Agilent 7500 ICP-MS Application Handbook

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Preface

Preface

The *Agilent 7500 ICP-MS Application Handbook* provides the user more in-depth information on many of the day-to-day tasks associated with routine operation of the *Agilent 7500* ICP-MS.

Who Should Read This Book

The primary audience for the *Agilent 7500 ICP-MS Application Handbook* consists of chemists and instrument operators in a laboratory. To use this manual effectively, you should have some experience using an inductively coupled plasma mass spectrometer (ICP-MS), a strong knowledge of chemistry and at least a basic level of computer experience.

How to Use This Book

The *Agilent 7500 ICP-MS Application Handbook* contains five chapters that are intended to be accessed independently, as needed. This manual contains the following chapters:

Chapter 1, Agilent 7500 Performance, describes limit of detection, precision and accuracy.

Chapter 2, Sample Preparation for ICP-MS, describes sample preparation for ICP-MS analysis.

Chapter 3, Analysis of Environmental Samples, describes analysis for environmental samples.

Chapter 4, Analysis of Semiconductor Samples, describes analysis of semiconductor samples.

Conventions Used in This Book

This book uses certain conventions to distinguish different types of information easily. This section describes these conventions.

Instructions

All step-by-step instructions are numbered and in bold, as in the following example.

1 Select Instrument»Tune from the ICP-MS Top.

The **Sensitivity** tuning window appears.

Alternatives

Lines beginning with a bullet (•) in step-by-step instructions indicate alternative steps, as in the following example:

2 Change the parameter value in one of the following ways:

- Click the right or left arrow at the end of the scroll bar, which changes the parameter value in small increments.
- Click the scroll bar, which changes the parameter value in larger increments.
- Double-click the box above the scroll bar and enter a new parameter value.

Menu Items

This book uses the following format for referring to menu items:

Instrument >> Tune

The text before the arrow symbol is the name of the menu; the text after the arrow symbol is the menu choice. This example refers to the Tune menu choice in the Instrument menu.

Terminology

This book frequently uses the following terms:

Convention	**Information**
Press	To hold down a button on the keyboard.
Click	To press and release the mouse button.
Double-click	To click the mouse button twice in rapid succession.
Drag	To press and hold the mouse button while moving the pointer.
Active Window	The window in which the cursor is currently located.
Radio Buttons	Choices where you can select only one item from a list. The selected radio button contains a solid dot. A grayed out radio button is a choice that is unavailable at a given time.
Check Box	Choice where you can select or clear the named item. Multiple items can be chosen simultaneously and are each marked with an X in a square. You cannot use a grayed out check box.
Push Button	Button used to initiate an immediate action. Cancel and Help are examples of push buttons. Push buttons are labeled on the buttons themselves.
ICP-MS	An inductively coupled plasma mass spectrometer.
Agilent 7500	The Agilent Technologies 7500 ICP-MS.
ChemStation	The ChemStation software for Agilent Technologies ICP-MS.

Notes

Notes contain a reminder about the effect of particular actions. They are indicated as follows:

NOTE This example shows how a note is displayed.

Cautions

Cautions indicate situations that could overwrite data or require immediate attention to prevent harm to the instrument. Cautions are indicated as follows:

CAUTION This example shows how a caution is displayed.

Warnings

Warnings indicate situations that could cause bodily harm. Warnings are indicated as follows:

WARNING This example shows how a warning is displayed.

Where to Go for More Information

In addition to the *Agilent 7500 ICP-MS Application Handbook*, you can reference the following resources:

- *Agilent 7500 ICP-MS ChemStation Operator's Manual*
- *Agilent 7500 ICP-MS Hardware Manual*
- *Online Help*

Your computer system has additional manuals that document the software and hardware. For more information on using or maintaining your computer, printer, or peripheral equipment, consult the respective hardware user's guide. Microsoft® Windows™ have a user's guide that explains how to install, use, and troubleshoot the software.

Agilent Technologies on Internet

For the latest information on products and services visit our worldwide web site on the internet at:

http://www.agilent.com/chem/icpms

1

Performance

Performance

To confirm if sample preparation method and the instrument performance are really performed correctly, the limit of detection, precision and accuracy should be verified.

Limit of Detection

Limit of detection (LOD) is normally calculated from three times the standard deviation (σ) of the blank water signal counts, divided by the sensitivity factor based on analysis of a standard solution. Sensitivity means counts per unit concentration.

$$\mathbf{LOD} = \frac{3\sigma \times \text{concentration of standard soln.}}{(S - B)}$$

σ: standard deviation in counts of a blank solution

S: counts of a 10 ppb solution

B: counts of the blank background

According to statistics, 7 repetitions are required to achieve the 95% confidence level.

In order to understand the relationship between the LOD and the integration time, the following example is used to illustrate this idea:

When counts are not high, the standard deviation (σ) is roughly equal to the square root of the signal of the blank. Assume that the sensitivity is 10,000 cps for 1 ppb, and the background is 5 cps. When the integration time is 10 seconds, the signal for a 1 ppb solution and the background will be 100,000 counts and 50 counts, respectively. The standard deviation will be the square root of 50 counts, which is 7.07. Then, the LOD is 0.21 ppt.

When the integration time is 1 second, the signal for a 1 ppb solution and the background will be 10,000 counts and 5 counts, respectively. The s.d. will be 2.236, and the LOD will be 0.67 ppt.

When the integration time is 0.1 seconds, the signal for 1 ppb solution and the background will be 1,000 counts and 0.5 counts, respectively. The s.d. will be 0.707, and the LOD will be 2.1 ppt.

From these calculations, the LOD will be improved by the square root of the integration time, and 10 seconds is an acceptable integration time to get best LODs Even if 100 seconds integration time is used, the LOD will be improved only by about a factor of three times. This is why 10 seconds integration time is commonly used for calculating best LODs.

It has to be noted that at least 1,000 counts will be required to get reproducible data: the S.D. will be 33 counts that will be 3.3 % rsd. 10,000 counts will be required to achieve a precision of ~1% rsd on the signal.

The detector will be switched from pulse counting mode to analog mode at around 1,000,000 cps, which corresponds to 100 ppb when the sensitivity is 10,000 cps/ppb at an analyte mass. The maximum count rate of the EM in analog mode is about 4,000,000,000 cps. That corresponds to about 400 ppm when the sensitivity is 10,000 cps/ppb at an analyte mass.

For real detection limit calculations, sometimes called the quantitative detection limit, 10 σ is often used instead of 3 σ.

Precision

The precision of ICP-MS is commonly expressed by repeatability of isotope ratio measurements.

To analyze isotope ratios, a 10 ppb Ag standard solution is commonly used because Ag has two isotopes that have almost the same isotopic abundance, at masses 107 and 109. The precision is expressed by the rsd of isotope ratio measurements with 10 repetitions. Typical rsd's are better than 0.2 %, about 0.18 - 0.15% with 30 seconds integration time per mass and three points per mass.

To get good precision, the important factor is stability of the signal: rsd's in the tuning mode should be as low as possible. Faster scan speeds compensate for instability of signal. The number of scans is switched from 100 times to 1000 times when the isotope ratio analysis mode is selected. When the integration time per point is 1 second, the dwell time in the spectrum mode is 10 msec and that of the isotope ratio analysis mode is 1 msec.

To get best precision, self-aspiration with the MCN is a good choice; better than 0.2% rsd has been obtained for ^{235}U /^{238}U over a period of one hour in HP laboratories.

Accuracy

Accuracy may be determined by analyzing reference materials with certified values and comparing the analytical results to the certified values. It should be kept in mind that accuracy depends not only on instrument performance but also on the laboratory techniques of the analyst. There are several analytical laboratory techniques which can affect accuracy. Accurately preparing calibration standards involves the use of grade A volumetric flasks and pipettes which have been verified for accuracy of delivery. The correct technique in using the flasks and pipettes is just as important. The flasks and pipettes must be clean, so they must be cleaned in a manner appropriate to the analysis and kept in a clean environment after cleaning. If flasks or pipettes are not cleaned, then they should be clean and free from impurities when purchased from the vendor.

Calibration standards should have analyte concentrations which are traceable to certified standard reference materials which have low impurity levels. They should be stored in a manner and environment which preserves their original concentration for as long a period as they are certified to be accurate. Keep in mind chemical incompatibilities between elements in solution which may cause precipitation of the elements. The matrix of stock solutions may also cause other elements in multielement solutions to precipitate.

Configuring and using the instrument properly for analysis, such as selecting tuning conditions appropriate to the analysis improves performance and accuracy (refer to the sections on tuning). Making a good standard calibration curve from which to quantitate the data is essential. Both the slope of the response and the y-intercept at zero concentration of the calibration curve must be accurate. Calibration curves with more than two levels for each element depend on the accuracy of each level for the r value of the curve to be good. The r value is an expression of the linearity of all the points on the curve.

In order for the least squares determination of the r value to be statistically valid, the calibration points should be evenly spaced with respect to their concentrations although this is often not done. In general it is a good idea to use calibration standards whose concentrations are evenly spaced. Sometimes various curve fitting techniques other than simple linear curves are used to compensate for calibration points that are not linear with respect to the calibration curve. If this is necessary then it indicates that the accuracy of the calibration curve (its slope or y-intercept) may not be good.

Quantitative sample preparation, that is, techniques which promote complete recovery of the analytes from the sample and avoid contamination of the prepared samples, are other issues important for accuracy. While performing analyses it is also necessary to verify their accuracy by following a quality control protocol for the analysis which monitors the accuracy of the data while it is being obtained.

One can see that there are many issues which affect the accuracy of the results obtained but which are determined by the technique of the analyst and not the performance of the instrument.

