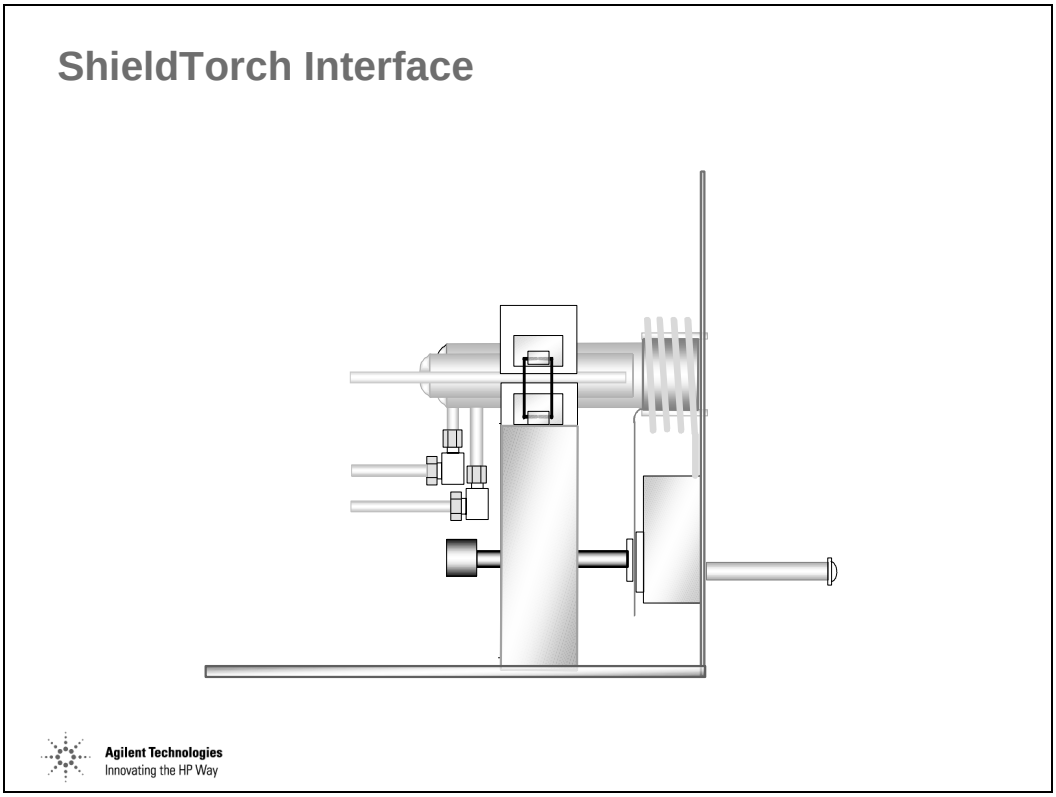


Figure 253

Normal and "Cool" Plasmas

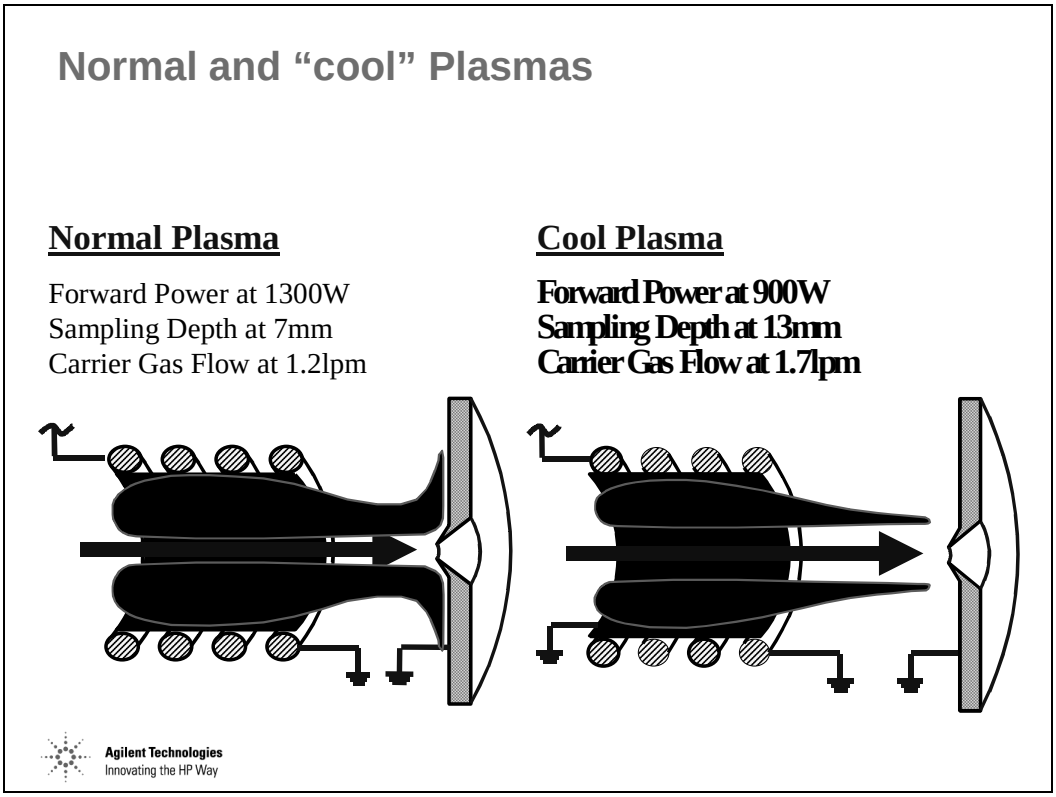


Figure 254

Shield Plate removes potential difference between plasma and interface, so no polyatomic ions form behind the sample cone. Cool central channel of plasma gives low Ar and Ar-based ion populations. Shield Plate can be used at high powers.

High temperature gives good ionization and matrix tolerance, but high population of Ar and Ar-based polyatomic species form in the plasma and behind the sample cone, due to potential difference between plasma and interface.

Shield Torch "Cool Plasma"

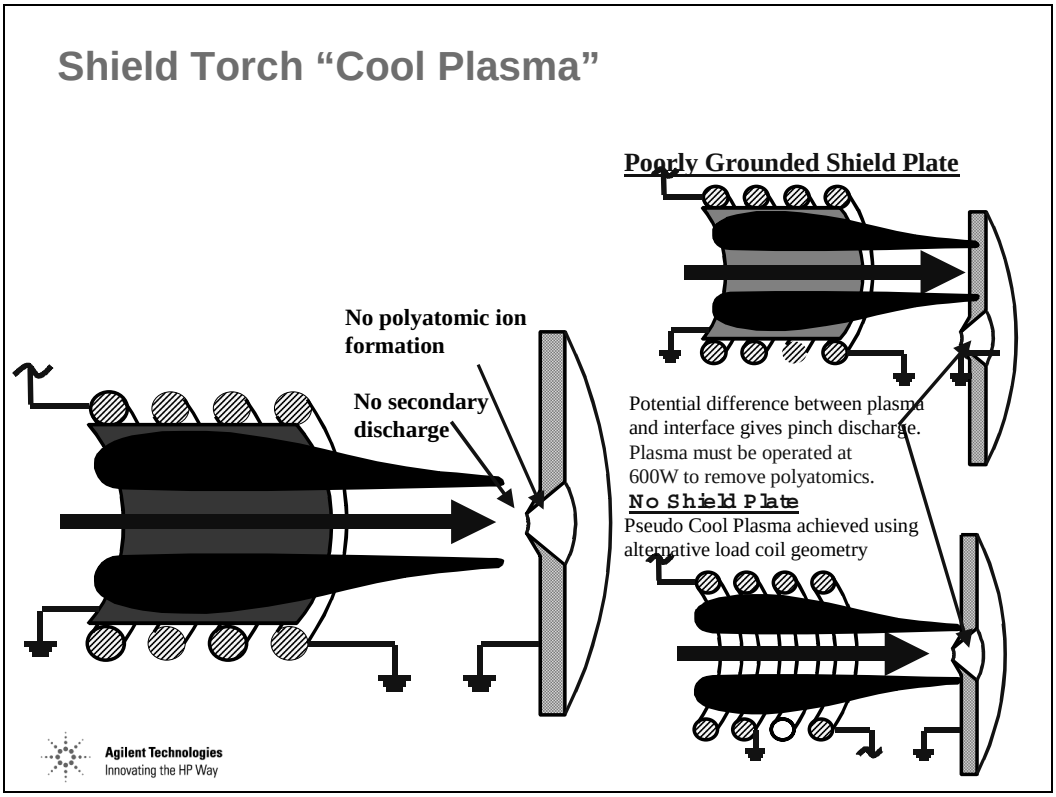


Figure 255

Shield Torch Installation

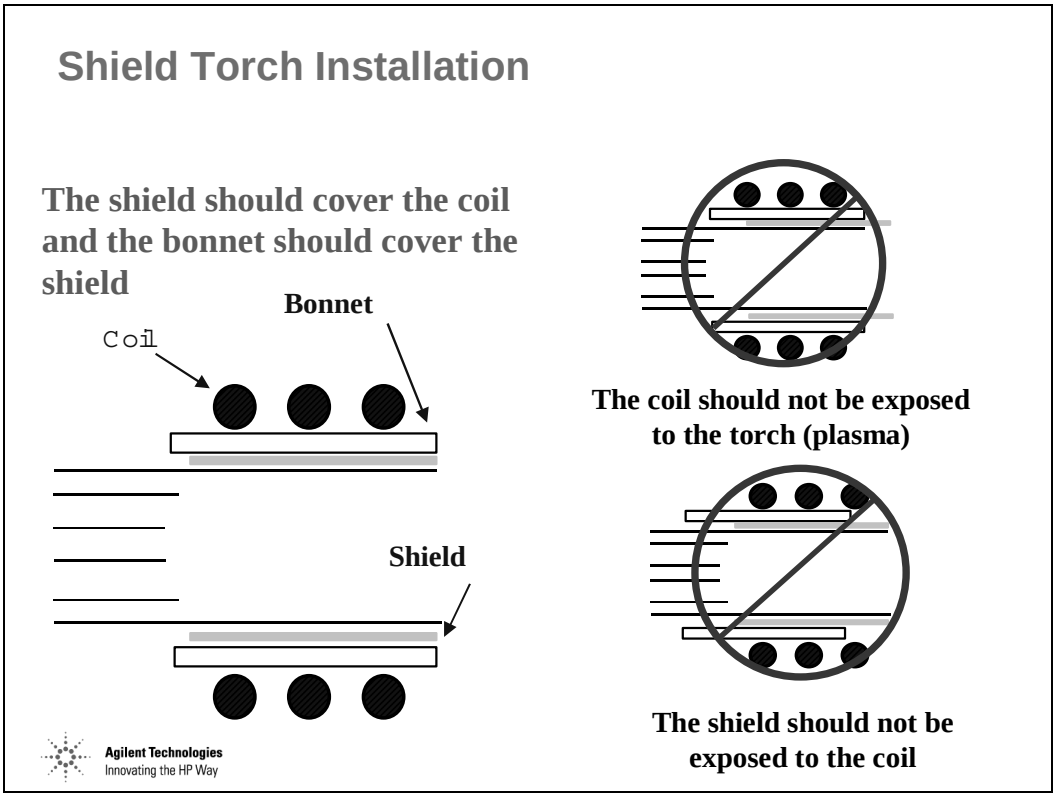


Figure 256

Cool Plasma Tuning

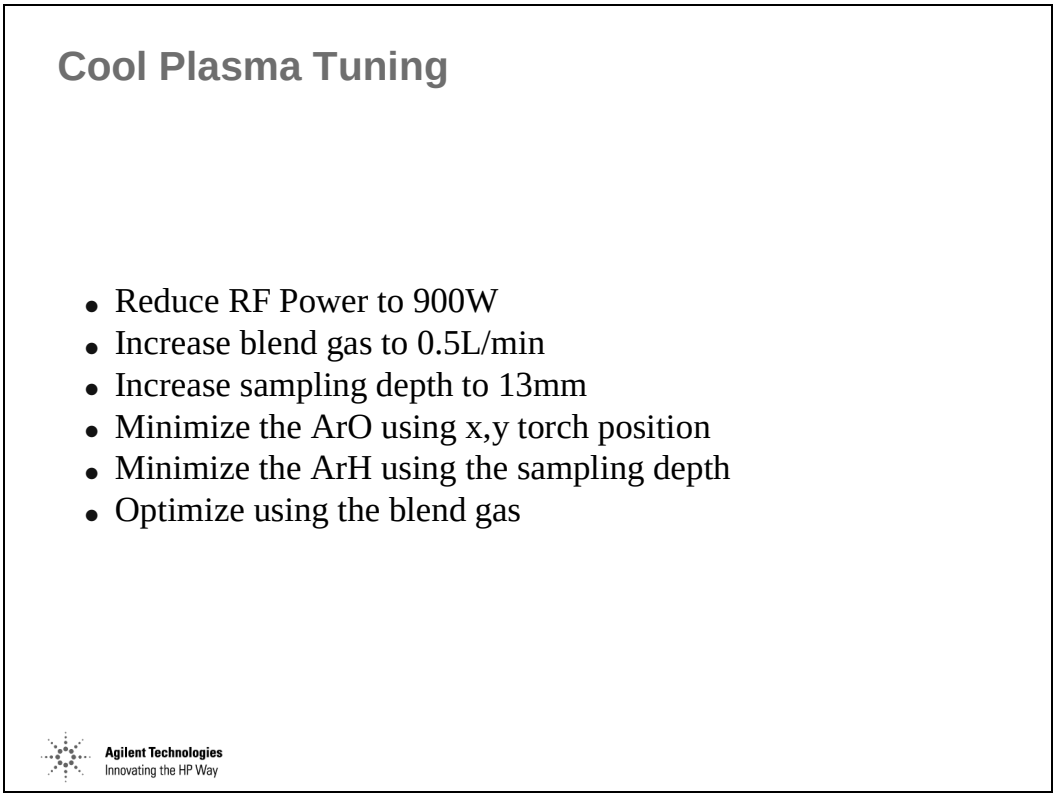


Figure 257

Advantages of Cool Plasma at Higher Power (900 - 1100 W)

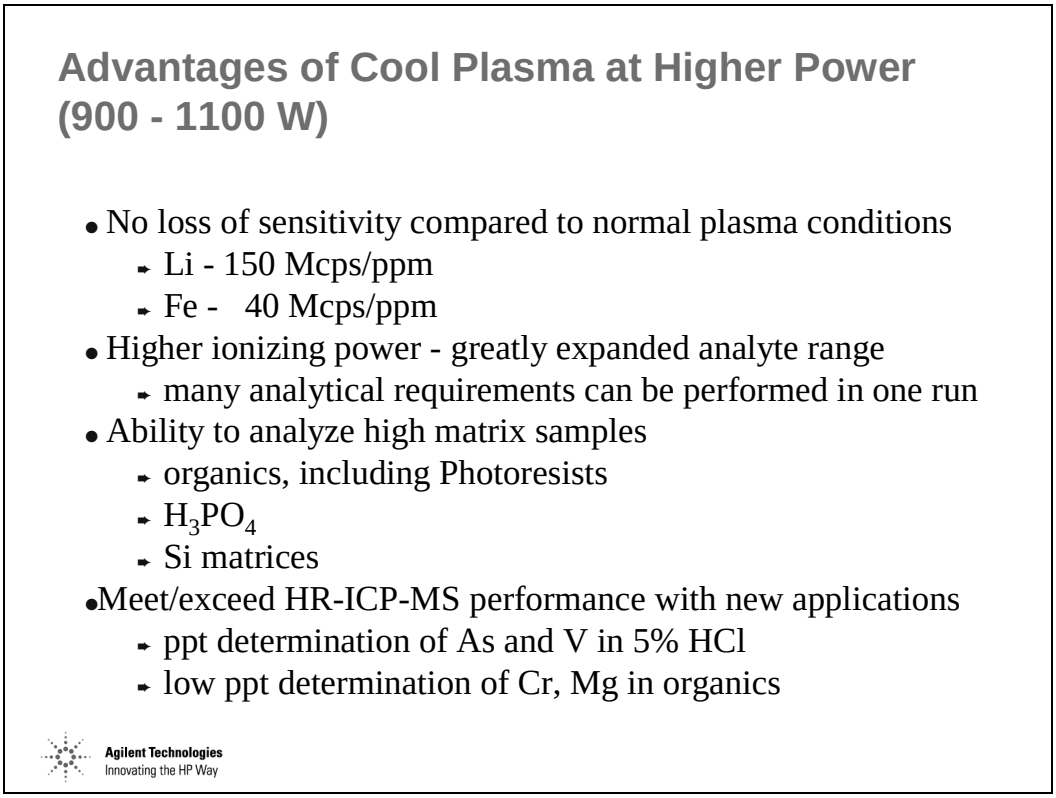


Figure 258

Advantages of Cool Plasma at Lower Power (700-800 W)

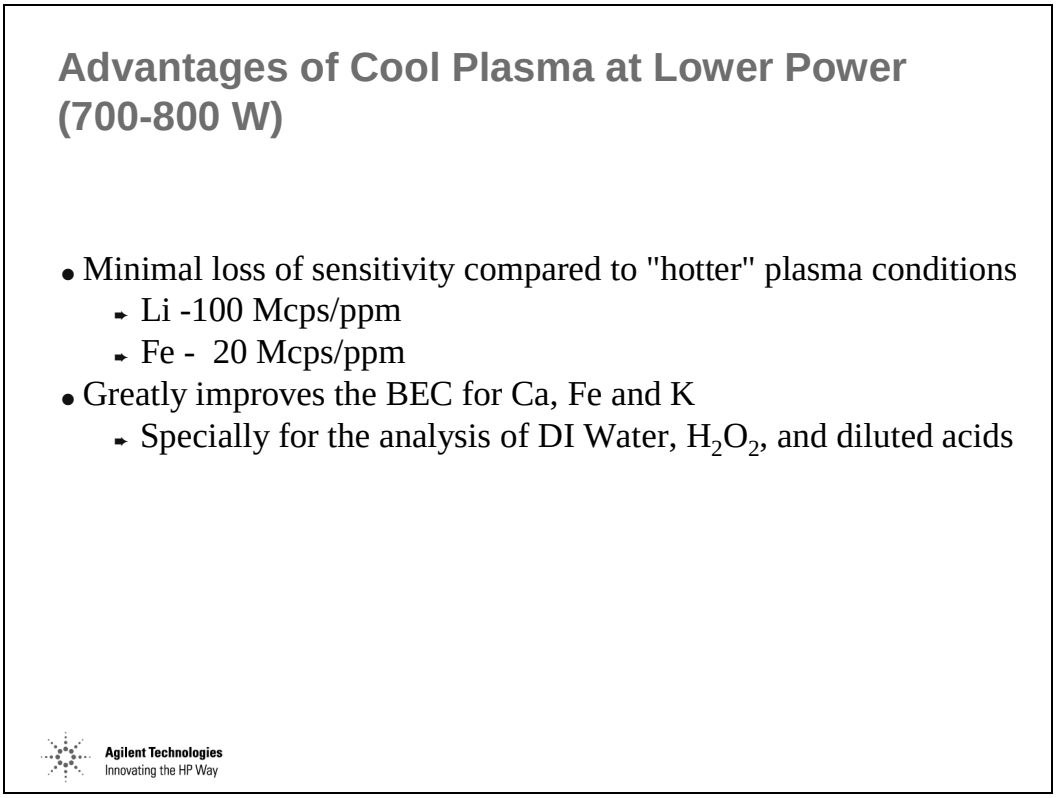


Figure 259

Detection Limits Study [1]

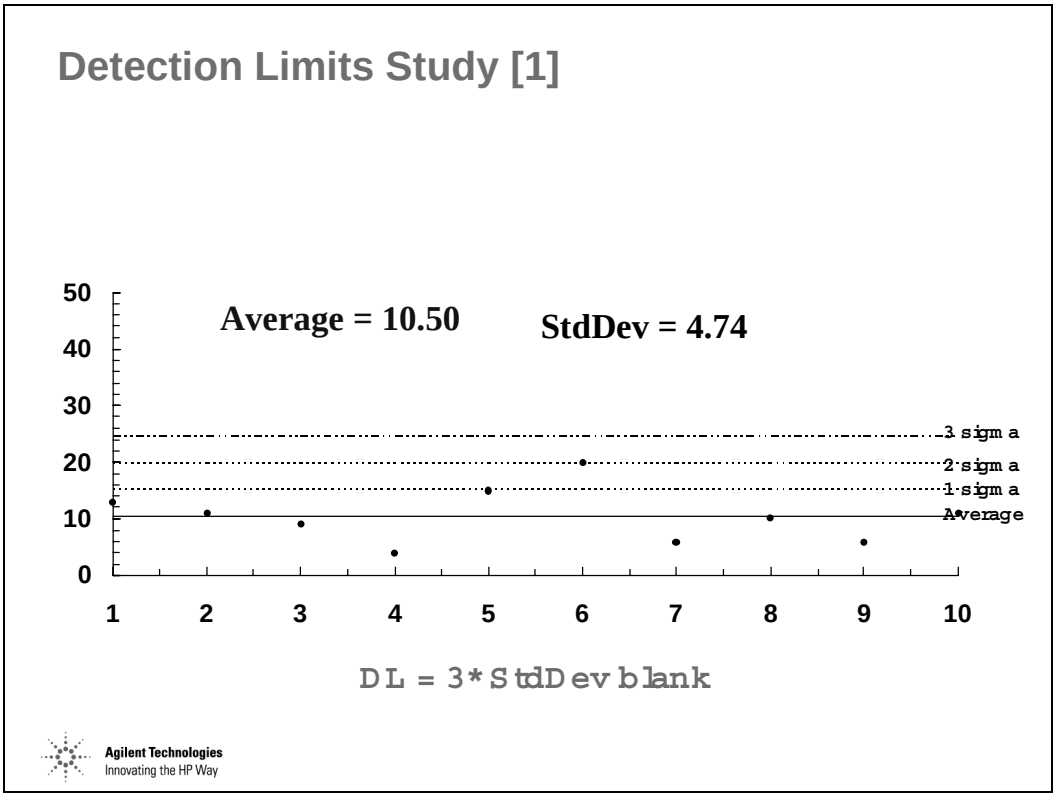


Figure 260

Detection Limits Study [2]

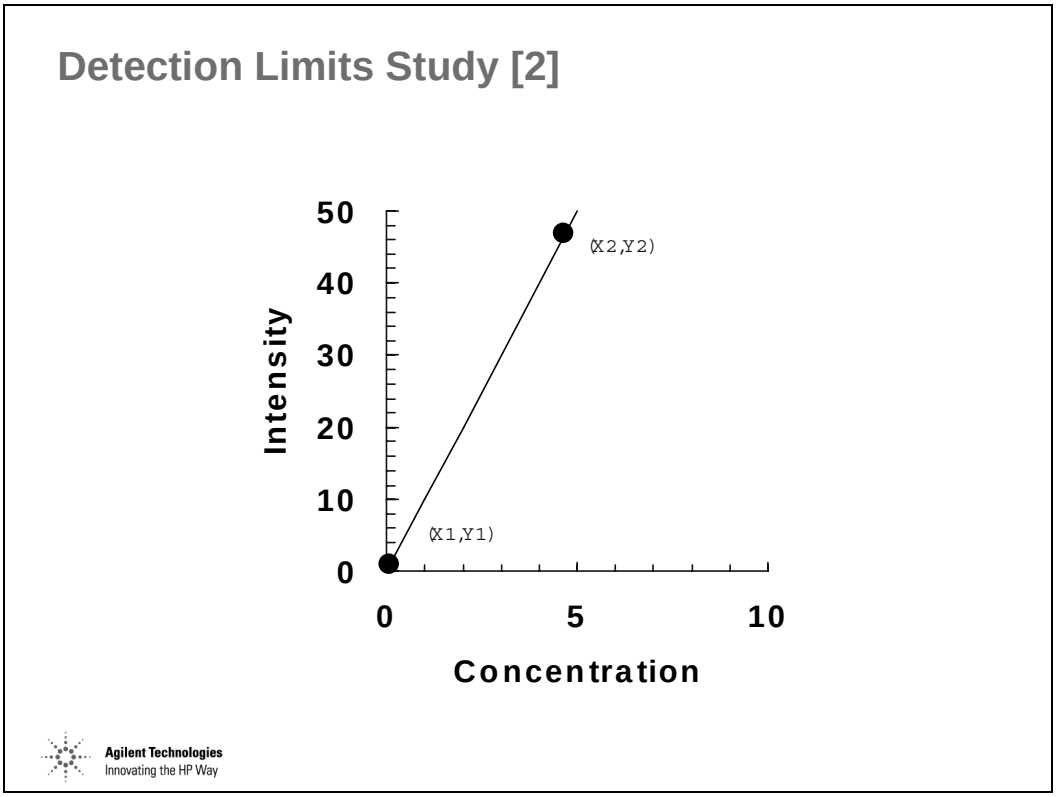


Figure 261

Automatic Switching Between Normal and Cool Plasma

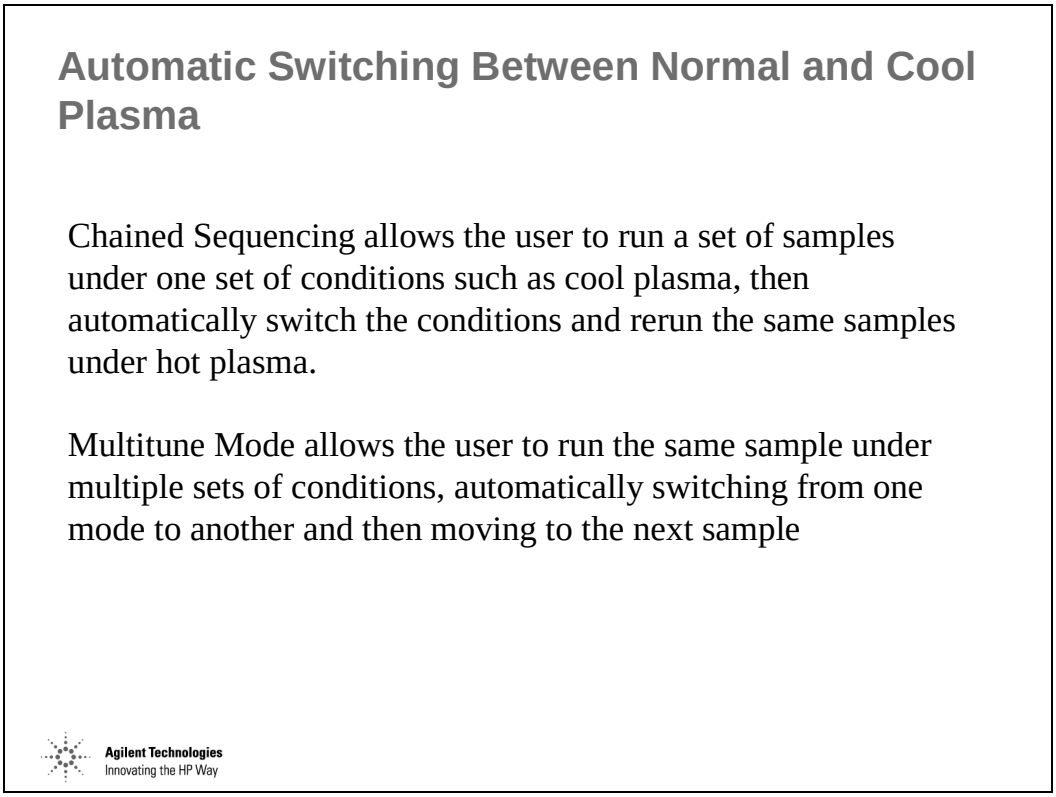


Figure 262

Agilent Technologies

Innovating the HP Way

Intelligent Sequence Training Text

What is Intelligent Sequence?

