



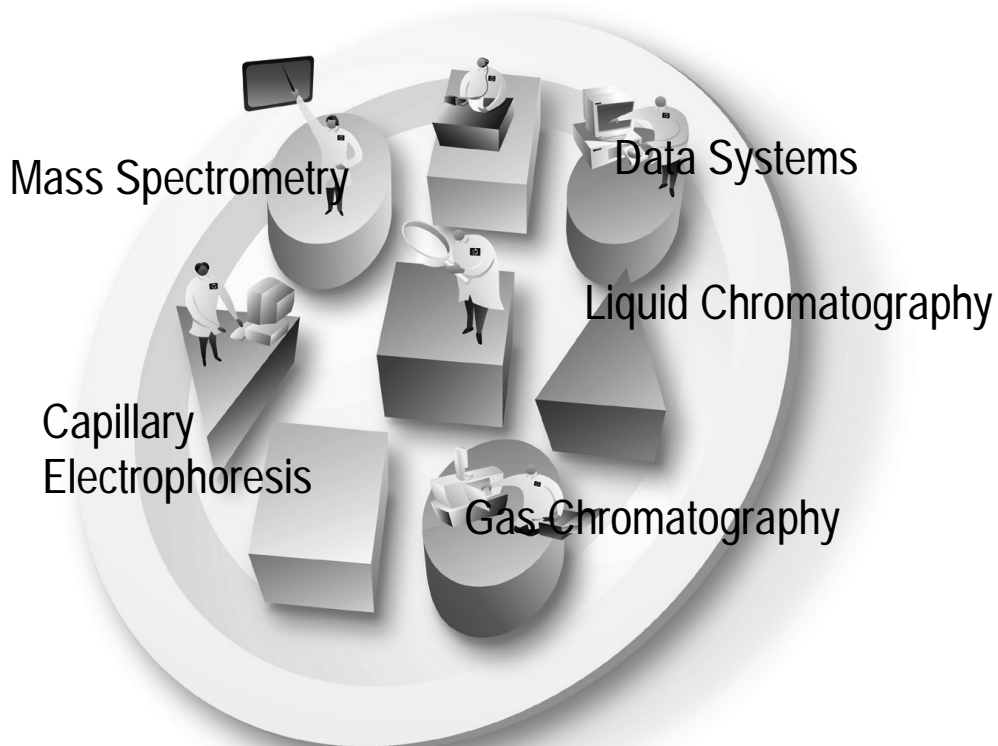
Agilent Technologies

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**





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

Manual Part Number H8974-90000

Printed in the USA January, 2001

Notice

The information contained in this document is subject to change without notice.

Agilent Technologies makes no warranty of any kind with regard to this material, including but not limited to the implied warranties of merchantability and fitness for a particular purpose.

Agilent Technologies shall not be liable for errors contained herein or for incidental, or consequential damages in connection with the furnishing, performance, or use of this material.

No part of this document may be photocopied or reproduced, or translated to another program language without the prior written consent of Agilent Technologies, Inc.

Agilent Technologies, Inc
11575 Great Oaks Way
Suite 100, MS 304B
Alpharetta, GA 30319

© 2000 by Agilent Technologies, Inc.

All rights reserved

Printed in the United States of America

Table Of Contents

INTRODUCTION: ELEMENTAL ANALYSIS.....	1
ATOMIC SPECTROMETRY	2
ATOMIC MASS AND WEIGHT.....	3
ISOTOPES AND ISOBARS	4
ANALYTICAL TECHNIQUES FOR ELEMENTAL ANALYSIS	5
ELEMENTAL ANALYSIS: FAAS.....	6
ELEMENTAL ANALYSIS: GFAAS	7
ELEMENTAL ANALYSIS: ICP-OES.....	8
ELEMENTAL ANALYSIS: ICP-MS.....	9
COMPARISON OF ELEMENTAL TECHNIQUES.....	10
GRAPHICAL COMPARISON OF ELEMENTAL TECHNIQUES	11
COMPARISON OF THE COMPLEXITY OF MULTI-ELEMENTAL TECHNIQUES.....	12
USERS/APPLICATIONS OF ICP-MS.....	13
MULTI-ELEMENTAL ANALYSIS OF METALS	14
INTRODUCTION: INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY	15
WHAT IS ICP-MS?.....	16
ADVANTAGES OF ICP-MS	17
AGILENT TECHNOLOGIES AND ICP-MS	18
PROCESSES IN ICP-MS.....	19
OVERVIEW OF AGILENT 7500 FEATURES	20
SCHEMATIC DIAGRAM OF AGILENT 7500A	21
SCHEMATIC DIAGRAM OF AGILENT 7500S.....	23
ISIS FOR APPLICATION FLEXIBILITY.....	24
SAMPLE INTRODUCTION.....	25
AGILENT 7500 SAMPLE INTRODUCTION.....	26
AUTOSAMPLERS.....	27
TYPICAL NEBULIZER.....	28
SPECIALIZED SAMPLE INTRODUCTION SYSTEMS.....	29
TYPICAL SPRAY CHAMBER – DOUBLE PASS	30
DROPLET DISTRIBUTION WITH AND WITHOUT SPRAY CHAMBER.....	31
NEW DESIGN AGILENT ICP TORCH BOX	32
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY	33
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (CONTINUED)	34
WHY ARGON?.....	35
DISTRIBUTION OF IONS IN THE PLASMA	36
SAMPLE IONIZATION IN THE PLASMA.....	37
FULL MASS CONTROL OF ALL GAS FLOWS.....	38
INTERFACE.....	39
AGILENT 7500 ION LENS SYSTEM.....	40
DISTRIBUTION OF IONS AND ELECTRONS AROUND THE INTERFACE.....	41
ION ENERGY DISTRIBUTION IN THE INTERFACE	42
THE ELECTROSTATIC LENSES	43
WHY “OFF-AXIS”?.....	44
LOW TRANSMISSION PHOTON STOP SYSTEM	45
AGILENT HIGH TRANSMISSION OFF-AXIS SYSTEM	46
ION FOCUSING – NEW OMEGA II LENS	47
FLAT RESPONSE CURVE – HIGH SENSITIVITY AT ALL MASSES.....	48
AGILENT 7500 QUADRUPOLE	49

RESOLUTION AND ABUNDANCE SENSITIVITY	50
NEW SIMULTANEOUS DUAL MODE DETECTOR & HIGH SPEED LOG AMPLIFIER – TRUE 9 ORDER DYNAMIC RANGE.....	51
THE DETECTOR	52
INTERFERENCES IN ICP-MS	53
INTERFERENCES IN ICP-MS	54
MASS SPECTROSCOPIC INTERFERENCES.....	55
ISOBARIC INTERFERENCES	56
POLYATOMIC INTERFERENCES	57
MASS SPECTROSCOPIC INTERFERENCES.....	58
OPTIMIZING TO MINIMIZE INTERFERENCE FORMATION IN THE PLASMA [1].....	59
OPTIMIZING TO MINIMIZE INTERFERENCE FORMATION IN THE PLASMA [2].....	60
OPTIMIZING TO MINIMIZE INTERFERENCE FORMATION IN THE PLASMA [3].....	61
EFFECT OF PLASMA TEMPERATURE ON DEGREE OF IONIZATION.....	62
EFFICIENT AEROSOL DECOMPOSITION	63
OXIDES AND DOUBLY CHARGED IONS	64
DEALING WITH MASS SPECTROSCOPIC INTERFERENCES	65
INTERFERENCE EQUATIONS	66
AS INTERFERENCE CORRECTION.....	67
INTERFERENCE CORRECTION EQUATIONS - AGILENT 7500.....	68
NON-SPECTROSCOPIC INTERFERENCES	69
EFFECT OF HIGH DISSOLVED SOLIDS	70
FIRST IONIZATION POTENTIAL	71
IONIZATION EFFICIENCY	72
SIGNAL SUPPRESSION	73
MATRIX EFFECTS – ON LOW MASS ANALYTE	74
MATRIX EFFECTS – ON MEDIUM MASS ANALYTE.....	75
MATRIX EFFECTS – ON HIGH MASS ANALYTE	76
SPACE CHARGE INTERFACE AND LENS REGION	77
IONIZATION SUPPRESSION PLASMA REGION	78
WHAT CAN BE DONE ABOUT MATRIX EFFECTS	79
TUNING THE AGILENT 7500.....	81
WHY TUNE THE ICP-MS?	82
TUNING PROCEDURE OVERVIEW.....	83
AGILENT 7500 ICP-MS MANUAL TUNE CHECKLIST [1].....	84
AGILENT 7500 ICP-MS MANUAL TUNE CHECKLIST [2].....	85
AUTOTUNE SCREEN	86
AUTOTUNING OF ICP TORCH POSITION AND NEW TARGET TUNE	87
FEATURES OF AUTOTUNE (1)	88
FEATURES OF AUTOTUNE (2)	89
CHOOSING THE AUTOTUNE MODE	90
BASICS OF THE SOFT EXTRACTION MODE.....	91
COMPARISON OF EXTRACTION MODES SETTINGS	92
AUTOTUNE - TARGET SETTING	93
TARGET SETTING - RANGE SETTING	94
SENSITIVITY TUNING	95
PEAK SHAPE AND RESOLUTION.....	96
ABUNDANCE SENSITIVITY	97
QUADRUPOLE MASS FILTER - SCAN LINE.....	98
DETECTION LIMITS IN NORMAL MODE	99
DETECTION LIMITS IN SOFT EXTRACTION MODE.....	100
LOW BECS IN SOFT EXTRACTION MODE	101
PULSE/ANALOG (P/A) TUNING	102

MAINTENANCE OF THE AGILENT 7500.....	103
MAINTENANCE SCHEDULE.....	104
RUNNING TIME MAINTENANCE SCREEN	105
EARLY MAINTENANCE FEEDBACK (EMF)	106
NORMAL MAINTENANCE OF THE SAMPLE INTRODUCTION SYSTEM	107
OVERNIGHT CLEANING OF THE SAMPLE INTRODUCTION SYSTEM.....	108
SAMPLE INTRODUCTION MAINTENANCE.....	109
NEBULIZER CONNECTIONS.....	110
MAINTENANCE OF A BABINGTON NEBULIZER.....	111
TORCH MAINTENANCE.....	112
INTERFACE MAINTENANCE	113
MAINTENANCE OF THE CONES	114
EXTRACTION LENSES MAINTENANCE	115
EXTRACTION LENSES	116
CLEANING OF THE EINZEL LENS AND OMEGA LENS ASSEMBLY	117
INSTRUMENT SHUTDOWN	118
REMOVAL OF THE EINZEL LENS - OMEGA LENS ASSEMBLY	119
EXPANDED VIEW OF EINZEL LENS - OMEGA LENS ASSEMBLY	120
PLATE BIAS LENS.....	121
PENNING GAUGE.....	122
ROTARY PUMP MAINTENANCE	123
CHANGING ROTARY PUMP OIL	124
MAINTENANCE LOGBOOK SETTING	125
MAINTENANCE LOGBOOK	126
SAMPLE INTRODUCTION MAINTENANCE.....	127
AIR FILTERS MAINTENANCE	128
INSTRUMENT START-UP	129
INTERNAL STANDARDIZATION IN ICP-MS.....	131
THE ROLE OF INTERNAL STANDARDS	132
HOW THE INTERNAL STANDARDS WORK - 1	133
HOW THE INTERNAL STANDARDS WORK - 2	134
CHOICE OF THE INTERNAL STANDARD	135
CONCENTRATION OF INTERNAL STANDARDS	136
ON-LINE ADDITION OF INTERNAL STANDARDS	137
SAMPLE PREPARATION TECHNIQUES FOR ICP-MS.....	139
CONTAMINATION	140
TYPES OF CONTAMINATION	141
CHALLENGES OF TRACE ANALYSIS.....	142
WHEN A CONTAMINATION CAN OCCUR.....	143
REAGENTS.....	144
WATER - MILLIPORE.....	145
NITRIC ACID	146
SELECTED METHODS OF SAMPLE PREPARATION.....	147
COMMONLY USED REAGENTS (1)	148
COMMONLY USED REAGENTS (2)	149
COMMONLY USED REAGENTS (3)	150
SEMI-QUANTITATIVE ANALYSIS OF SAMPLES.....	151
SEMI-QUANTITATIVE ANALYSIS.....	152
WHAT IS SEMI-QUANTITATIVE ANALYSIS?	153
DATA ACQUISITION	154
METHOD SET-UP FOR SEMI-QUANTITATIVE ANALYSIS	155
PARAMETERS SELECTION - SPECTRUM ACQUISITION.....	156

PARAMETERS SELECTION - SELECTION OF MASSES	157
MORE ACQUISITION PARAMETERS.....	158
REPORT GENERATION	159
SEMI-QUANT PARAMETERS	160
SEMI-QUANTITATIVE DATA ANALYSIS	161
EDITING PARAMETERS	162
DAILY UPDATE OF THE SEMI-QUANT PARAMETERS	163
INTERNAL STANDARD CORRECTION FOR OFF-LINE INTERNAL STANDARD ADDITION	164
INTERNAL STANDARD CORRECTION FOR ON-LINE INTERNAL STANDARD ADDITION.....	165
EXAMPLE OF SEMI-QUANT REPORT [1].....	166
EXAMPLE OF SEMI-QUANT REPORT [2].....	167
GENERATING A SEMI-QUANT REPORT.....	168
MANUAL VERIFICATION OF THE DATA	169
QUANTITATIVE ANALYSIS OF SAMPLES	171
WHAT IS QUANTITATIVE ANALYSIS?	172
METHOD SET-UP FOR QUANTITATIVE ANALYSIS	173
STEP ONE: EDITING THE AMU SELECT FILE	174
EDITING A METHOD FOR QUANTITATIVE ANALYSIS	175
METHOD INFORMATION	176
ACQUISITION MODES	177
ACQUISITION PARAMETERS - MULTITUNE METHOD	179
PERIODIC TABLE	180
MASS TABLE	181
PERISTALTIC PUMP PROGRAM	182
RAW DATA CORRECTIONS	183
CONFIGURE REPORTS.....	184
CALIBRATION.....	185
CALIBRATION TABLE	186
SAVE THE CALIBRATION AND THE METHOD	187
QUANTITATIVE DATA ANALYSIS	188
STANDARD DATA FILES	189
CALIBRATION CURVES.....	190
EXAMPLES OF THE CALIBRATION CURVES FOR “EXCLUDED”	191
SIMPLE SEQUENCING (INTELLIGENT SEQUENCING DISABLED)	193
SEQUENCING	194
ASX-500 VIAL POSITION NOMENCLATURE.....	195
SEQUENCING	196
SAMPLE LOG TABLE - SEQUENCE FLOW AND PERIODIC BLOCK	197
SAMPLE LOG TABLE	198
SPECIAL FEATURES - KEYWORDS	199
RUNNING A SEQUENCE.....	200
CHAINED SEQUENCE.....	201
CHAINED SEQUENCE	202
METHOD OF STANDARD ADDITIONS (MSA).....	203
EXTERNAL CALIBRATION.....	204
PROS AND CONS OF EXTERNAL CALIBRATION	205
METHOD OF STANDARD ADDITION (MSA)	206
PROS AND CONS OF METHOD OF STANDARD ADDITIONS.....	207
DETERMINATION OF URANIUM IN URINE BY MSA.....	208
CONVERTING FROM MSA TO EXTERNAL CALIBRATION	209
MATRIX-MATCHED URANIUM IN URINE EXTERNAL CALIBRATION	210
OFF-LINE DATA ANALYSIS AND SEQUENCE REPROCESSING	211

OFF-LINE DATA ANALYSIS	212
PROCEDURE FOR OFF-LINE DATA ANALYSIS	213
OFF-LINE CALIBRATION REVIEW OF CURRENTLY RUNNING METHOD	214
USING DOList FOR OFF-LINE DATA REPROCESSING.....	215
HOW TO USE DOList	216
SELECTING FILES USING DOList	217
SEQUENCE - REPROCESSING DATA BATCH	218
SEQUENCE REPROCESSING.....	219
CUSTOM REPORTS AND DATABASES	221
WHAT YOU WILL LEARN.....	222
CUSTOM REPORTS AND DATABASES	223
CREATING AND EDITING A REPORT TEMPLATE.....	224
CUSTOM REPORTS - REPORT WIZARD.....	225
CUSTOM REPORTS - DRAG AND DROP (1)	227
CUSTOM REPORTS - DRAG AND DROP (2)	228
FORMATTING CUSTOM REPORTS.....	229
CUSTOM REPORTS - PRINTING SET-UP	230
CUSTOM REPORTS - SAVING THE TEMPLATE	231
PRINTING CUSTOM REPORTS - INTERACTIVELY	232
PRINTING CUSTOM REPORTS - PRINTING MULTIPLE FILES [1]	233
PRINTING CUSTOM REPORTS - PRINTING MULTIPLE FILES [2]	234
DATABASES	235
DATABASE WIZARD.....	236
DATABASE - DRAG AND DROP	237
DATABASE - FORMATTING.....	238
DATABASE - CHARTS	239
GLOBAL CHART OPTIONS	240
DATABASE - SAVING.....	242
UPDATING THE DATABASE - INTERACTIVELY	243
UPDATE THE DATABASE - MULTIPLE FILES [1].....	244
UPDATE THE DATABASE - MULTIPLE FILES [2].....	245
ISOTOPE RATIO MEASUREMENTS.....	247
EDITING A METHOD FOR QUANTITATIVE ANALYSIS	248
ACQUISITION MODES	249
ACQUISITION PARAMETERS FOR ISOTOPIC RATIO MEASUREMENTS.....	251
REPORT SELECTION	252
SETTING PARAMETERS FOR ISOTOPIC RATIOS.....	253
EXAMPLE OF THE ISOTOPIC RATIO REPORT	254
AGILENT ICP-MS CHEMSTATION AND WINDOWS OVERVIEW	255
THE WINDOWS INTERFACE	256
WINDOWS MENUS.....	257
USEFUL WINDOWS TIPS	258
MAINTAINING THE COMPUTER SYSTEM.....	259
WINDOWS NT EXPLORER - ENHANCED FILE MANAGEMENT.....	260
DIRECTORY STRUCTURE OF THE AGILENT CHEMSTATION.....	261
FILE NAMING	262
CHEMSTATION FILE EXTENSIONS	263
AN OVERVIEW OF ICP-MS ENVIRONMENTAL APPLICATIONS	265
OPTIMIZING AGILENT 7500 FOR ENVIRONMENTAL SAMPLES ANALYSIS	266
ENVIRONMENTAL TUNING	267
THREE GOALS OF ENVIRONMENTAL TUNING.....	269
TUNING FLOW CHART.....	271

RECOMMENDATIONS ON INTERFERENCE EQUATIONS	272
MORE INTERFERENCE CORRECTIONS	274
CALIBRATION STANDARDS	276
LINEAR RANGE DETERMINATION.....	277
INTERFERENCE CHECK SAMPLES	278
TROUBLESHOOTING ENVIRONMENTAL APPLICATIONS [1]	279
TROUBLESHOOTING ENVIRONMENTAL APPLICATIONS [2]	281
TROUBLESHOOTING ENVIRONMENTAL APPLICATIONS [3]	283
TROUBLESHOOTING ENVIRONMENTAL APPLICATIONS [4]	285
SEMICONDUCTOR APPLICATIONS OF ICP-MS AND ADVANTAGES OF AGILENT 7500S SYSTEM.....	287
CHEMICALS AND MATERIALS USED IN SEMICONDUCTOR INDUSTRY	288
METALS ANALYSIS IN THE SEMICONDUCTOR INDUSTRY - CUSTOMER GROUPS AND REQUIREMENTS.....	289
SHIELDTORCH INTERFACE	290
SHIELDTORCH INTERFACE	291
NORMAL AND “COOL” PLASMAS	292
SHIELD TORCH “COOL PLASMA”	293
SHIELD TORCH INSTALLATION.....	294
COOL PLASMA TUNING.....	295
ADVANTAGES OF COOL PLASMA AT HIGHER POWER (900 - 1100 W)	296
ADVANTAGES OF COOL PLASMA AT LOWER POWER (700-800 W)	297
DETECTION LIMITS STUDY [1]	298
DETECTION LIMITS STUDY [2]	299
AUTOMATIC SWITCHING BETWEEN NORMAL AND COOL PLASMA.....	300
INTELLIGENT SEQUENCE TRAINING TEXT.....	301
WHAT IS INTELLIGENT SEQUENCE?	302
TYPICAL ANALYTICAL FLOW.....	303
USING INTELLIGENT SEQUENCING	304
SETTING UP A QC CONFIGURATION.....	319
LABORATORY 1: AGILENT 7500 CONFIGURATION, STARTUP AND TUNING.....	327
CONFIGURATION	328
STARTUP AND TUNING	329
AGILENT 7500 STARTUP CHECKLIST	330
SHUTDOWN CHECKLIST	331
LABORATORY 2: AGILENT 7500 ROUTINE MAINTENANCE	333
GENERAL	334
SAMPLE INTRODUCTION.....	335
INTERFACE.....	336
NEBULIZER, SPRAY CHAMBER AND TORCH.....	337
RE-IGNITE THE PLASMA AND CHECK THE TUNE	338
LABORATORY 3: SEMI-QUANTITATIVE ANALYSIS.....	339
SEMI-QUANTITATIVE ANALYSIS	340
LABORATORY 4: QUANTITATIVE ANALYSIS OF UNKNOWN SAMPLE.....	341
QUANTITATIVE ANALYSIS	342
APPENDIX 1 – GENERAL INFORMATION.....	343
PROFESSIONAL ORGANIZATIONS.....	344
JOURNALS	345
SELECTED WEB SITES (1).....	346

SELECTED WEB SITES (2).....	347
APPENDIX 2 – FLOW CHATS	349
MANUAL TUNE TROUBLESHOOTING FLOWCHART [1].....	350
MANUAL TUNE TROUBLESHOOTING FLOWCHART [2].....	351
APPENDIX 3 – DEALING WITH POLYATOMICS	353
THE PROBLEM.....	354
STRATEGY #1: (HIGH POWER) COOL PLASMA ANALYSIS	355
COMMERCIALIZATION OF COOL PLASMA ANALYSIS	356
SCHEMATIC OF AGILENT SHIELDTORCH	357
NOT ALL COOL PLASMAS* ARE THE SAME! [1]	358
NOT ALL COOL PLASMAS* ARE THE SAME! [2]	359
FE IN 31% H ₂ O ₂ - 5 PPT SPIKE RECOVERY.....	360
SHIELDTORCH TECHNOLOGY ELIMINATES INTERFERENCES BEFORE THEY FORM!	361
CAN HEAVY MATRICES BE ANALYZED?	362
CR IN UNDILUTED METHANOL.....	363
EXAMPLE OF HEAVY MATRIX ANALYSIS.....	364
CALIBRATION FOR ⁵⁶ Fe IN 1000 PPM PT.....	365
CALIBRATION FOR ⁶⁶ Zn IN 1000 PPM PT	366
DETERMINATION OF Se BY HIGH POWER COOL PLASMA	367
SPECTRUM OF 10 PPB Se AND BLANK	368
CALIBRATION FOR ⁸⁰ Se.....	369
DETECTION LIMITS FOR Se BY COOL PLASMA	370
CURRENT RESEARCH DEVELOPMENTS USING THE SHIELDTORCH.....	371
AS CALIBRATION IN 10% HCL	372
LOW LEVEL P CALIBRATION.....	373
LOW LEVEL S CALIBRATION.....	374
LOW LEVEL Si CALIBRATION.....	375
STRATEGY #2: RESOLVE THE INTERFERENCES.....	376
LIMITATIONS OF HR-ICP-MS	377
RESOLUTION VS. SENSITIVITY	378
OTHER FACTS ABOUT HR-ICP-MS [1].....	379
OTHER FACTS ABOUT HR-ICP-MS [2].....	380
OTHER FACTS ABOUT HR-ICP-MS [3].....	381
STRATEGY #3: DISSOCIATE INTERFERENCES WITHIN THE SPECTROMETER	382
PRINCIPLE OF COLLISION TECHNOLOGY	383
SELECTING A GAS PHASE REAGENT.....	384
OPTIMIZING THE GAS PHASE REAGENT	385
SIDE REACTIONS ARE INEVITABLE!!.....	386
SIDE REACTIONS CREATE NEW INTERFERENCES	387
HYDROCARBONS ARE PARTICULARLY PRONE TO COMPLEX CHEMISTRIES EVEN AT TRACE LEVELS	388
EFFECTS OF SAMPLE MATRIX	389
STRATEGIES TO OVERCOME THE PROBLEM OF SIDE REACTIONS	390
LIMITATION OF SCANNING THE ANALYZER QUAD	391
COLLISION CELLS CAN CREATE INTERFERENCES	392
IN SUMMARY	393



Agilent Technologies
Innovating the HP Way

Introduction: Elemental Analysis

Atomic Spectrometry

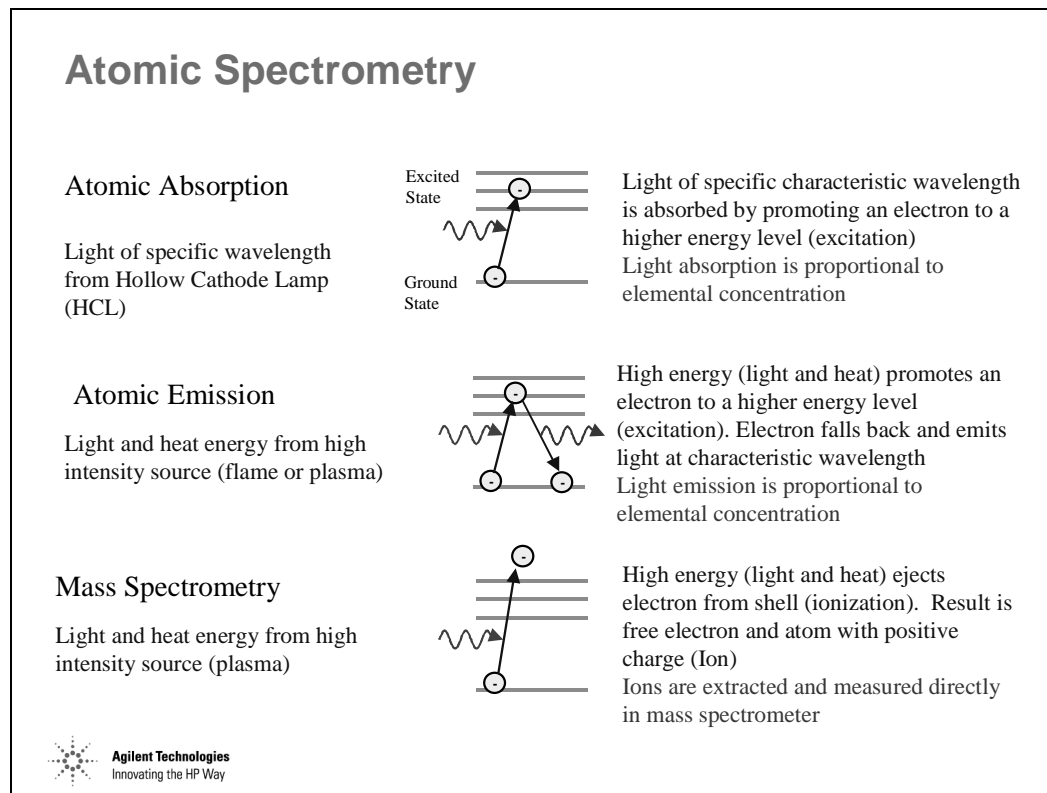


Figure 1

Atomic Mass and Weight

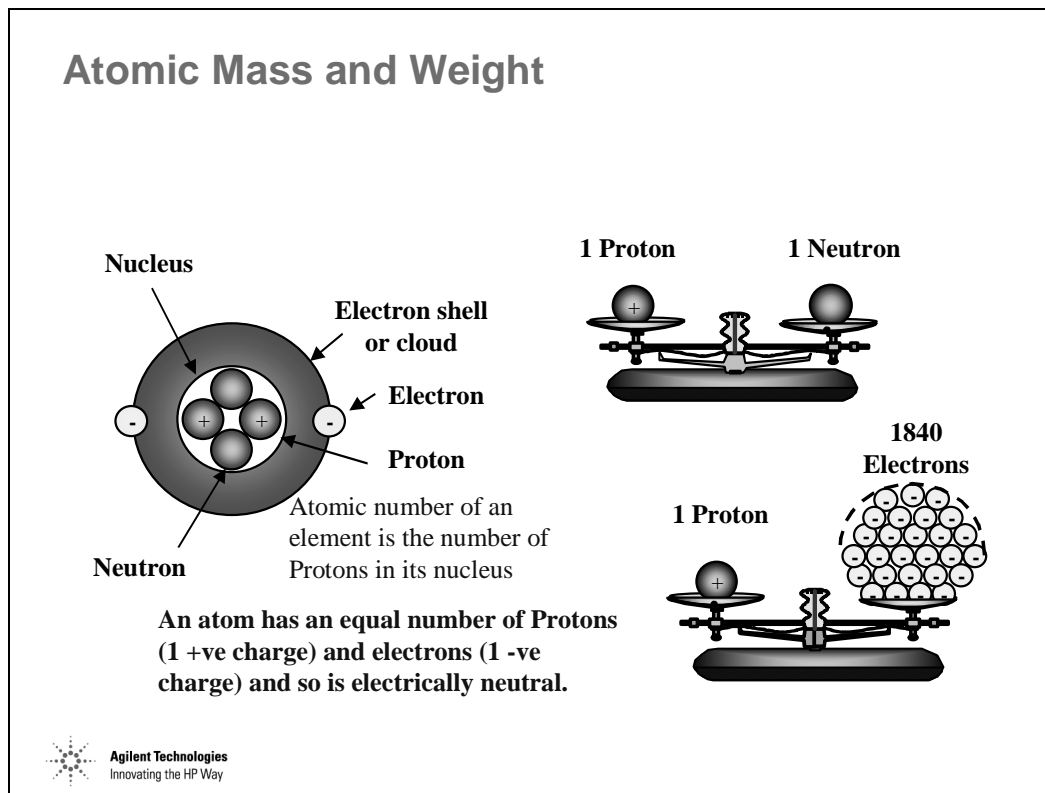


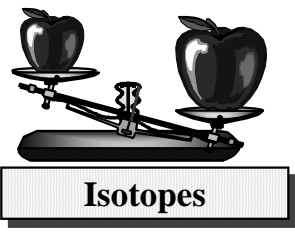
Figure 2

Isotopes and Isobars

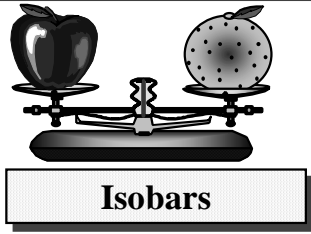
Isotopes and Isobars

Isotopes: Atomic number (number of protons) is the same, but number of neutrons is different (e.g. Pb204 & Pb 208)
Chemical characteristics are same, but physical properties are different.


Isobars: Atomic number is different, but atomic weight is almost identical so species appear at same mass (e.g. Pb204 & Hg204)
Chemical characteristics are different, but physical properties are similar.



Isotopes



Isobars



Agilent Technologies
Innovating the HP Way

Figure 3

Analytical Techniques for Elemental Analysis

Analytical Techniques for Elemental Analysis

FAAS - Flame Atomic Absorption Spectrometry

GFAAS - Graphite Furnace Atomic Absorption Spectrometry

ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometry = Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

ICP-MS - Inductively Coupled Plasma Mass Spectrometry



Agilent Technologies
Innovating the HP Way

Figure 4

Elemental Analysis: FAAS

Elemental Analysis: FAAS

Advantages:

- Inexpensive
- Rapid for few selected elements
- Limited use for organic solvents

Disadvantages

- Poor sensitivity (high detection limits)
- Single element determination at-the-time
- Requires large amount of sample
- Narrow linear range



Agilent Technologies
Innovating the HP Way

Figure 5

Elemental Analysis: GFAAS

Elemental Analysis: GFAAS

Advantages:

- Relatively inexpensive
- Requires small sample volume
- Excellent sensitivity (low detection limits)

Disadvantages

- Single element determination at-the-time
- High operating costs (consumables)
- Very narrow linear range
- Cumbersome and time-consuming technique
- Not suited for organic solvents
- Requires matrix modifiers



Agilent Technologies
Innovating the HP Way

Figure 6

Elemental Analysis: ICP-OES

Elemental Analysis: ICP-OES

Advantages:

- Good general-purpose technique
- Good dynamic range
- Accommodates organic solvents
- Multi-elemental technique

Disadvantages

- Cost of the instrument
- Limits of detection
- Sample volume requirements
- Spectral interferences for unknown/complicated matrices



Agilent Technologies
Innovating the HP Way

Figure 7

Elemental Analysis: ICP-MS

Elemental Analysis: ICP-MS

Advantages:

- Requires small amount of sample
- Excellent dynamic range
- Accommodates organic solvents
- Multi-elemental technique
- Isotope differentiation and determination
- Scanning (semi-quant) capabilities
- Superior limits of detection
- Limited and well defined interferences

Disadvantages

- Cost of the instrument



Agilent Technologies
Innovating the HP Way

Figure 8

Comparison of Elemental Techniques

Comparison of Elemental Techniques

<u>Criteria¹</u>	<u>GFAAS</u>	<u>Sequential</u>	<u>Simultaneous</u>	<u>ICP-MS</u>
		<u>ICP-OES</u>	<u>ICP-OES</u>	
Detection Limits	ppt	ppb	ppb	ppq-ppt
Linear Range	2-3	4-6	4-6	9*
Interferences	Moderate	Many	Many	Few
Speed	Slow	Slow	Fast	Fast
Elemental Coverage	Poor	Good	Good	Excellent
Multi-element	No	Yes	Yes	Yes
Simultaneous	No	No	Yes	Yes
Sample Size	uL	mL	mL	uL or mL
Capital Cost	\$	\$	\$\$	\$\$
Operating Cost	\$\$\$	\$\$	\$\$	\$



Figure 9

Graphical Comparison of Elemental Techniques

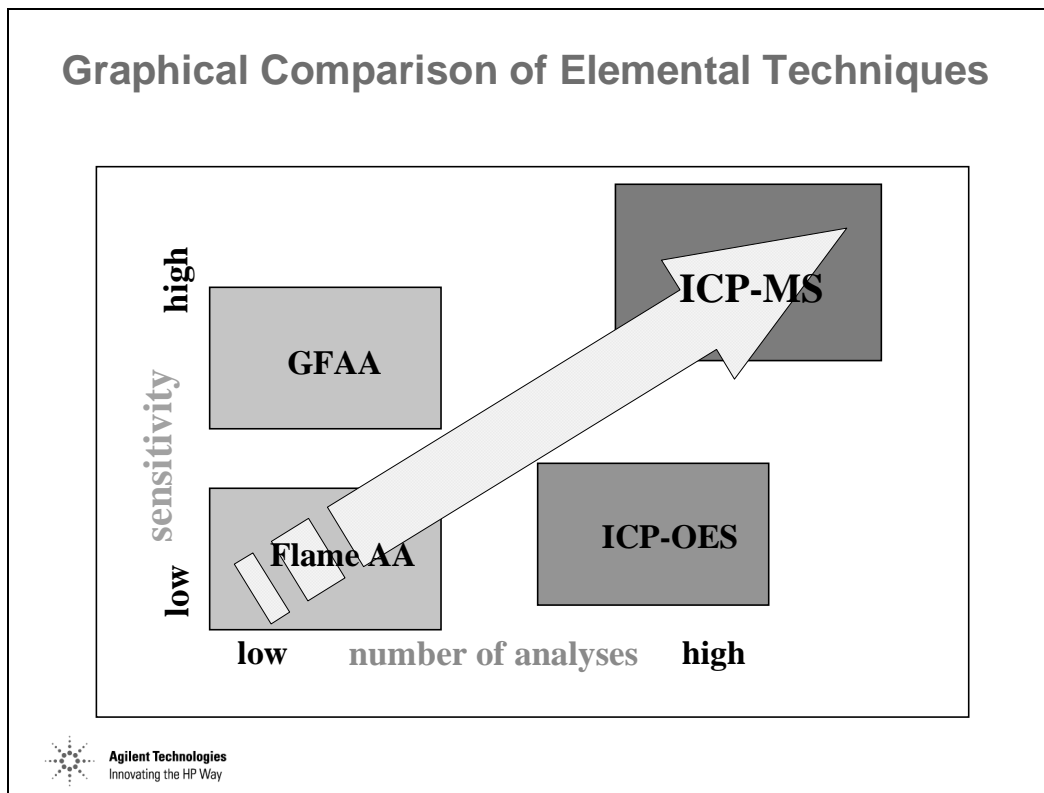


Figure 10

Comparison of the Complexity of Multi-elemental Techniques

Comparison of the Complexity of Multielemental Techniques		
	<u># emission lines</u>	<u># (natural) isotopes</u>
<u>alkali metals</u>		
lithium	30	2
cesium	645	1
<u>alkali earths</u>		
magnesium	173	3
calcium	662	6
<u>transition metals</u>		
chromium	2277	4
iron	4757	4
cerium	5755	4

Figure 11

Users/Applications of ICP-MS

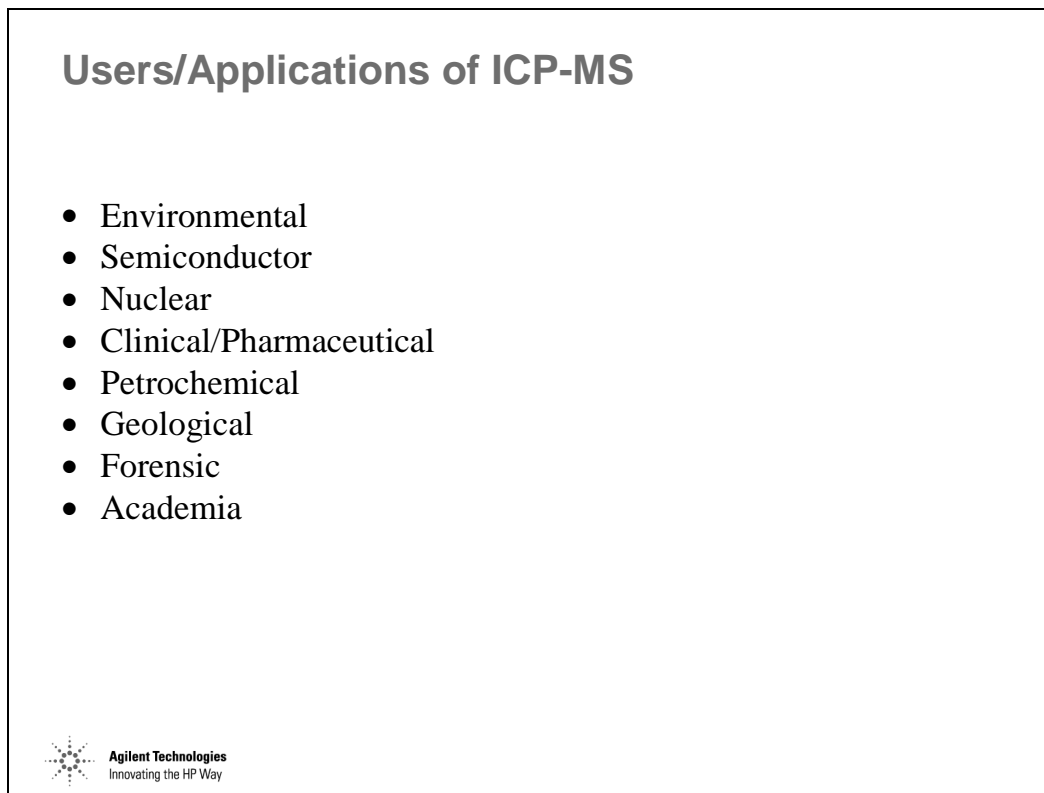


Figure 12

Multi-elemental Analysis of Metals

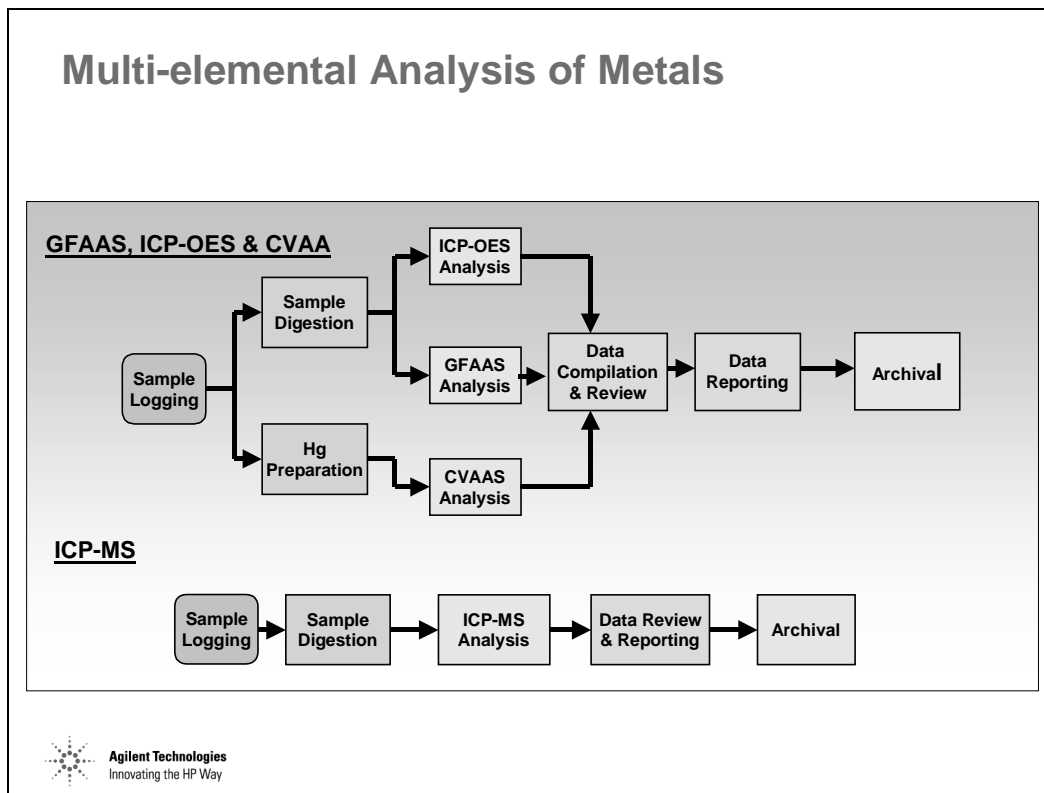


Figure 13



Agilent Technologies

Innovating the HP Way

Introduction: Inductively Coupled Plasma Mass Spectrometry

What is ICP-MS?

What is ICP-MS?

- Inorganic (elemental) analysis technique.
- **ICP - Inductively Coupled Plasma**
high temperature ion source
- **MS - Mass Spectrometer**
 - quadrupole scanning spectrometer
 - mass range from 7 to 250 amu (Li to U...)
 - separates all elements in rapid sequential scan
 - ions measured using dual mode detector
 - *ppt to ppm levels*
 - *isotopic information available*



Agilent Technologies
Innovating the HP Way

Figure 14

Advantages of ICP-MS

Advantages of ICP-MS

- Trace and ultratrace measurement of >70 elements - from Li to U
 - Agilent 7500 can measure from <1ppt to >500ppm (9 orders linear range)
- Spectral simplicity
 - Every element (except In) has an isotope which is free from direct overlap
- Speed of multi-element analysis
 - Typical multi-element acquisition in 1-2 min (~4 min including rinse)
- Flexibility to optimize for specific applications
 - Automated set-up and autotuning give improved ease of use
- Fast semi-quantitative analysis - accurate data without calibration
 - measurement is based on comparison of relative isotope sensitivity
- Isotope ratio measurements
 - nuclear, geological, environmental and nutrition studies



Figure 15

Agilent Technologies and ICP-MS

Agilent Technologies and ICP-MS

- 1987 - **PMS 100** - first computer controlled ICP-MS
- 1988 - **PMS 200** - 2nd generation ICP-MS
- 1990 - **PMS 2000** - featuring Omega lens system - lowest random background in ICP-QMS
- 1992 - **ShieldTorch** interface developed - interferences fundamentally reduced for the first time in ICP-QMS - enables analysis of K, Ca, Fe by ICP-QMS
- 1994 - **HP 4500** introduced - World's first benchtop system
- 1998 - **Over 500** systems installed
- 1999 - **HP 4500 Series 100, 200, 300** introduced
- 2000 - *Agilent 7500 series. 7500a, 7500i and 7500s - the next generation in ICP-MS instrumentation*



Figure 16

Processes in ICP-MS

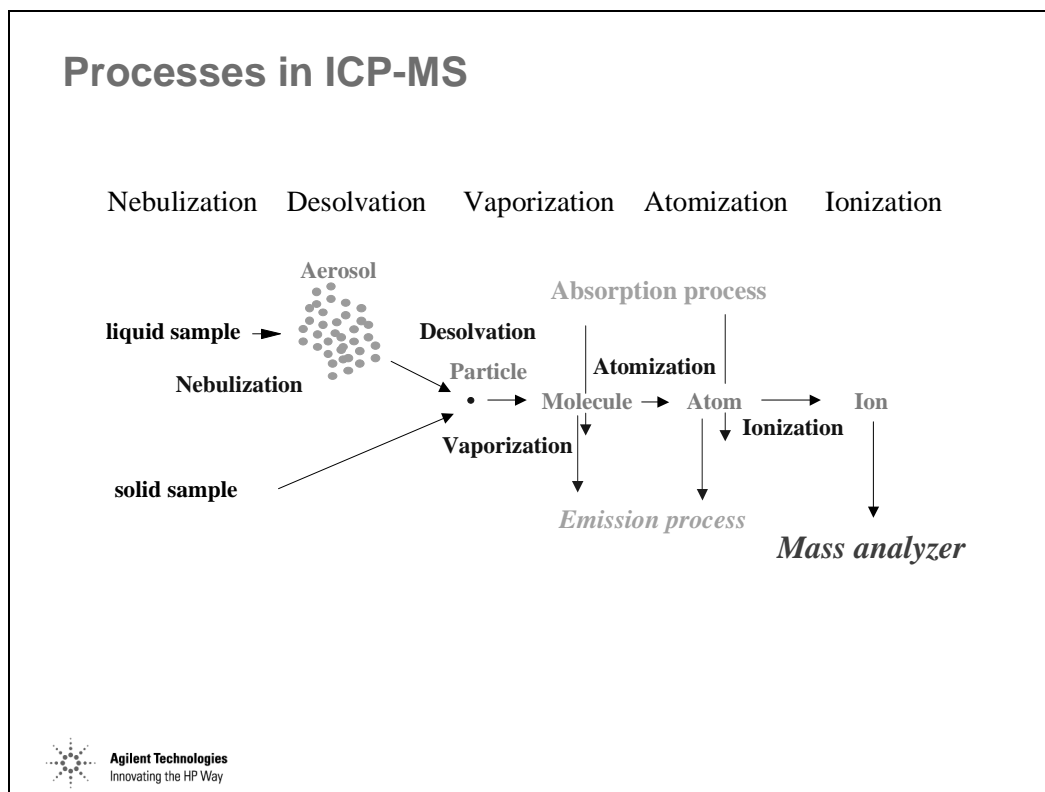


Figure 17

Overview of Agilent 7500 Features

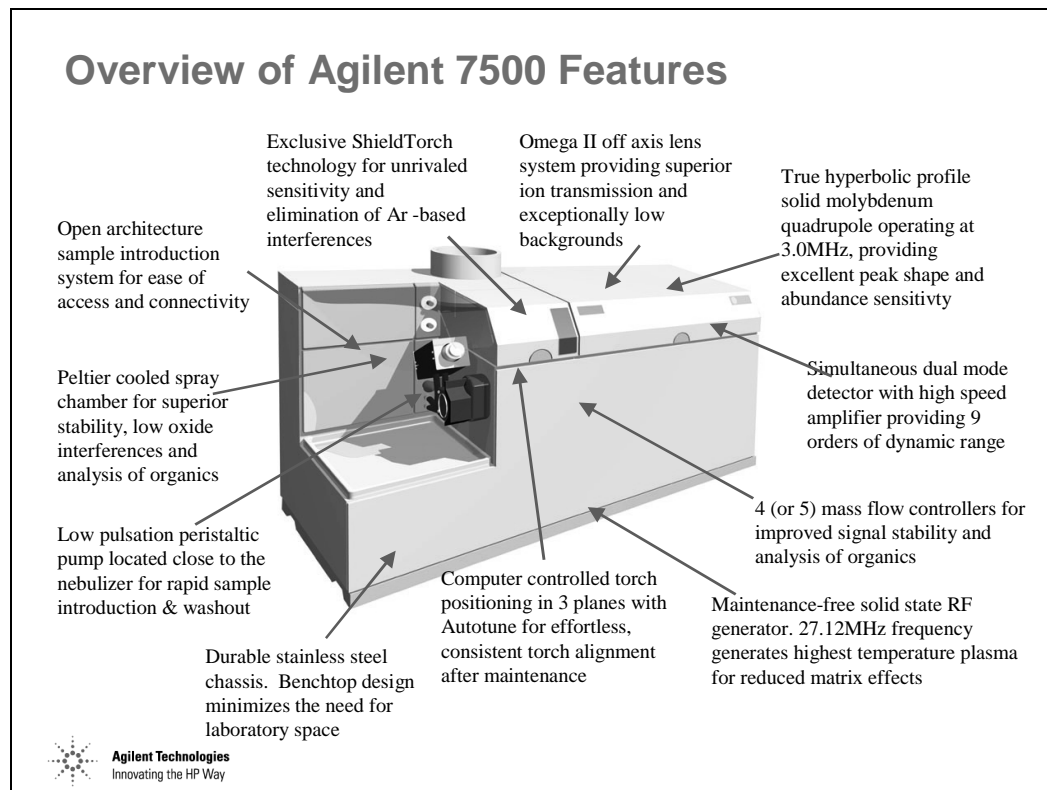


Figure 18

Schematic Diagram of Agilent 7500a

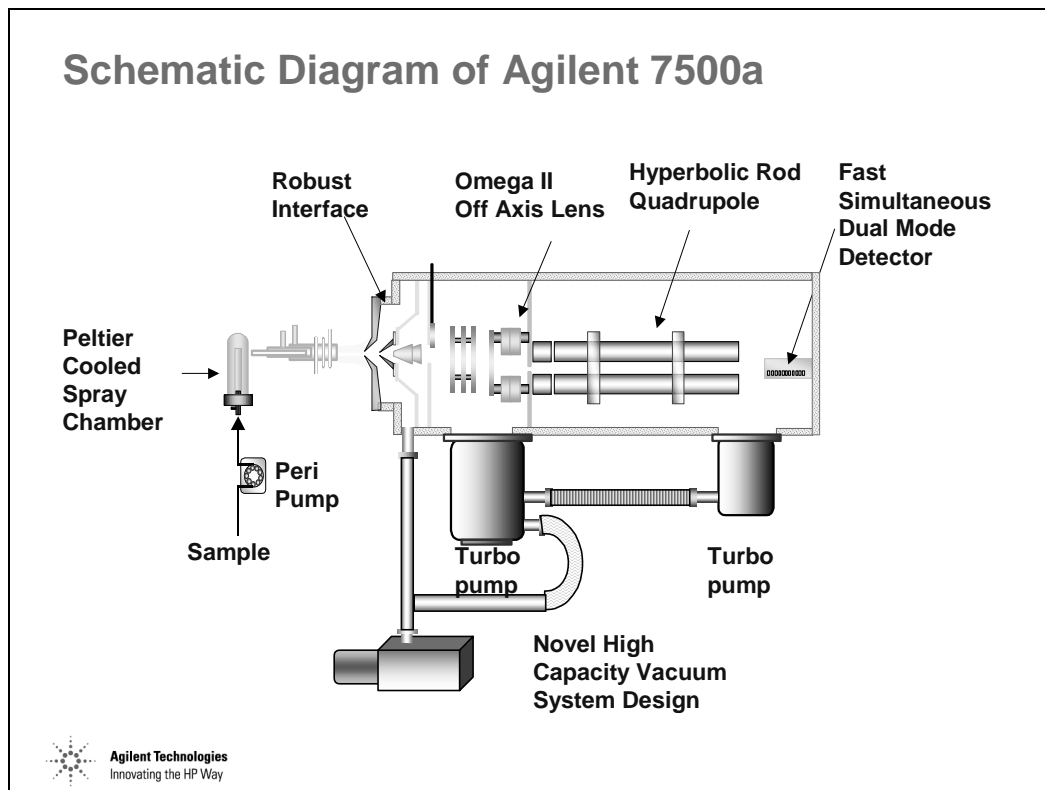


Figure 19

- 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

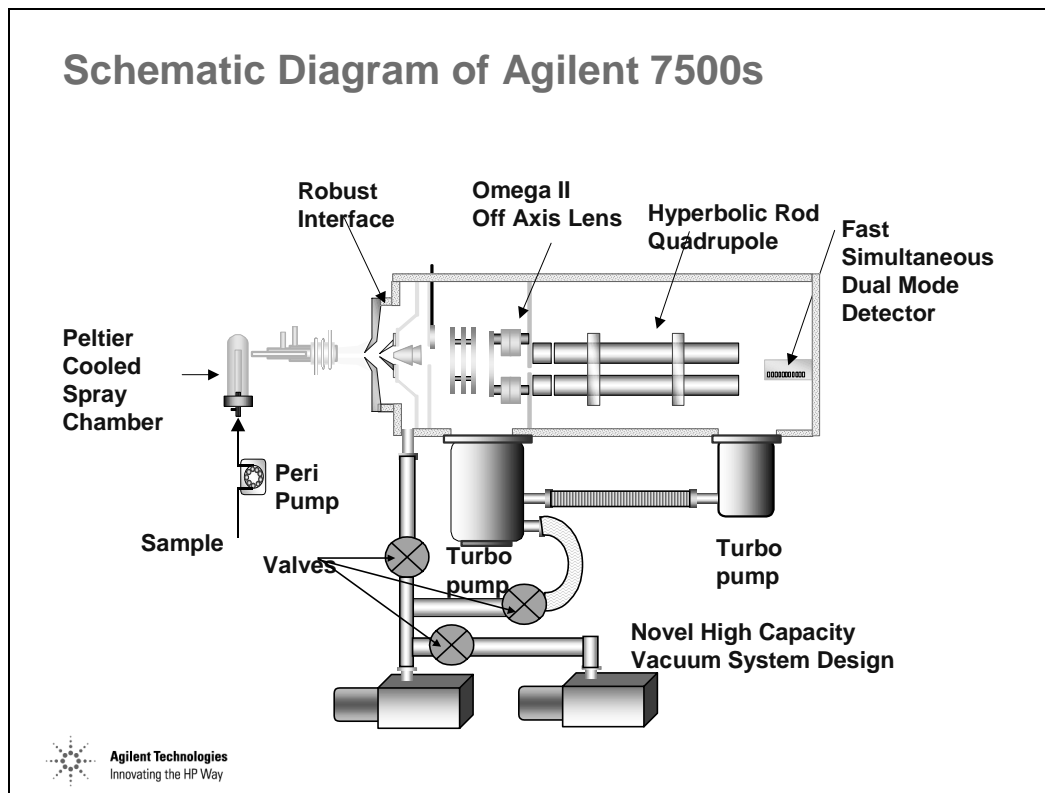


Figure 20

ISIS for Application Flexibility

ISIS for Application Flexibility



Agilent Technologies
Innovating the HP Way

Figure 21

Sample Introduction

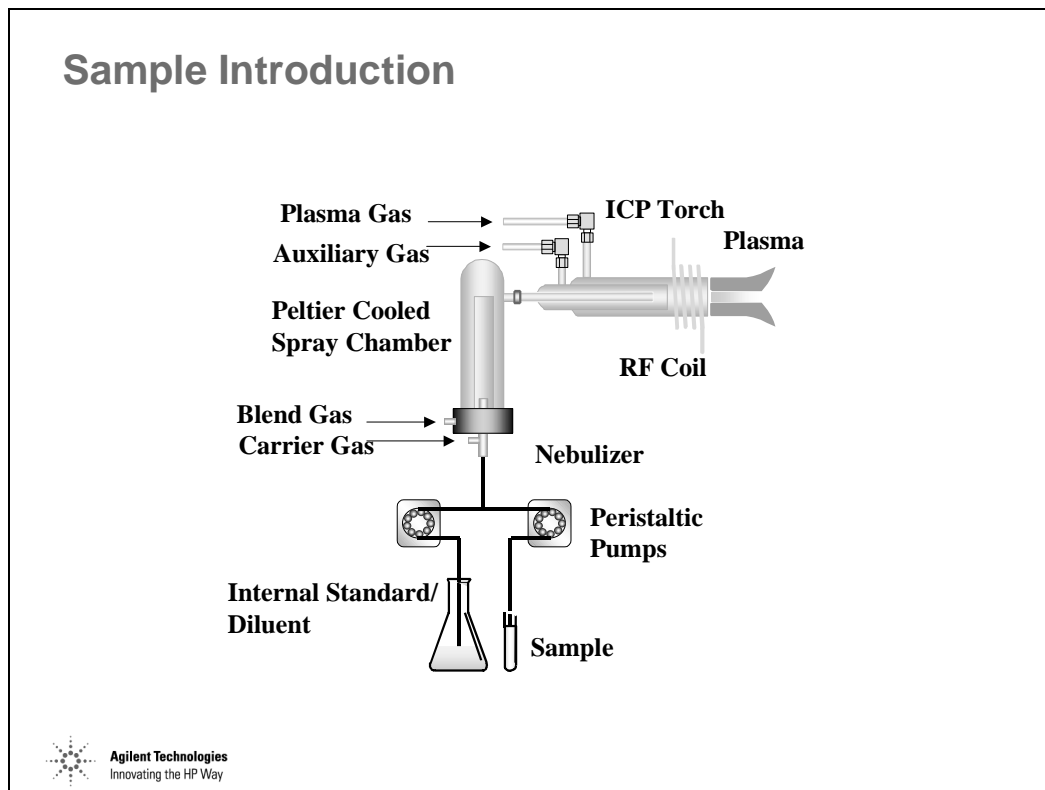


Figure 22

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

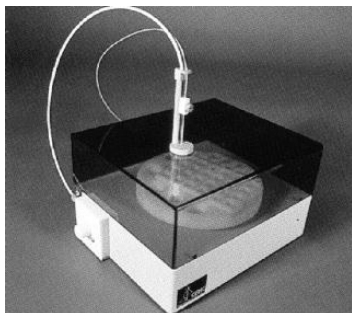


Agilent Technologies
Innovating the HP Way

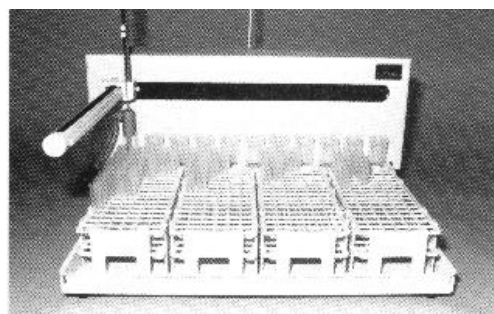
Figure 23

Autosamplers

Autosamplers



ASX -100



ASX -500



Figure 24

Typical Nebulizer

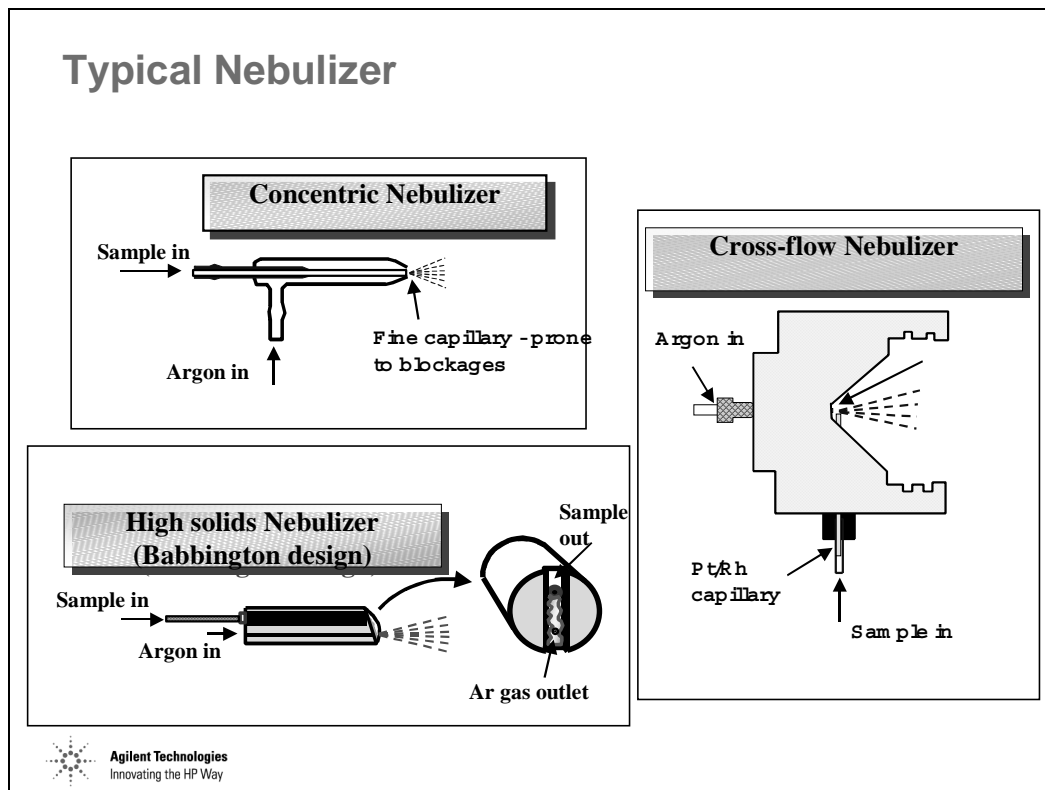


Figure 25

Specialized Sample Introduction Systems

Specialized Sample Introduction Systems



Inert sample kit with unique polypropylene spray chamber

Organic analysis kit including exclusive oxygen inlet connector for safe addition of oxygen for organics analysis



Exclusive Agilent Micro Flow Nebulizer for trouble-free analysis of microvolume samples

Widest range of ICP torches including exclusive platinum injector torch for HF and unique photoresist torch for photoresist matrices



Agilent Technologies
Innovating the HP Way

Figure 26

Typical Spray Chamber – Double Pass

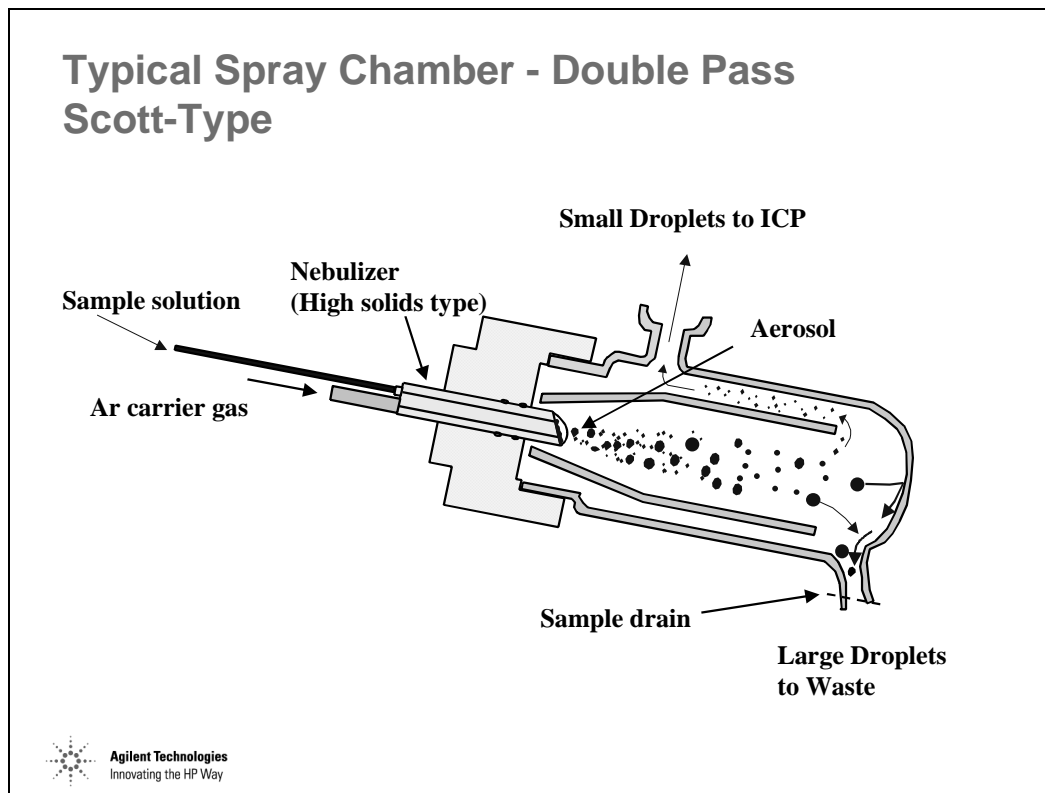


Figure 27

Droplet Distribution With and Without Spray Chamber

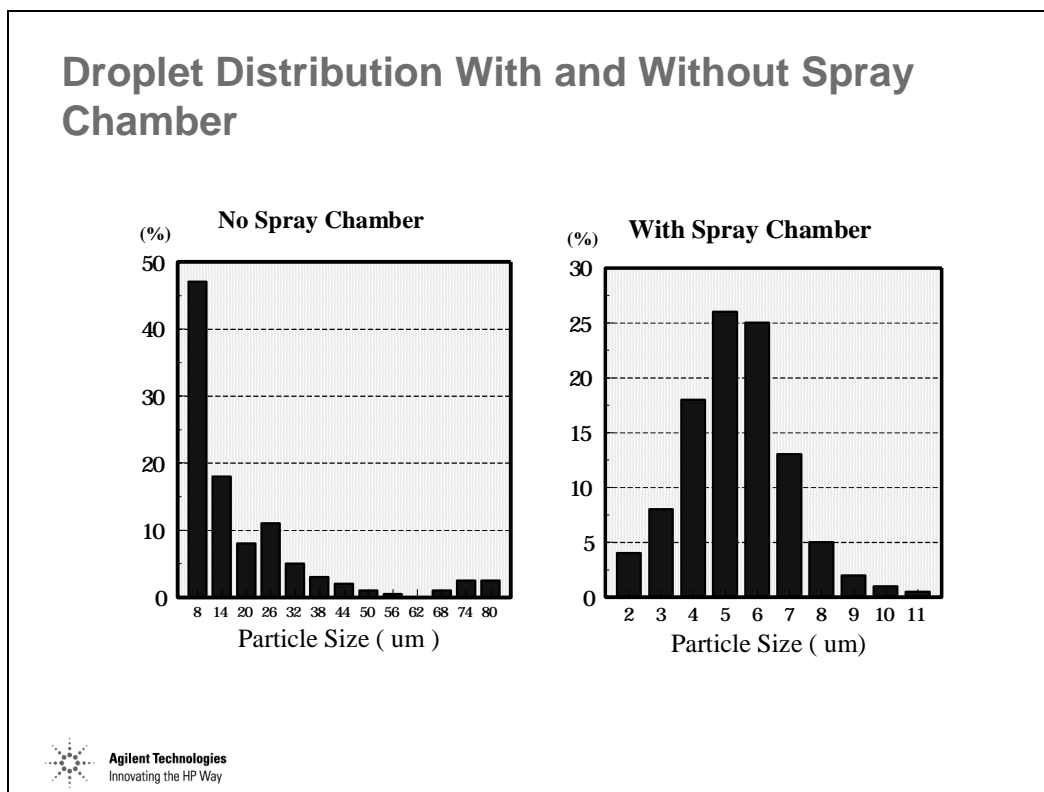
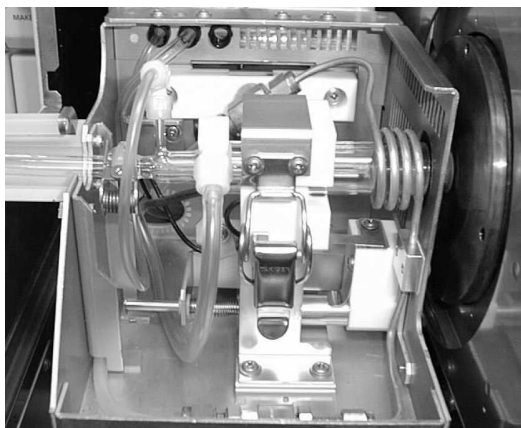


Figure 28

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.