Performance

Accuracy

2

Sample Preparation for ICP-MS

Sample Preparation for ICP-MS

In this chapter, sample preparation for ICP-MS analysis is described. In order to use the Agilent 7500 effectively, an appropriate sample preparation technique has to be selected and there are many preparation procedures for elemental analysis.

General Considerations

Environment for the Instrument

The environment required for the ICP-MS instrument depends on the application. If you want to analyze ultra trace levels (ppt) of Na, Al and Fe, a clean room is required. For semiconductor applications, better than class 1,000 is preferable for the Agilent 7500 itself and better than class 100 is preferable for the sample preparation facility.

For other applications such as environmental, biological, botanical and geological, a clean room is not required. However, it is recommended that the ICP-MS is located in a separate area to avoid cross-contamination. In particular, the sample preparation facility used for open vessel digestions must be isolated.

People are one of the main sources of contamination. Wash hands before experiments and wear clean gloves.

Equipment

The sample bottles and volumetric flasks used are also very important. A new sample bottle may contain high concentrations of Na, Al, K, Fe, Zn, Sn and Pb. Bottles and flasks must be washed prior to use in a 5%(v/v) HNO_3 solution for at least one night. They should be kept in a 5% (v/v) HNO_3 solution while not in use, and washed with plenty of pure water just before use.

Nalgene **PMP** volumetric flasks are recommended for the preparation of standard solutions, polyethylene bottles for stock standard solutions and samples, and **PFA** bottles for pure water and acids. **Teflon** is difficult to clean because of its higher hydrophobicity.

The following procedure for Teflon and quartz cleaning has been suggested by an acid manufacturer in Japan:

1. Cleaning by an organic alkali solution

2. Cleaning by acetone

3. Heating in conc. HNO_3 for a day (only for quartz)

4. Soak in a 3M HF for 10 min. (only for quartz)

5. Heating in aqua regia for a day (only for quartz)

6. Heating in conc. HNO_3 for 3-5 days

7. Heating in 0.1N HNO_3 for 5 days

Pure Water

Since the normal sample type for ICP-MS is an aqueous solution, water quality is critical. Water is also used for making standard solutions and diluting samples. The suitability for ICP-MS applications of three types of pure water: distilled water, deionized water and sub-boiling water is discussed below.

♦ Distilled water

Distilled water is obtained by boiling and condensing water. This is a classical and easy way to obtain pure water. However, the quality of this water is not good enough for ICP-MS applications because some volatile elements are vaporized with water. Pb, B and Zn are common impurities in distilled water.

♦ Deionized water

Deionized water is obtained by passing water through ion exchange columns. This technique effectively reduces impurities in water. Modern pure water systems use this technique, for example the Millipore Milli-Q series deionized water units. Water purity is normally expressed in terms of resistivity and **18.3 MΩcm** is theoretically the maximum resistivity for pure water. However, there are non-conductive impurities in pure water and resistivity is only one of the indicators of water quality.

♦ Sub-boiling water

Sub-boiling water is a type of distilled water, but there is a difference in the boiling procedure. The water is not completely boiled, but heated usually by an infrared lamp. Deionized water is used as the source water and heated up to about 40 to 50 °C. The vaporized water is recovered by a condenser. Since the water vapor pressure is very low at this temperature, the amount of pure water recovered is only about 2 L/day with a normal system. In order to obtain high purity water, the material used for the sub-boiling system is important. There are two types of material used: Teflon and Quartz.
This system can be used for purifying not only water, but also acids used in the semiconductor industry.

Boron is a very difficult element to remove because of its low dissociation in water and high volatility. To reduce the boron background from the sample introduction system, use the inert sample introduction kit. Boron memory comes from the glass parts of the sample introduction system, even from quartz.

Which method should be used to analyze impurities in pure water? Since ICP-MS is not an absolute analytical technique, standard samples have to be analyzed and pure water is used as a blank solution. Therefore, a water sample must be concentrated prior to analysis. The preconcentration will be made by simply evaporating the water, taking care not to evaporate volatile elements with low boiling points. A high purity closed quartz vessel is used in order to avoid contamination.

NOTE

Elements are very unstable in pure water and adsorbed onto the inner surface of vessels, transport tubes and the peristaltic pump tube. Therefore a small amount of nitric acid should be added to the water: at least 0.1% as nitric acid is recommended, 100 µL conc. HNO_3 in 100 mL of sample gives about a 0.06% nitric acid concentration. A concentration of 0.1% is not high enough to form a stable solution, therefore the sample should be analyzed directly after preparation. At least 1% HNO_3 acid is required to make a solution that will be stable for more than a few minutes.

Acids and Alkalis

Many samples are digested by acids and alkalis. There are many types of grade for chemicals. Refer to the certified values which manufacturers provide with the reagent to select a suitable one.

Since the final solution to be analyzed often contains acids and alkalis, analysis of these chemicals is very important. The following section gives some basic information about these chemicals.

Main polyatomic ions due to acid are shown in Table 2-1.

CAUTION

Analyte signals will be stable up to the concentrations described within this section. However, direct analysis of minerals acids or alkalis at high concentration levels, for long periods, may cause corrosion damage to the sample introduction area.

Table 2-1. Main Polyatomic Ions Due to Acids

m / z	Element	HNO_3	HCl	H_2SO_4
20	Ne (90.5 %)	OH_2		
21	Ne (0.27 %)	OH_3		
22	Ne (9.2 %)			
23	Na (100 %)			
24	Mg (79.0 %)			
25	Mg (10.0 %)			
26	Mg (11.0 %)			
27	Al (100 %)			
28	Si (92.2 %)	CO, N_2		
29	Si (4.7 %)	N_2H, COH		
30	Si (3.1 %)	NO		
31	P (100 %)	NOH		
32	S (95.0 %)	O_2		S
33	S (0.75 %)	O_2H		SH, S
34	S (4.2 %)	O_2		S, SH
35	Cl (75.8 %)	O_2H	Cl	SH
36	S (0.02 %), Ar (0.34 %)	Ar	ClH	S
37	Cl (24.2 %)	ArH	Cl	SH
38	Ar (0.06 %)	Ar	ClH	
39	K (93.2 %)	ArH		
40	Ar (99.6 %), K (0.01 %), Ca (96.9 %)	Ar		
41	K (6.7 %)	ArH		
42	Ca (0.65 %)	ArH_2		
43	Ca (0.14 %)			
44	Ca (2.1 %)	CO_2		
45	Sc (100 %)	CO_2H		
46	Ti (8.2 %)	NO_2		SN
47	Ti (7.4 %)			SN
48	Ca (0.19 %), Ti (73.7 %)			SO, SN
49	Ti (5.4 %)		ClN	SO
50	Ti (5.2 %), V (0.25 %), Cr (4.4 %)	ArN		SO
51	V (99.8 %)		ClO, ClN	
52	Cr (83.8 %)	ArC, ArO	ClOH	SO
53	Cr (9.5 %)		ClO	
54	Cr (2.4 %), Fe (5.8 %)	ArN	ClOH	
55	Mn (100 %)	ArNH		
56	Fe (91.8 %)	ArO		
57	Fe (2.2 %)	ArOH		
58	Fe (0.29 %), Ni (68.3 %)			
59	Co (100 %)			
60	Ni (26.1 %)			
61	Ni (1.1 %)			
62	Ni (3.6 %)			
63	Cu (69.2 %)			
64	Ni (0.91 %), Zn (48.6 %)			SO_2, S_2
65	Cu (30.8 %)			SO_2, S_2
66	Zn (27.9 %)			SO_2, S_2
67	Zn (4.1 %)		ClO_2	
68	Zn (18.8 %)	ArN_2		SO_2, S_2
69	Ga (60.1 %)		ClO_2	
70	Zn (0.62 %), Ge (20.5 %)	ArNO		
71	Ga (39.9 %)		ArCl	
72	Ge (27.4 %)	Ar_2		ArS
73	Ge (7.8 %)		ArCl	ArS
74	Ge (36.5 %), Se (0.87 %)	Ar_2		ArS
75	As (100 %)		ArCl	
76	Ge (7.8 %), Se (9.0 %)	Ar_2		ArS
77	Se (7.6 %)	Ar2H	ArCl	
78	Se (23.5 %), Kr (0.36 %)	Ar_2		
79	Br (50.7 %)	Ar_2H		
80	Se (49.8 %), Kr (2.3 %)	Ar_2		SO_3
81	Br (49.3 %)	Ar_2H		SO_3H

- **Nitric acid (HNO_3)**

HNO_3 is the most suitable acid for ICP-MS because there are fewer interferences due to the acid itself and it is a strong oxidizing agent. Typical impurities in HNO_3 are Pb, Sn and Zn, which are volatile elements and are carried through the distillation process. To get better quality HNO_3, a sub-boiling system is commonly used, e.g. TAMAPURE guarantees impurity levels lower than 10 ppt. Typical ICP-MS interferences are N_2, NO with Si and ArN with a minor isotope of Fe. HNO_3 solutions up to 40% can be introduced.

- **Hydrochloric acid (HCl)**

HCl is also a very good acid to digest metal oxides and metals, but rarely used alone for digestion. HCl is a reducing agent and not used for digesting organic materials. Typical impurities in HCl are As, Sb and Sn because of their volatility. To get better quality HCl, the sub-boiling system is used.

Typical ICP-MS interferences are ClO and ArCl with V, Cr, As and Se. Therefore, HCl should be avoided when analyzing these elements.

Platinum group elements are stable in an HCl matrix solution. Chlorides of As, Sb, Sn, Se, Ge and Hg are readily lost during open vessel digestions at higher temperatures. Utilization of HCl should be avoided, if possible, for ICP-MS, as HCl has to be removed from the sample by evaporation. Up to 18% HCl solutions can be introduced into the ICP-MS.