Intelligent Sequence is designed to dramatically improve sample throughput and reporting accuracy while decreasing the time spent by the operator and data reviewer. Intelligent Sequence automates a variety of QA/QC control procedures as well as all the EPA-mandated quality control procedures (EPA Methods 200.8, 6020 and 6020-CLP) from analysis through reporting.

Features

Intelligent sequence has several unique features.

Smart Sequencing

Intelligent Sequence recognizes all EPA designated QA/QC sample types and, when used with an autosampler, allows automatic, unattended analysis of batches of samples with all necessary calibrations, checks and controls. During sequencing, sample results are evaluated for pass/fail against a user-editable database of QC criteria. If a QC parameter is out of range, sequencing automatically performs a user-selectable action to attempt to remedy the problem. All sample results and QC actions are logged and a QC exception report is created.

QC Reporting

During sequencing, sample-type specific reports are generated and stored for all runs. A QC summary report is also generated. This report can be viewed at any time during or after the sequence. The summary report includes, in an easily reviewed format, a list of samples run and any QC failures which may have occurred. All batch or Sample Delivery Group relevant data are automatically stored together in system-generated “batch directories” for convenient archival and retrieval.

Tune Compliance Checking

A simple, graphical user interface allows user selectable tune compliance criteria to be stored with each method. Evaluating a tune sample can be automatic or manual via a simple pull-down menu item.

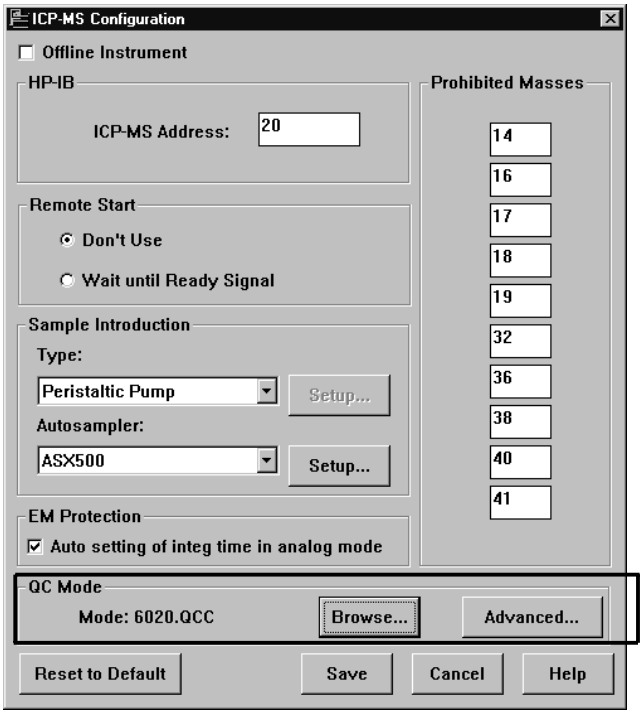
Typical Analytical Flow

1) Select appropriate QC configuration — ***Configuration*** >> ***QC Mode***
2) Load ICP-MS method — ***Methods*** >> ***Load***
3) Edit method and QC parameters — ***Methods*** >> ***Edit Entire Method***
   - Method Information
   - Interference Equation
   - Acquisition
   - Data Analysis
   - ❑ Report… Select ***QC report***
   - ❑ Calibration Table… Select ***Load Mass from Current Acq.*** in ***New***
   - QC Parameters
   - ❑ QC Database
4) Set unreported elements — ***Methods*** >> ***Set Unreported Elements***
5) Save the method and calibration — ***Methods*** >> ***Save***
   - Verify QC Method
6) Load the tuning method — ***Methods*** >> ***Load***
7) Edit method and QC parameters — ***Methods*** >> ***Edit Entire Method***
   - Method Information
   - Acquisition
   - Data Analysis
   - ❑ Report… Select ***QC report***
   - QC Parameters
   - QC Tune Criteria
8) Save the method and calibration — ***Methods*** >> ***Save***
9) Edit the sample log table — ***Sequence*** >> ***Edit Sample Log Table***
10) Simulate the sequence — ***Sequence*** >> ***Simulate Sequence***
11) Save the sequence — **Sequence** >> **Save**
12) Run the sequence — ***Sequence*** >> ***Run***

Using Intelligent Sequencing

QC Configuration

To use Intelligent Sequencing, the appropriate QC configuration must be selected in Configuration.



The following QC modes are provided as default.

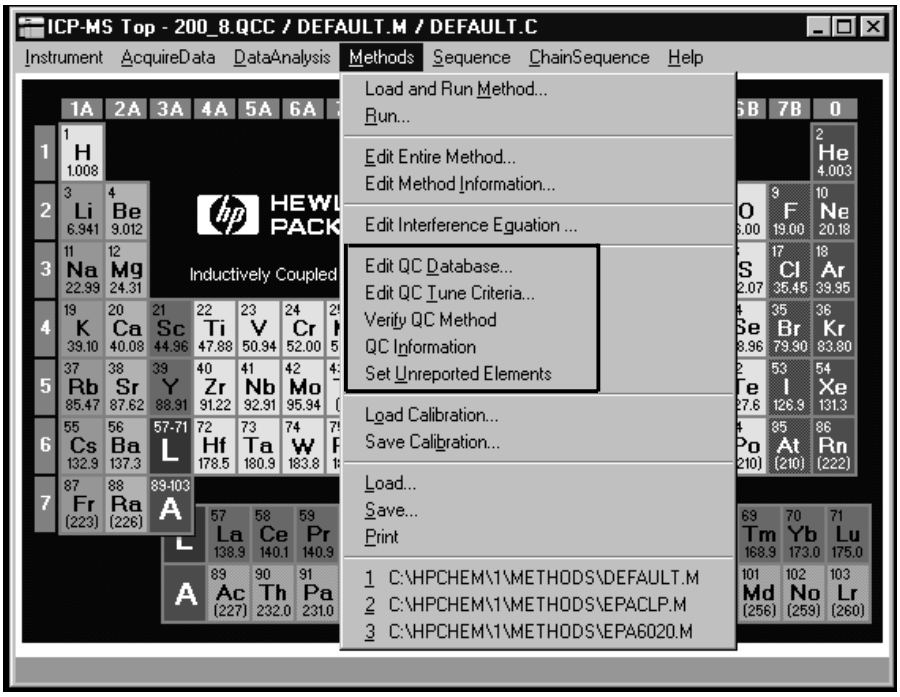
- EPA2008.QCC --- intelligent functions defined by EPA Method 200.8.
- EPA6020.QCC --- intelligent functions defined by EPA Method 6020.
- EPA6020C.QCC --- intelligent functions defined by EPA Method 6020 CLP.
- EPAGEN.QCC --- Intelligent functions designed to meet both EPA 200.8 and 6020 requirements
- GENERAL.QCC --- Intelligent sequencing disabled (no expected values or failure actions defined)

When selecting GENERAL.QCC, the sequencing mode is changed to the general sequencing mode. When selecting other QC modes, the sequencing mode is changed to intelligent sequencing mode.

For more information about sample types included in each QC mode, see Appendix of "AGILENT 7500 ChemStation Intelligent Sequence Manual".

ICP-MS Method

When intelligent sequencing mode is selected, additional menus become available in the Methods menu.



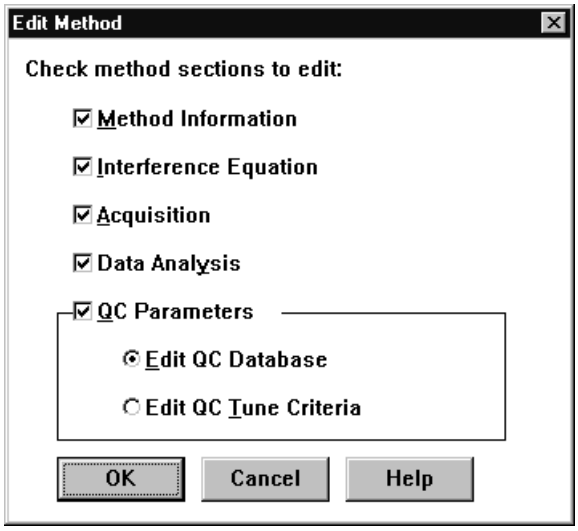
- Edit QC Database… Enables editing of QC related items on a sample type basis such as high limit values, low limit values and error action.
- Edit QC Tune Criteria… Enables editing of tune compliance criteria such as sensitivity, mass resolution and %RSD.
- Verify QC Method… Checks the QC database and QC tune criteria for configuration errors.
- QC Information… Indicates the QC mode name which was used to make the current method.
- Set Unreported Elements… Allows the user to select the elements which are not to be reported on QC custom reports.

Default Methods Provided

EPA Method	200.8	6020	CLP	Remark
QC Mode (.qcc)	200_8	6020	6020CLP	
Method (.m)	***EPA20_8***	***EPA6020***	***EPACLP***	For QC Database
Tuning Method (.m)	***TN200-8***	***TN6020***	***TNCLP***	For QC Tune Criteria

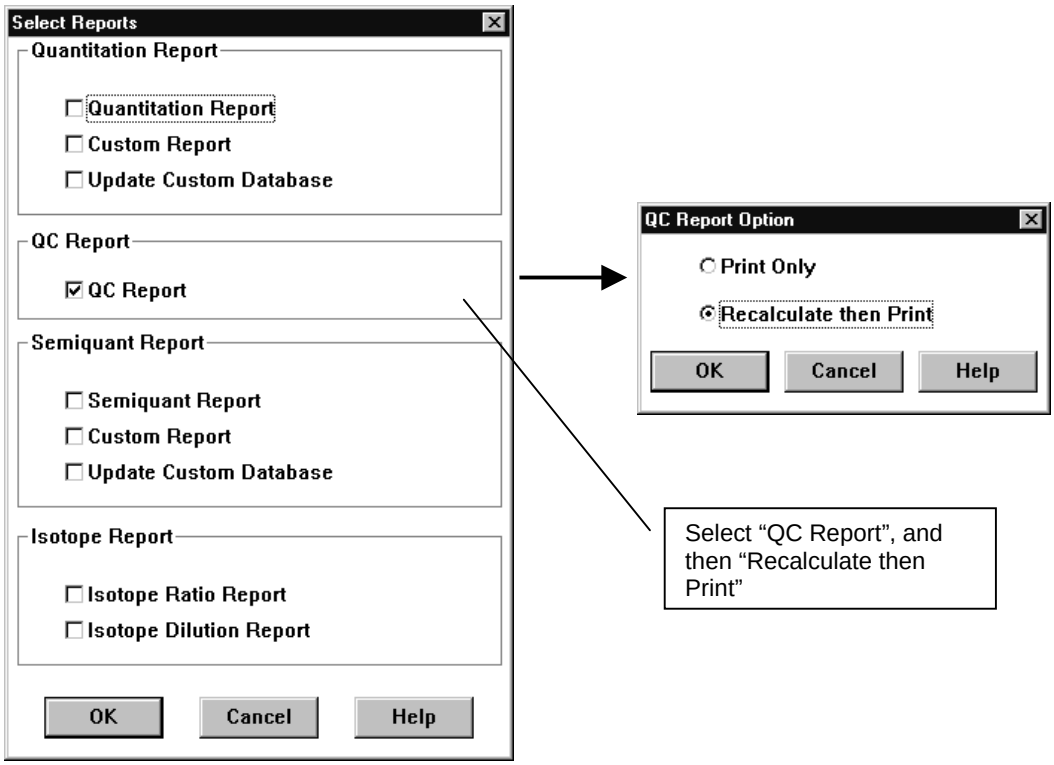
Edit Entire Method

Use Edit Entire Method to make a complete method including QC parameters.



- Method Information… Same settings as general use.
- Interference Equation… Same settings as general use.
- Acquisition… Same settings as general use.

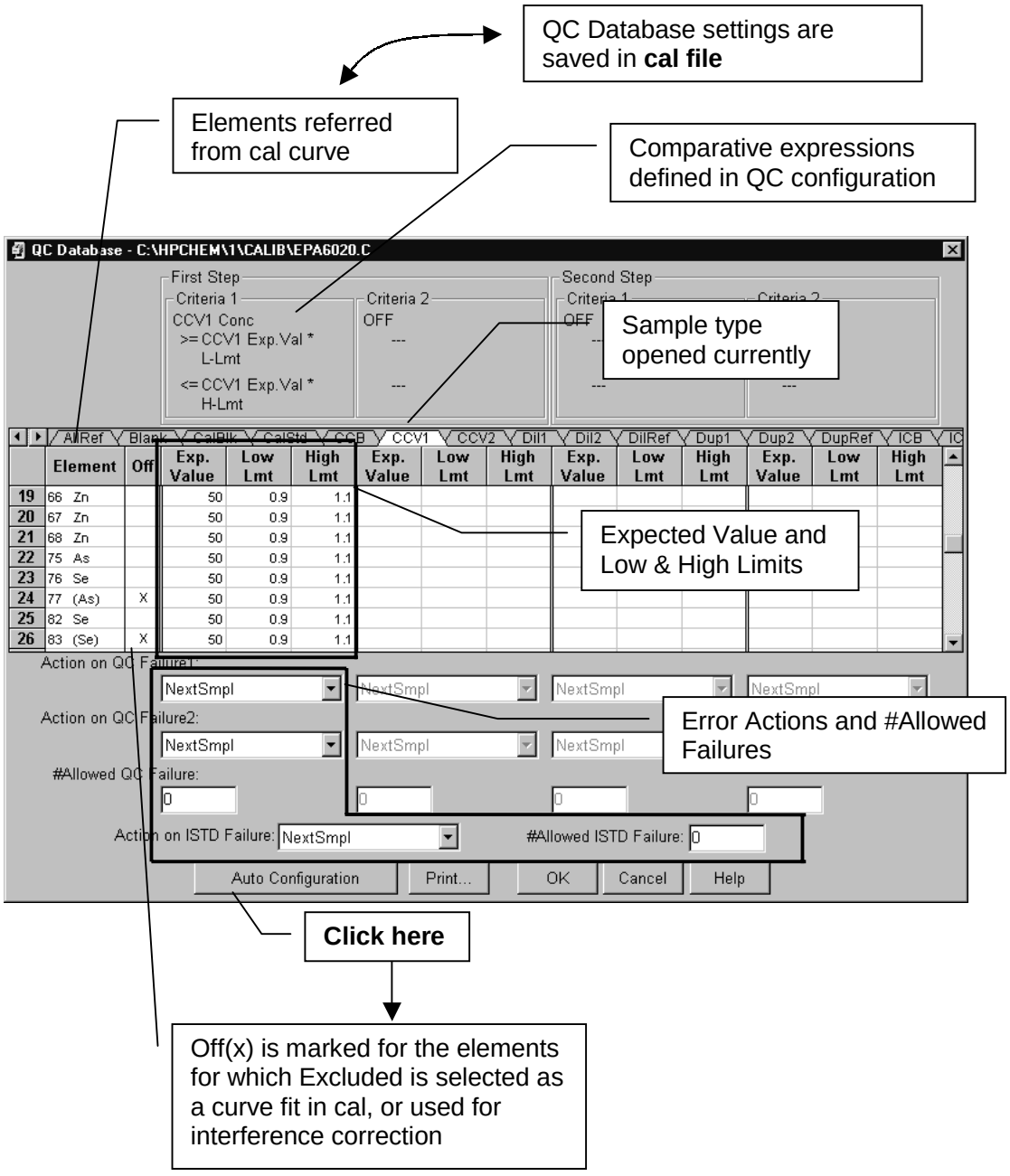
- Data Analysis… Same except Select Reports.



- QC Parameters… ***New menu***
  - (A) QC Database
  - (B) QC Tune Criteria

(A) QC Database

For information about how to read comparative expressions (definition of criteria), see “Setting Up a Method” of “AGILENT 7500 ChemStation Intelligent Sequence Manual”.



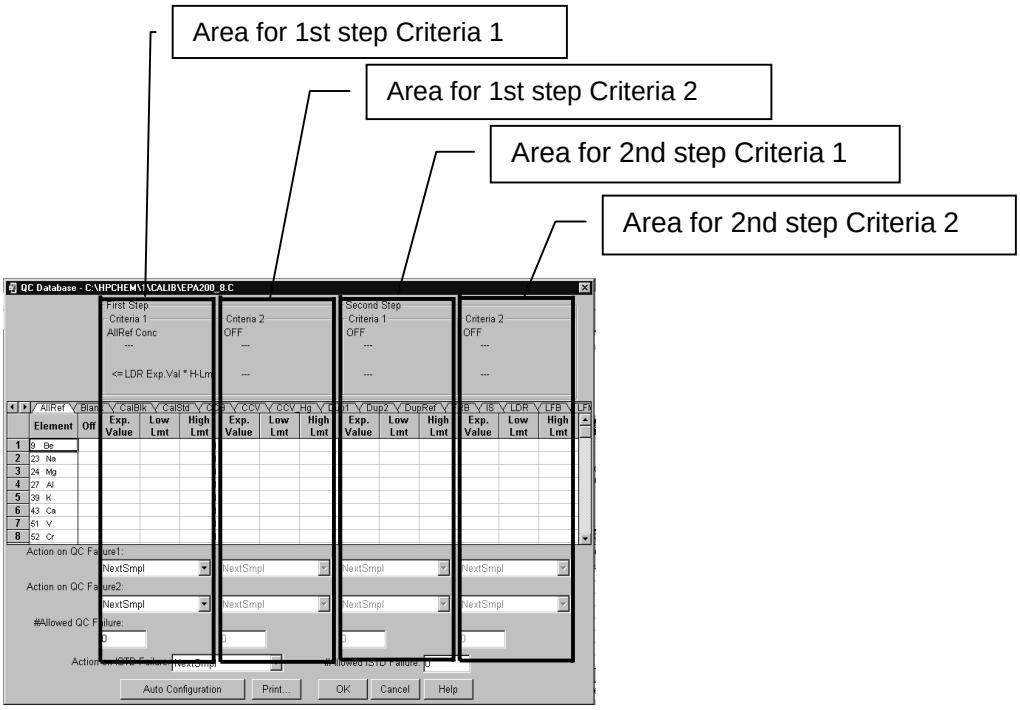
<Error Actions supported>

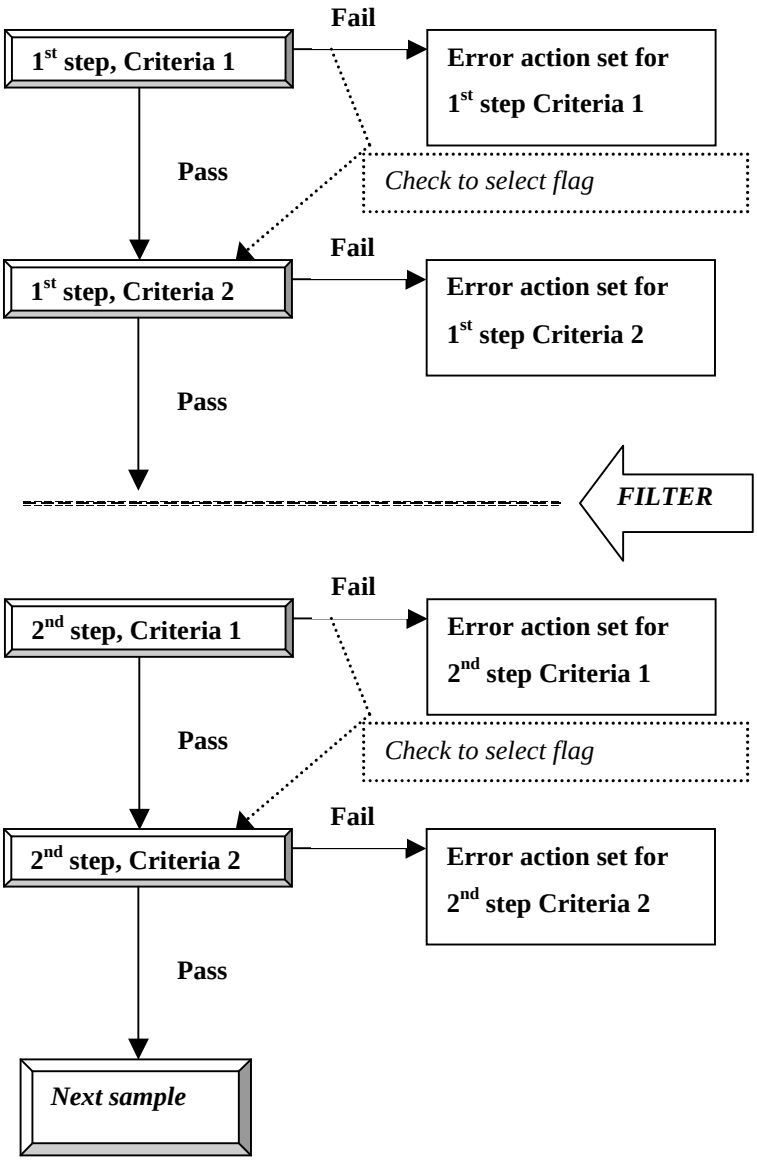
- NextSmpl… Next sample
- Abort… Abort the run

- Blk (Abort) – NextSmpl… Run the blank block then continue (Abort if all of the samples in the blank block fail).
- Blk (Cont.) – NextSmpl… Run the blank block then continue (Continue even if all of the samples in the blank block fail)
- Blk (Abort) – SameSmpl… Run the blank block and re-run same sample (Abort if all of the samples in the blank block fail).
- Blk (Cont.) – SameSmpl… Run the blank block and re-run same sample (Continue even if all of the samples in the blank block fail).
- Cal – SameSmpl… Recalibrate and re-run same sample.
- Cal – AllSmpls… Recalibrate and re-run all samples since last CCV block.
- NextLot… Run next lot of samples
- Run User Macro… Run the user macro which must be placed under the method currently running, and named "QCUSER.MAC".

<How proceed Criteria>

Up to four criteria for each sample type (except ISTD).





Normally just one Criteria (1st step Criteria 1), or two Criteria (1st step Criteria 1 & 2nd step Criteria 1, or 1st step Criteria 1&1st step Criteria 2) is used.

<Examples>

- 1st step Criteria 1

"Check whether the analytical concentrations of certified reference material (CRM) are 90-110% of the certified values (expected values)."

1st step Criteria 1
Low limit: CRM conc >= 0.9 x CRM expected values
High limit: CRM conc =< 1.1 x CRM expected values

- 1st step Criteria 1 & 2nd step Criteria 1

"Check whether the analytical concentrations of CRM are 90-110% of the certified values for elements whose counts are equal or more than 1000 cps"

1st step Criteria 1
Low limit: CRM cps >= 1000
High limit: none

2nd step Criteria 1
Low limit: CRM conc >= 0.9 x CRM expected values
High limit: CRM conc =< 1.1 x CRM expected values

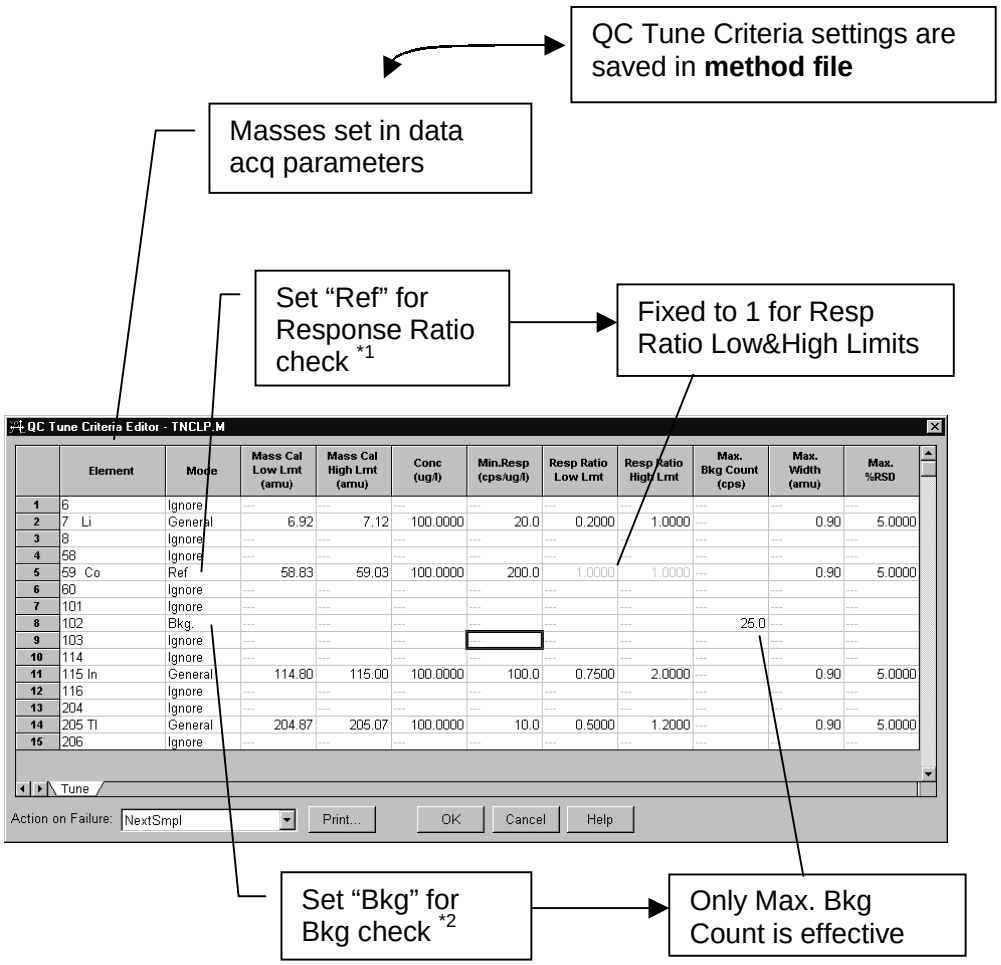
- 1st step Criteria 1 & 1st step Criteria 2

"Check whether the analytical concentrations of certified reference material (CRM) are 85-115% of the certified values. If not, recalibrate and then analyze again. Also check whether concentrations are 90-110% of the certified values. If not, have a error flag on a report."