Agilent Technologies
Innovating the HP Way

Figure 29

Inductively Coupled Plasma Mass Spectrometry

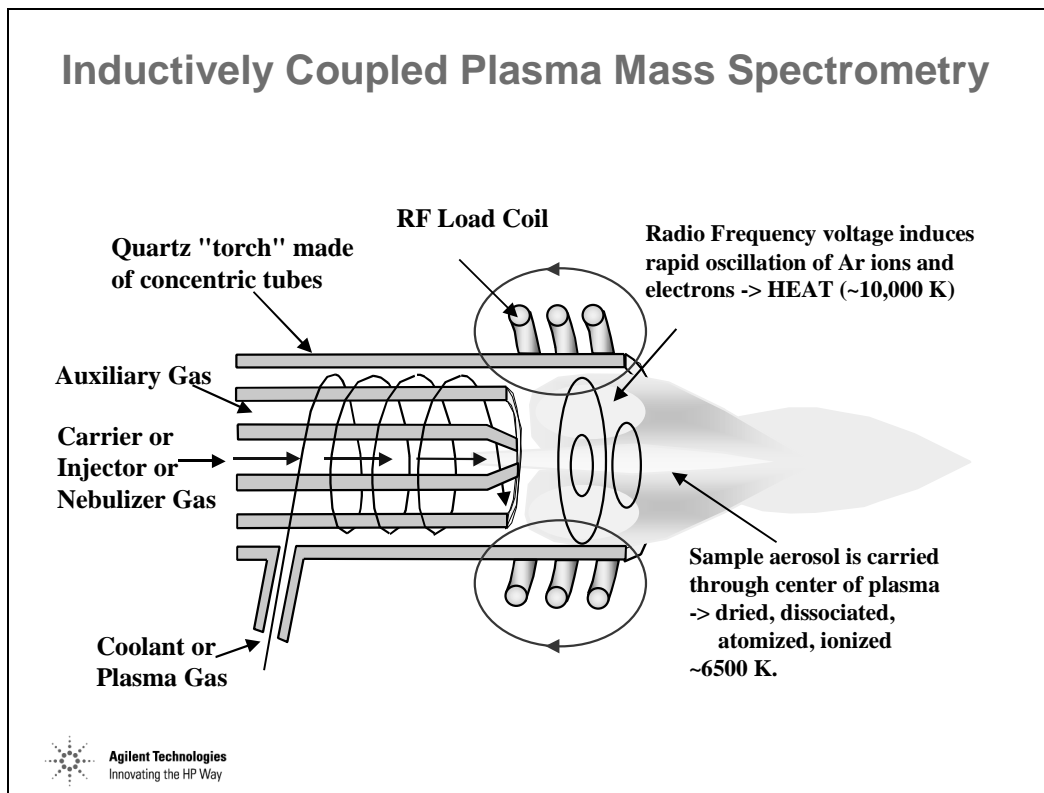


Figure 30

Inductively Coupled Plasma Mass Spectrometry (continued)

Inductively Coupled Plasma Mass Spectrometry

- **Plasma is electrical discharge, not chemical flame**
 - Ar gas used
 - plasma at atmospheric pressure -> very high temperature
 - *(a low pressure plasma is a fluorescent lamp)*
 - plasma is generated through inductive coupling of free electrons with rapidly oscillating magnetic field (27 MHz)
 - Energy is transferred collisionally to argon molecules
 - plasma is contained in gas flow in a quartz tube (torch)
 - sample aerosol is carried through the center of the plasma
 - proximity to 10,000 °C plasma causes dissociation, atomization and ionization
 - ions are extracted into the spectrometer



Figure 31

Why Argon?

Why Argon?

- Ar is inert
- Ar is relatively inexpensive!
- Ar is easily obtained at very high purity

Most importantly -

- Ar has a 1st ionization potential of **15.75** electron volts (eV)
 - higher than the 1st ionization potential of most other elements (except He, F, Ne) and
 - lower than the 2nd ionization potential of most other elements (except Ca, Sr, Ba, etc)
- **Since the plasma ionization environment is defined by the Ar, most analyte elements are efficiently singly charged**



Figure 32

Distribution of Ions in the Plasma

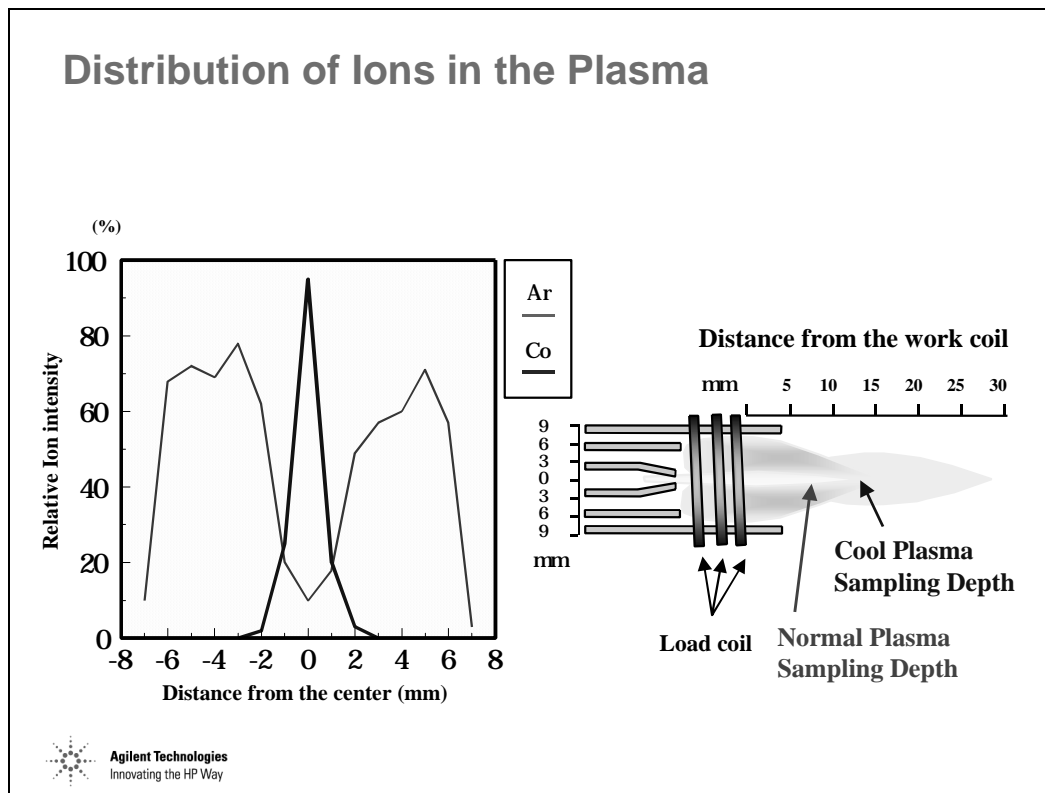


Figure 33

Sample Ionization in the Plasma

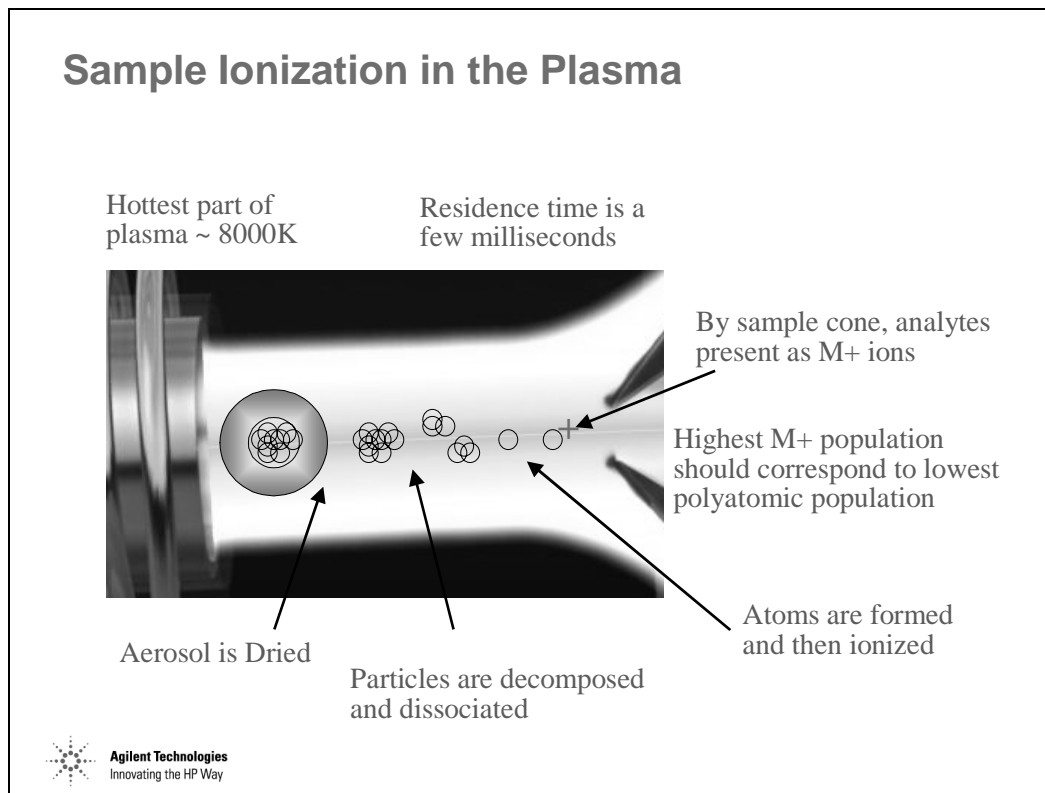
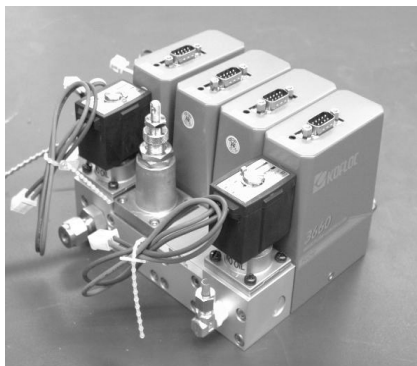


Figure 34

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



Figure 35

Interface

Interface

- Sampling cone
- Skimmer cone

Allows introduction of ions into the vacuum chamber

Material : Nickel
 Platinum

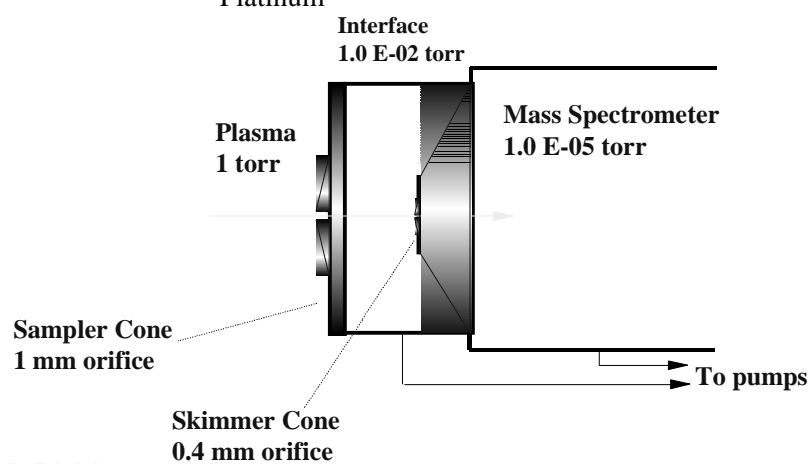


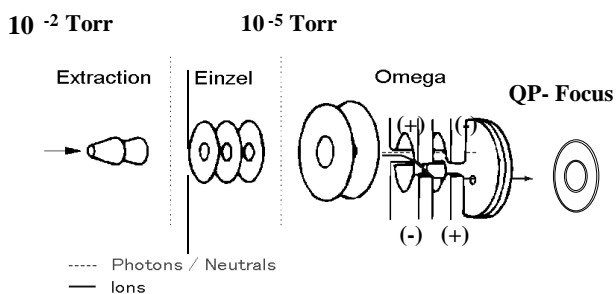
Figure 36

Agilent 7500 Ion Lens System

Agilent 7500 Ion Lens System

Serves to focus ions coming from the skimmer into the mass filter. Rejects neutral atoms and minimizes the passage of any photons from ICP.

- **Extraction** - Extract and accelerate ions from the plasma
- **Einzel** - Collimate and focus ion beam
- **Omega** - Bend ion beam to eliminate photons and neutrals
- **QP focus** - Refocus ion beam



Agilent Technologies
Innovating the HP Way

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

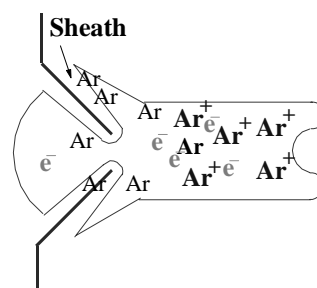


Figure 38

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.

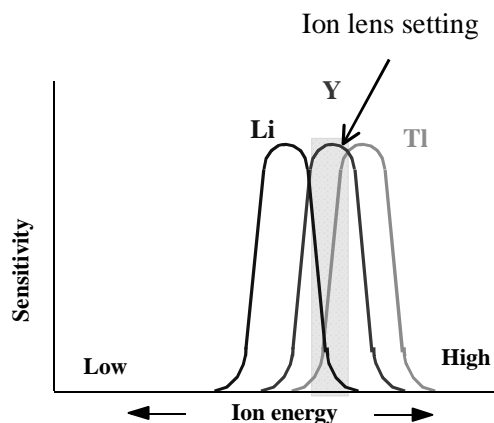


Figure 39

The Electrostatic Lenses

The Electrostatic Lenses

- Ions, photons and neutrals all enter the spectrometer through the interface
 - the detector is sensitive to photons/neutrals, as well as ions
- Ions are charged particles
 - can be deflected using electric fields
- Photons travel in straight lines
- If ions can be deflected off-axis, they will be separated from non-charged species (photons/neutrals)
 - must ensure that mass bias is not introduced when ions are deflected



Figure 40

Why “Off-Axis”?

Why “Off-Axis”?

- Detector must be screened from Plasma
 - Plasma is an intense source of photons and neutrals
 - Electron Multiplier is photon/neutral sensitive
- Common approach is to place a metal disc in the light path
 - "Photon Stop"
 - "Shadow Stop"
- BUT -With the "Photon Stop" or "Shadow Stop" ions must be defocused around the disc and then re-focused on the other side
 - *This is very inefficient and will introduce mass bias*



Figure 41

Low Transmission Photon Stop System

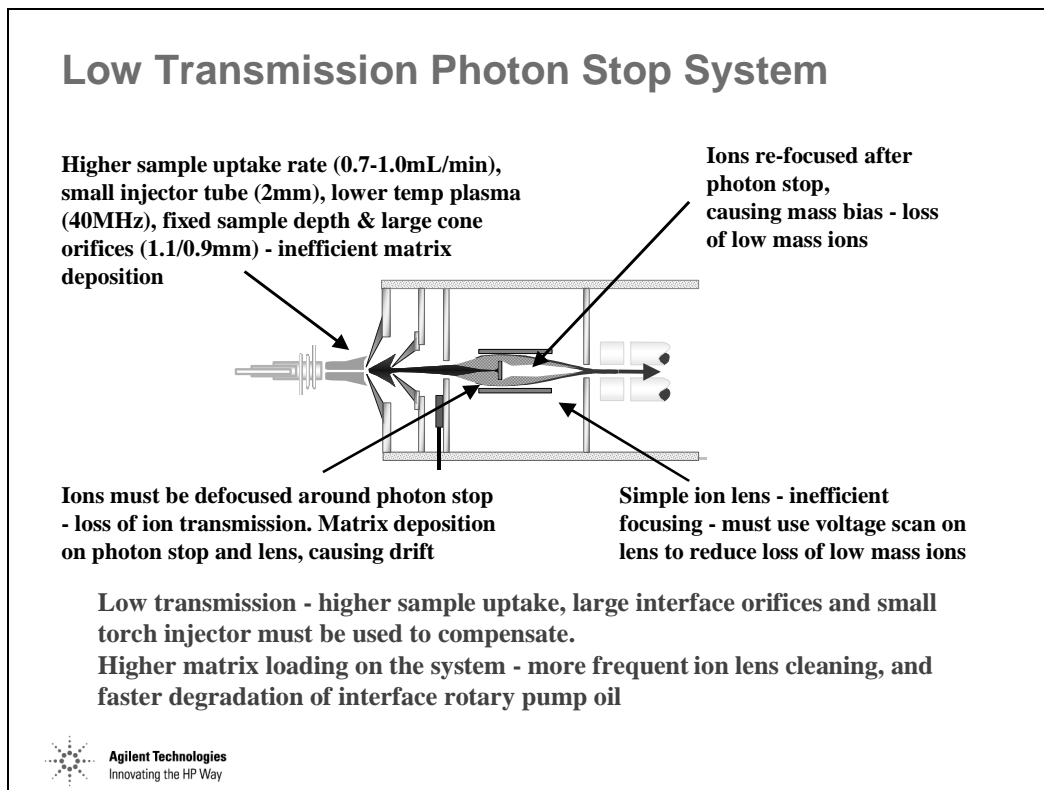


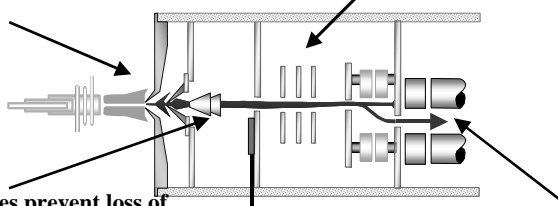
Figure 42

Agilent High Transmission Off-Axis System

Agilent High Transmission Off-Axis System

Lower sample uptake rate (0.3mL/min), larger injector tube (2.5mm), higher temp plasma (27MHz), variable sample depth & small cone orifices (1.0/0.4mm) - efficient matrix deposition

Compound ion lens - efficient focusing, high transmission across the mass range



Dual extraction lenses prevent loss of low mass ion on exit from interface. Also serve to protect main ion lenses by trapping sample matrix.

Photons and neutrals removed - ions are deflected off axis into quadrupole with minimal mass bias

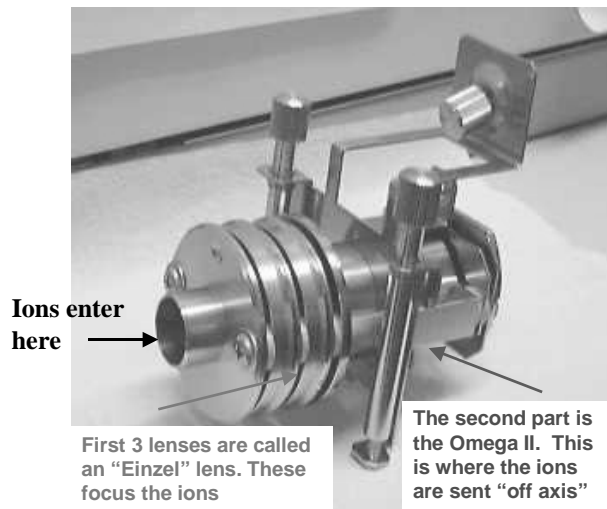
High transmission - sensitivity maintained with less sample loading on system - lower sample uptake, small interface orifices and larger diameter torch injector. Results in much less frequent ion lens cleaning and extended interface rotary pump oil lifetime.



Figure 43

Ion Focusing – New Omega II Lens

Ion Focusing - New Omega II lens



Integrated 1 piece design for easy cleaning (when required)

No wires to attach, makes replacement fast and easy

Gives very high sensitivity and low background performance



Agilent Technologies
Innovating the HP Way

Figure 44

Flat Response Curve – High Sensitivity at All Masses

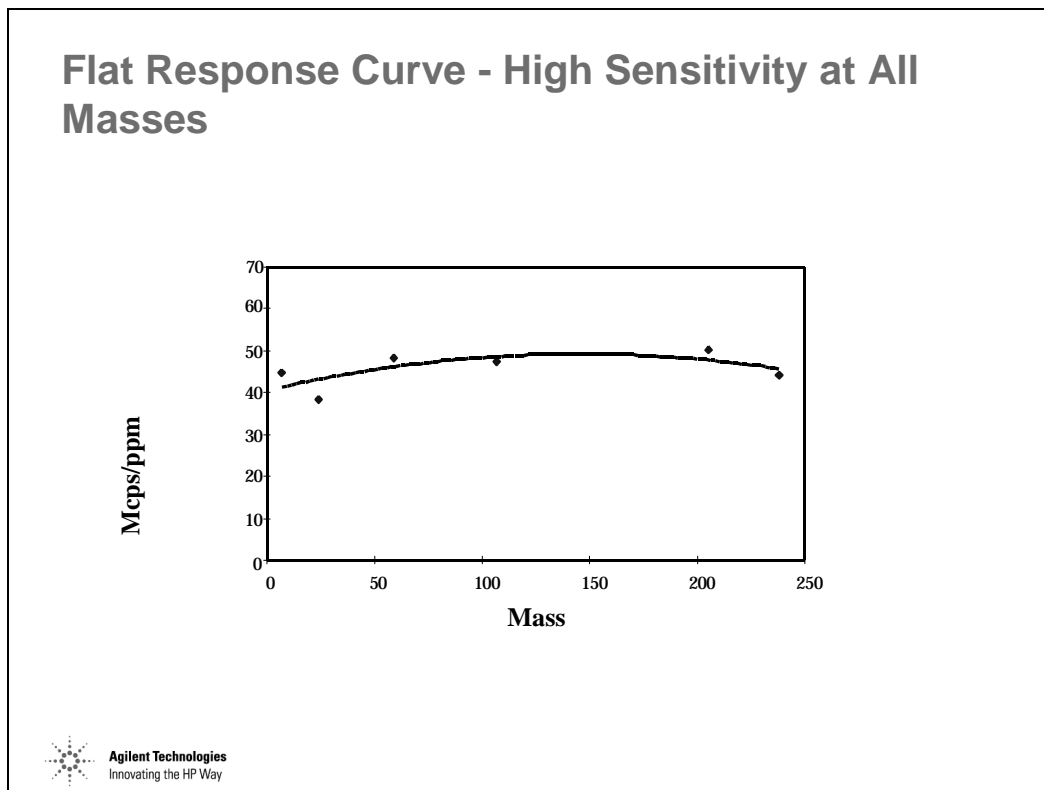
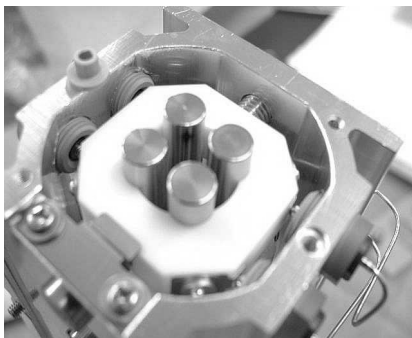


Figure 45

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

Agilent 7500 Quadrupole

Agilent 7500 Quadrupole



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



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

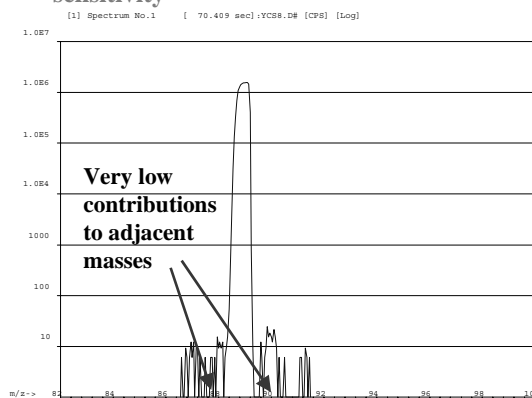


Figure 46

Resolution and Abundance Sensitivity

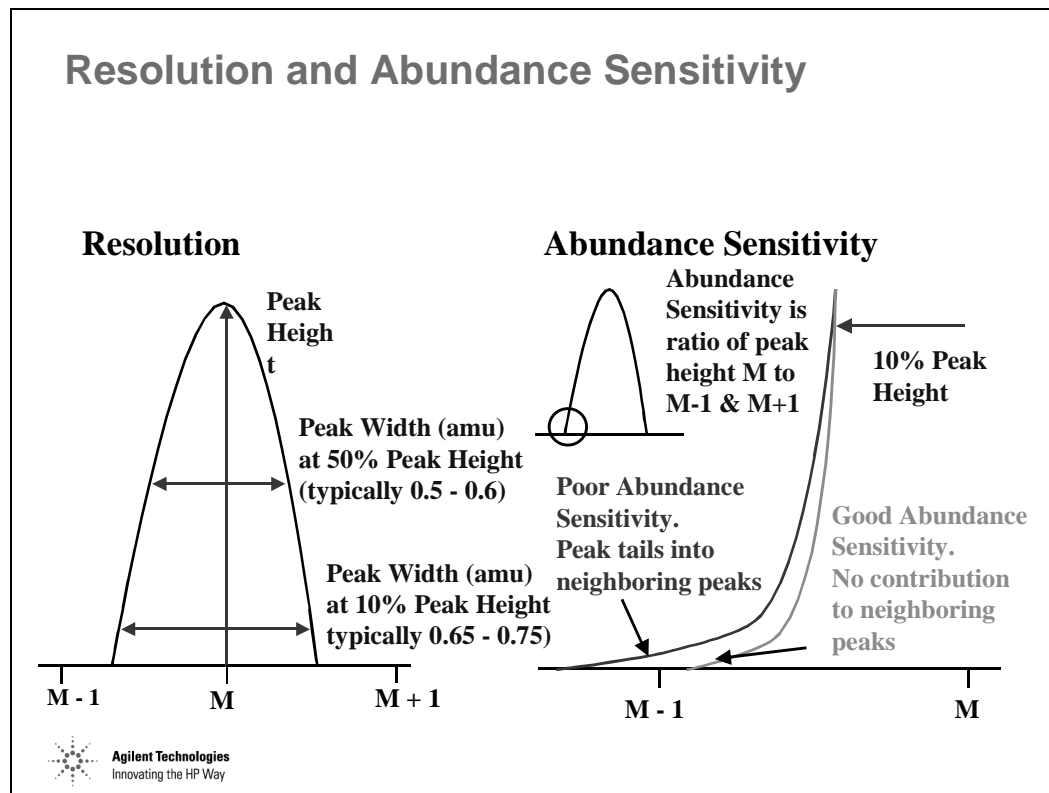
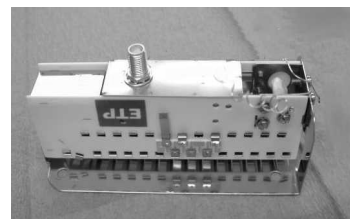
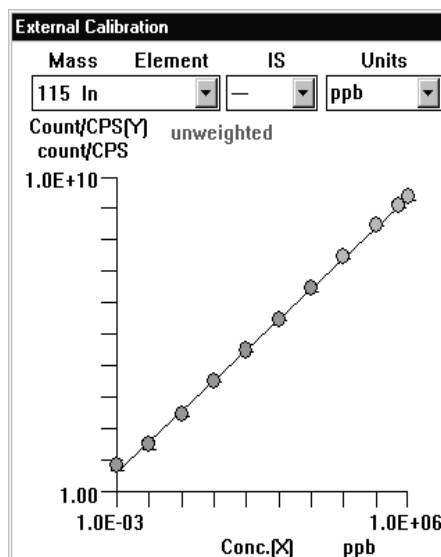


Figure 47

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



Agilent Technologies
Innovating the HP Way

Figure 48

The Detector

The Detector

- Electron multiplier
 - discrete dynode detector (ETP)
 - each dynode gives "cascade" of electrons
 - -> signal is multiplied

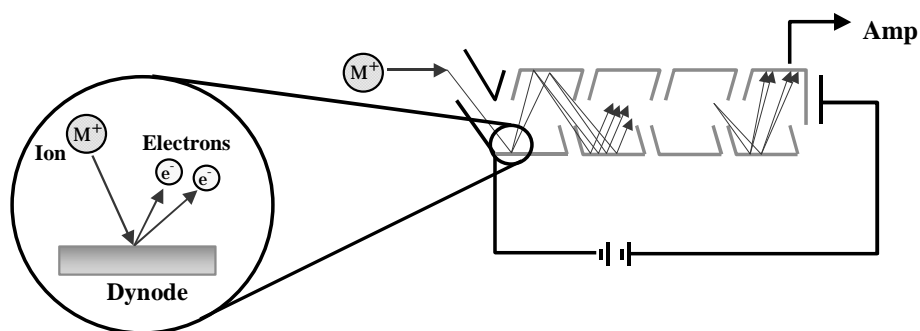


Figure 49



Agilent Technologies

Innovating the HP Way

Interferences in ICP-MS

Interferences in ICP-MS

Interferences in ICP-MS

- Mass Spectroscopic Interferences
 - Inability to resolve same nominal masses
- Non-spectroscopic Interferences
 - Result from sample matrix



Figure 50

Mass Spectroscopic Interferences

Mass Spectroscopic Interferences

- Isobaric
- Polyatomic
 - Argides
 - Oxides
 - Other (i.e. Chlorides, Hydrides, etc.)
- Doubly-charged



Figure 51

Isobaric Interferences

Isobaric Interferences

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

Figure 52

Polyatomic Interferences

Polyatomic Interferences

<i>Interferent</i>	<i>m/z</i>	<i>Overlaps with</i>
N_2^+	28	Si
NO^+	30	Si
O_2^+	32	S
	34	S
Ar^+	40	Ca
ArO^+	56	Fe
Ar_2^+	80	Se
	78	Se
	76	Se

Figure 53

Mass Spectroscopic Interferences

Mass Spectroscopic Interferences

- **Choose an isotope free of interferences**
 - ^{137}Ba instead of ^{138}Ba
- **Optimize instrument to minimize interference**
 - Oxides, Doubly-charged ions
- **ShieldTorch**
 - Reduces polyatomic ions with high ionization potential
 - Removes ArO
 - Removes ArH



Figure 54

Optimizing to Minimize Interference Formation in the Plasma [1]

Optimizing to Minimize Interference Formation in the Plasma [1]

Minimize 'matrix' loading

- low sample uptake rate

- reduce water loading

 - cooled spray chamber

 - desolvation

Maximize residence time in plasma

- maximum sampling depth

- large diameter torch injector for lower aerosol velocity



Figure 55

Optimizing to Minimize Interference Formation in the Plasma

[2]

Optimizing to Minimize Interference Formation in the Plasma [2]

Maximize available energy for ionization

- high forward power

- reduce sample and carrier flow

- eliminate/reduce matrix easily ionizable elements where practical

- dilute if necessary



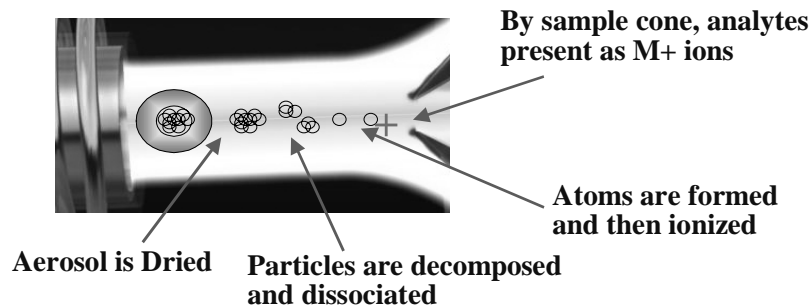
Agilent Technologies
Innovating the HP Way

Figure 56

Optimizing to Minimize Interference Formation in the Plasma [3]

Optimizing to Minimize Interference Formation in the Plasma [3]

Residence time is on the order of milliseconds. It is essential to optimize plasma energy input ensure sample matrix breakdown!



 **Agilent Technologies**
Innovating the HP Way

Figure 57

Effect of Plasma Temperature on Degree of Ionization

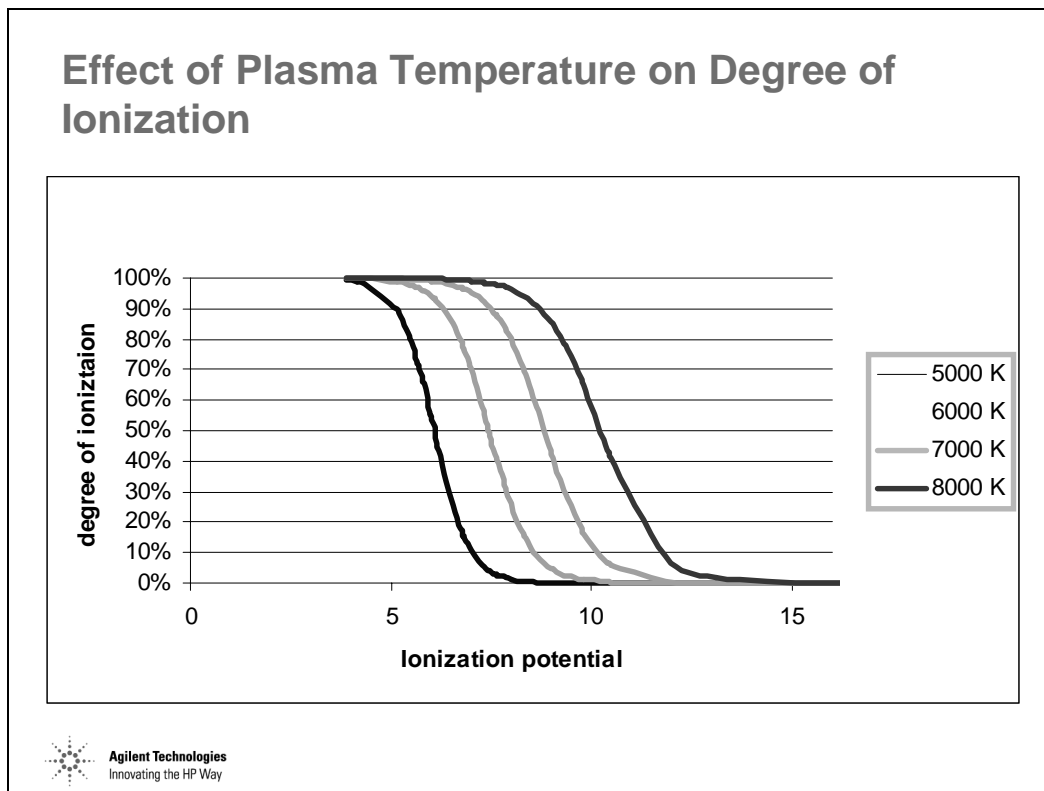
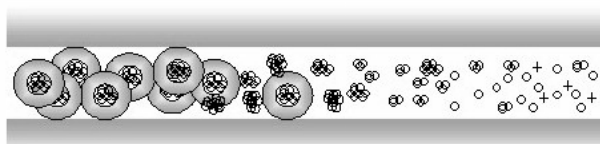


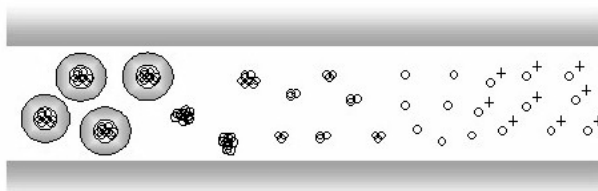
Figure 58

Efficient Aerosol Decomposition

Efficient Aerosol Decomposition



High sample load, narrow central channel → inefficient matrix decomposition



Low sample load, wide central channel → efficient matrix decomposition

Wide bore torch injector results in a diffuse aerosol to minimize localized cooling as the aerosol droplets are dried and minimizes potential sample deposition on the inner surface



Figure 59

Oxides and Doubly Charged Ions

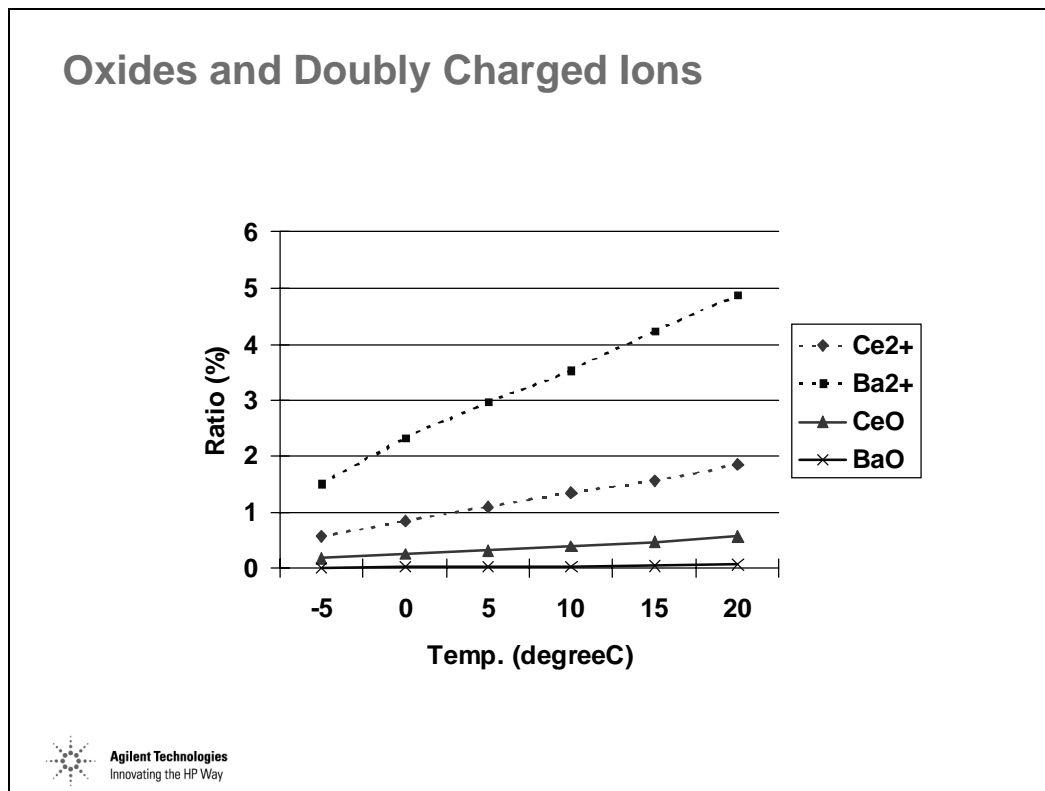


Figure 60

Dealing with Mass Spectroscopic Interferences

Dealing with Mass Spectroscopic Interferences

- **Matrix Elimination**
 - *Chelation*
 - *Chromatography*
 - *ETV*
 - *Desolvation*
 - membrane
 - thermal
- **Interference correction equations**



Agilent Technologies
Innovating the HP Way

Figure 61

Interference Equations

Interference Equations

Mathematical equations used to minimize the effect of elemental, doubly-charged and polyatomic isobaric interferences in ICP-MS analysis.

Isobaric

^{204}Hg on ^{204}Pb

Polyatomic

$^{75}\text{ArCl}$ on ^{75}As

Doubly charged ions

$^{88}\text{Sr}^{++}$ on ^{44}Ca

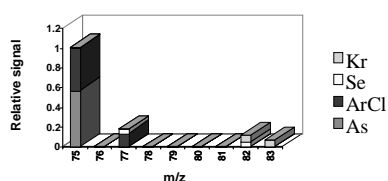


Agilent Technologies
Innovating the HP Way

Figure 62

As Interference Correction

As interference Correction



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

$$^{75}\text{As} = ^{75}\text{M} - \{ ^{77}\text{ArCl} (3.127) \} \quad (1)$$

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

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

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

So equation 1 and 2 becomes:

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

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

But, there is Krypton at 82...

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

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

So equation 3 and 4 becomes:

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

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

Figure 63

Interference Correction Equations - Agilent 7500

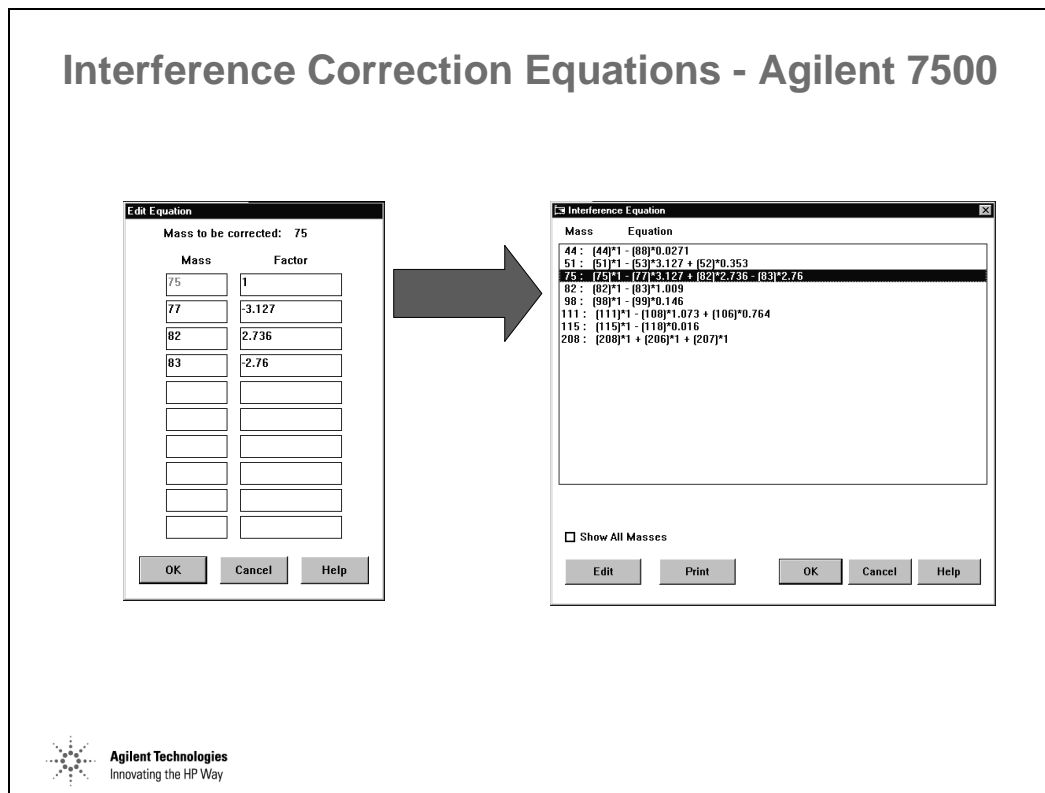


Figure 64

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

Non-Spectroscopic Interferences

- **Total Dissolved Solids**
- **High Mass Elements**
 - High mass elements affect the signal of low mass element. (Space Charge)
- **Easily Ionized Elements**
 - Limited ionization energy is consumed by easily ionized elements such as Na and K.

Result from sample matrix



Figure 65

Effect of High Dissolved Solids

Effect of High Dissolved Solids

- Signal suppression
- Deposits on sampler and skimmer cones
- Deposits on ion optics



Figure 66

First Ionization Potential

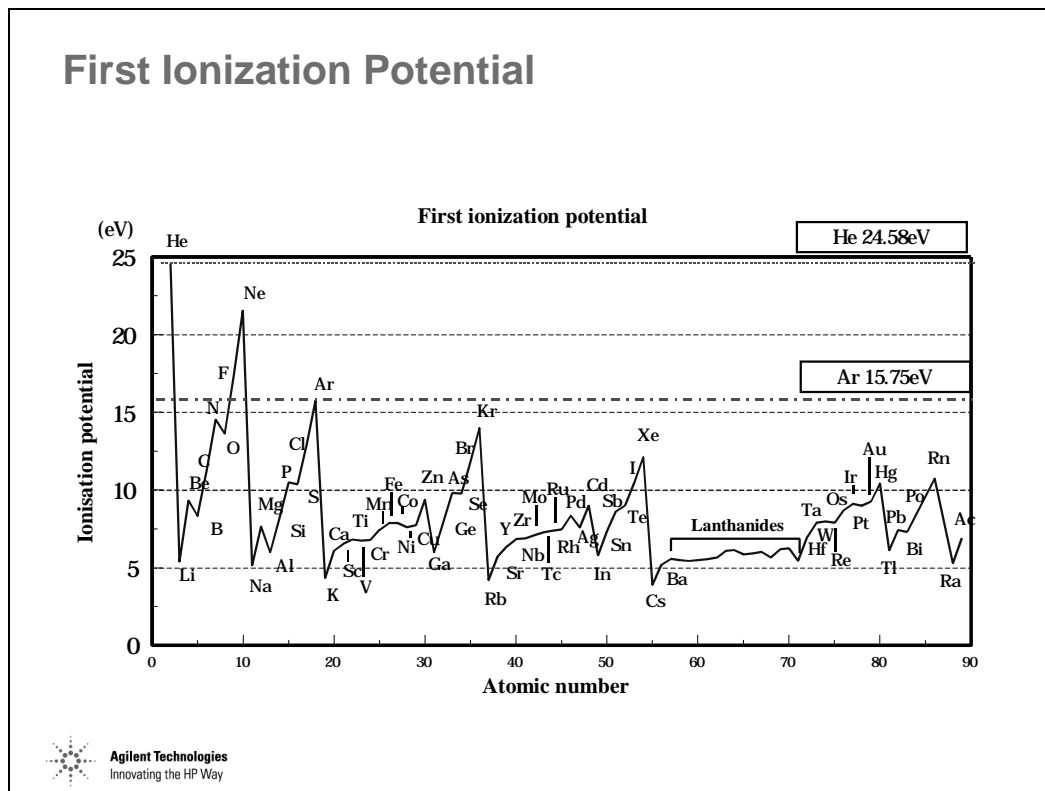


Figure 67

Ionization Efficiency

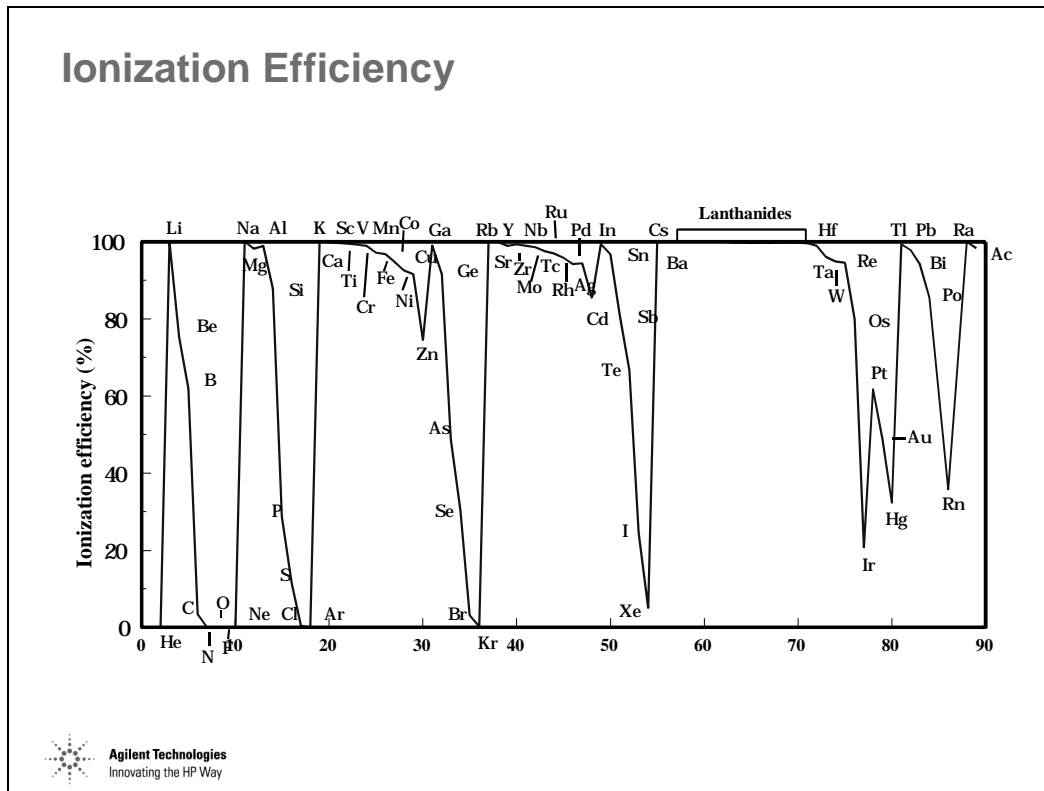


Figure 68

Signal Suppression

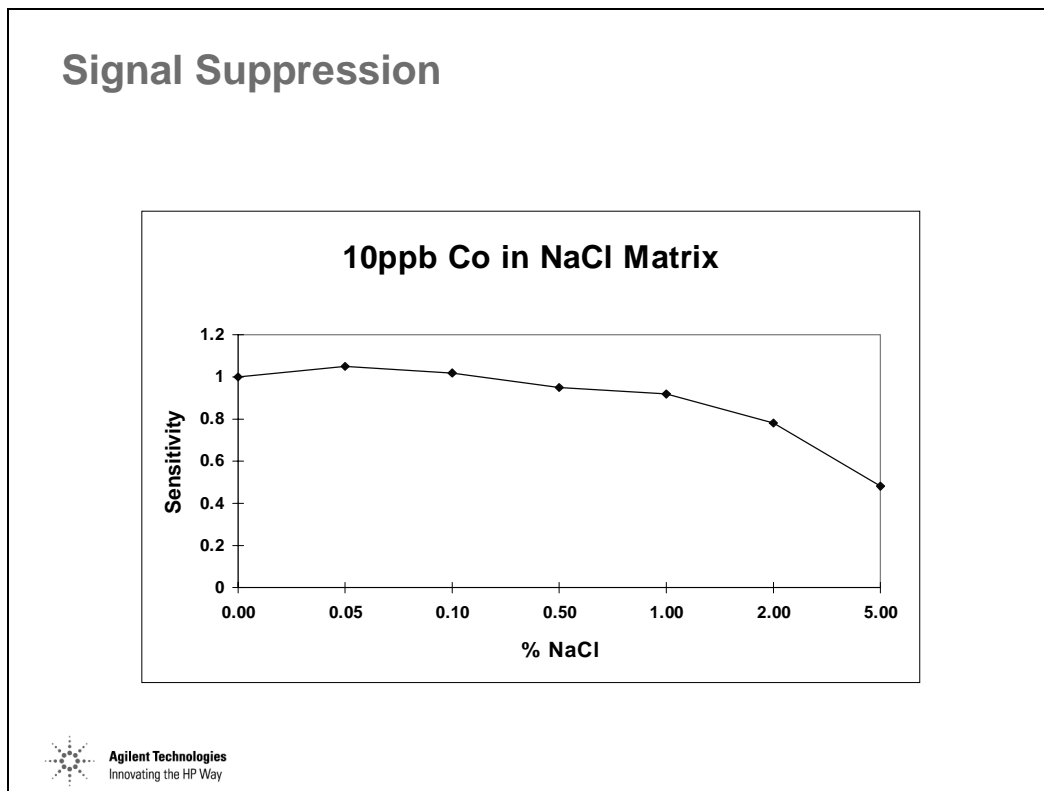
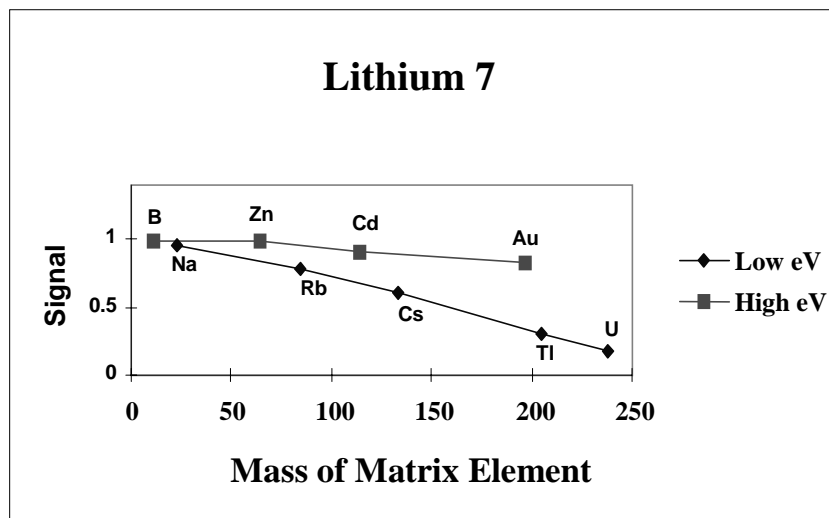


Figure 69

Matrix Effects – On Low Mass Analyte Analyte

Matrix Effects - on Low Mass Analyte



Molar Ratio of Matrix Element to Analyte = 1000:1

Figure 70

Matrix Effects – On Medium Mass Analyte

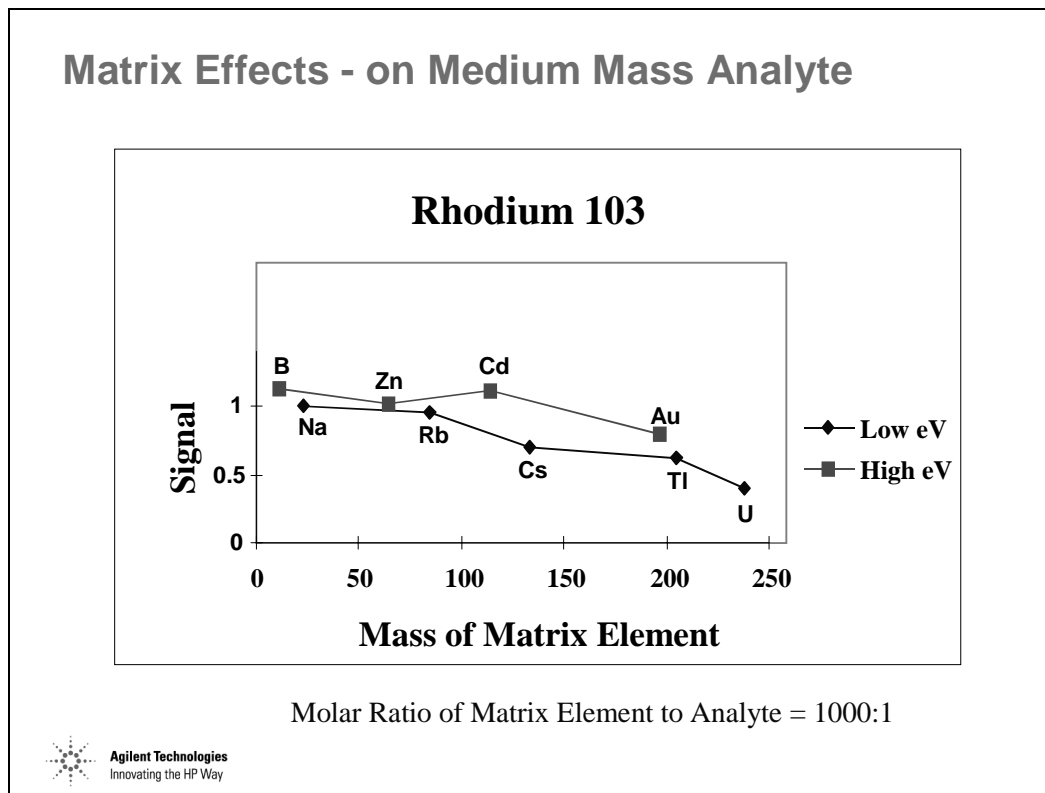


Figure 71

Matrix Effects – On High Mass Analyte

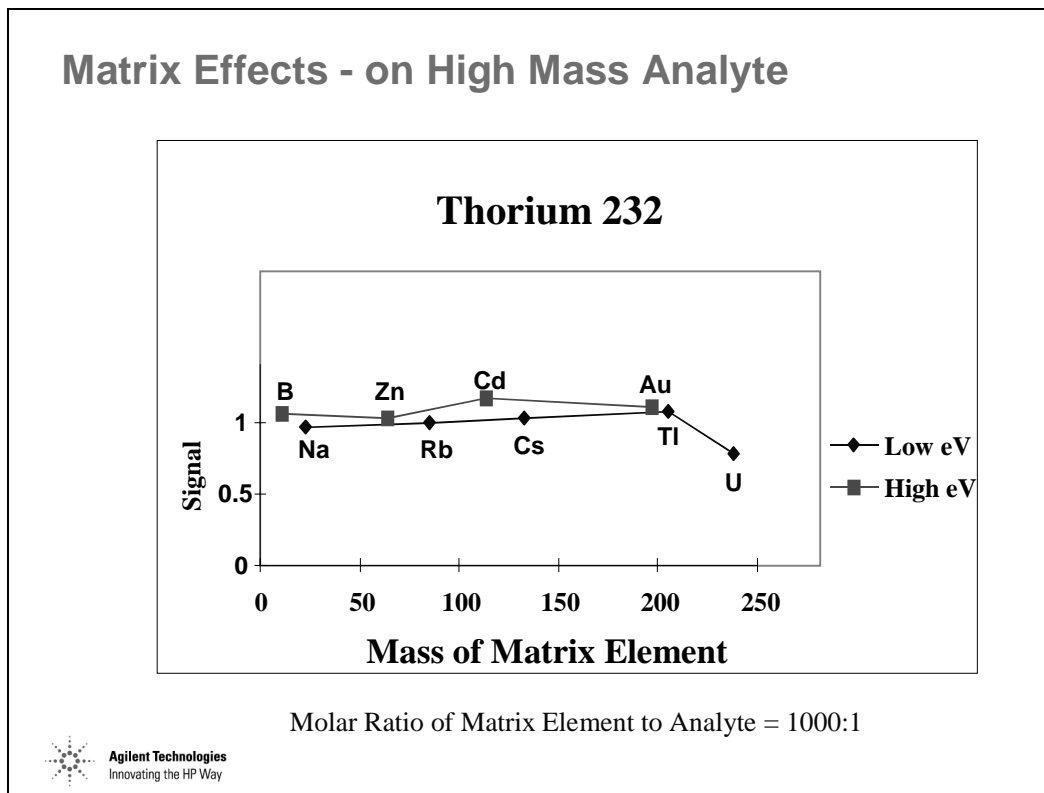


Figure 72

Space Charge Interface and Lens Region

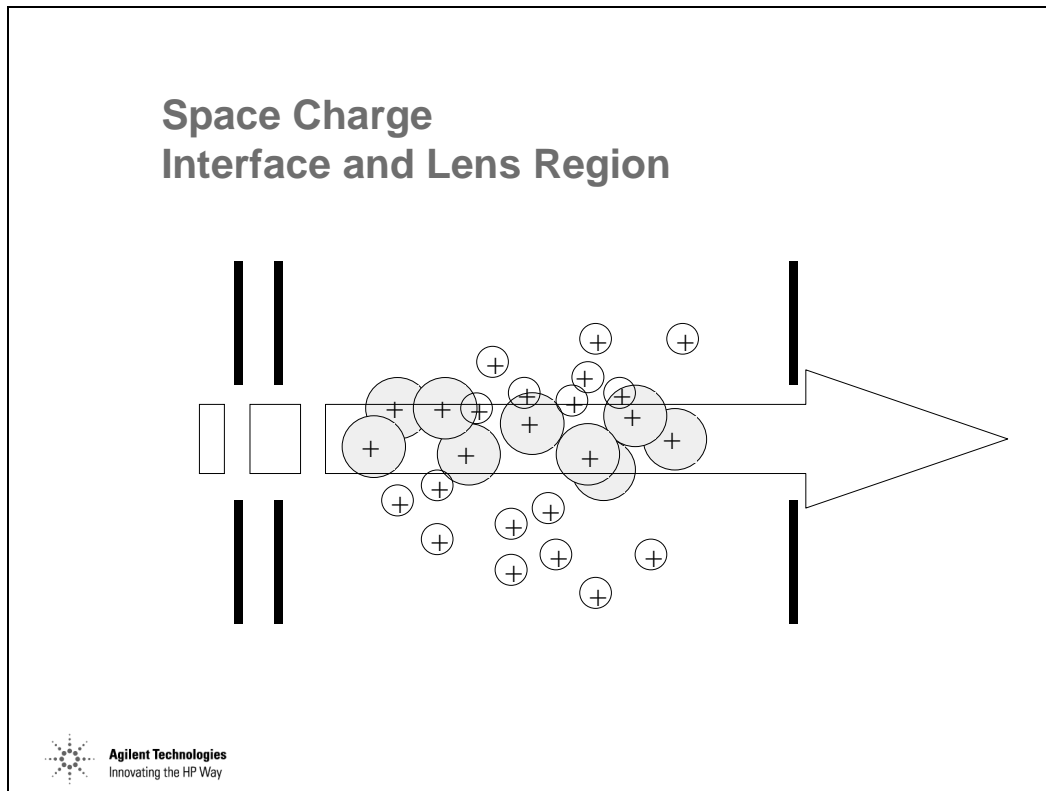


Figure 73

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

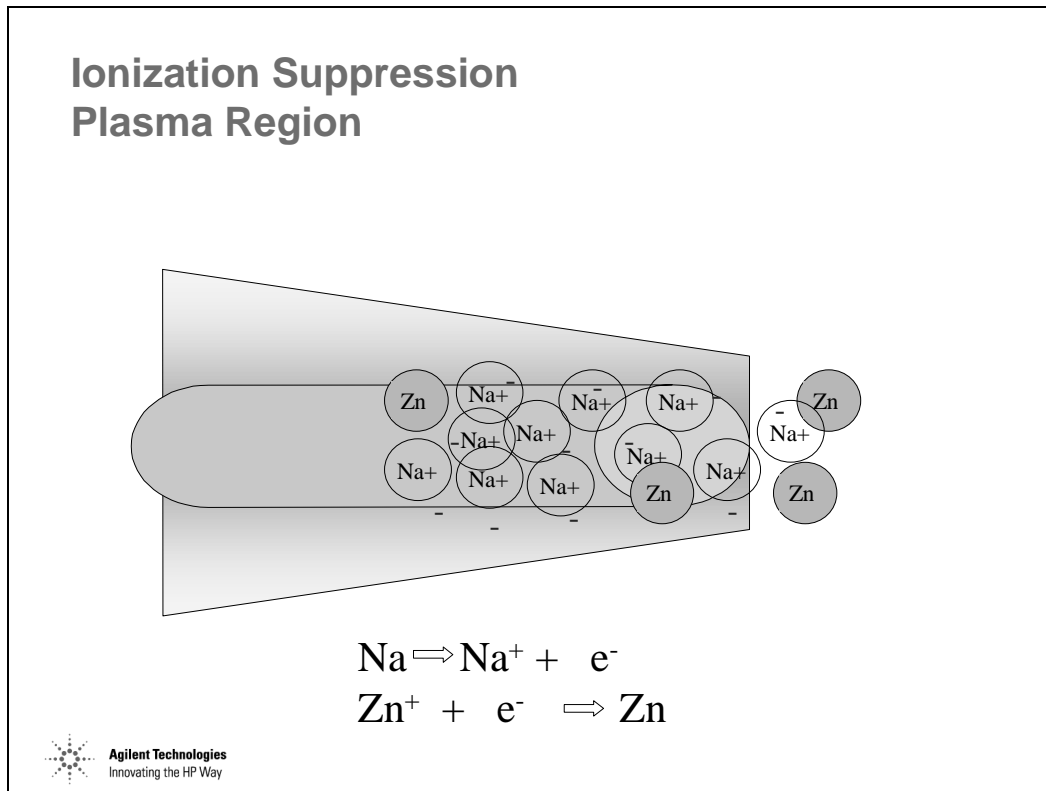


Figure 74

What Can Be Done About Matrix Effects

What Can Be Done About Matrix Effects

- Dilution of Sample
- Internal Standardization
- Standard Additions
- Matrix Elimination
 - Chromatography
 - ETV
 - Membrane desolvation



Figure 75

What Can Be Done About Matrix Effects



Agilent Technologies

Innovating the HP Way

Tuning the Agilent 7500

Why Tune the ICP-MS?