- **Hydrofluoric acid (HF)**

HF is an acid which dissolves silica and attacks Ni interface cones, therefore a special sample introduction system must be used. The inert sample introduction kit consists of a crossflow nebulizer, a polypropylene spray chamber and a Pt injector torch. Interferences due to HF aren't critical; ArF would interfere with Co although formation of ArF is insignificant.

Fluorides of B, Si, As and Sb might be lost along with HF, while salts of Ca and K are poorly soluble in HF. HF can be removed from the sample by evaporation. Up to 30% HF can be introduced into ICP-MS.

- **Hydrogen peroxide (H_2O_2)**

H_2O_2 is a strong oxidizing agent and used with other acids for digestion instead of $HClO_4$. The H_2O_2 background shows a similar background to water and H_2O_2 is one of the best chemicals for ICP-MS analysis. A 30% H_2O_2 solution can be analyzed. Up to 60% H_2O_2 solutions exist, but higher concentrations of H_2O_2 are extremely dangerous, therefore the ultrasonic nebulizer should not be used for higher concentrations of H_2O_2. Since the dissociation constant of H_2O_2 is low in water, a small amount of HNO_3, to give about 0.1%, should be added.

- **Sulfuric acid (H_2SO_4)**

H_2SO_4 is an oxidizing agent and used for the digestion of organic materials and geological materials with other acids. Since the boiling point of H_2SO_4 is extremely high, 338 °C, it is hard to decompose in the plasma. It adheres to the interfaces and the lenses, causing deterioration of Ni and Cu interfaces and instability of signal. Pt interfaces have to be used. In addition, H_2SO_4 forms polyatomic ions; SO, SO_2 and S_2 interfering with major isotopes of Ti and Zn and minor isotopes of V and Cr. The quality of H_2SO_4 is not as good as other acids because the distillation requires higher temperatures.

Sulfates of Ba, Ca, Pb and Sr have very low solubility, and those of Ag, As, Ge, Hg, Re and Se are volatile and might be lost during open vessel digestion. H_2SO_4 cannot be removed from the sample by evaporation unlike HCl and HF, therefore utilization of H_2SO_4 is not recommended for ICP-MS. The maximum recommended concentration that should be aspirated for long periods of time is 1% with the concentric nebulizer (CN), crossflow nebulizer (CF) and babington nebulizer (BN), and 5% with the micro flow nebulizer.

- **Phosphoric acid (H_3PO_4)**

H_3PO_4 is not commonly used for digestion, but used as a buffer agent with other acids. Its extremely high boiling point limits its application in ICP-MS, as H_3PO_4 cannot be decomposed in the plasma, and it deteriorates Ni interfaces. In addition, H_3PO_4 forms several polyatomic ions, $H_xP_yO_z$. Therefore utilization of H_3PO_4 should be avoided. The maximum concentration that can be analyzed is less than **0.1%** with CN, CF and BN.

- **Perchloric acid ($HClO_4$)**

$HClO_4$ is one of the strongest oxidizing agents and it reacts explosively with organic materials. Therefore, organic materials should be pretreated with HNO_3 or a mixture of HNO_3 and $HClO_4$.

Removal of $HClO_4$ is more difficult than for HCl, and ArCl and ClO will interfere with As, Se and V. Therefore, H_2O_2 is preferred rather than $HClO_4$ as an oxidizing agent for ICP-MS samples.

- **Aqua regia (1 part conc. HNO_3 + 3 parts conc. HCl)**

Aqua regia is commonly used for the digestion of metals and alloys, especially for precious metals such as Au, Pt and Pd. Since aqua regia includes HCl, there are polyatomic interferences due to Cl. An HCl matrix is generally removed by evaporation.

- **Sodium hydroxide (NaOH)**

NaOH is not commonly used for digestion and is rarely analyzed by ICP-MS. Alkali solutions dissolve glass slightly at room temperature, therefore the inert introduction system has to be used. Higher (%) concentrations of Na may cause matrix suppression and interfere with m/z 63 on Cu.

- **Lithium metaborate ($LiBO_2$)**

$LiBO_2$ is the most commonly used reagent for the alkali fusion technique which is applied to the digestion of refractory compounds such as geological and metallurgical samples.

However, higher concentrations of Li and B cause matrix suppression. The microwave digestion that is described later will be used instead of the alkali fusion technique.

- **Ammonium hydroxide (NH_4OH)**

NH_4OH is one of the commonly used alkali solutions in semiconductor manufacturing for cleaning organic compounds. Because of its constituents, N, H and O, the polyatomic interferences are similar to those caused by water in the plasma. However, 5% is the maximum recommended concentration that can be analyzed with the CN, CF and BN because of higher vapor pressures at room temperature. To stabilize signals of analytes and neutralize samples, adding HNO_3 might be better.

- **Tetramethyl ammonium hydroxide (TMAH)**

TMAH is also commonly used in semiconductor manufacturing for cleaning organic compounds, and is now also used for the digestion of blood and biological materials. Because of its constituents, C, H, N and O, there are few significant polyatomic interferences except ArC which interferes with Cr. Because of its strong alkaline character, the inert sample introduction system has to be used, and 5% is the maximum concentration that can be used with the CF and BN because of higher vapor pressures at room temperature**.**

Applications

When a sample contains a high matrix concentration, a signal suppression or enhancement due to a matrix effect might be seen. Clogging at the nebulizer or interfaces might also occur. In general, the maximum concentration for a matrix should be no more than 1000 ppm.

The following are the comments on each application field.

Environmental

- **Drinking water**

Drinking water can be directly analyzed after acidification with HNO_3. Drinking water typically contains a few tenths ppm of Na, Ca, Mg, K and Cl. In general, ArNa at m/z 63 interferes with Cu, but m/z 65 can be used. ArMg interferes with Zn at m/z 64, but m/z 66 and 68 can be used. CaO and KO interferences at m/z 60 and 55 are negligible; ClO and ArCl interferences are also negligible in most cases, the signal from ArCl at m/z 75 for As is corrected by an interference correction equation and m/z 82 is used for Se.

- **River water and sea water**

These samples are filtered by a 0.45 µm membrane filter right after collection to separate particulate and dissolved materials. Then the sample has to be acidified in order to prevent absorption on the inner surface of the container and precipitation of trace elements with major elements; HNO_3 should be used for acidification to obtain a pH less than 2.

Although higher salt concentrations might cause clogging at the tip of the interface cones, high matrix samples, even undiluted seawater which contains about 3% (w/v) salts can be directly introduced using the BN and Ni interface cones. Matrix suppression, however, occurs in the case of seawater. The signal can be reduced to about 1/3 to 1/5 of normal sensitivity, and polyatomic ions such as ArNa, CaO, CaOH, ArMg, ArCl and ClO interfere with elements at m/z less than 80. Se can not be analyzed at m/z 82 due to BrH interference. However, heavier elements such as Cd and Pb can be analyzed using internal standards.

NOTE

Matrix suppression is compensated for by internal standard correction. An element whose mass is close to that of the analyte is used as an internal standard . However, the behavior of higher ionization potential elements such as As and Cd are sometimes different from that of lower ionization potential elements. Therefore, Te would be recommended as an internal standard element for Cd.

For analysis of lighter mass elements in seawater, matrix separation is the only way to analyze them. Cation exchange chromatography separates matrix elements from the analytes.

Many different matrix elements may be found in waste waters. Therefore it is difficult to give a general description of their analysis. Matrix interference and matrix suppression are important considerations. The best way to analyze such an unknown sample is to dilute it 100 times with pure water and do a semiquantitative analysis. That will give an approximate concentration for each element in the sample, then proceed to a more detailed analysis using that information.

- **Soils and sediments**

To digest these samples completely, HF is commonly used with other acids such as HNO_3 or $HClO_4$. Open or closed vessel digestions are commonly used, however there are several advantages in using the microwave digestion that is described later, therefore this technique is recommended. A combination of HNO_3, HF and H_2O_2 with the microwave can digest these samples completely. For more details, refer to Chapter 3.

In the case of EPA Method 6020, a mixture of HNO_3 and H_2O_2 is used for sample preparation. The purpose of these analyses is to monitor toxic elements leached out from landfills, therefore complete digestion is not required. A 1 g sample is acid digested, and the digested sample is diluted with water up to 100 mL and filtered. The matrix concentration in the final solution will be much less than 1% because silicates cannot be digested by the acids.

In general, for long term analyses, the maximum matrix concentration in a sample solution should be less than 0.1%, or 1000 ppm.

The alkali fusion method is also used for digestion of these samples, but this method should be limited to the determination of Si.

Geological

It is basically same as the digestion procedure for soils and sediments.

Biological

- **Animal tissues**

Animal tissues are digested by HNO_3 using the microwave digester. The classic open vessel digestion with HNO_3 and $HClO_4$ is not recommended because As and Se, which are very important elements in biological study, may be lost during the digestion.

- **Urine**

Urine contains some particulates as well as higher concentrations of salt and protein. Therefore, filtration by a 0.45 μm membrane filter, followed by 10 times dilution with dilute HNO_3 is the commonly used technique.

- **Blood**

Because of its high viscosity and matrix, the direct analysis of whole blood is not possible, and many researchers are working on best digest methods. The following are some preparation procedures:

- Dilution by 1% HNO_3 by a factor of 10 and centrifugation. Then the supernatant fluid is analyzed. This technique is used at the Harvard School of Public Health and the Mayo Clinic, among others.
- Microwave digestion with HNO_3.
- Dilution by alkali solution. 0.5 mL of blood is diluted with 2 mL of diluent (ammonia / ammonium hydrogen phosphate / EDTA / TritonX-100).
- Digestion by TMAH.

Metallurgical

Metals can be dissolved by the chemicals described above. The final concentration of matrices should be less than 0.1%. Polyatomic interferences and matrix suppression should be taken into account.