1st step Criteria 1
Low limit: CRM conc >= 0.85 x CRM expected values
High limit: CRM conc =< 1.15 x CRM expected values

1st step Criteria 2
Low limit: CRM conc >= 0.9 x CRM expected values
High limit: CRM conc =< 1.1 x CRM expected values

(B) QC Tune Criteria



*1: “Ref” appears in the Mode list when Response Ratio check is enabled.

*2: “Bkg” appears in the Mode list when Max Bkg Count check is enabled.

Notes on Setting a Method

- Use ***Auto Configuration*** first, when there are more Off (x) elements other than the elements for which Excluded is selected as a curve fit in the calibration table and the elements with parentheses. When ***Auto Configuration*** is used, all Off column settings are always reinitialized.
- In the event of a simultaneous QC failure and ISTD failure, the action on QC failure will take precedence.
- The error action for third failure is set in QC configuration on a sample type basis.
- Set equal or more number of acquired elements for ***#Allowed QC Failure*** when the Second Step is used. Otherwise, the First Step does not work as a filter, and QC check won't go to the Second Step.
- Expected values for Reference part (right side of comparative expressions) always refer to the values set in the First Step Criteria 1. Expected values for Measured part (left side of comparative expressions) refer to the values set in each criteria.
- Use ***Set Unreported Elements***, when there are elements which are not to be reported on QC custom reports.

Before Saving the Method

- Use ***Verify QC Method*** to check whether there is any error on settings. (Click this in ***Method Save Options*** when method is saved.)

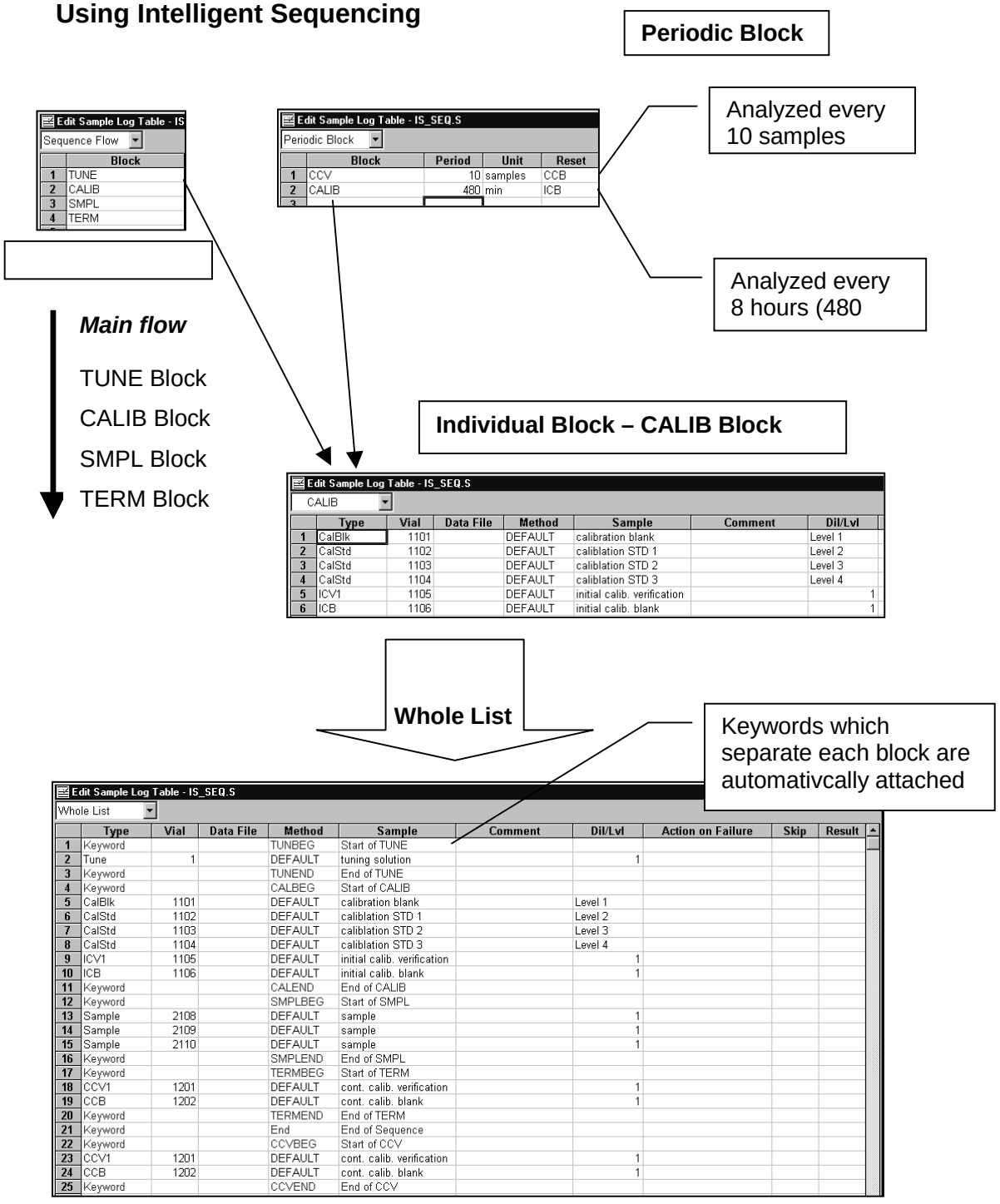
Setting Up a Sequence

Structure of Sample Log Table

Sample Log Table is arranged in subroutines or "Blocks".

The Sample Log Table is composed of four kinds of sheets as follows:

- Sequence Flow sheet
- Periodic Block sheet
- Individual Block sheet
- Whole List sheet



Notes on Setting Each Sheet

<Periodic Block>

The upper block setting has priority when there is a conflict with multiple blocks.

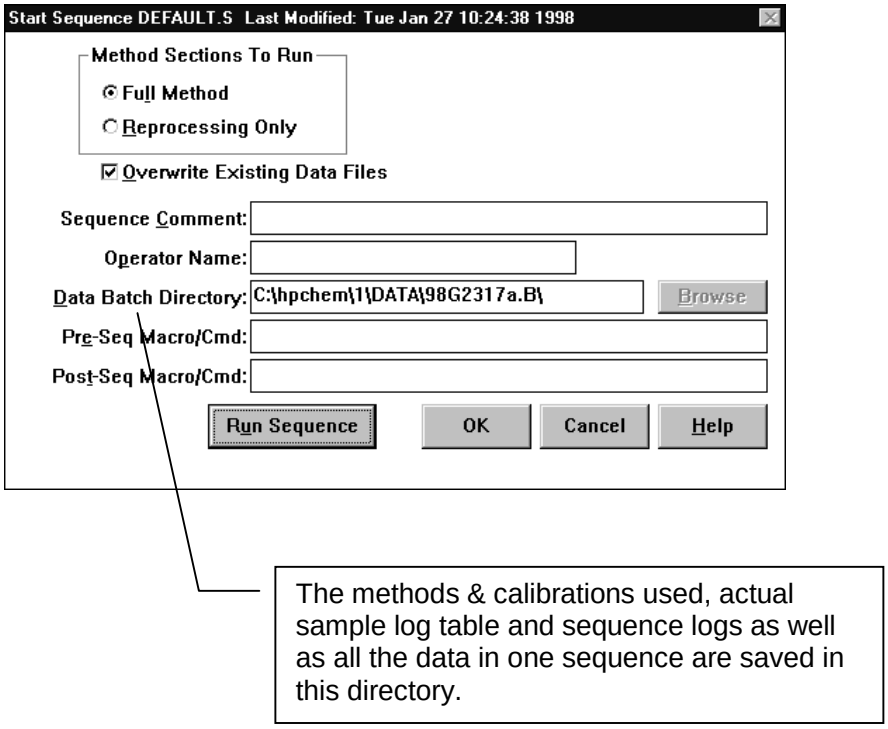
<Individual Block>

- Blanks which are analyzed when the error actions “Blk…….” are taken should be set in BLANK Block.
- Samples which are analyzed when the sequence is aborted should be set in ERRTERM Block.
- When ISTD check is set, the CalBlk should be set at first except Tune since the ISTD counts from the CalBlk are used to establish the reference values.
- When recovery, dilution or duplication check is set, a reference sample type should be set prior to recovery, dilution or duplication sample.

Before Running the Sequence

- Use ***Simulate Sequence*** to check whether there is any error on settings.

Running a Sequence



Note on Running a Sequence

- Insure the same QC configuration as the one used when the methods and sequence to be executed were made.
- After editing the sample log table (online) during sequence run, close the table immediately. The sequence is paused while the sample log table is opened.

- If the data analysis parameters, QC Database or QC Tune Criteria in the method currently used needs to be changed instantly, load the method using Offline Data Analysis, and change it. The modified method can be saved to online using ***Offline Data Analysis >> Method >> Save to Online***.

Sequence Reprocessing of Data

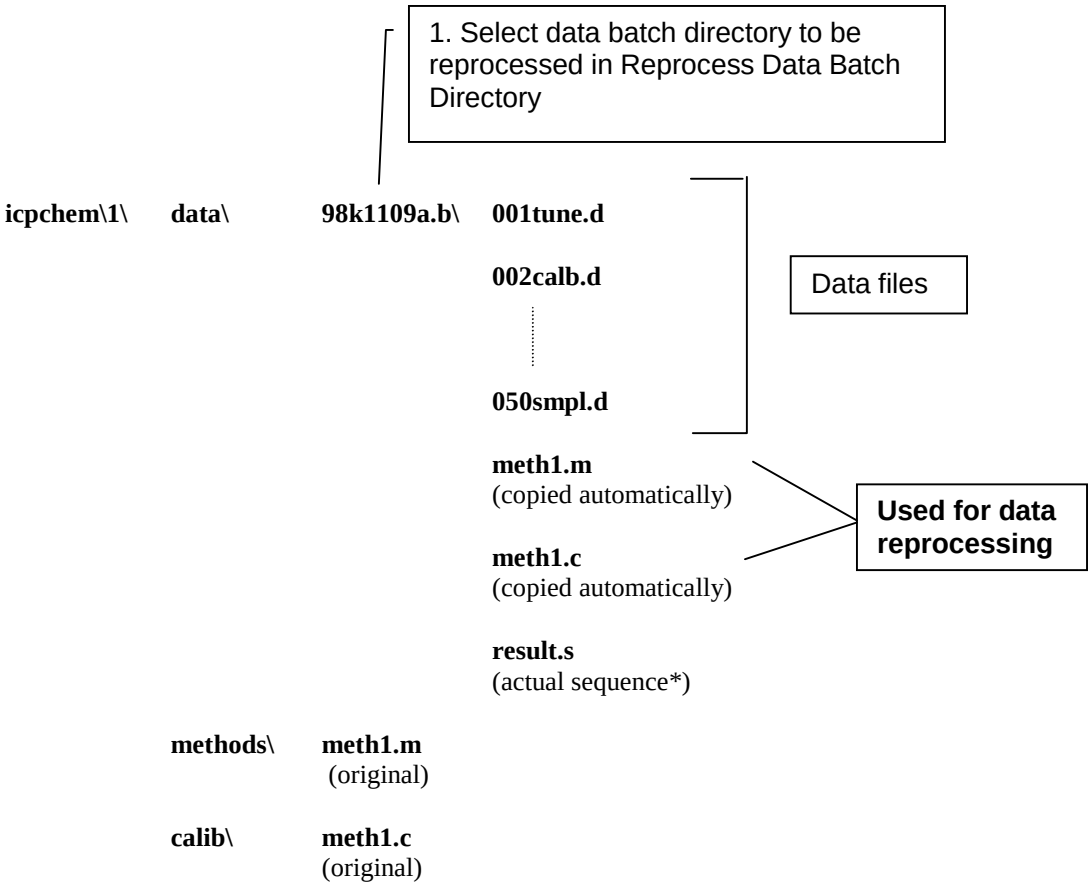
Two ways for batch reprocessing of data:

A. Reprocessing Data Batch Directory

B. Running a Sequence with Reprocessing Only

(A) Reprocess Data Batch Directory

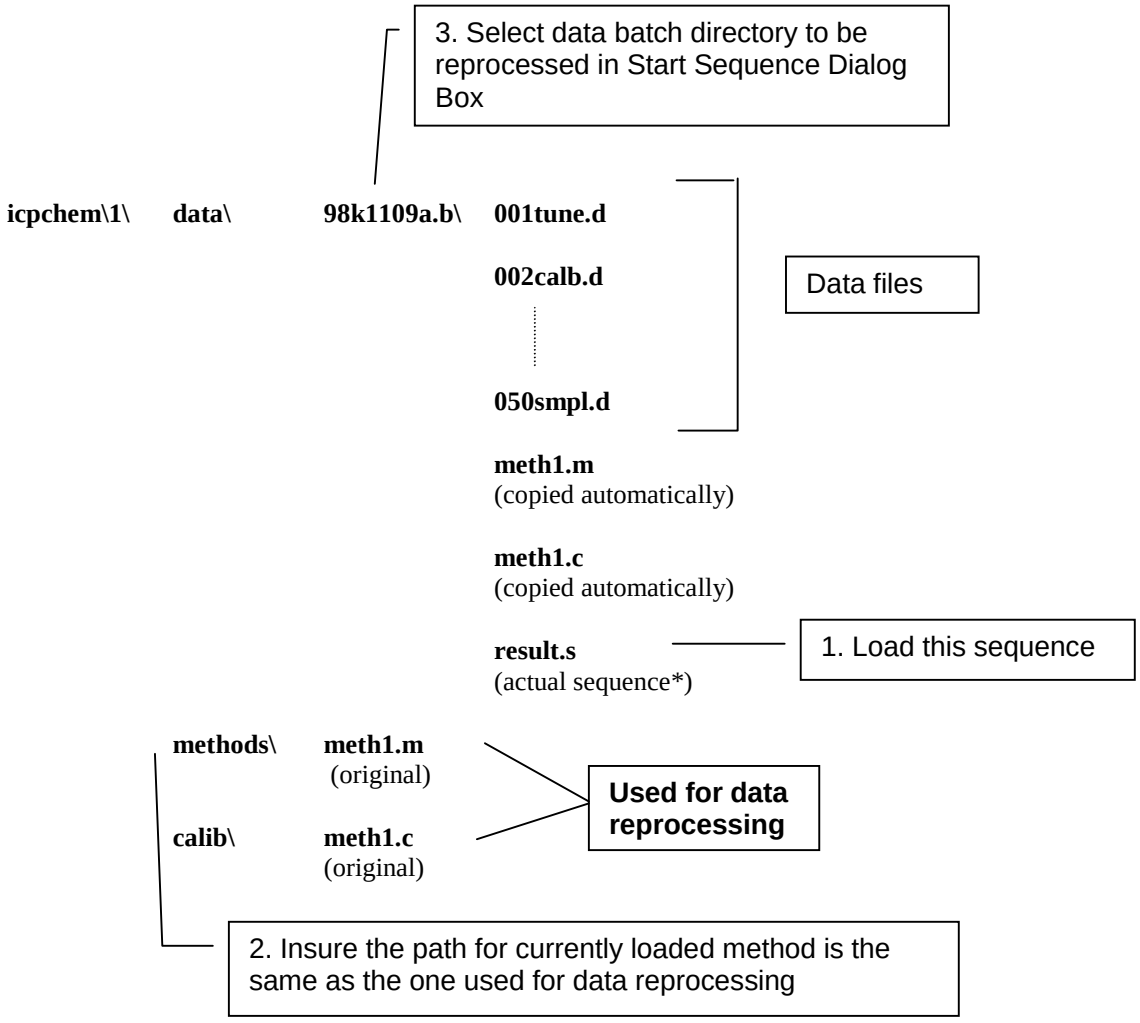
<Files to be selected and used>



- The name for actual sequence is always **result.s**.

(B) Running a Sequence with Reprocessing Only

<Files to be selected and used>



* The name for actual sequence is always **result.s**.

Notes on Reprocessing Data

- Insure the correct method and calibration file are selected when changing parameters for reprocessing; change the copied method and calibration in the data batch directory when using ***Reprocess Data Batch Directory***, and change the original method and calibration when running the sequence with reprocessing only.
- The header information updated using ***Data Analysis*** >> ***File*** >> ***Edit Header*** is not reflected when using batch reprocessing (both ways). Change the Sample Log Table of **result.s** if needed. However, the

header information to be printed out is not changed until the header information is updated using ***Data Analysis*** >> ***File*** >> ***Edit Header***.

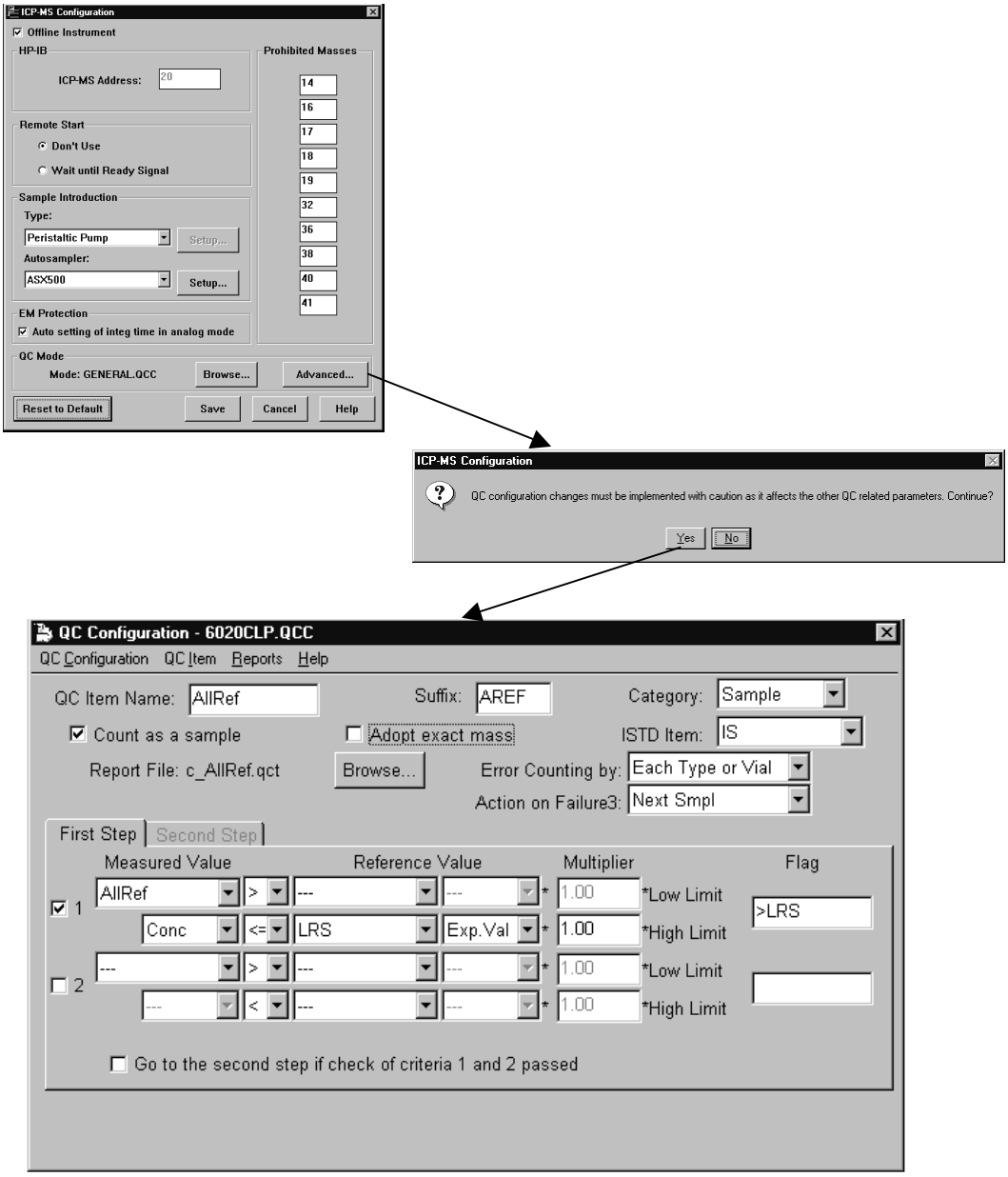
Setting Up a QC Configuration

QC configuration defines the QC sample type set which contains…

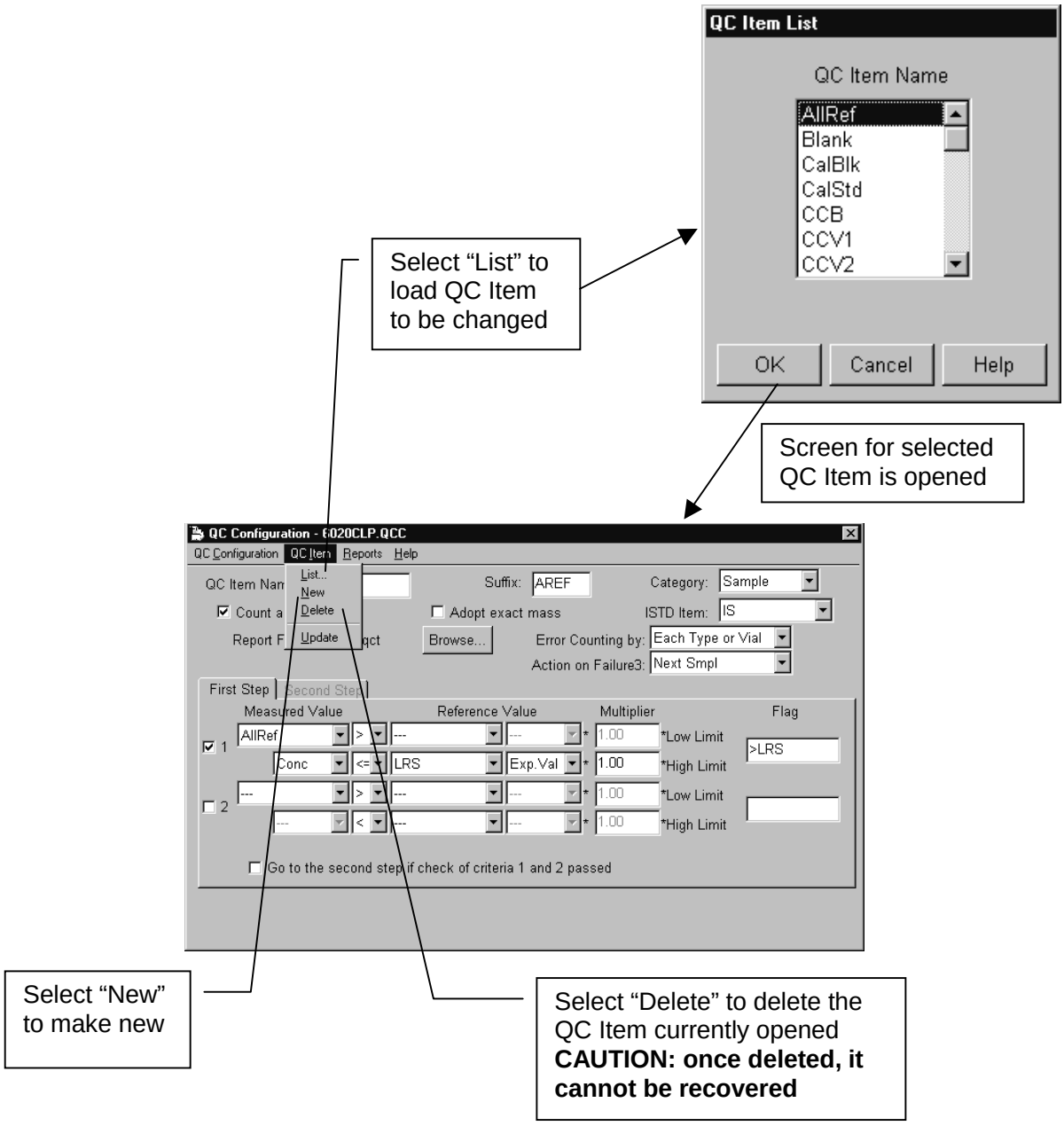
- Sample type name
- Data name suffix
- QC report template
- Type category
- QC Item name to be used for ISTD check
- Error counting way
- Action on 3rd failure
- Comparative expressions
- Error flags for QC report

The Changes in QC Configuration must be implemented with **CAUTION** as it affects the settings in the QC Database, QC Tune Criteria, or Sample Log Table directly.