Why Tune the ICP-MS?

- Optimize Sensitivity
 - *Maximize Signal*
 - *Minimize Noise*
- Verify Correct Mass Calibration
- Verify Correct Ion Ratio Response
- Minimize Interferences
 - *Oxides*
 - *Doubly-Charged Ions*
 - *Argides*



Figure 76

Tuning Procedure Overview

Tuning Procedure Overview

- Tune Plasma Parameters
 - RF Power*
 - Gas Flows*
 - Peristaltic Pump Flow*
 - Torch Position*
- Tune Ion Optics
 - Extraction and Ion focusing lenses*
 - Omega Lenses*
- Tune Quadrupole Mass Analyzer
 - Optimum Mass Resolution and Response*
 - Correct Mass Assignments*
- Tune Detector
 - Optimum Sensitivity*
 - Optimum Dual Mode (Pulse and Analog) linearity*
- Save Tune Conditions
- Generate Tune Report



Agilent Technologies
Innovating the HP Way

Figure 77

Agilent 7500 ICP-MS Manual Tune Checklist [1]

Agilent 7500 ICP-MS Manual Tune Checklist [1]

See “Manually Tuning the HP-4500 ICP-MS” for detailed instructions

I. Verify Hardware

- vacuum, gas pressures and flows, peri-pump tubes and connections, error log
- examine cones with magnifier

II. Verify Plasma Parameters

- Aspirate tune solution #1, Warm up for 15-30 min
- Check sensitivity, and precision
- Fine tune carrier and/or blend gas flows for maximum signal, minimum RSDs (high Li RSDs are usually related to worn or damaged cones)
- Verify torch position and run torch position autotune if in doubt
- Check oxides (<0.8% is fine). If high: 1. Decrease carrier and/or blend gas flow. 2. Decrease peri-pump flow. 3. Increase sampling depth. 4. Increase RF power

III. Ion Lenses

- Adjust Ion lenses for maximum (or desired) signal and minimum noise and RSDs in this order :
 - Extract 1 and Extract 2 simultaneously (maintain ~ 50 V difference)
 - Einzel 2
 - Omega Bias, Omega + and Omega - in that order
 - QP focus if necessary



Agilent Technologies
Innovating the HP Way

Figure 78

Agilent 7500 ICP-MS Manual Tune Checklist [2]

Agilent 7500 ICP-MS Manual Tune Checklist [2]

IV. Quadrupole Parameters

- **Select Resolution/Axis**
- **Observe peak shapes, optimize by increasing Plate Bias and Pole Bias together if necessary**
- **Adjust peak widths (0.7-0.75 AMU at 10%) if necessary with AMU offset for low mass and AMU gain for mid- and high-mass**
- **Adjust mass calibration (nominal mass +/- 0.05 AMU) with Mass Offset for low mass and Mass Gain for mid and high mass**

V. Detector Parameters

- **Automatically: Select SetEM from Tune menu**
- **Run P/A factor Autotune from Tune while aspirating 100 ppb standard**

VI. Save Tune and Print Tune Report



Figure 79

Autotune Screen

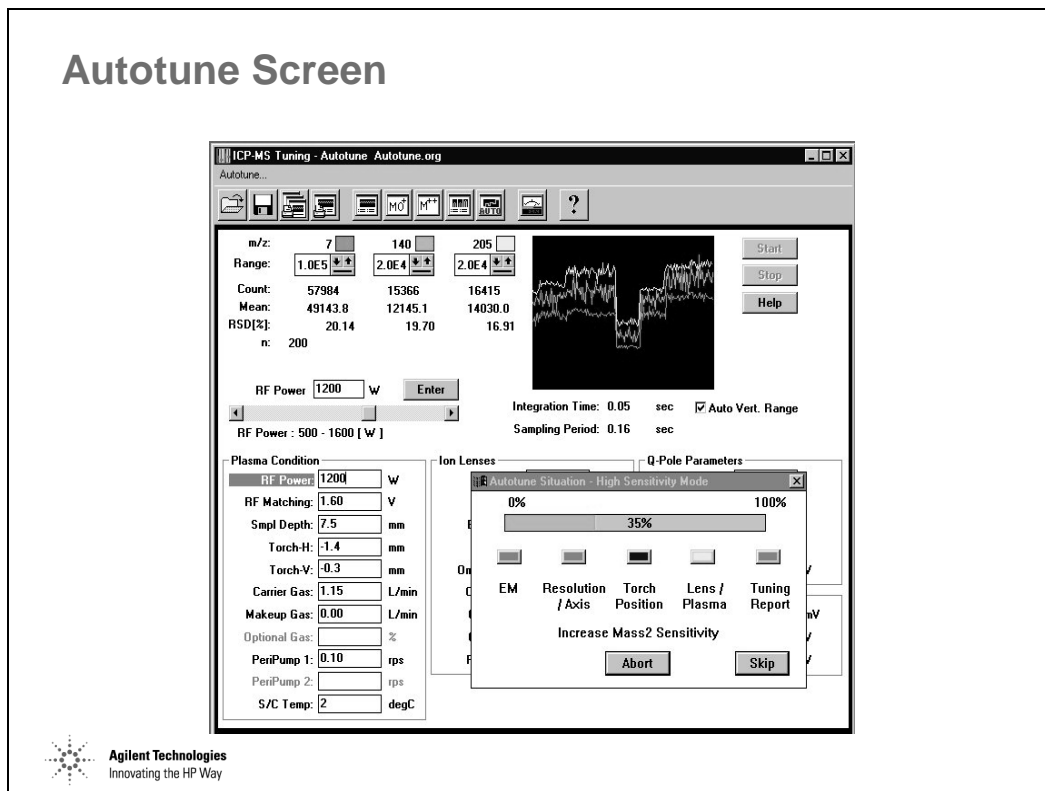


Figure 80

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

Autotuning of ICP Torch Position and New Target Tune

- Autotuning is used for consistent optimization, against a pre-defined set of tuning criteria (sensitivity, background, oxides, etc.)
- ICP torch position is critical for obtaining best sensitivity and lowest molecular interferences - manual ICP torch adjustment is imprecise and highly dependent on operator skill and experience. Can also be VERY time consuming.
- Target tune - user can specify the required sensitivity - even at different parts of the mass range. Target tune gives the novice user the expertise of an ICP-MS expert!
- Not limited to pre-defined suite of tune elements.



Figure 81

Features of Autotune (1)

Features of Autotune (1)

- **Customizing**

- ⇒ *Tune mass selection*
- ⇒ *Target tune set up for sensitivities, etc. (*)*
- ⇒ *Tune parameter range set up, fixed tune parameter set up, etc. (*)*

- **Speed**

- ⇒ *Quick Mode Option*
- ⇒ *Fix parameter set up (*)*
- ⇒ *Quick measurement*

- **Visualizing**

- ⇒ *Real time display of the Indicator*

(*) These items were realized in the Agilent 4500, but enforced in the Agilent 7500



Figure 82

Features of Autotune (2)

Features of Autotune (2)

- **Multiple Functions and Abilities**
 - 4 tuning modes
 - ◆ *Extraction,*
 - ◆ *Soft Extraction,*
 - ◆ *Cool Plasma*
 - ◆ *Hot ShieldTorch*
 - Target Tune
 - RSD Option
 - Saving function of Autotune's target set up file
 - Skip function
 - Intelligence of Autotune sequence



Figure 83

Choosing the Autotune Mode

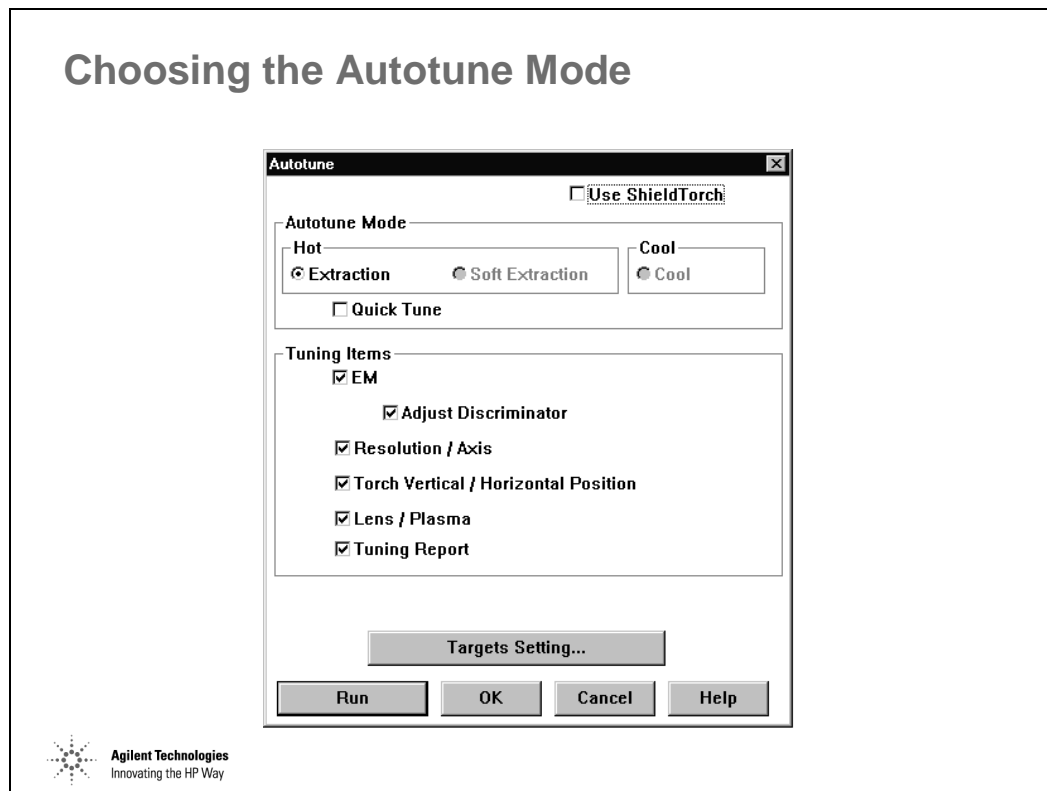


Figure 84

Basics of the Soft Extraction Mode

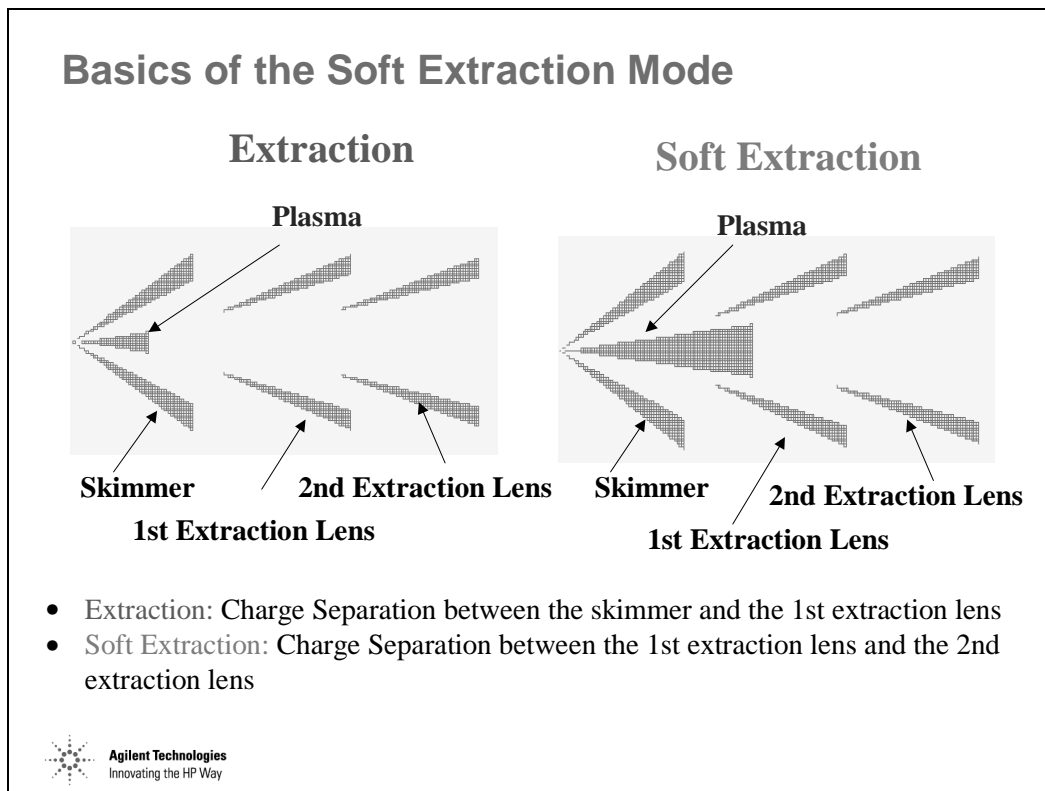


Figure 85

Comparison of Extraction Modes Settings

Comparison of Extraction Modes Settings				
	Extraction Mode		Soft Extraction Mode	
	Cool	Hot	Cool	Hot
Shield Torch	Li: 20000 (Co: 1000) Y : --- Tl: 300 BKG: < 1cps CeO: >>>	Li: 200 Y : 700 Tl: 300 BKG: <20cps CeO: 30%	-----	Li: 6 Y : 300 Tl: 200 BKG: < 1cps CeO: 8%
Non-Shield Torch	-----	Li: 15 Y : 30 Tl: 15 BKG: < 5cps CeO: 0.5 %	-----	-----
Typical Sensitivity for Each Mode By Agilent 7500s (Mcps/ppm)				



Figure 86

Autotune - Target Setting

Autotune - Target Setting

Set Autotune Targets - Extraction Mode

-EM
Tuning Mass [amu]: ☐ Auto Selection ☒ Manual Setting

-Resolution / Axis ☒ Mass1 ☒ Mass2 ☒ Mass3
Tuning Mass [amu]:

-Torch Position and Lens / Plasma
Tuning Mass [amu]: Mass1 Mass2 Mass3

Sensitivity
Increase Sensitivity: ☒ Lower Limit [cps]: ☒ ☒
Decrease Sensitivity: ☐ Upper Limit [cps]: ☐ ☐

☒ Oxide Ratio
☐ Mass1 ☒ Mass2 ☐ Mass3 %

☒ Doubly Charged Ratio
☐ Mass1 ☒ Mass2 ☐ Mass3 %

☒ Background cps

☐ RSD Option

Reset to Default Load... Save... Range Setting...

OK Cancel Help



Figure 87

Target Setting - Range Setting

Target Setting - Range Setting

Set Autotune Targets - Extraction Mode

EM
 Tuning Mass [amu]: ☐ Auto Selection ☒ Manual Setting

Resolution / Axis ☒ Mass1 ☒ Mass2 ☒ Mass3
 Tuning Mass [amu]:

Torch Position and Lens / Plasma
 Tuning Mass [amu]: Mass1 Mass2 Mass3

Sensitivity
 Increase Sensitivity: ☒ Lower Limit [cps]:
 Decrease Sensitivity: ☐ Upper Limit [cps]:

☒ Oxide Ratio
☐ Mass1 ☐ Mass2 ☐ Mass3 %

☒ Doubly Charged Ratio
☐ Mass1 ☐ Mass2 ☐ Mass3 %

☒ Background cps

☐ RSD Option

Reset to Default Load... Save... Range Setting...

OK Cancel Help

<Parameter Range> Current Value << Min Max >> << Fix >>

Plasma Parameters

RF Power [W]: 1350	<input type="text" value="1200"/>	<input type="text" value="1400"/>	<input type="radio"/> 1300
Smpl Depth [mm]: 8.0	<input type="text" value="6.0"/>	<input type="text" value="10.0"/>	<input type="radio"/> 7.0
Torch-H [mm]: -0.5	<input type="text" value="-2.0"/>	<input type="text" value="2.0"/>	
Torch-V [mm]: 0.2	<input type="text" value="-2.0"/>	<input type="text" value="2.0"/>	
Carrier Gas [L/min]: 1.22	<input type="text" value="1.10"/>	<input type="text" value="1.40"/>	<input type="radio"/> 1.20
Makeup Gas [L/min]: 0.00	<input type="text" value="0.10"/>	<input type="text" value="0.40"/>	<input type="radio"/> 0.00

Lens Parameters

Extract 1 [V]: -170.0	<input type="text" value="-200.0"/>	<input type="text" value="0.0"/>	<input type="radio"/> -180.0
Extract 2 [V]: -130.0	<input type="text" value="-200.0"/>	<input type="text" value="0.0"/>	<input type="radio"/> -80.0
Einzel 1,3 [V]: -100	<input type="text" value="-200"/>	<input type="text" value="-100"/>	<input type="radio"/> -100
Einzel 2 [V]: 5	<input type="text" value="0"/>	<input type="text" value="10"/>	<input type="radio"/> 10
Omega Bias [V]: -45	<input type="text" value="-50"/>	<input type="text" value="-40"/>	<input type="radio"/> -40
Omega+ [V]: 7.0	<input type="text" value="5.0"/>	<input type="text" value="10.0"/>	<input type="radio"/> 10.0
Omega- [V]: 10.0	<input type="text" value="0.0"/>	<input type="text" value="10.0"/>	<input type="radio"/> 5.0
QP Focus [V]: 7.0	<input type="text" value="5.0"/>	<input type="text" value="10.0"/>	<input type="radio"/> 0.0
Plate Bias [V]: -7.0	<input type="text" value="-20.0"/>	<input type="text" value="0.0"/>	<input type="radio"/> 0.0

Mass Parameters

AMU Gain: 129	0	255
AMU Offset: 123	0	511
Axis Gain: 1.0000	0.9800	1.0200
Axis Offset: 0.05	-0.50	0.50
QP Bias [V]: 0.0	-20.0	20.0
		<input type="checkbox"/> -10.0

EM Parameters

Discriminator [mV]: 9.9	0.0	200.0
Analog HV [V]: 1940	0	3500
Pulse HV [V]: 1150	0	2000



Agilent Technologies
 Innovating the HP Way

Figure 88

Sensitivity Tuning

Sensitivity Tuning

ICP-MS Tuning - Sensitivity NORMALS.U

File Tune Acq Params Meters Maintenance Log Help

m/z: 7 89 205

Range: 1000 1000 1000

Count:

Mean:

RSD[%]:

n:

Extract 1: -170.0 V Enter

Extract 1: -200.0 - 10.0 [V]

Integration Time: 0.10 sec ☒ Auto Vert. Range

Sampling Period: 0.31 sec

Plasma Condition

RF Power: 1350 W

RF Matching: 1.71 V

Smpl Depth: 8.0 mm

Torch-H: -0.5 mm

Torch-V: 0.2 mm

Carrier Gas: 1.22 L/min

Makeup Gas: 0.00 L/min

Optional Gas: 0.0 %

PeriPump 1: 0.10 rps

PeriPump 2: rps

S/C Temp: 2 degC

Ion Lenses

Extract 1: -170.0 V

Extract 2: -130 V

Einzel 1,3: -100 V

Einzel 2: 5 V

Omega Bias: -45 V

Omega (+): 7.0 V

Omega (-): 10.0 V

QP Focus: 7.0 V

Plate Bias: -7.0 V

Q-Pole Parameters

AMU Gain: 129

AMU Offset: 123

Axis Gain: 1.0000

Axis Offset: 0.05

QP Bias: 0.0 V

Detector Parameters

Discriminator: 9.9 mV

Analog HV: 1940 V

Pulse HV: 1150 V



Figure 89

Peak Shape and Resolution

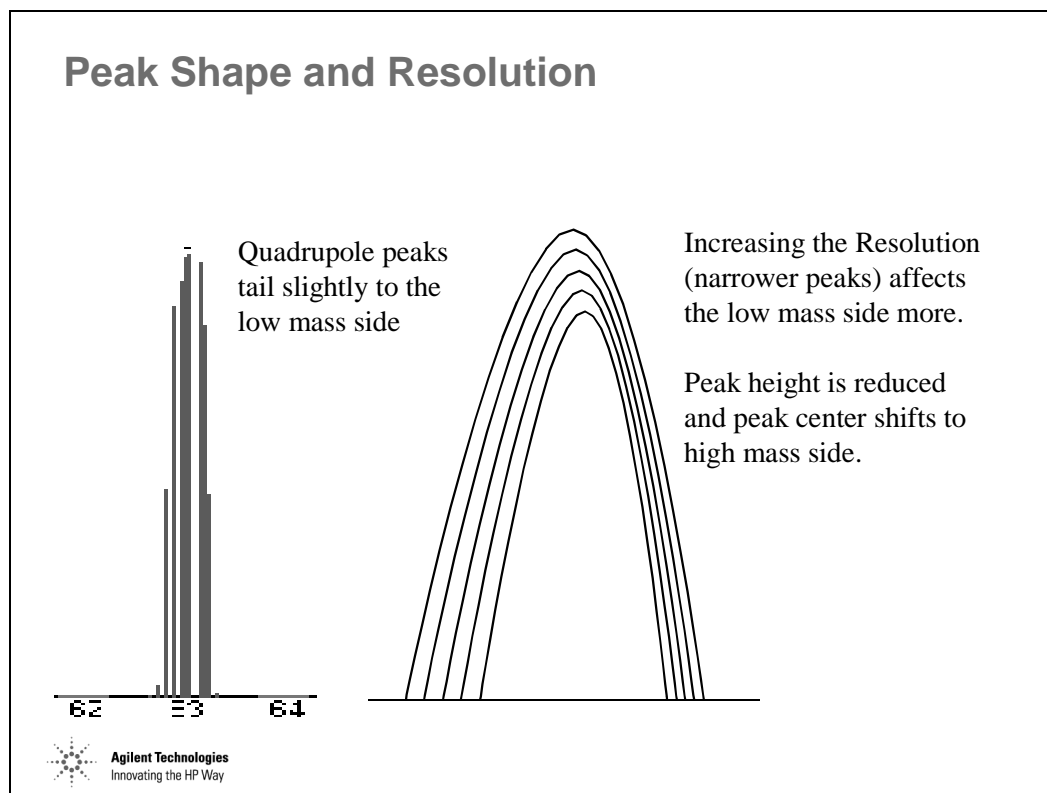


Figure 90

Abundance Sensitivity

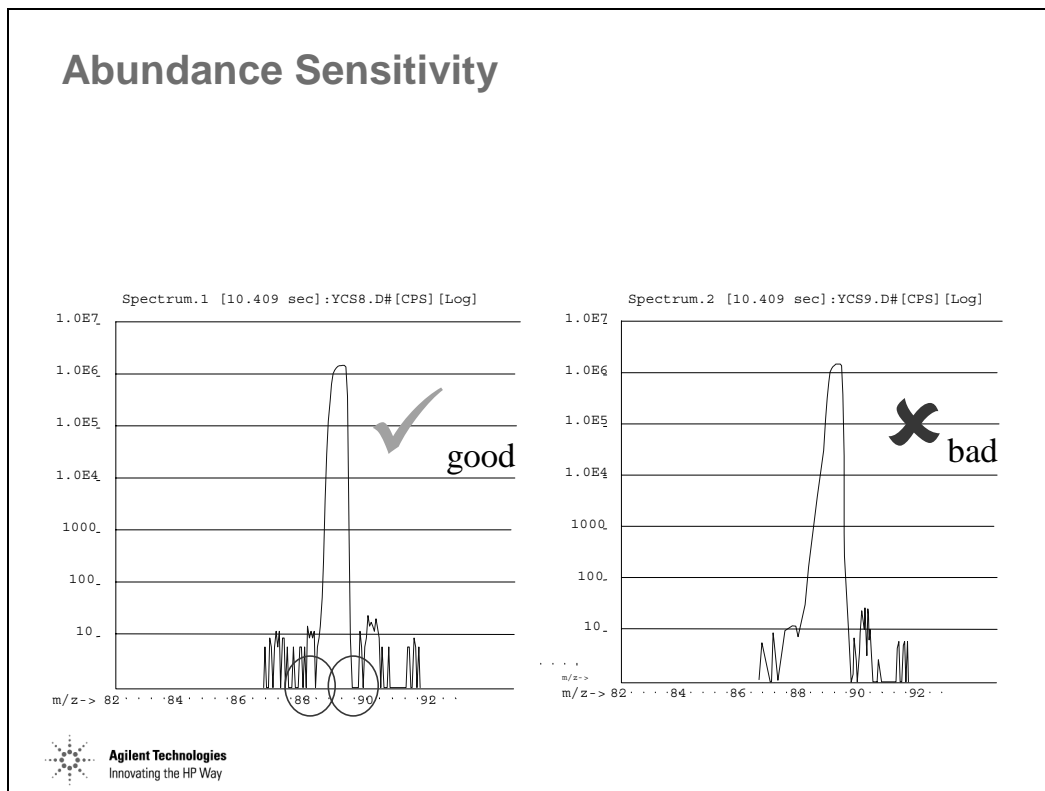


Figure 91

Quadrupole Mass Filter - Scan Line

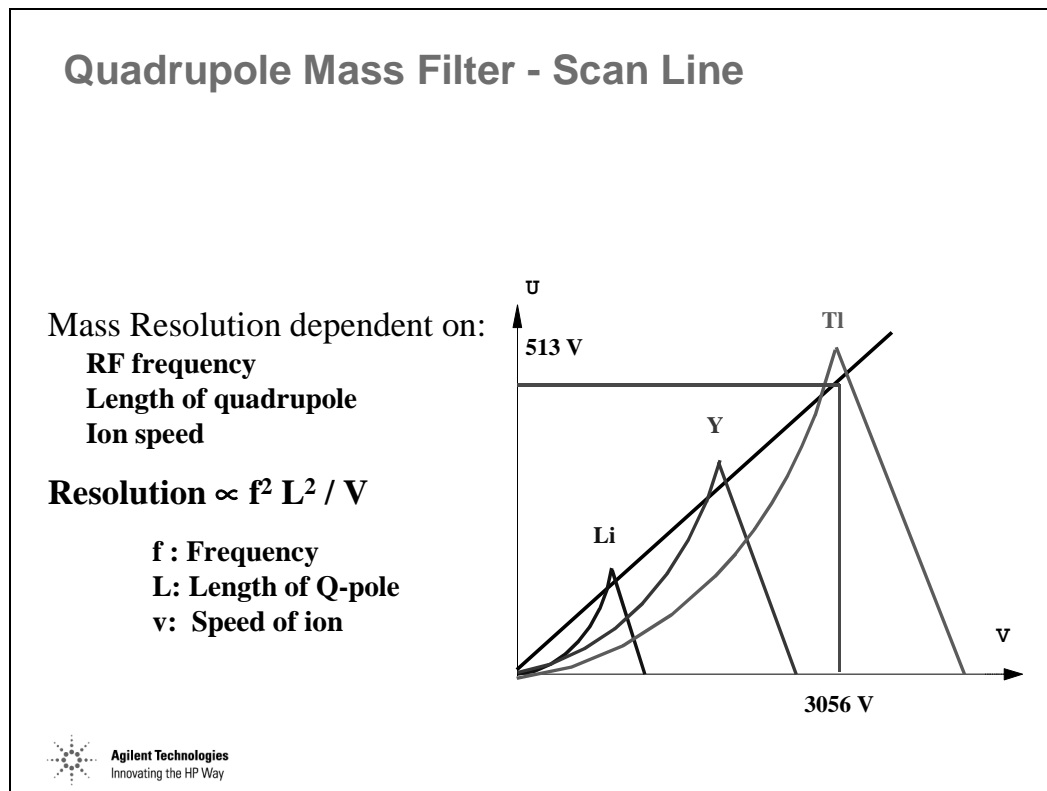


Figure 92

Detection Limits in Normal Mode

Detection Limits in Normal Mode																		
Unit : ng/L(ppt)																		
3 sigma Integration Time :3sec.																		
Upper Value : Detection Limit Lower Value : BEC																		
Li 5 51	Be 2.8 0.9																B 11 93	C 5000 82000
Na 100 730	Mg 40 110																Al 10 64	Si 700 16000
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	Ne	
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 0.8 0.8	Ru 7 100	Rh 1 2	Pd 0.7 1.4	Ag 0.7 1.7	Cd 0.7 1.2	In 0.1 0.2	Sn 0.6 2	Sb 0.7 1	Te 7 7	I 70 230	Ar	
Cs 0.5 2.7	Ba 2.5 3.5	* 30 4	Hf 0.3 0.1	Ta 0.08 0.5	W 0.3 0.3	Re 0.3 0.3	Os 0.2 310	Ir 0.2 2.3	Pt 18 2.3	Au 0.8 1.2	Hg 1.6 1.8	Tl 1 6	Pb 1 0.3	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 0.2 0.2	Th 0.2 0.2	Pa 0.6 0.8	U 0.6 0.8	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		



Figure 93

Detection Limits in Soft Extraction Mode

Detection Limits in Soft Extraction Mode																	
Unit : ng/L(ppt)																	
3 sigma Integration Time :3sec.																	
Upper Value : Detection Limit Lower Value : BEC																	
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	



Agilent Technologies
 Innovating the HP Way

Figure 94

Low BECs in Soft Extraction Mode

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

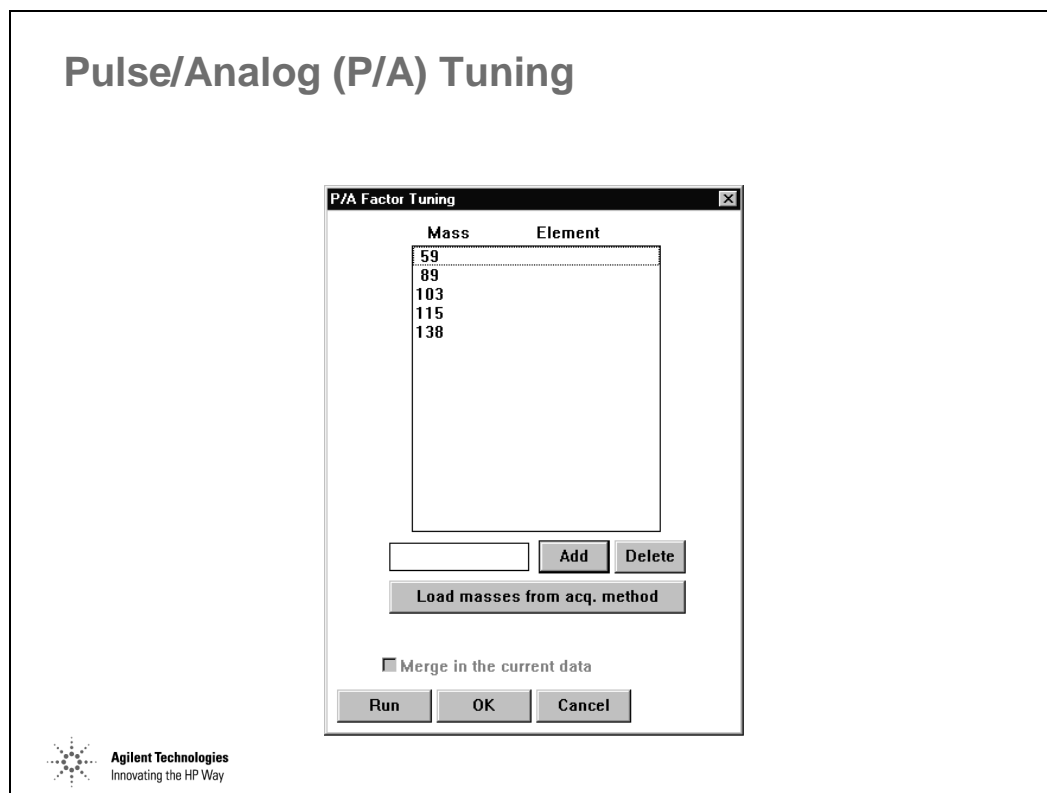


Figure 96



Agilent Technologies

Innovating the HP Way

Maintenance of the Agilent 7500

Maintenance Schedule

Maintenance Schedule

- Daily
 - Lab conditions, Argon, drain, peristaltic pump tubing, cones
- When Needed
 - Cones, nebulizer, peristaltic pump tubing, torch, water filter, electron multiplier
- Weekly
 - tuning solution preparation, torch, spray chamber, nebulizer, carrier gas line, cooling system
- Monthly
 - check rotary pump, oil mist filter, check extraction lens
- 6 months
 - clean lenses, change rotary pump oil, replace gas tubing
- Yearly
 - replace o-rings, clean penning gauge, check/replace mist filter



Agilent Technologies
Innovating the HP Way

Figure 97

Running Time Maintenance Screen

Running Time Maintenance Screen

Running Time

	Current Time [Hour(s)]		Current Data [Count(s)]		Maintenance Period [Count(s)]
Power ON:			EM Total Current: 0.00E+000	Reset	<input checked="" type="checkbox"/> 1.00E+015
Vacuum ON:					
Plasma ON:					

<Vacuum Running Time>

	Current Time [Hour(s)]		Maintenance Period [Hour(s)]
Rotary Pump:	0	Reset	
Turbo Pump (I):	0	Reset	
Turbo Pump (A):	0	Reset	
check the rough pump oil	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 720
replace the rough pump oil	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
replace the mist-filter	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
user defined	<input type="text"/>	Reset	<input type="checkbox"/> 0
user defined	<input type="text"/>	Reset	<input type="checkbox"/> 0

<Plasma Running Time>

	Current Time [Hour(s)]		Maintenance Period [Hour(s)]
clean the einzel lens	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
clean the extract lens	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
clean the sampling cone	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
clean the skimmer	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
change the peri-pump tube	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
clean the nebulizer	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
clean the spray chamber	<input type="text"/>	Reset	<input checked="" type="checkbox"/> 4320
user defined	<input type="text"/>	Reset	<input type="checkbox"/> 0

OK

Cancel

Help


 Agilent Technologies
Innovating the HP Way

Figure 98

Early Maintenance Feedback (EMF)

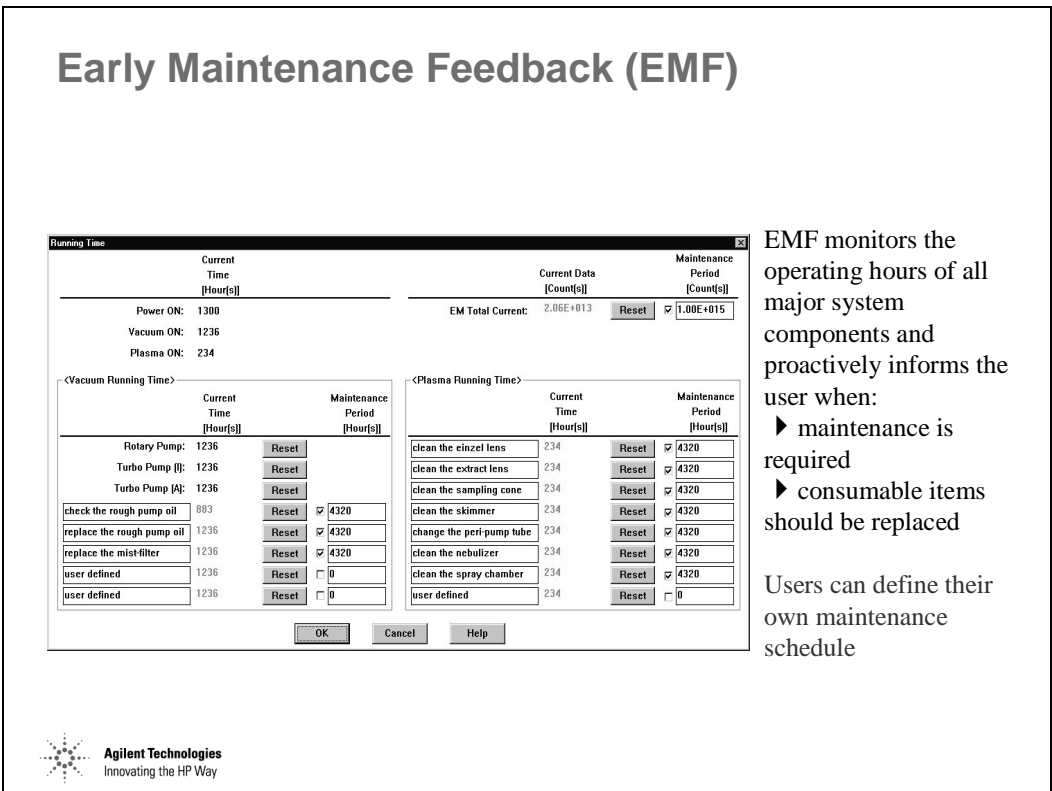


Figure 99

Normal Maintenance of the Sample Introduction System

Normal Maintenance of the Sample Introduction System

Non-Glassware Components

- Sample tubing
 - Peristaltic pump tubing
 - Babington nebulizer
 - Crossflow nebulizer
 - Nebulizer end caps
 - O-rings
1. Soak in 1% to 5% nitric acid (5 min.)
 2. Clean in ultrasonic bath (5 min.)
 3. Rinse with DI water

Glassware

- Concentric nebulizer
 - Spray chamber
 - Ball joint connector
 - Torch
1. Soak in 1% to 5% nitric acid (5 min.)
or sonicate in 10% Citranox[®]
 2. Rinse with DI water



Figure 100

Overnight Cleaning of the Sample Introduction System

Overnight Cleaning of the Sample Introduction System

For severely contaminated glassware and non-glassware components

Procedure

1. Soak in 5% nitric acid overnight or boil in 10% Citranox[®] for 1 hour, rinse in 5% nitric acid
2. Rinse with DI water



Agilent Technologies
Innovating the HP Way

Figure 101

Sample Introduction Maintenance

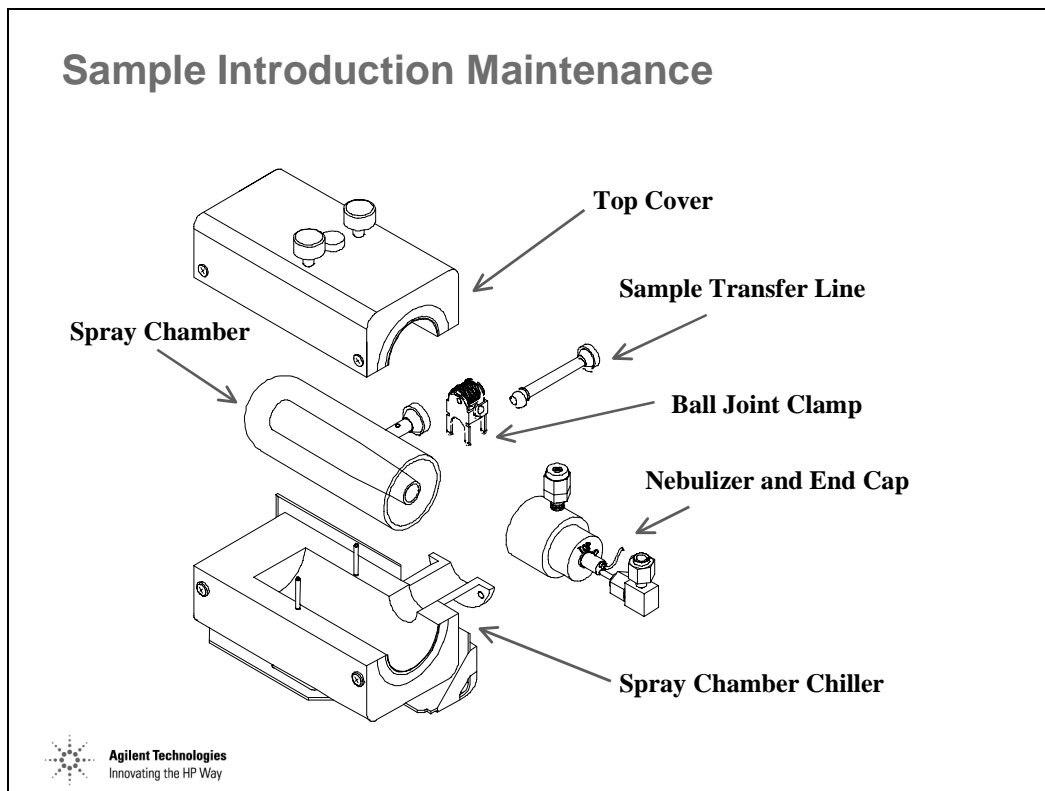


Figure 102

Nebulizer Connections

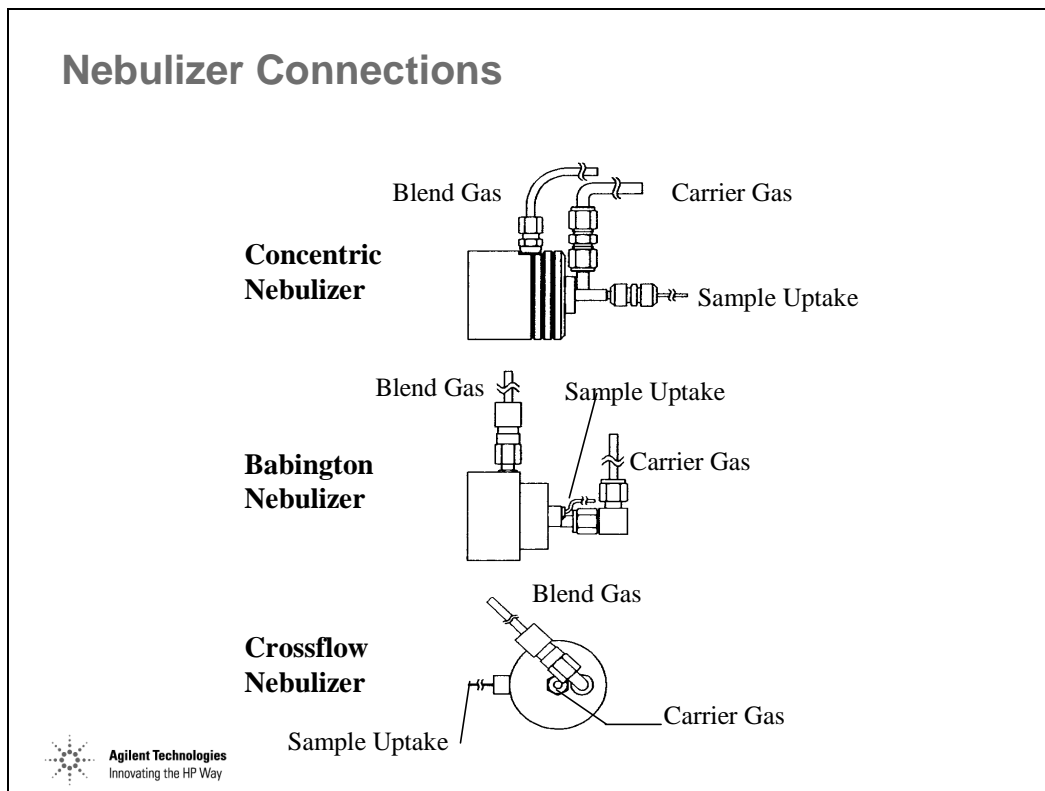


Figure 103

Maintenance of a Babington Nebulizer

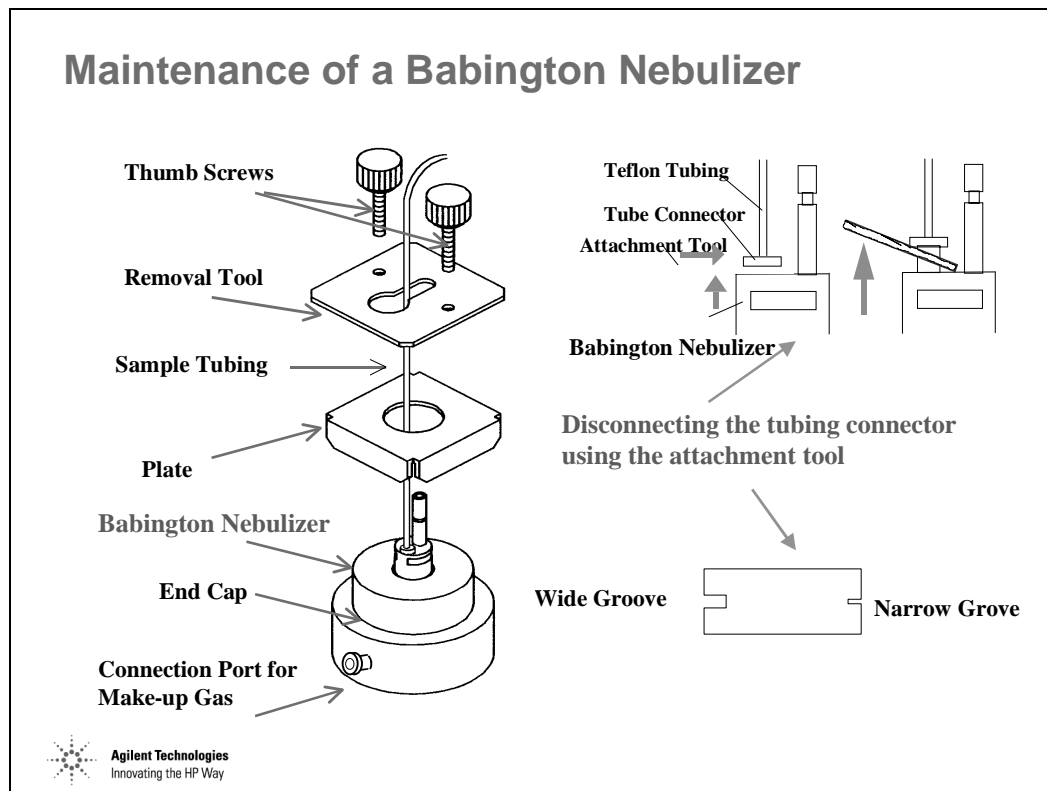


Figure 104

Torch Maintenance

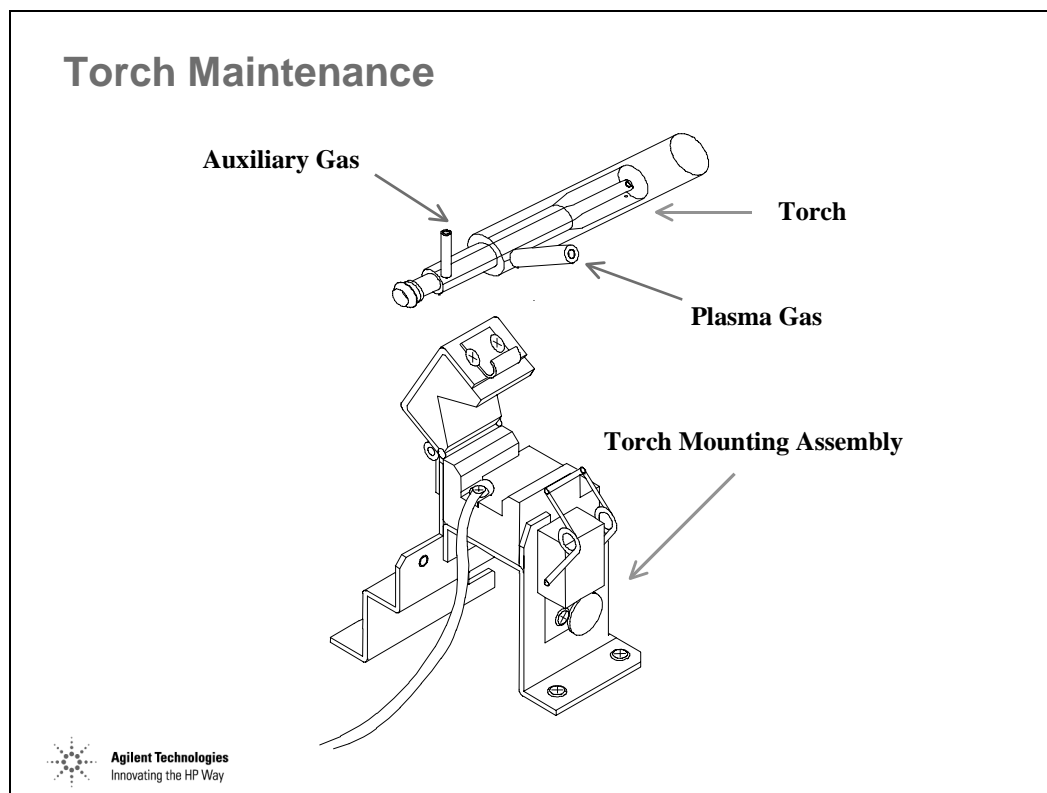


Figure 105

Interface Maintenance

Interface Maintenance

Routine Maintenance

Components

- Sampling cone
- Skimmer cone

Procedure

1. Soak in 1-5% nitric acid (<10 min.)
2. Rinse with DI water

Removing Severe Deposits

Components

- Sampling cone
- Skimmer cone

Procedure

1. Polish with waterproof abrasive paper
 - be careful not to damage the orifice
2. Rinse with DI water



Agilent Technologies
Innovating the HP Way

Figure 106

Maintenance of the Cones

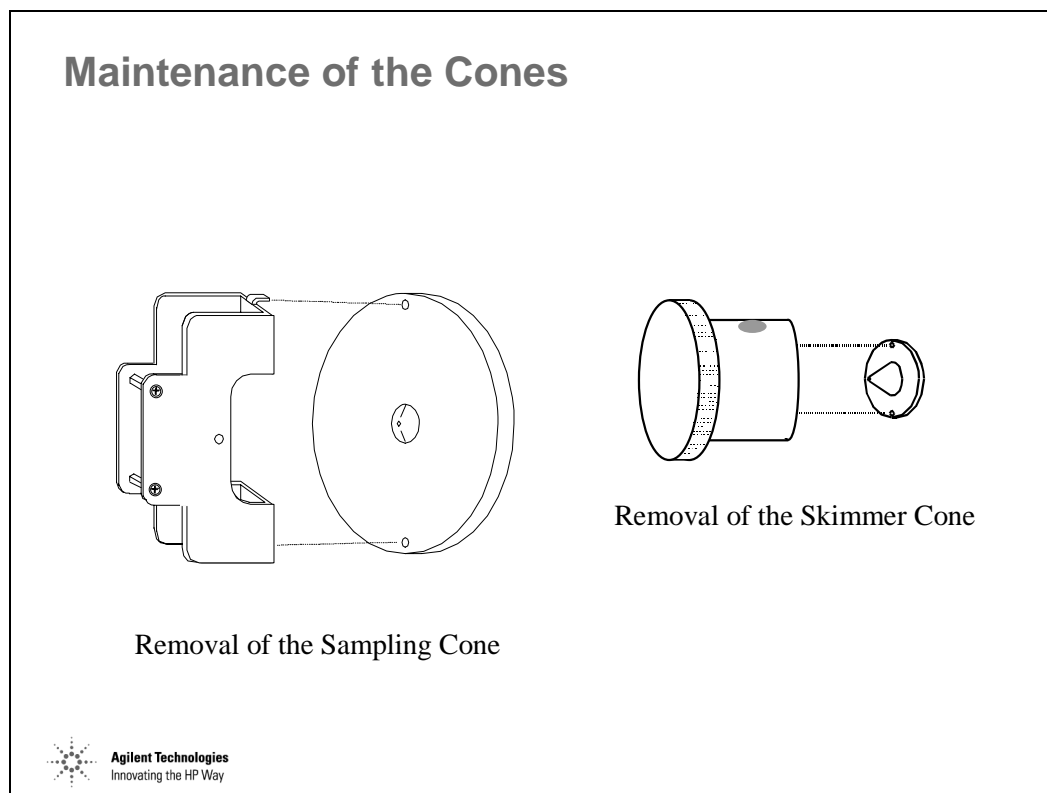


Figure 107

Extraction Lenses Maintenance

Extraction Lenses Maintenance

- Remove skimmer base from vacuum manifold
- Disassemble extraction lenses, screws and spacers
- Polish extraction lenses with waterproof abrasive paper
- Wash extraction lenses in DI water
- Sonicate lenses, spacers and screws in DI water for 5 minutes
- Sonicate lenses, spacers and screws in acetone for 5 minutes
- Reassemble lenses, spacers and screws on skimmer base
- Install skimmer base on vacuum manifold



Figure 108

Extraction Lenses

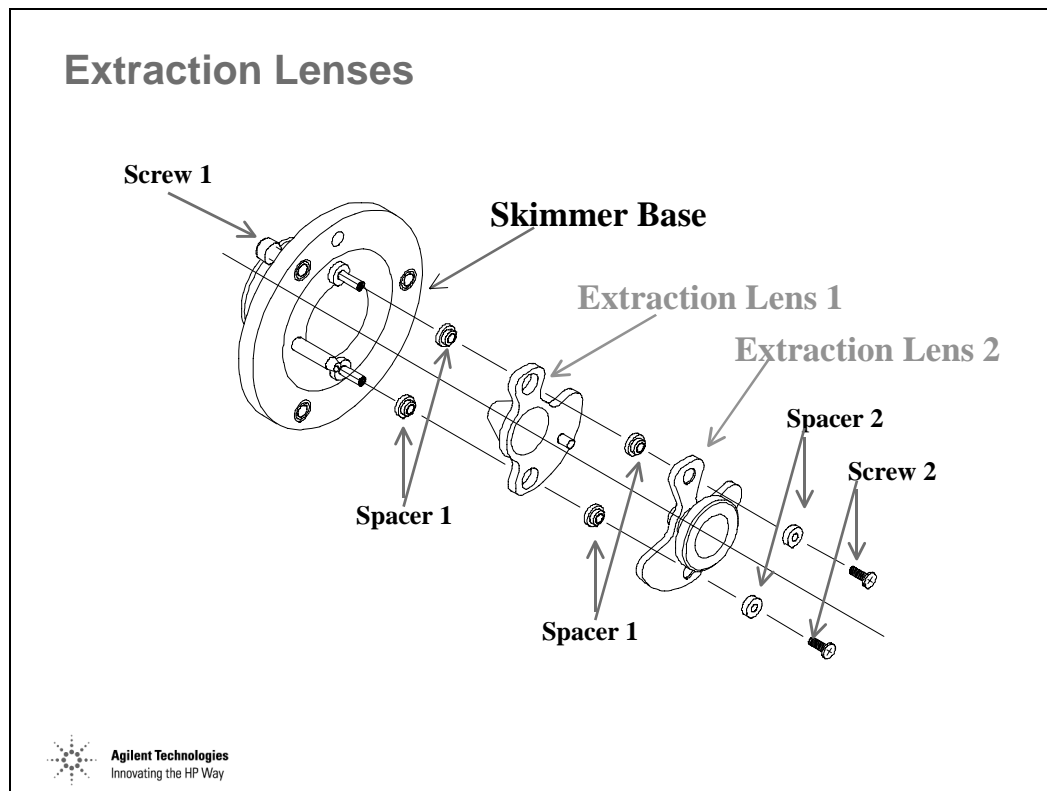


Figure 109

Cleaning of the Einzel Lens and Omega Lens Assembly

Cleaning of the Einzel Lens and Omega Lens Assembly

- Disassemble lenses, remove screws and spacers
- Polish each lens, lens orifice and the curved surfaces of the Omega lenses using waterproof abrasive paper
- Wash lenses in DI water
- Sonicate lenses, spacers and screws in DI water for 5 minutes
- Sonicate lenses, spacers and screws in acetone or alcohol for 5 minutes
- Reassemble and install the lens assemblies and install them in the vacuum manifold
- Replace top cover and vent nut and restart system.