Petrochemical

This sample type is one of the more difficult for ICP-MS. Carbon may deposit at the tip of the sampling cone, higher vapor pressure solvents may extinguish the plasma, lower vapor pressure solvents may remain in the sample introduction devices and some organic solvents dissolve the plastic used for the sample introduction system.

Some organic solvents can be analyzed directly by ICP-MS. The following is a brief summary of organic samples.

NOTE When O_2 is added to keep the interface free from carbon build-up, it is recommended to use the Pt interface, as this is more durable in the presence of excess O_2.

- **Methanol (CH_3OH)**

Methanol has a high vapor pressure which restricts its introduction into the plasma and too much sample loading may put out the plasma. Therefore, a special introduction device has to be used.

Using a small inner diameter torch injector reduces sample loading into the plasma, allowing the analysis of 100% methanol. The standard torch injector is 2.5 mm i.d., and there are 1.5 mm i.d. torch injectors as an option. Tygon tubing can be used, although the silicon tube is better.

The recommended preparation is dilution by water after pre-concentration by evaporation to dryness.

- **Acetone (CH_3COCH_3)**

Acetone also has a high vapor pressure and the same technique as for methanol can be applied. However, the Tygon tube cannot be used. Therefore, self-aspiration must be used. The addition of oxygen is required to prevent carbon deposition by forming CO_2. The recommended preparation is dilution by water after pre-concentration by evaporation to dryness.

- **Xylene ($C_6H_4(CH_3)_2$)**

Xylene is commonly used for solvent extraction. 100% xylene can be analyzed with the addition of oxygen. In general, 5% oxygen in the total flow of carrier and blend gas should be added. Excessively high concentrations of oxygen might cause deterioration of the interfaces.

- **Crude oil**

Crude oil is one of the difficult organic samples to analyze because of its higher boiling point and viscosity. There are two techniques for its analysis:

The **micro-emulsion** technique can mix crude oil with water: 1% of the crude oil and 1% surfactant solution such as TRITON-X100 are mixed and sonicated. The advantage of this technique is that it does not require a digestion process, which prevents loss of volatile organic compounds such as Hg and As.

Another good technique is microwave digestion with HNO_3. HNO_3 can digest almost all organic solvents.

- **Photoresist**

Photoresist is also extremely difficult because of its higher viscosity and boiling point.

NOTE

The difficult part of photoresist analysis is in the sample introduction: the photoresist remains in the spray chamber and sometimes in the torch, causing clogging in the torch. Since the photoresist reacts with ultraviolet radiation it can form a solid organic material, so ultraviolet radiation from the plasma can cause crystallization in the torch.

- **Gasoline**

Gasoline can be digested by microwave digestion.

Digestion Procedures

Open Vessel Digestion

Open vessel digestion is the classical technique that requires complex mixtures of acids and takes a few hours to a few days to digest a sample. For ICP-MS applications, this technique is not recommended and should be avoided. There is a contamination problem during the digestion and acid fumes cause pollution of the environment. Unfortunately, the EPA method requires this technique for the digestion of environmental samples.

Closed Vessel Digestion

The closed vessel digestion is a better technique than the open vessel. Teflon is commonly used as a container with a stainless steel jacket. The advantages of this technique over the open vessel are as follows:

- The pressure inside a vessel is higher than atmospheric, which increases the temperature of the solution.
- Contamination from the atmosphere can be avoided.
- Volatile elements such as As, Hg, Sb, Se and Sn will remain in the solution.

All these features reduce the time of digestion. However, extreme care should be taken, or the pressure inside the vessel may becomes too high and the vessel could explode.

Microwave Digestion

The most convenient technique will be the microwave digestion. Microwave energy is absorbed by dipole rotation and ionic conductance, causing rapid heating of not only the aqueous phase, but also the sample itself. Teflon is transparent to microwave radiation and favored for the vessel. The microwave digester is different from a conventional microwave oven used for cooking foods and is specially designed for digestion of samples, taking into account safety issues. The temperature of the inside vessel is measured and controlled; the pressure of the inside vessel is also measured and controlled. There is a place which releases pressure generated suddenly by reactions between chemicals and samples preventing explosion of the vessel.

There are several types of vessels for microwave digestion: PTFE is the most popular material but its purity is not high enough for ICP-MS; PFA has recently been applied to high purity samples, its purity is better than PTFE; quartz is also used for high purity samples.

Chromatography

One of the advantages of ICP-MS as a chromatography detector is that ICP-MS is a very good element specific detector. In the future, this technique is very important for the analysis of environment samples and biochemical samples.

Chromatography is also a very good technique to separate the sample matrix from the analytes of interest. There are four types of chromatography that can be used with ICP-MS: ion chromatography (IC), liquid chromatography (LC) and capillary electrophoresis (CE).

IC

Since most elements form cations or anions in solution, IC is a very good technique to use with ICP-MS. There are two types of columns, cation exchange and anion exchange.

Basically, the IC effluent conditions can be directly applied to ICP-MS, because the normal eluent flow rate for IC is about 1 mL/min which is acceptable for the ICP-MS. However, some eluents cause matrix suppression or clogging at the tip of the nebulizer and the interfaces cones.

The following separations have been performed using IC-ICP-MS and published:

- As speciation
- Cr speciation

- Transition metals analysis
- REEs analysis

LC

The application of LC to ICP-MS is more difficult than for IC, because the LC eluent is not always suitable for ICP-MS. Higher concentrations of methanol or acetonitrile can not be analyzed with the normal sample introduction system and phosphoric acid buffers are hard to introduce into the ICP-MS.

CE

CE shows remarkable separation capability. However, the flow rate is too small for ICP-MS. The typical sample uptake rate of the Agilent 7500 is 400 µL/min, and about 2 % of the sample actually goes into the plasma (10 µL/min). On the other hand, the typical flow rate of CE is 10 nL/min which is less than 1/10000 of the normal required flow rate of ICP-MS. Therefore, the additional eluent flow is required. Consequently, the detection limit of CE-ICP-MS becomes worse, around the ppb level at the best, similar to the detection limit of CE itself.

3

Analysis of Environmental Samples

Analysis of Environmental Samples

In this chapter, the analysis of environmental samples is described. River water and soil are used as typical examples.

Sample Preparation

There are several ways to prepare environmental samples as described in Chapter 3. EPA (Environmental Protection Agency) Method 200.8, 6020 (CLP-M) and Japanese regulations use the following procedures.

Aqueous Samples

♦ **EPA Method 200.8**

For the determination of dissolved elements, the sample must be filtered through a 0.45 µm pore membrane filter at the time of collection or as soon as practically possible. Use a portion of the sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid to pH < 2 immediately following filtration.

For the determination of total recoverable analytes, samples are not filtered, but acidified with (1+1) nitric acid to pH < 2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient).

Before analysis, add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) HNO_3 solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL sample).

Soil

♦ **EPA Method 200.8 (Reference - not yet approved for soil)**

For the determination of total recoverable elements in soils, mix the sample thoroughly to achieve homogeneity and accurately weigh a 1.0 ± 0.01 g portion of the sample. Transfer to a 250 mL beaker. Add 4 mL (1+1) HNO_3 and 10 mL (1+4) HCl. Cover with a watch glass and reflux the sample on a hot plate for 30 min.

Very slight boiling may occur, however, vigorous boiling must be avoided to prevent the loss of the HCl-H_2O azeotrope. (NOTE: adjust the temperature control of the hot plate such that an uncovered beaker containing 50 mL of water located in the center of the hot plate can be maintained at a temperature of approximately, but no higher than 85° C). Allow the sample to cool, and quantitatively transfer to a 100 mL volumetric flask. Dilute to volume with deionized water and mix. Centrifuge the sample or allow to stand overnight to separate insoluble material. Prior to analysis, pipette 20 mL into a 100 mL volumetric flask and dilute to volume with deionized water.

♦ EPA Method 6020 CLP-M Ver.9.0

Hot plate digestion procedure

Mix the sample thoroughly to achieve homogeneity. For each sample, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion and transfer to a beaker. Add 2 mL of (1+4) HNO_3, mix the slurry, and cover with a watch glass. Heat the sample and reflux for 40 min. (without boiling) at 95° C. Do not allow the volume to be reduced to less than 5 mL to maintain a covering of solution over the bottom of the beaker.

After the reflux step has been completed and the sample has cooled, add 2 mL of deionized water and 3 mL of 30% (v/v) H_2O_2. Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker. Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL of 30% H_2O_2.) Add 4 mL of (1+4) HCl and 10 mL of deionized water, return the covered beaker to the hot plate and heat for an additional 10 min. After cooling, filter and dilute to 200 mL with deionized water. The sample is now retained for analysis.

Block digestion procedure

Mix the sample thoroughly to achieve homogeneity. For each sample, weigh (to the nearest 0.01 g) a 1.25 to 1.85 g portion and transfer to a digestion tube. Add 12.5 mL of (1+1) HNO_3 and mix the slurry. Heat the sample and reflux for 40 min. without exceeding 95° C. Do not allow the volume to be reduced to less than 5 mL to maintain a covering of solution over the bottom of the digestion tube.

After the reflux step has been completed and the sample has cooled, add 2.5 mL of deionized water and 3.75 mL of 30% (v/v) H_2O_2. Return the digestion tubes to the block digestion unit for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the digestion tubes. Continue to add 30% H_2O_2 in 1.25 mL aliquots with warming until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 12.5 mL 30% H_2O_2.) Add 5 mL of (1+4) HCl and 12.5 mL of deionized water, return the covered beaker to the hot plate and heat for an additional 10 min. After cooling, filter and dilute to 250 mL with deionized water.