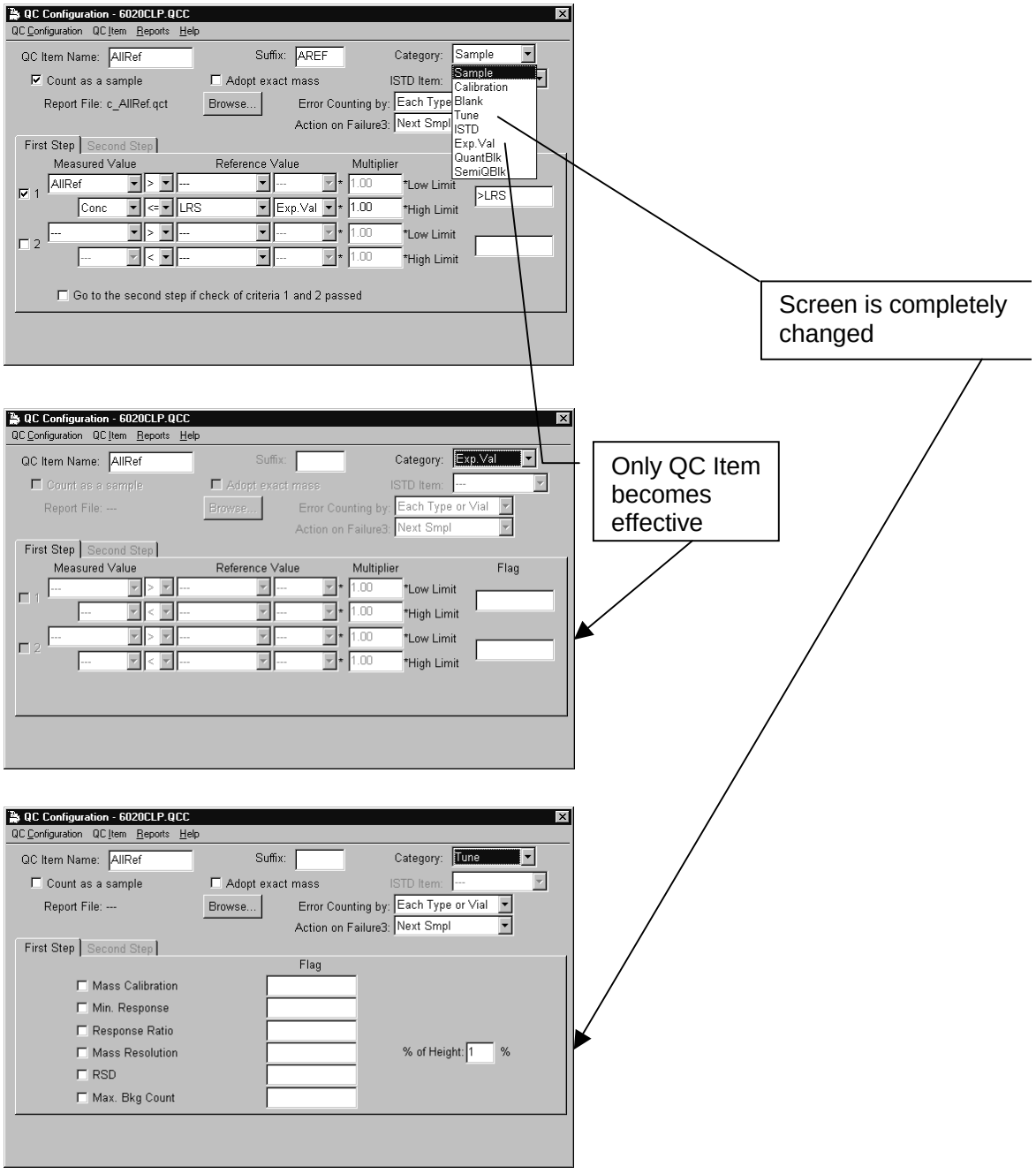
Configuring QC Items



How to Create or Change a QC Item



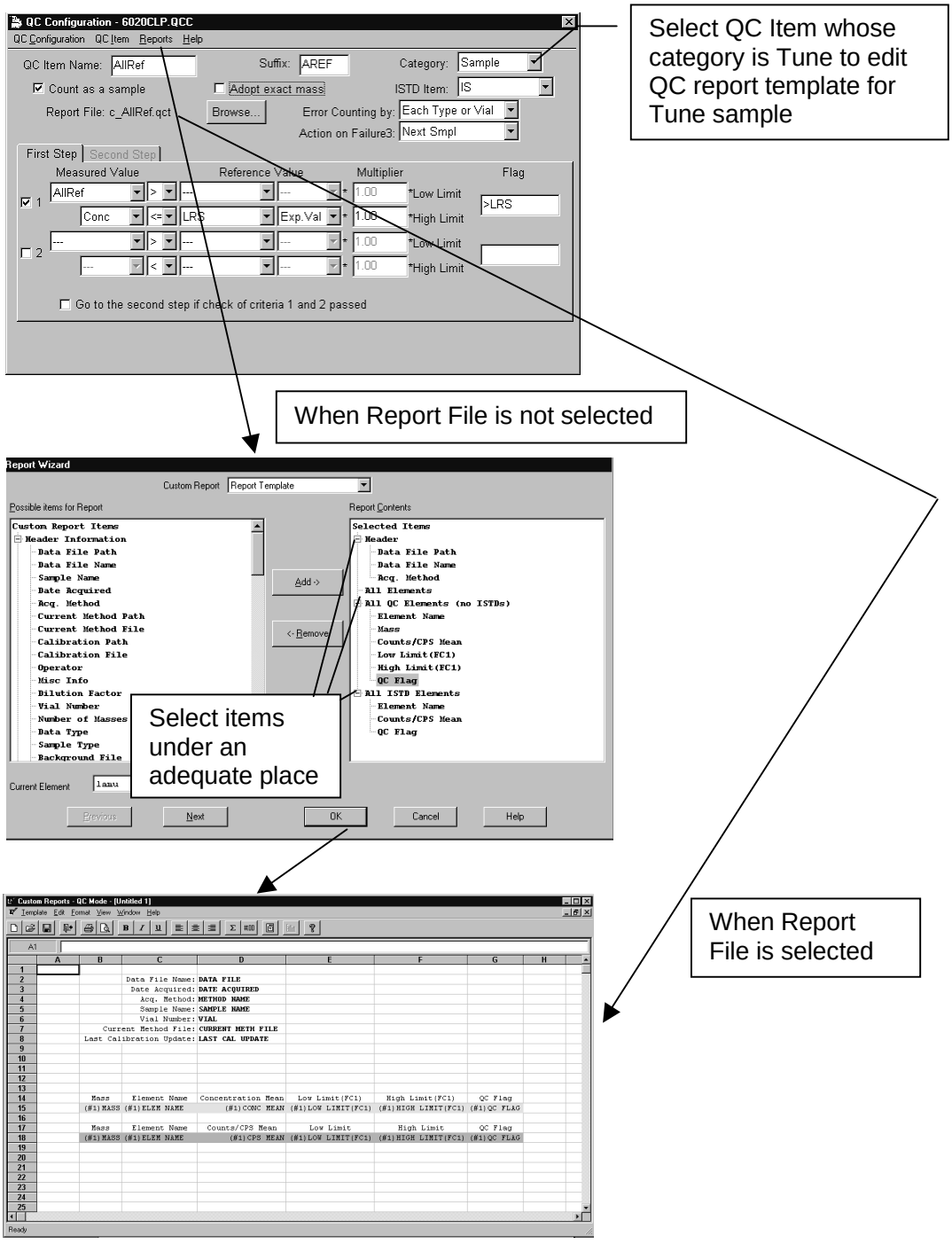
Special Screens



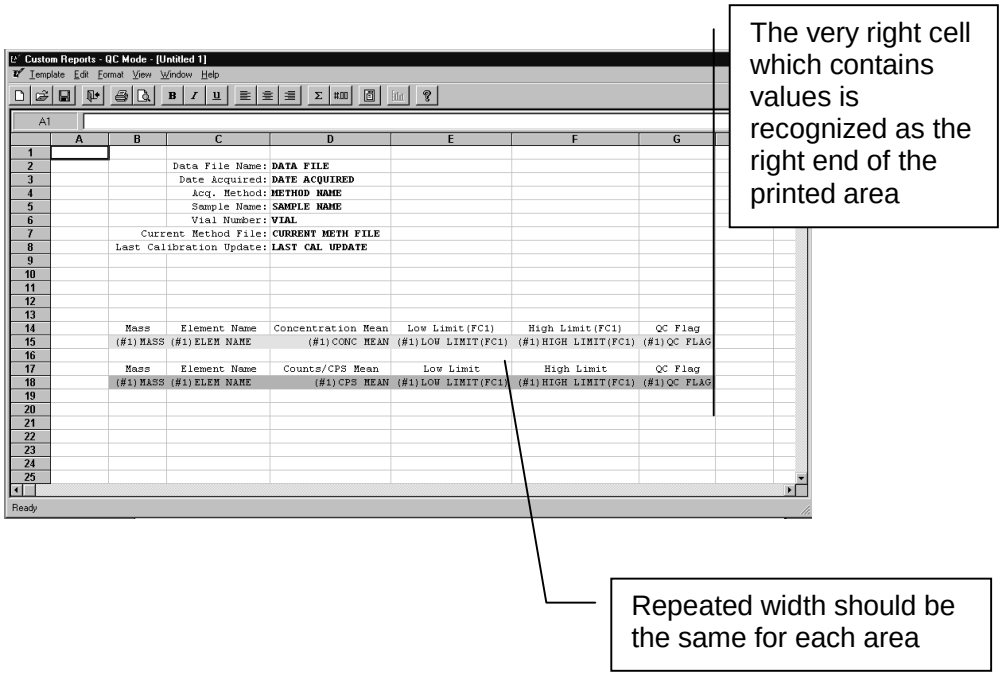
Notes on Setting QC Items

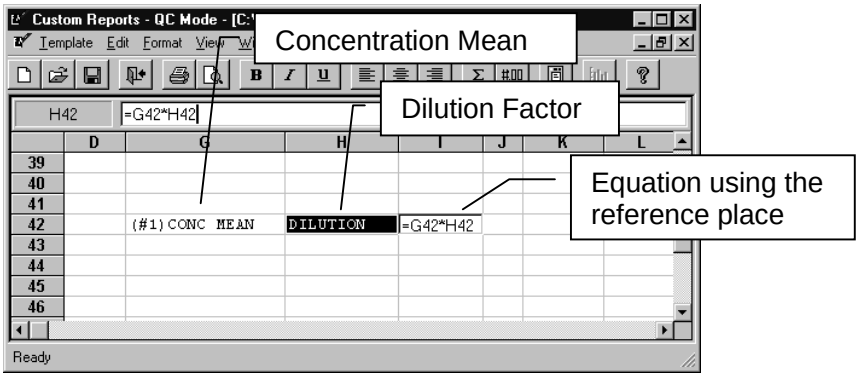
- Preservation of the original QC mode files is recommended.
- Once a QC Item is deleted, it will change the setting of related items in the QC Database, QC Tune Criteria, or Sample Log Table even when the same QC Item in the QC mode is restored.
- Also, once a Category of a QC Item is changed, it will change the setting of related items in the QC Database, QC Configuration, or Sample Log Table even when the same Category for the QC Item is restored.
- Basically the AGILENT 7500 ChemStation does a mass defect correction. Therefore, ***Adopt exact mass*** should be **OFF** if not necessary.

Creating a QC Report Template



Notes on Editing QC Report Template





- The raw concentrations (not taken into account dilution factor) are always indicated. To get the corrected concentration, set ***Concentration Mean*** and ***Dilution Factor*** as printed Items. And then set the equation which expresses ***Concentraion Mean*** multiplied by ***Dilution Factor*** using the reference place.

- There is no function to select the printed area. When there is a column you don't want to print out, select the column, and then select ***Format*** >> ***Column Width*** >> ***Hide.***
- When adding graph (spectrum) on a Tune type template, the repeat setting cannot be applied. Individual setting is required.

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Laboratory 1: Agilent 7500 Configuration, Startup and Tuning

Reference:

- Agilent 7500 ChemStation Operators Manual
- Agilent 7500 Customer Training Class, Module 4
- Agilent 7500 Customer Training Class, Appendix 2

Configuration

1) Close ChemStation if open and open 'Configuration' under Agilent 7500 Program Group
2) Check: Offline Instrument – NOT CHECKED
3) Check: Remote Start – Don't Use except for synchronization with external sampling devices
4) Check: Sample Introduction as appropriate including peristaltic pump and autosampler
5) Check: EM Protection – select Auto setting of integration time in analog mode
6) Check: QC Mode – GENERAL.QCC
7) Save and Exit

Startup and Tuning

1) Review Startup Checklist

2) Initiate Plasma and Warm-up Instrument
   Position ALS in distilled water
   Go to Tune
   Select Tune >> PeriPump program for Autotune, review the values here
   Select Sensitivity and Start
   (Allow instrument to scan for 10-15 minutes to warm up the quadrupole)
   Place the ALS probe in position 3 (10 ppb tune solution, Li, Y, Ce, Tl)
   (Allow time for uptake, 1-2 min)

3) Select Sensitivity >> Start
   Watch for awhile
   Select File >> Print, (keep this for reference as your starting point)

4) Select Tune >> Autotune…
   Select Torch Position, Sensitivity, Resolution/Axis and Tune Report
   Run Autotune (watch what happens)
   Compare the new tune report with the original one which you printed

5) Load "poor_s.u" (This has been deliberately mis-tuned for poor sensitivity)
   Using the ChemStation Manual, Student Manual and Tune Flowcharts, fix this tune

6) Load "high-ox.u"
   Try to reduce the oxides in this tune

7) Ask the instructor to "Fix" the system so that it generates high %RSDs. Fix this!

8) Save your best tune as best.u

9) Place the internal standard solution on line

10) Under Acq. Parms select masses 6, 140 and 209 (what are these elements and where do they come from, e.g. why would we be interested in monitoring them?)

11) Allow time for ISTD uptake and monitor the ISTD counts and %RSDs, do they make sense?

12) Discuss your results with the instructor.

Agilent 7500 Startup Checklist

CHILLER

ARGON

PERIPUMP TUBES CLAMPED

INTERNAL STANDARD MIX

Out for tune

In for analysis

TUNE SOLUTION FULL

BLANK RINSE SOLUTION FULL

DRAIN RESERVOIRS **NOT** FULL

ALS RINSE PORT RESERVOIR OK

SHIELD IN or OUT (application dependent)

PLASMA ON

Shutdown Checklist

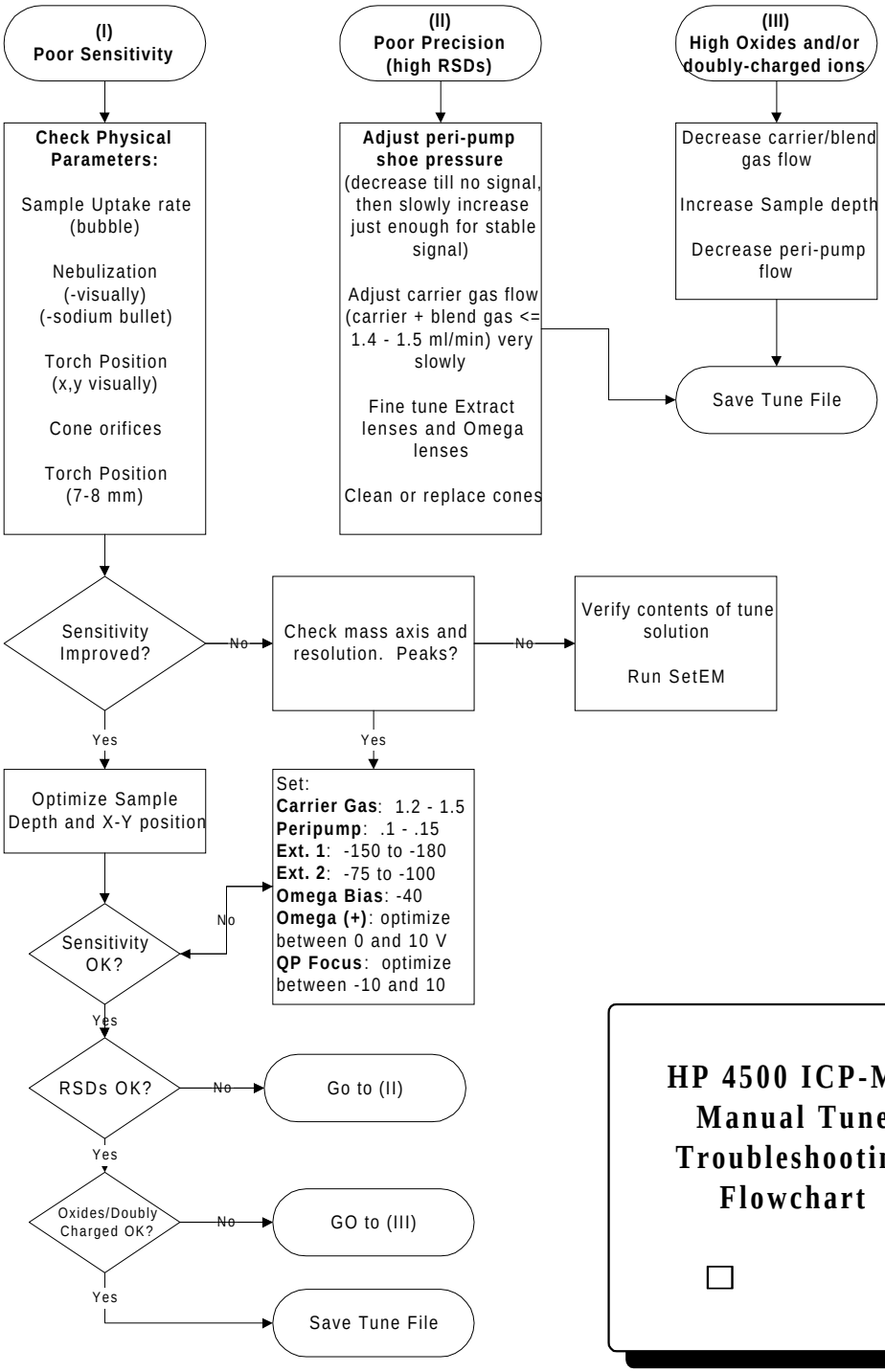
ALS IN RINSE SOLUTION, WAIT 1 MINUTE

PLASMA OFF

PERIPUMP TUBES UNCLAMPED

CHILLER

Shutdown Checklist



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Laboratory 2: Agilent 7500 Routine Maintenance

Reference:

- Agilent 7500 Administration and Maintenance Manual
- Agilent 7500 Customer Training Class – Module 5
- Maintenance Log Table

General

1) Remove and examine air filters
2) Examine level and color of oil in Rough Pumps
3) Check all fluids, belts and hoses (just kidding)
4) Check for corrosion and wipe down cabinet as necessary with damp cloth

Sample Introduction

Remove:

- Peri-pump tubes
- Nebulizer
- Spray Chamber
- Torch

Clean or replace as necessary (refer to maintenance manual)

Interface

1) Remove Sampler and Skimmer Cones and Extraction Lens assembly
2) Sonicate cones in 10% Citranox with occasional careful wiping until visibly clean (10-30 minutes)
3) Rinse cones with water, then DI water, blow dry and set aside.
4) Disassemble extract lens assembly, examine lenses and insulators for discoloration.
5) Sonicate in 10% Citranox and rinse thoroughly as above. Do not sonicate the insulators unless obviously discolored as they take longer to dry.
6) Reassemble and reinstall extraction lenses and interface cones

Nebulizer, Spray chamber and Torch

1) Babbington and Crossflow nebulizers can be sonicated in either dilute Citranox or, 5-10% nitric acid as needed. Babbington nebulizers can be unclogged (argon line) with a tiny GC syringe cleaning wire if needed. Rinse well after cleaning.
2) GLASSWARE SHOULD NOT BE SONICATED! However, torches and spray chambers can be boiled in hot 10% Citranox and then rinsed well. This greatly improves the wetability of the spray chamber. Soaking in strong (10-50%) nitric acid solution overnight may also be necessary for extremely dirty or contaminated glassware.
3) Remove the glassware, examine carefully and replace. Be sure all gas and spray chamber drain connections are leak free.

Re-ignite the plasma and check the tune

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Laboratory 3: Semi-Quantitative Analysis

Reference:

- Agilent 7500 ChemStation Operators Manual
- Agilent 7500 Customer Training Class Manual, Module 08

Semi-Quantitative Analysis

1) From Top Level, load default.m
2) Select 'Edit Entire Method'
3) Edit all method sections to create a semiquant method for unknown sample screening

Do not waste time acquiring nonsense elements such as inert gasses, air, carbon, halogens etc. Also exclude the transuranic elements.

4) Use 0.1 second integration for all elements
5) Use 60 second uptake, 5 second optional rinse, and 60 second stabilization.
6) Do not configure the use of internal standards, since we will be using this method to screen for the presence if internal standard elements in the unknown sample.
7) Examine your tune report and estimate the semiquant response factor threshold (Minimum Peak in cps) necessary to exclude results lower than ~0.1 ppb from the report.
8) Save the method as a unique name.
9) Analyze a blank and a 10 ppb (or 100 ppb) multielement calibration standard with your method.
10) Using the blank and 10 ppb (or 100 ppb) standard, enable blank subtraction and reset the semiquant response factors.
11) Analyze the unknown sample to screen for the presence of the internal standard elements, as well as the presence and approximate concentrations of other analyte elements. This information will be used to develop a quantitative method for analysis of the unknown sample(s).
12) Compare the results with the certified values.

Are semiquant results subject to interferences?

Can they be corrected?

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Laboratory 4: Quantitative Analysis of Unknown Sample

Reference:

- Agilent 7500 ChemStation Operators Manual
- Agilent 7500 Customer Training Class, Module 09
- HP/Agilent Standard Operating Procedure, EPA Method 200.8

Quantitative Analysis

1) Using your SemiQuant results for the Unknown sample and the EPA 200.8 SOP as guidelines, build a quantitative method for analysis of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn.
2) Include at least two calibration levels plus a blank for each element. If the element is likely to trigger analog mode, include a calibration point which will also be acquired in analog mode. (Why is this?)
   Multi-element calibration standards will be available in 1; 10; 100; 500; 1,000 ppb concentrations.
3) Build a simple sequence to update your calibration and analyze your unknown sample at two dilutions.
4) Compare your results with the certified values.
5) Discuss your results with the instructor.

Hints:

Always run at least 2 calibration blanks at the beginning of a sequence to insure adequate flush-out of previously run samples.

Always run a blank after the high calibration standard and before any samples to detect possible memory effects.

Always analyze a blank and mid-point calibration as samples at the end of a sequence and every 10 samples to verify that the system is under control.

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Appendix 1 – General Information

Professional Organizations

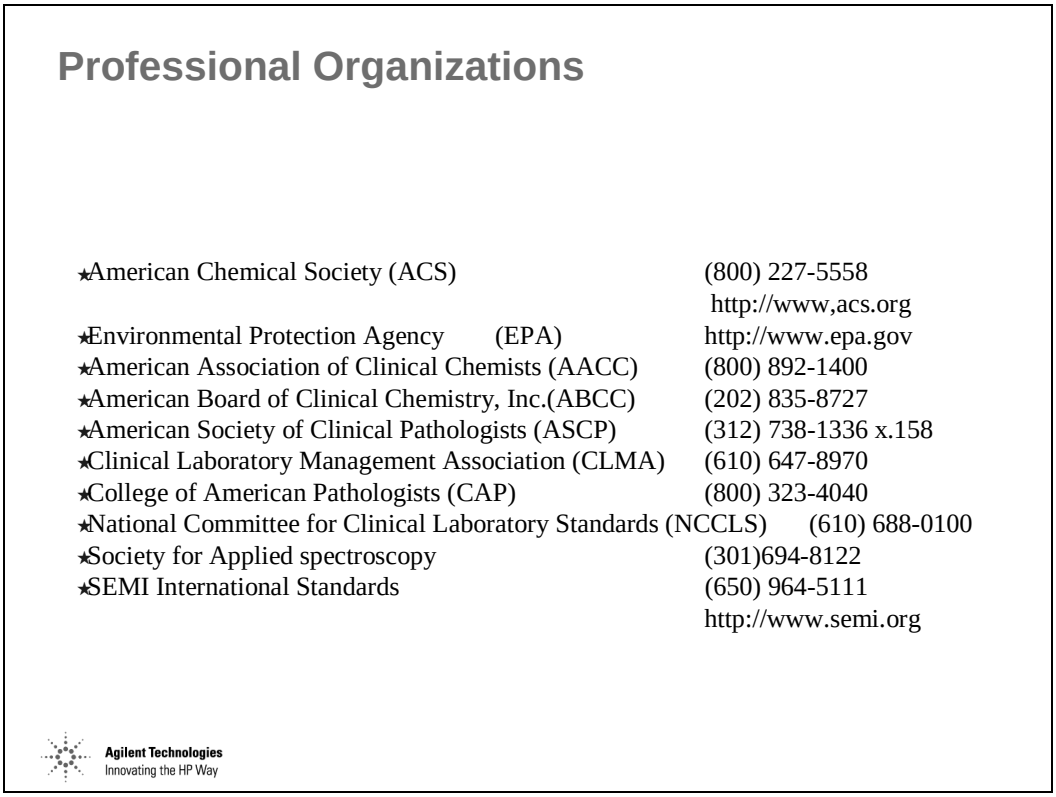

Figure 263

Journals

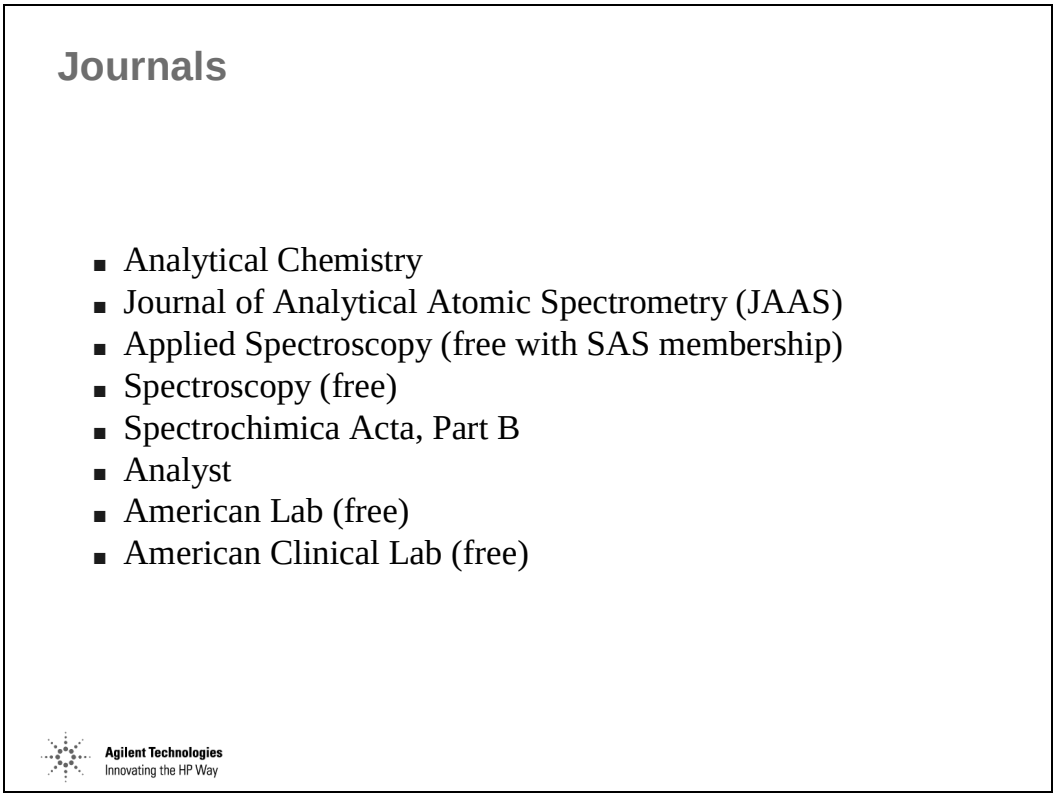

Figure 264

Selected Web Sites (1)