Figure 110

Instrument Shutdown

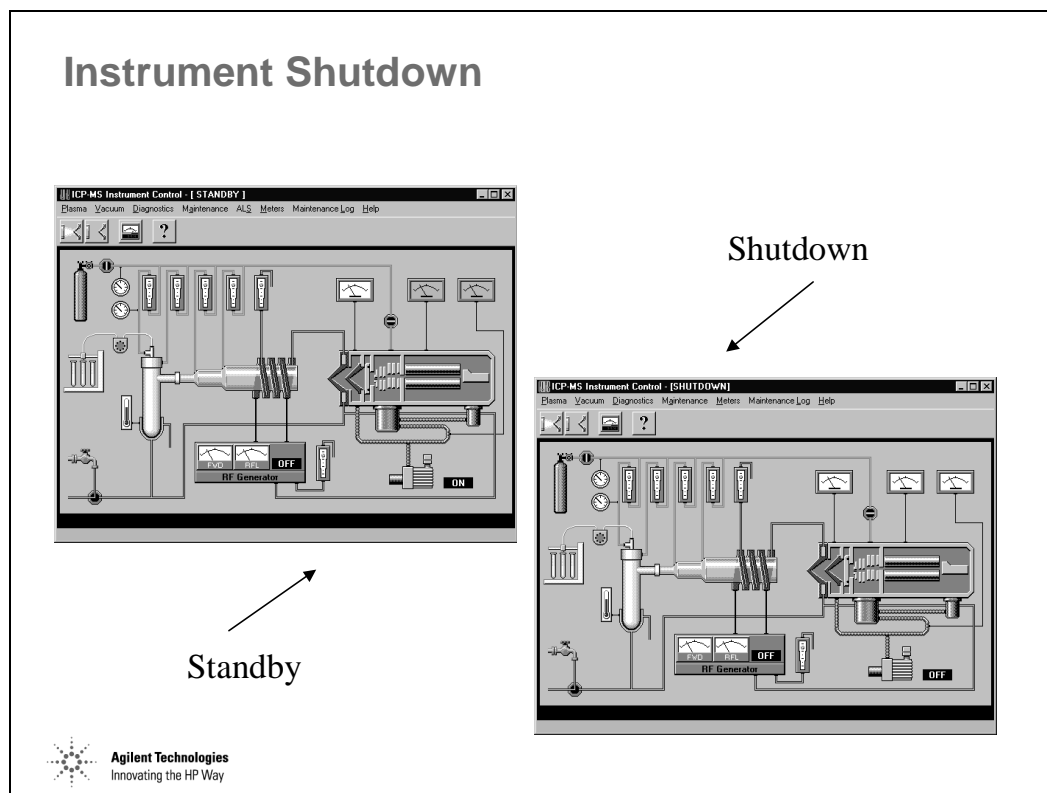


Figure 111

Removal of the Einzel Lens - Omega Lens Assembly

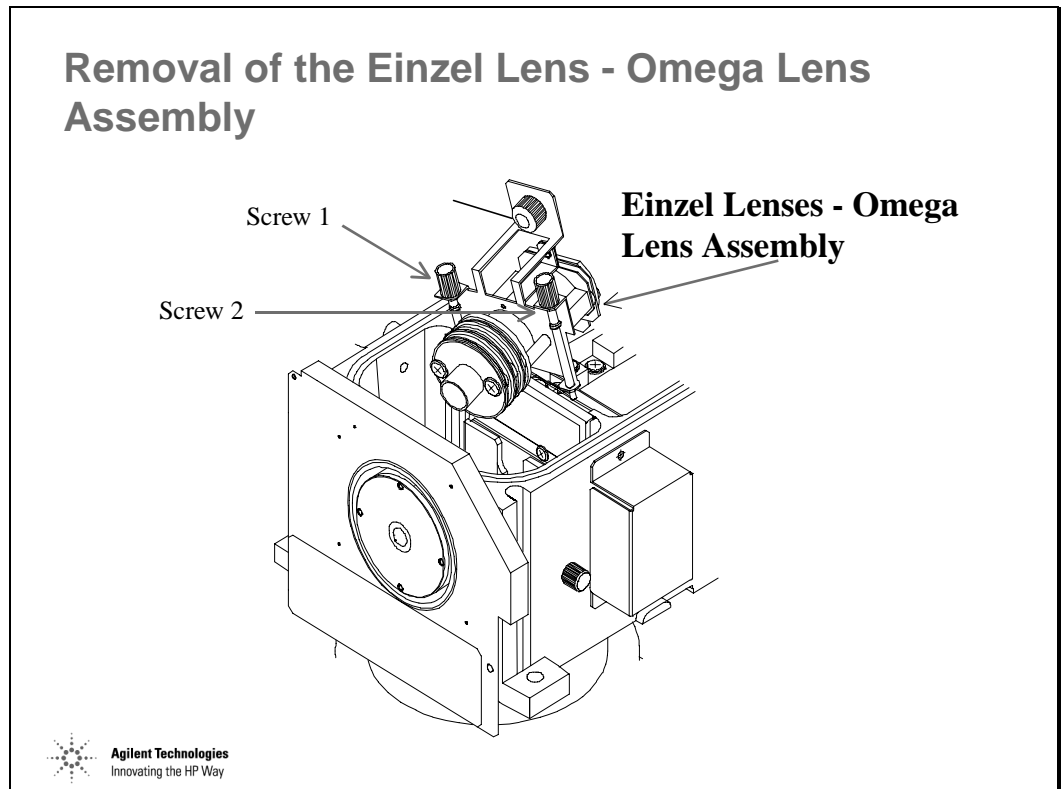


Figure 112

Expanded View of Einzel Lens - Omega Lens Assembly

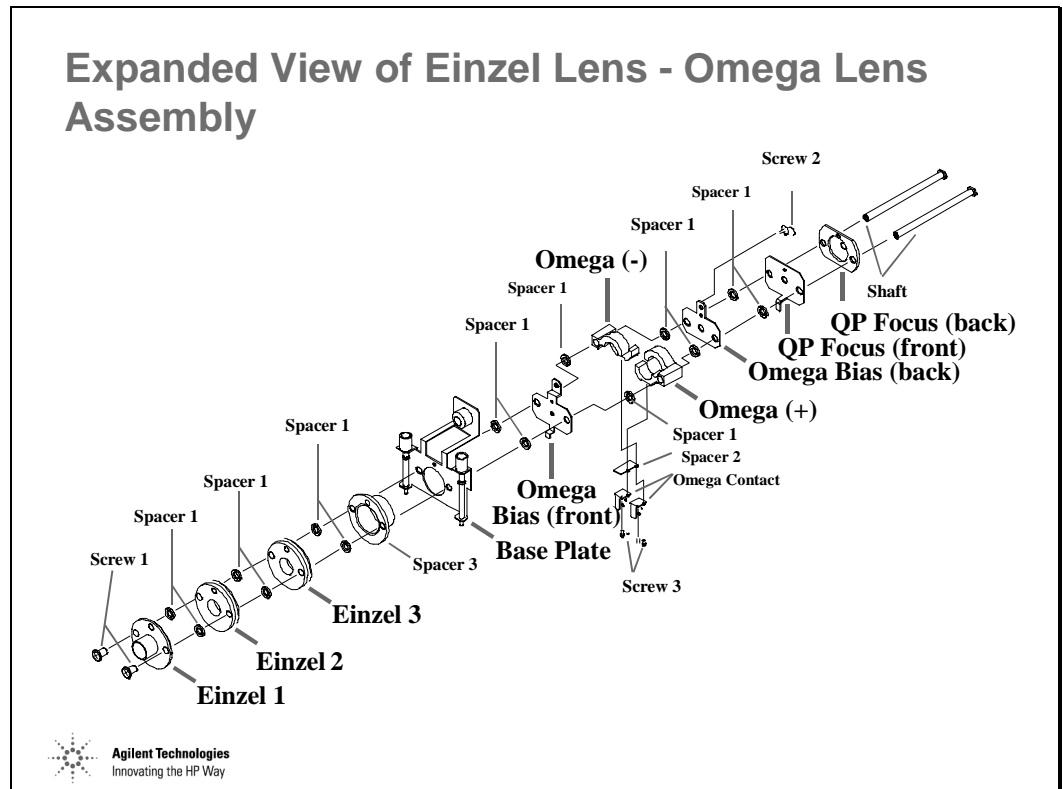


Figure 113

Plate Bias Lens

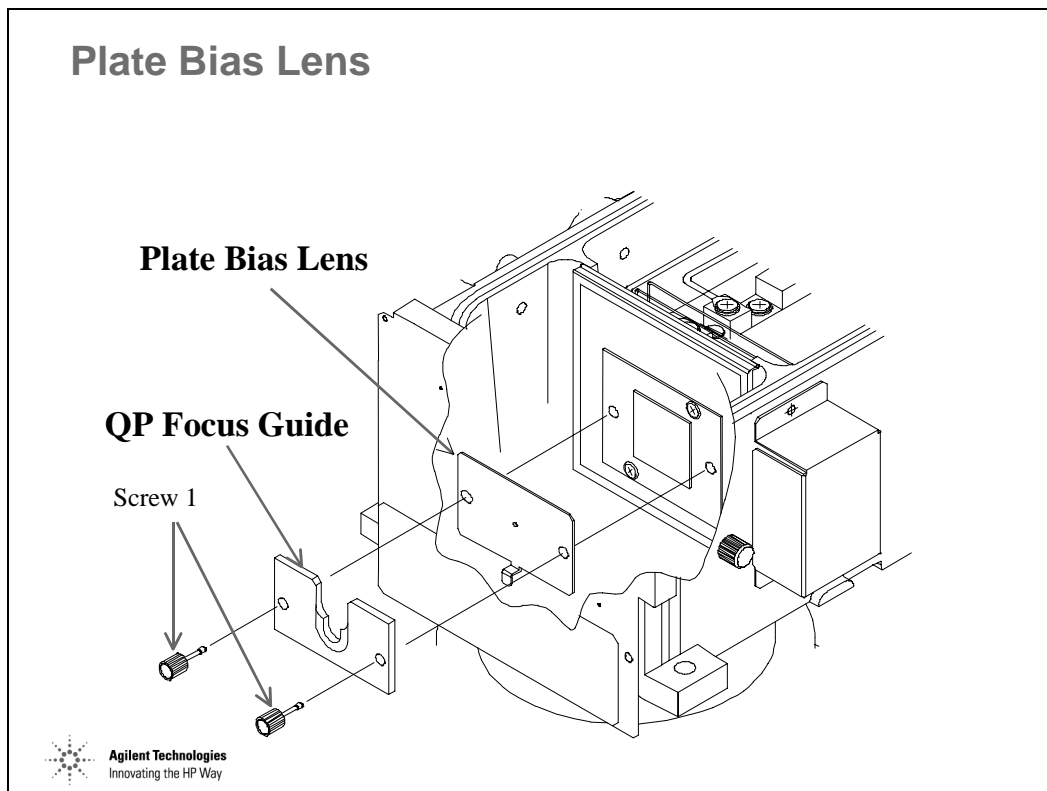


Figure 114

Penning Gauge

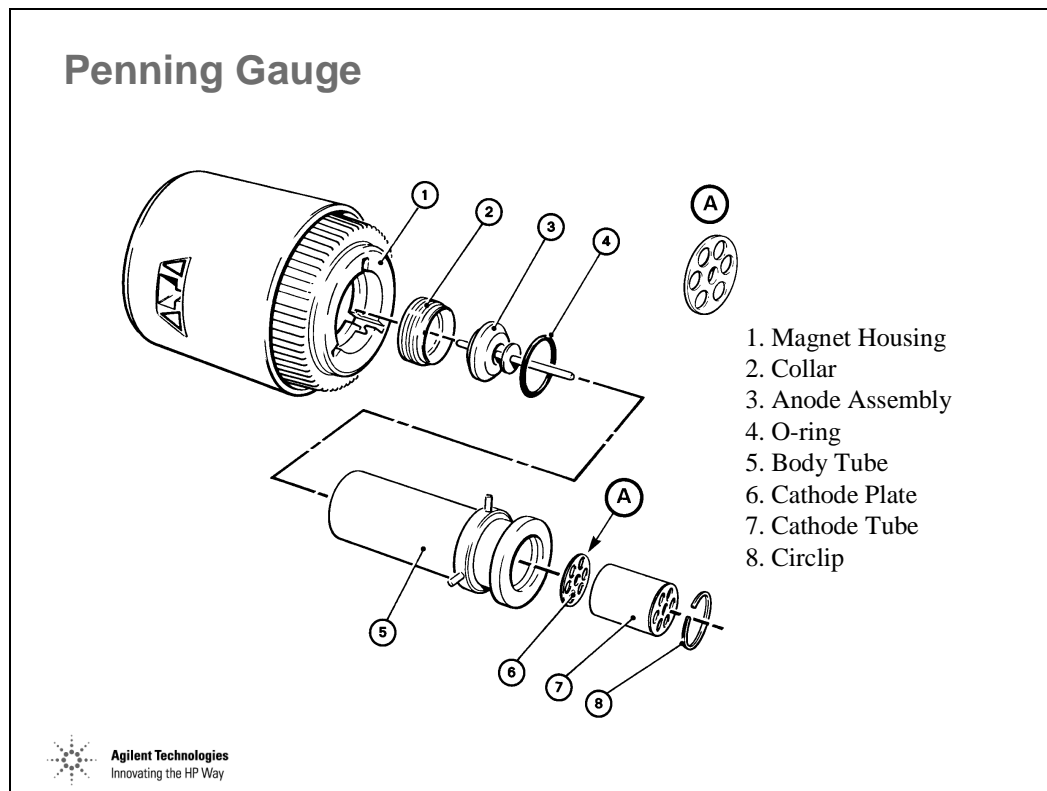


Figure 115

Rotary Pump Maintenance

Rotary Pump Maintenance

- Put system in Shutdown mode (Turn vacuum off)
- Turn off pump circuit breakers on front panel
- Remove oil inlet cap on top of pump
- Remove oil drain plug using a flat blade screwdriver and allow oil to drain into a waste container
- Replace oil drain plug and add new oil through the oil inlet until the oil level window is 80% full
- Replace oil inlet cap, turn on pump breakers on front panel, and start system (Turn vacuum on)



Figure 116

Changing Rotary Pump Oil

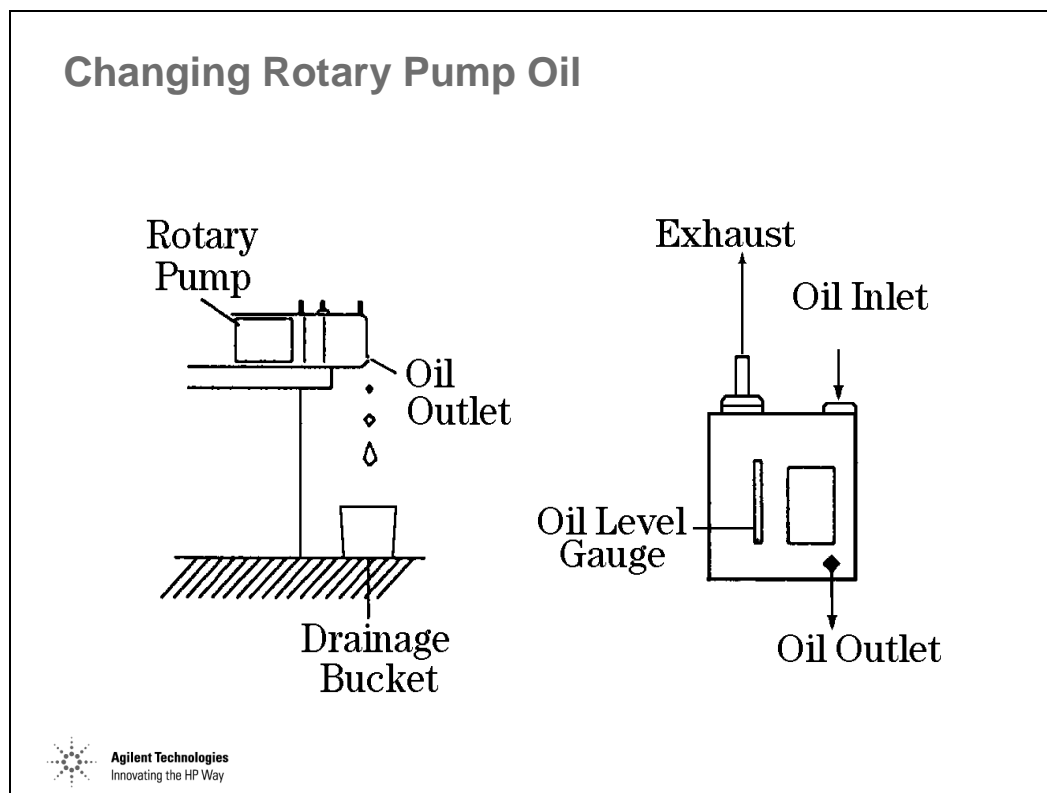


Figure 117

Maintenance Logbook Setting

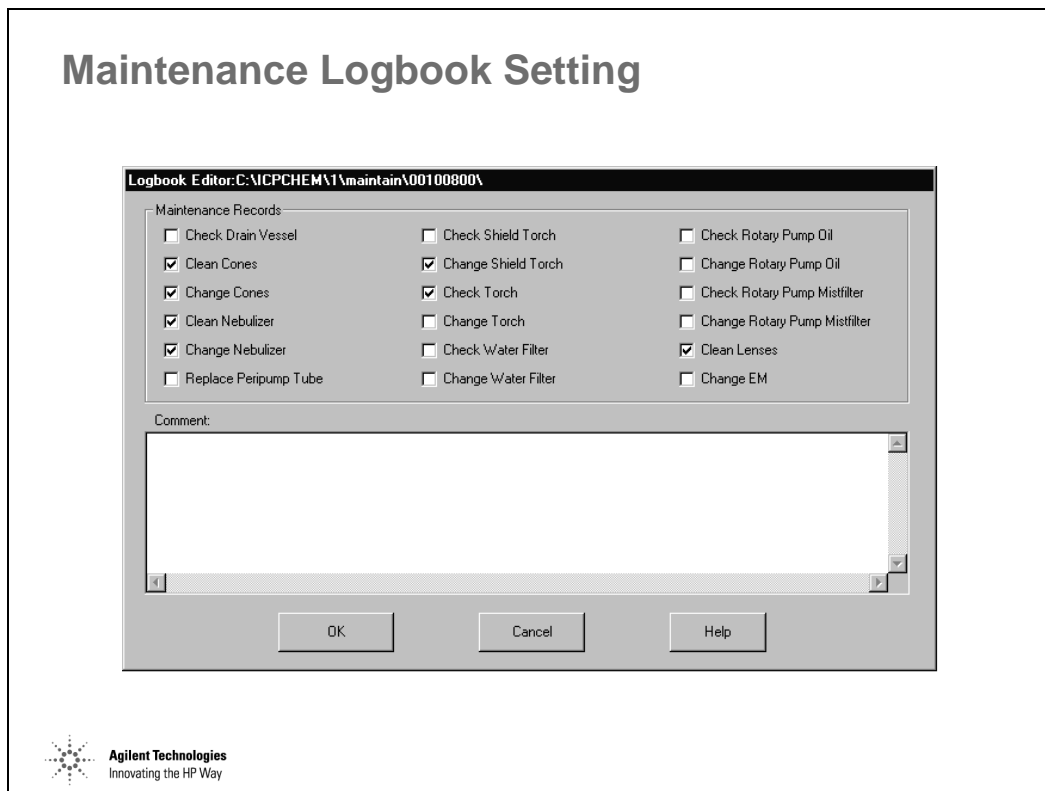


Figure 118

Maintenance Logbook

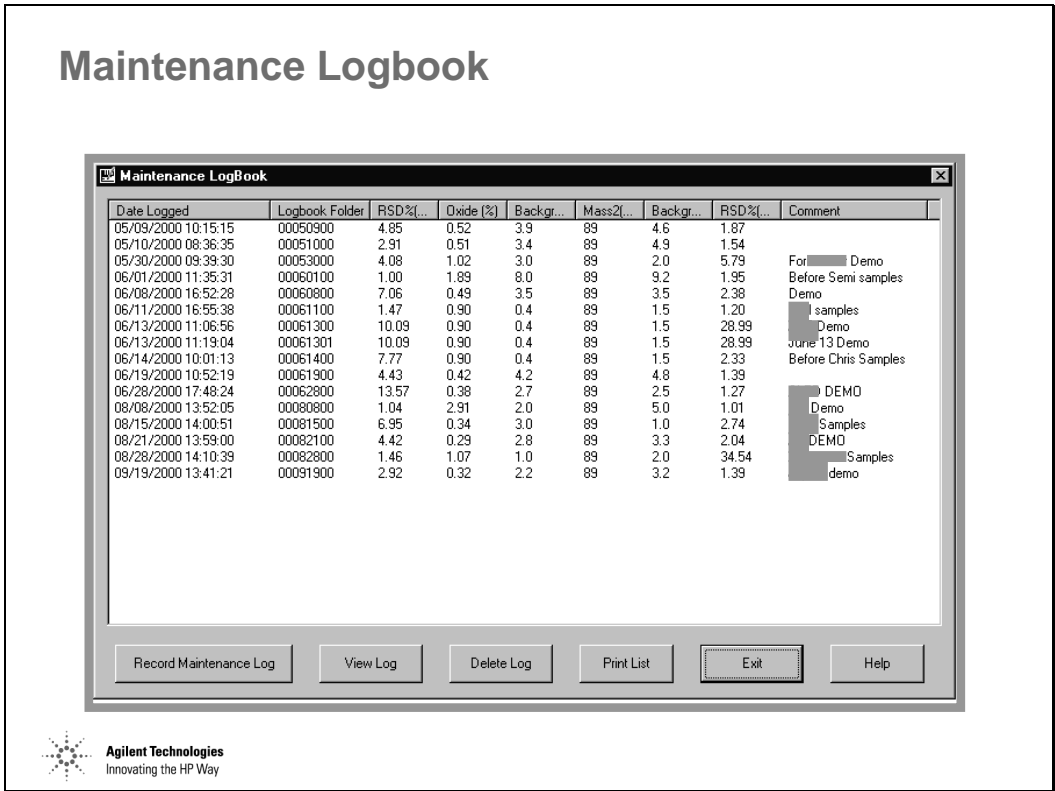


Figure 119

Sample Introduction Maintenance

Sample Introduction Maintenance

Outputs

☐ Open Ar Gas Valve
☐ Open OP Gas Valve

Plasma Gas: L/min
Aux Gas: L/min
Carrier Gas: L/min
MakeUp Gas: L/min
Optional Gas: %

PeriPump

Pump 1: rps
Pump 2: rps

Inputs

Ar Gas Tank Press: 0.0 kPa
OP Gas Tank Press: 0.0 kPa
Carrier Gas Press: 0.0 kPa
OP Gas Press: 0.0 kPa
Plasma Gas: 0.0 L/min
Aux Gas: 0.00 L/min
Carrier Gas: 0.00 L/min
MakeUp Gas: 0.00 L/min
Optional Gas: 0.00 %

Torch Position

Gas Controller


 **Agilent Technologies**
Innovating the HP Way

Figure 120

Air Filters Maintenance

Air Filters Maintenance

- Remove air filters from the instrument
- Remove dust from the filters using a vacuum cleaner
- Wash filters with water if necessary and allow to dry
- Return filters to the instrument



Figure 121

Instrument Start-up

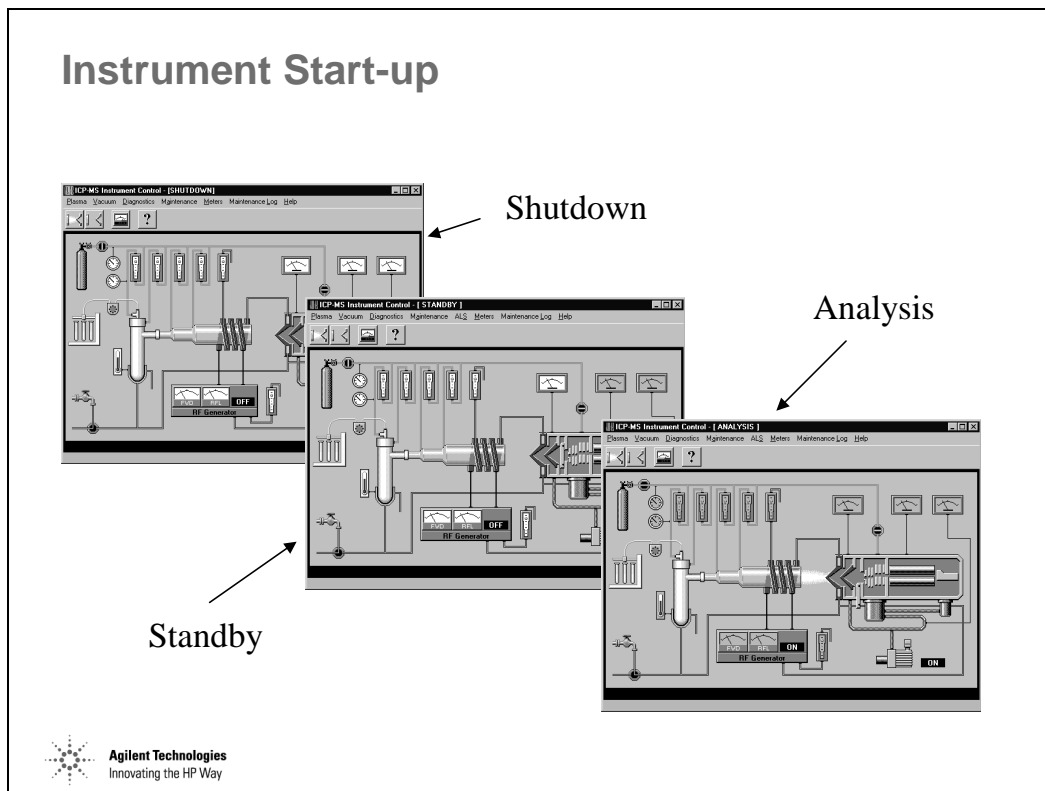


Figure 122



Agilent Technologies
Innovating the HP Way

Internal Standardization in ICP-MS

The Role of Internal Standards

The Role of Internal Standards

Correct for variations in response due to:

Matrix Effects

Transport effects

Nebulization effects

Ionization effects

Space-charge effects

Instrument Drift



Agilent Technologies
Innovating the HP Way

Figure 123

How the Internal Standards Work - 1

How the Internal Standards Work - 1

- Added to each sample, standard and blank at identical concentration
- System therefore expects identical response from ISTDs in each solution
- Ratio of measured ISTD response to expected ISTD response is used to correct the response of the non-internal standard elements accordingly.



Figure 124

How the Internal Standards Work - 2

How the Internal Standards Work - 2

- In all cases where potential matrix suppression exists, the use of internal standards is necessary.
- The calibration curve is plotted using the ratio of the analyte signal to IS signal (i.e. a_x/is_x), thereby canceling the effect of matrix suppression.
- Each analyte in the sample will then be quantitated using the ratio of the IS and the analyte in the sample.

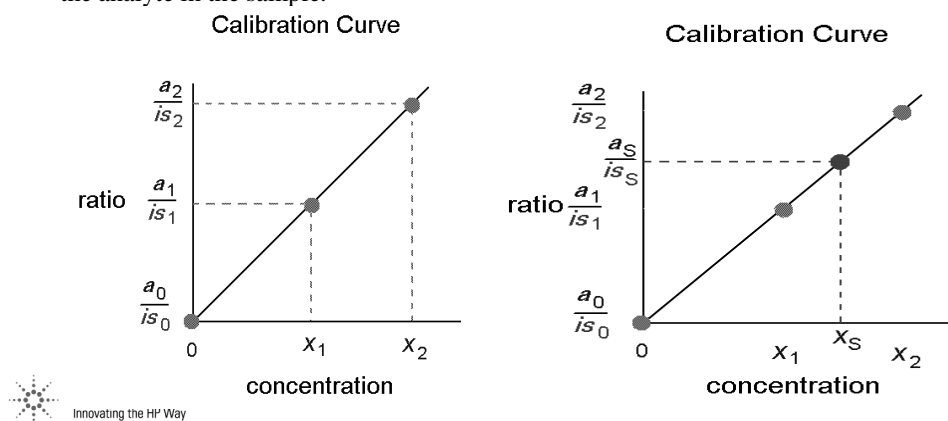


Figure 125

Choice of the Internal Standard

Choice of the Internal Standard

It is assumed that the IS elements behave in the same way that the analytes do in the plasma when using this correction. Therefore, selecting the appropriate IS element is very important.

These are the things to take into consideration:

- The element is not contained in the sample solution.
- The mass number is close to that of the analyte.
- The ionization potential is similar to that of the analyte.
- Chemical characteristics

The ionization potential matching is extremely important for analytes with high ionization potentials.

Elements that are commonly used as IS are:

6Li, Sc, Ge, Y, Rh, In, Tb, Ho, Bi



Agilent Technologies
Innovating the HP Way

Figure 126

Concentration of Internal Standards

Concentration of Internal Standards

The IS elements can be added to the sample in 2 ways:

- **On-line addition by peristaltic pump**
- **Spike in each standard and sample**

In either case, it is recommended to add IS in concentration levels around mid-calibration range (exact concentration is application-specific)

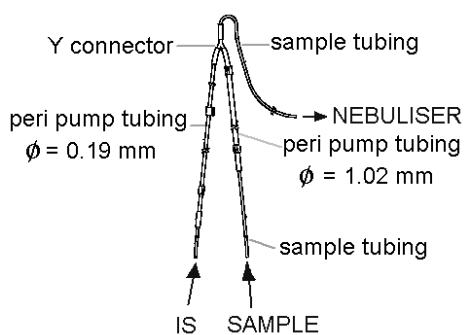
*For environmental applications 50 ppb concentration is usually applied.
For on-line IS addition use 1 ppm IS stock solution, and use the peristaltic pumps as recommended.*



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 ($\phi = 0.19 \text{ mm}$), 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 % HNO_3 would yield approximately 50 ppb in the sample. At least 5 % HNO_3 is needed to avoid absorption of elements to the tubing, as absorption is more severe using narrow tubing.



Figure 128



Agilent Technologies
Innovating the HP Way

Sample Preparation Techniques for ICP-MS

Contamination

Contamination

- "Contamination is the introduction of any component which affects the numerical value finally attributed to a constituent relative to the amount present prior to sampling"
- Types of contamination:
 - positive
 - negative
 - pseudocontamination

D.E. Robertson "Ultrapurity, Methods and Techniques",
M. Zeif and R. Speights, Eds., Marcel Dekker, NY, 1972



Agilent Technologies
Innovating the HP Way

Figure 129

Types of Contamination

Types of Contamination

Positive contamination - results in additive errors. Caused by

- impurities in reagents
- lab environment
- desorption from container walls

Negative contamination - results in subtractive errors. Caused by

- losses in handling
- adsorption to container walls

Pseudocontamination - results in either positive or negative errors.

Caused by

- irreproducibility of experimental conditions



Figure 130

Challenges of Trace Analysis

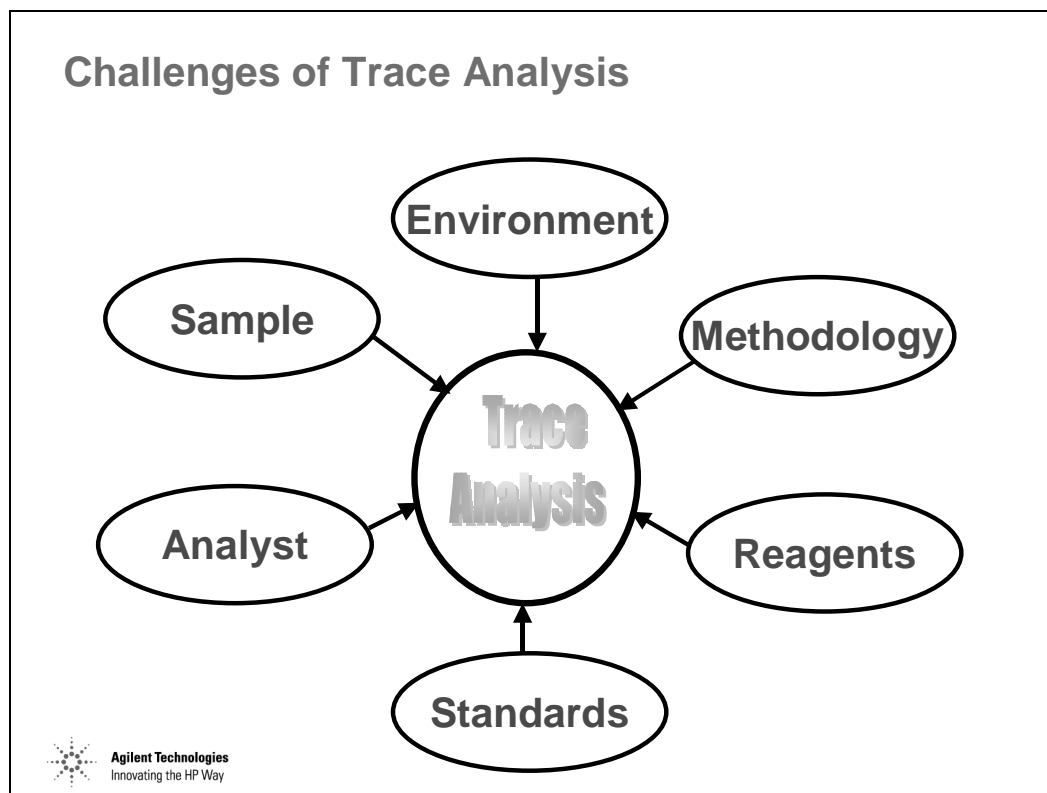


Figure 131

When a Contamination Can Occur

When a Contamination Can Occur

- **Sample collection**
 - collection techniques
 - collection devices
- **Sample storage**
 - prevention of positive contamination
 - prevention of negative contamination
- **Sample preparation**
 - reagents
 - lab environment
 - apparatus
- **Sample measurement**
 - instrument sample introduction system
 - standards



Figure 132

Reagents

Reagents

- **Water**
- Nitric acid
- Hydrochloric acid
- Sulfuric acid
- Hydrofluoric acid
- Other inorganic acids
- Hydrogen peroxide
- Alkaline solutions
- Organic solvents



Agilent Technologies
Innovating the HP Way

Figure 133

Water - Millipore

Water - Millipore

Millipore Corporation
80 Ashby Road
P.O. Box 9125
Bedford, MA 01730-9903
Tel 1-800-MILLIPORE (1-800-645-5476)
fax 781-533-8873
Internet: <http://www.millipore.com/H2O>



Figure 134

Nitric Acid

Nitric Acid

From Fisher Scientific (1-800-766-7000)

“TraceMetal” - for environmental analysis -
500 mL in glass, catalog # A509-500,
Certificate of Lot Analysis included with each shipment

“Optima” - for semiconductor and clinical applications -
catalog # A467-250, 250 mL in Teflon™,
catalog # A467-500, 500 mL in Teflon™,
Certificate of Lot Analysis included with each bottle

from Mallinkrodt-Baker (1-800-444-0880)

“INSTRA-ANALYZED” (equivalent of “TraceMetal”),
500 mL in poly coated glass, catalog # 9598-00

“ULTREX II” (equivalent of “Optima”)
500 mL in Teflon™, catalog # 6901-05



Figure 135

Selected Methods of Sample Preparation

Selected Methods of Sample Preparation

- ⇒ Dilution
- ⇒ Preconcentration
- ⇒ Filtration
- ⇒ Acidification
- ⇒ Digestion
 - ⇒ *Open vessel digestion*
 - ⇒ *Closed vessel digestion*
 - ⇒ *Microwave digestion*
- ⇒ Fusion
- ⇒ Matrix separation
 - ⇒ *Chromatography*
 - ⇒ *Electrothermal Vaporization*



Figure 136

Commonly Used Reagents (1)

Commonly Used Reagents (1)

Nitric Acid (HNO₃)

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.



Agilent Technologies
Innovating the HP Way

Figure 137

Commonly Used Reagents (2)

Commonly Used Reagents (2)

Hydrogen Peroxide (H_2O_2)

Strong oxidizing agent used with other acids for digestion.

Useful for ICP-MS work, as backgrounds are similar to water (H_2O).

Sulfuric Acid (H_2SO_4)

Oxidizing agent used with other acids for digestion.

Causes numerous polyatomic ion interferences.

Difficult to decompose in plasma due to high boiling point and viscosity.

Deteriorates Ni and Cu interface material.

Not recommended for use if it can be avoided.

Phosphoric Acid (H_3PO_4)

Used to buffer other acids.

Causes numerous polyatomic ion interferences.

Difficult to decompose in plasma due to high boiling point and viscosity.

Deteriorates Ni interface material.

Should be avoided.



Agilent Technologies
Innovating the HP Way

Figure 138

Commonly Used Reagents (3)

Commonly Used Reagents (3)

Perchloric Acid (HClO_4)

Strong oxidizing agent used with other acids for digestion of organic materials.

Generates Cl derived polyatomic ions.

More difficult to evaporate than HCl.

Not recommended for use if it can be avoided.

Handle with care as many solid perchlorates are explosive.

Aqua Regia

(1 part conc. HNO_3 + 3 parts conc. HCl)

Used for metal digestion, especially precious metals.

Generates Cl derived polyatomic ions.

Cl matrix can be removed by evaporation.



Agilent Technologies
Innovating the HP Way

Figure 139



Agilent Technologies
Innovating the HP Way

Semi-quantitative Analysis of Samples

Semi-quantitative Analysis

Semi-quantitative Analysis

- What is Semi-quantitative Analysis
- Setting Semi-quantitative acquisition parameters
- Analyzing the samples
- Semi-quantitative data analysis



Figure 140

What is Semi-quantitative Analysis?

What is Semi-quantitative Analysis?

- Is an analytical procedure used to calculate concentrations of all elements present in an unknown sample
- Is useful as a screen prior to Quantitative Analysis
 - *concentration ranges of analytes*
 - *selection of internal standards*
- Does not require an external calibration
- Is generally accurate to +/- 30% or better on completely unknown samples



Figure 141

Data Acquisition

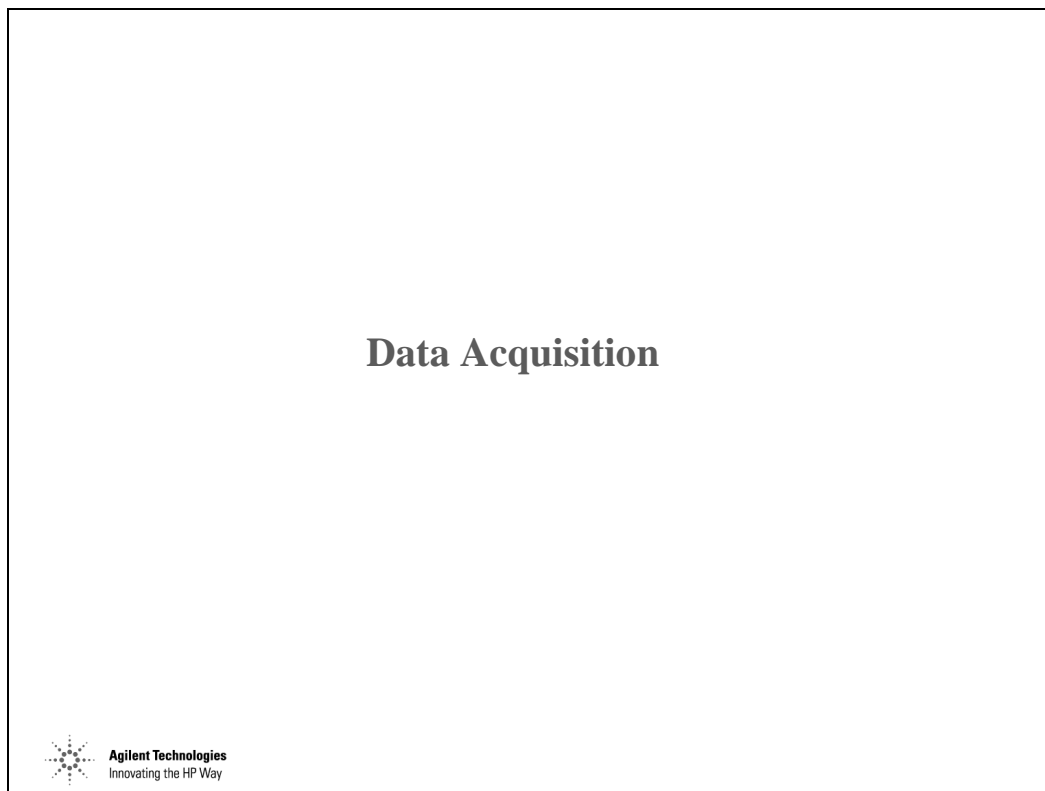


Figure 142

Method Set-up for Semi-quantitative Analysis

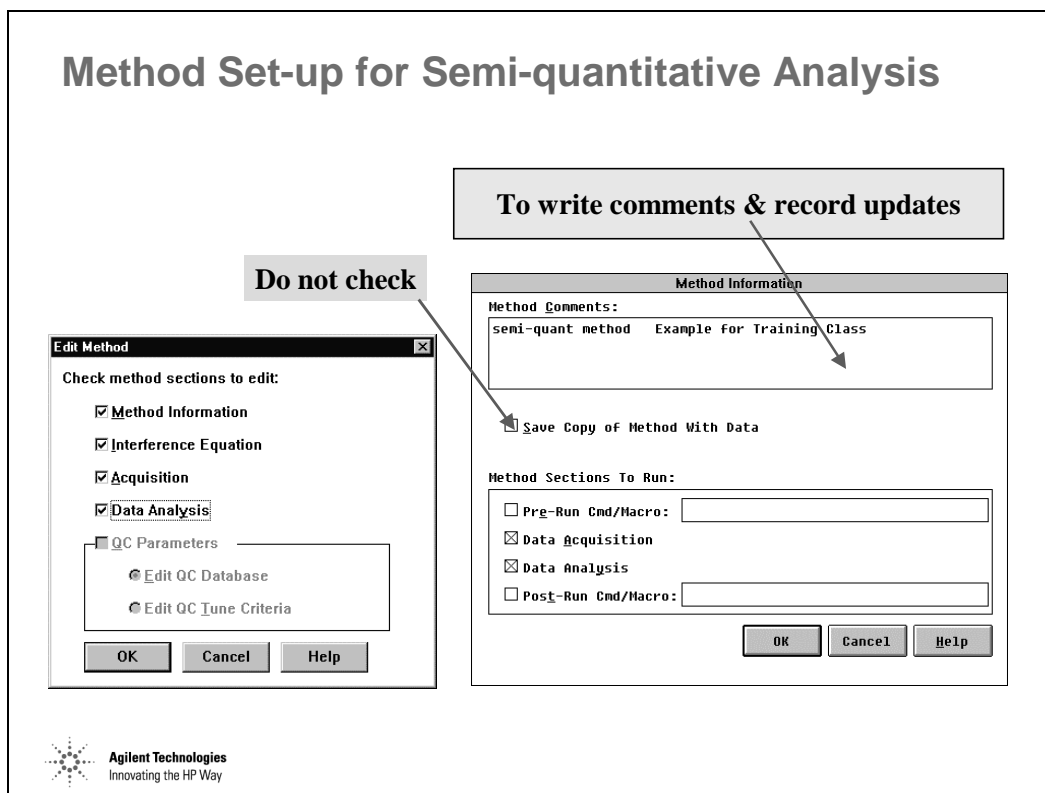


Figure 143

Parameters Selection - Spectrum Acquisition

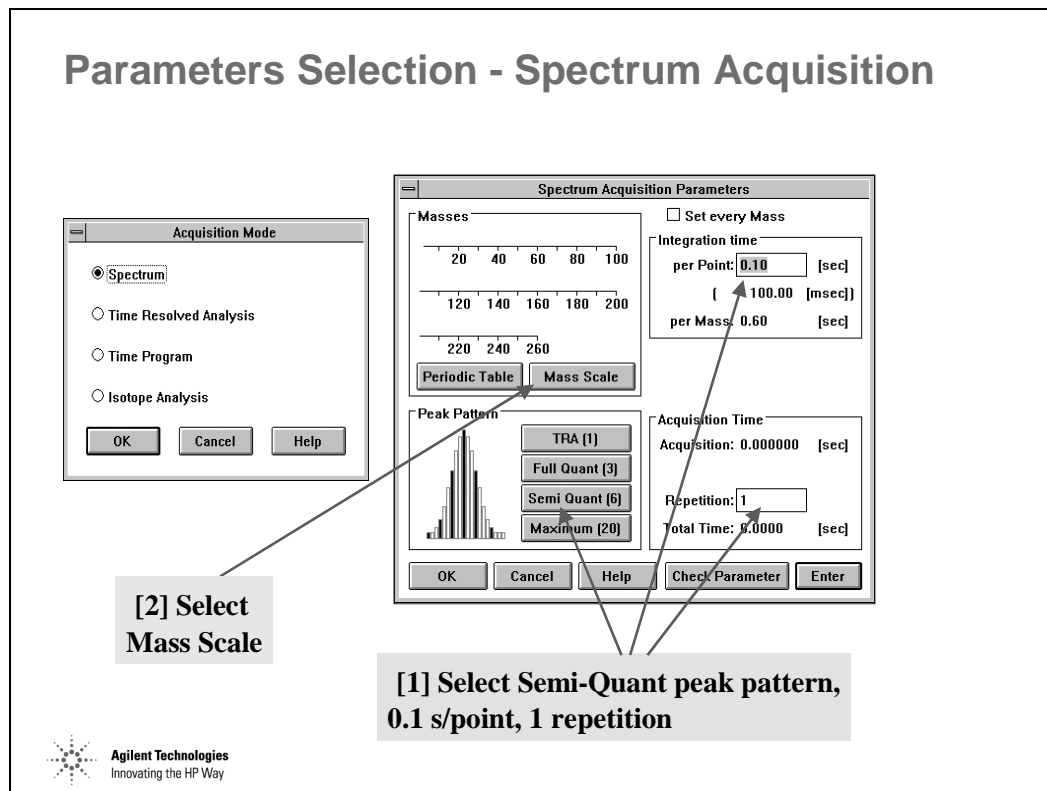


Figure 144

Parameters Selection - Selection of Masses

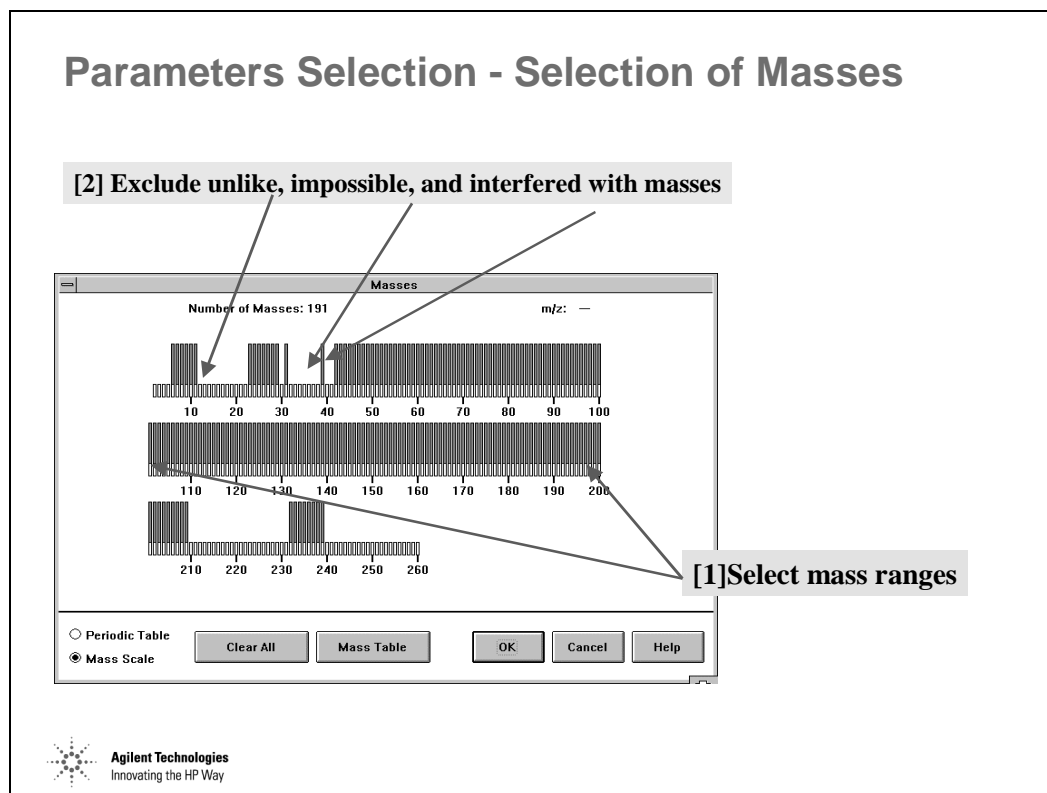


Figure 145

More Acquisition Parameters

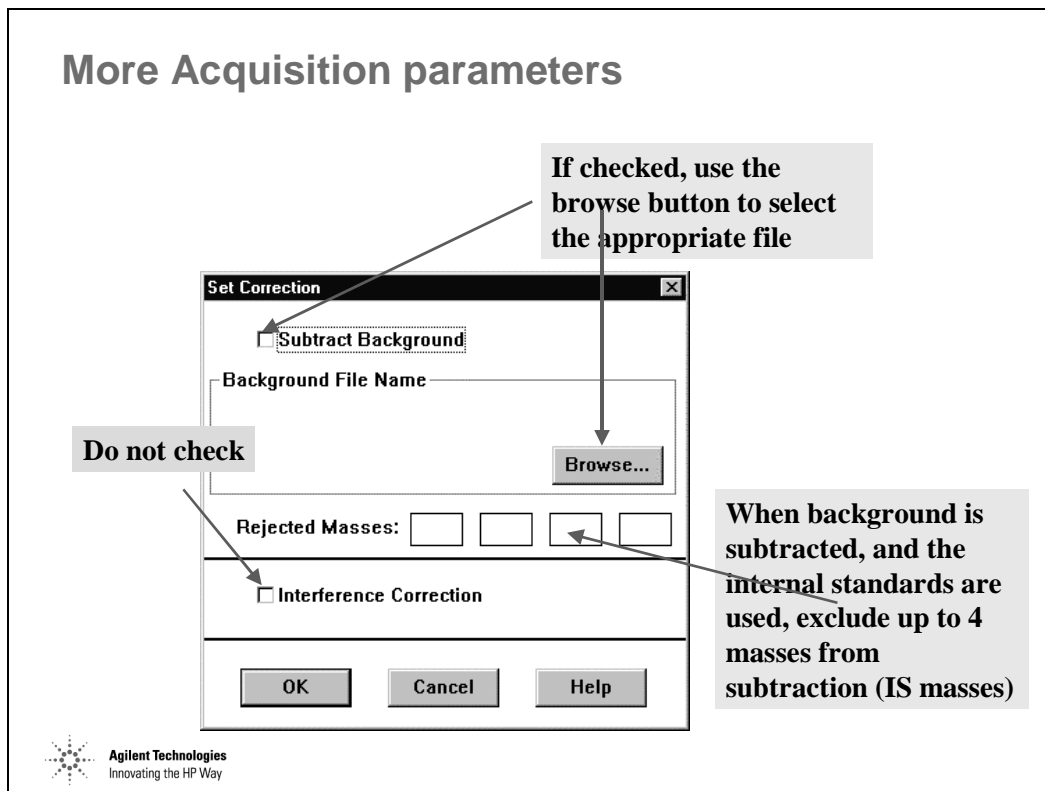


Figure 146

Report Generation

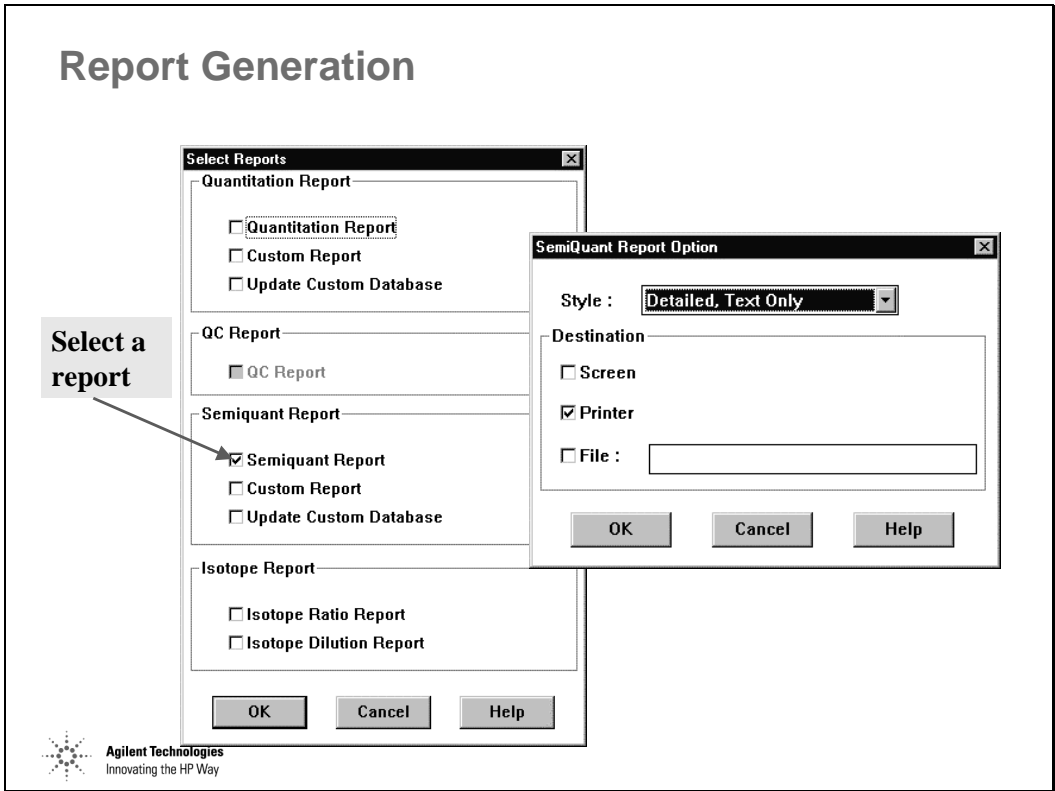


Figure 147

Semi-quant Parameters

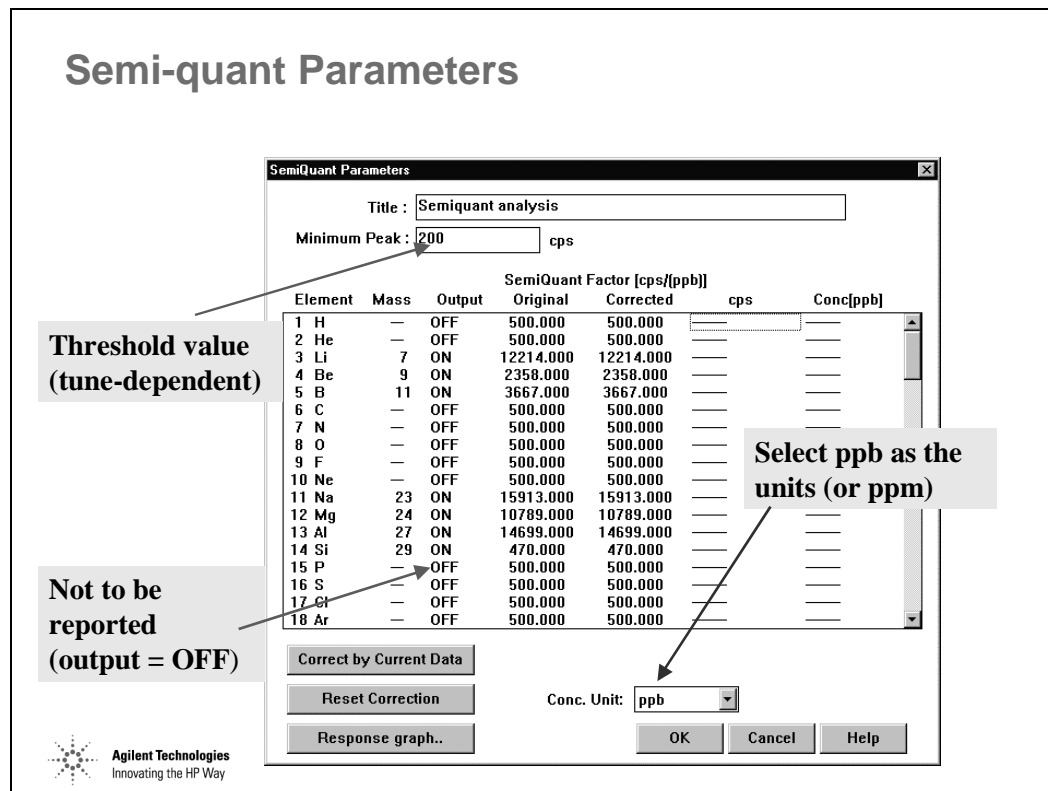


Figure 148

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

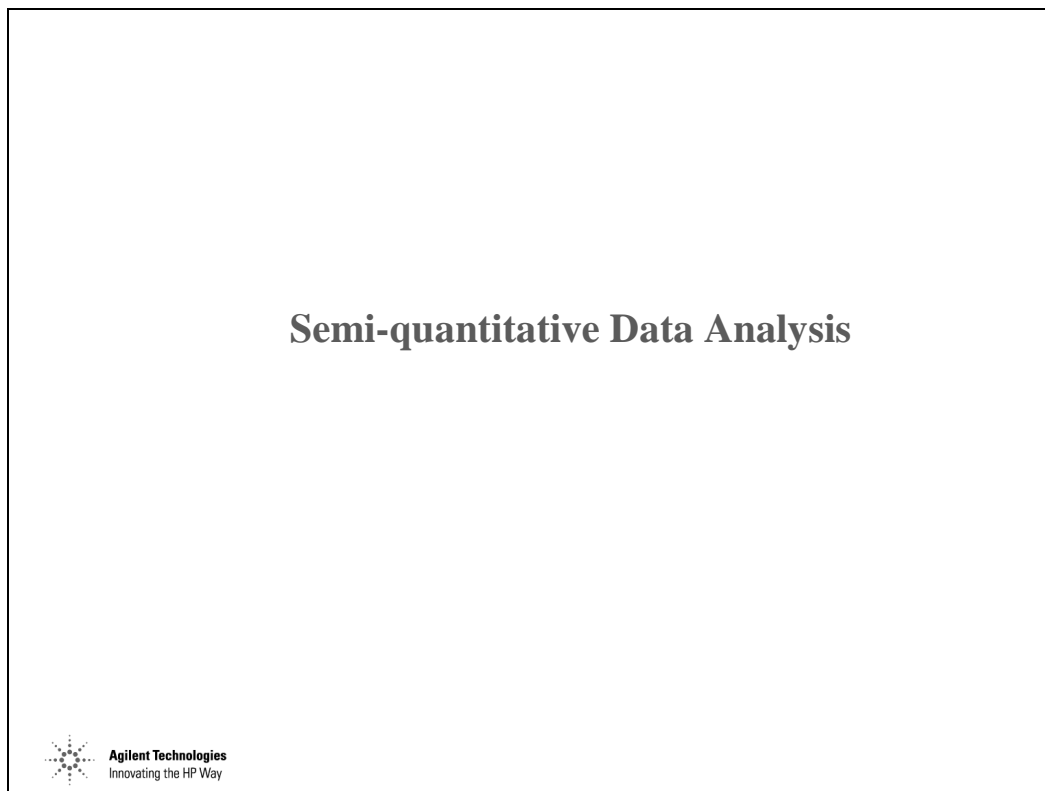


Figure 149

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

Editing Parameters

Holding <ctrl> select elements to be reported

Change default mass for Cu from 63 to 65

Enter the concentration of calibration standard

SemiQuant Parameters

Title : These are the default semiquant parameters

Minimum Peak : 200 cps

Element	Mass	Output	SemiQuant Factor [cps/[ppb]]		cps	Conc[ppb]
			Original	Corrected		
19 K	39	ON	22392.000	22392.000		
20 Ca	43	ON	34.000	34.000		
21 Sc	45	ON	13800.000	13800.000		
22 Ti	47	ON	966.000	966.000		
23 V	51	ON	13816.000	13816.000		
24 Cr	53	ON	1483.000	1483.000		
25 Mn	55	ON	15710.000	15710.000		
26 Fe	57	ON	354.000	354.000		
27 Co	59	ON	14042.000	14042.000		
28 Ni	60	ON	2968.000	2968.000		
29 Cu	65	ON	8123.000	8123.000		
30 Zn	66	ON	1852.000	1852.000		
31 Ga	69	ON	9082.000	9082.000		
32 Ge	72	ON	2518.000	2518.000		
33 As	75	ON	1739.000	1739.000		
34 Se	82	ON	165.000	165.000		
35 Br	79	ON	270.000	270.000		
36 Kr	—	OFF	500.000	500.000		

Correct by Current Data

Reset Correction

Response graph..

Conc: 100 ppb

Conc. Unit: ppb

Enter

OK Cancel Help

Agilent Technologies
Innovating the HP Way

Figure 150

Daily Update of the Semi-Quant Parameters

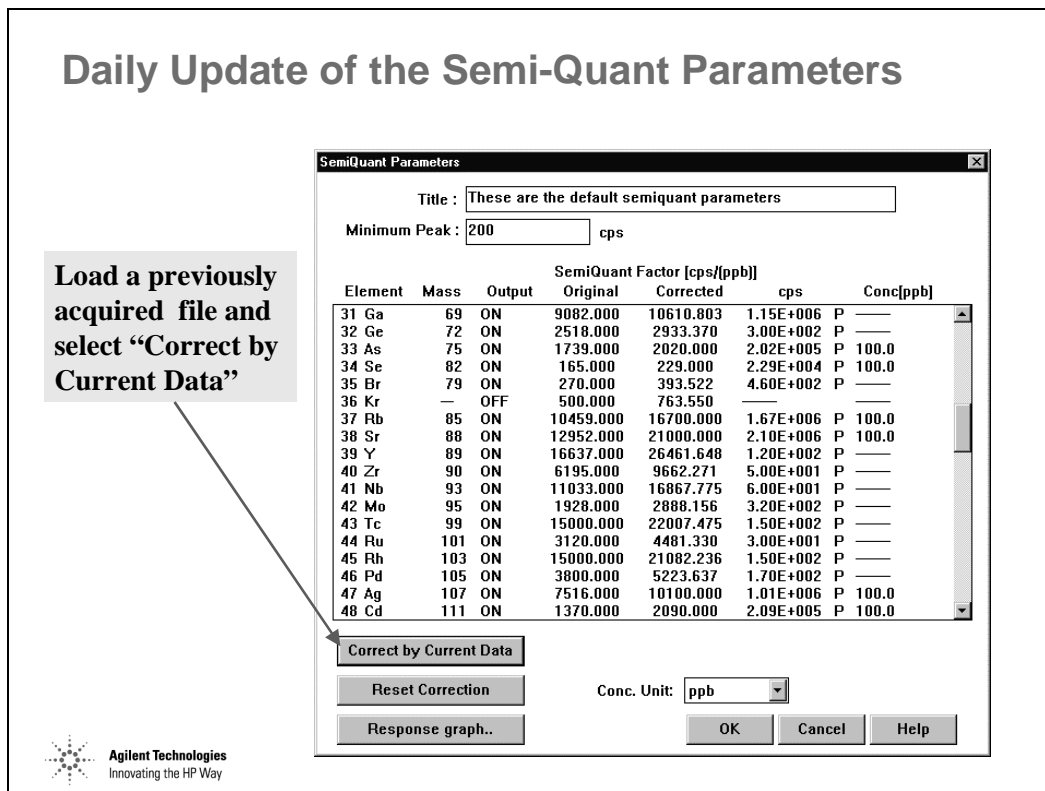


Figure 151

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

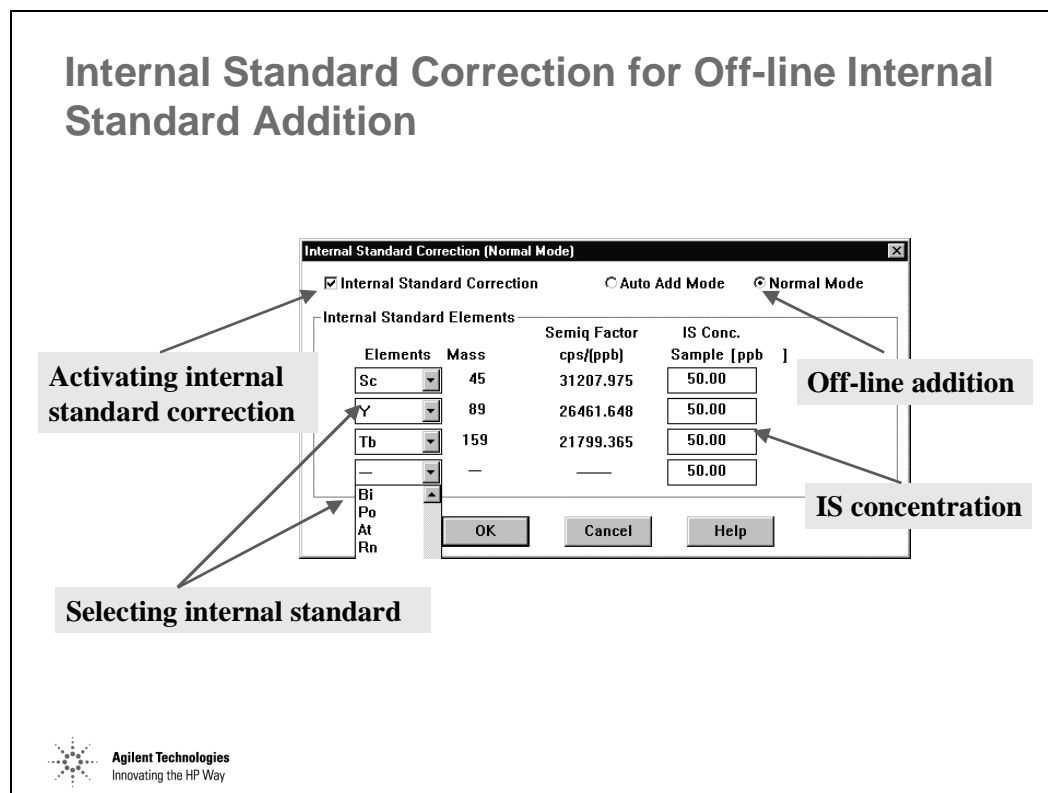


Figure 152

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

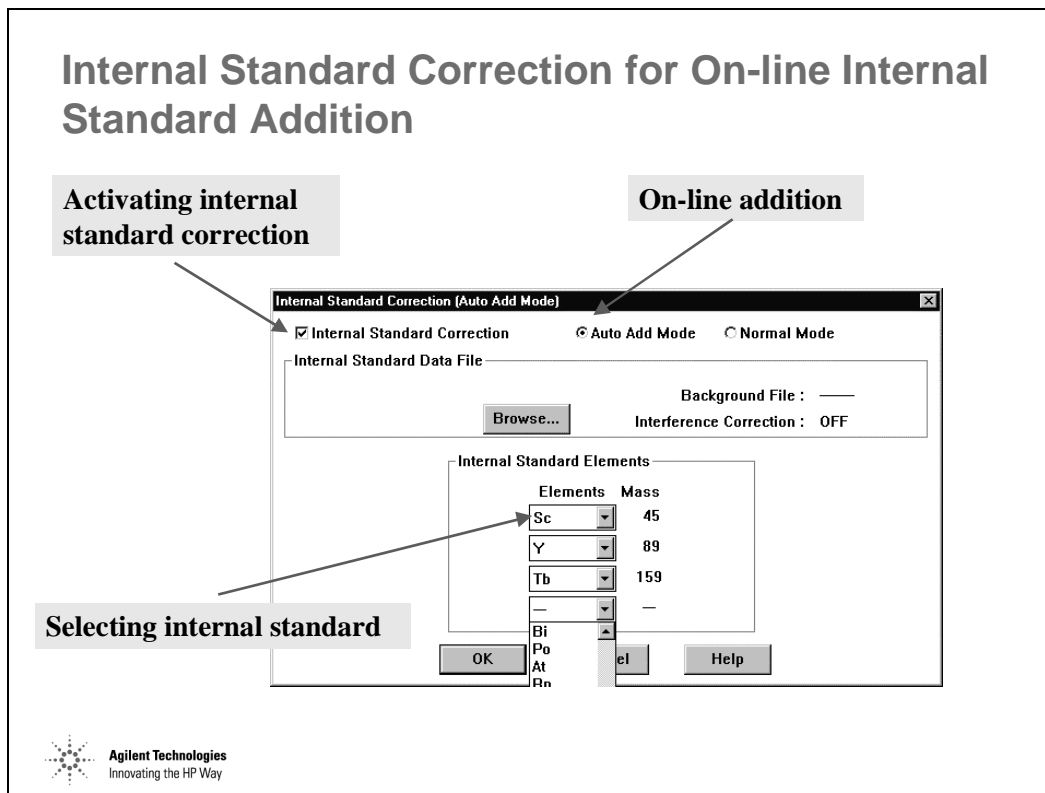


Figure 153

‘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]

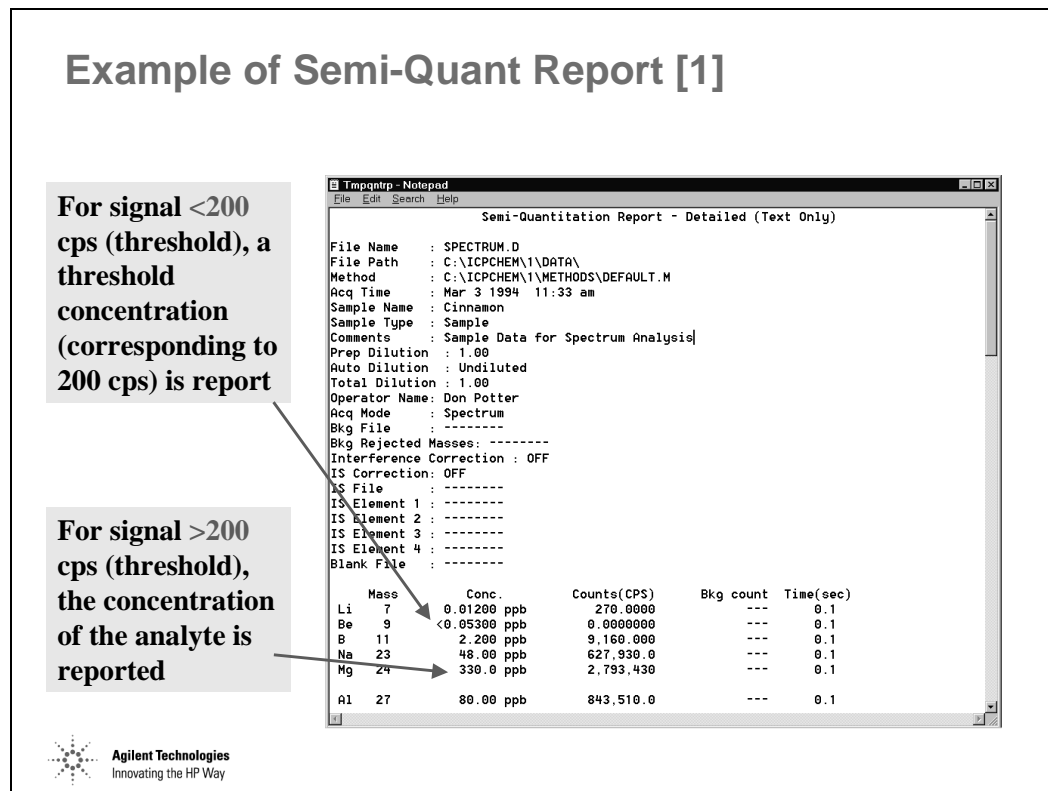


Figure 154

Example of Semi-Quant Report [2]

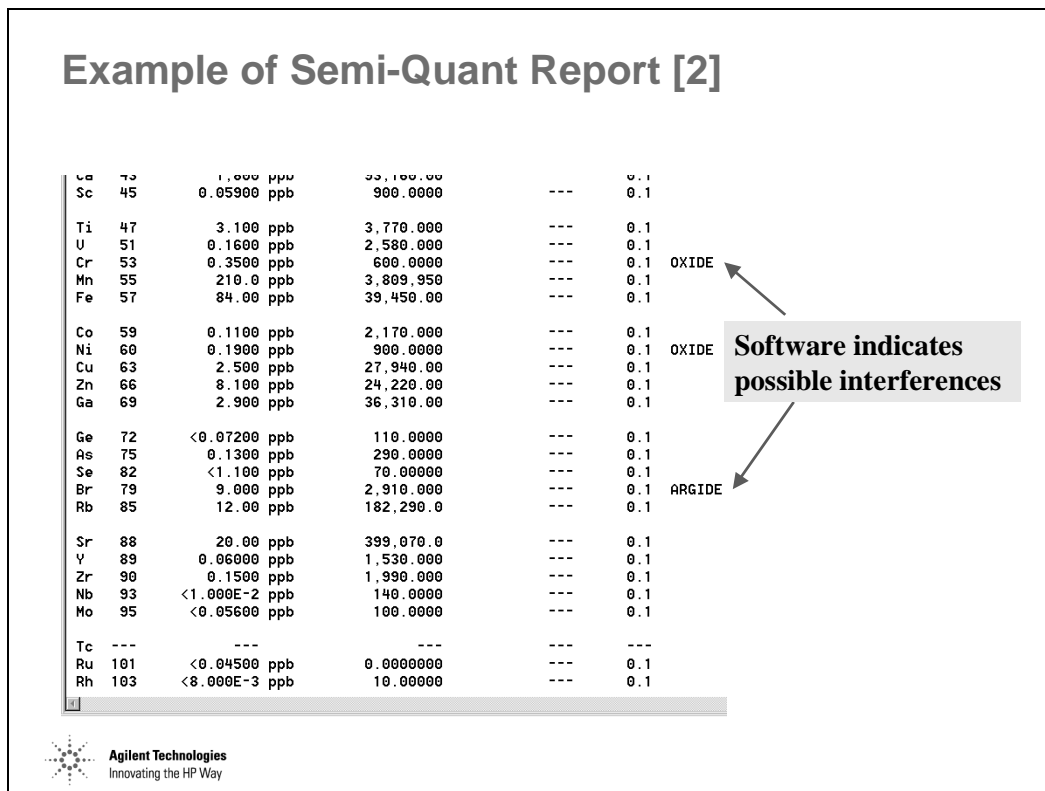


Figure 155

Generating a Semi-quant Report

Generating a Semi-quant Report

- Automatically as part of Run Method or Run Sequence
- Manually from Data Analysis
- SemiQuant also allows Custom Reports and Custom Databases
- Use of DoList for multiple reports



Figure 156

Manual Verification of the Data

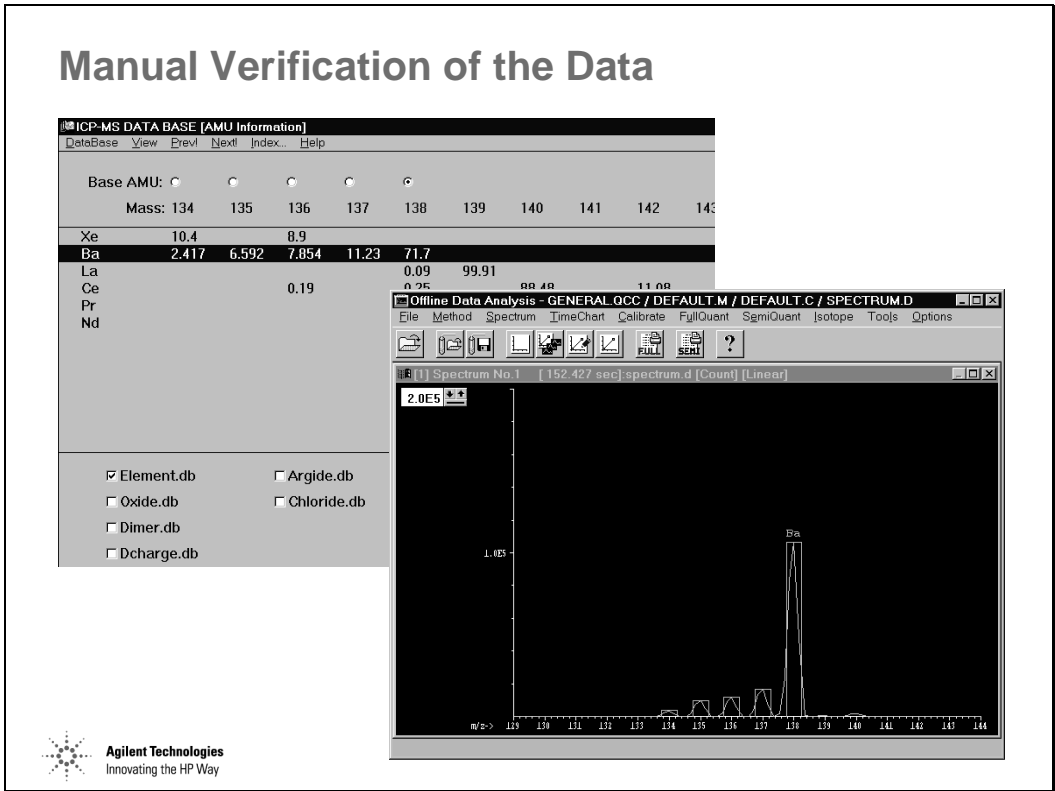


Figure 157



Agilent Technologies
Innovating the HP Way

Quantitative Analysis of Samples

What is Quantitative Analysis?