- **EPA Method 3050B (related to EPA Method 6020)**

Mix the sample thoroughly to achieve homogeneity and sieve if necessary using a USS #10 sieve. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with low percent solids a larger sample size may be used as long as digestion is completed. Add 10 mL of (1+1) HNO_3 , mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to 95° C and reflux for 10-15 min. without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 min. If brown fumes are generated, indicating oxidation of the sample by HNO_3. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling of solution over the bottom of the vessel at all times. After cooling, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel. Continuing to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.) Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95° C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times. After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

♦ Microwave Digestion Procedure

EPA Method 3015

This method is used as a digestion procedure for analysis of aqueous samples, mobility-procedure extracts and wastes that contain suspended solids. A part of this method was approved for ICP-AES, DCP-AES and FLAA, and is under investigation for ICP-MS. The digestion should be performed with HNO_3.

EPA Method 3051

This method is under investigation and will be applicable to analysis of sludges, sediments, soils and oils. Digestion should be performed with HNO_3 and the sample has to be filtered after digestion.

Tuning

Tuning for environmental applications is a little different than tuning for other applications.
When a sample with a high matrix concentration is introduced to the plasma, plasma energy is consumed to break down the matrix. This may mean that the target measurement elements are not fully ionized. In this case, the elements are measured at lower concentrations than are actually present. The best countermeasure is to dilute the sample. However, this problem can also be reduced to a certain extent by adjusting the tuning. 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. This can be achieved by the following adjustments:

- Higher RF power (1.3 to 1.6 kW)
- Lower combined gas flow rate for carrier gas and blend gas (0.05 to 0.10L/min less than usual)
- Longer sampling depth position (6 to 9 mm)
- Lower peristaltic pump speed

The lower the CeO to Ce ratio (CeO/Ce), the better the results you will get. The typical value of CeO/Ce should be $< 0.5\%$. It should be noted that these changes might cause instability of signal and lower sensitivity. However, instability of signal in the tuning mode doesn't always cause bad precision in data acquisition mode. The number of scans in data acquisition mode is 100, while that in tuning is 1, which compensates for signal instability in the tuning mode. The recommendation is $< 15\%$ rsd in tuning mode (10 ppb solution, 0.1 sec).

The required dynamic range for typical environmental samples is on the order of very low ppb to mid ppm.

Standard Solutions Preparation

Standard Solution

In general, the error in the calibration curve produced by the least squares method is lowest in the higher concentration range. Therefore, a calibration curve should be made for a concentration range that covers the concentration of the sample. However, the ICP-MS has a wide linear dynamic range in practice and quantitative results can be obtained with comparatively little error at down to one tenth the maximum concentration level of the calibration curve.

In contrast, the error is large for quantitative analysis at lower concentrations when the range of the calibration curve includes several high concentration levels: points at the high end of the range may significantly shift the line of best fit if the least squares method is used directly, and the error in these points may affect the entire range (Fig. 3-1). In this case, the weighted least squares method should be used to weight the standard deviation of each point that gives more weight to points with a low standard deviation. For example, accurate quantitative analysis cannot be achieved for 1 ppb samples if the calibration curve is produced from levels of 0, 50 and 100 ppb. For such samples, use a calibration curve with a maximum concentration of about 10 ppb.

When the concentrations of analytes in samples vary through a wide range, calibration curves should include several points such as 0, 0.1, 1, 10 and 100 ppb, and selecting adequate calibration points for each sample improves the accuracy of quantitative calculations.

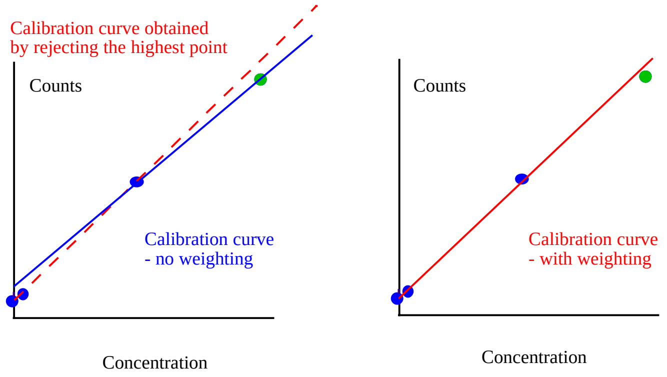

Fig. 3-1 Weighted and Unweighted Calibration Curves

Internal Standard Solution

This method is recommended in the following cases:

1. When measuring samples with a high matrix concentration.

   When the total matrix concentration exceeds 100 ppm in, for example, sewage or environmental water. In such cases, there are Non-spectroscopic Interferences. They are physical effects which occur in the plasma and the center chamber region of the instrument which effect the analyte signal in a non-specific way. Typically, the result is suppression of signal across a range of masses or sometimes across a range of ionization potentials. For example, very high concentrations of high mass matrix elements can suppress lower mass elements via space charge effects. Lighter mass ions are repelled from the ion beam by the presence of heavier ions.

   These interferences can be also corrected by the method of standard additions.

2. When measurement takes a long time due to large numbers of samples, internal standardization compensates for sensitivity drift.

   This is the method by which the analyte signal drift is corrected by the signal of another element (the internal standard element) added to both the standard solution and the sample. If the signal of the analyte is affected for any of the above reasons, the internal standard element should also be affected in the same way, therefore the ratio of analyte to internal standard element is not affected (Fig. 3-2).

   When the signals of blank, standard solution and sample are **a0, a1, a2**, **a3**, and **as,** and the signals of internal standard in each solution are **b0, b1, b2, b3** and **bs**, then the vertical and horizontal axes of calibration curve are the **a to b ratio** and the concentration as shown in Fig. 3-2. When the ratio of sample is **as/bs**, the concentration of sample (**cs**) can be calculated according to the calibration curve.

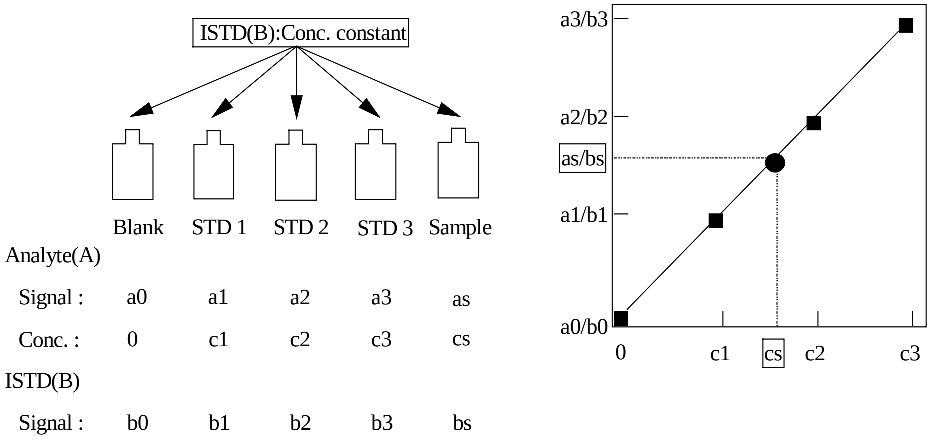

Fig. 3-2 Internal Standard Method

In the calibration report or the calibration graphs, the ratio of the analyte to internal standard is given, not the counts.

Matrix effects are not normally an issue with drinking water, but the use of internal standards is recommended if the water hardness is high. The method of standard additions can also be used for this purpose.

Selecting Internal Standard Elements

Since the analytes and internal standard elements should show the same behavior, the internal standard elements should be selected to have mass numbers and/or ionization potentials similar to the analytes: e.g. Bi (209 AMU) is a good internal standard for the measurement of Pb (208 AMU) because of the proximity in mass number, and Zn (9.39 eV) is good for measurement of Cd (8.99 eV) because of it’s similar ionization potential.

As a rule, elements that are not originally present in the sample should be selected. However, an element that is present in the sample might be used when the quantity of the element is sufficiently small compared to the signal of the added internal standard. As a guide, semiquantitative analysis should be performed first to determine which elements are present in a sample. Elements that are commonly used as internal standards are Li, Be, Sc, Co, Ga, Rb, Y, Rh, In, Cs, Ce, Tl and Bi.

Recommendation

EPA Method 200.8	Li (6 AMU), **Sc**, **Y**, Rh, **In**, **Tb**, Ho, Lu and **Bi**

Internal standards recommended for use with this method are shown in bold face.

EPA Method 6020	Li (6 AMU), Sc, Y, Rh, In, Tb, Ho and Bi

Li may be present in environmental samples, therefore a solution artificially enriched in ^{6}Li is recommended, although it is expensive.

Concentration of Internal Standards

When the internal standard elements are directly added to the sample and standard solutions, the concentration of each internal standard element after addition should be the same in both the sample and the standard solutions used to produce the calibration curve. In addition, the concentration of internal standards in the standard solution at level 1 (the calibration blank in the calibration table) and that in the samples must be the same and must not be 0.

When the peristaltic pump is used for on-line introduction of an internal standard, the internal standard solution must be prepared separately from the sample and the calibration curve standard solutions. The inner diameter of the internal standard introduction tubing is much smaller than the inner diameter of the sample introduction tubing and so the uptake rate of the internal standard solution is about 1/20 of the sample uptake rate. The internal standard solution is diluted by about 20 times by the sample, and therefore the internal standard solution must be prepared with a higher concentration; 1 ppm ISTD is normally appropriate.

Measurement

The internal standard elements must be selected in the acquisition parameters as well as the analytes. An integration time of 1 to 3 seconds per element is recommended. Since the inner diameter of the internal standard tube is small, it can take extra time to get a stable signal due to analyte adsorption, so that the first analysis must be started 3 minutes after the signal of the internal standard element appears. In general, longer stabilization times are required for on-line internal standard addition.