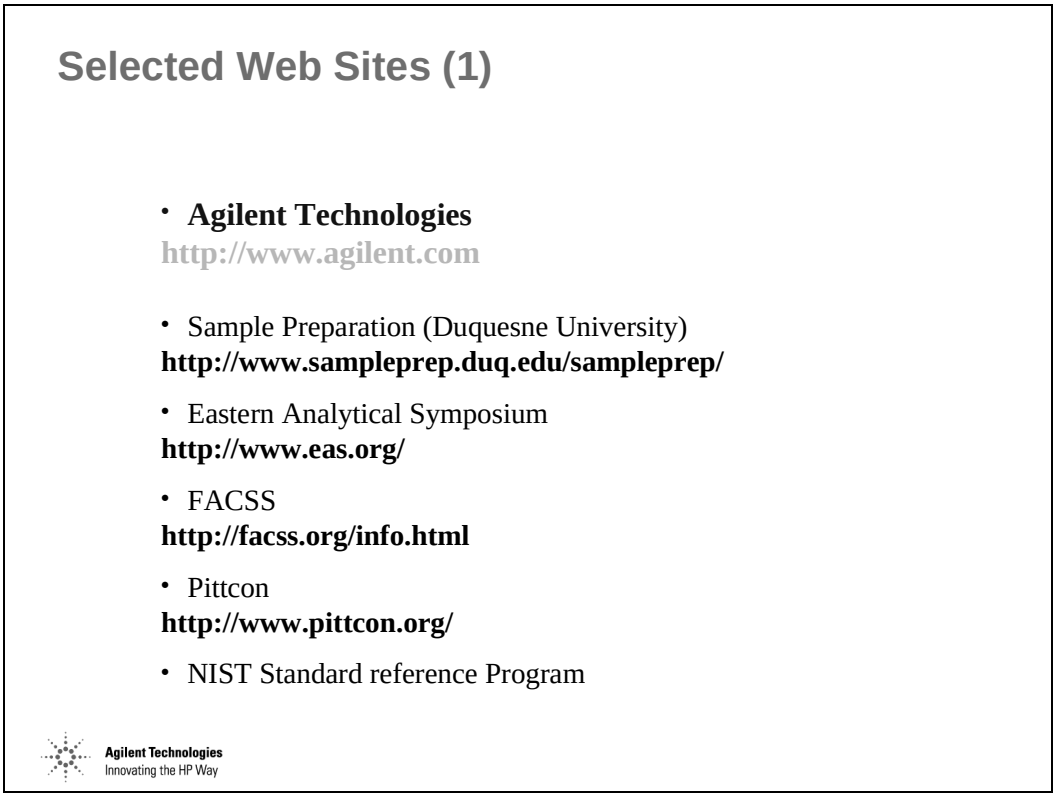

Figure 265

Selected Web Sites (2)

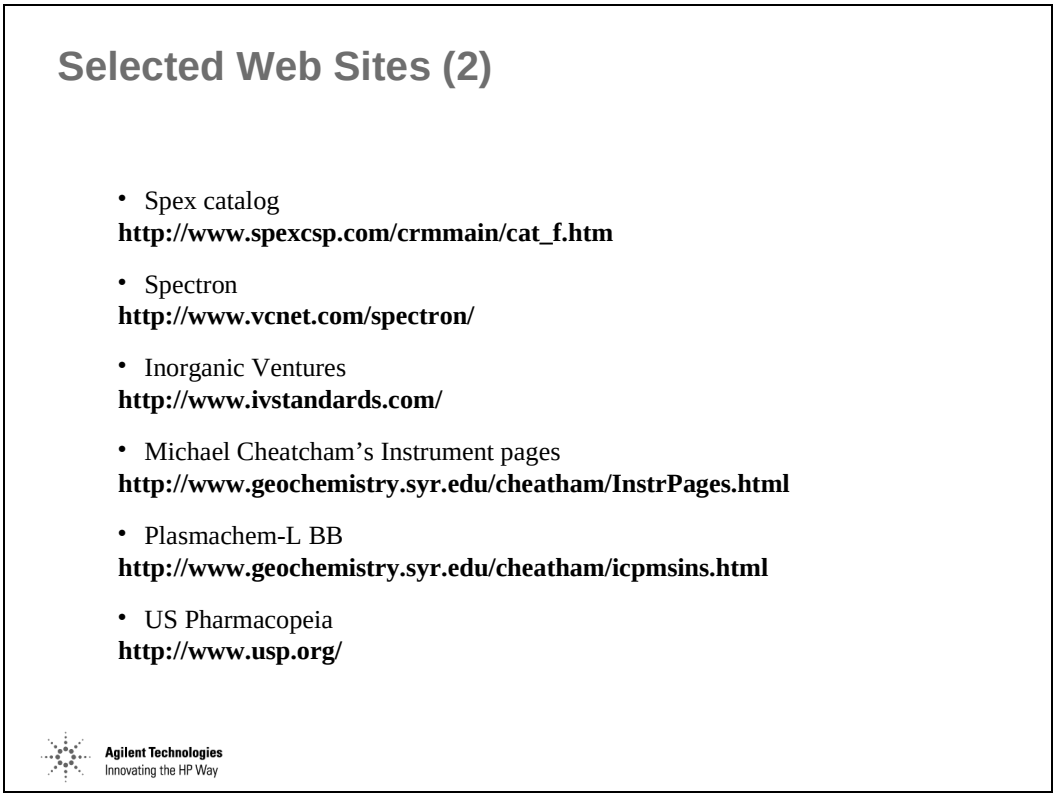

Figure 266

Selected Web Sites (2)

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Appendix 2 – Flow Chats

Manual Tune Troubleshooting Flowchart [1]

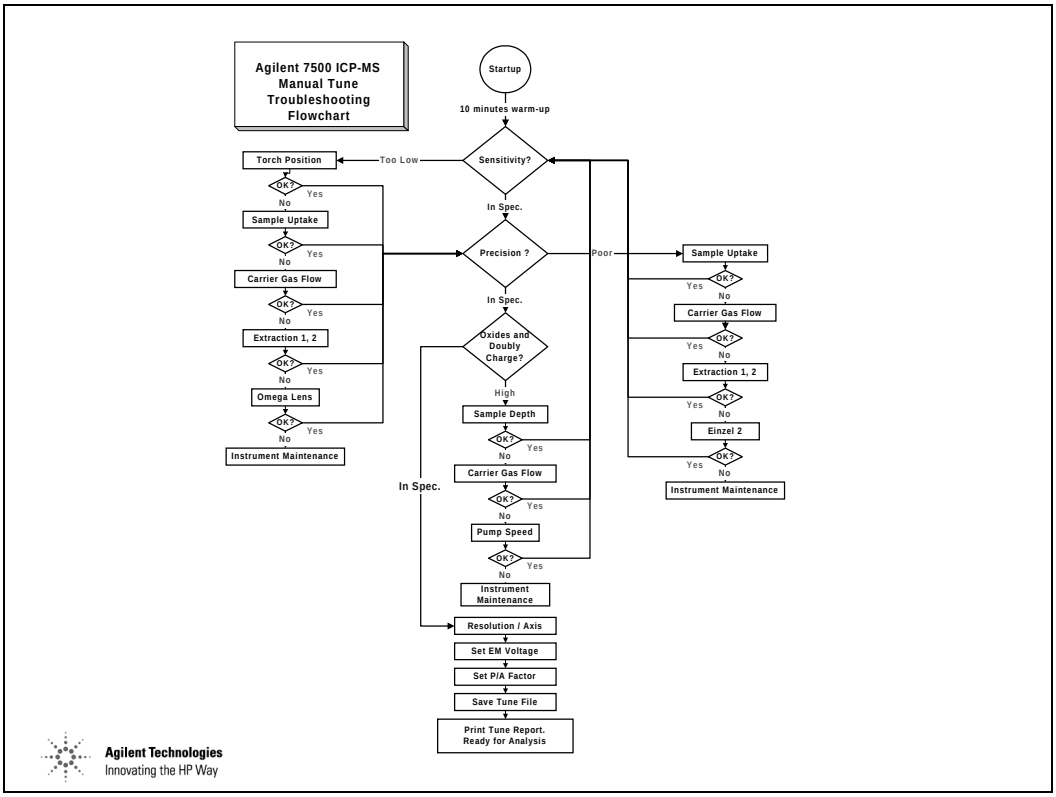

Figure 267

Manual Tune Troubleshooting Flowchart [2]

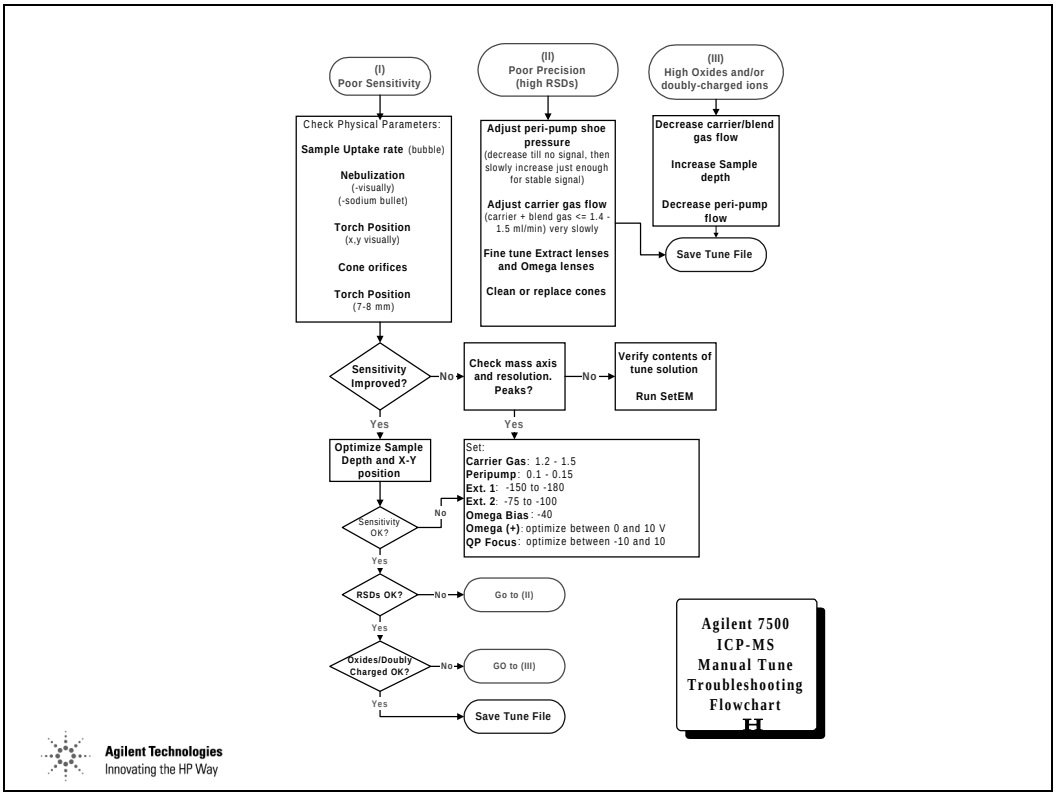

Figure 268

Manual Tune Troubleshooting Flowchart [2]

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Appendix 3 – Dealing with Polyatomics

The Problem

The Problem...

Bulk argon from the plasma can combine with entrained atmospheric gases and matrix constituents to form argon polyatomic ions.

The resulting polyatomic ions can overlap analyte masses of interest compromising detection limits

Common examples are:

- ArO^+ interferes with ^{56}Fe
- ArH^+ interferes with ^{39}K
- Ar^+ interferes with ^{40}Ca
- $ArCl^+$ interferes with ^{75}As

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Figure 269

Strategy #1: (High Power) Cool Plasma Analysis

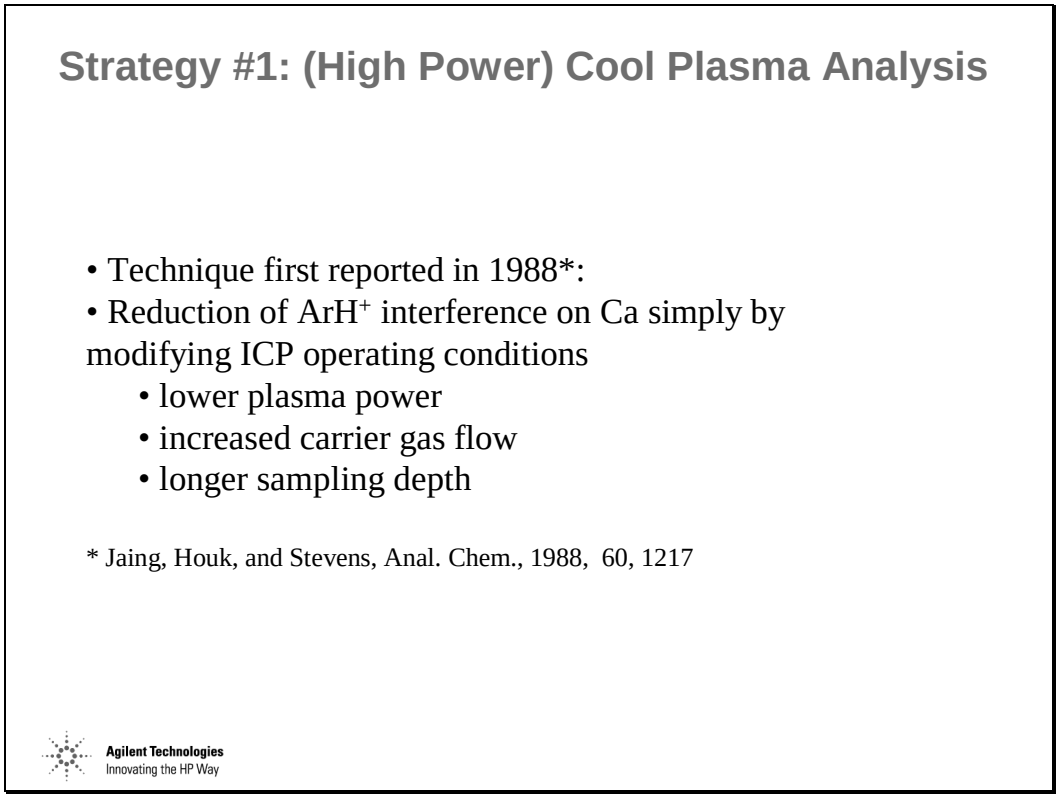


Figure 270

Commercialization of Cool Plasma Analysis

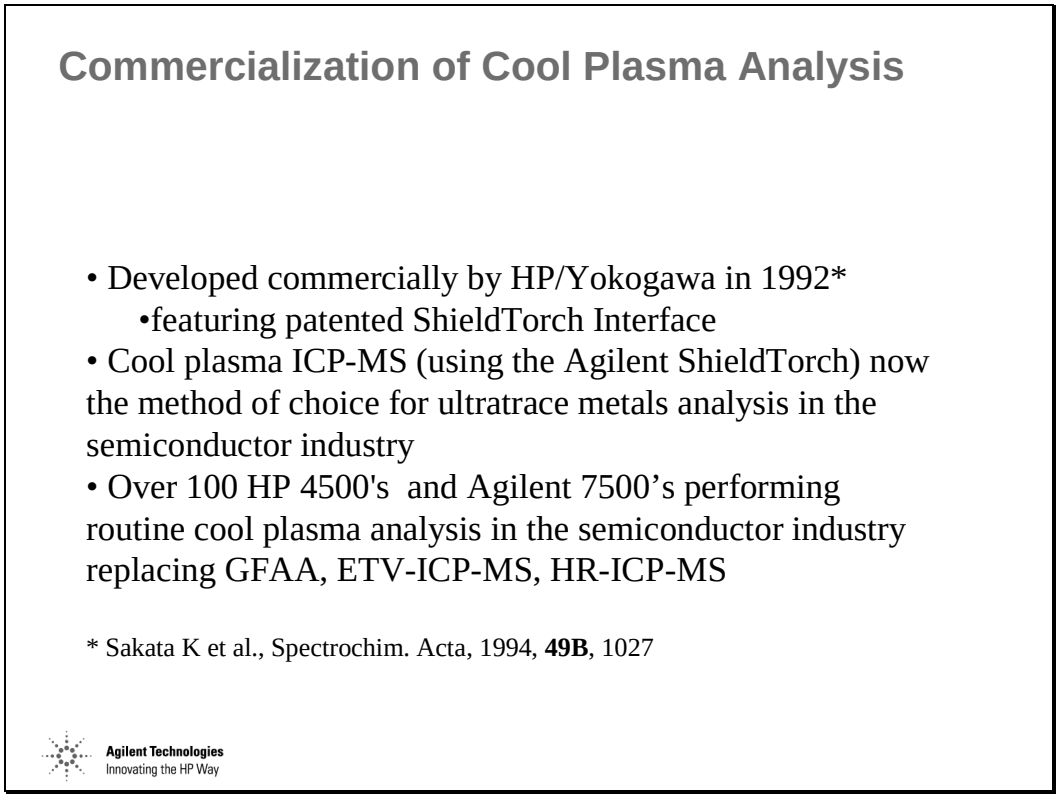
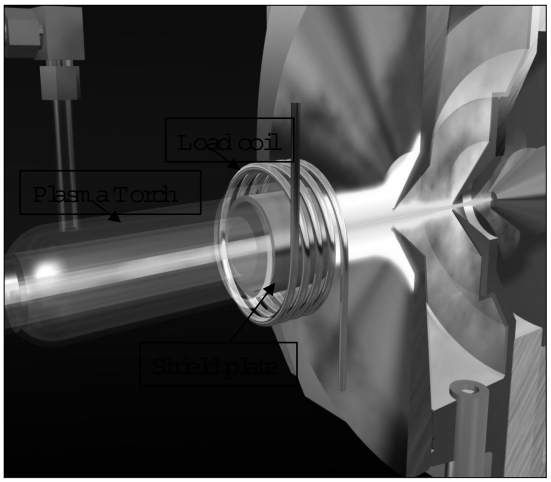


Figure 271

Schematic of Agilent ShieldTorch

Schematic of Agilent ShieldTorch



- Shield plate removes capacitive coupling of the coil to the plasma
- Plasma is at **true** ground potential
- Cooler central channel
- No re-ionization of polyatomic species
- Background spectrum is virtually free from plasma-based peaks.

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Figure 272

Not All Cool Plasmas* Are the Same! [1]

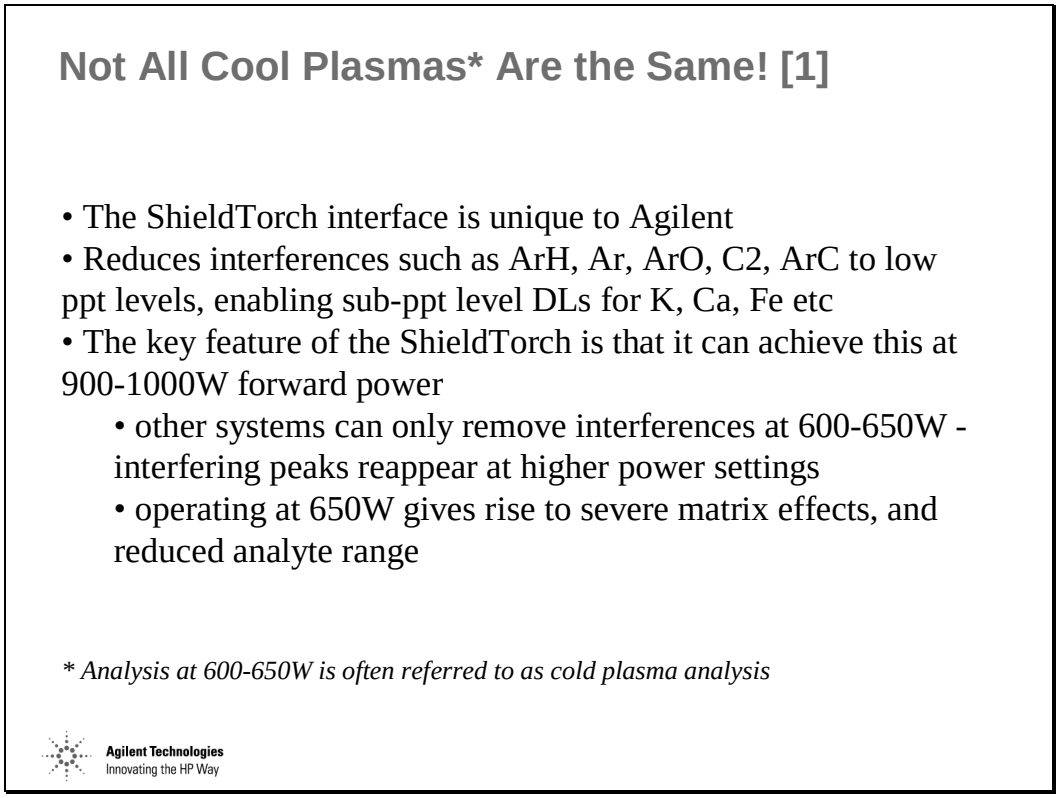


Figure 273

Not All Cool Plasmas* Are the Same! [2]

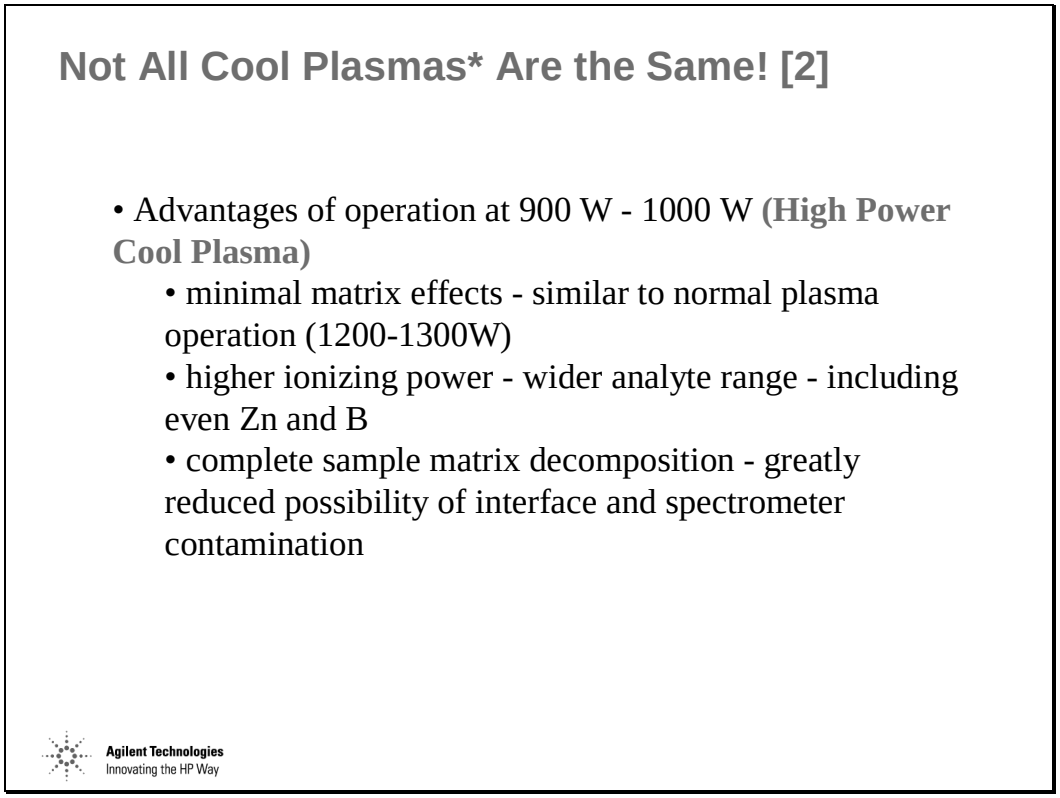
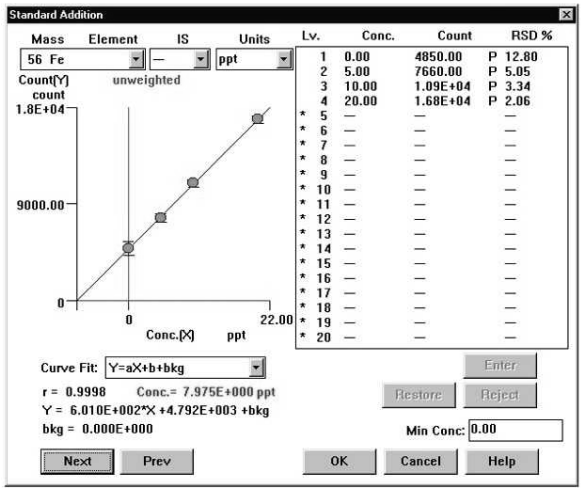


Figure 274

Fe in 31% H_2O_2 - 5 ppt Spike Recovery

Fe in 31% H_2O_2 - 5 ppt Spike Recovery



Excellent linearity even at 5ppt using high power cool plasma

DL - 0.3ppt in the H2O2 matrix

No collision cell or HR-ICP-MS data reported to date showing Fe linearity at 5ppt

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Figure 275

ShieldTorch Technology Eliminates Interferences Before They Form!