What is Quantitative Analysis?

Quantitative Analysis:

- **An analytical procedure used to calculate concentrations of specific elements in unknown samples**
- **Uses calibration curves based on the response of one or more levels of standards to calculate unknown concentrations**
- **Allows the use of internal standards to correct for instrument drift and matrix differences between standards and samples**



Figure 158

Method Set-up for Quantitative Analysis

Method Set-up for Quantitative Analysis

Steps in Setting up a Quantitative Analysis:

- Editing the AMU Select file, if necessary
- Interference correction equations
- Spectrum acquisition parameters
- Peripump program
- Calibration table
- Acquiring calibration standards and updating the calibration table
- Analyzing unknown samples



Figure 159

Step One: Editing the AMU Select File

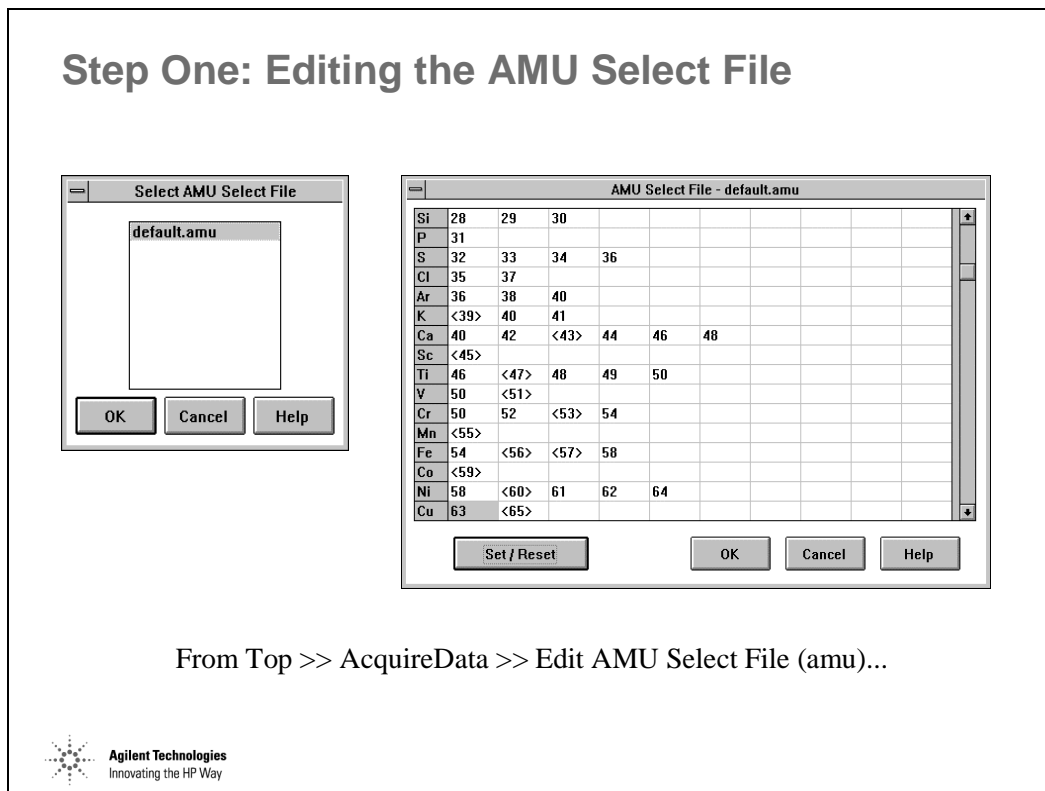


Figure 160

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

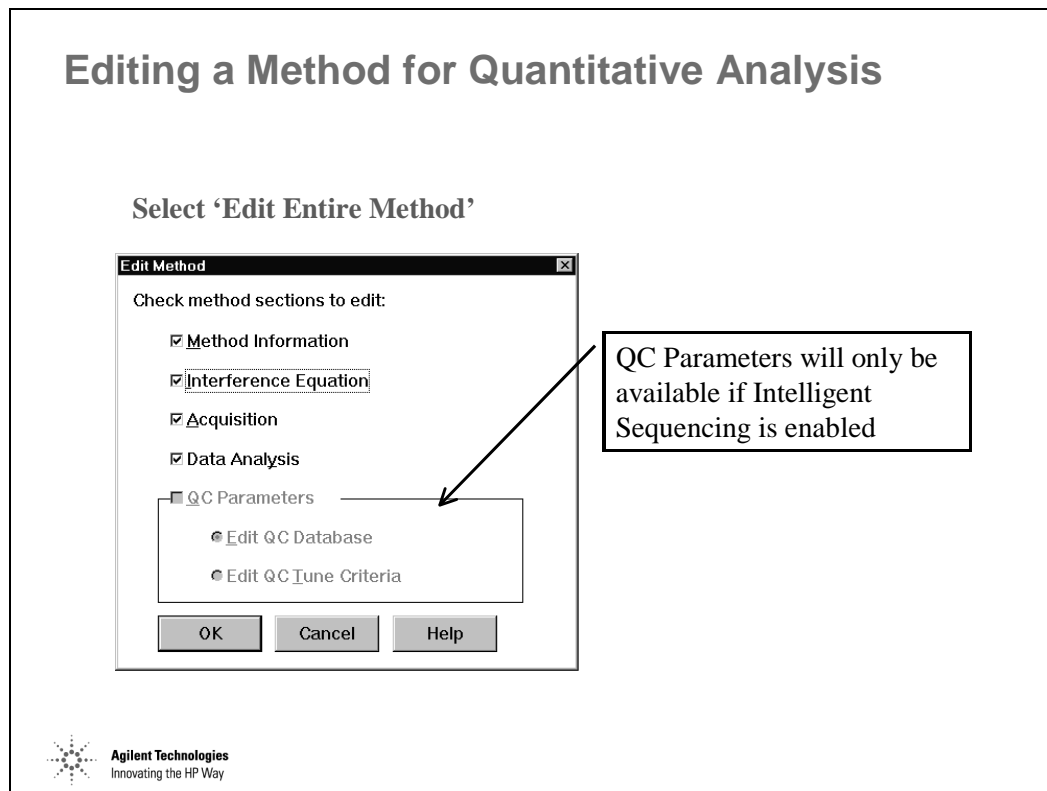


Figure 161

Method Information

Method Information

Method Information

Method Comments:
chemical samples: Multitune mode

☐ Save Copy of Method With Data

Method Sections To Run:

☐ Pre-Run Cmd/Macro:

☒ Data Acquisition

☒ Data Analysis

☐ Post-Run Cmd/Macro:

OK Cancel Help



Figure 162

Acquisition Modes

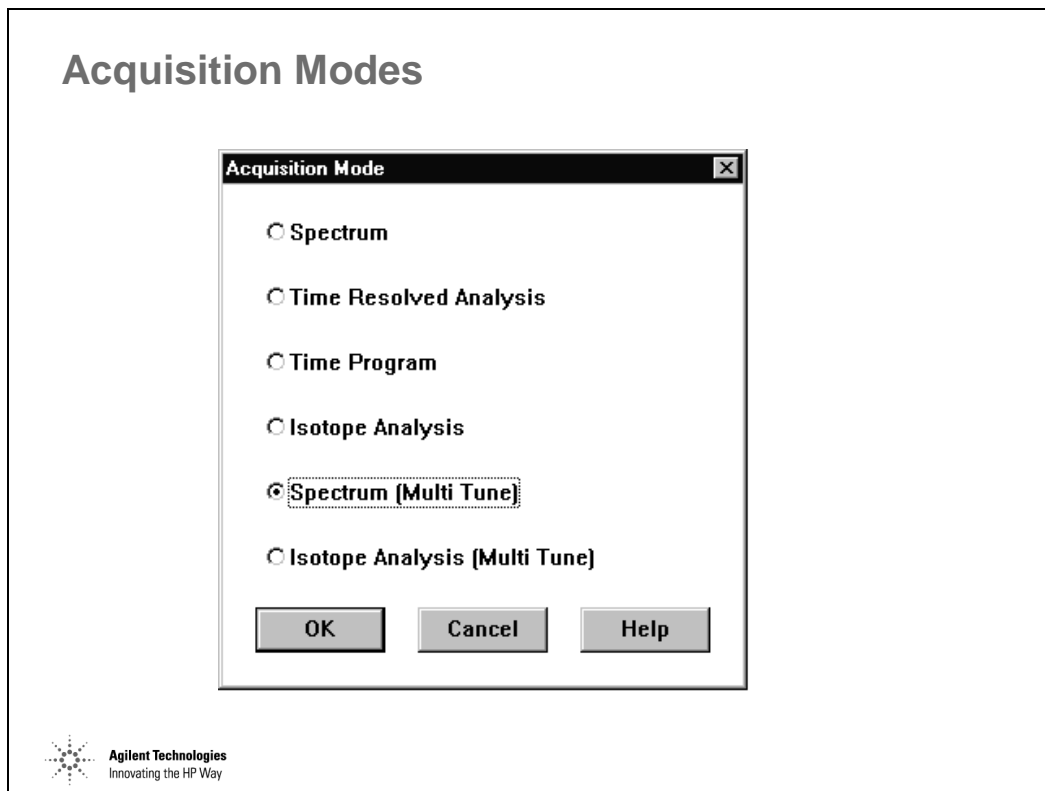


Figure 163

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

Acquisition Parameters - Multitune Method

Spectrum (Multi Tune) Acquisition Parameters

Masses

20 40 60 80 100
120 140 160 180 200
220 240 260

Periodic Table Mass Scale

Integration time

per Point: 0.30 [sec]
(300.00 [msec])

Detector: Auto

Tune Step: 2

Peak Pattern

TRA (1)
Full Quant (3)
Semi Quant (6)
Maximum (20)

Acquisition Time

Repetition: 3
Total Time: 155 [sec]

Integration Time [sec]

Mass Elem.	per Point	per Mass	Detector	Tune Step
7 Li	0.30	0.90	Auto	2
10 B	0.30	0.90	Auto	1
11 B	0.30	0.90	Auto	1
23 Na	0.30	0.90	Auto	2
24 Mg	0.30	0.90	Auto	2
27 Al	0.30	0.90	Auto	2
39 K	0.30	0.90	Auto	2
40 Ca	0.30	0.90	Auto	2
45 SiOH	0.30	0.90	Auto	2
52 Cr	0.30	0.90	Auto	2
55 Mn	0.30	0.90	Auto	1
56 Fe	0.30	0.90	Auto	2
57 Fe	0.30	0.90	Auto	2
58 Ni	0.30	0.90	Auto	2
63 Cu	0.30	0.90	Auto	1
64 Zn	0.30	0.90	Auto	1
66 Zn	0.30	0.90	Auto	1
68 Zn	0.30	0.90	Auto	2
118 Sn	0.30	0.90	Auto	1
138 Ba	0.30	0.90	Auto	1
157 Gd	0.30	0.90	Auto	3
197 Au	0.30	0.90	Auto	1

Tune

Step	Tune File	Stabilization Time [sec]	Date Updated
1	normal.u	5	Oct 19 2000 07:27 pm
2	cool.u	70	Oct 19 2000 07:25 pm
3	normal.u	5	Oct 19 2000 07:27 pm
4	—	—	—
5	—	—	—
6	—	—	—

Tune File: Browse...

Stabilization Time: 5 [sec]

Remove Tune Step

OK Cancel Help Check Parameter Enter

Figure 164

Periodic Table

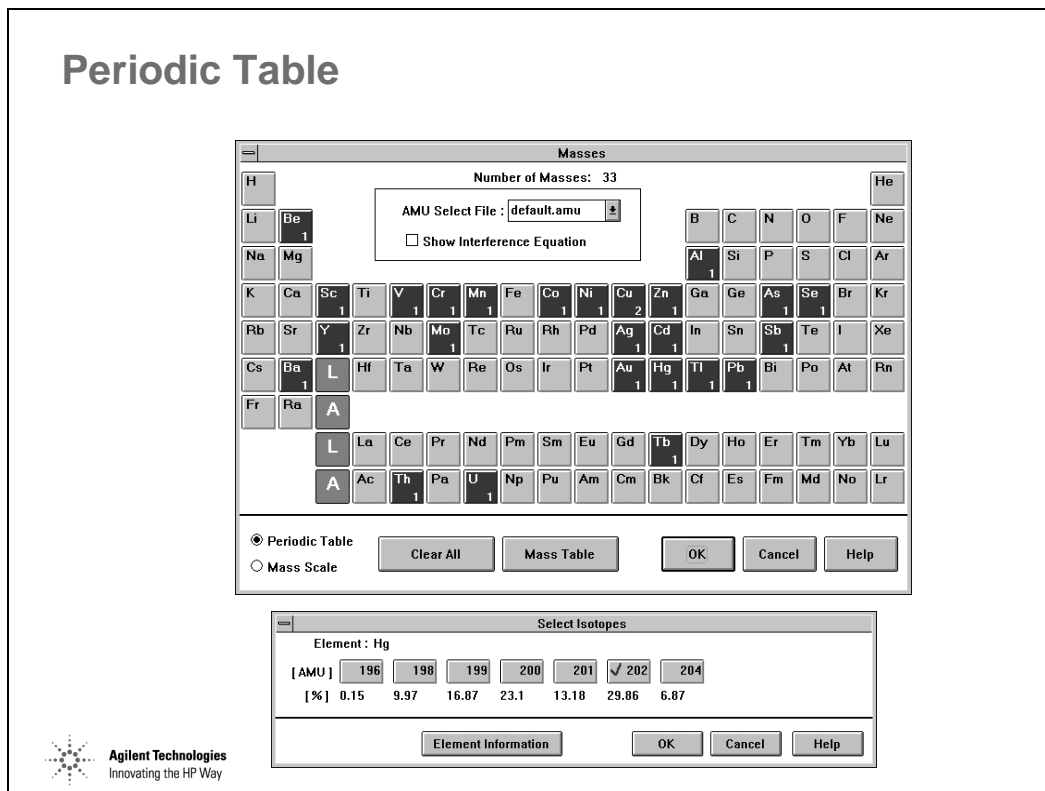


Figure 165

Mass Table

Mass Table

Mass Table

Number of Masses: 33

2amu - 100amu	101amu - 200amu	201amu - 260amu
9 Be	106 (Cd)	202 Hg
27 Al	107 Ag	205 Tl
45 Sc	108 (Cd)	206 (Pb)
51 V	111 Cd	207 (Pb)
52 Cr	121 Sb	208 Pb
53 (As)	137 Ba	232 Th
55 (Cs)		
59 (Pr)		
60 (Nd)		
63 (Eu)		
65 (Gd)		
66 (Tm)		
75 (Re)		
77 (Ir)		
82 Se		
89 Y		
98 Mo		
99 (Mo)		

SetMasses

! Selected mass (Se, 82) is already set as ' (As) '.
Overwrite?

Yes No

OK Cancel Help Enter Delete Mass

Figure 166

Peristaltic Pump Program

Peristaltic Pump Program

Peristaltic Pump Program

Before Acquisition

Uptake Speed: 0.30 rps

Uptake Time: 50 sec

Stabilization Time: 50 sec

After Acquisition (Probe Rinse)

Rinse Speed: 0.30 rps

Rinse Time(Sample): 1 sec

Rinse Time(STD): 1 sec

After Acquisition (Rinse)

Rinse Vial: 1

Rinse Speed: 0.10 rps

Rinse Time: 10 sec

OK Cancel Help

**Maximum Speed should not exceed
0.30 rps with online ISTDs addition**

Typical Stabilization Time is 50-60 sec

**Probe Rinse should be very short (~1
sec)**

**Rinse time is sample/matrix dependent
(30-90 sec)**



Agilent Technologies
Innovating the HP Way

Figure 167

Raw Data Corrections

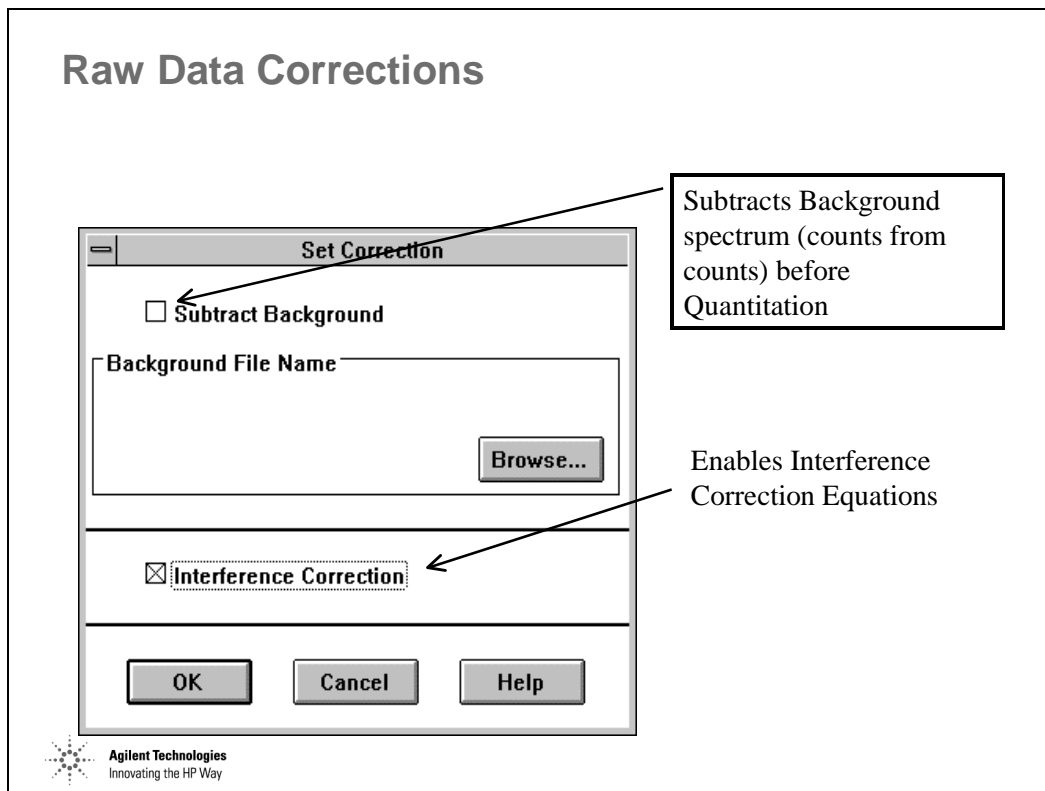


Figure 168

Configure Reports

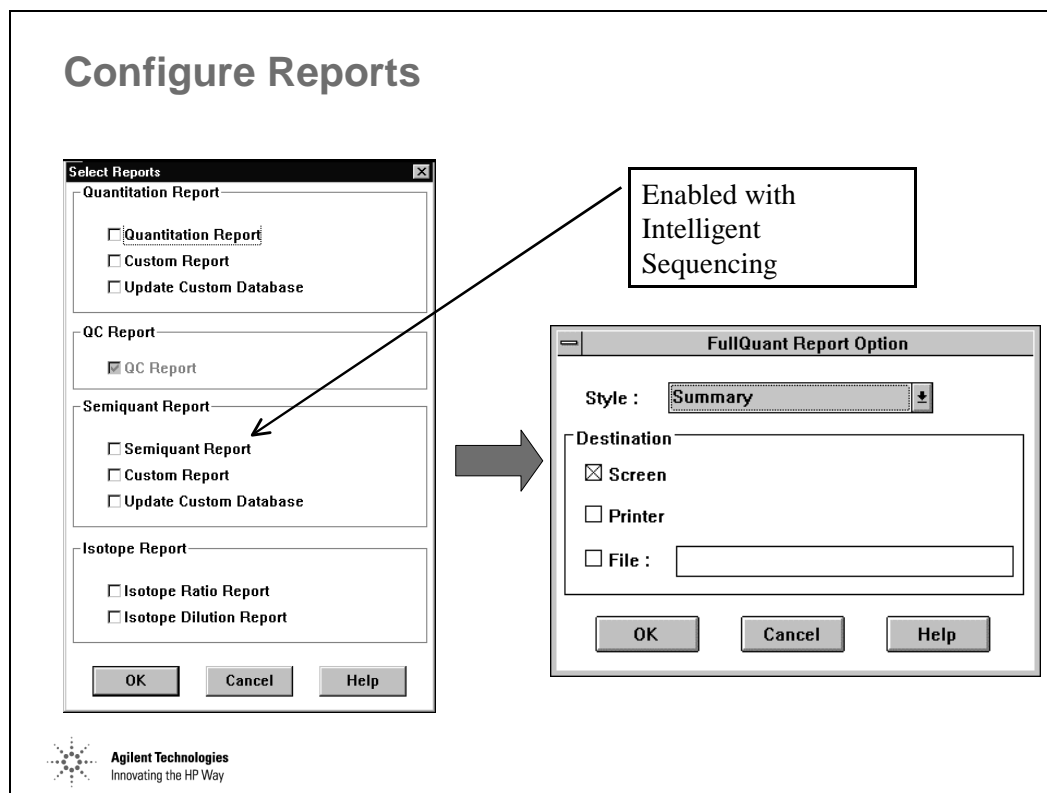


Figure 169

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



Figure 170

Calibration Table

Calibration Table

Edit Levels										
					Concentration of Standard Solution					
Mass Element	Curve Fit	Units	IS	Min Conc	Level 1	Level 2	Level 3	Level 4	Level 5	
6 Li	Excluded	ppb	—	0.00	20.00	20.00	20.00	20.00	20.00	▲
9 Be	Y=aX+b	ppb	6	5.00E-03	0.00	10.00	50.00	200.00	—	
23 Na	Y=aX+b	ppb	45	5.00E-03	0.00	1000.00	5000.00	2.00E+04	—	
24 Mg	Y=aX+b	ppb	45	5.00E-03	0.00	1000.00	5000.00	2.00E+04	—	
27 Al	Y=aX+b	ppb	45	5.00E-03	0.00	10.00	50.00	200.00	—	
39 K	Y=aX+b	ppb	45	5.00E-03	0.00	1000.00	5000.00	2.00E+04	—	
43 Ca	Y=aX+b	ppb	45	5.00E-03	0.00	1000.00	5000.00	2.00E+04	—	
45 Sc	Excluded	ppb	—	0.00	20.00	20.00	20.00	20.00	20.00	
51 V	Y=aX+b	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	
52 Cr	Y=aX+b	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	
53 [V]	Excluded	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	
55 Mn	Y=aX+b	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	
56 Fe	Y=aX+b	ppb	72	5.00E-03	0.00	1000.00	5000.00	2.00E+04	—	
57 Fe	Y=aX+b	ppb	72	5.00E-03	0.00	1000.00	5000.00	2.00E+04	—	
59 Co	Y=aX+b	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	
60 Ni	Y=aX+b	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	
63 Cu	Excluded	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	
66 Zn	Y=aX+b	ppb	72	5.00E-03	0.00	10.00	50.00	200.00	—	▼

Calibration Title:

☐ Weight

OK Cancel Help

Added Element: Add Conc. Multiply

Enter


 Agilent Technologies
Innovating the HP Way

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

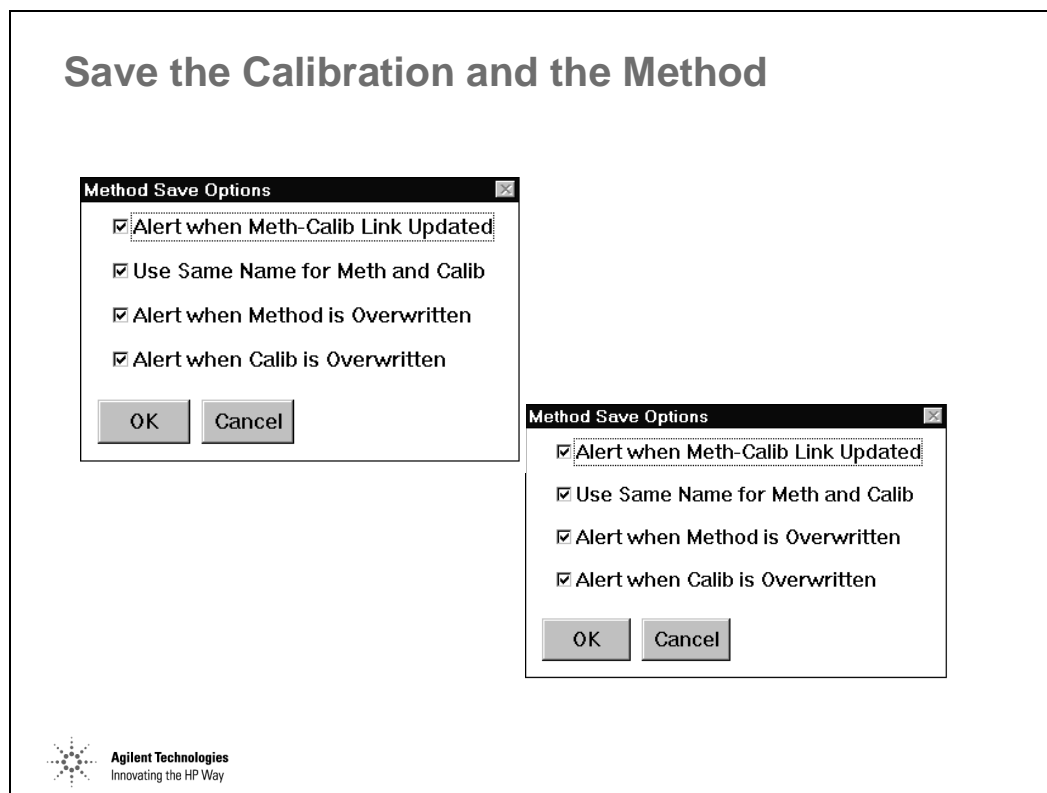


Figure 172

Quantitative Data Analysis

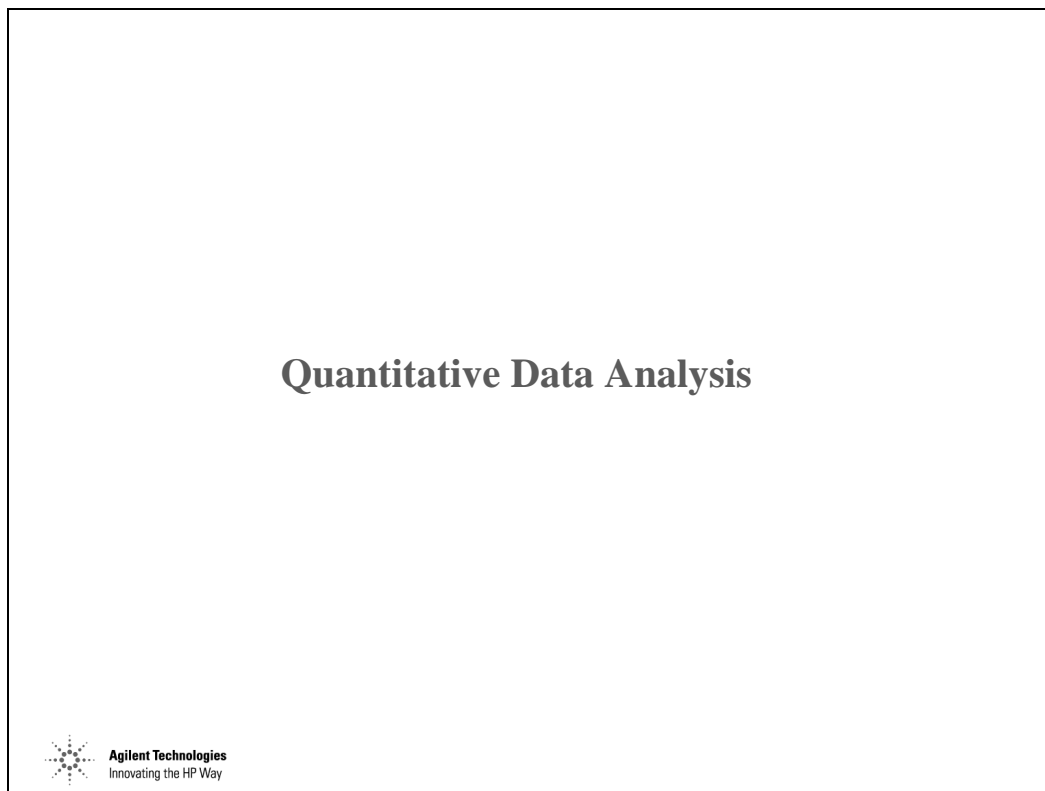


Figure 173

Standard Data Files

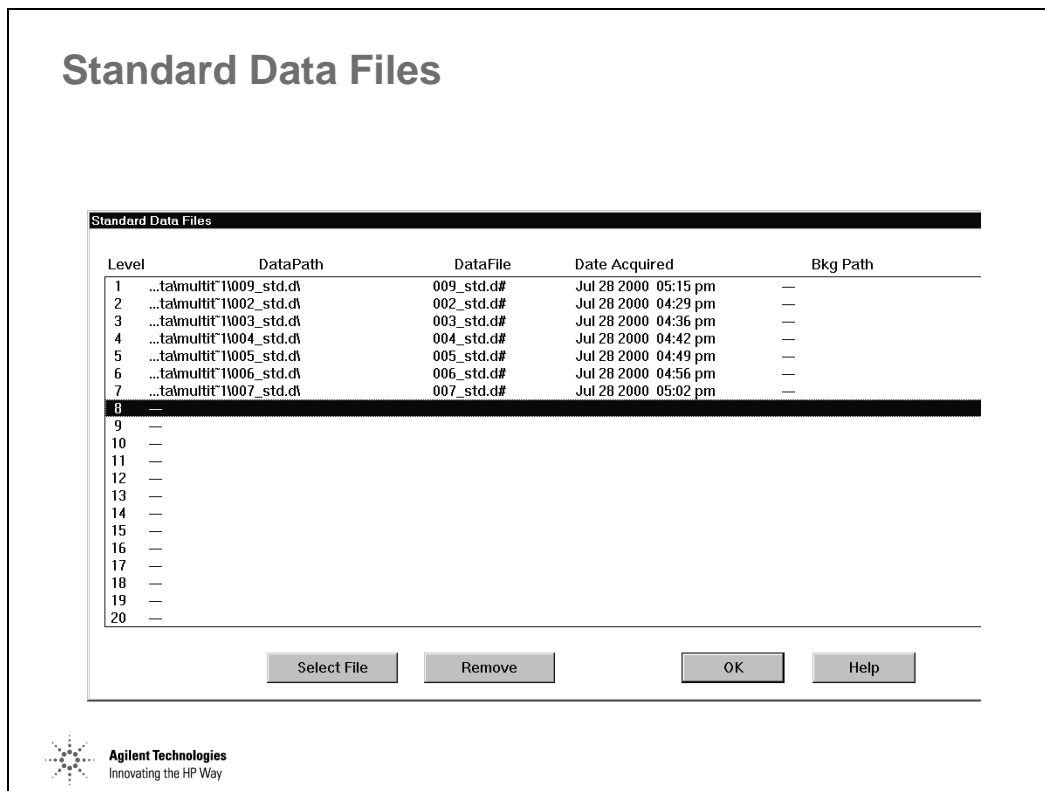
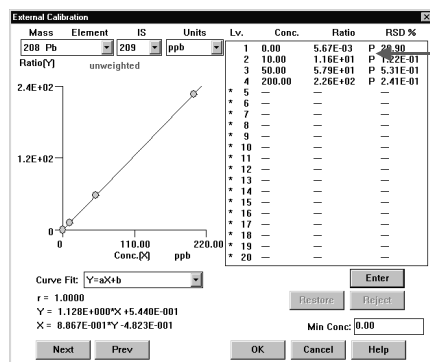


Figure 174

Calibration Curves

Calibration Curves



All measurements in Pulse counting mode

Some measurements in Pulse counting mode, some in Analog mode

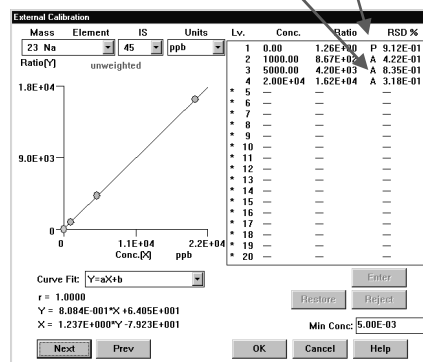


Figure 175

Examples of the Calibration Curves for “Excluded”

Examples of the Calibration Curves for “Excluded”

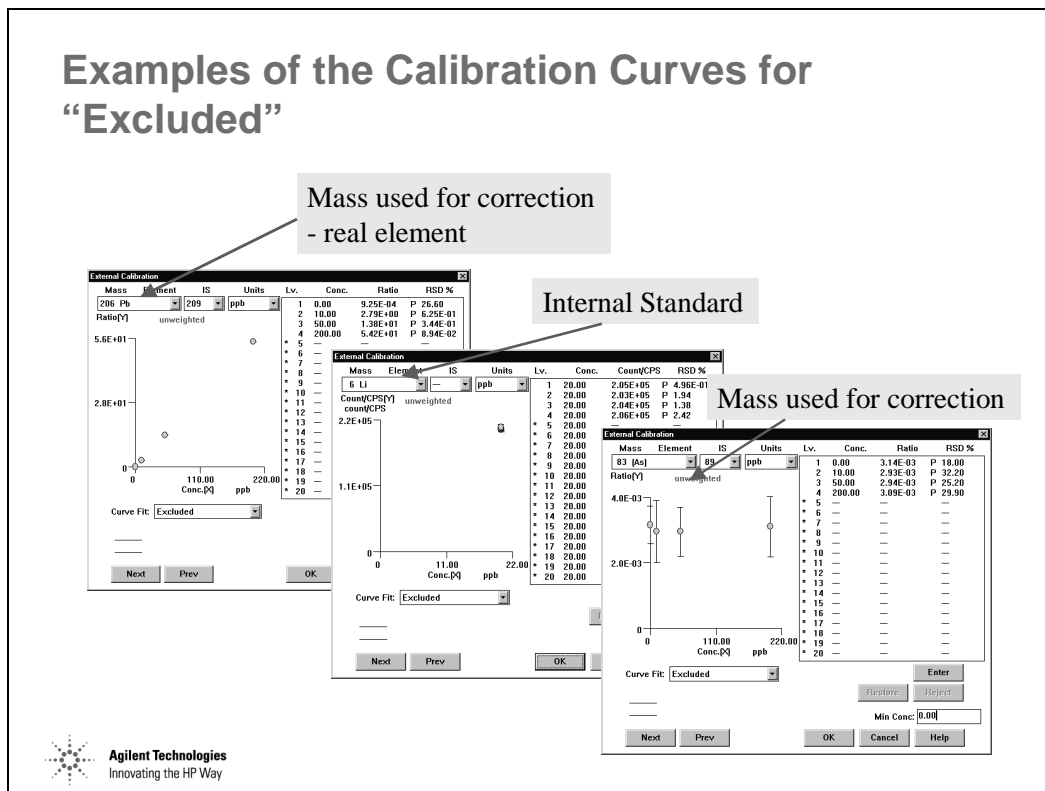


Figure 176

Examples of the Calibration Curves for “Excluded”



Agilent Technologies

Innovating the HP Way

Simple Sequencing (Intelligent Sequencing Disabled)

Sequencing

Sequencing

Sequencing

- Associates a list of samples with ALS positions and analytical methods
- Allows unattended analysis of multiple samples using multiple acquisition and reporting methods including all calibration updates.
- Designed to be used with an Autosampler (ASX-500 or ASX-100), can be used in a manual mode
- Allows automatic shutdown upon completion of the sequence



Agilent Technologies
Innovating the HP Way

Figure 177

ASX-500 Vial Position Nomenclature

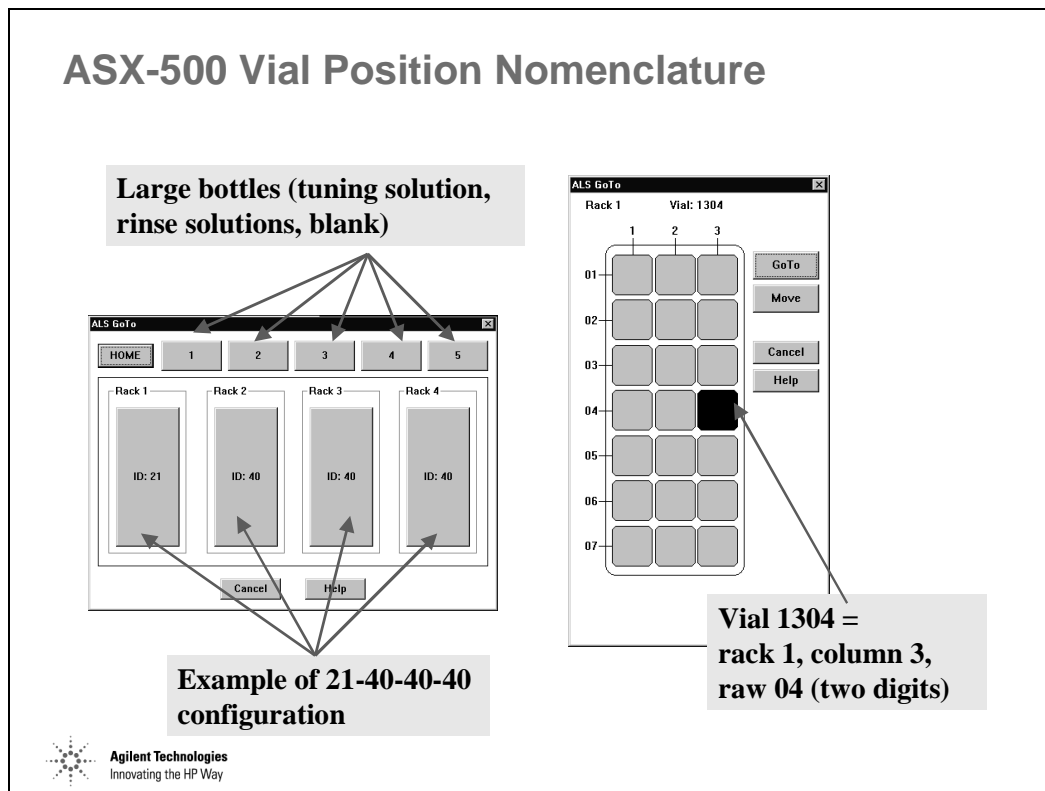


Figure 178

Sequencing

Sequencing

- NT ChemStation Sequencing is Spreadsheet based
- Allows shortcuts such as
 - *cut*,
 - *copy*,
 - *paste*,
 - *repeat*,
 - *fill down*
- Allows sample list to be inserted from other applications by
 - **importing .csv file**
 - **copy and paste from other application**



Agilent Technologies
Innovating the HP Way

Figure 179

Sample Log Table - Sequence Flow and Periodic Block

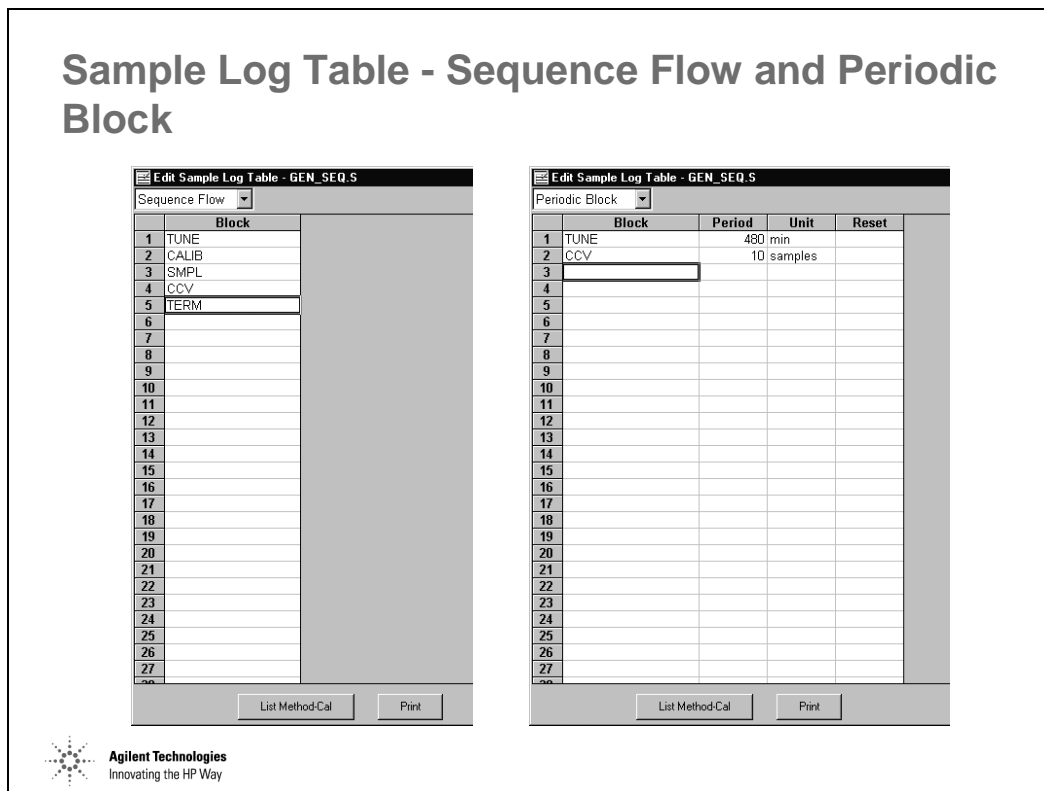


Figure 180

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

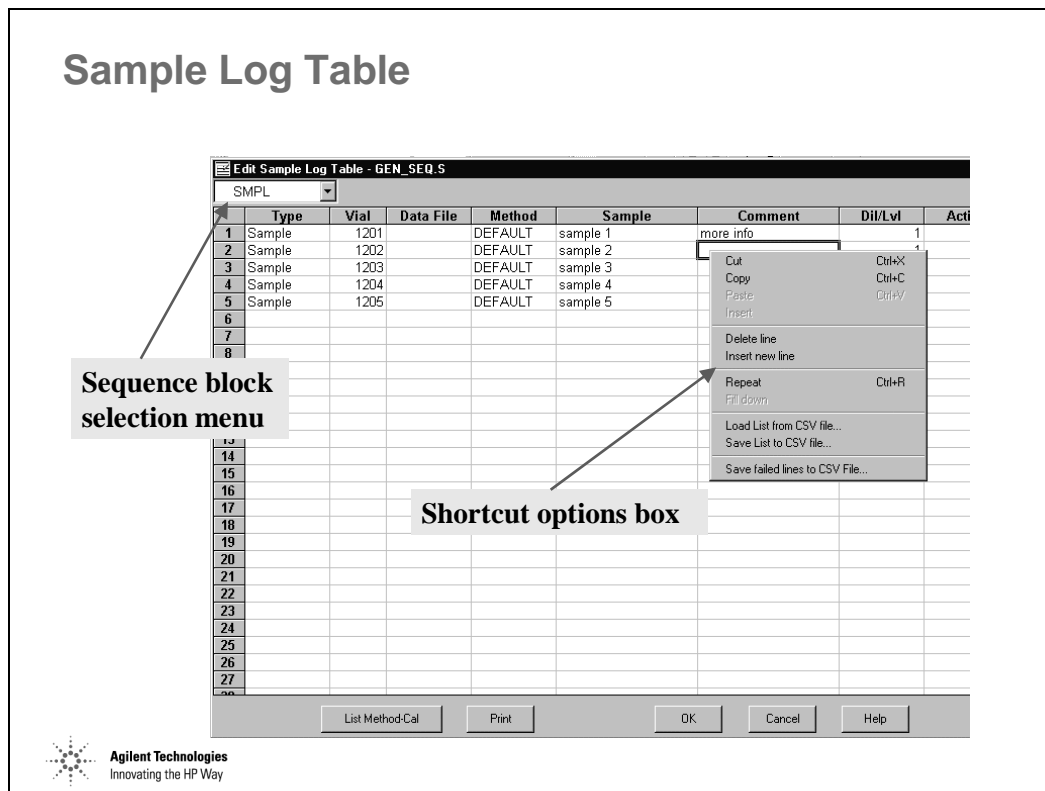


Figure 181

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 **incremented** 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

Special Features - Keywords

Command - a macro program

Methpath - specifies a method path (different than the normal ICPCHEM pathway)

Overwrit - overwrites a data file without asking for confirmation

Pause - pauses a sequence

Lotsep - separates sample batches (used mostly in intelligent sequencing)

StdToExt - converts MSA calibration to external calibration

Standby - puts the instrument in Standby mode



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

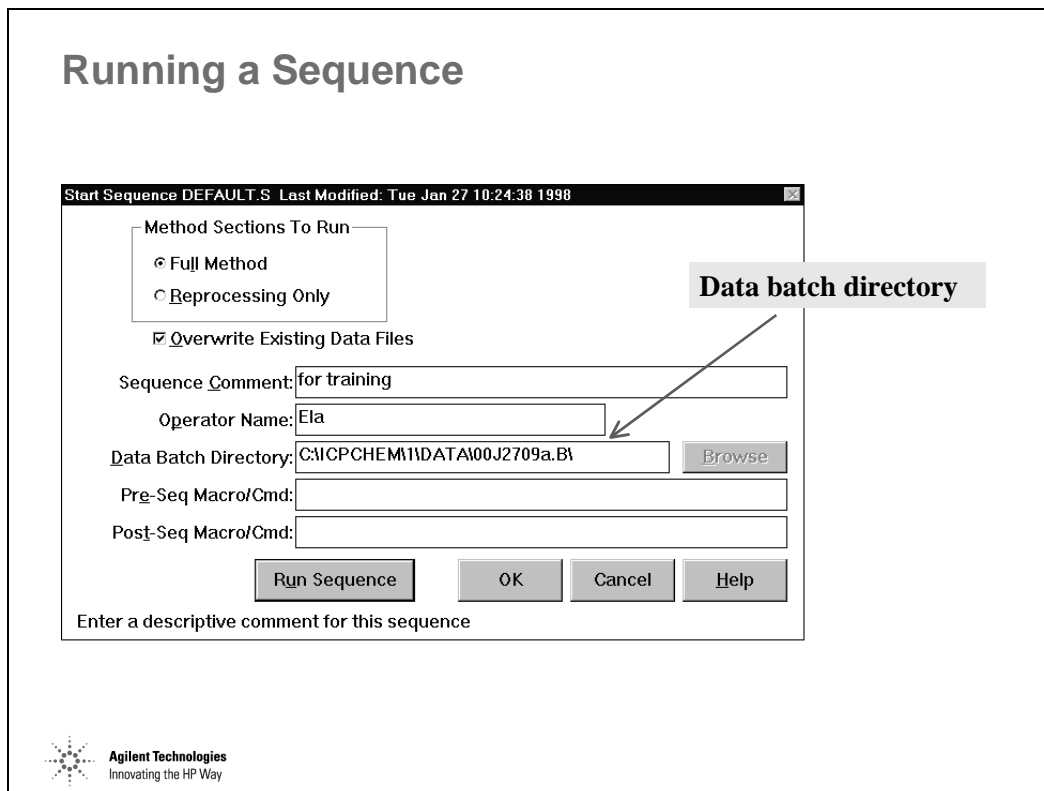


Figure 183

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

Chained Sequence

- **Allows Multiple Sequences to be Run in Series**
- **Allows Different Tune Conditions to be Used for Each Sequence**
 - **for example Hot and Cool Plasma**
 - **high and low sensitivity etc.**

*Tunes to be used in a chained sequence must be created (verified)
prior to running the sequence*



Agilent Technologies
Innovating the HP Way

Figure 184

Chained Sequence

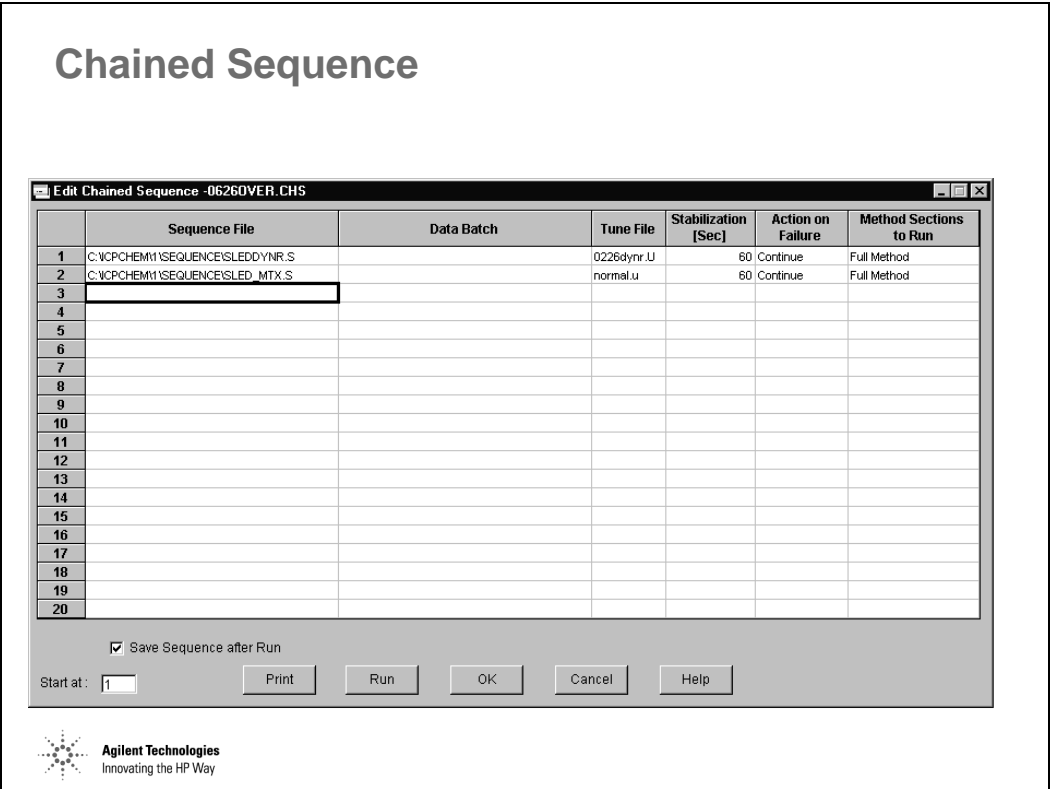


Figure 185



Agilent Technologies
Innovating the HP Way

Method of Standard Additions (MSA)

External Calibration

External Calibration

- **All Standards are prepared in one matrix**
- **A calibration curve is generated by plotting the intensity vs. concentration**
- **Sample concentration is calculated using the slope of the calibration curve**
- **Internal standards are used to correct for matrix-related signal changes**
 - IS can be added on-line



Figure 186

Pros and Cons of External Calibration

Pros and Cons of External Calibration

Pros

Minimal sample preparation

Good accuracy for simple matrices

Cons

IS additions increases contamination potential

Limited with difficult matrices (Photoresist)

It doesn't work well with cool plasma



Agilent Technologies
Innovating the HP Way

Figure 187

Method of Standard Addition (MSA)

Method of Standard Addition (MSA)

- **Standards are prepared in the sample matrix**
- **A calibration curve is generated by plotting the intensity vs. spiked concentration**
- **Sample concentration is calculated by extrapolating to the Y intercept**
- **Calibration can be converted into an external to run subsequent samples of the same matrix.**



Figure 188

Pros and Cons of Method of Standard Additions

Pros and Cons of Method of Standard Additions

Pros

- Method of choice for ultra-trace levels**
- Good accuracy for all matrices**
- No need for internal standards**
 - Compensate for differences in sample nebulization and transport efficiency**

Cons

- Different calibrations for each matrix**
- All signal is accounted for**
 - can't distinguish between true signal or background**
- BEC for Ca, Fe and K can be affected**



Figure 189

Determination of Uranium in Urine by MSA

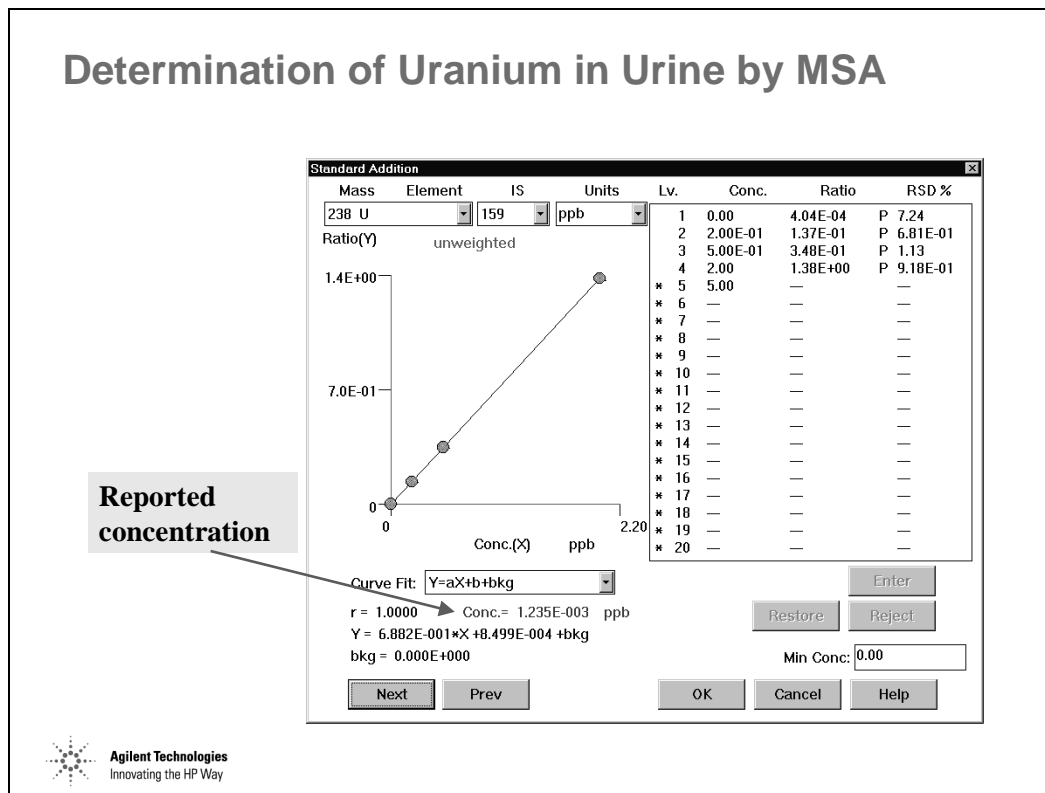


Figure 190

Converting from MSA to External Calibration

Converting from MSA to External Calibration

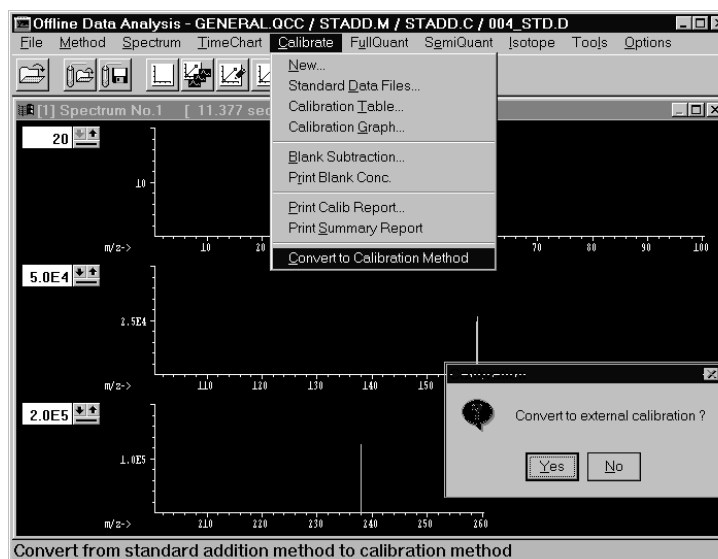


Figure 191

Matrix-matched Uranium in Urine External Calibration

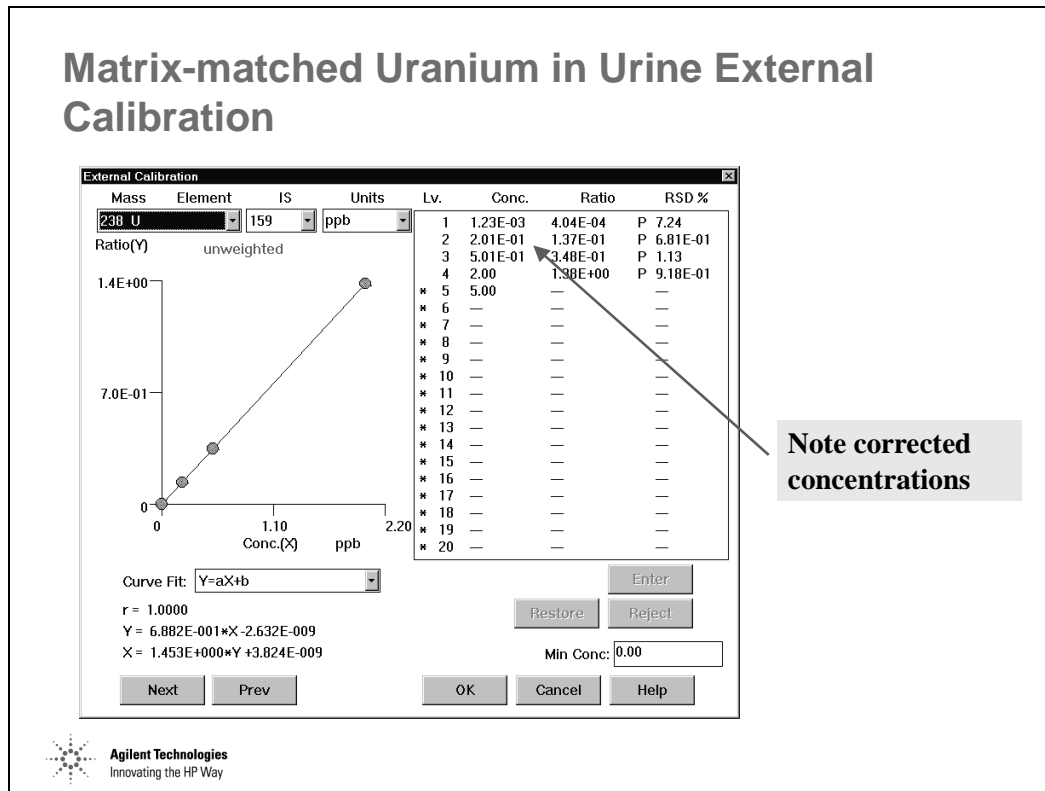


Figure 192



Agilent Technologies

Innovating the HP Way

Off-line Data Analysis and Sequence Reprocessing

Off-line Data Analysis

Off-line Data Analysis

- Reviews calibration and data for currently running sequence
- Edits currently running data analysis method
- Saves modifications to currently running data analysis method (if needed)
- Reprocesses data for currently running sequence
- Reviews/Reprocesses previously acquired data



Figure 193

Procedure for Off-line Data Analysis

Procedure for Off-line Data Analysis

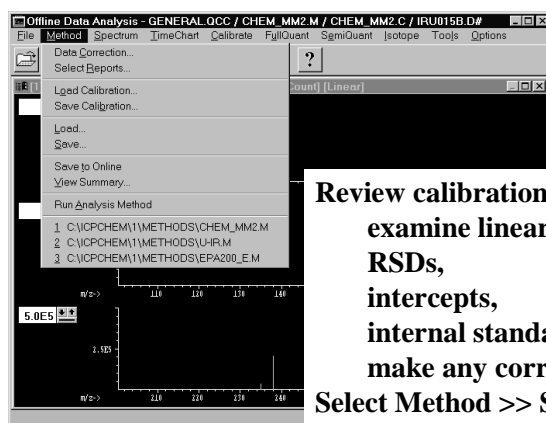
- Start Off-line Data Analysis
- Load appropriate method
- Verify calibration data files
- Make corrections/modifications (if needed)
- Reprocess data



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

Figure 195

Using DoList for Off-line Data Reprocessing

Using DoList for Off-line Data Reprocessing

Dolist automatically reprocesses a batch or list of data files according to the options selected using to the currently loaded method and calibration.