Standard Addition to a Sample

This method is recommended to correct matrix effects such as signal suppression or enhancement. A standard solution is directly added to a sample. Since a small amount of the standard solution is added to the sample, the matrix effect must show the same behavior for both the sample and the spiked solution. This effect can be used to correct for signal suppression or enhancement.

When the signals of sample and spiked solutions are **s0, s1** and **s2**, and the signal of a blank is ***bkg***, the calibration curve obtained by a least squares fit of the points will be as shown in Fig. 3-3. Using the ***bkg*** may be a problem if the sample matrix is quite different from the ***bkg*** matrix.

The concentration of analyte added is **p1** and **p2**, and consequently **c0** is the concentration of analyte in the sample. When the concentration of the sample is c0, the actual analyte concentrations in the spiked solutions are **c1** and **c2**; e.g. when 10 ppb (p1) and 20 ppb(p2) are added to the sample and the sample concentration is 2 ppb(c0), the actual concentrations of the spiked samples are 12 ppb (c1) and 22 ppb (c2).

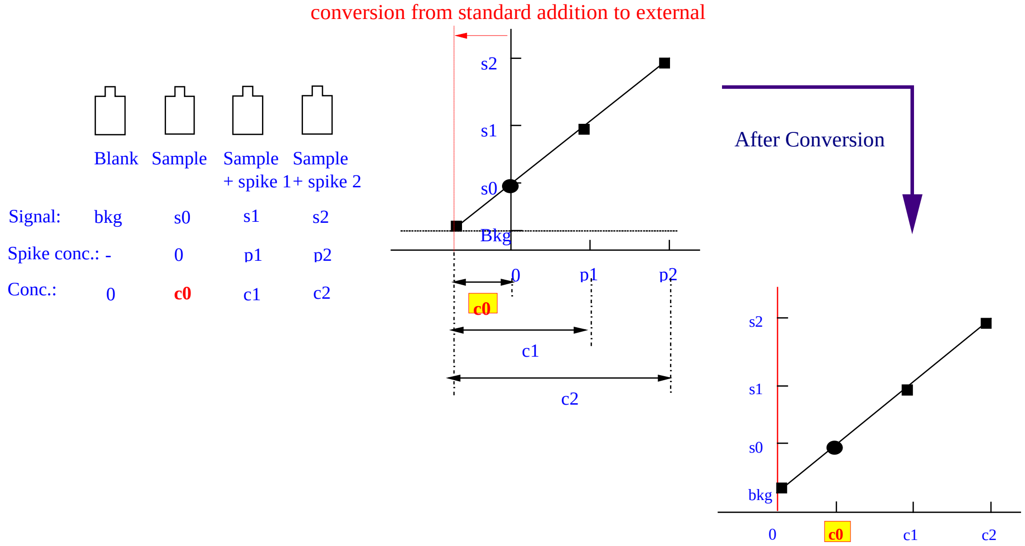

Fig. 3-3 Method of Standard Additions

Once a standard addition calibration curve is made for one sample, this calibration curve can be converted to an external calibration curve. After conversion, the vertical axis shifts to the ***bkg*** point and the point at the concentration of the background becomes the y-intercept. The concentration of the background becomes 0 and the concentrations of other points are recalculated relative to the background; concentrations of other points are combined values of spiked sample concentrations and sample concentrations. After the conversion, the calibration point of a 10 ppb spiked solution becomes 12 ppb when using the above example. The calibration table is also updated according to the calibration curve.

If the matrix of other samples is similar to the first sample, the converted external calibration curve can be used.

NOTE

The method of standard additions should not be used for an analyte that suffers from significant polyatomic interference, since it is impossible to know what part of the signal in the sample is due to analyte, and what part is due to an interference.

Concentration of Standard Solutions

The concentration of each element after addition to the sample should be of the same order (preferably half to x2) the original concentration in the sample. If the concentration of the standard and the original concentration of the sample are very different, the calculation error will become significant.

Measurement

If a signal contains some background such as random background and/or memory from the sample introduction system, it may also be calculated as the analyte concentration contained in the sample, which might cause a quantitation error. To avoid that, the measurement of pure water or nitric acid diluted with pure water is recommended and used as the background file.

Data Acquisition

There are two ways to set data acquisition parameters such as acquisition mode, measurement mass, peak pattern, integration time and repetition. One is from ***Acquire Data>>Main Panel*** and the other is from ***Method>>Edit Entire Method.*** Refer to the *Agilent 7500 ChemStation Operator's Manual* to set each parameter. In addition, the setting of interference equations is also described.

Interference Equations

Possibility of Interferences

Spectroscopic Interferences are interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass to charge (m/z) ratio as the analyte elements.

They can be isobaric, polyatomic, oxide, and doubly charged ions. Isobaric interferences are isotopes of other elements which have the same nominal mass, which can usually be corrected for by the use of elemental interference equations (mathematical interference correction; called an Interference Equation in the ChemStation). These equations are defined in the various EPA methods and use the naturally occurring isotope ratios of most elements to estimate and allow the subtraction of isobaric interferences.

Interference Equation

The following are examples of interference equations:

<Example>

When As is measured in a Cl matrix sample, Cl bonds with Ar and ArCl polyatomic ions are formed, one of which has the same m/z as As (75). As a result, quantitative analysis can have an error due to ArCl. In this case, the knowledge that ArCl is present at m/z 75 and m/z 77 in the proportion to the isotope ratio of ^{35}Cl : ^{37}Cl, 75.8% : 24.2%, can be used to correct for the interference at m/z 75. The ArCl counts at m/z 75 are calculated based on the m/z 77 ArCl count. By subtracting ArCl from the count at m/z 75, the correct As concentration can be obtained.

However, as Se has an isotope at m/z 77, any Se in the sample will increase the m/z 77 counts accordingly. Fortunately, Se also has an isotope at m/z 82. By measuring the Se at m/z 82, the Se count at m/z 77 can be estimated (Fig. 3-4), and subtracted from the counts at m/z 77 to calculate the counts due to ArCl.

(1) Estimate ^{77}Se based on ^{82}Se.

(2) Estimate ^{75}ArCl based on ^{77}ArCl.

(3) The remaining m/z 75 counts are due to As.

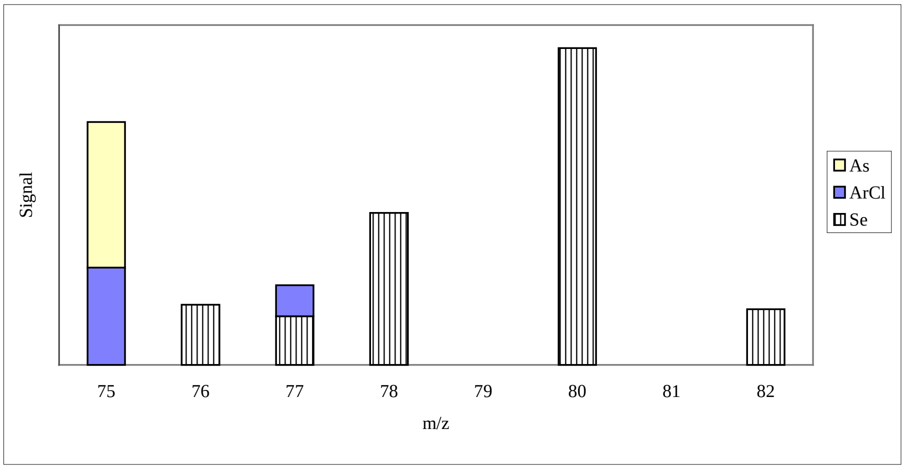

Fig. 3-4 Isotope Patterns of As, Se, and ArCl

As the result, the As count is obtained by the following interference equation:

(1.000)(75C) - (3.127)[(77C) - (0.874)(82C)]

(where 75C, 77C and 82C are the counts on m/z 75, 77 and 82 respectively)

Therefore, m/z 77 and m/z 82 must be measured as well as m/z 75 to perform quantitative analysis of As by using the interference equation. Be sure to select the additional mass numbers specified in the interference correction equation. These are automatically selected by the ChemStation provided the interference correction equations are loaded at the time masses are selected in the method.

The interference equation can also be used for elements such as Pb, for which the isotope ratio varies for different sample sources. In this case, the sum of the Pb isotopes should be measured and used to calculate the Pb concentration.

The equations for As and Cd are derived as follows:

- **ArCl on As**

If there is an ArCl interference at m/z 75, it will be corrected for by the following equations:

As(75) = M(75) - 75.8/24.2 * ArCl(77)
= M(75) - 3.132 * ArCl(77) --- (1)

But at m/z 77 there is Se, and ArCl at m/z 77 will be corrected for by the following equation:

ArCl(77) = M(77) - 7.6/8.7 * Se(82)
= M(77) - 0.874 * Se(82) --- (2)

Then this equation should be applied to equation (1):

As(75) = M(75) - 3.132 * (M(77) - 0.874 * Se(82))
= M(75) - 3.132 * M(77) + 2.736 * Se(82)
--- (3) considering ArCl and Se

But there is a Kr interference at m/z 82 in some cases, arising from Kr found in the Ar supply (mainly from bottled Ar) therefore the signal at m/z 82 should be corrected as follows:

Se(82) = M(82) - 11.6/11.5 * Kr(83)
= M(82) - 1.009 * Kr(83) --- (4)

If this equation is applied to the equation (3):

As(75) = M(75) - 3.132 * M(77) + 2.736 * (M(82) - 1.009 * Kr(83))
= M(75) - 3.132 * M(77) + 2.736 * M(82) - 2.760 * Kr(83)
--- (5) considering ArCl, Se and Kr

There can sometimes be an additional, small interference on m/z 77, due to ArArH. It can be compensated for in the following way:

At first, a blank solution must be analyzed, and m/z 77 and 80 should be measured. The ratio of 77/80 will be calculated and this ratio will be entered into equation (3) with (4).