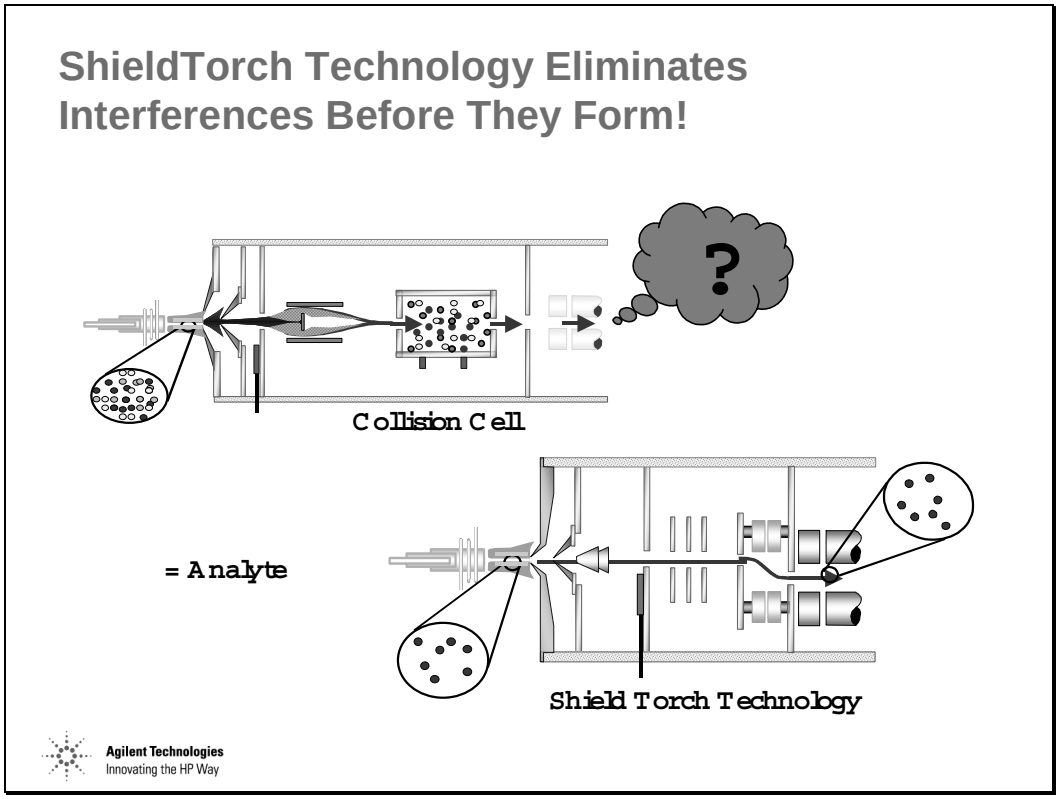


Figure 276

Can Heavy Matrices be Analyzed?

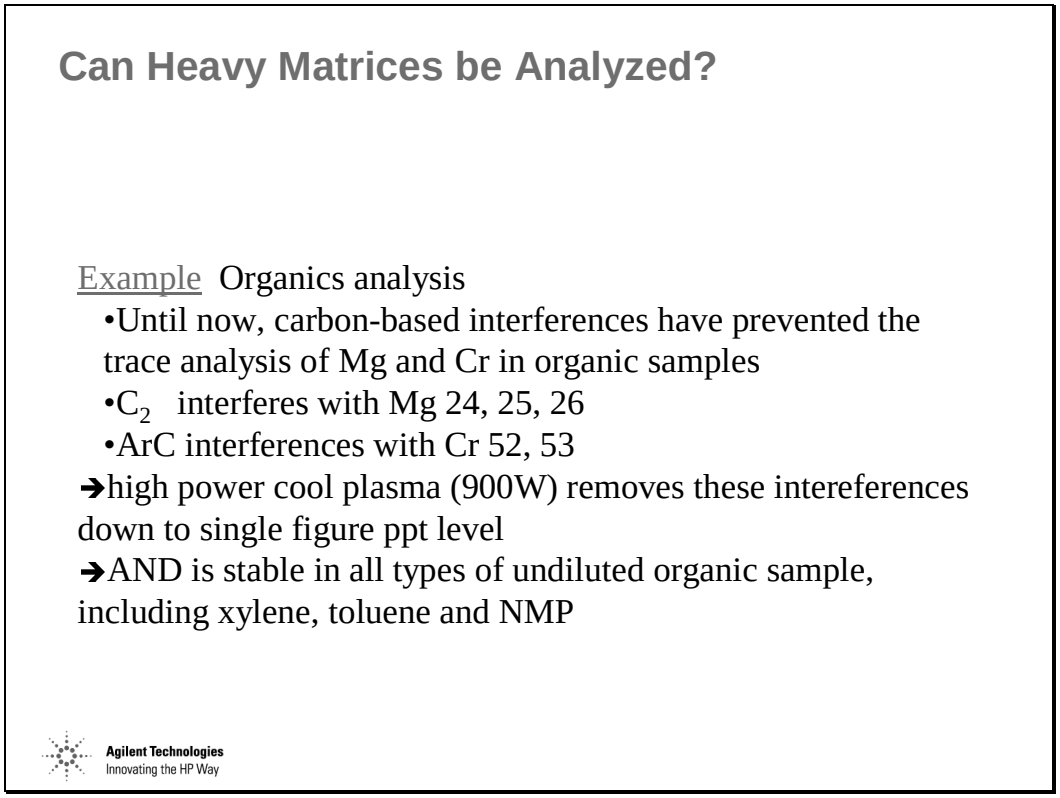
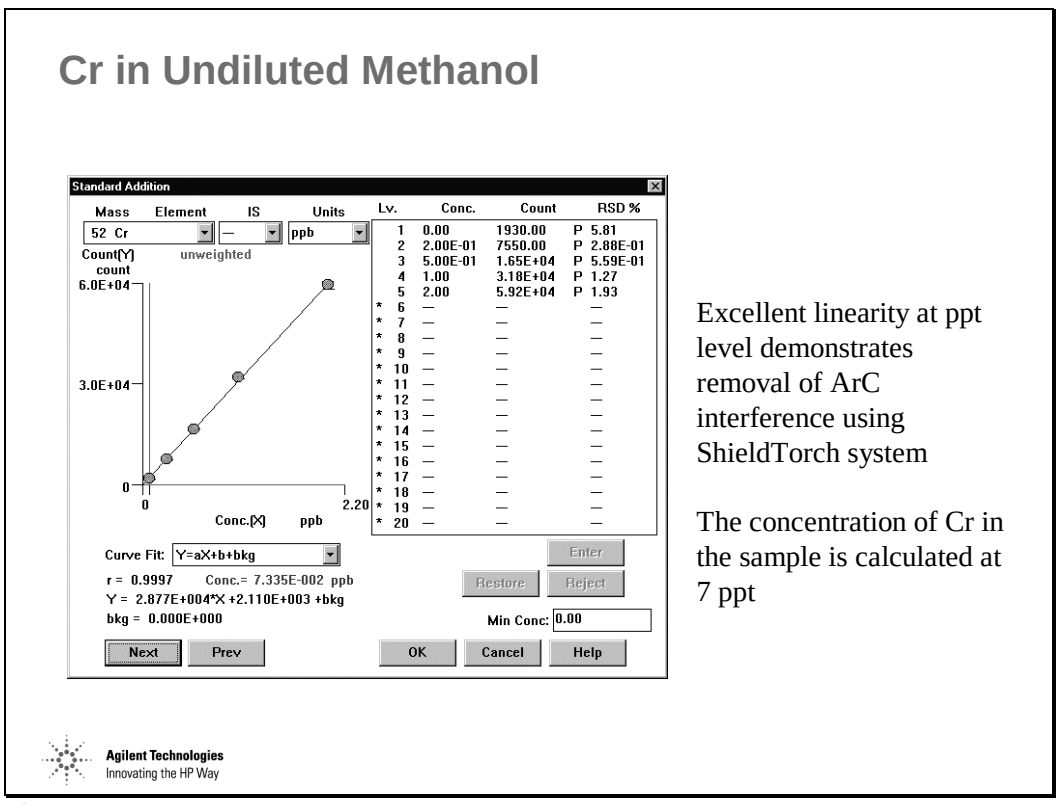


Figure 277

Cr in Undiluted Methanol



Excellent linearity at ppt level demonstrates removal of ArC interference using ShieldTorch system

The concentration of Cr in the sample is calculated at 7 ppt

Figure 278

Example of Heavy Matrix Analysis

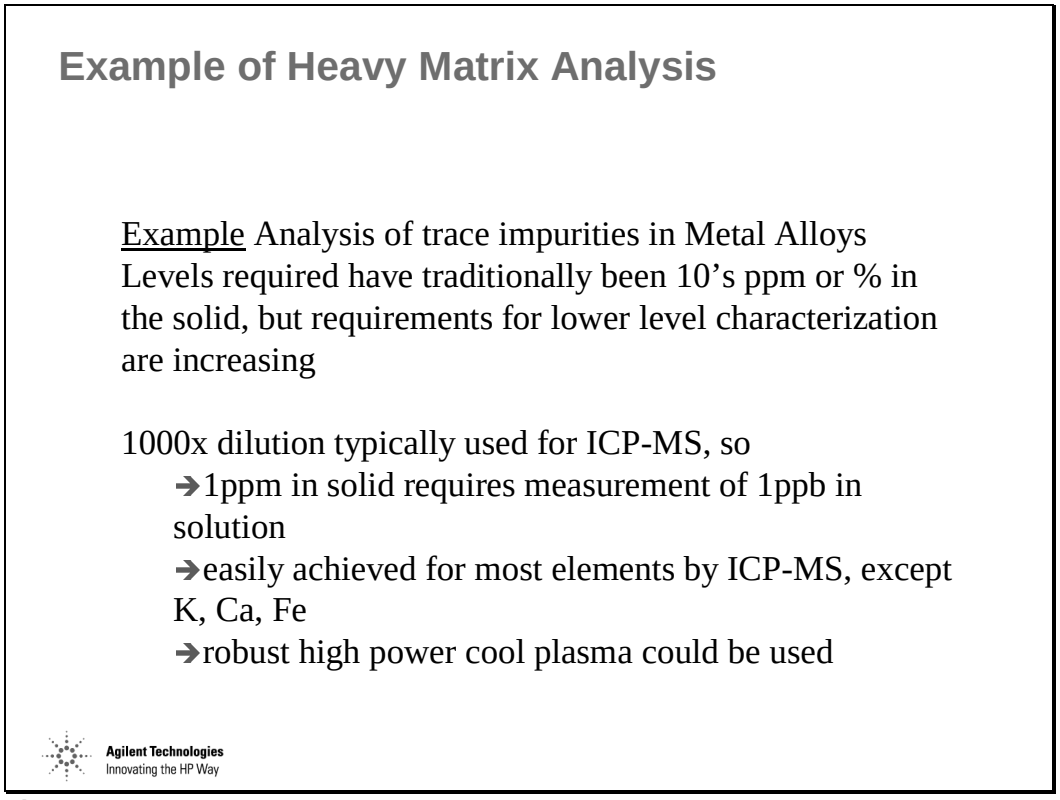


Figure 279

Calibration for ^{56}Fe in 1000 ppm Pt

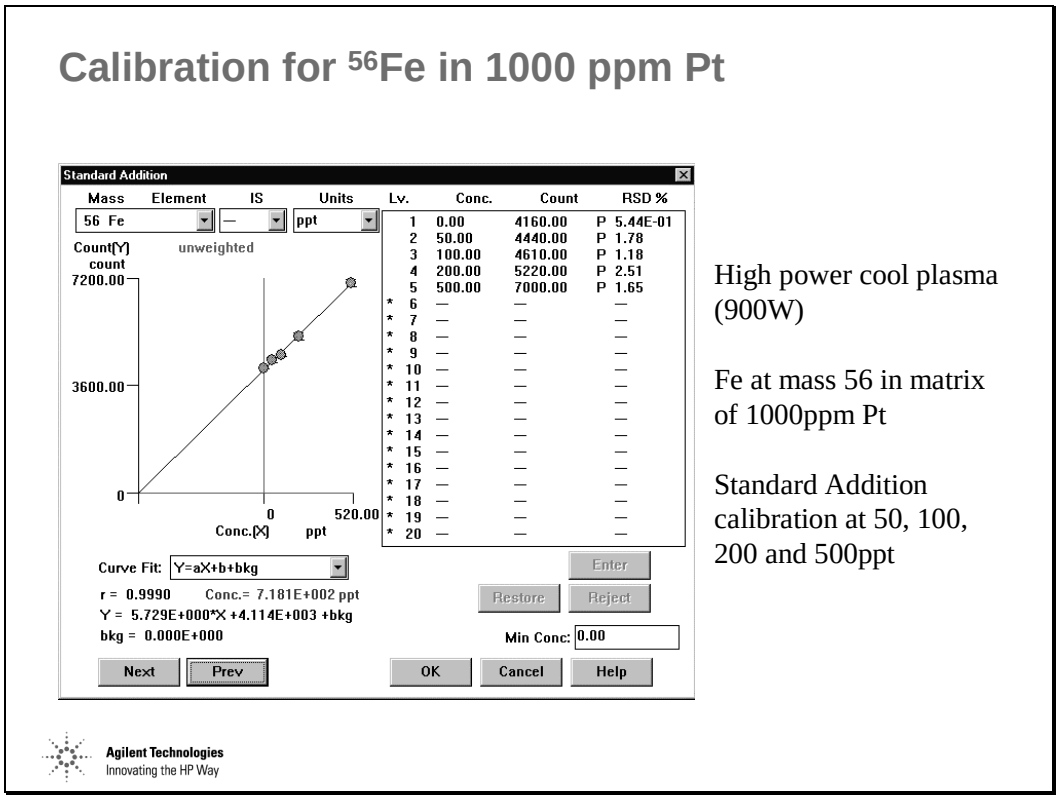
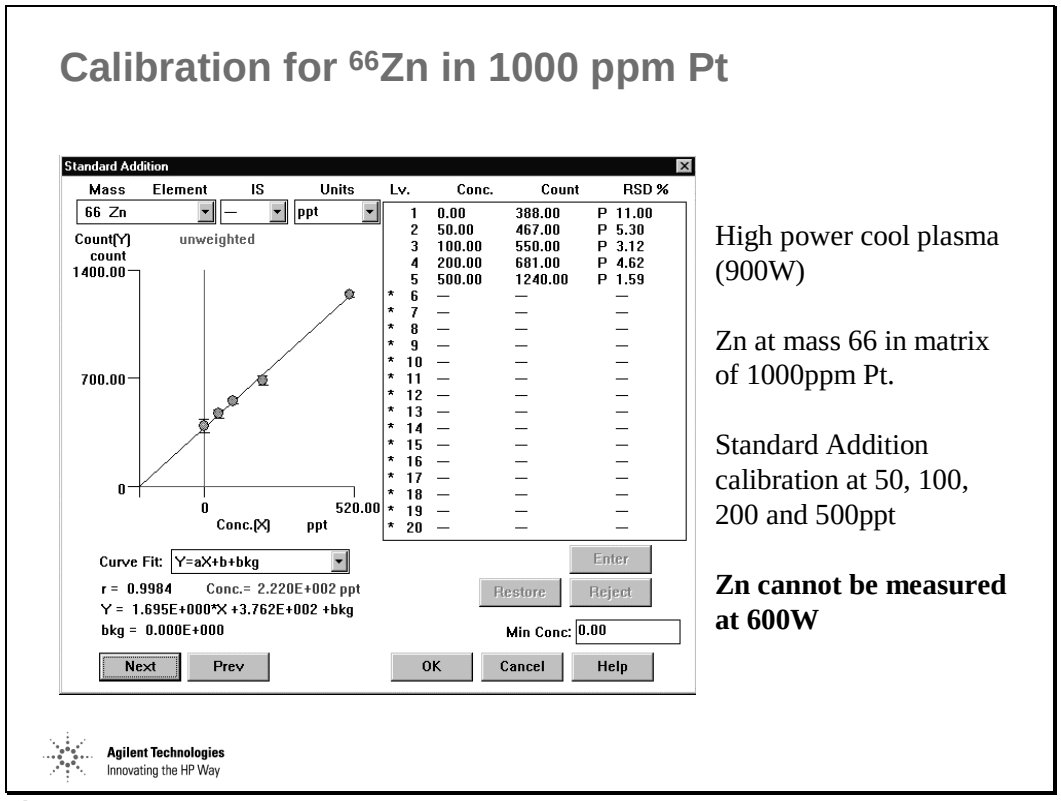


Figure 280

Calibration for ^{66}Zn in 1000 ppm Pt



High power cool plasma (900W)

Zn at mass 66 in matrix of 1000ppm Pt.

Standard Addition calibration at 50, 100, 200 and 500ppt

Zn cannot be measured at 600W

Figure 281

Determination of Se by High Power Cool Plasma

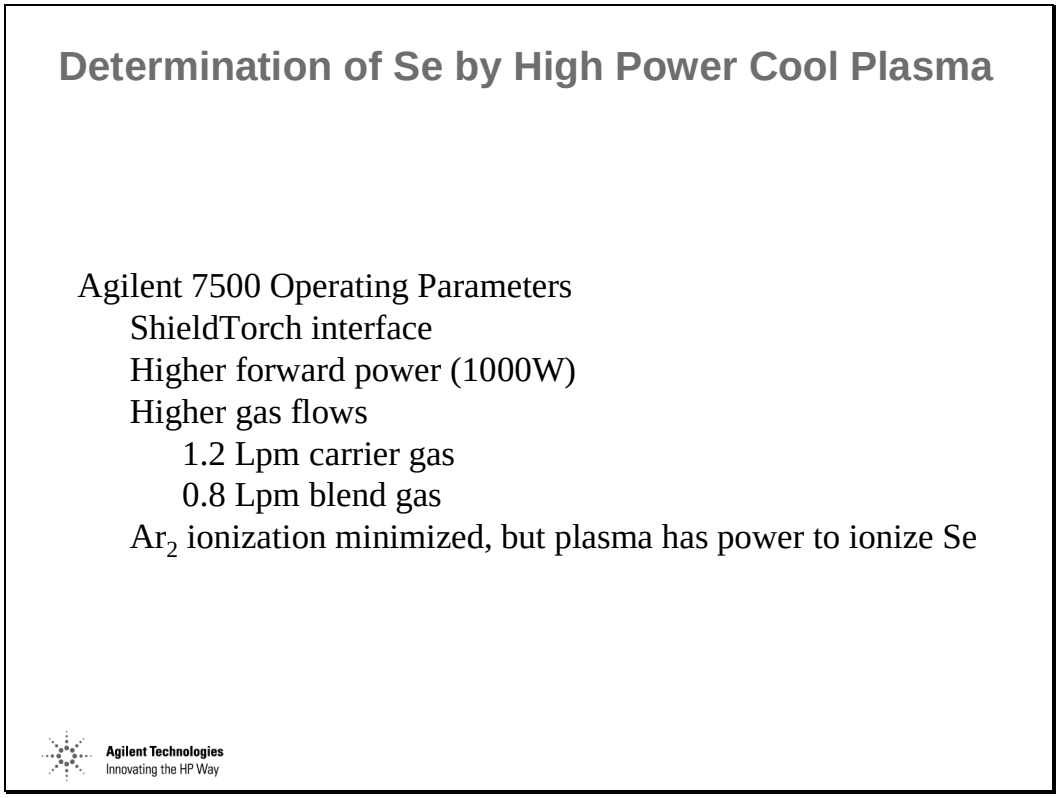


Figure 282

Spectrum of 10 ppb Se and Blank

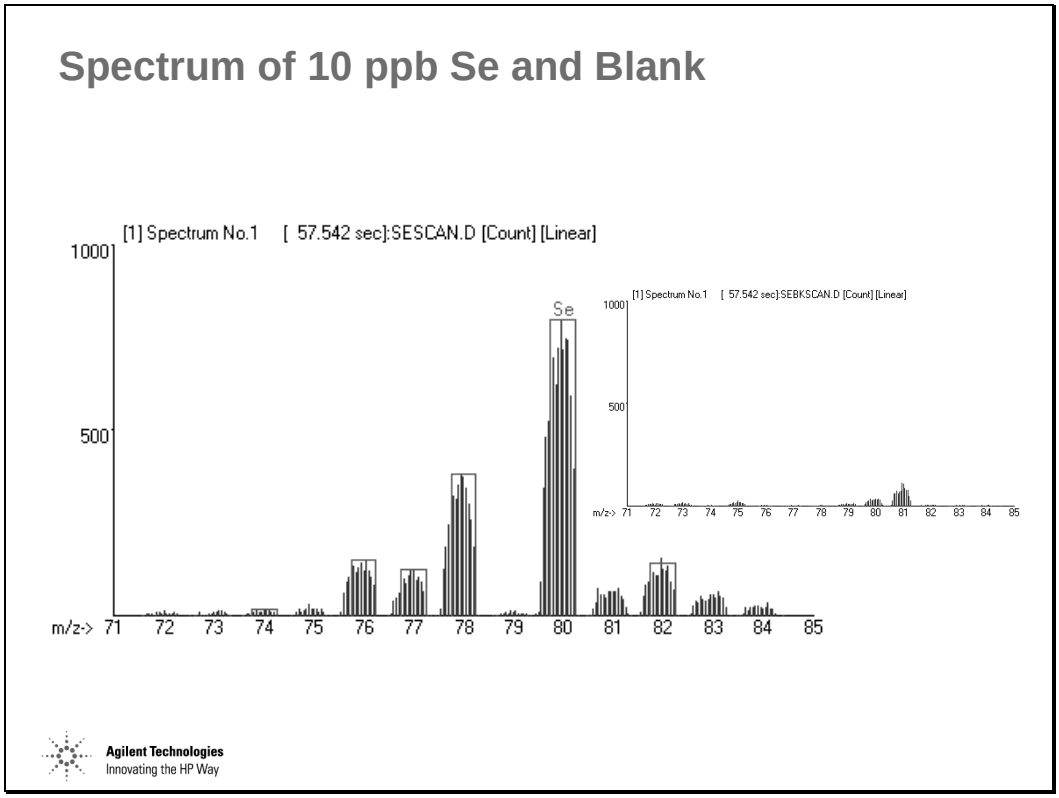


Figure 283

Calibration for ^{80}Se

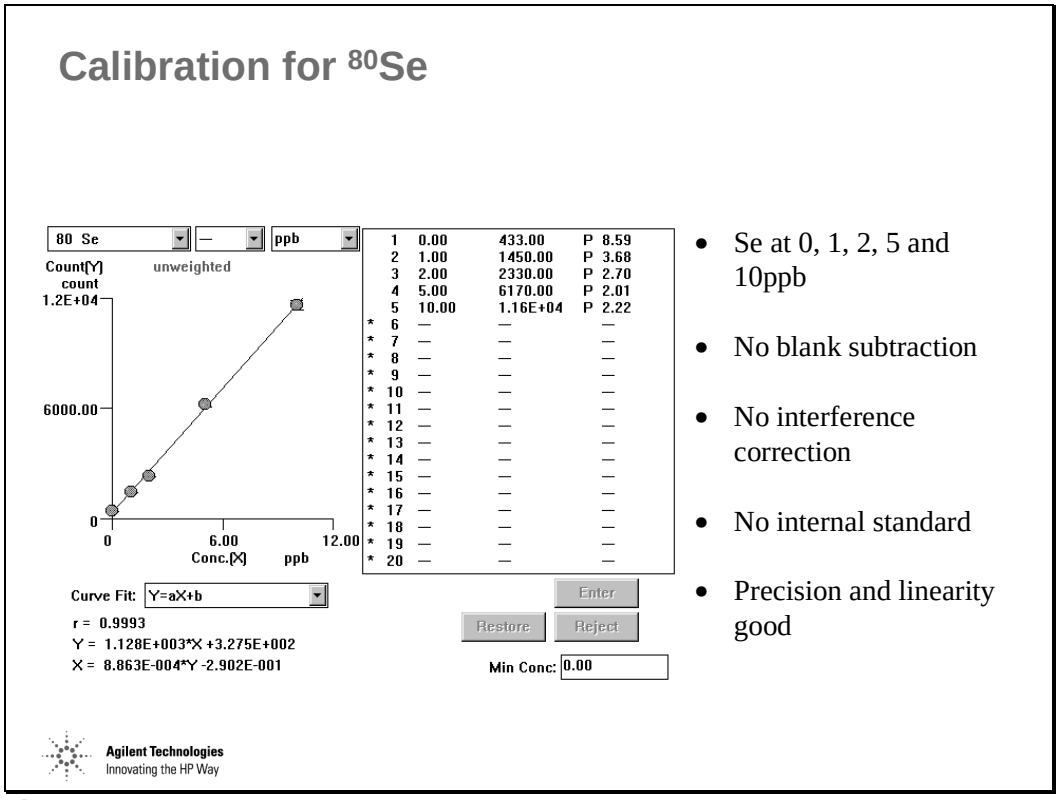


Figure 284

Detection Limits for Se by Cool Plasma

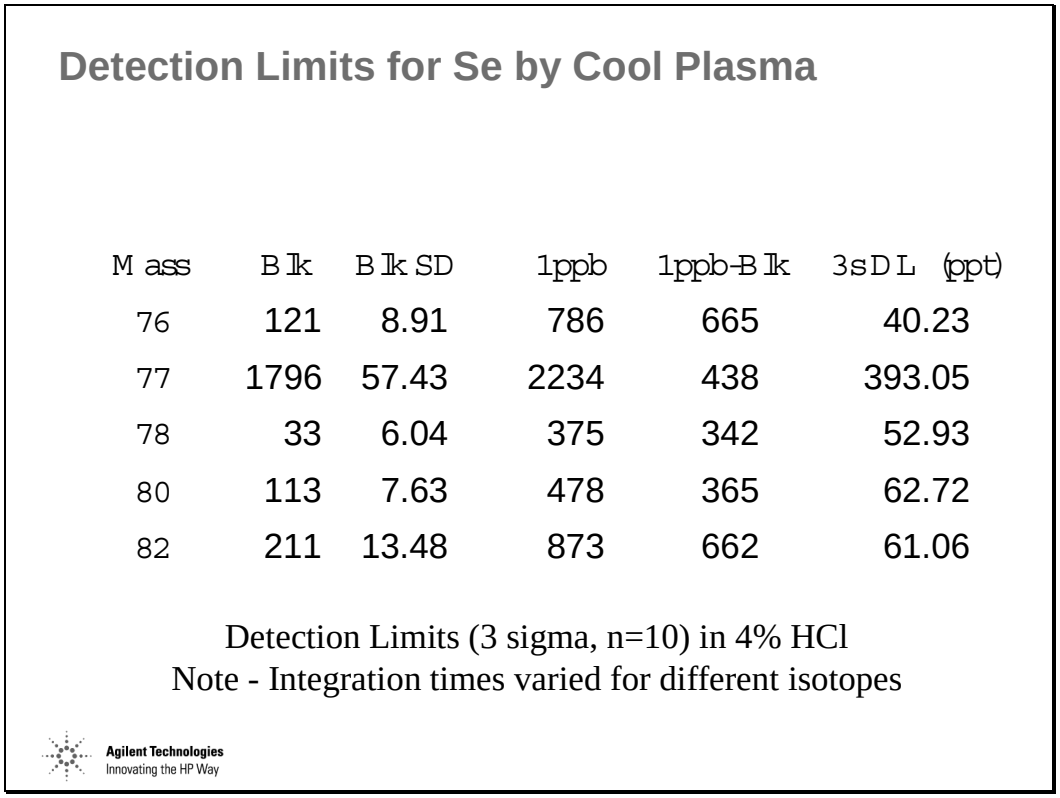


Figure 285

Current Research Developments Using the ShieldTorch

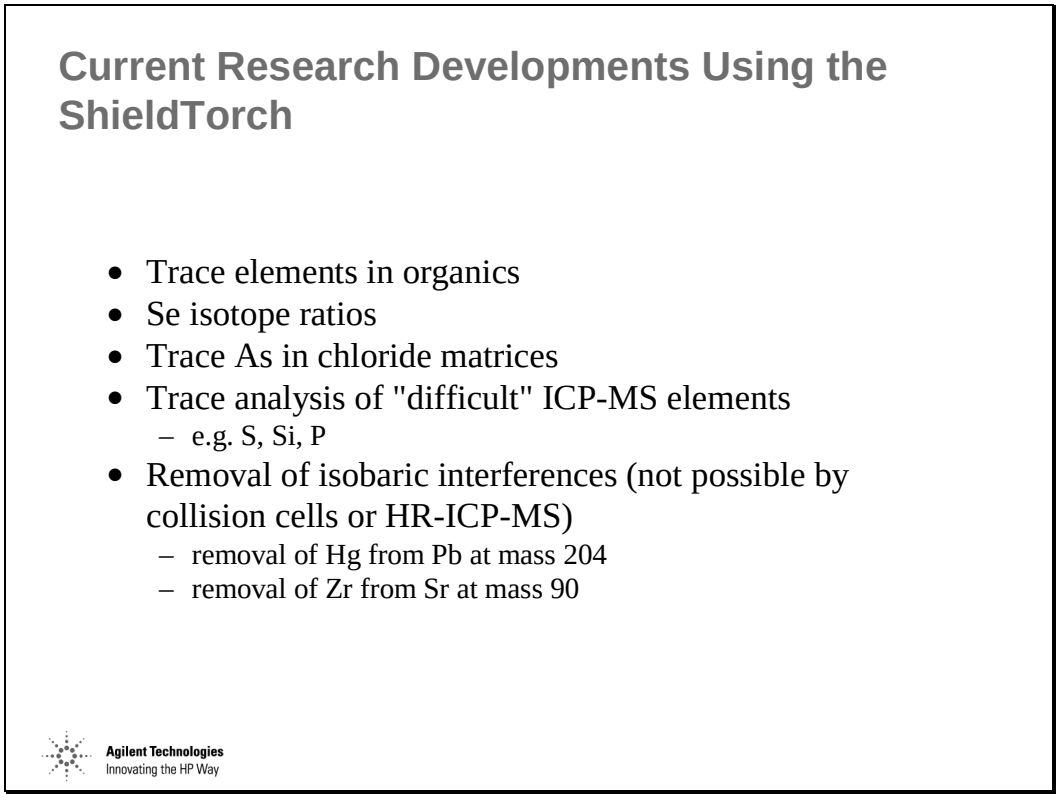
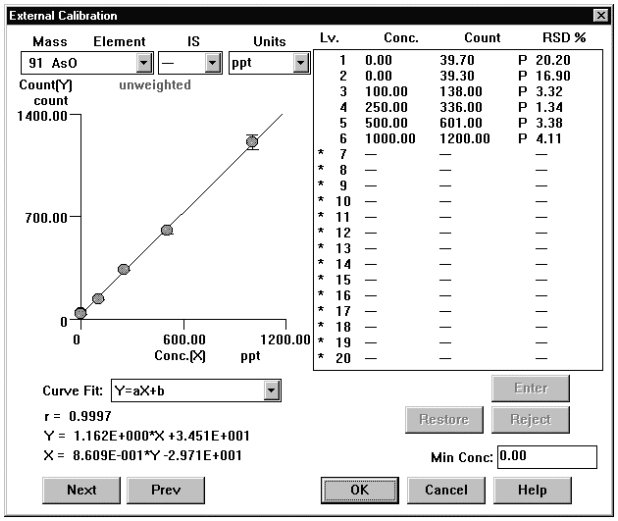