DoList does NOT update the method or calibration



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

How to Use DoList

Data Analysis >> Tools >> Configure DoList
Data Analysis >> Tools >> DoList

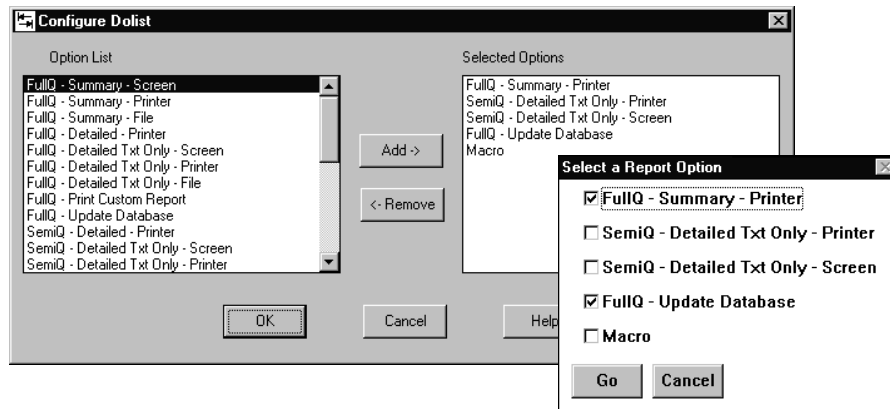


Figure 197

Selecting Files Using DoList

Selecting Files Using DoList

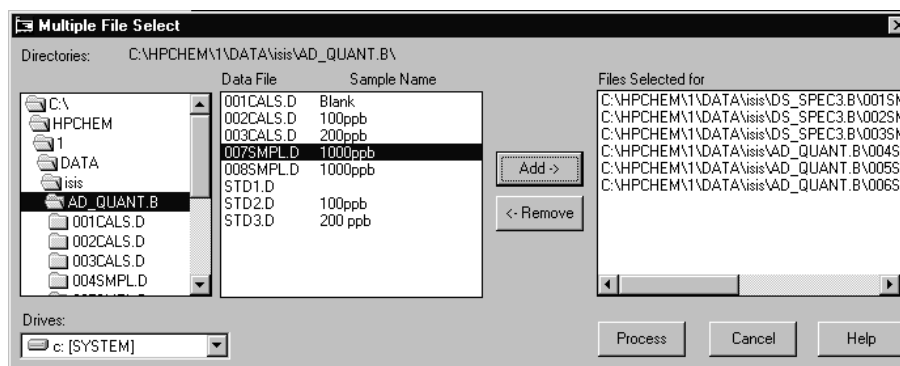


Figure 198

Sequence - Reprocessing Data Batch

Sequence - Reprocessing Data Batch

Used to reprocess entire (or partial) sequence

Does

- Load methods from disk as specified

- Update calibrations in order acquired

- Recalculate (Requant) data and regenerate reports

- Save updated calibrations to disk



Agilent Technologies
Innovating the HP Way

Figure 199

Sequence Reprocessing

Sequence Reprocessing

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

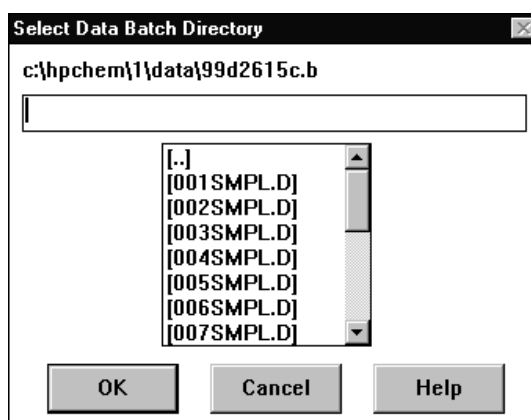


Figure 200

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 to remove necessary files such as calibration files or reference files for sample types such as spikes or duplicates.



Agilent Technologies

Innovating the HP Way

Custom Reports and Databases

What You Will Learn

What You Will Learn

- How to create a template and generate reports
- how to create a database and update it



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.

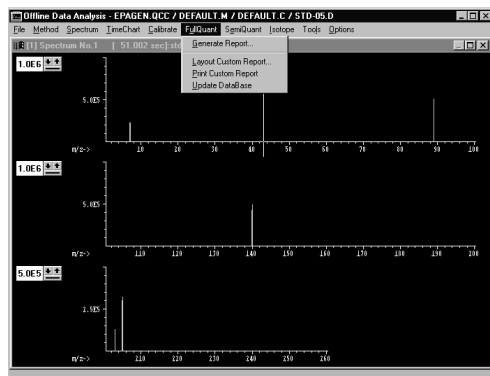
Custom databases contain information from many samples.

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

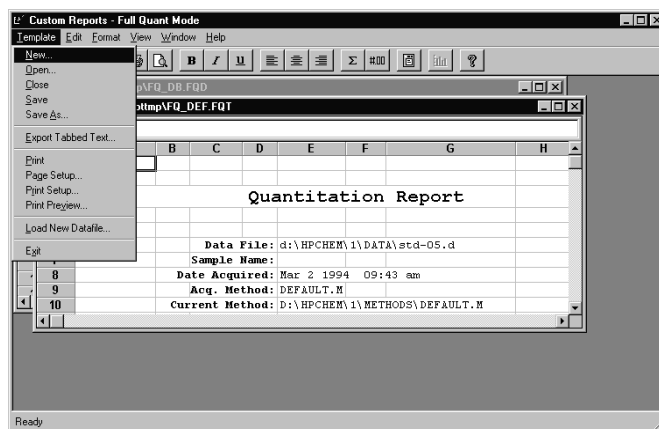


Figure 202

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



Figure 203

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

Custom Reports - Report Wizard

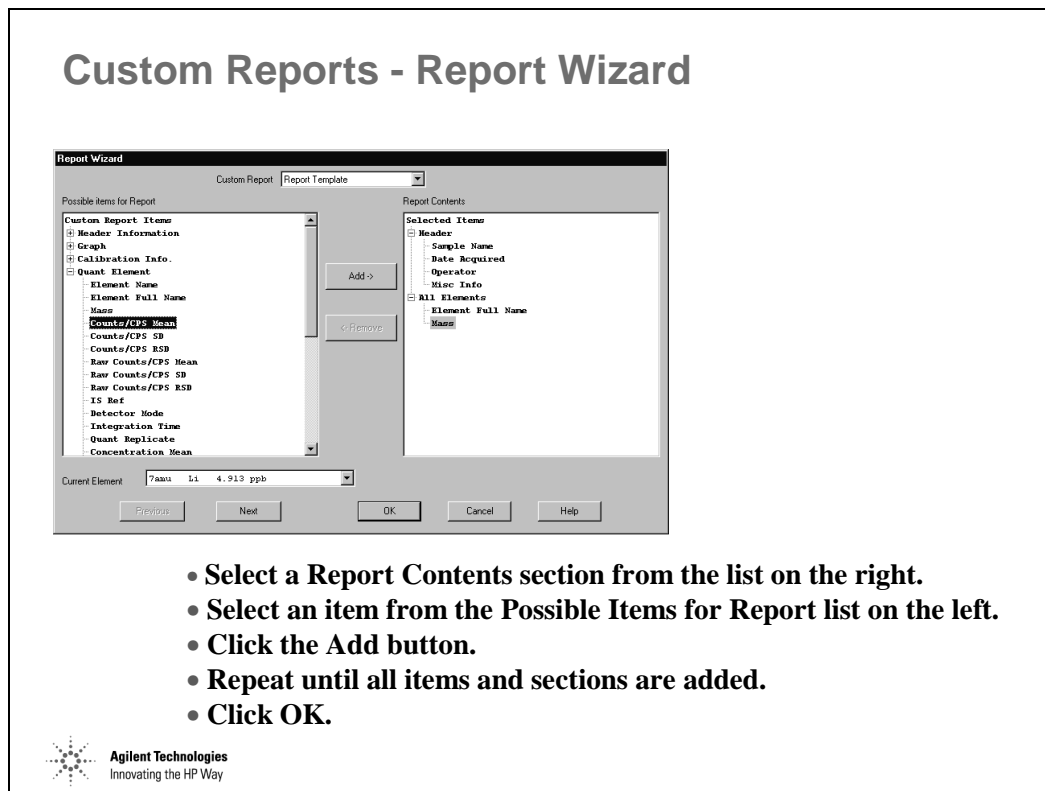


Figure 204

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

Custom Reports - Report Wizard

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)

Custom Reports - Drag and Drop (1)

Custom Reports - Full Quant Mode - [Untitled 1]

	A	B	C	D	E
1					
2			Sample Name:		
3			Date Acquired:	Mar 2 1994 09:43 am	
4			Operator:		
5			Misc Info:		
6					
7					
8		Element Full Name	Mass	Counts/CPS Mean	Concentration Mean
9		lithium	7	69037.03	4.91
10		yttrium	89	155520.80	4.95
11		cerium	140	143303.59	5.08
12		thallium	203	40159.74	4.77
13		thallium	205	95924.12	4.75
14					
15					
16					
17					
18					
19					
20					

Ready

Edit Box: Drag and Drop

7amu L1 4.913 ppb

Previous Next

Header Information

- Data File Path
- Data File Name
- Sample Name
- Date Acquired
- Acq. Method
- Current Method Path
- Calibration Path
- Calibration File
- Operator
- Misc Info
- Dilution Factor
- Vial Number
- Number of Masses
- Data Type
- Sample Type
- Background File
- Bkg Rejected Masses
- Interference Correction
- Scan Number
- Data Points

Close Help

Agilent Technologies
Innovating the HP Way

Figure 205

Custom Reports - Drag and Drop (2)

Custom Reports - Drag and Drop (2)

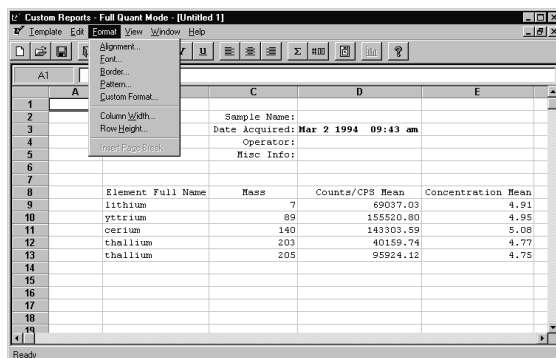
- Accessed by selecting View / Edit Box or clicking Edit Box button of the toolbar.
- Select an item and drag it to any cell on the spreadsheet.
- Use the Next button or select from the list to view other elements.
- The current value for the highlighted item is displayed.



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



Figure 207

Column width and row height can be controlled from 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

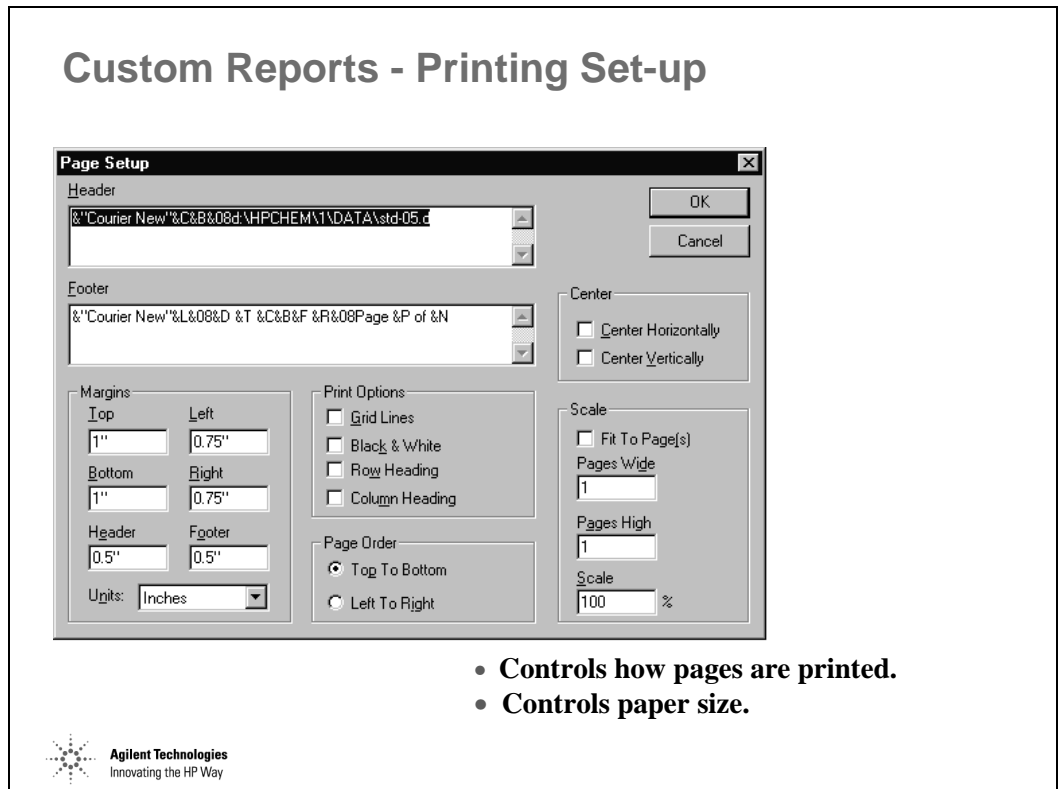


Figure 208

The following “Print Options” are available:

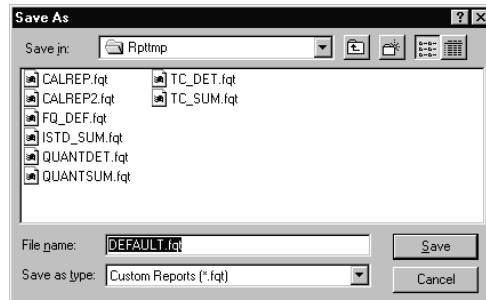
- Grid Lines - lets you print grid lines (otherwise they are visible on the screen only)
- Black & White - prints color in black and white on a color printer

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

Custom Reports - Saving the Template



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

- Click Yes to link the template with the current method



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

Printing Custom Reports - Interactively

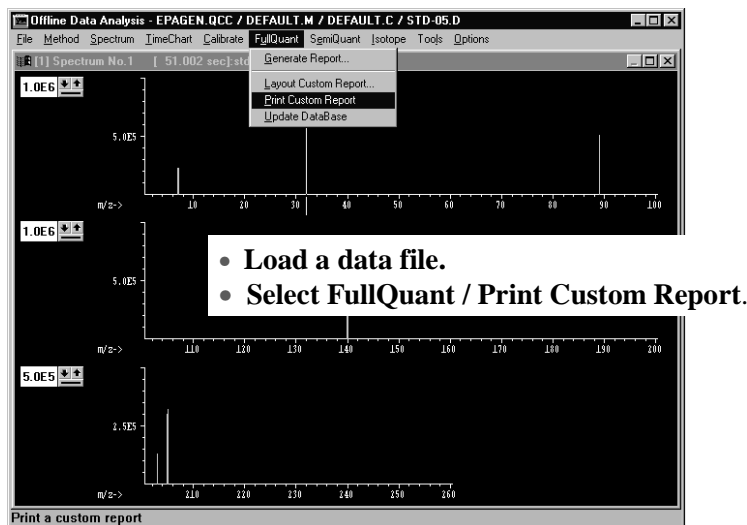


Figure 210

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]

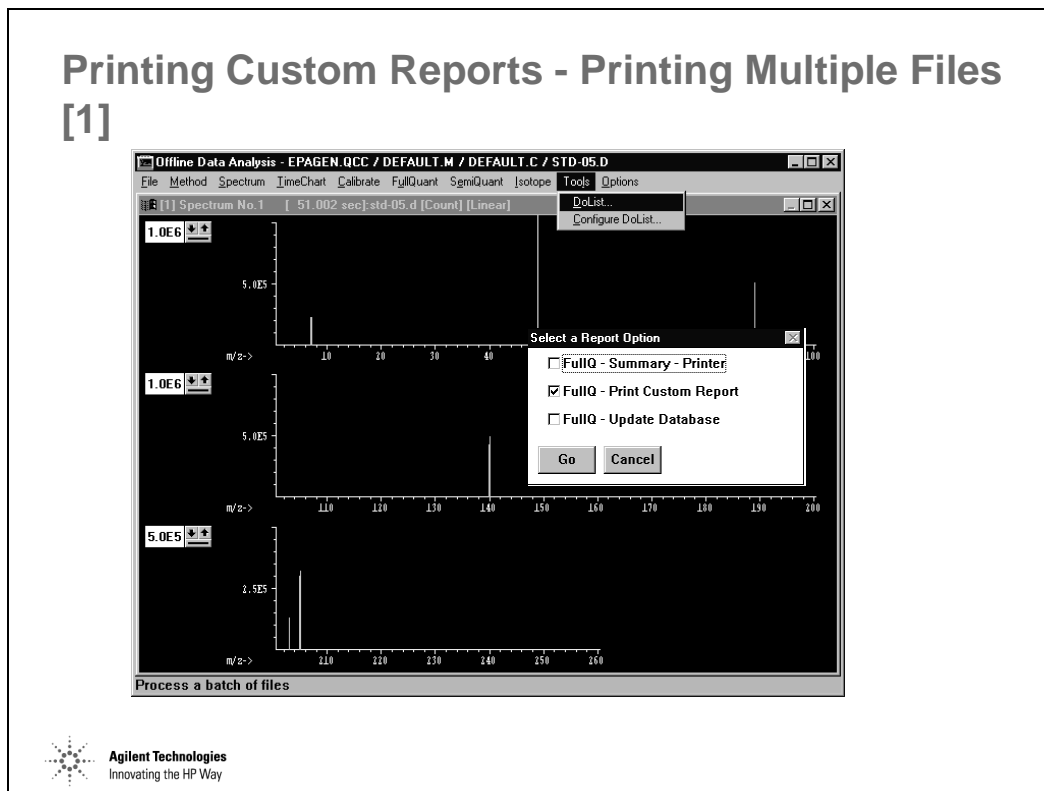


Figure 211

Printing Custom Reports - Printing Multiple Files [2]

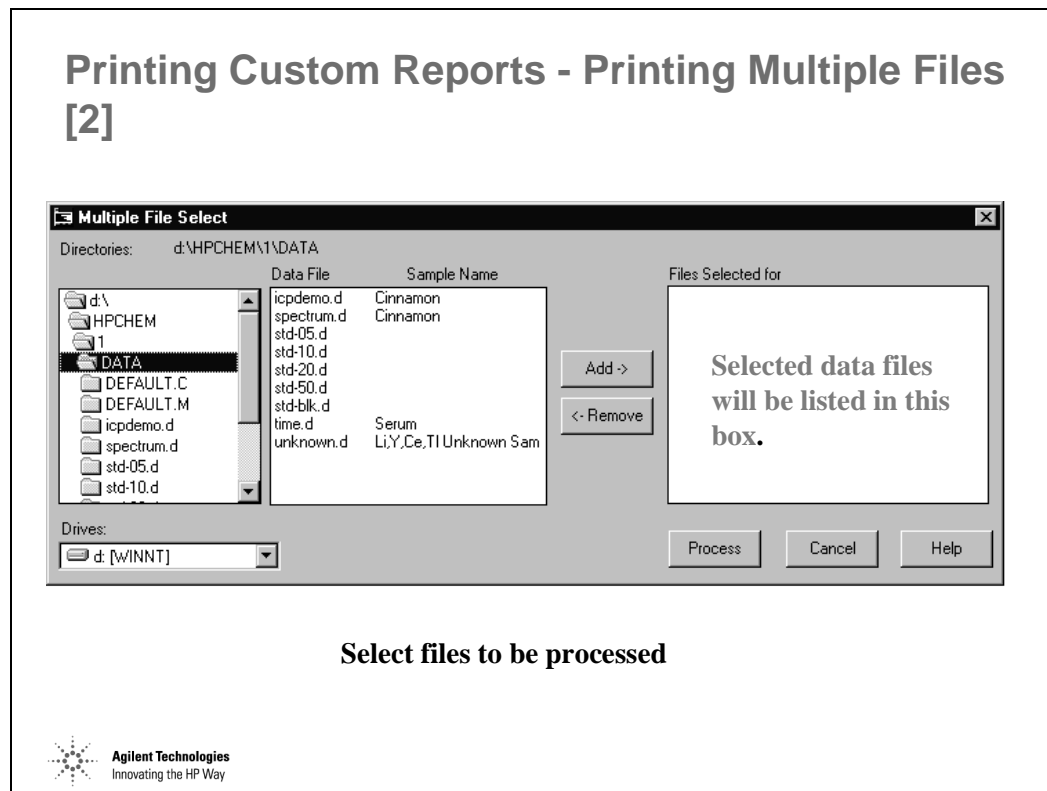


Figure 212

Select files from the Data File listing:

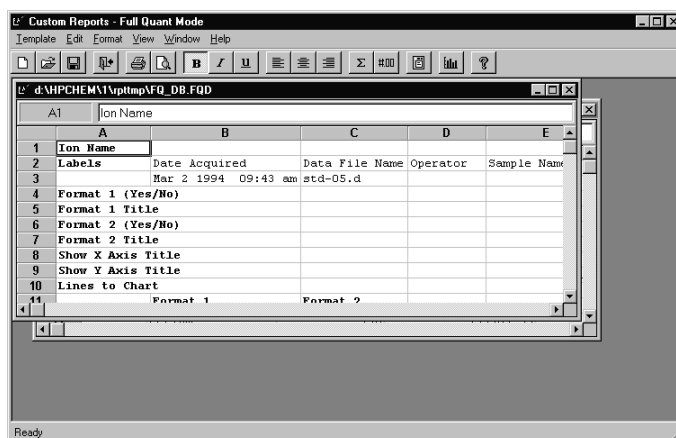
- multiple continuous
- multiple discontinuous
- a single file can be removed from the “Files Selected for Processing” by double clicking on it.

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

Click the Process button.

Databases

Databases



- Create new database
- Edit the current database and/or create charts
- Specify new database

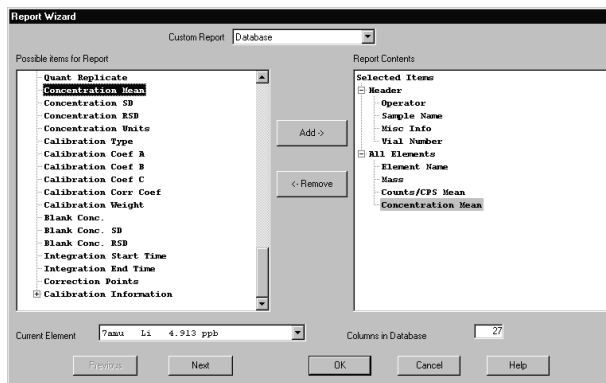


Figure 213

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

Database Wizard

Database Wizard



- Select a Database section from the list of the right.
- Select an item from the Possible Items for Database list on the left.
- Click the Add button.
- Repeat until all items and sections are added.
- Click OK.



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

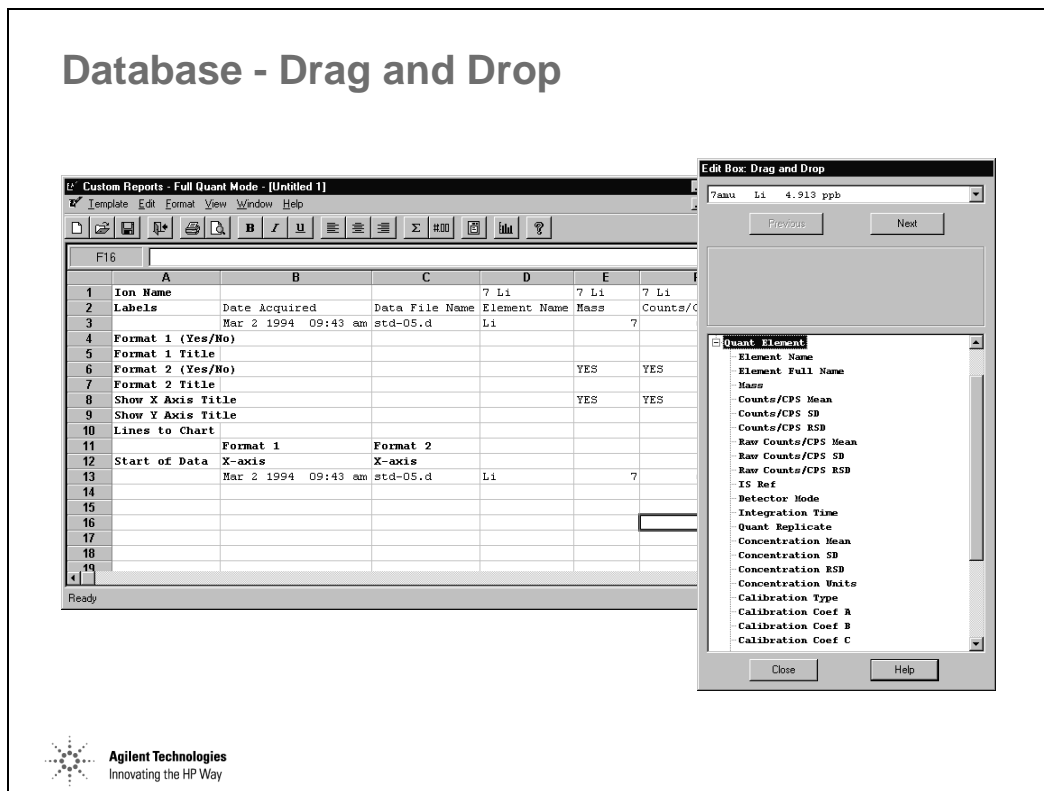


Figure 215

- 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

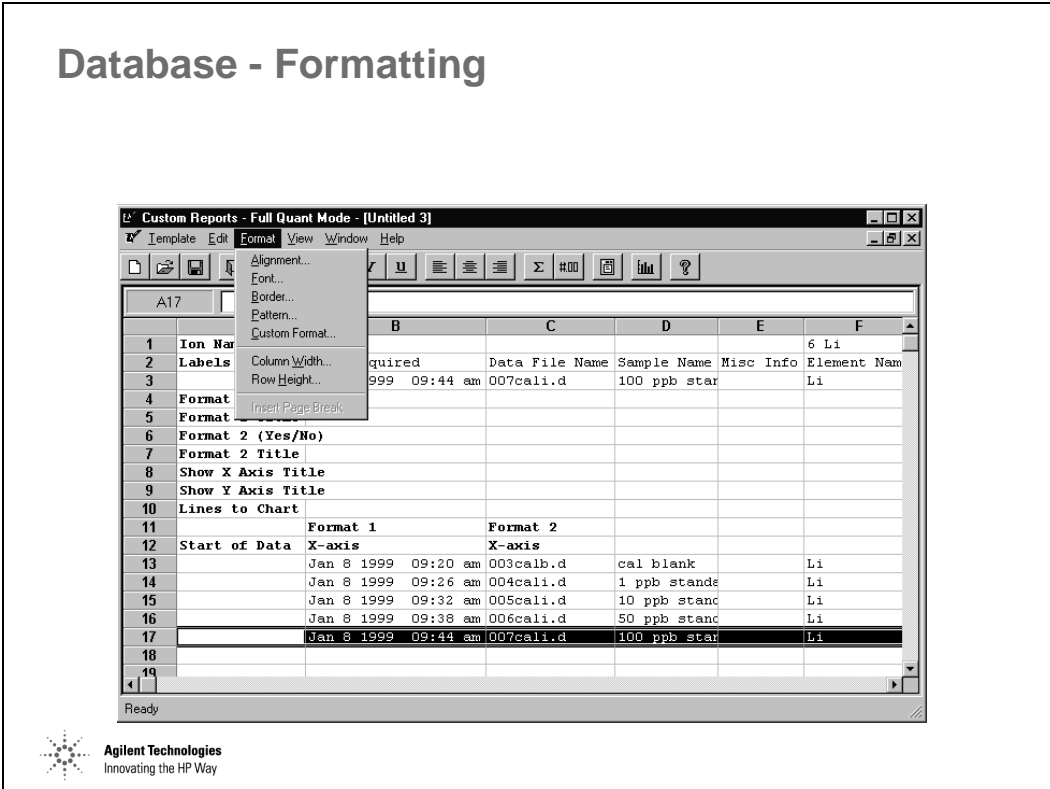


Figure 216

Database - Charts

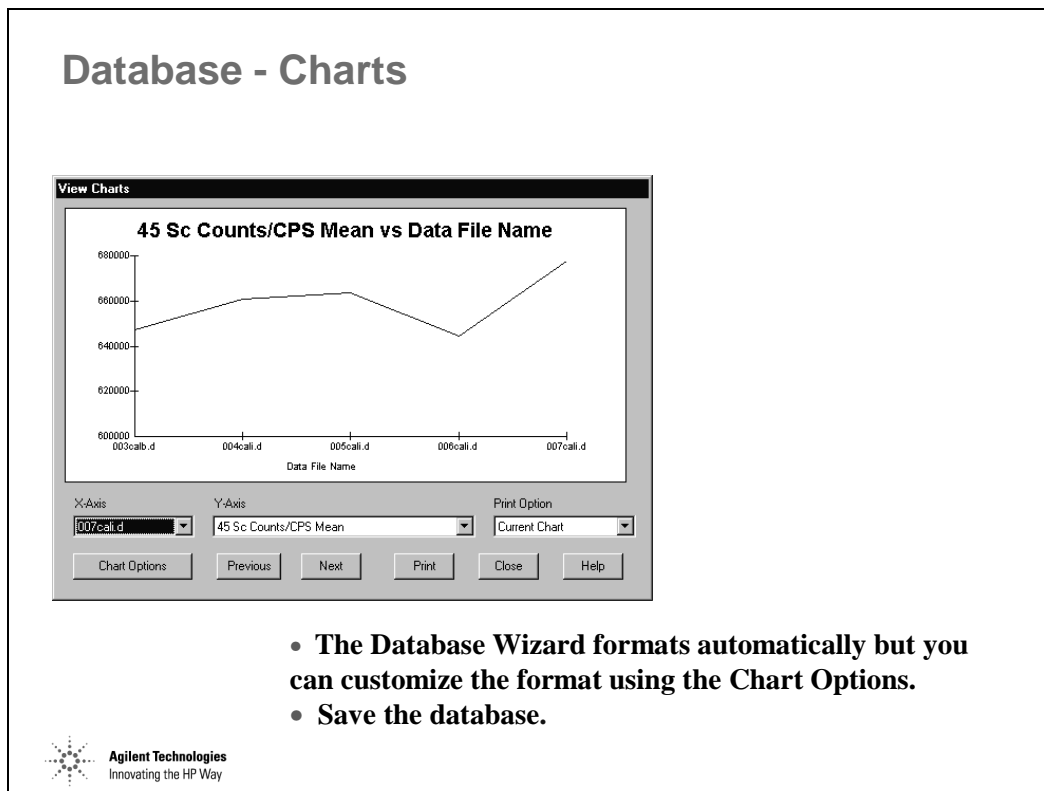


Figure 217

“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

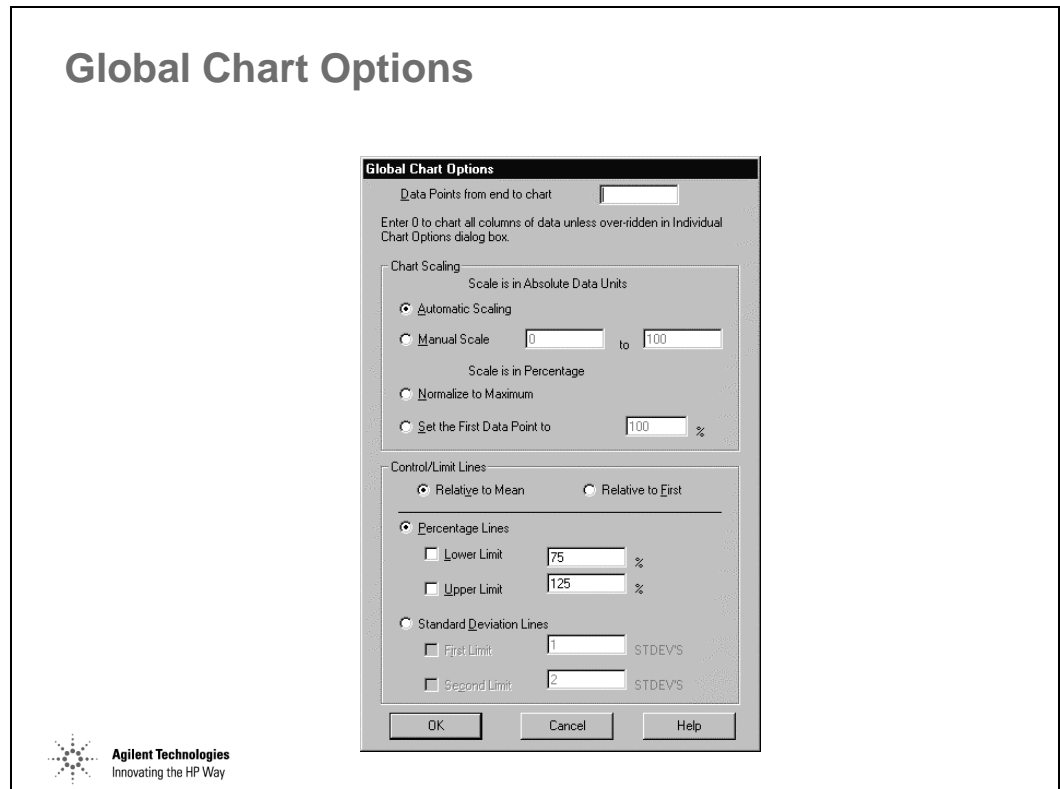


Figure 218

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.

Global Chart Options

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.

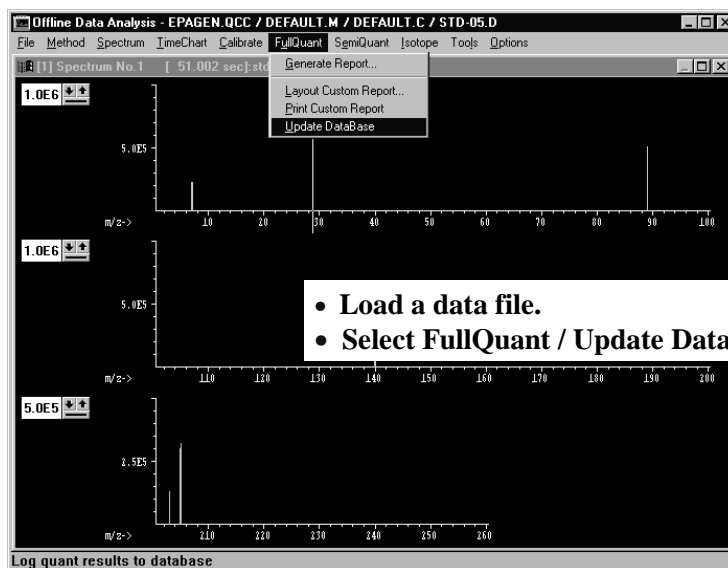
- Click Yes to link the template with the current method



Figure 219

Updating the Database - Interactively

Updating the Database - Interactively



- Load a data file.
- Select FullQuant / Update Database.

Figure 220

Update the Database - Multiple Files [1]

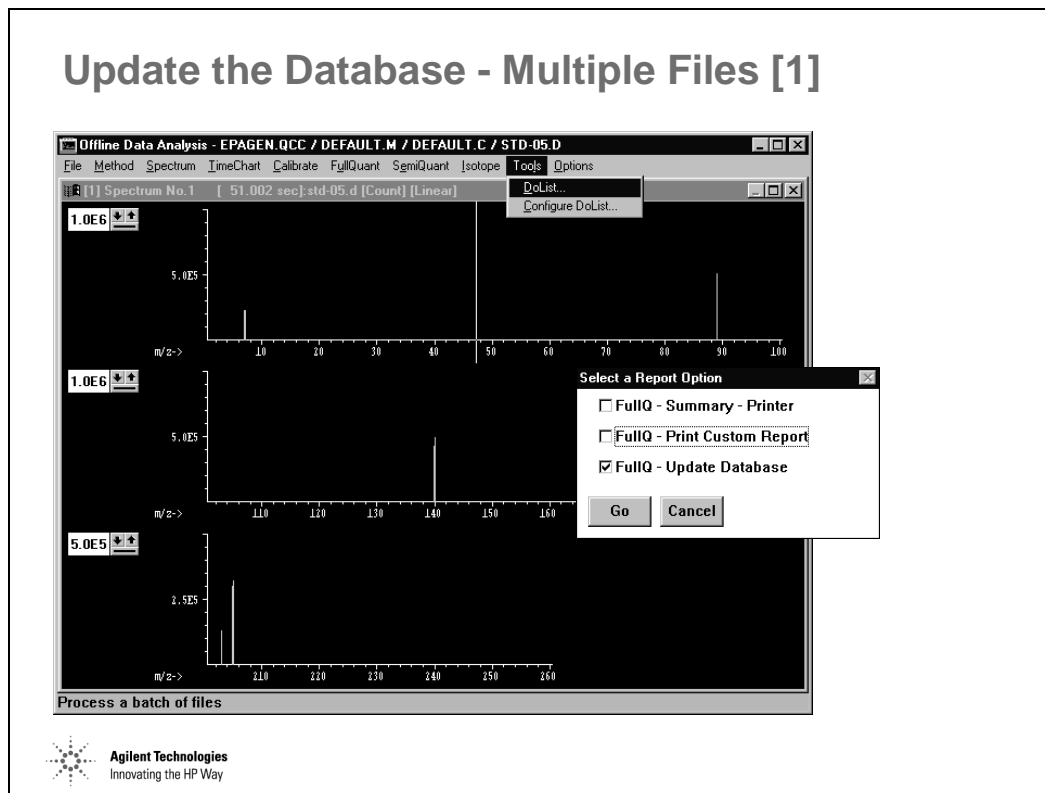
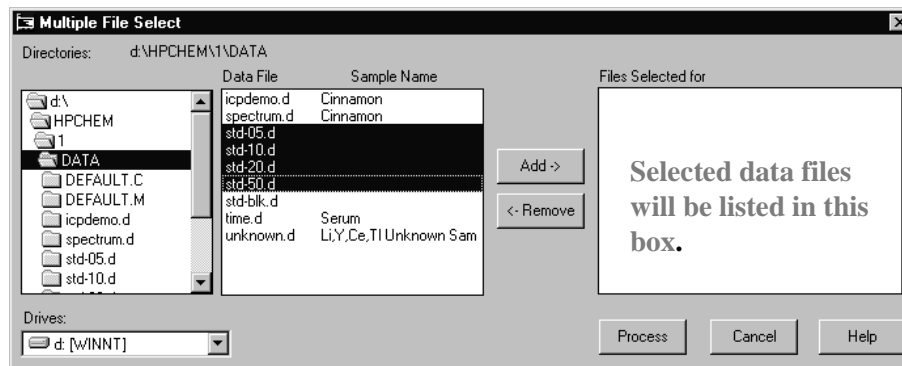


Figure 221

Update the Database - Multiple Files [2]

Update the Database - Multiple Files [2]



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

Figure 222

Update the Database - Multiple Files [2]



Agilent Technologies

Innovating the HP Way

Isotope Ratio Measurements

Editing a Method for Quantitative Analysis

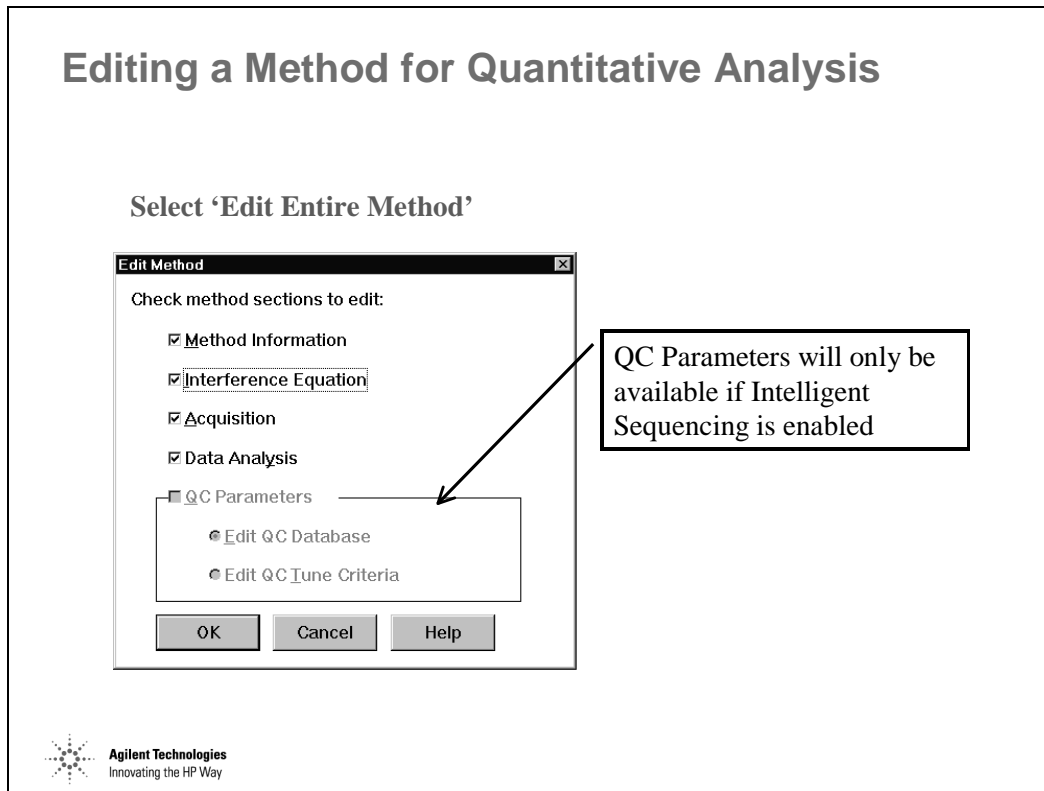


Figure 223

Acquisition Modes

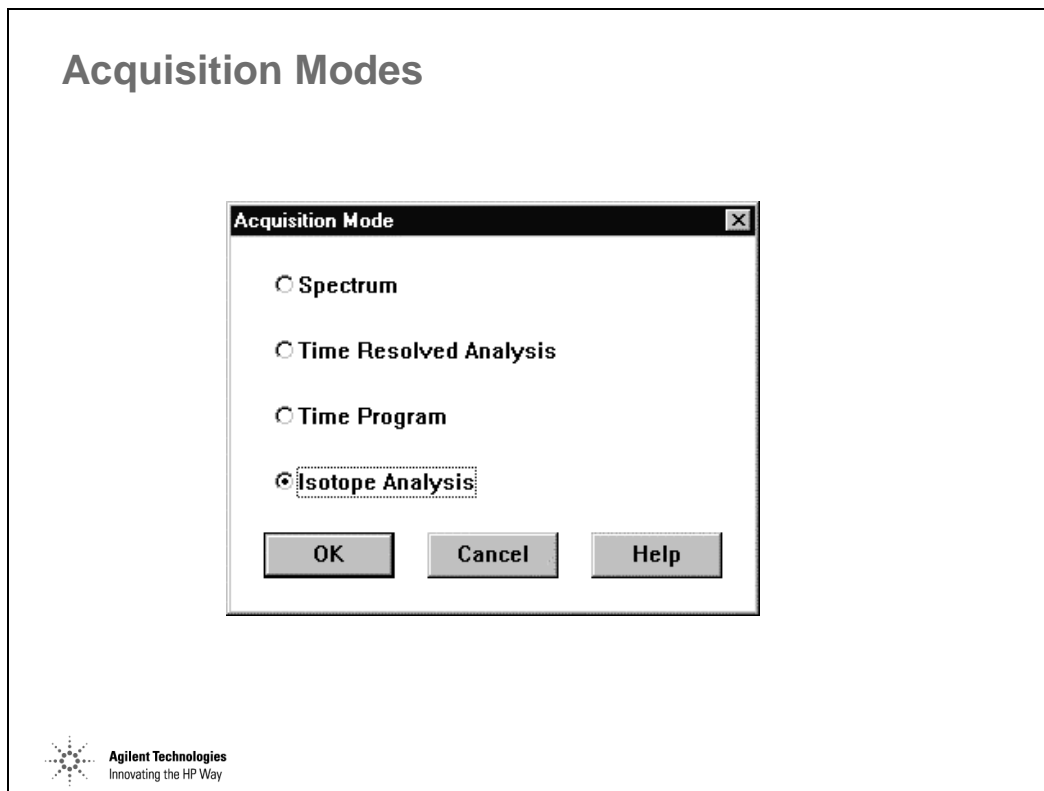


Figure 224

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

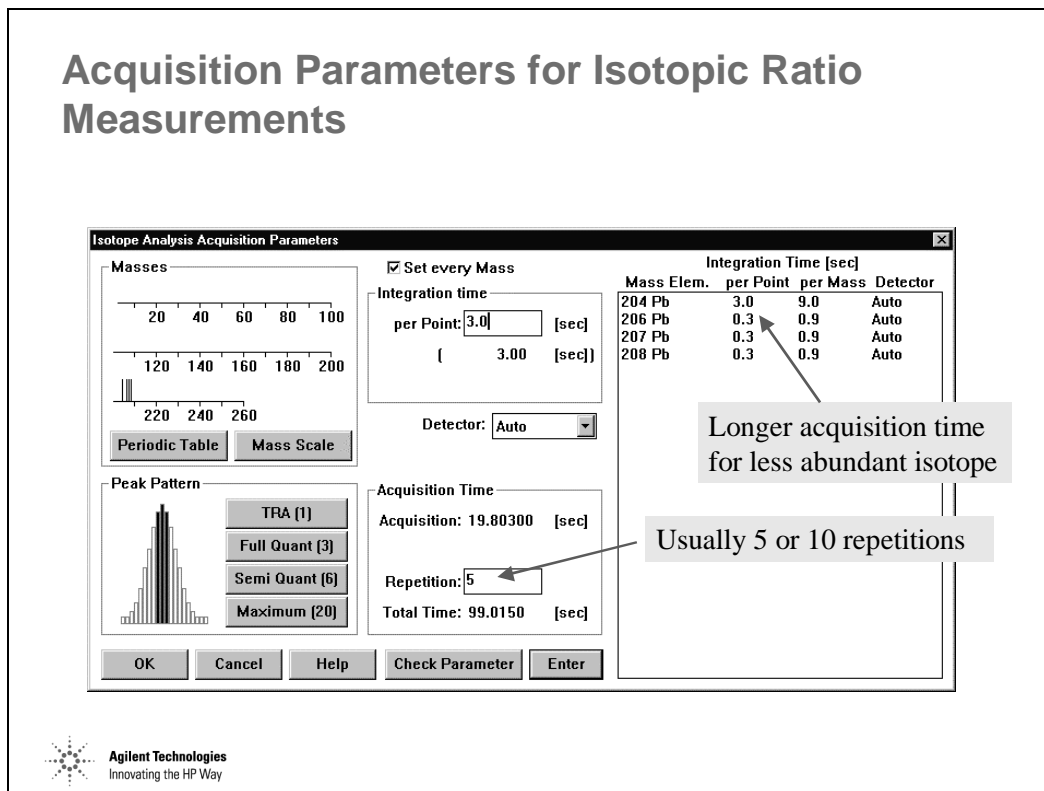


Figure 225

Report Selection

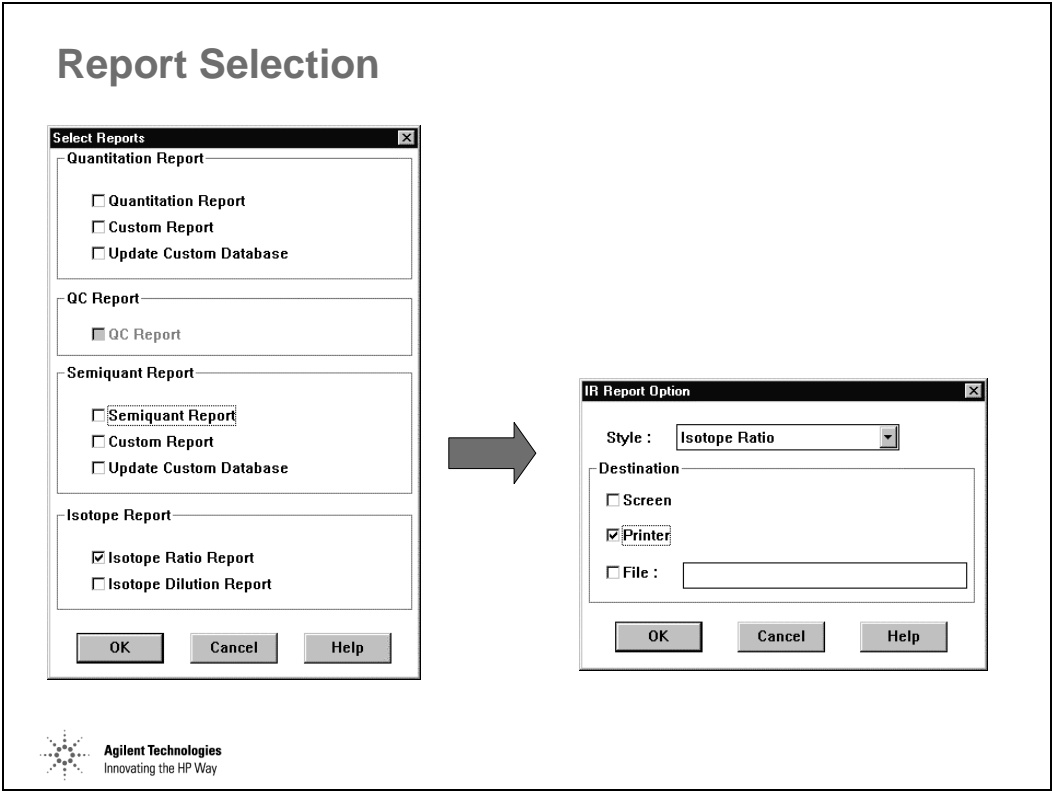


Figure 226

Setting Parameters for Isotopic Ratios

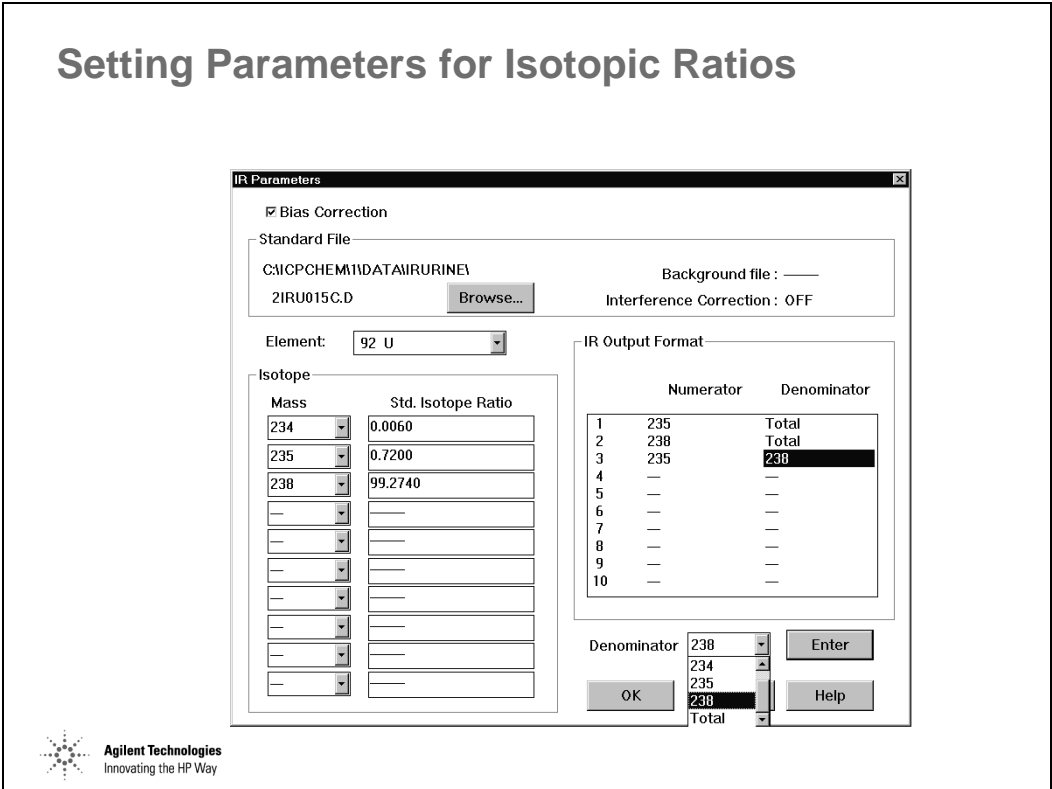
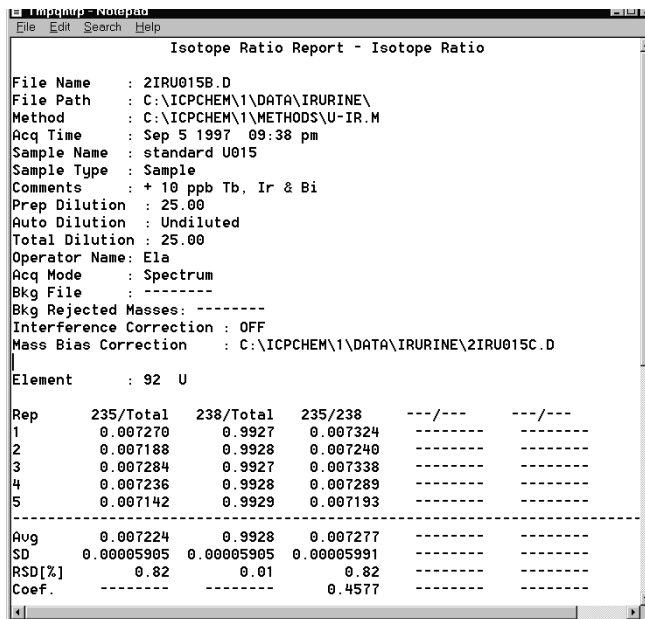


Figure 227

Example of the Isotopic Ratio Report

Example of the Isotopic Ratio Report



Isotope Ratio Report - Isotope Ratio

File Name : 2IRU015B.D
File Path : C:\ICPCHEM\1\DATA\IRURINE\
Method : C:\ICPCHEM\1\METHODS\U-IR.M
Acq Time : Sep 5 1997 09:38 pm
Sample Name : standard U015
Sample Type : Sample
Comments : + 10 ppb Tb, Ir & Bi
Prep Dilution : 25.00
Auto Dilution : Undiluted
Total Dilution : 25.00
Operator Name: Ela
Acq Mode : Spectrum
Bkg File : -----
Bkg Rejected Masses: -----
Interference Correction : OFF
Mass Bias Correction : C:\ICPCHEM\1\DATA\IRURINE\2IRU015C.D

Element : 92 U

Rep	235/Total	238/Total	235/238	---/---	---/---
1	0.007270	0.9927	0.007324	-----	-----
2	0.007188	0.9928	0.007240	-----	-----
3	0.007284	0.9927	0.007338	-----	-----
4	0.007236	0.9928	0.007289	-----	-----
5	0.007142	0.9929	0.007193	-----	-----
Avg	0.007224	0.9928	0.007277	-----	-----
SD	0.00005905	0.00005905	0.00005991	-----	-----
RSD[%]	0.82	0.01	0.82	-----	-----
Coef.	-----	-----	0.4577	-----	-----

Agilent Technologies
Innovating the HP Way

Figure 228



Agilent Technologies
Innovating the HP Way

Agilent ICP-MS ChemStation and Windows Overview

The Windows Interface

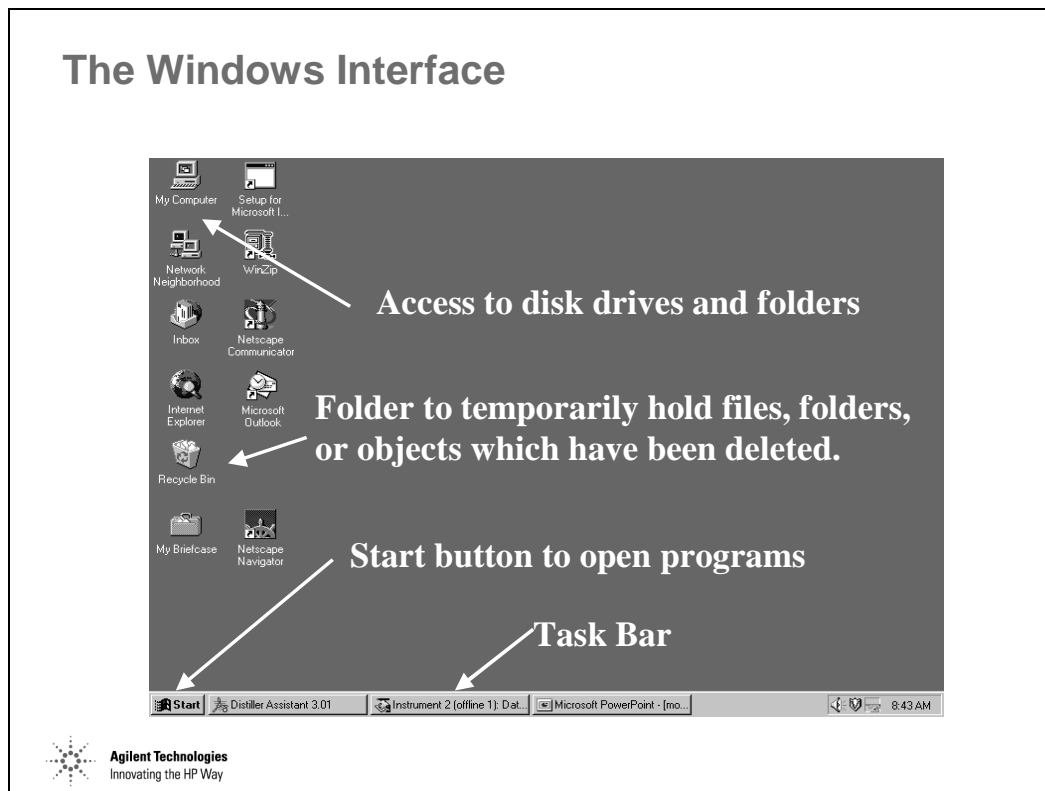


Figure 229

Windows Menus

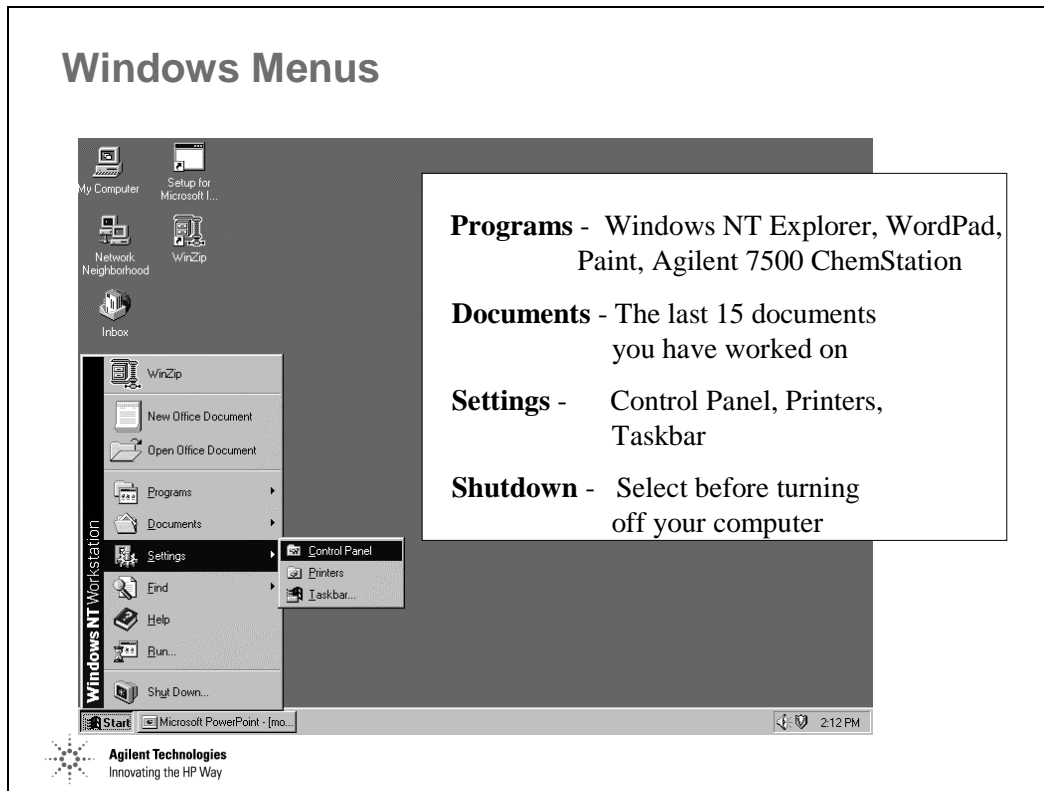


Figure 230

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.