As(75) = M(75)-3.132 * (M(77)-0.874 * M(82) + 1.009 * Kr(83)
- ratio of 77/80 * M(80))
= M(75) - 3.132 * M(77) + 2.736 * M(82) - 2.760 * Kr(83)
+ 3.132 * ratio of 77/80 * M(80)
--- (6) considering ArCl, Se, Kr and ArArH

♦ **Cd on MoO and Sn and Pd**

For Cd analysis, interference due to mainly MoO and Sn is possible. There are two variants of equation recommended by the EPA:

When m/z 114 is used (EPA Method 6020), MoO and Sn should be corrected based on m/z 108 and 118.

Cd(114) = M(114) - 24.1/14.8 * MoO(108) - 0.65/24.2 * Sn(118)
= M(114) - 1.628 * MoO(108) - 0.0269 * Sn(118) --- (7)

But, at m/z 108 there is a contribution from Cd and it must be corrected for:

MoO(108) = M(108) - 0.89/1.3 * Cd(106)
= M(108) - 0.685 * Cd(106) --- (8)

When this equation is put into equation (7):

Cd(114) = M(114) - 1.628 * (M(108) - 0.685 * Cd(106)) - 0.0269 * Sn(118)
= M(114) - 1.628 * M(108) + 1.115 * Cd(106) - 0.0269 * Sn(118)
--- (9) considering MoO and Sn

If there is a Pd contribution, which interfere with m/z 106 and 108. Therefore m/z 106 on Cd and m/z 108 on Mo must be corrected as follows:

Cd(106) = M(106) - 27.3/22.3 * Pd(105)
= M(106) - 1.224 * Pd(105) --- (10)

MoO(108) = M(108) -0.89/1.3 * Cd(106) - 26.5/22.3 * Pd(105)
= M(108) - 0.685 * (M(106) - 1.224 * Pd(105)) - 1.188 * Pd(105)
= M(108) - 0.685 * M(106) - 0.349 * Pd(105) --- (11)

When equation (11) is put into equation (7):

$$\begin{aligned}
\mathrm{Cd}(114) &= \mathrm{M}(114) - 1.628 \ast (\mathrm{M}(108) - 0.685 \ast \mathrm{M}(106) - 0.349 \ast \mathrm{Pd}(105)) \\
&\qquad - 0.0269 \ast \mathrm{Sn}\ (118) \\
&\mathbf{= M(114) - 1.628 \ast M(108) + 1.115 \ast M(106) + 0.568 \ast Pd(105)} \\
&\qquad \mathbf{- 0.0269 \ast Sn\ (118)} \\
&\qquad \textbf{--- (12) considering MoO, Cd and Pd}
\end{aligned}$$

When m/z 111 is used (EPA 200.8), MoO should be corrected based on m/z 108. Cd contribution on m/z 106 must also be considered as described in equation (8):

$$\begin{aligned}
\mathrm{Cd}(111) &= \mathrm{M}(111) - 15.9/14.8 \ast \mathrm{MoO}(108) \\
&= \mathrm{M}(111) - 1.074 \ast (\mathrm{M}(108) - 0.685 \ast \mathrm{Cd}(106)) \\
&\mathbf{= M(111) - 1.074 \ast M(108) + 0.735 \ast Cd(106)} \textbf{ --- (13) considering MoO}
\end{aligned}$$

When there is a Pd contribution, m/z 108 must be corrected using equation (11):

$$\begin{aligned}
\mathrm{Cd}(111) &= \mathrm{M}(111) - 15.9/14.8 \ast \mathrm{MoO}(108) \\
&= \mathrm{M}(111) - 1.074 \ast (\mathrm{M}(108) - 0.685 \ast \mathrm{M}(106) - 0.349 \ast \mathrm{Pd}(105)) \\
&\mathbf{= M(111) - 1.074 \ast M(108) + 0.736 \ast M(106) + 0.375 \ast Pd(105)} \\
&\qquad \textbf{--- (14) considering MoO and Pd}
\end{aligned}$$

The folowing equations are EPA recommendation.

EPA Method 200.8

As	(1.000)(75C) - (3.127)[(77C) - (0.815)(82C)]
Cd	(1.000)(111C) - (1.073)[(108C) - (0.712)(106C)]
Pb	(1.000)(206C) + (1.000)(207C) + (1.000)(208C)
Mo	(1.000)(98C) - (0.146)(99C)
V	(1.000)(51C) - (3.127)[(53C) - (0.113)(52C)]
In	(1.000)(115C) - (0.016)(118C)

EPA Method 6020 (CLP-M Ver.9)

As	(1.0000)(75C) - (3.1278)(77C) + (1.0177)(78C)
Cd	(1.0000)(114C) - (0.0149)(118C) - (1.6285)(108C)
Pb	(1.0000)(208C) + (1.0000)(207C) + (1.0000)(206C)
Se	(1.0000)(78C) - (0.1869)(76C)
V	(1.0000)(51C) - (3.1081)(53C) + (0.3524)(52C)
^{6}Li	(1.0000)(6C) - (0.0813)(7C)
In	(1.0000)(115C) - (0.0149)(118C)

‘m’ C = the total ion count at m/z ‘m’

In the case of EPA methods, the values are different from the theoretical values, because they contain some experimental factors. Moreover, interferences are matrix dependent. They might also vary depending on the instrument and conditions

NOTE

Interference Equations are not applicable when polyatomic ion signals are much higher than the analyte signal. If the signal of a polyatomic ion is 10,000 counts, the standard deviation will be theoretically about 100 counts. This deviation will affect an analyte signal and if the analyte signal is 100 counts, it will be impossible to calculate accurately. If several correction factors are used in an equation, errors will also be accumulated with each term. In addition, the imprecision from an internal standard will affect the measurement when an internal standard correction is applied.

Entering Interference Equations

To enter interference equations, select ***Methods>>Edit Interference***.

Refer to the *Agilent 7500 ChemStation Operator's Manual* for more details.

NOTE

All parentheses in the interference equation should be multiplied out before creating the equation in the ChemStation software, since the software does not recognize parentheses.

The interference equation must be set up before selecting element in the acquisition parameters. When an element is selected, related masses based on the interference equation will be automatically selected. However, there is no direct link between the database of edit interference equation and edit acquisition parameters, and the related mass is not selected automatically, only when the interference equation is set.
It is recommended to always acquire data with the interference equations selected, to ensure that all the appropriate masses are selected.

Acquisition Parameters

Measurement Mass Number

Depending on the isotope, interferences can occur due to polyatomic ions or isobaric overlap. Therefore, isotopes that do not suffer interferences but still have a sufficiently high isotopic abundance should be chosen.

The following isotopes are normally recommended for analysis (Table 3-1). Some of them are different from the default mass numbers recommended by the ChemStation. In this case, double-click on the element button in the periodic table to display the ***isotope selection*** window, then select the mass number to be analyzed. Select multiple isotopes if in doubt. The default mass can be edited by selecting ***AcquireData>>Edit AMU select file***. There are also remarks regarding interferences, given here for guidance.

The Background Equivalent Concentrations (BEC) of common interferences due to polyatomic ions is given in Table 3-2.

Table 3-1 Recommended Masses for Analysis

Analyte	Mass number (AMU)	Remarks
Ag	107	
Al	27	Dilution sometimes required.
As	75	Interference from ArCl occurs if the Cl concentration is high.
B	11	**Do not introduce high concentrations** as this element causes memory problems in the sample introduction system.
Ba	138	
Be	9	Difficult to ionize. Increased plasma temperatures help.
Cd	111, 114	Difficult to ionize. Increased plasma temperatures help.
Ca	43, 44	Use m/z 43 for samples in the order of several tens of ppm.
Cr	52	ClO interferes at m/z 53.
Co	59	
Cu	65	m/z 63 suffers interference from ArNa.
Fe	54, 56, 57	Suffers interference from ArN, ArO and ArOH respectively. m/z 54 or 57 are normally the best choices using normal. CaO/Ca is about 0.02%.
Hg	202	Difficult to ionize. Also, easily adsorbed into containers, etc. **Do not introduce high concentrations** as this element causes memory problems in the sample introduction system
K	39	Dilution sometimes required.
Mg	24, 25	Use m/z 25 for samples containing ppm levels..
Mn	55	Interference from KO can occur if the K concentration is very high.
Mo	95, 98	
Na	23	Dilution sometimes required.
Ni	60	Interference from CaO occurs if the Ca concentration is high.
Pb	206, 207, 208	Somewhat susceptible to memory effects if high concentrations are aspirated.
Sb	121	
Se	77, 82	Interference from BrH can occur if the Br concentration is high.
Th	232	
Tl	205	
U	238	
V	51	Interference from ClO occurs if the Cl concentration is high.
Zn	66	Difficult to ionize. Increasing the plasma temperature helps.

Table 3-2 Background Equivalent Concentrations (BEC) of Common Interferences (each matrix conc. is 50 ppm)

m/z	Element	Pure water	1% HNO3	Na	Mg	Si	Cl	K	Ca
52	Cr	ArC 1							
53	Cr						ClO 0.2		
54	Fe		ArN 10						
55	Mn								
56	Fe	ArO 100			MgO2 60				CaO 10
57	Fe	ArOH 15			MgO2 8				CaOH 30
60	Ni								CaO 0.1
61	Ni								CaOH 2
62	Ni								
63	Cu			ArNa 1					
64	Zn				ArMg 2				
65	Cu				ArMg 0.2				
66	Zn				ArMg 0.4				
67	Zn						ClO2 0.1		
68	Zn					ArSi 0.8			
75	As						ArCl 0.05		
76	Se	Ar2 150							
77	Se						ArCl 0.2		
78	Se	Ar2 15							
82	Se								
92	Mo								
94	Mo								
95	Mo							ArOK 0.04	
96	Mo					ArSi2 0.2			
97	Mo								
98	Mo					ArSi2 0.01			
100	Mo								

<Conditions> (Unit : ppb)

RF power : 1.35 kW Carrier gas : 1.2 L/min.