Figure 286

As Calibration in 10% HCl

As Calibration in 10% HCl

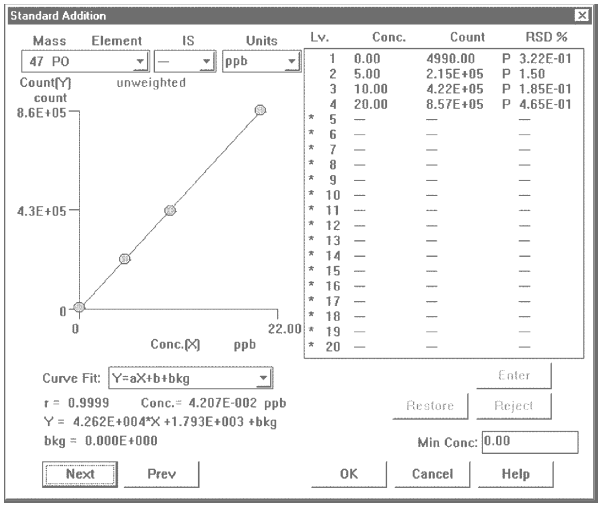


- As at 0, 100, 250, 500 and 1000ppt
- ShieldTorch cool plasma
  - ArCl removed but As not ionised
  - measure AsO at mass 91
- As DL - 40ppt (in 10% HCl)

Figure 287

Low Level P Calibration

Low Level P Calibration



- P at 0, 5, 10, 20 ppb
- ShieldTorch cool plasma
  - measure PO at mass 47
- P DL - 30ppt

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Figure 288

Low Level S Calibration

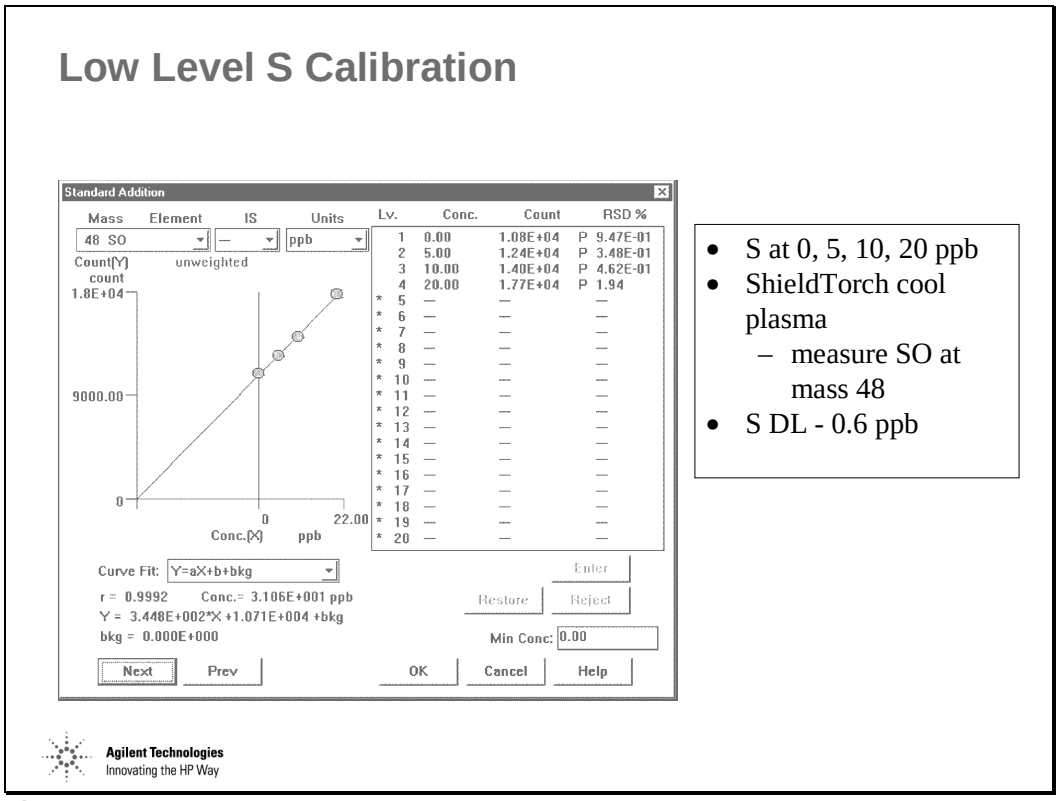
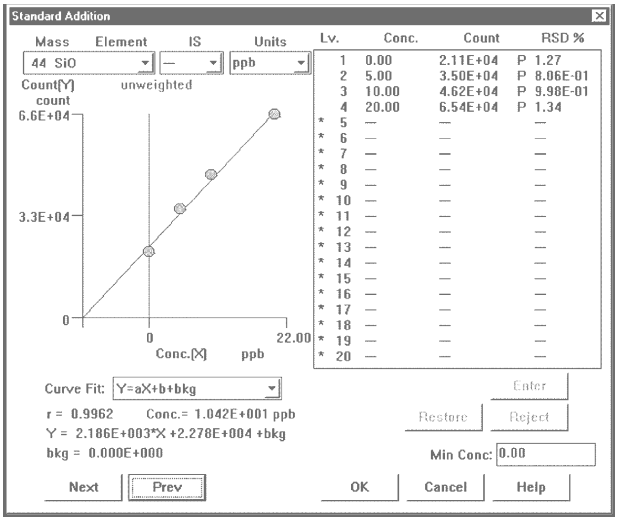


Figure 289

Low Level Si Calibration

Low Level Si Calibration



- Si at 0, 5, 10, 20 ppb
- ShieldTorch cool plasma
  - measure SiO at mass 44
- Si DL - 1.2 ppb

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Figure 290

Strategy #2: Resolve the Interferences

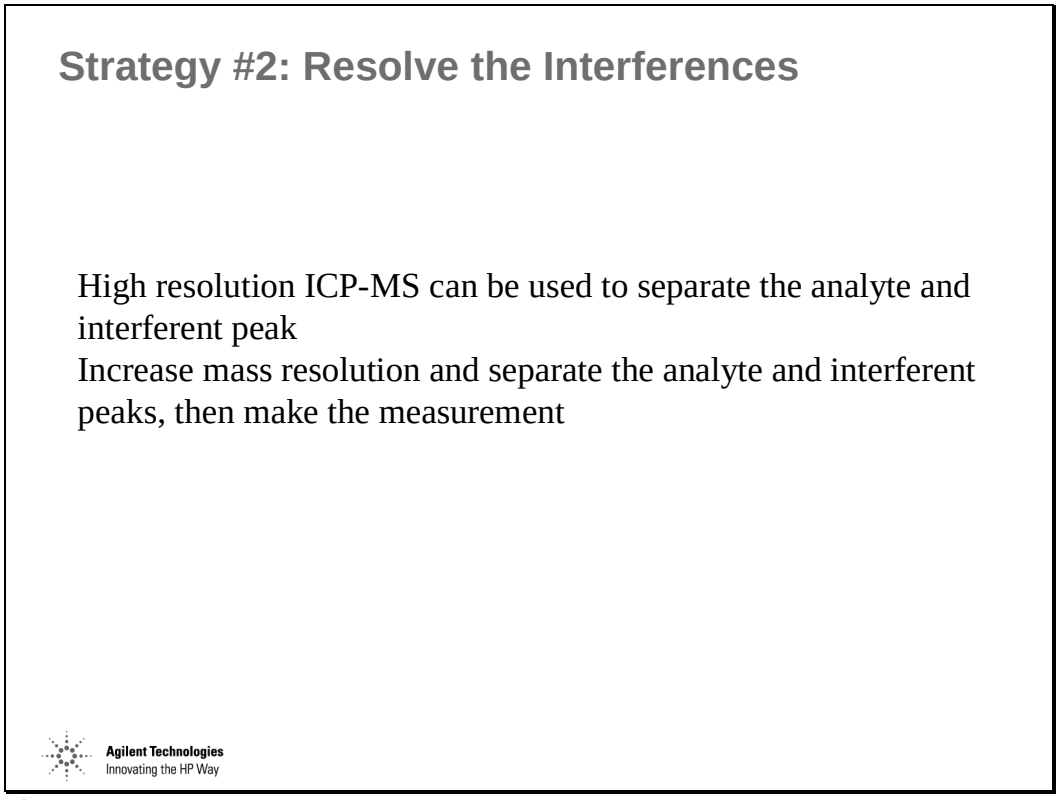

Figure 291

Limitations of HR-ICP-MS

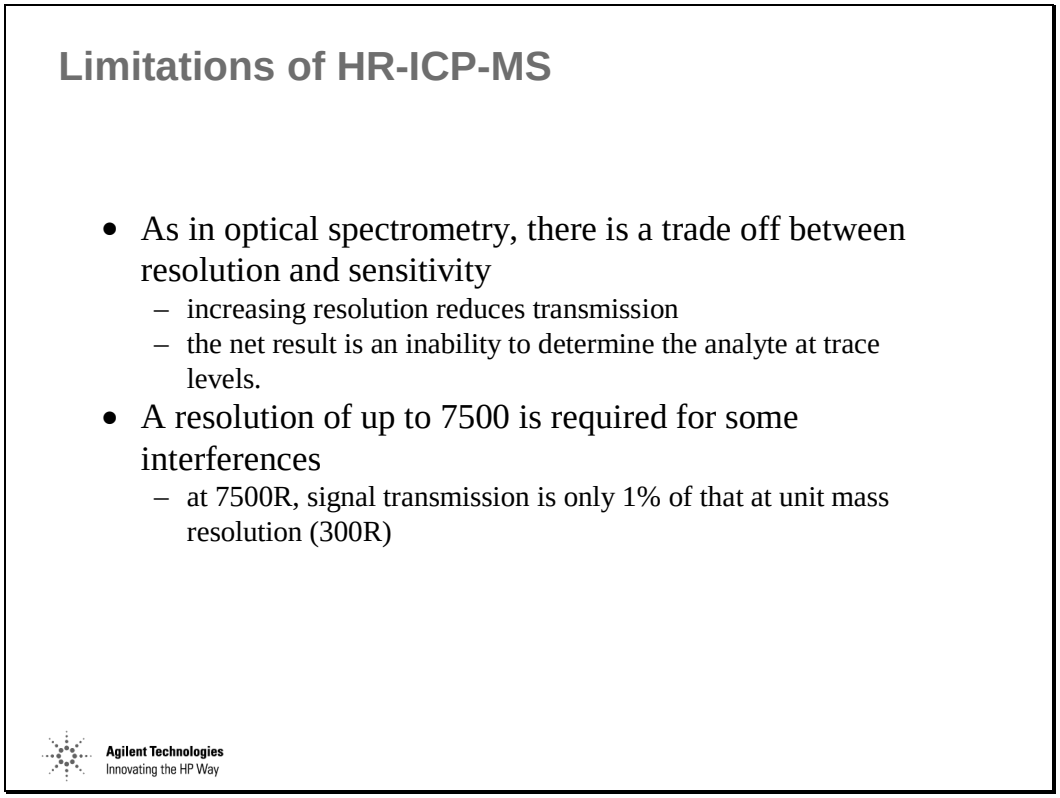

Figure 292

Resolution vs. Sensitivity

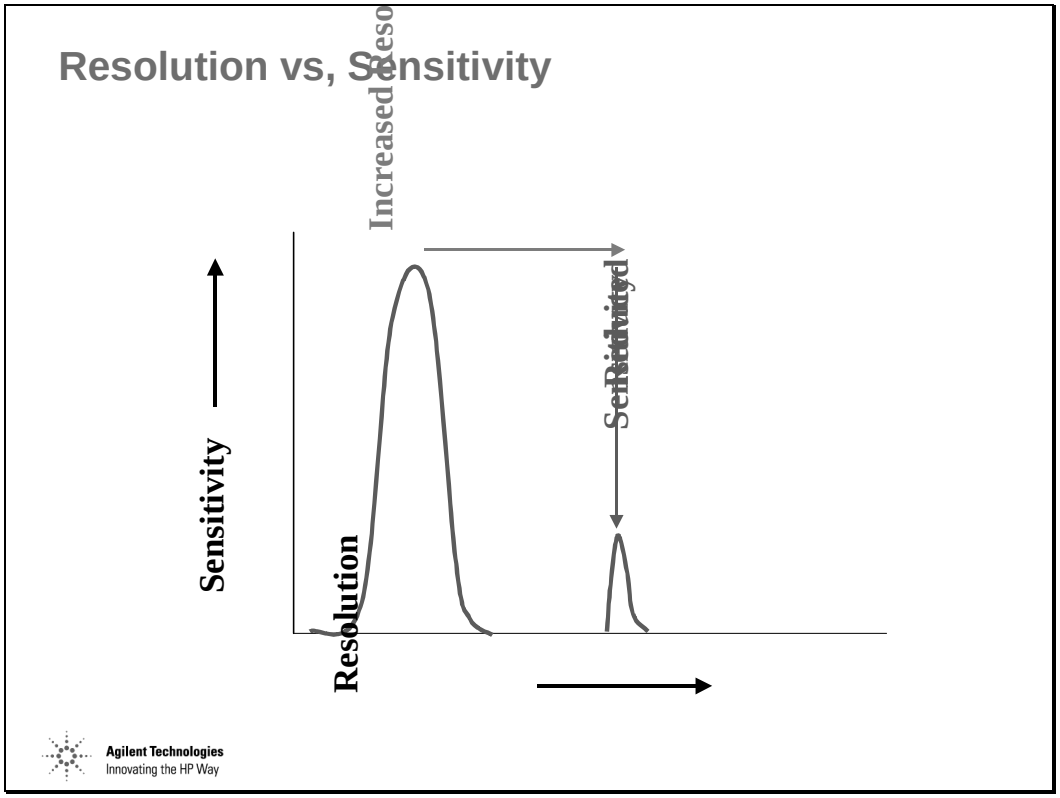

Figure 293

Other Facts About HR-ICP-MS [1]

Other Facts About HR-ICP-MS [1]

- Abundance sensitivity (tailing) is much worse in a magnetic sector than a quadrupole
  - if the analyte peak is adjacent to a large interferent peak, eg ^{39}K next to ^{40}Ar, the tail from the Ar overwhelms the K signal
  - in these cases, increasing the resolution does not help

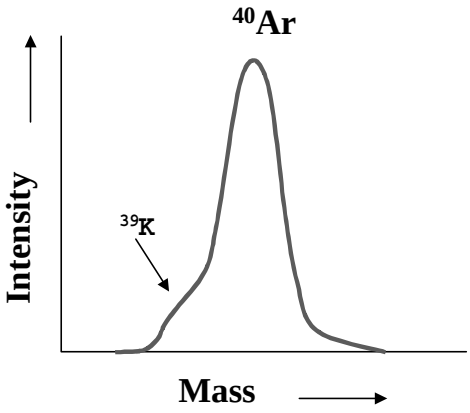

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Figure 294

Other Facts About HR-ICP-MS [2]

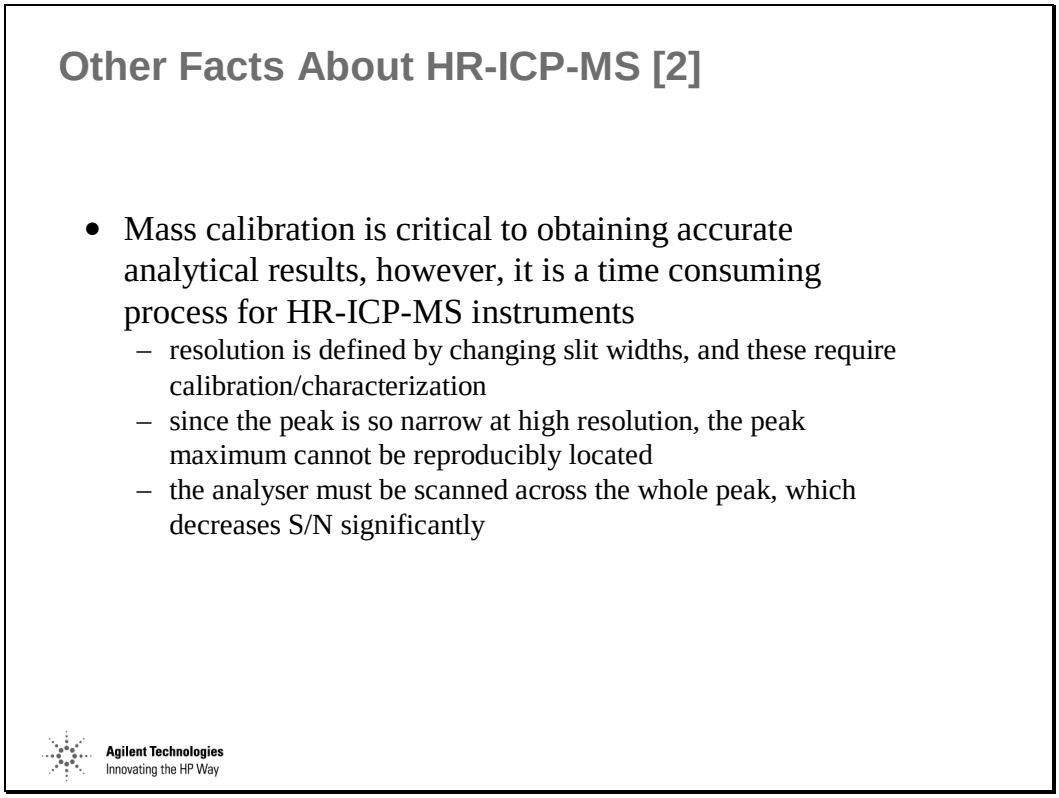

Figure 295

Other Facts About HR-ICP-MS [3]

Other Facts About HR-ICP-MS [3]

- High resolution instruments cost >$350k
- Not perceived to be appropriate for routine analysis
- Require a higher level of operator skill than ICP-QMS