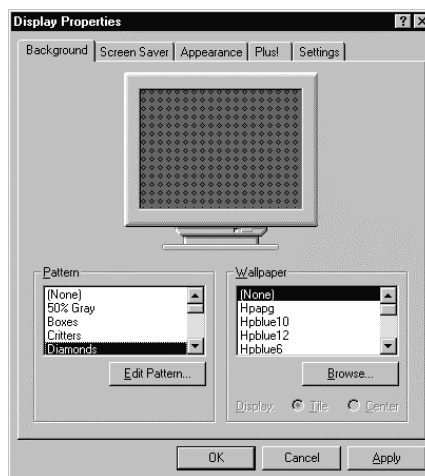


Figure 231

Maintaining the Computer System

Maintaining the Computer System

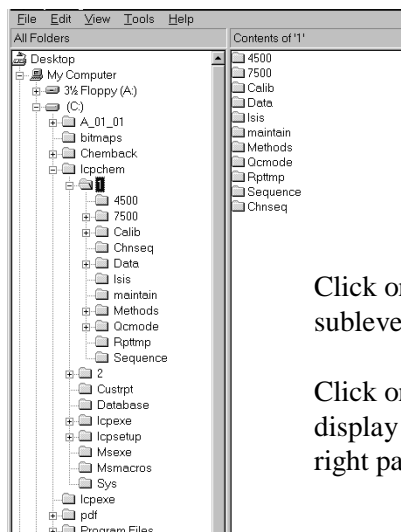
- Delete temporary files on a regular basis
- Use Checkdisk to check for errors on the disk
- Defragment the hard drive using a WinNT utility
- Use Virus detection software
- Create a Windows NT Emergency Repair disk



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.

Figure 233

Directory Structure of the Agilent ChemStation

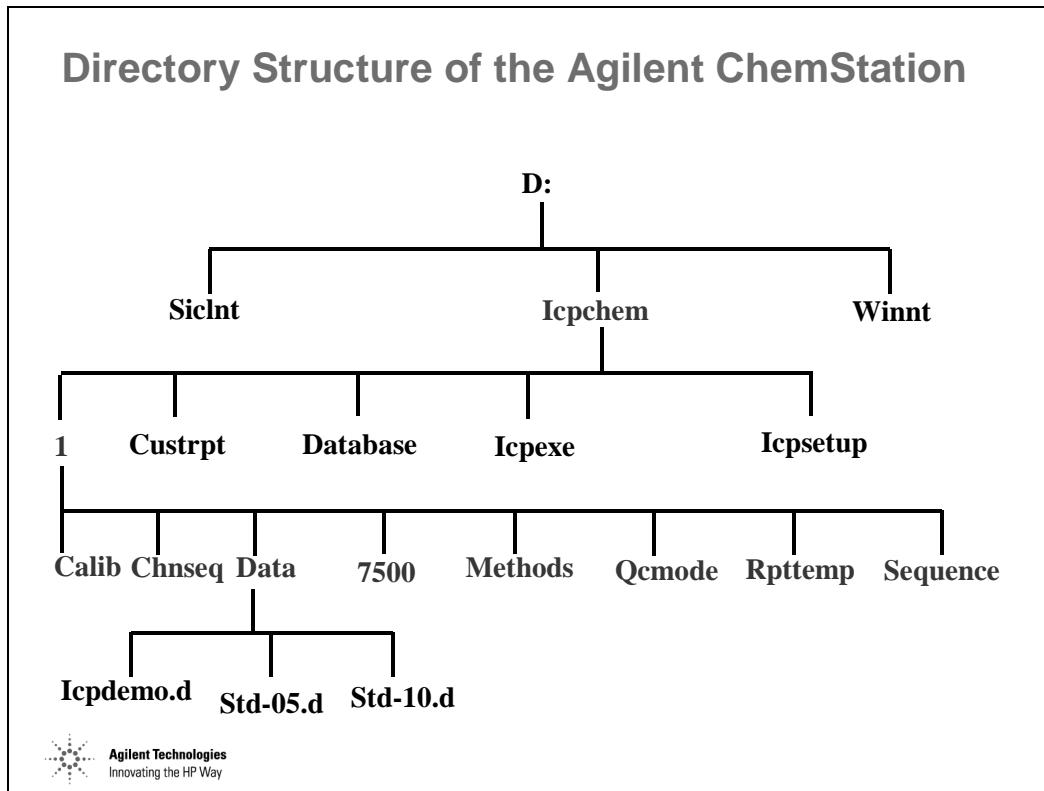


Figure 234

File Naming

File Naming

Files have the form:

<filename>. <extension>

<up to 8 characters> . <up to 3 characters>

Period Separator

Forbidden characters for filenames:

. / \ : <space> [] + ; , ? = * < >



Agilent Technologies
Innovating the HP Way

Figure 235

ChemStation File Extensions

ChemStation File extensions

.d	data "file"	.qcc	QC mode
.m	method "file"	.qct	QC template
.s	sequence file	.fmt	full quant template
.chs	chained sequence	.fqd	database template
.mac	macro file	.u	tune file
.exe	program	.pa	P/A file
.txt	text file	.prm	tune parameters
.db	database		
.log	logfile		



Figure 236



Agilent Technologies
Innovating the HP Way

An Overview of ICP-MS Environmental Applications

Optimizing Agilent 7500 for Environmental Samples Analysis

Optimizing Agilent 7500 for Environmental Samples Analysis

→ Tuning

Match instrument dynamic range to analyte concentration range

- Detune sensitivity, especially low mass
- Dilute samples as necessary (off-line or auto-dilute with ISIS)

→ Minimize Effects of Sample Matrix

- High RF power
- Longer sampling depth ==> longer residence time
- Appropriate use/selection of internal standards
- Appropriate selection of isotopes



Figure 237

Environmental Tuning

Environmental Tuning

Three Steps:

- Initial Setup and Hardware Checkout
- Optimize Physical & Plasma Parameters
- Detune Sensitivity via Ion Lenses



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

Three Goals of Environmental Tuning

Optimize aerosol formation
Maximize analyte exposure to plasma temperature
Minimize matrix exposure to mass spectrometer components



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

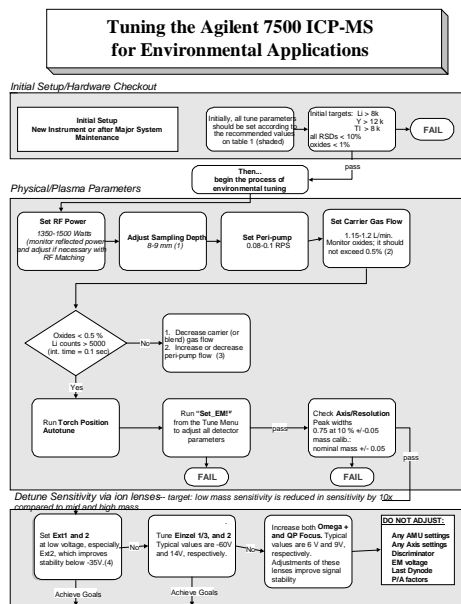


Figure 240

Recommendations on Interference Equations

Recommendations on Interference Equations

Generally Use Equations Specified in EPA Method 200.8

May require slight adjustment based on measured values



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 ^{82}Kr is considered, the equation should be changed as follows:

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

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

$$\begin{aligned} Se(82) &= M(82) - 11.6/11.5 * Kr(83) \\ &= M(82) - 1.0087 * Kr(83) \end{aligned}$$

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

More Interference Corrections

Some correction factors are based on formation of doubly charged species or oxides rather than on isotope ratios and need to be updated periodically.

- Iron-54
- Ca-44



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 HNO₃ should be the same. If the concentration of HNO₃ 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:

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

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

Calibration Standards

Calibration Standards

Calibrate no higher than necessary

Minimize memory effects and the detector wear

- typical ranges for 'trace elements': 0, 1, 10, 100 ppb
- major elements such as Na, K, Ca, Mg, Fe: 0, 100, 1000, 10,000 ppb
- Hg: 0, 0.1, 0.5, 1, 5 ppb

Major and trace elements are available in a single solution with their concentration in 100:1 ratios, respectively

Mercury supplied in a separate solution

Addition of 100 ppb gold to ALL solutions required for mercury determination



Agilent Technologies
Innovating the HP Way

Figure 243

Linear Range Determination

Linear Range Determination

‘Practical Linear Range’

Reasonable upper range of analyte concentrations after sample dilution to avoid excessive carryover after running LRS

Typically:

- ~1 ppm for most elements,
- 10-50 ppm for ‘minerals’,
- < 500 ppb for Ag, Mo, Sb, Tl, Pb and other memory prone elements,
- < 20 ppb for Hg!

Much lower than actual **Instrument Linear Range**



Figure 244

Interference Check Samples

Interference Check Samples

Purpose is to test effectiveness of plasma conditions and correction equations:

High concentrations of 'Interfering Elements'
Trace concentrations (~20 ppb) of analyte elements
Only the analyte elements need be measured



Figure 245

Troubleshooting Environmental Applications [1]

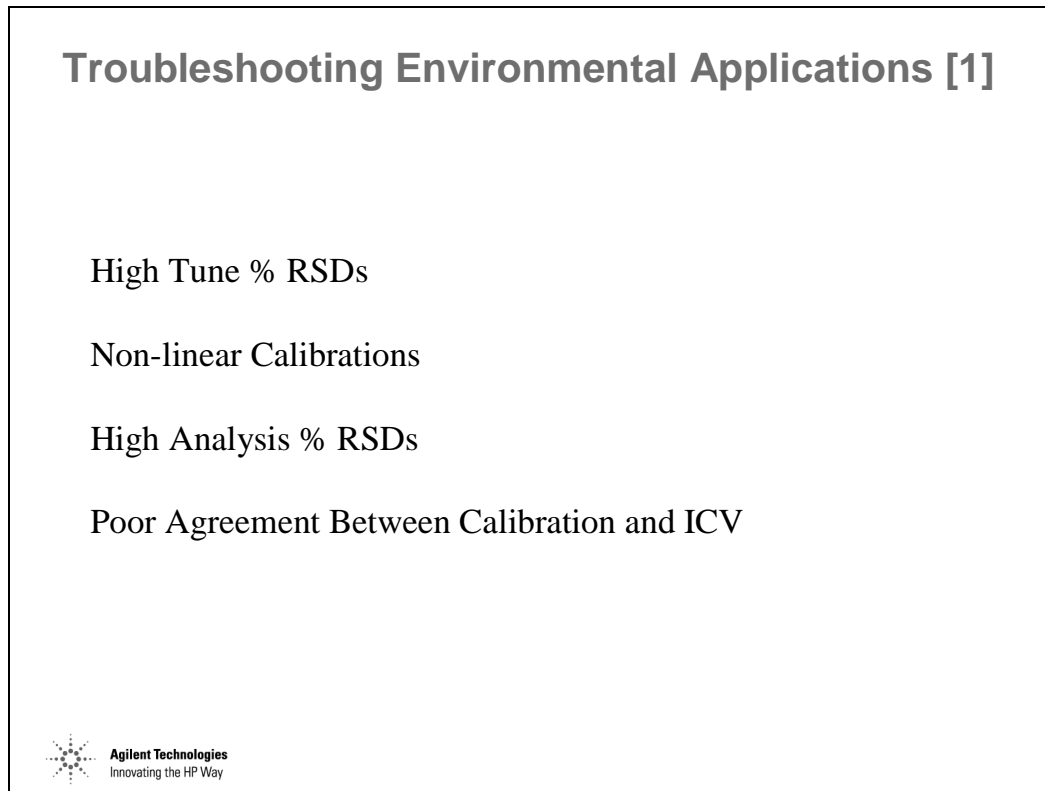


Figure 246

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]

Troubleshooting Environmental Applications [2]

Poor Analyte Recovery in Spiked Samples for Selected Analytes

Carry-over or Memory Effects for Certain Elements



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% HNO₃) will help. If

Troubleshooting Environmental Applications [2]

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]

Troubleshooting Environmental Applications [3]

Calibration Drift Over Time

Poor Internal Standard Recoveries in Certain Samples



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]

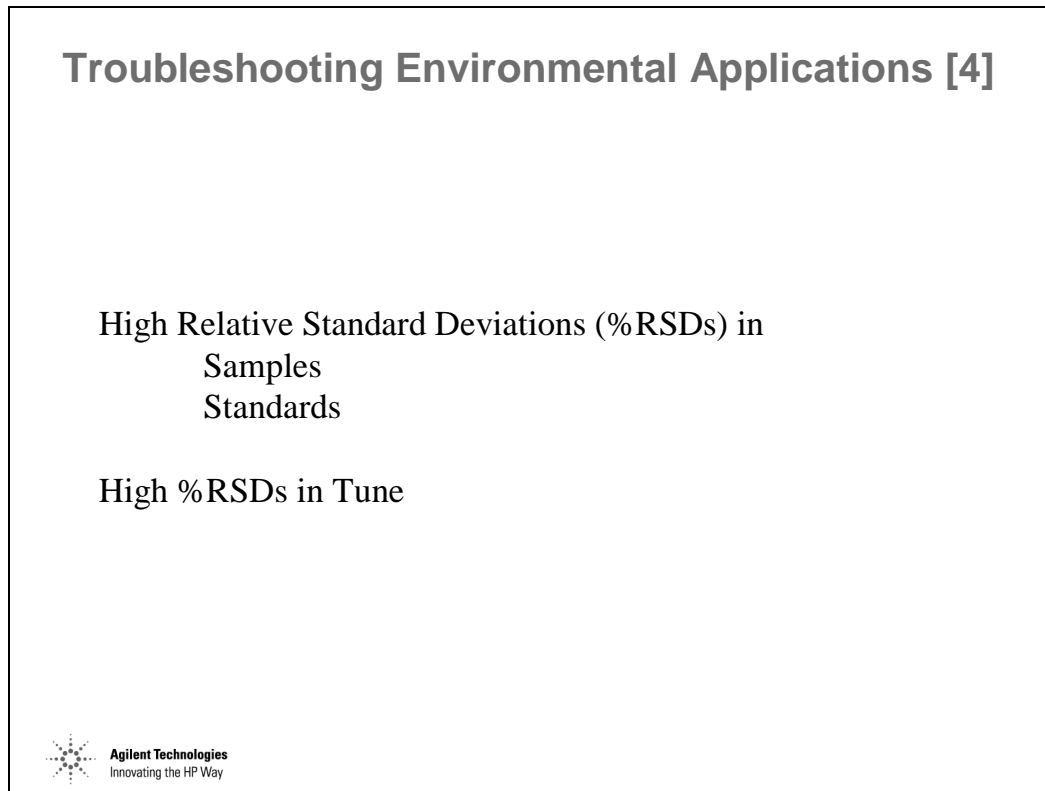


Figure 249

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

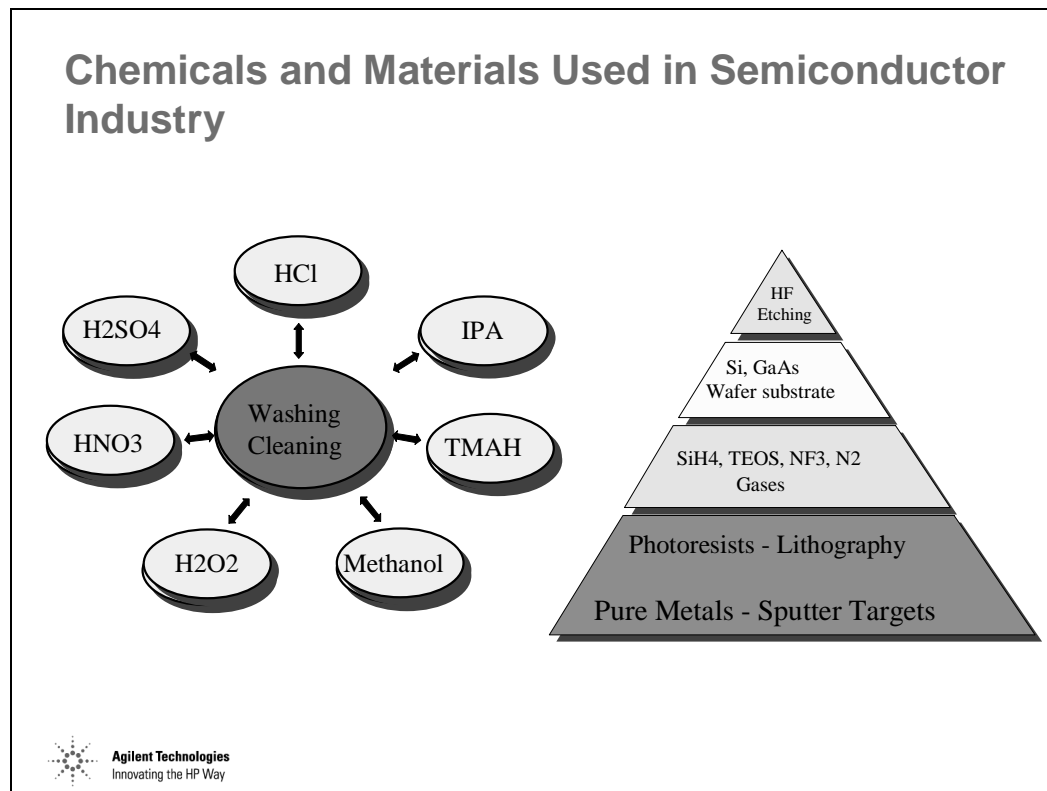


Figure 250

BPSG = boron phosphorus silicon glass used for doping.

TEOS = tetra ethoxy silane (used for depositing SiO₂ 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

Metals Analysis in the Semiconductor Industry - Customer Groups and Requirements

- Chemical manufacturers
 - need for QC analysis of products
 - inorganic chemicals
 - organic chemicals
- Wafer manufacturers
 - characterize bulk polysilicon
 - monitor contamination control in wet stations
 - analysis of chemicals and various mixes
 - wafer surface characterization
- Device manufacturers
 - monitor contamination control in wet stations
 - analysis of chemicals and various mixes
 - photoresist/stripper analysis



Figure 251

ShieldTorch Interface

ShieldTorch Interface

- Developed by HP/Yokogawa in 1992
 - led to widespread use of "cool" plasmas
- Prevents secondary discharge in the ICP-MS interface
 - virtually eliminates many polyatomic interferences
 - Shield plate design assures complete discharge removal
- Enables the determination of Fe, Ca and K at low ppt levels
 - 3 orders of magnitude improvement in detection limits
- Improved DLs for most other SEMI elements
 - dramatically reduced interface background
 - **sub-ppt DLs for Na**
- Operates at higher power levels - up to 1100W
 - other systems must be operated at 500-600W
- No consumables
 - Shield plate lasts indefinitely - *never has to be removed*



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

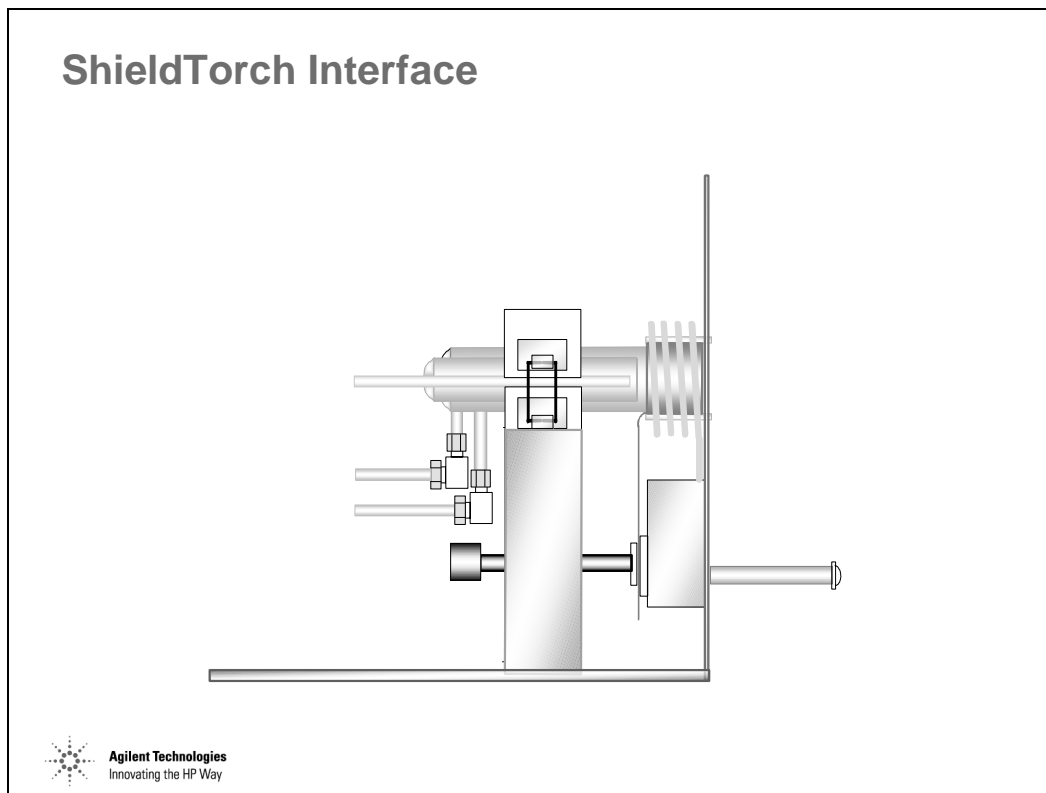


Figure 253

Normal and “Cool” Plasmas

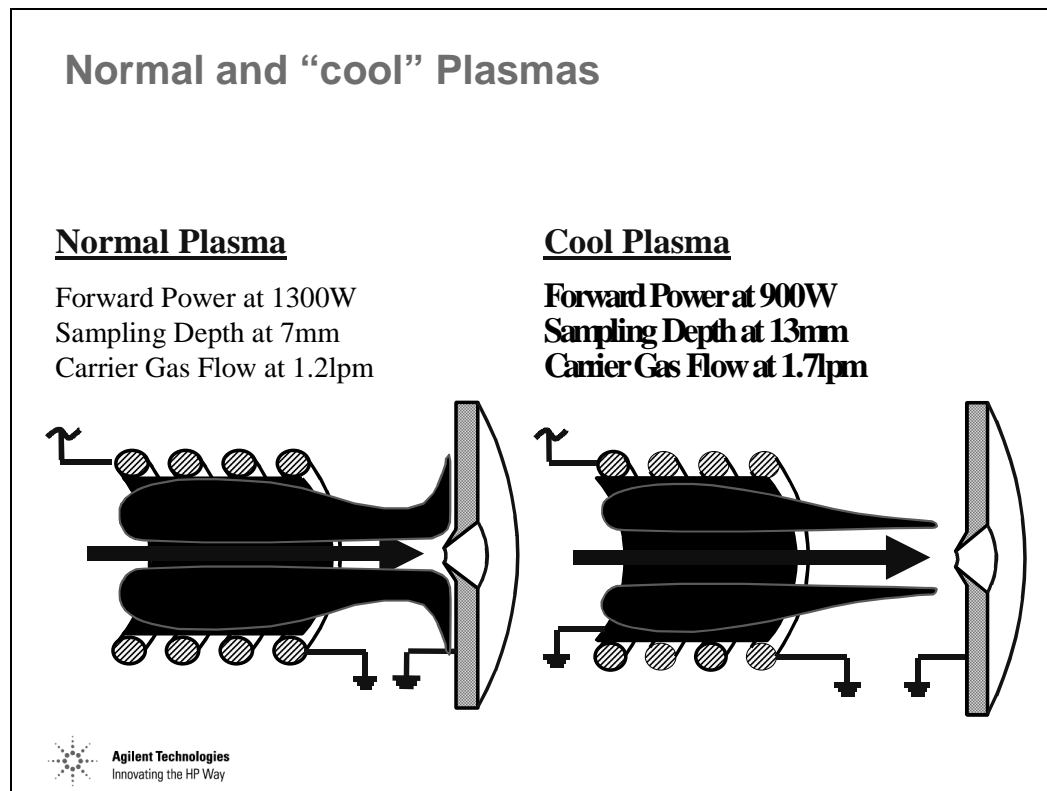


Figure 254

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”

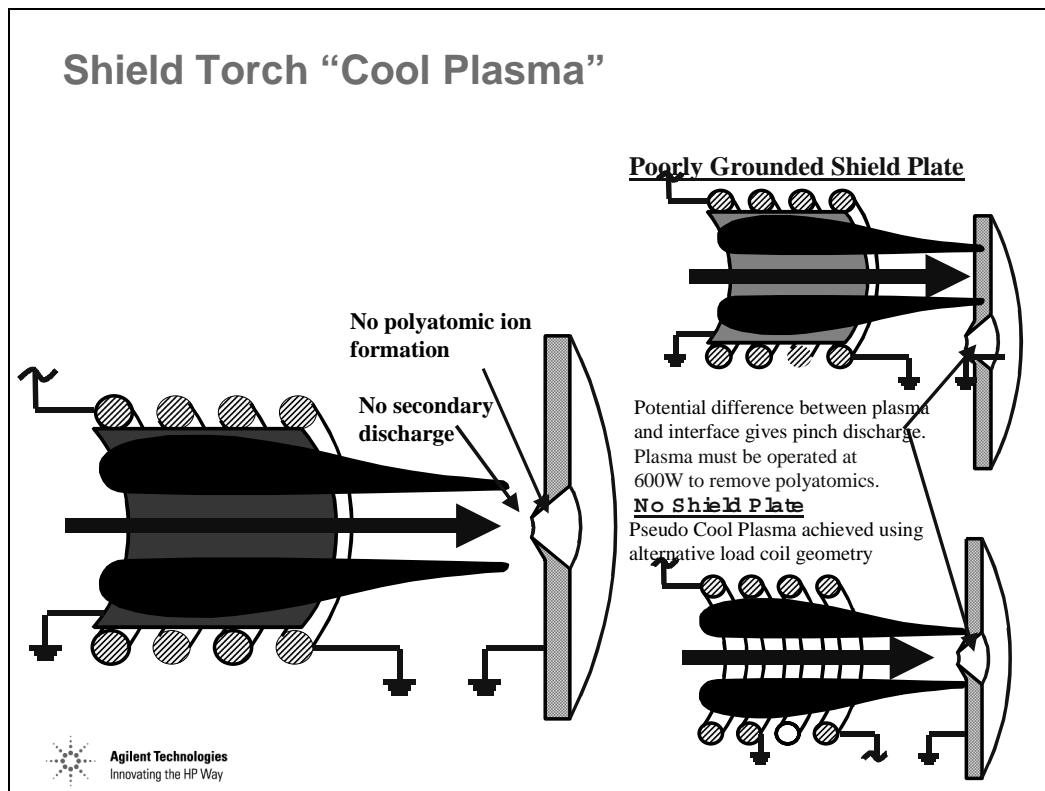


Figure 255

Shield Torch Installation

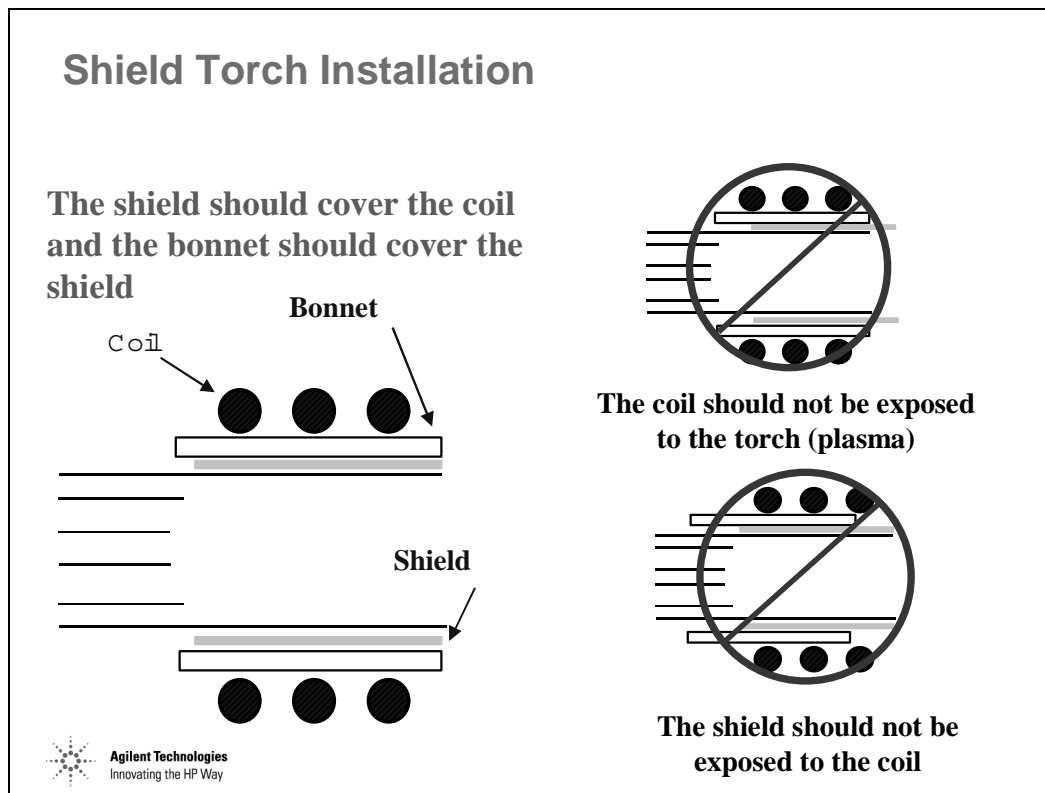


Figure 256

Cool Plasma Tuning

Cool Plasma Tuning

- Reduce RF Power to 900W
- Increase blend gas to 0.5L/min
- Increase sampling depth to 13mm
- Minimize the ArO using x,y torch position
- Minimize the ArH using the sampling depth
- Optimize using the blend gas



Figure 257

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

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

- No loss of sensitivity compared to normal plasma conditions
 - Li - 150 Mcps/ppm
 - Fe - 40 Mcps/ppm
- Higher ionizing power - greatly expanded analyte range
 - many analytical requirements can be performed in one run
- Ability to analyze high matrix samples
 - organics, including Photoresists
 - H_3PO_4
 - Si matrices
- Meet/exceed HR-ICP-MS performance with new applications
 - ppt determination of As and V in 5% HCl
 - low ppt determination of Cr, Mg in organics



Figure 258

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

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

- Minimal loss of sensitivity compared to "hotter" plasma conditions
 - Li -100 Mcps/ppm
 - Fe - 20 Mcps/ppm
- Greatly improves the BEC for Ca, Fe and K
 - Specially for the analysis of DI Water, H₂O₂, and diluted acids



Figure 259

Detection Limits Study [1]

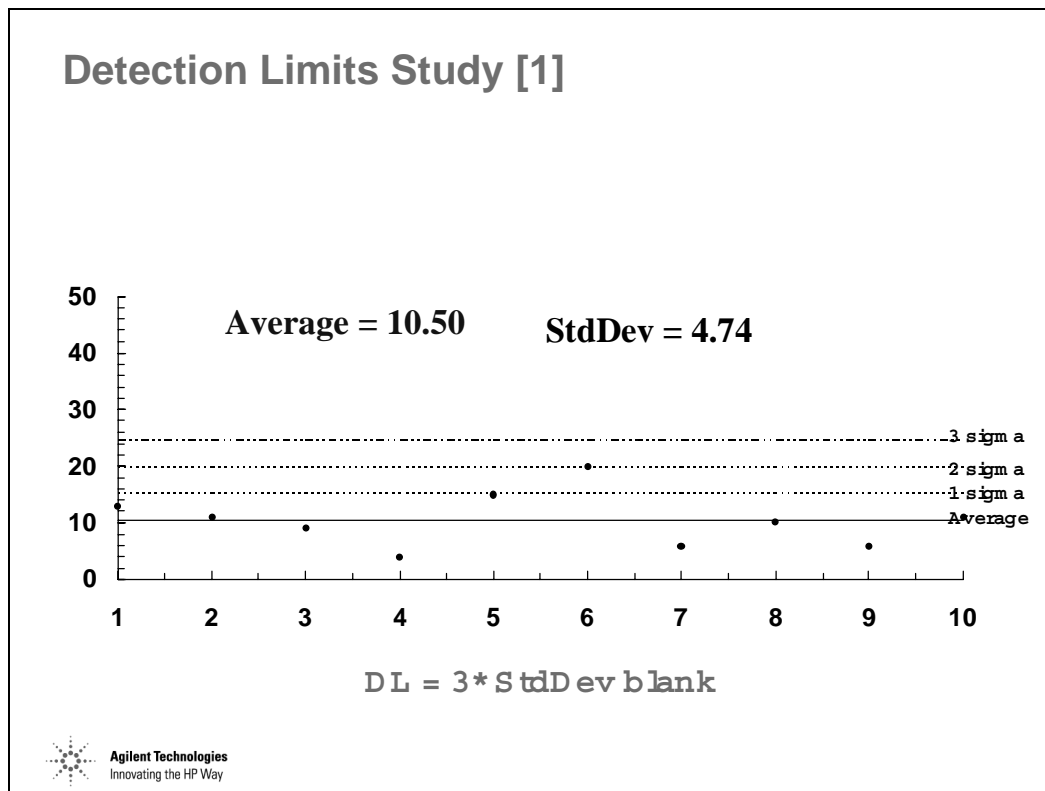


Figure 260

Detection Limits Study [2]

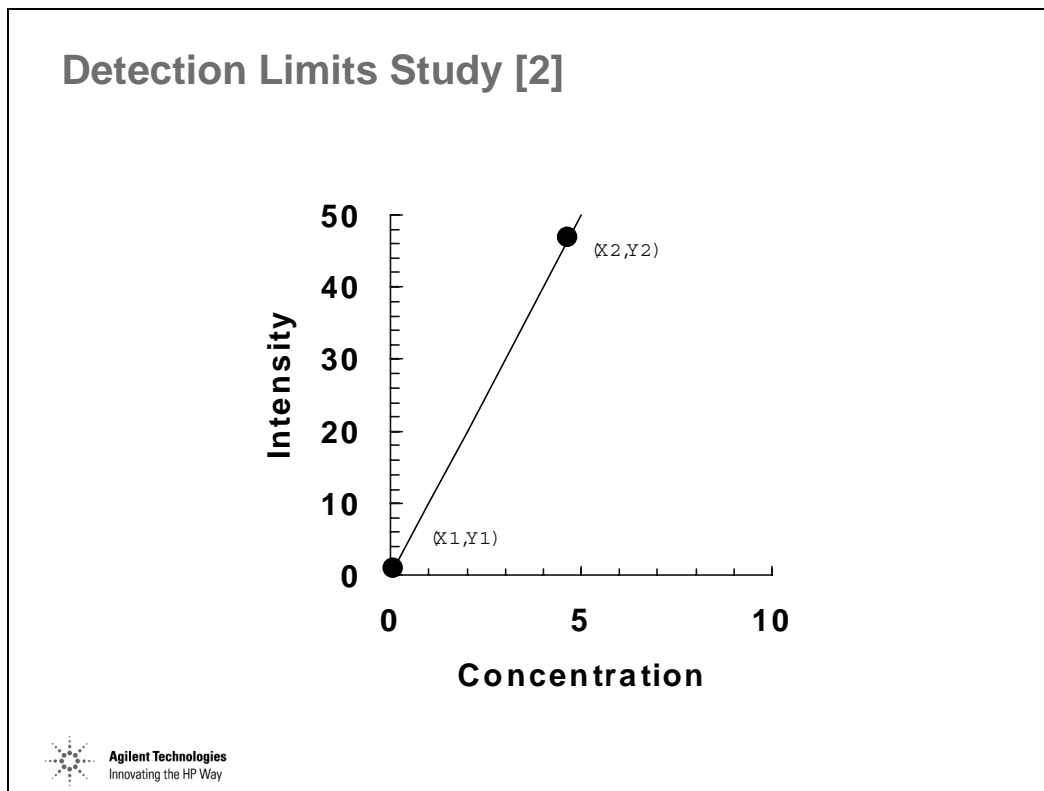


Figure 261

Automatic Switching Between Normal and Cool Plasma

Automatic Switching Between Normal and Cool Plasma

Chained Sequencing allows the user to run a set of samples under one set of conditions such as cool plasma, then automatically switch the conditions and rerun the same samples under hot plasma.

Multitune Mode allows the user to run the same sample under multiple sets of conditions, automatically switching from one mode to another and then moving to the next sample



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.

ICP-MS Configuration

☐ Offline Instrument

HP-IB

ICP-MS Address: 20

Remote Start

☒ Don't Use

☐ Wait until Ready Signal

Sample Introduction

Type: Peristaltic Pump Setup...

Autosampler: ASX500 Setup...

EM Protection

☒ Auto setting of integ time in analog mode

Prohibited Masses

14

16

17

18

19

32

36

38

40

41

QC Mode

Mode: 6020.QCC Browse... Advanced...

Reset to Default Save Cancel Help

The following QC modes are provided as default.

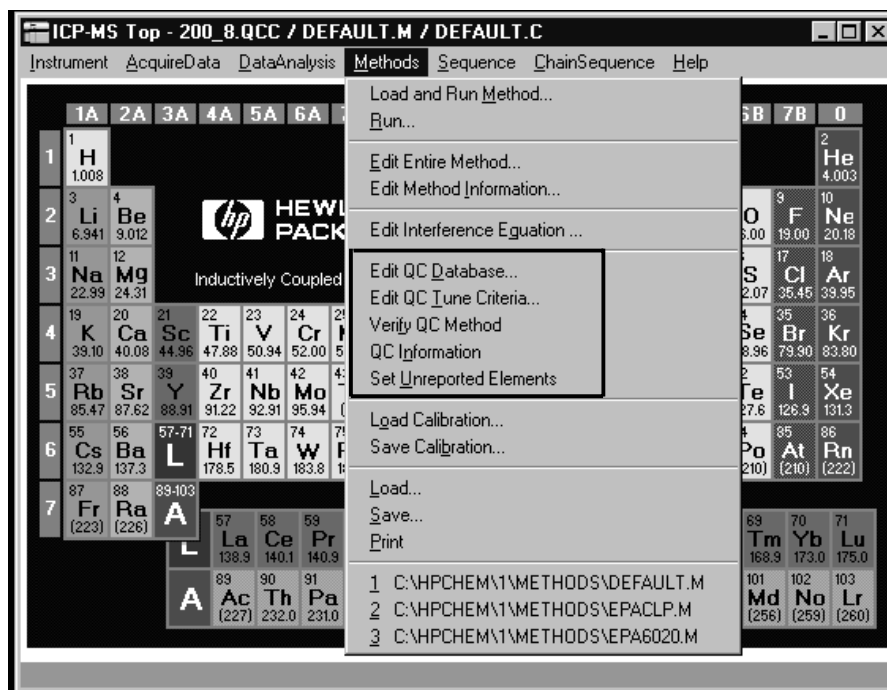
- EPA2008.QCC --- intelligent functions defined by EPA Method 200.8.
- EPA6020.QCC --- intelligent functions defined by EPA Method 6020.
- EPA6020C.QCC --- intelligent functions defined by EPA Method 6020 CLP.
- EPAGEN.QCC --- Intelligent functions designed to meet both EPA 200.8 and 6020 requirements
- 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

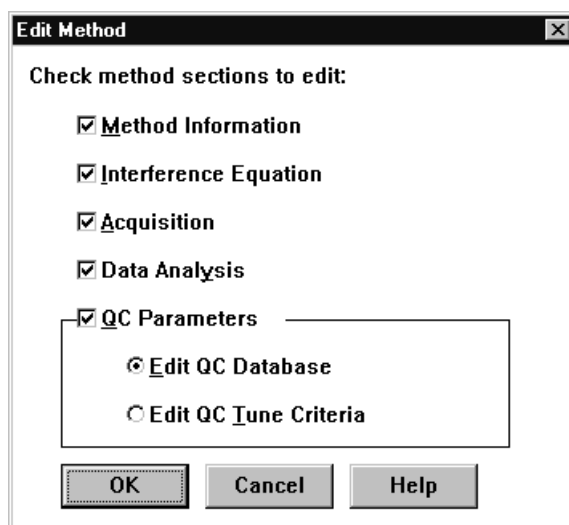
Intelligent Sequence Training Text

Using Intelligent Sequencing

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

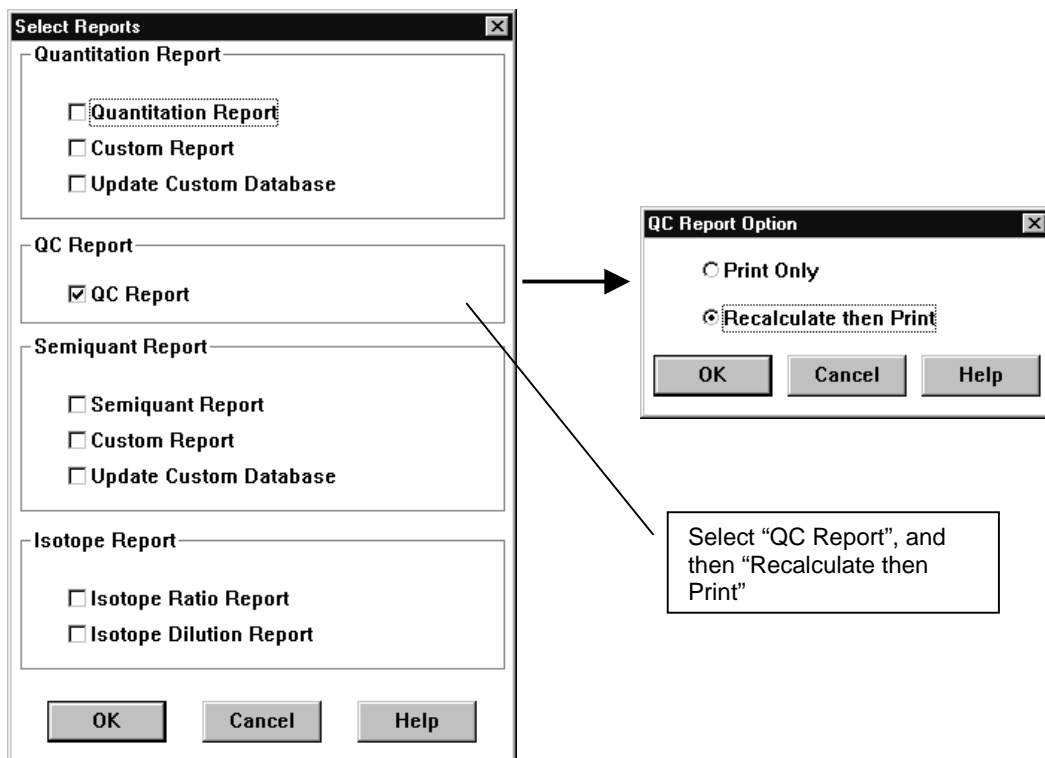
Edit Entire Method

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

Intelligent Sequence Training Text Using Intelligent Sequencing

(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”.

QC Database settings are saved in **cal file**

Elements referred from cal curve

Comparative expressions defined in QC configuration

Sample type opened currently

	Element	Off	Exp. Value	Low Lmt	High Lmt	Exp. Value	Low Lmt	High Lmt	Exp. Value	Low Lmt	High Lmt	Exp. Value	Low Lmt	High Lmt
19	66 Zn		50	0.9	1.1									
20	67 Zn		50	0.9	1.1									
21	68 Zn		50	0.9	1.1									
22	75 As		50	0.9	1.1									
23	76 Se		50	0.9	1.1									
24	77 (As)	X	50	0.9	1.1									
25	82 Se		50	0.9	1.1									
26	83 (Se)	X	50	0.9	1.1									

Expected Value and Low & High Limits

Error Actions and #Allowed Failures

Action on QC Failure1: NextSmpl

Action on QC Failure2: NextSmpl

#Allowed QC Failure: 0

Action on ISTD Failure: NextSmpl

#Allowed ISTD Failure: 0

Auto Configuration Print... OK Cancel Help

Click here

Off(x) is marked for the elements for which Excluded is selected as a curve fit in cal, or used for interference correction

<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).

Area for 1st step Criteria 1

Area for 1st step Criteria 2

Area for 2nd step Criteria 1

Area for 2nd step Criteria 2

Element	Off	Exp. Value	Low Lmt	High Lmt
1	0			
2	23			
3	24			
4	27			
5	39			
6	43			
7	51			
8	52			

Element	Off	Exp. Value	Low Lmt	High Lmt
1	0			
2	23			
3	24			
4	27			
5	39			
6	43			
7	51			
8	52			

Action on QC Failure1: NextSmpl

Action on QC Failure2: NextSmpl

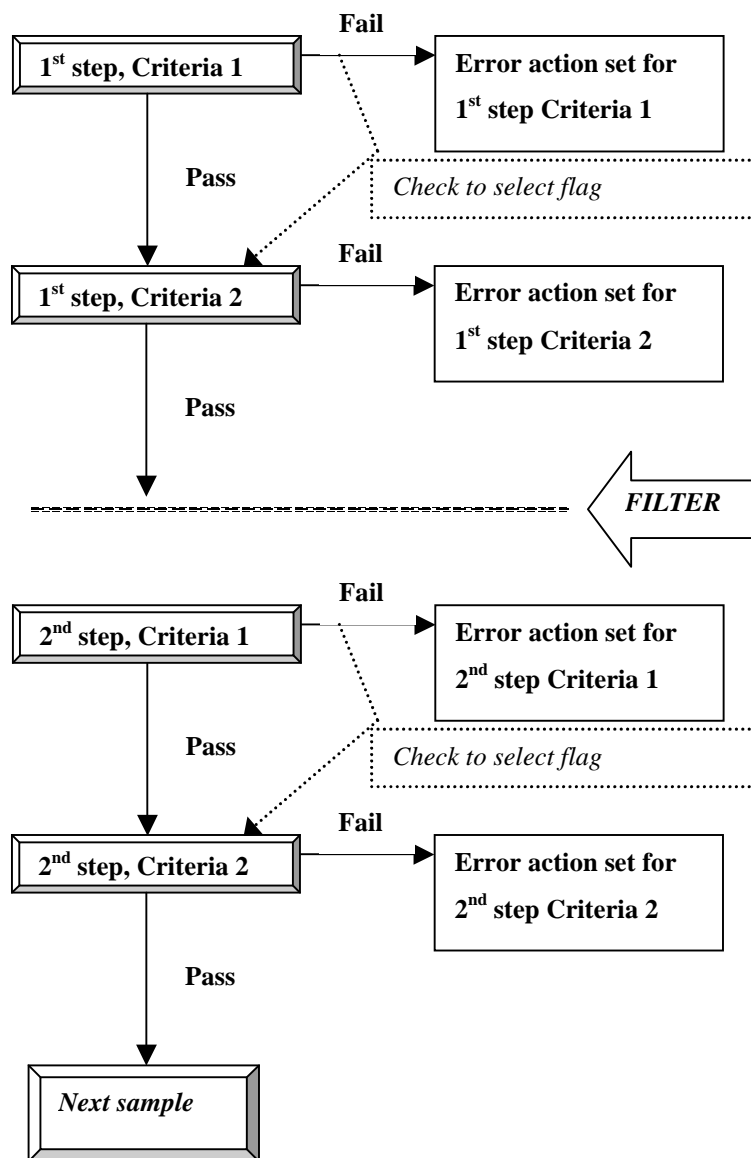
#Allowed QC Failure: 0

Action on ISTD Failure: NextSmpl

Action on ISTD Failure2: NextSmpl

Buttons: Auto Configuration, Print..., OK, Cancel, Help

Intelligent Sequence Training Text
Using Intelligent Sequencing



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 $\geq 0.9 \times$ CRM expected values

High limit: CRM conc $\leq 1.1 \times$ 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 \geq 1000

High limit: none

2nd step Criteria 1

Low limit: CRM conc \geq 0.9 x CRM expected values

High limit: CRM conc \leq 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 \geq 0.85 x CRM expected values

High limit: CRM conc \leq 1.15 x CRM expected values

1st step Criteria 2

Low limit: CRM conc \geq 0.9 x CRM expected values

High limit: CRM conc \leq 1.1 x CRM expected values

Intelligent Sequence Training Text Using Intelligent Sequencing

(B) QC Tune Criteria

QC Tune Criteria settings are saved in **method file**

Masses set in data acq parameters

Set "Ref" for Response Ratio check ^{*1}

Fixed to 1 for Resp Ratio Low&High Limits

Set "Bkg" for Bkg check ^{*2}

Only Max. Bkg Count is effective

	Element	Mode	Mass Cal Low Lmt (amu)	Mass Cal High Lmt (amu)	Conc (ug/l)	Min.Resp (cps/ug/l)	Resp Ratio Low Lmt	Resp Ratio High Lmt	Max. Bkg Count (cps)	Max. Width (amu)	Max. %RSD
1	6	Ignore									
2	7 Li	General	6.92	7.12	100.0000	20.0	0.2000	1.0000		0.90	5.0000
3	8	Ignore									
4	58	Ignore									
5	59 Co	Ref	58.83	59.03	100.0000	200.0	1.0000	1.0000		0.90	5.0000
6	60	Ignore									
7	101	Ignore									
8	102	Bkg.							25.0		
9	103	Ignore									
10	114	Ignore									
11	115 In	General	114.80	115.00	100.0000	100.0	0.7500	2.0000		0.90	5.0000
12	116	Ignore									
13	204	Ignore									
14	205 Tl	General	204.87	205.07	100.0000	10.0	0.5000	1.2000		0.90	5.0000
15	206	Ignore									

*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

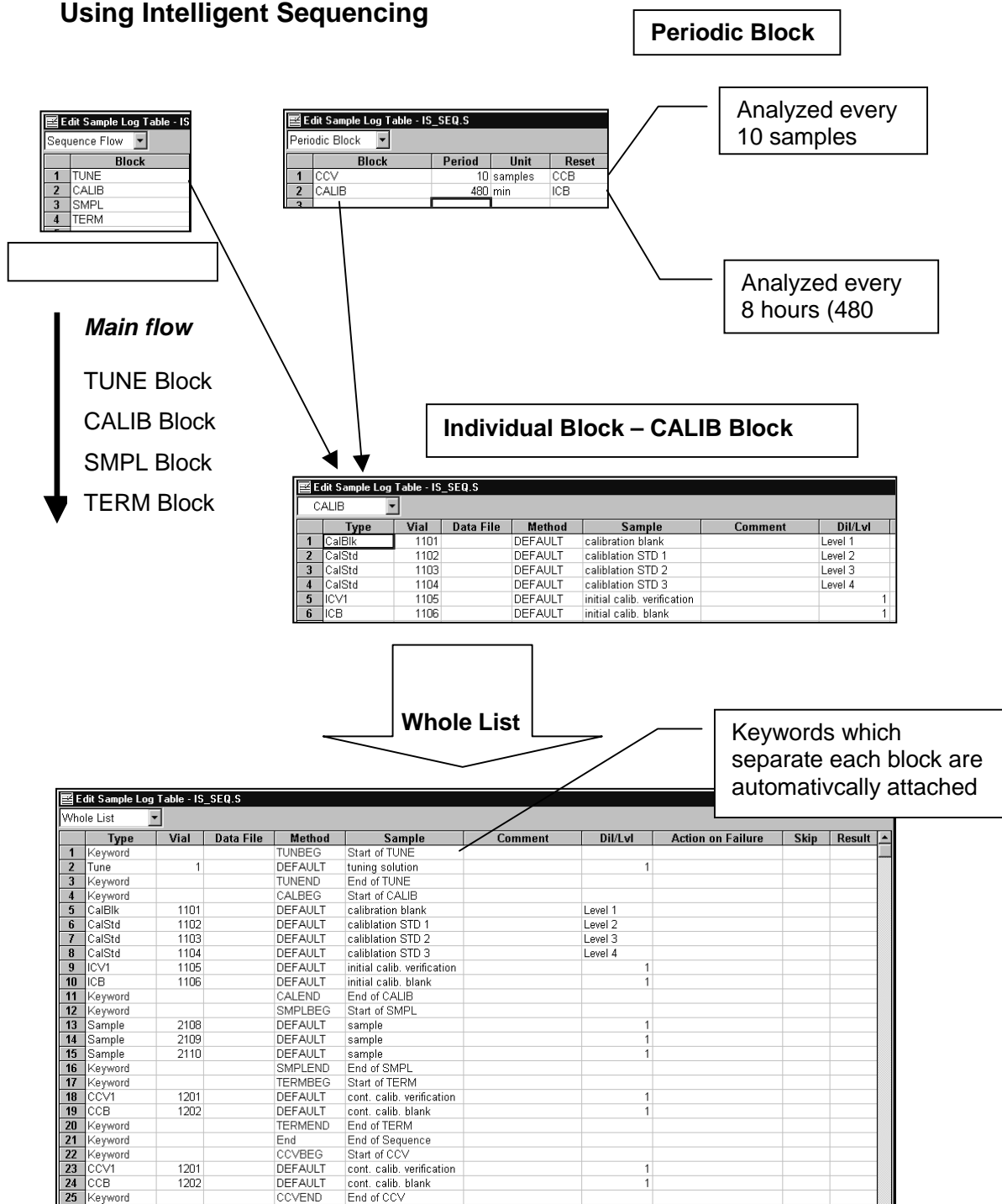
Structure of Sample Log Table

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

Intelligent Sequence Training Text Using Intelligent Sequencing



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

Start Sequence DEFAULT.S Last Modified: Tue Jan 27 10:24:38 1998

Method Sections To Run

☒ Full Method

☐ Reprocessing Only

☒ Overwrite Existing Data Files

Sequence Comment: _____

Operator Name: _____

Data Batch Directory: C:\hpcchem\1\DATA\98G2317a.B\ Browse

Pre-Seq Macro/Cmd: _____

Post-Seq Macro/Cmd: _____

Run Sequence OK Cancel Help

The methods & calibrations used, actual sample log table and sequence logs as well as all the data in one sequence are saved in this directory.

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.

Intelligent Sequence Training Text

Using Intelligent Sequencing

- 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*.

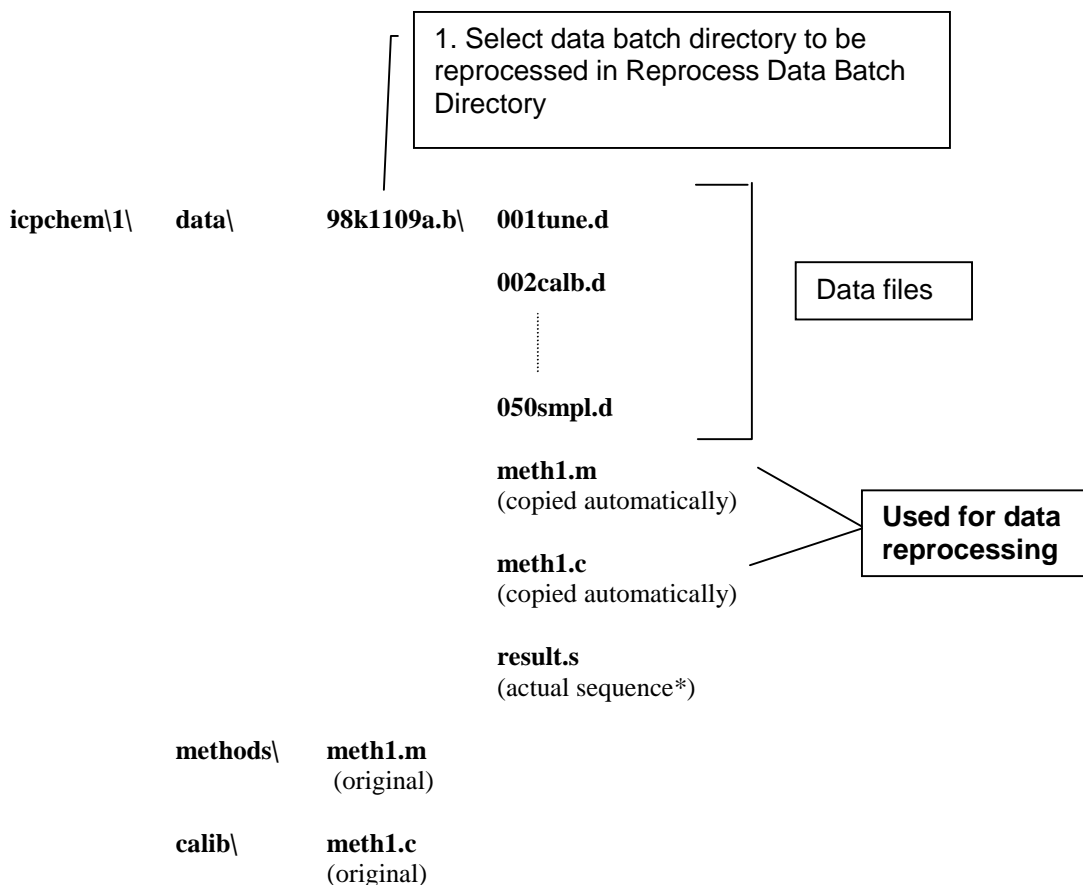
Sequence Reprocessing of Data

Two ways for batch reprocessing of data:

- A. Reprocessing Data Batch Directory
- B. Running a Sequence with Reprocessing Only

(A) *Reprocess Data Batch Directory*

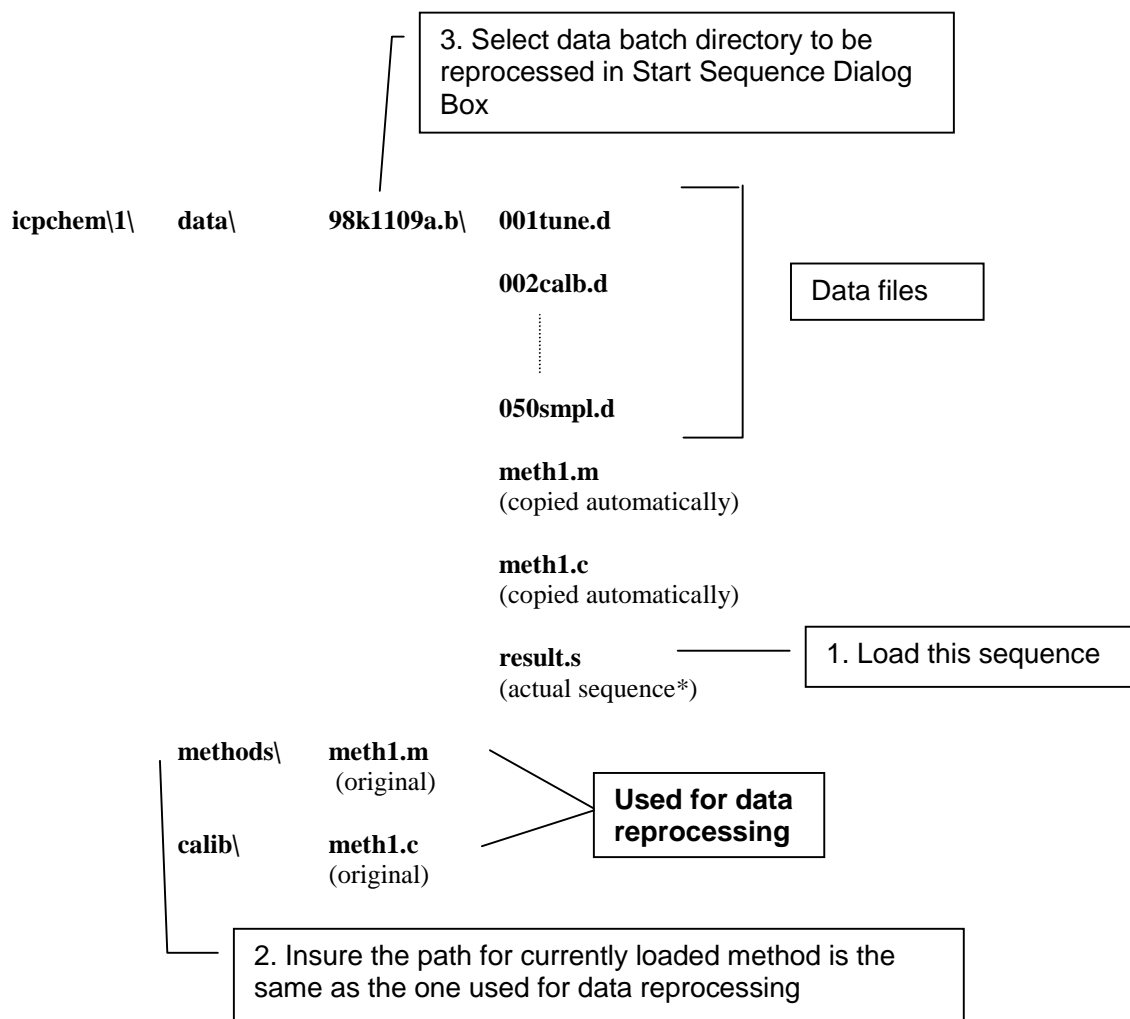
<Files to be selected and used>



- 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

Intelligent Sequence Training Text
Using Intelligent Sequencing

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...

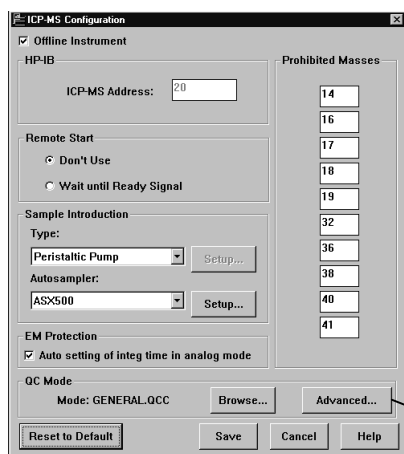
- Sample type name
- Data name suffix
- QC report template
- Type category
- QC Item name to be used for ISTD check
- Error counting way
- Action on 3rd failure
- Comparative expressions
- Error flags for QC report

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.

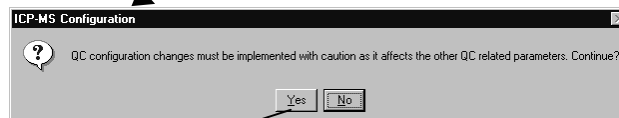
Intelligent Sequence Training Text

Setting Up a QC Configuration

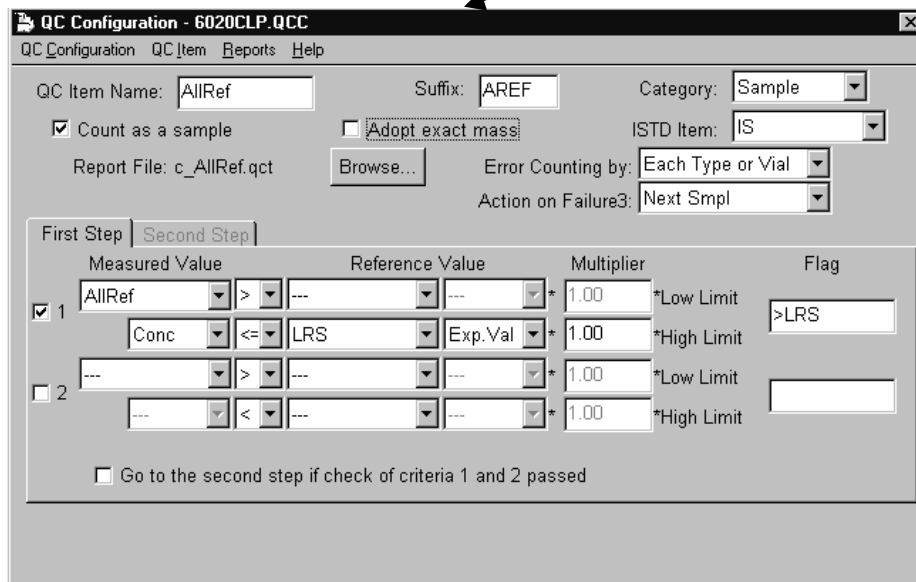
Configuring QC Items



ICP-MS Configuration dialog box. It includes sections for Offline Instrument, Remote Start, Sample Introduction, EM Protection, and QC Mode. The QC Mode section shows 'Mode: GENERAL.QCC' and buttons for 'Browse...', 'Advanced...', 'Reset to Default', 'Save', 'Cancel', and 'Help'.