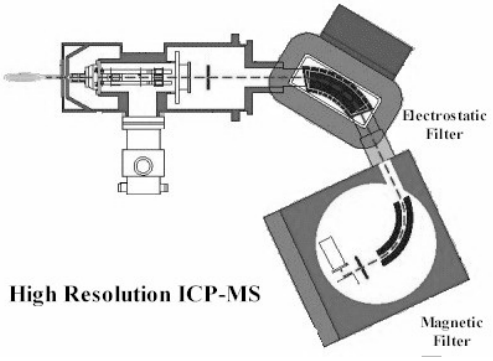

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Figure 296

Strategy #3: Dissociate Interferences Within the Spectrometer

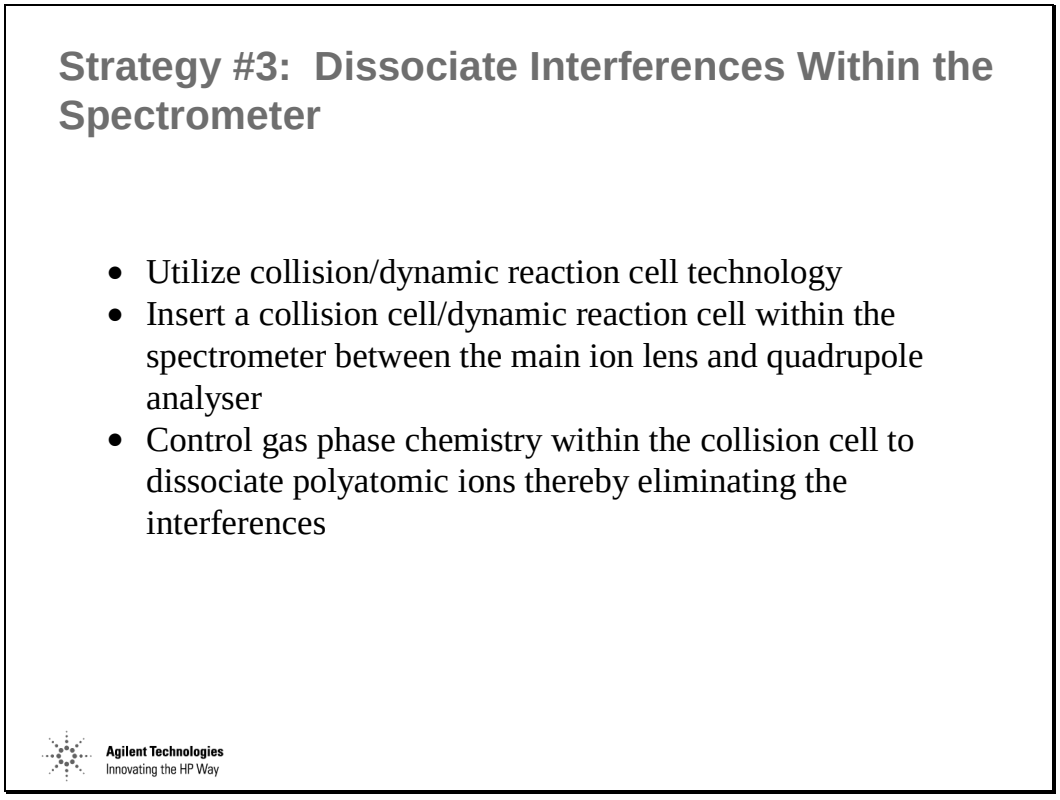

Figure 297

Principle of Collision Technology

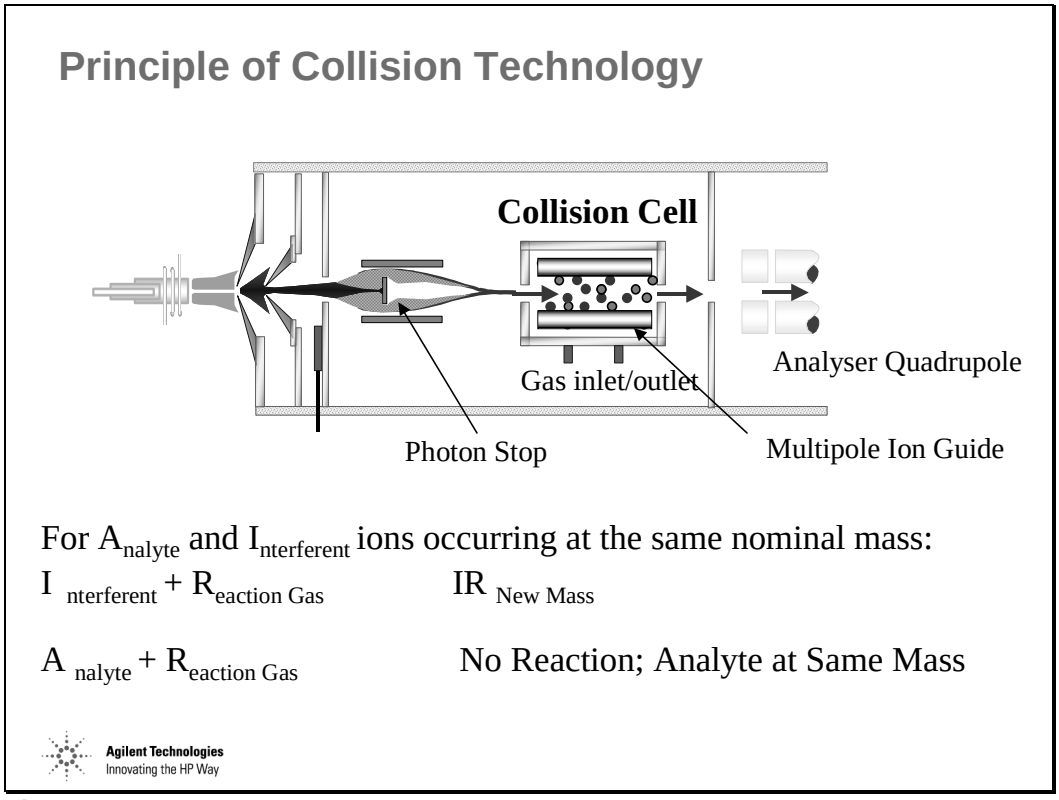

Figure 298

Selecting a Gas Phase Reagent

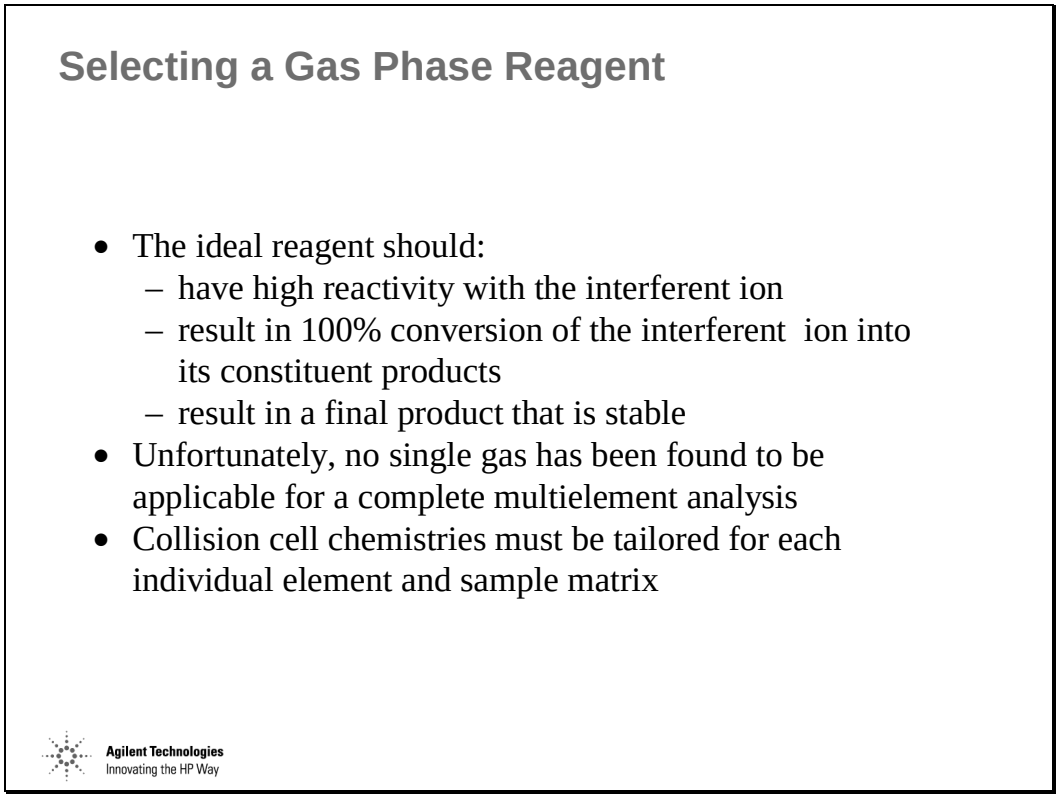

Figure 299

Optimizing the Gas Phase Reagent

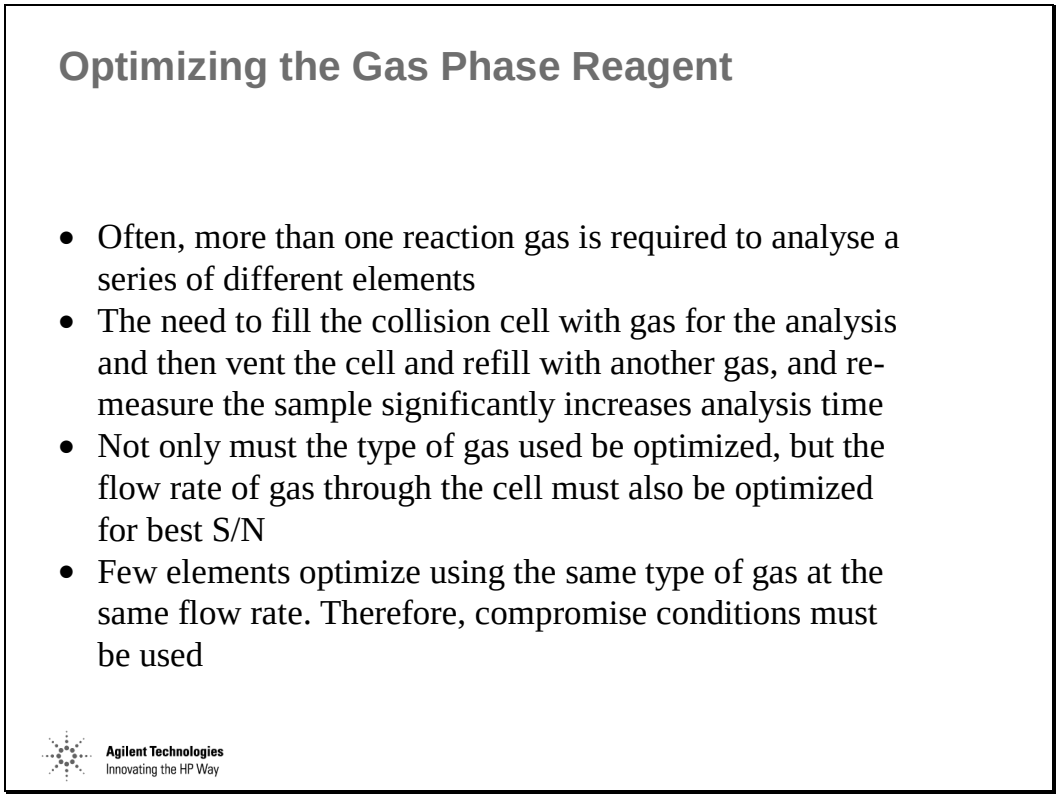

Figure 300

Side Reactions Are Inevitable!!

Side Reactions are Inevitable!!

- Side reactions i.e. unexpected reactions of the collision gas with other matrix components, have always been reported when using this technology
- For example, when using NH_3 as a collision gas when Ni is present in the sample:

Reaction		Product
$Ni^+ + NH_3$	→	$Ni(NH_3)^+$
$Ni^+ + Ni(NH_3)^+$	→	$Ni(NH_3)_2^+$
$Ni^+ + Ni(NH_3)_2^+$	→	$Ni(NH_3)_3^+$
$Ni^+ + Ni(NH_3)_3^+$	→	$Ni(NH_3)_4^+$

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Figure 301

Side Reactions Create New Interferences

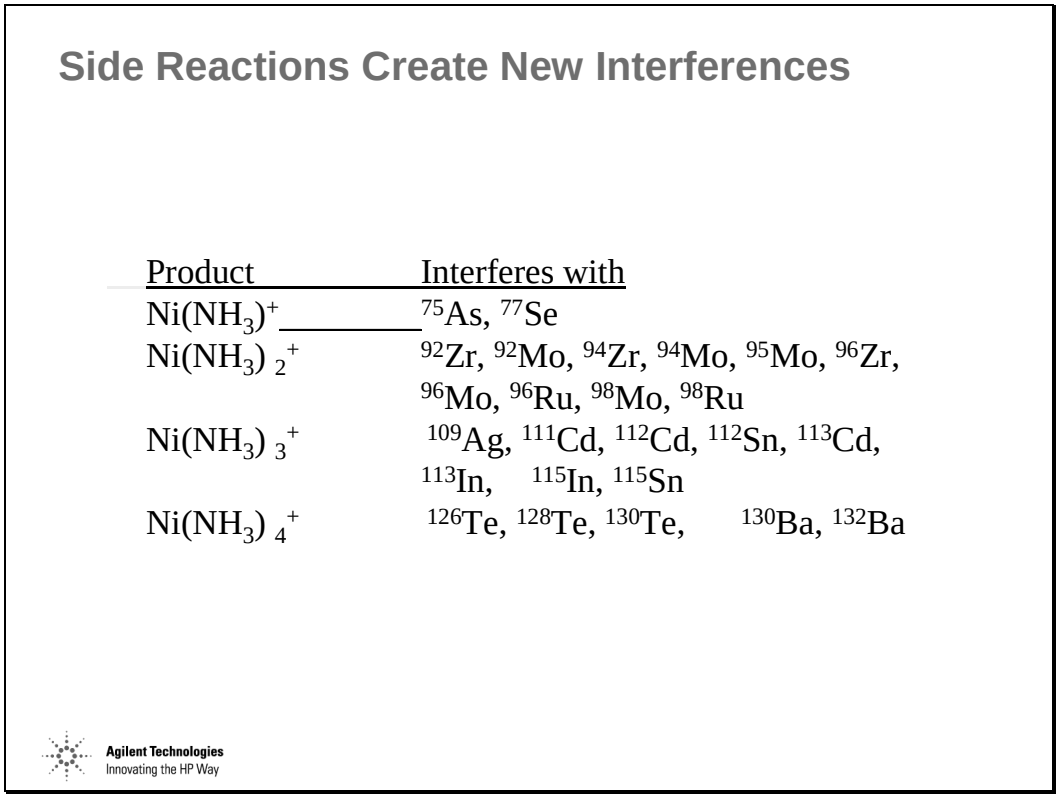

Figure 302

Hydrocarbons Are Particularly Prone To Complex Chemistries Even at Trace Levels

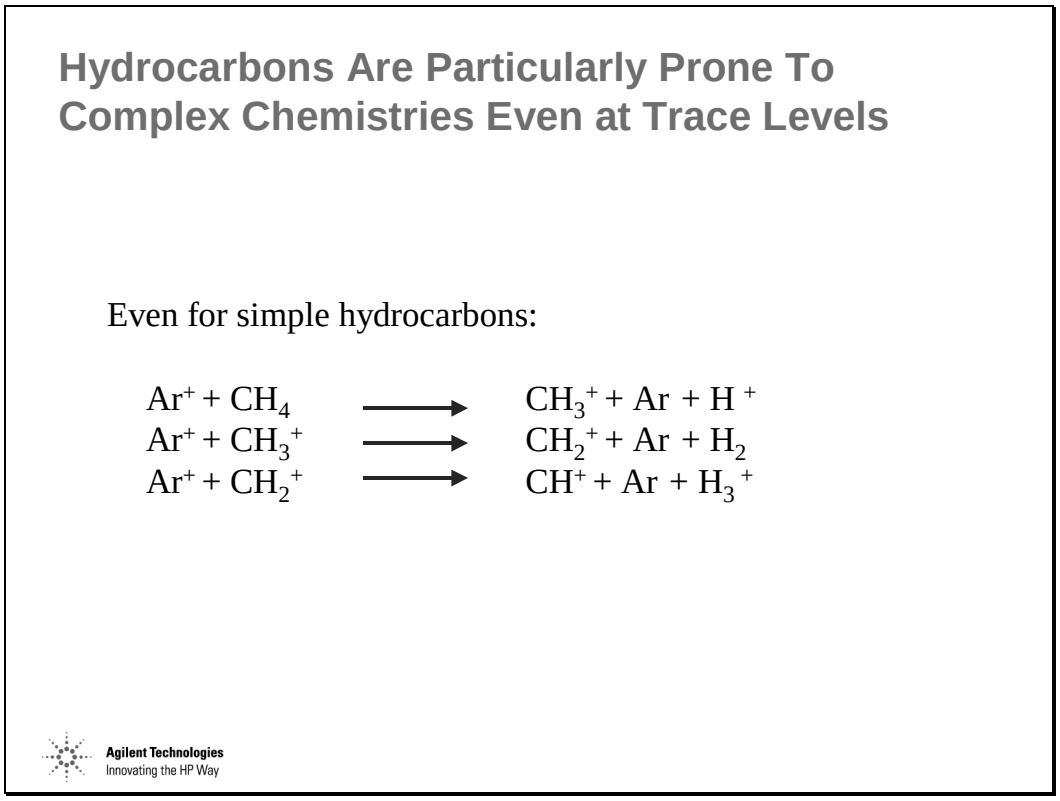

Figure 303

Effects of Sample Matrix

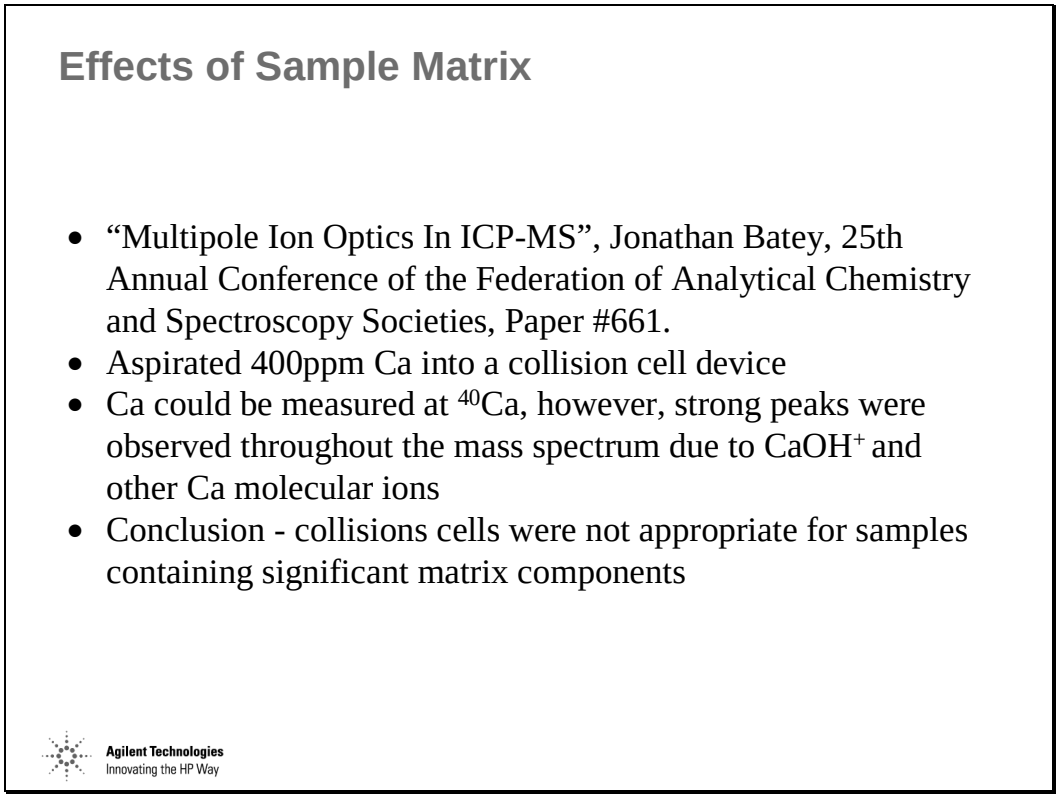

Figure 304

Strategies to Overcome the Problem of Side Reactions

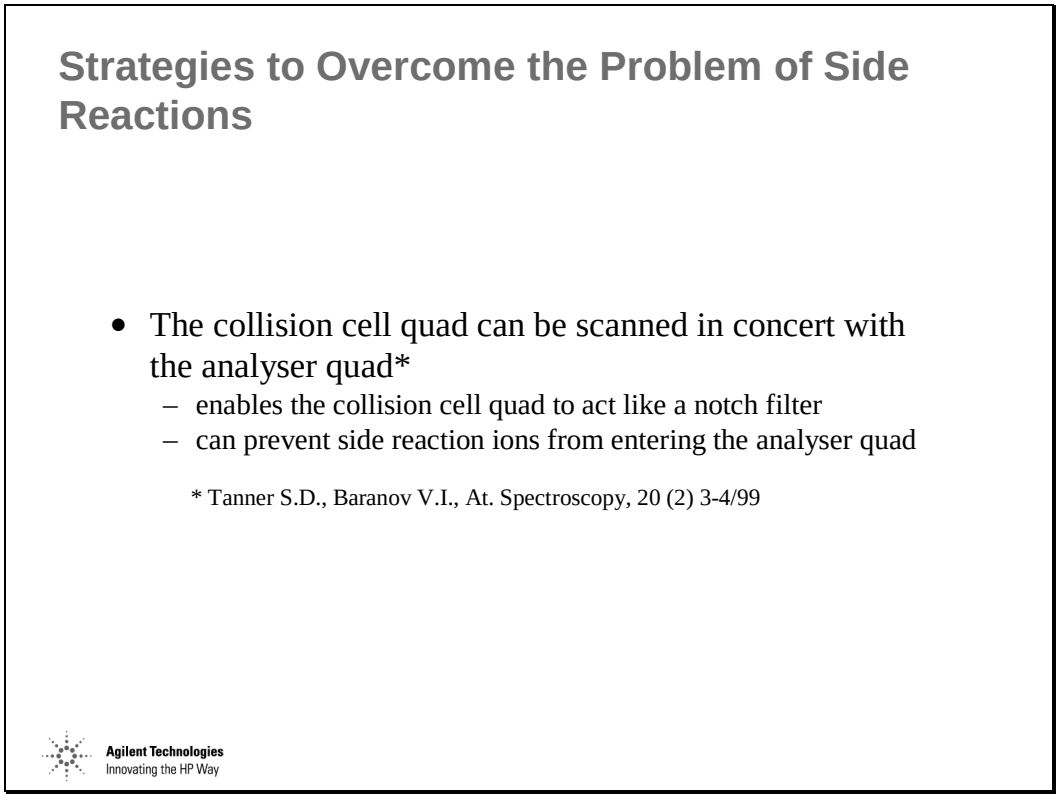

Figure 305

Limitation of Scanning the Analyzer Quad

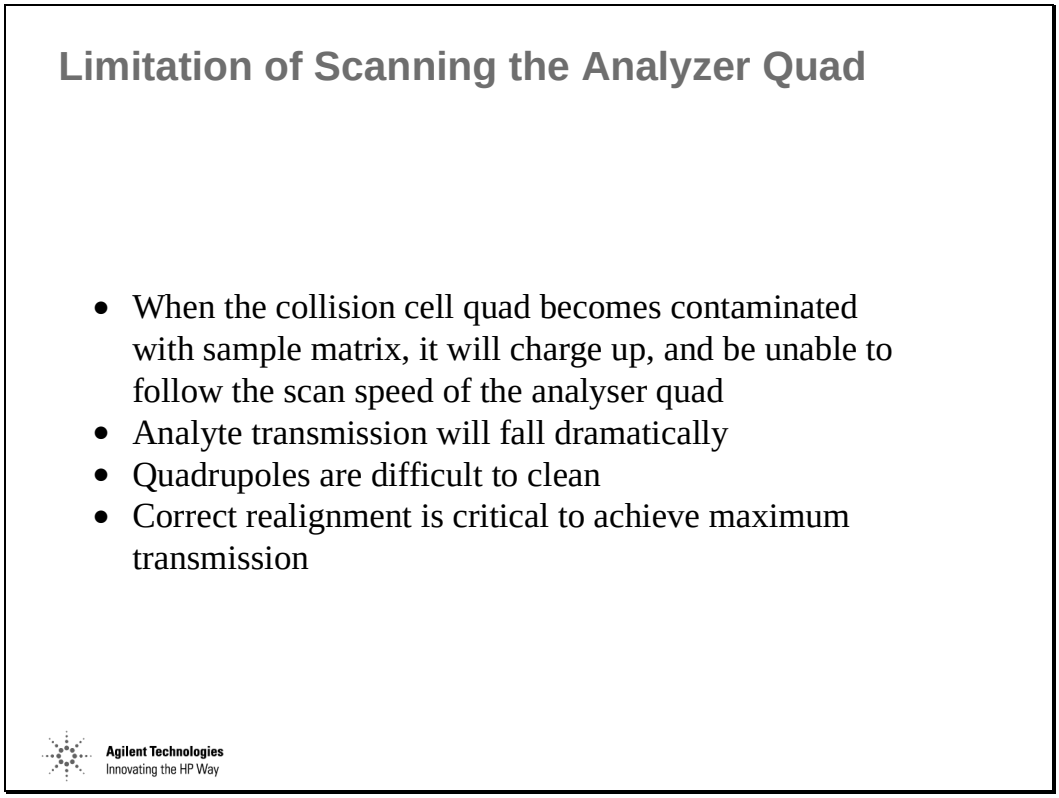

Figure 306

Collision Cells Can Create Interferences

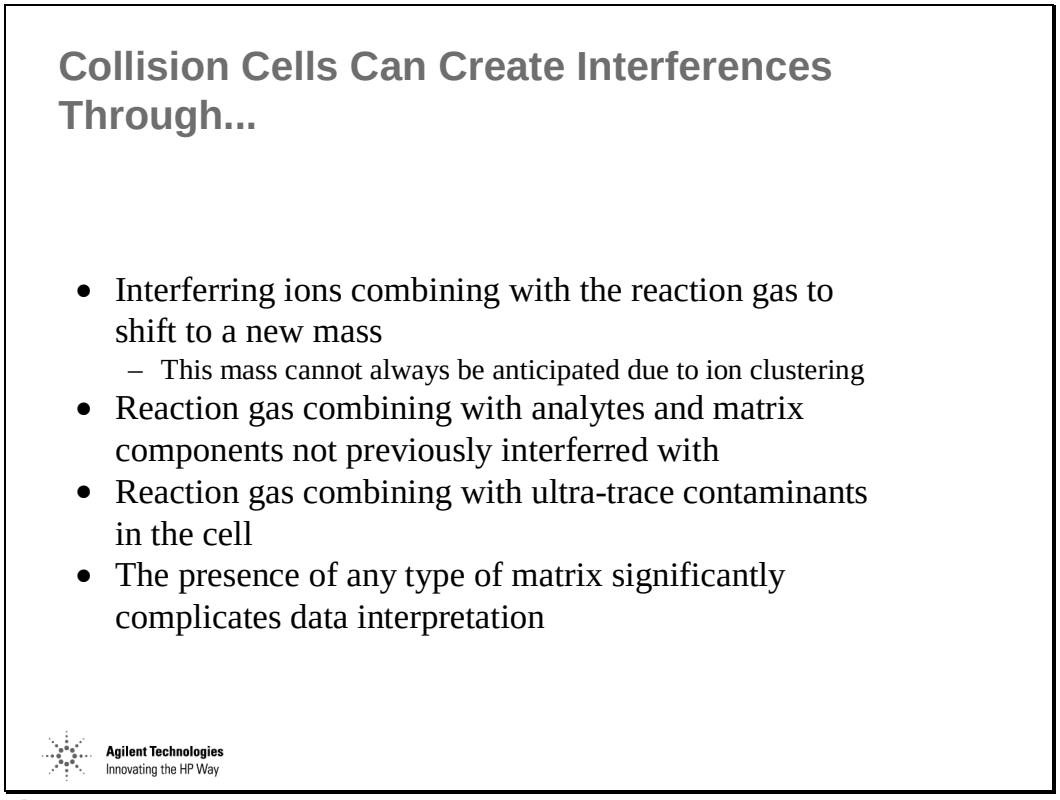

Figure 307

In Summary

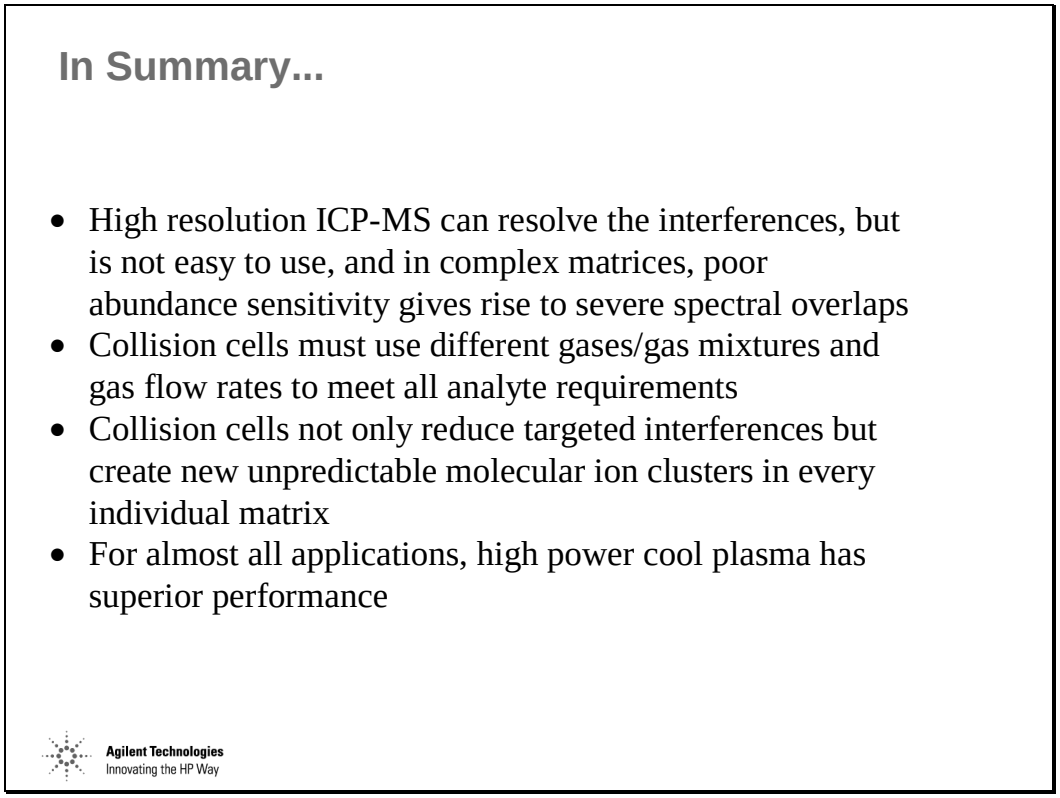

Figure 308

In Summary