Warning dialog box: "QC configuration changes must be implemented with caution as it affects the other QC related parameters. Continue?" with 'Yes' and 'No' buttons.

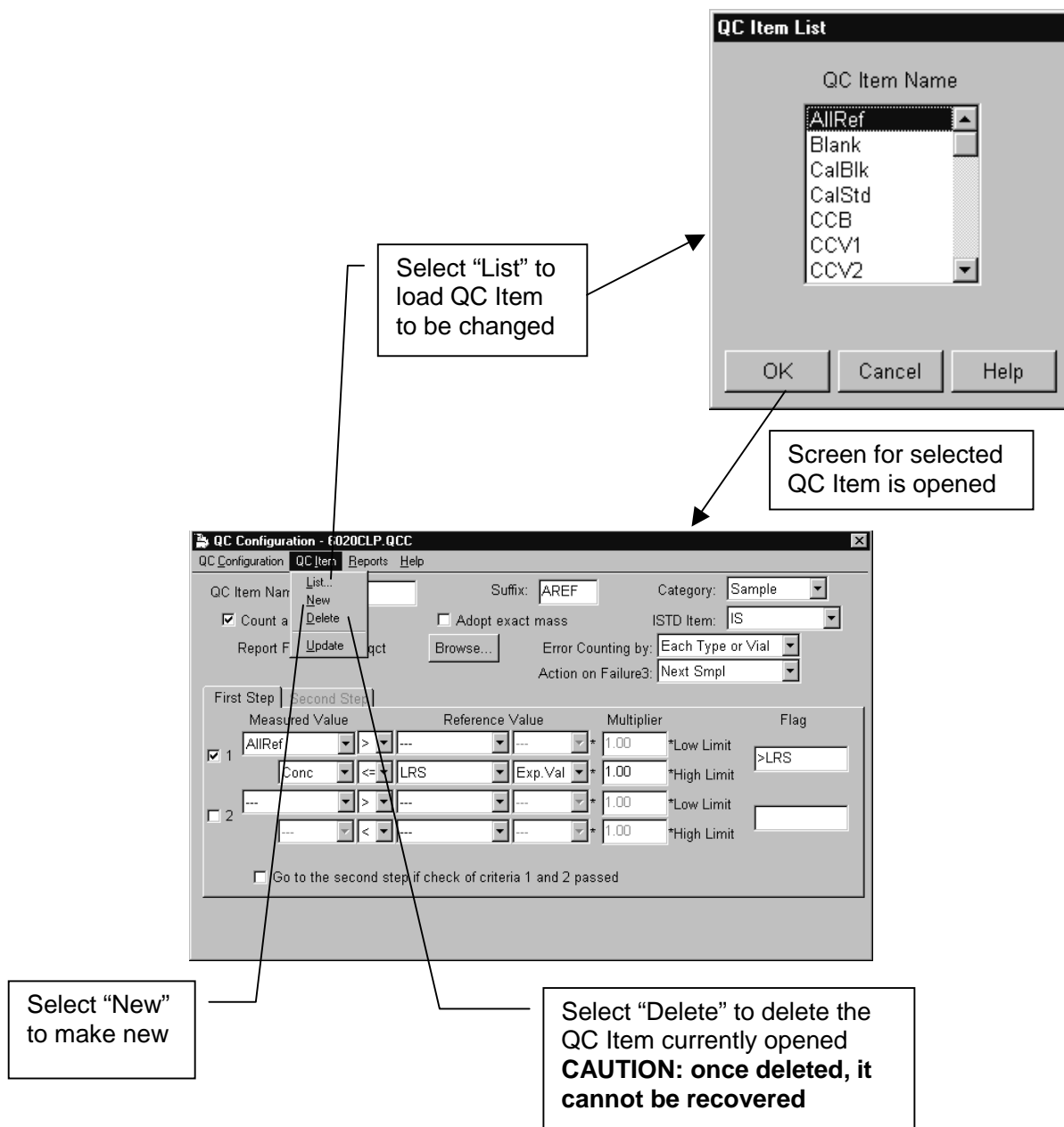


QC Configuration - 6020CLP.QCC dialog box. It includes fields for QC Item Name, Suffix, Category, and ISTD Item. It also has checkboxes for 'Count as a sample' and 'Adopt exact mass'. The 'First Step' tab is active, showing a table for Measured Value, Reference Value, Multiplier, and Flag.

	Measured Value	Reference Value	Multiplier	Flag
1	AllRef	>	---	*Low Limit
	Conc	<=	LRS	*High Limit
2	---	>	---	*Low Limit
	---	<	---	*High Limit

☐ Go to the second step if check of criteria 1 and 2 passed

How to Create or Change a QC Item



Intelligent Sequence Training Text

Setting Up a QC Configuration

Special Screens

QC Configuration - 6020CLP.QCC

QC Configuration QC Item Reports Help

QC Item Name: AllRef Suffix: AREF Category: Sample

☒ Count as a sample ☐ Adopt exact mass

Report File: c:\AllRef.qct Browse...

Error Counting by: Each Type

Action on Failure3: Next Smpl

ISTD Item: Sample

First Step Second Step

	Measured Value	Reference Value	Multiplier	Low Limit	High Limit
1	AllRef	LRS	1.00	>LRS	
2			1.00		

☐ Go to the second step if check of criteria 1 and 2 passed

Screen is completely changed

QC Configuration - 6020CLP.QCC

QC Configuration QC Item Reports Help

QC Item Name: AllRef Suffix: AREF Category: Exp.Val

☐ Count as a sample ☐ Adopt exact mass

Report File: --- Browse...

Error Counting by: Each Type or Vial

Action on Failure3: Next Smpl

ISTD Item: ---

First Step Second Step

	Measured Value	Reference Value	Multiplier	Flag
1			1.00	*Low Limit
2			1.00	*High Limit

Only QC Item becomes effective

QC Configuration - 6020CLP.QCC

QC Configuration QC Item Reports Help

QC Item Name: AllRef Suffix: AREF Category: Tune

☐ Count as a sample ☐ Adopt exact mass

Report File: --- Browse...

Error Counting by: Each Type or Vial

Action on Failure3: Next Smpl

ISTD Item: ---

First Step Second Step

	Flag
<input type="checkbox"/> Mass Calibration	
<input type="checkbox"/> Min. Response	
<input type="checkbox"/> Response Ratio	
<input type="checkbox"/> Mass Resolution	
<input type="checkbox"/> RSD	
<input type="checkbox"/> Max. Bkg Count	

% of Height: 1 %

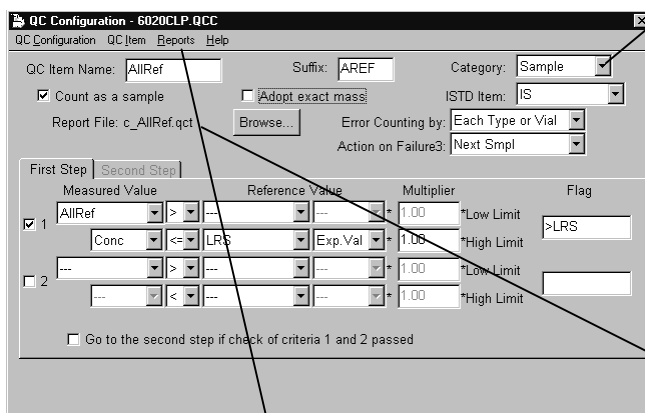
Notes on Setting QC Items

- 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.

Intelligent Sequence Training Text

Setting Up a QC Configuration

Creating a QC Report Template



QC Configuration - 6020CLP.QCC

QC Configuration QC Item Reports Help

QC Item Name: AllRef Suffix: AREF Category: Sample

☒ Count as a sample ☐ Adopt exact mass ISTD Item: IS

Report File: c:\AllRef.qct Browse... Error Counting by: Each Type or Vial

Action on Failure3: Next Smpl

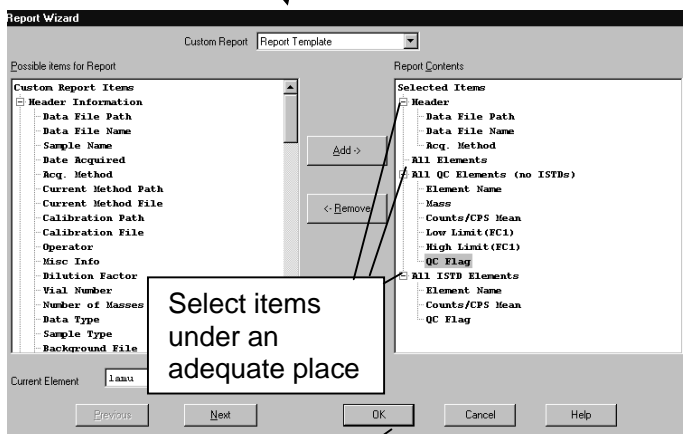
First Step Second Step

	Measured Value	Reference Value	Multiplier	Flag
<input checked="" type="checkbox"/> 1	AllRef >	LRS	1.00	*Low Limit
	Conc <=	Exp.Val	1.00	*High Limit
<input type="checkbox"/> 2			1.00	*Low Limit
			1.00	*High Limit

☐ Go to the second step if check of criteria 1 and 2 passed

Select QC Item whose category is Tune to edit QC report template for Tune sample

When Report File is not selected



Report Wizard

Custom Report Report Template

Possible Items for Report

Custom Report Items

- Header Information
 - Data File Path
 - Data File Name
 - Sample Name
 - Date Acquired
 - Acq. Method
 - Current Method Path
 - Current Method File
 - Calibration Path
 - Calibration File
 - Operator
 - Misc Info
 - Dilution Factor
 - Vial Number
 - Number of Masses
 - Data Type
 - Sample Type
 - Background File

Report Contents

Selected Items

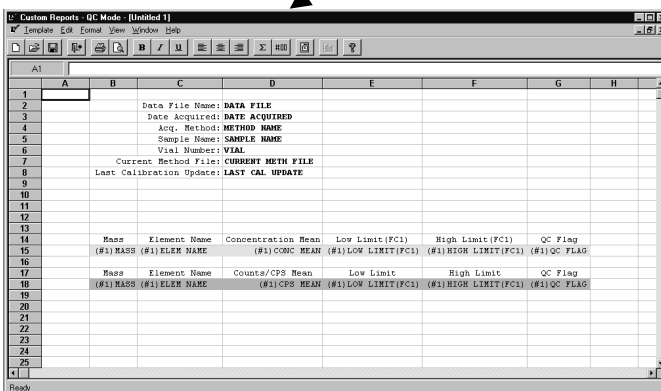
- Header
 - Data File Path
 - Data File Name
 - Acq. Method
- All Elements (no ISTDs)
 - Element Name
 - Mass
 - Counts/CPS Mean
 - Low Limit (FC1)
 - High Limit (FC1)
 - QC Flag
- All ISTD Elements
 - Element Name
 - Counts/CPS Mean
 - QC Flag

Current Element: 1amu

Previous Next OK Cancel Help

Select items under an adequate place

When Report File is selected



Custom Reports - QC Mode - [Untitled 1]

	A	B	C	D	E	F	G	H
1								
2								
3			Data File Name: DATA FILE					
4			Date Acquired: DATE ACQUIRED					
5			Acq. Method: METHOD NAME					
6			Sample Name: SAMPLE NAME					
7			Vial Number: VIAL					
8			Current Method File: CURRENT METH FILE					
9			Last Calibration Update: LAST CAL UPDATE					
10								
11								
12								
13								
14		Mass	Element Name	Concentration Mean	Low Limit (FC1)	High Limit (FC1)	QC Flag	
15		(#1) MASS	(#1) ELEM NAME	(#1) CONC MEAN	(#1) LOW LIMIT (FC1)	(#1) HIGH LIMIT (FC1)	(#1) QC FLAG	
16								
17		Mass	Element Name	Counts/CPS Mean	Low Limit	High Limit	QC Flag	
18		(#1) MASS	(#1) ELEM NAME	(#1) CPS MEAN	(#1) LOW LIMIT (FC1)	(#1) HIGH LIMIT (FC1)	(#1) QC FLAG	
19								
20								
21								
22								
23								
24								
25								

Ready

Notes on Editing QC Report Template

The very right cell which contains values is recognized as the right end of the printed area

Repeated width should be the same for each area

Concentration Mean

Dilution Factor

Equation using the reference place

- 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 **Concentration Mean** multiplied by **Dilution Factor** using the reference place.

Intelligent Sequence Training Text

Setting Up a QC Configuration

- 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.



Agilent Technologies
Innovating the HP Way

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

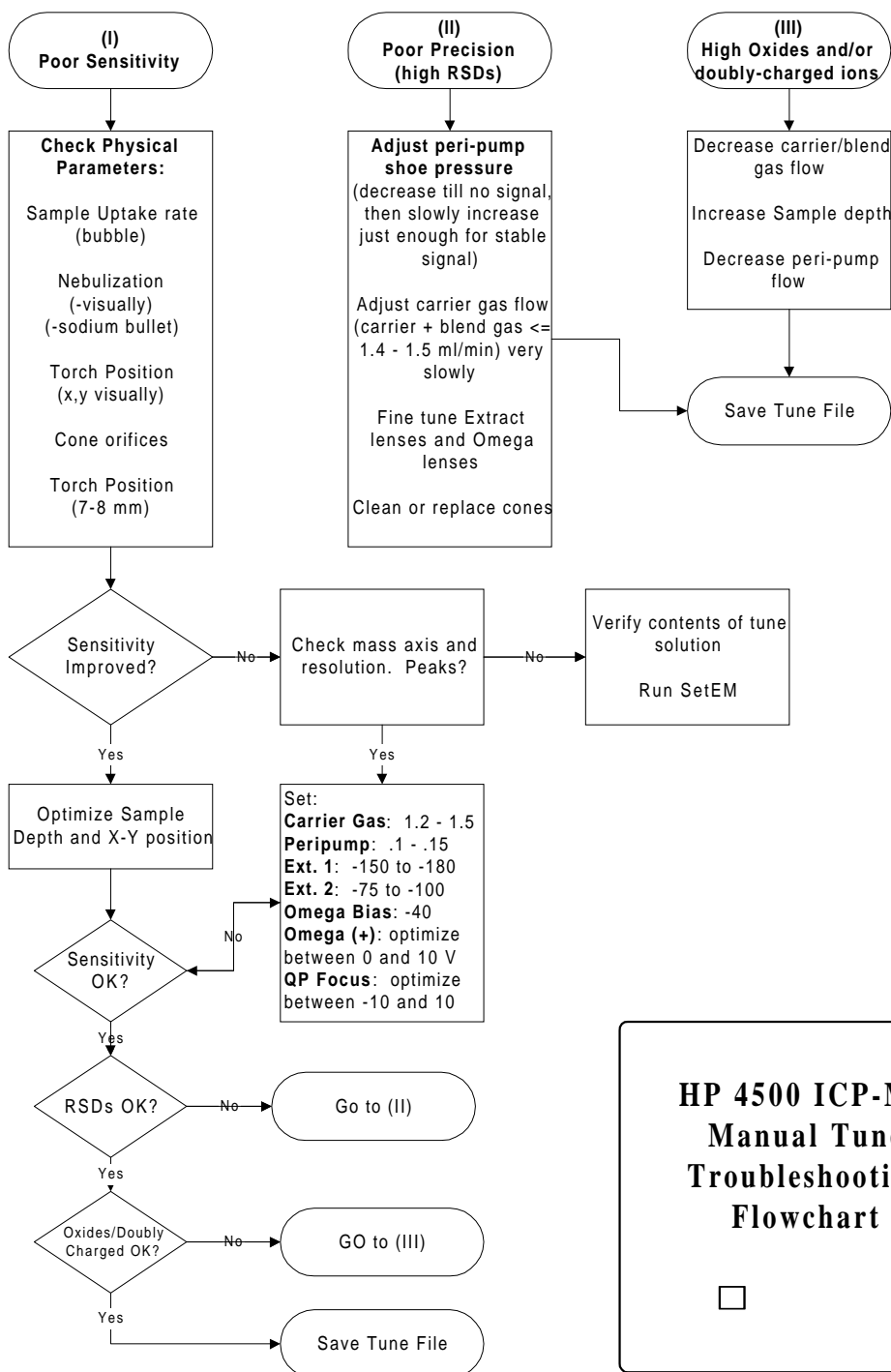
ALS IN RINSE SOLUTION, WAIT 1 MINUTE

PLASMA OFF

PERIPUMP TUBES UNCLAMPED

CHILLER

Laboratory 1: Agilent 7500 Configuration, Startup and Tuning
Shutdown Checklist





Agilent Technologies

Innovating the HP Way

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 wettability 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



Agilent Technologies
Innovating the HP Way

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 of 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?



Agilent Technologies
Innovating the HP Way

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.



Agilent Technologies
Innovating the HP Way

Appendix 1 – General Information

Professional Organizations

Professional Organizations

★American Chemical Society (ACS)	(800) 227-5558 http://www.acs.org
★Environmental Protection Agency (EPA)	http://www.epa.gov
★American Association of Clinical Chemists (AACC)	(800) 892-1400
★American Board of Clinical Chemistry, Inc.(ABCC)	(202) 835-8727
★American Society of Clinical Pathologists (ASCP)	(312) 738-1336 x.158
★Clinical Laboratory Management Association (CLMA)	(610) 647-8970
★College of American Pathologists (CAP)	(800) 323-4040
★National Committee for Clinical Laboratory Standards (NCCLS)	(610) 688-0100
★Society for Applied spectroscopy	(301)694-8122
★SEMI International Standards	(650) 964-5111 http://www.semi.org



Figure 263

Journals

Journals

- Analytical Chemistry
- Journal of Analytical Atomic Spectrometry (JAAS)
- Applied Spectroscopy (free with SAS membership)
- Spectroscopy (free)
- Spectrochimica Acta, Part B
- Analyst
- American Lab (free)
- American Clinical Lab (free)



Figure 264

Selected Web Sites (1)

Selected Web Sites (1)

- **Agilent Technologies**
<http://www.agilent.com>
- Sample Preparation (Duquesne University)
<http://www.sampleprep.duq.edu/sampleprep/>
- Eastern Analytical Symposium
<http://www.eas.org/>
- FACSS
<http://facss.org/info.html>
- Pittcon
<http://www.pittcon.org/>
- NIST Standard reference Program



Figure 265

Selected Web Sites (2)

Selected Web Sites (2)

- Spex catalog
http://www.spexcsp.com/crmmain/cat_f.htm
- Spectron
<http://www.vcnet.com/spectron/>
- Inorganic Ventures
<http://www.ivstandards.com/>
- Michael Cheatcham's Instrument pages
<http://www.geochemistry.syr.edu/cheatham/InstrPages.html>
- Plasmachem-L BB
<http://www.geochemistry.syr.edu/cheatham/icpmsins.html>
- US Pharmacopeia
<http://www.usp.org/>



Agilent Technologies
Innovating the HP Way

Figure 266



Appendix 2 – Flow Chats

Manual Tune Troubleshooting Flowchart [1]

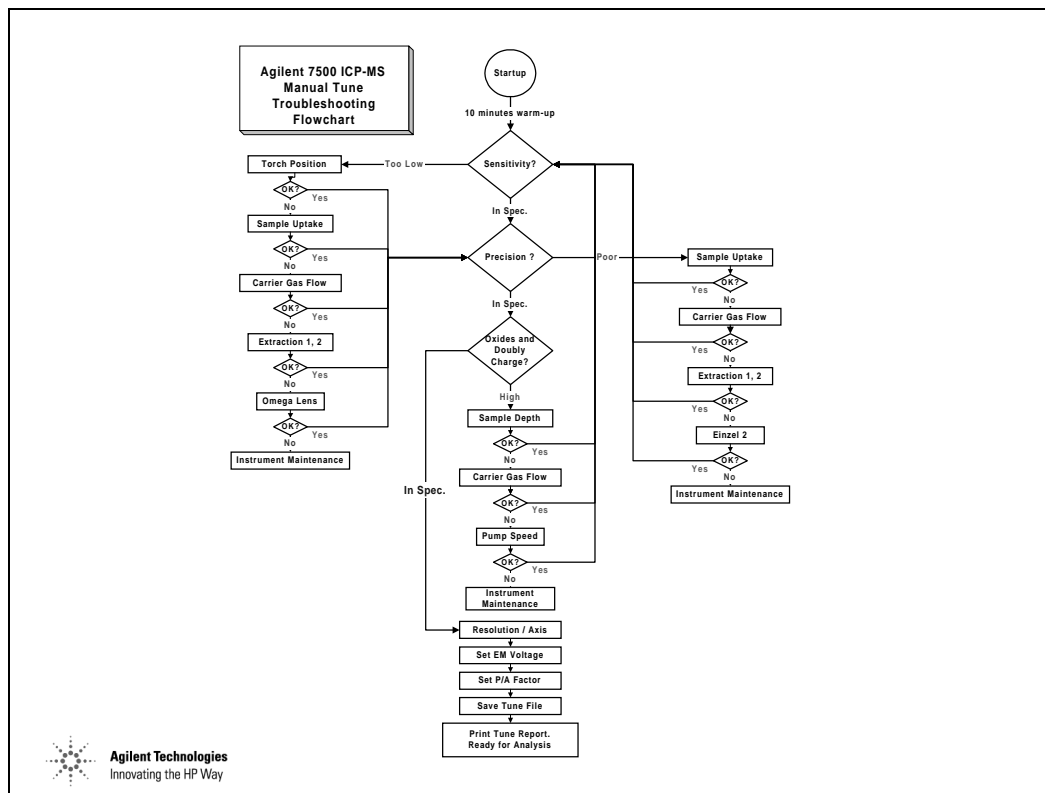


Figure 267

Manual Tune Troubleshooting Flowchart [2]

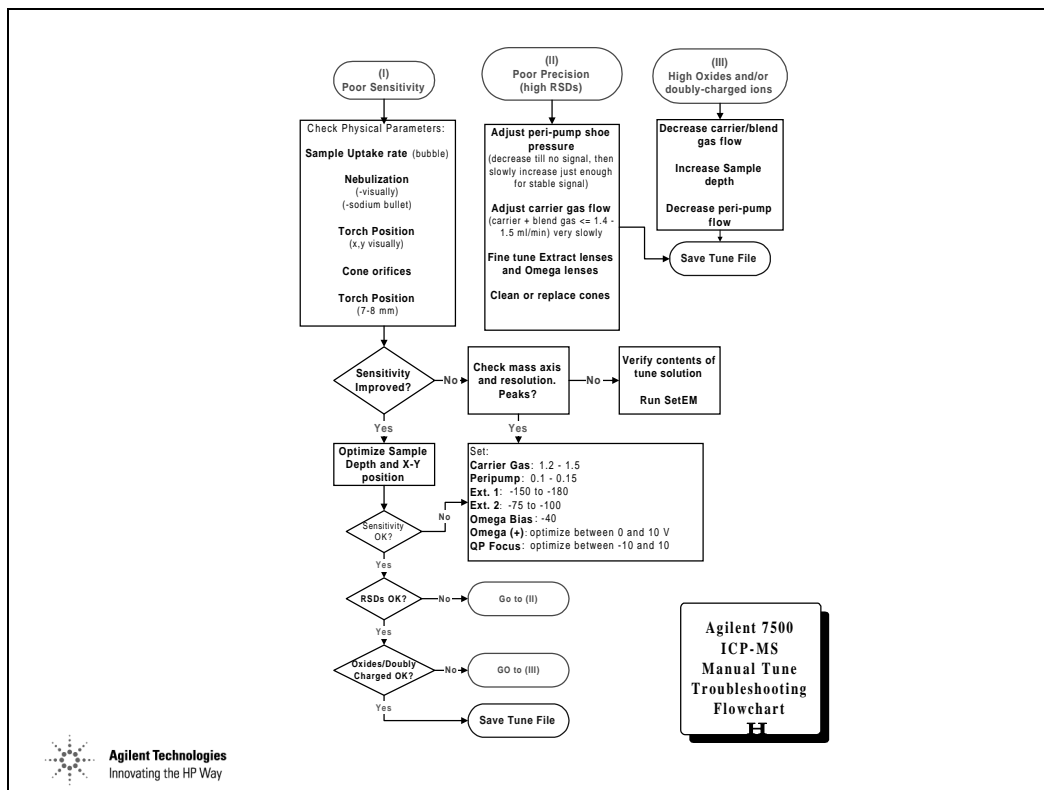


Figure 268

Manual Tune Troubleshooting Flowchart [2]



Agilent Technologies
Innovating the HP Way

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



Agilent Technologies
Innovating the HP Way

Figure 269

Strategy #1: (High Power) Cool Plasma Analysis

Strategy #1: (High Power) Cool Plasma Analysis

- Technique first reported in 1988*:
- Reduction of ArH^+ interference on Ca simply by modifying ICP operating conditions
 - lower plasma power
 - increased carrier gas flow
 - longer sampling depth

* Jaing, Houk, and Stevens, Anal. Chem., 1988, 60, 1217



Figure 270

Commercialization of Cool Plasma Analysis

Commercialization of Cool Plasma Analysis

- Developed commercially by HP/Yokogawa in 1992*
 - featuring patented ShieldTorch Interface
- Cool plasma ICP-MS (using the Agilent ShieldTorch) now the method of choice for ultratrace metals analysis in the semiconductor industry
- Over 100 HP 4500's and Agilent 7500's performing routine cool plasma analysis in the semiconductor industry replacing GFAA, ETV-ICP-MS, HR-ICP-MS

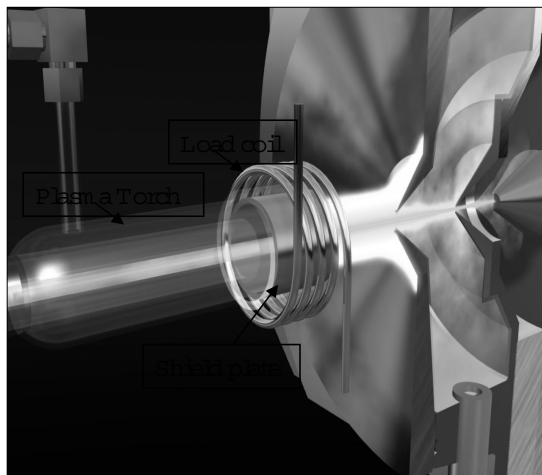
* Sakata K et al., Spectrochim. Acta, 1994, **49B**, 1027



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.



Figure 272

Not All Cool Plasmas* Are the Same!

[1]

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

- The ShieldTorch interface is unique to Agilent
- Reduces interferences such as ArH, Ar, ArO, C2, ArC to low ppt levels, enabling sub-ppt level DLs for K, Ca, Fe etc
- The key feature of the ShieldTorch is that it can achieve this at 900-1000W forward power
 - other systems can only remove interferences at 600-650W - interfering peaks reappear at higher power settings
 - operating at 650W gives rise to severe matrix effects, and reduced analyte range

** Analysis at 600-650W is often referred to as cold plasma analysis*



Figure 273

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

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

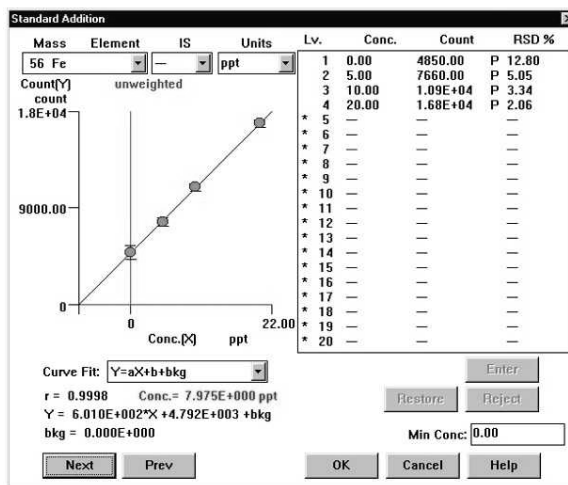
- Advantages of operation at 900 W - 1000 W (**High Power Cool Plasma**)
 - minimal matrix effects - similar to normal plasma operation (1200-1300W)
 - higher ionizing power - wider analyte range - including even Zn and B
 - complete sample matrix decomposition - greatly reduced possibility of interface and spectrometer contamination



Figure 274

Fe in 31% H₂O₂ - 5 ppt Spike Recovery

Fe in 31% H₂O₂ - 5 ppt Spike Recovery

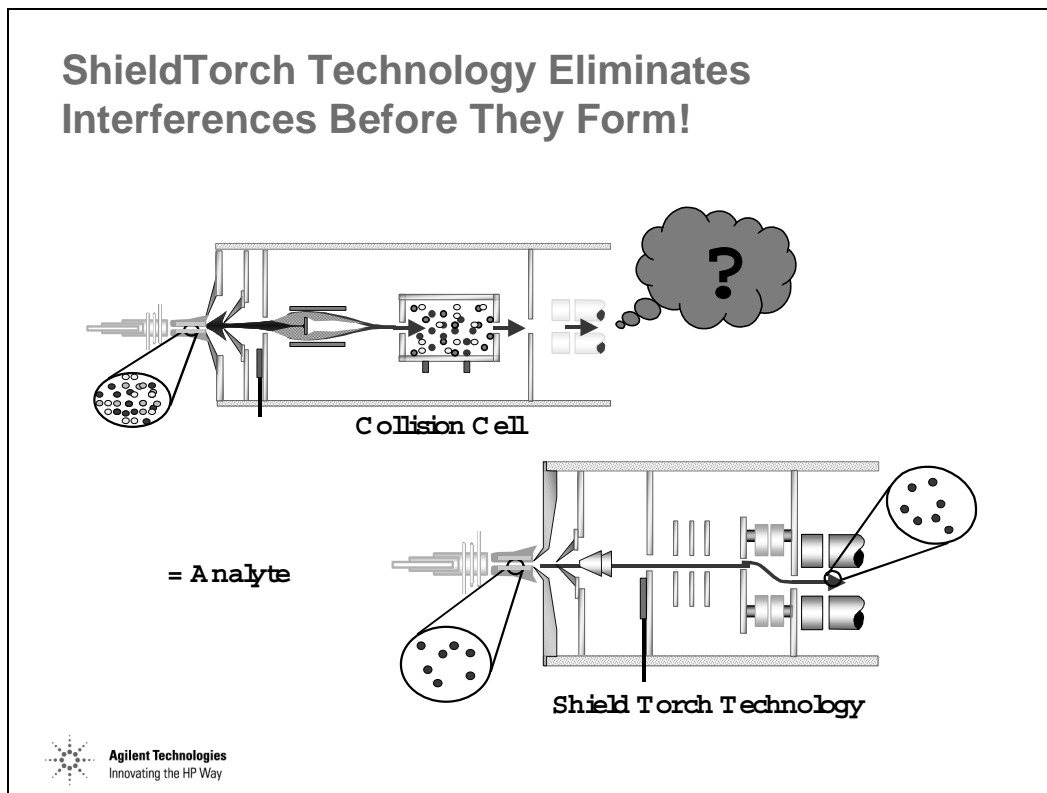


Excellent linearity even
 at 5ppt using high
 power cool plasma

DL - 0.3ppt in the
 H₂O₂ matrix

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

Figure 275

ShieldTorch Technology Eliminates Interferences Before They Form!**ShieldTorch Technology Eliminates Interferences Before They Form!****Figure 276**

Can Heavy Matrices be Analyzed?

Can Heavy Matrices be Analyzed?

Example Organics analysis

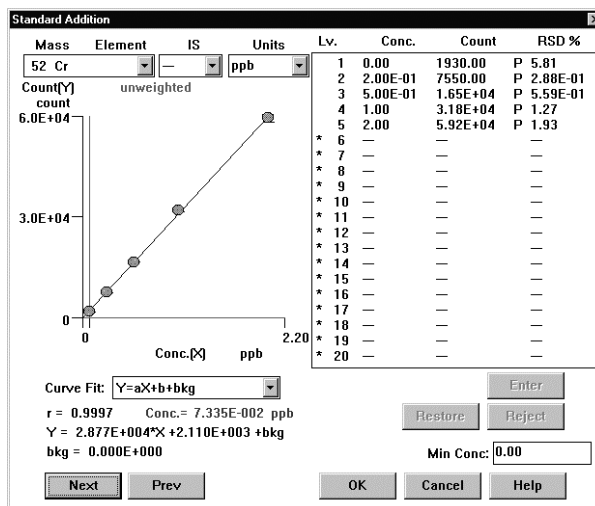
- Until now, carbon-based interferences have prevented the trace analysis of Mg and Cr in organic samples
- C_2 interferes with Mg 24, 25, 26
- ArC interferences with Cr 52, 53
- ➔ high power cool plasma (900W) removes these interferences down to single figure ppt level
- ➔ AND is stable in all types of undiluted organic sample, including xylene, toluene and NMP



Figure 277

Cr in Undiluted Methanol

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

Example of Heavy Matrix Analysis

Example Analysis of trace impurities in Metal Alloys
Levels required have traditionally been 10's ppm or % in the solid, but requirements for lower level characterization are increasing

1000x dilution typically used for ICP-MS, so

- 1ppm in solid requires measurement of 1ppb in solution
- easily achieved for most elements by ICP-MS, except K, Ca, Fe
- robust high power cool plasma could be used



Figure 279

Calibration for ⁵⁶Fe in 1000 ppm Pt

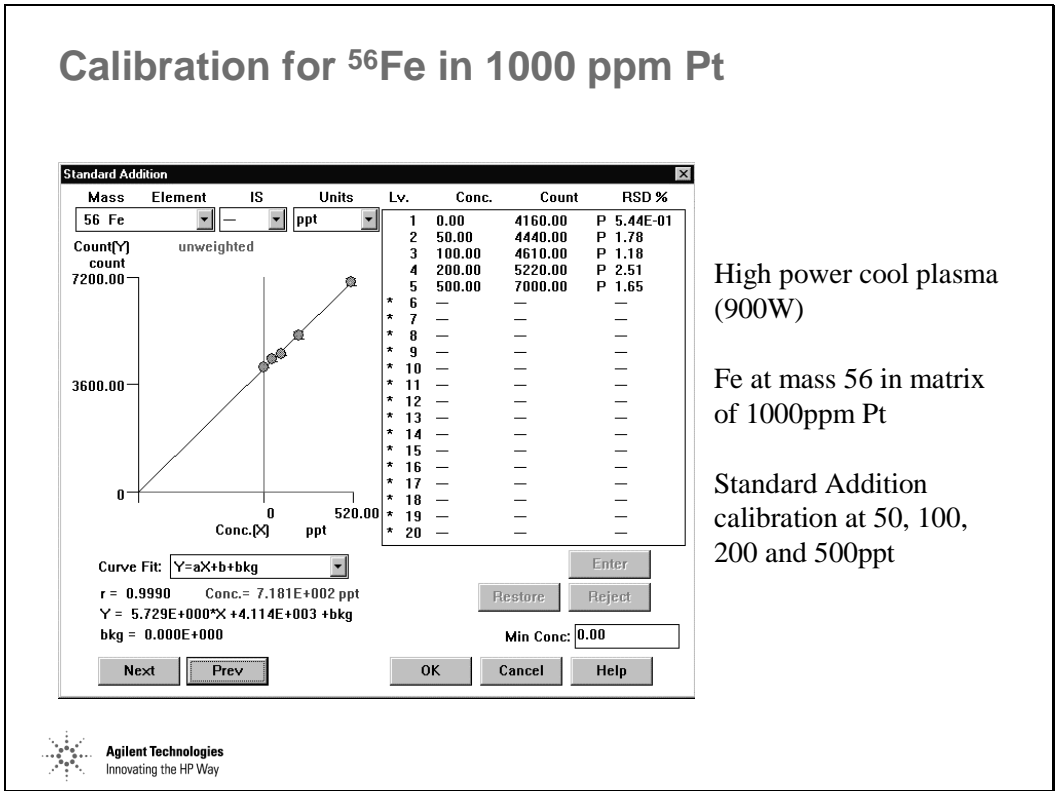
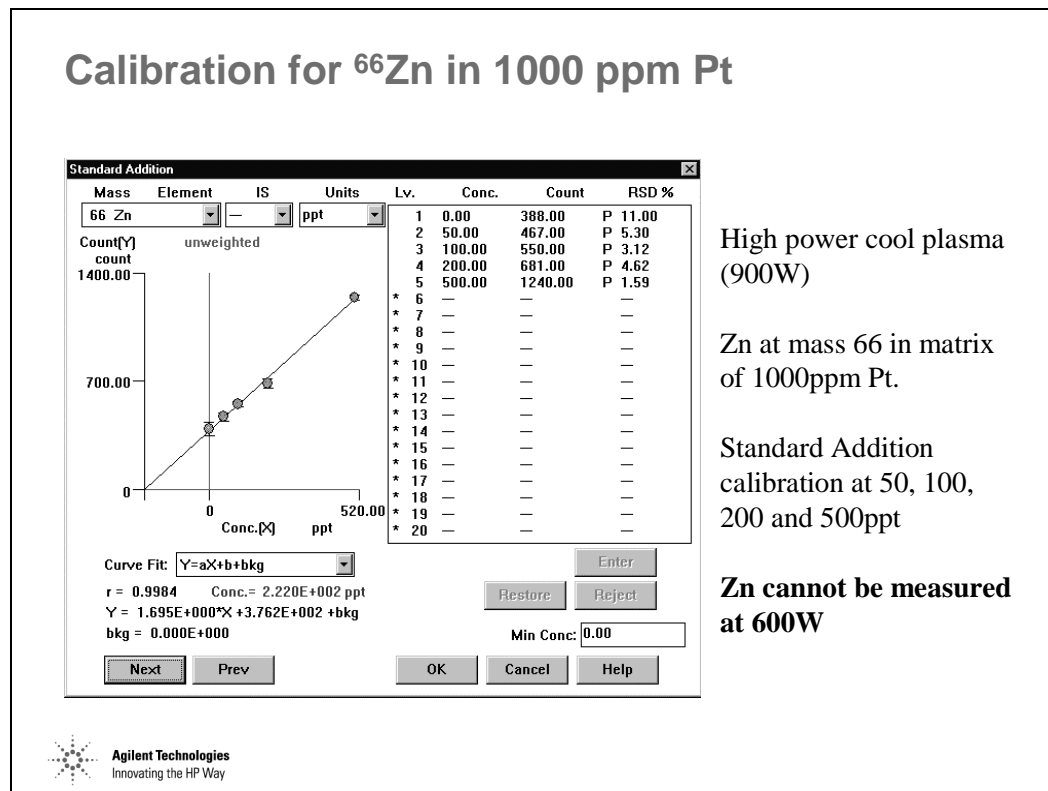


Figure 280

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

Determination of Se by High Power Cool Plasma

Agilent 7500 Operating Parameters

ShieldTorch interface

Higher forward power (1000W)

Higher gas flows

1.2 Lpm carrier gas

0.8 Lpm blend gas

Ar₂ ionization minimized, but plasma has power to ionize Se



Figure 282

Spectrum of 10 ppb Se and Blank

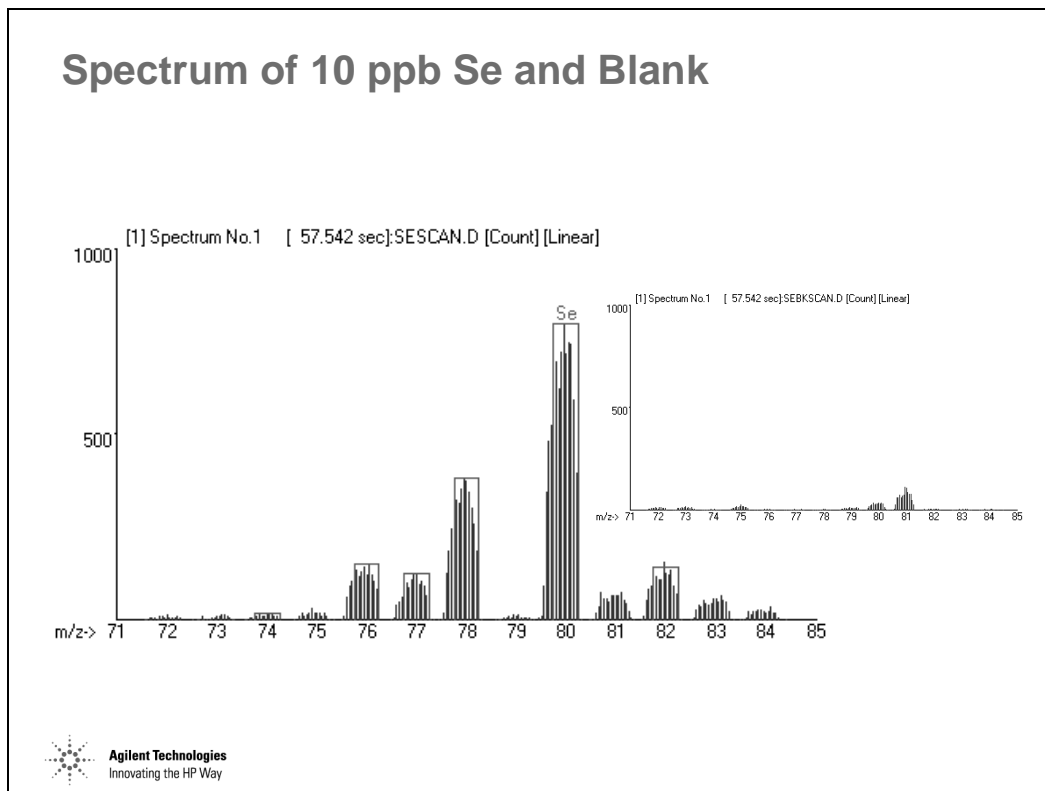


Figure 283

Calibration for ^{80}Se

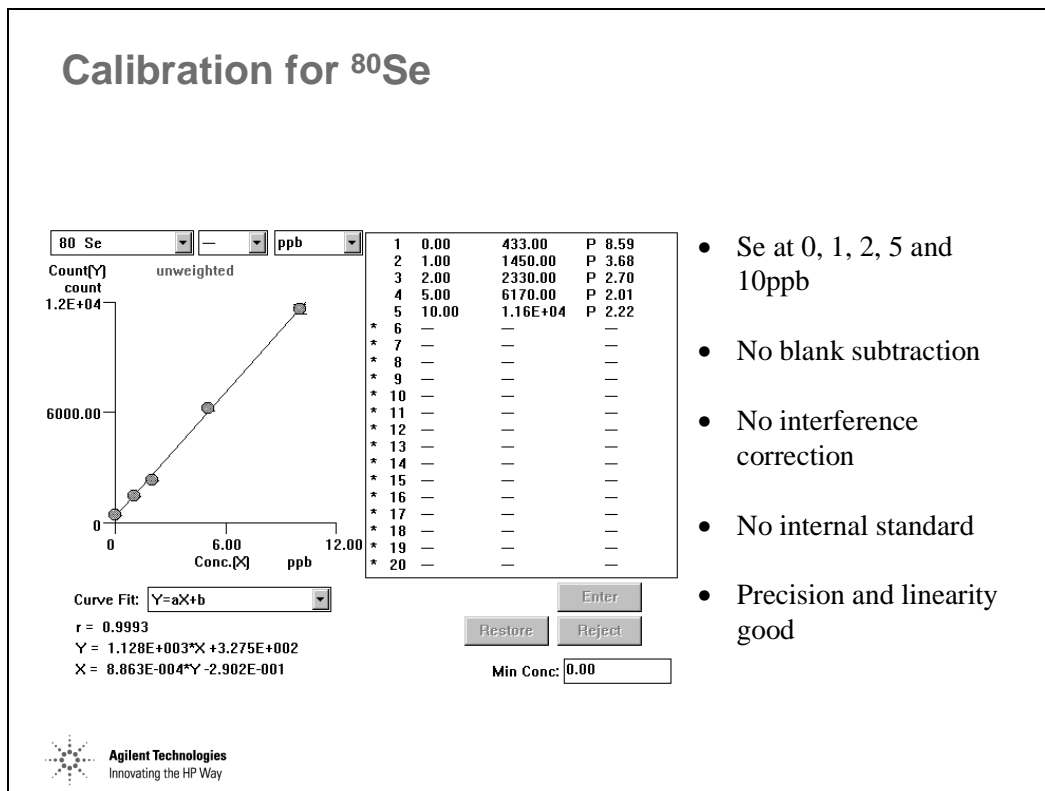


Figure 284

Detection Limits for Se by Cool Plasma

Detection Limits for Se by Cool Plasma

M ass	B lk	B lk SD	1ppb	1ppb-B lk	3sDL (ppt)
76	121	8.91	786	665	40.23
77	1796	57.43	2234	438	393.05
78	33	6.04	375	342	52.93
80	113	7.63	478	365	62.72
82	211	13.48	873	662	61.06

Detection Limits (3 sigma, n=10) in 4% HCl
 Note - Integration times varied for different isotopes



Figure 285

Current Research Developments Using the ShieldTorch

Current Research Developments Using the ShieldTorch

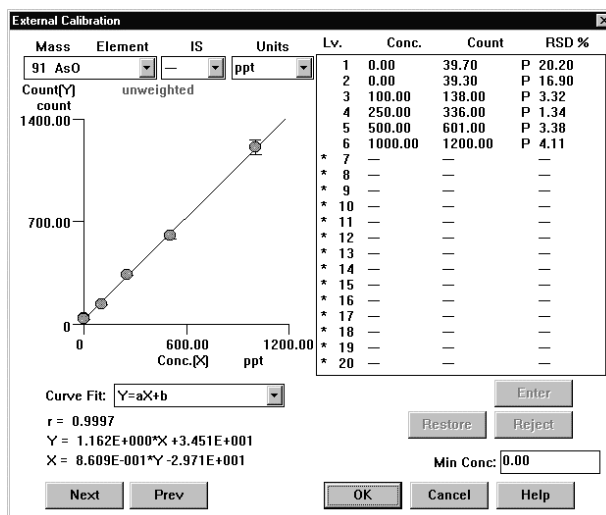
- Trace elements in organics
- Se isotope ratios
- Trace As in chloride matrices
- Trace analysis of "difficult" ICP-MS elements
 - e.g. S, Si, P
- Removal of isobaric interferences (not possible by collision cells or HR-ICP-MS)
 - removal of Hg from Pb at mass 204
 - removal of Zr from Sr at mass 90



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)

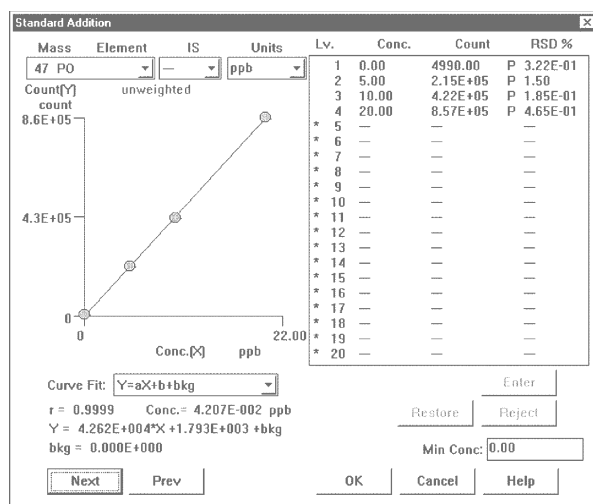


Agilent Technologies
Innovating the HP Way

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

Figure 288

Low Level S Calibration

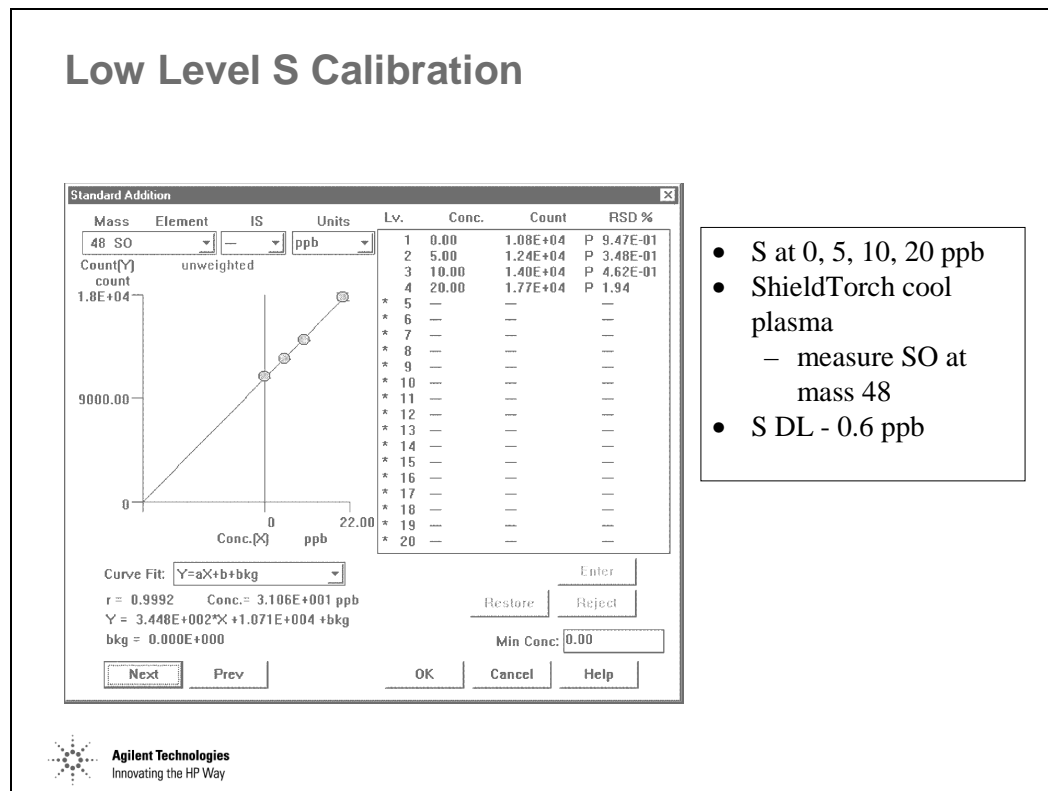
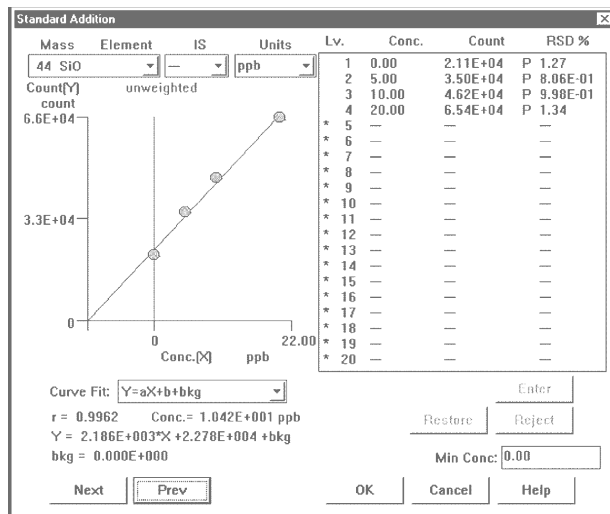


Figure 289

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

Figure 290

Strategy #2: Resolve the Interferences

Strategy #2: Resolve the Interferences

High resolution ICP-MS can be used to separate the analyte and interferent peak

Increase mass resolution and separate the analyte and interferent peaks, then make the measurement



Figure 291

Limitations of HR-ICP-MS

Limitations of HR-ICP-MS

- As in optical spectrometry, there is a trade off between resolution and sensitivity
 - increasing resolution reduces transmission
 - the net result is an inability to determine the analyte at trace levels.
- A resolution of up to 7500 is required for some interferences
 - at 7500R, signal transmission is only 1% of that at unit mass resolution (300R)



Figure 292

Resolution vs. Sensitivity

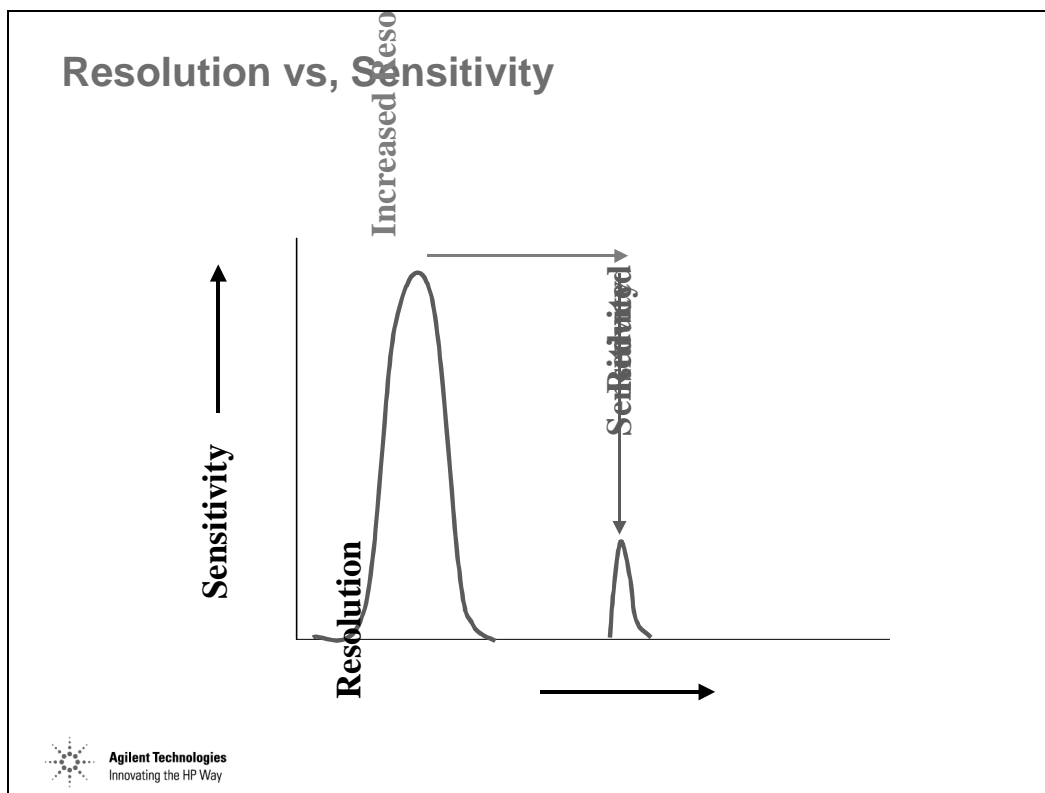


Figure 293

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

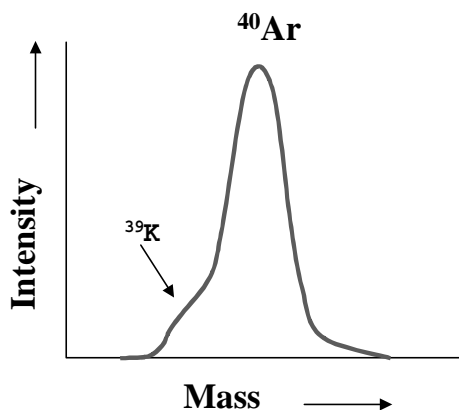


Figure 294

Other Facts About HR-ICP-MS [2]

Other Facts About HR-ICP-MS [2]

- Mass calibration is critical to obtaining accurate analytical results, however, it is a time consuming process for HR-ICP-MS instruments
 - resolution is defined by changing slit widths, and these require calibration/characterization
 - since the peak is so narrow at high resolution, the peak maximum cannot be reproducibly located
 - the analyser must be scanned across the whole peak, which decreases S/N significantly



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

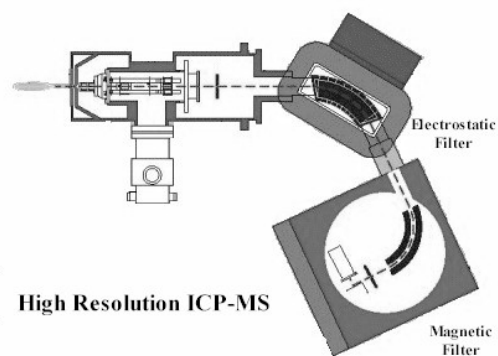


Figure 296

Strategy #3: Dissociate Interferences Within the Spectrometer

Strategy #3: Dissociate Interferences Within the Spectrometer

- Utilize collision/dynamic reaction cell technology
- Insert a collision cell/dynamic reaction cell within the spectrometer between the main ion lens and quadrupole analyser
- Control gas phase chemistry within the collision cell to dissociate polyatomic ions thereby eliminating the interferences



Figure 297

Principle of Collision Technology

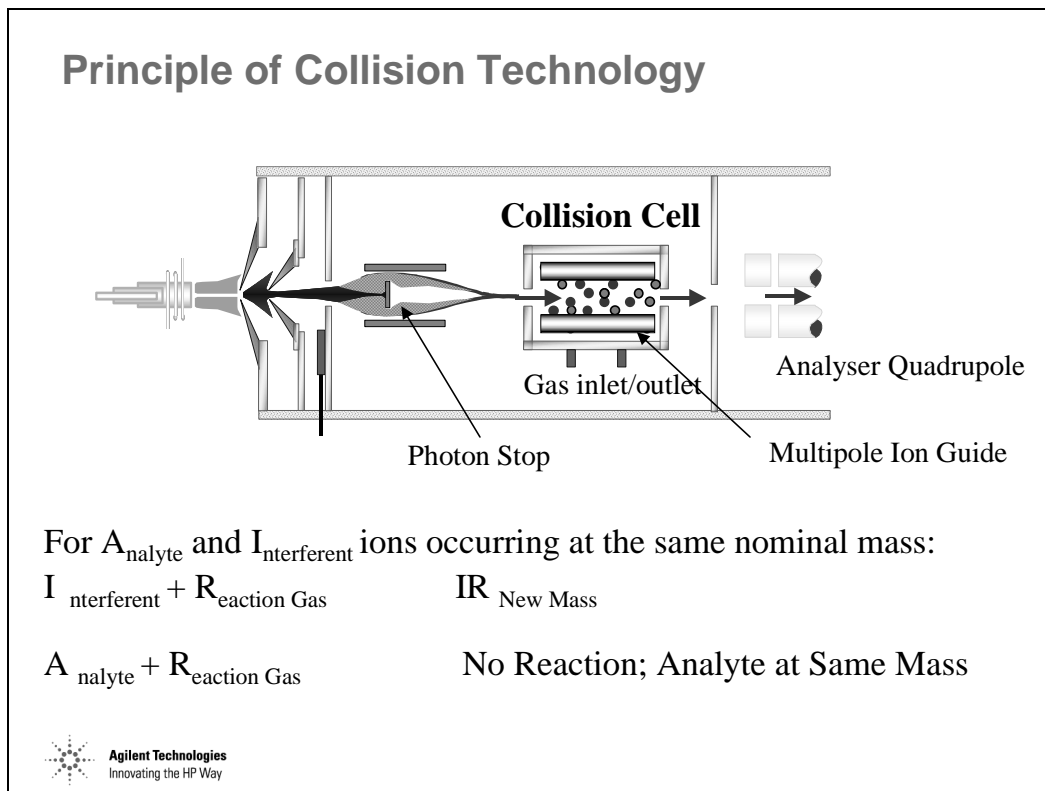


Figure 298

Selecting a Gas Phase Reagent

Selecting a Gas Phase Reagent

- The ideal reagent should:
 - have high reactivity with the interferent ion
 - result in 100% conversion of the interferent ion into its constituent products
 - result in a final product that is stable
- Unfortunately, no single gas has been found to be applicable for a complete multielement analysis
- Collision cell chemistries must be tailored for each individual element and sample matrix



Figure 299

Optimizing the Gas Phase Reagent

Optimizing the Gas Phase Reagent

- Often, more than one reaction gas is required to analyse a series of different elements
- The need to fill the collision cell with gas for the analysis and then vent the cell and refill with another gas, and re-measure the sample significantly increases analysis time
- Not only must the type of gas used be optimized, but the flow rate of gas through the cell must also be optimized for best S/N
- Few elements optimize using the same type of gas at the same flow rate. Therefore, compromise conditions must be used



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:

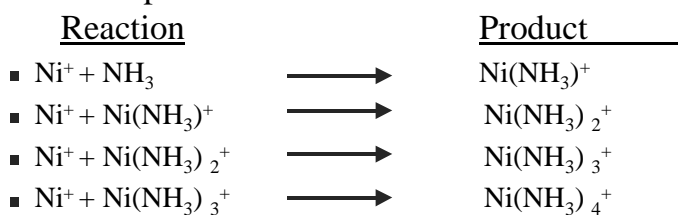


Figure 301

Side Reactions Create New Interferences

Side Reactions Create New Interferences

<u>Product</u>	<u>Interferes with</u>
$\text{Ni}(\text{NH}_3)^+$	^{75}As , ^{77}Se
$\text{Ni}(\text{NH}_3)_2^+$	^{92}Zr , ^{92}Mo , ^{94}Zr , ^{94}Mo , ^{95}Mo , ^{96}Zr , ^{96}Mo , ^{96}Ru , ^{98}Mo , ^{98}Ru
$\text{Ni}(\text{NH}_3)_3^+$	^{109}Ag , ^{111}Cd , ^{112}Cd , ^{112}Sn , ^{113}Cd , ^{113}In , ^{115}In , ^{115}Sn
$\text{Ni}(\text{NH}_3)_4^+$	^{126}Te , ^{128}Te , ^{130}Te , ^{130}Ba , ^{132}Ba



Figure 302

Hydrocarbons Are Particularly Prone To Complex Chemistries Even at Trace Levels

Hydrocarbons Are Particularly Prone To Complex Chemistries Even at Trace Levels

Hydrocarbons Are Particularly Prone To Complex Chemistries Even at Trace Levels

Even for simple hydrocarbons:

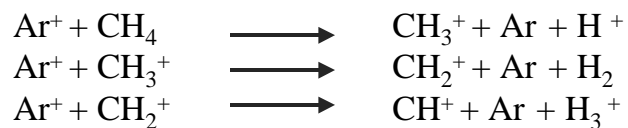


Figure 303

Effects of Sample Matrix

Effects of Sample Matrix

- “Multipole Ion Optics In ICP-MS”, Jonathan Batey, 25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, Paper #661.
- Aspirated 400ppm Ca into a collision cell device
- Ca could be measured at ^{40}Ca , however, strong peaks were observed throughout the mass spectrum due to CaOH^+ and other Ca molecular ions
- Conclusion - collisions cells were not appropriate for samples containing significant matrix components



Figure 304

Strategies to Overcome the Problem of Side Reactions

Strategies to Overcome the Problem of Side Reactions

- The collision cell quad can be scanned in concert with the analyser quad*
 - enables the collision cell quad to act like a notch filter
 - can prevent side reaction ions from entering the analyser quad

* Tanner S.D., Baranov V.I., At. Spectroscopy, 20 (2) 3-4/99



Figure 305

Limitation of Scanning the Analyzer Quad

Limitation of Scanning the Analyzer Quad

- When the collision cell quad becomes contaminated with sample matrix, it will charge up, and be unable to follow the scan speed of the analyser quad
- Analyte transmission will fall dramatically
- Quadrupoles are difficult to clean
- Correct realignment is critical to achieve maximum transmission



Figure 306

Collision Cells Can Create Interferences

Collision Cells Can Create Interferences Through...

- Interfering ions combining with the reaction gas to shift to a new mass
 - This mass cannot always be anticipated due to ion clustering
- Reaction gas combining with analytes and matrix components not previously interfered with
- Reaction gas combining with ultra-trace contaminants in the cell
- The presence of any type of matrix significantly complicates data interpretation



Figure 307

In Summary

In Summary...

- High resolution ICP-MS can resolve the interferences, but is not easy to use, and in complex matrices, poor abundance sensitivity gives rise to severe spectral overlaps
- Collision cells must use different gases/gas mixtures and gas flow rates to meet all analyte requirements
- Collision cells not only reduce targeted interferences but create new unpredictable molecular ion clusters in every individual matrix
- For almost all applications, high power cool plasma has superior performance



Figure 308