Sampling depth : 7 mm Sample uptake : 0.5 mL/min.

Peak Pattern

For normal quantitative analysis, select ***[Full Quant] (3 points/mass).***

Integration Time

Increasing the integration time gives better precision but the required measurement time increases.
Refer to ‘Detection Limits’ in Chapter 1.

Peri-pump Program

Peri-pump setting for environmental applications is a little different than normal conditions. Longer rinse time might be needed because of higher concentration samples. Optional Rinse (about 2% HNO_3) is also recommended when the ASX-500 Autosampler is used. A correctly working system should be able to wash out a 1 ppm solution of most elements to <= 1 ppb in a reasonable (1-2 min.) time. If not, check the following subjects.

- Shorten all sample introduction system tubing as much as possible, especially any tygon tubing, such as the tails on the peri-pump tubing.
- Look for sample leakage into the space between the inner and outer tubes on the ASX-500 sample probe.
- Replace the blank solution and the blank bottles, these can become contaminated.
- Look for dead volume in the throat of the concentric nebulizer and eliminate it.
- Clean, thoroughly, the entire sample introduction system. This includes replacing pump tubes, bottles, all sample tubing, cleaning nebulizer, spray chamber, spray chamber end cap, sampler and skimmer. Detailed instructions for cleaning are in the *Agilent 7500 ICP-MS Hardware Manual.*

Data Analysis

Set the ***[Interference Correction]*** check box to ***on*** in the window displayed by selecting ***Data Analysis>>Method>>Set Correction***. If set to ***on***, the data being analyzed will be corrected for interferences before being calculated, and the .**D#** file extension is used.

NOTE

The error “No Data to Correct” upon loading a data file into data analysis might be occurred. This is a result of not acquiring all the masses that are specified in the interference equations. It happens if equations are entered or edited after elements are selected for data acquisition.

Also, the data in any data file loaded while the check box is on is processed using the specified interference equation. If set to ***off***, subsequent data is loaded without correction. When using an interference equation in quantitative analysis, set the ***[Interference Correction]*** check box to ***on*** before selecting the data file for producing the calibration curve.

Background Subtraction and Blank Subtraction

There are two types of data correction in data analysis - background subtraction and blank subtraction.

The background subtraction only subtracts one spectrum from another, and is used only for visual inspection of spectral data. All data points in a sample spectrum are subtracted by each data point in the background spectrum; the internal standard signal will also be subtracted, so the background subtraction cannot be used for quantitation.

NOTE If the number of repetitions is more than two, subtraction will be performed in each repetition. In this case, the average data is used as the background data file. After the subtraction of each repetition, the average data will be calculated. Even though the same data file is used for the sample and the background, the subtraction result may not equal 0.

The blank subtraction is used for subtraction of the blank concentration from a sample concentration. This subtraction will be performed after quantitative results are calculated, and is used to correct for reagent blanks in quantitative analysis.

Semiquantitative Analysis

The Agilent 7500 has an intelligent semiquantitative analysis calculation routine that automatically checks for interferences. The process by which this takes place is described below, where every mass is examined individually for sufficient signal and the presence of interferences.

1. Check whether the signal is higher than the minimum peak value set in the ***SemiQuant*** parameters. If it is smaller than the minimum peak, the signal is reported ***'not detected'***. If the signal is higher than the minimum peak, go to the next step.

2. Check whether the signal after subtraction of the background signal is higher than 3 % of the background signal. If the signal is high enough, go to the next step.

3. Check whether the isotope ratio is better than or equal to ± 10% of theoretical ratio. All isotopes are measured and if the ratio is a good enough fit, calculation will proceed. If the ratio is a poor fit, go to the next step.

4. Check whether there is an interference due to oxide. If the signal 16 AMU lower than the target mass is high, there might be an oxide interference. The signal of the target mass must be higher than or equal to 1% of the signal that is 16 AMU lower than the target mass. Ge at mass 72 is an exception due to the presence of ArO at mass 56.

5. Check whether there is interference due to hydride. If a signal that is 1 AMU lower than a target mass is high, there might be a possibility of hydride interference. The signal of target mass must be higher than or equal to 1% of the signal that is 1 AMU lower than the target mass.

6. Check whether there is interference due to doubly charged species. If the signal at twice the target mass is high, there might be a possibility of doubly charged interference. The signal of target mass must be higher than or equal to 1% of the signal that is twice the target mass. Li at mass 7 is exception due to the presence of N_2 at mass 14.

7. Check whether there is interference due to a dimer. If the signal that is half the target mass is high, there might be a possibility of dimer interference. The signal of the target mass must be higher than or equal to 0.1% of the signal at half the target mass. Mass 7 for Li, 24 for Mg, 60 for Ni, 72 for Ge are exceptions due to the presence of H_2 at mass 3, C_2 at mass 12, NO at mass 30 and Ar at mass 36.

8. Check whether there is interference due to argide. If the signal at 40 AMU lower than the target mass is high, there might be a possibility of argide interference. The signal of the target mass must be higher than or equal to 0.1% of the signal at 40 AMU lower than the target mass.

To add checks for other interferences such as chlorides and nitrides, the factors can be edited in the ***win.ini*** file. Under the ***[PCS]*** section, the SEMIQFACTOR parameter must be edited. To set a check for chloride interference add the following SEMIQFACTOR line as follows:

```
SEMIQFACTOR8=CHLORIDE,35,0.01,75
```

Where:

CHLORIDE = flag
35 = amu difference from target mass
0.01 = limit value in %/100
75 = an exception mass

The algorithm created is as follows:

If a peak at a mass 35 amu lower than the target mass is greater than 1% of the target mass, flag “chloride” as the interference. An exception would be to As at mass 75 (since this is normally corrected for with an interference equation).

Up to 15 factors can be created and set.

NOTE

If the m/z number used for semiquantitative analysis is changed, the original response factor which is the value for the default m/z must also be changed as it doesn’t change automatically. Based on the natural isotope abundance, you can estimate the new response factor for the mass you select.

Verifying Quantitative Results

The following methods are available to verify that quantitative results are correct:

- Recovery test
  Perform quantitative analysis again after adding a known concentration of the measured elements to the sample, then compare the results with the results of the original sample. Verify that the added concentration was recovered accurately.

- Dilution test
  Dilute the sample, then check that the quantitative results for the diluted and undiluted samples match.

- Measure a reference standard material
  If you can obtain a reference standard material that is similar to the sample being measured, you can use the standard to verify your results.

All these methods are used in USEPA Method 6020 (CLP-M).

Worked Examples

The following examples take the user through some of the basic parts of the ChemStation software to provide some initial software training.

Soils (IAEA SOIL-7)

Sample Preparation

The following method allows almost complete digestion of soils and sediments: Mix the sample thoroughly to achieve homogeneity. For each sample, weigh about a 0.1 g portion of the sample and transfer to a digestion vessel. Add 0.7 mL of concentrated HNO_3 and 1 mL of deionized water. Digest the sample for 60 min. at 600 W by microwave heating. After cooling, add 0.3 mL of HF and digest the sample for 60 min. at 600 W by microwave heating. After cooling, dilute to 100 mL with deionized water.

Semiquantitative Analysis

Normally as a first step, semiquantitative analysis is recommended to give the approximate concentrations of analytes -this is useful to make standard solutions for the calibration curve.

1. Set the acquisition parameters as follows:
   Measurement m/z number --- all
   Peak pattern --- Semi Quant (6 points/mass) to check for spectral interferences
   Integration time --- 0.05 sec
   Repetition --- 1

2. Analyze a blank (1% HNO_3) first, then analyze a 10 ppb standard solution (normally used for tuning).

3. Correct for the response factor for semiquantitative analysis using the file for the standard solution, and use the file for the blank solution as the background file. Refer to the *Agilent 7500 ChemStation Operator's Manual* for more detail.

4. Analyze the sample, then identify some peaks using the ***[Template]*** and label them, then get the semiquantitative result in ***[Data Analysis]***.

Refer to the *Agilent 7500 ChemStation Operator's Manual* for more detail.

The following items can also be selected in SemiQuant.
- Internal standard correction
- Subtraction of the blank data file

Refer to the *Agilent 7500 ChemStation Operator's Manual* for more detail.

NOTE Only the highest point of the 6 points is used for semiquantitative analysis. Therefore the counts in **Tabulate/mass** and those in the semiquantitative report will be different.

Quantitative Analysis

1. Based on the semiquantitative result, quantitate by the method of standard additions as follows:
   Solutions --- pure water, sample, sample + STD 1, and sample + STD 2
   (Select the appropriate concentrations for STD 1 and 2 based on the semiquant results)
   Analytes --- V, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, and Pb

2. Set the acquisition parameters as follows:
   Measurement mass number and integration time ---Select as appropriate
   Peak Pattern --- Full Quant (3 points/mass)
   Repetition --- 3

3. Analyze pure water which is used for the background data file, then the sample and sample + spike solutions.

4. Make a calibration curve. ***Standard Addition*** must be selected in ***Data Analysi>>Calibrate>>New.*** And a background data file is also selected as well as sample data files in ***Standard Data Files.*** **-1 or bkg** must be entered as concentration. With the calibration curve of each element, the concentration is displayed.

When generating the report later on, the quantitative report represents the concentration of the sample used for the standard addition no matter what data file is loaded. The standard addition calibration curve must be converted to an external calibration curve prior to quantitating other samples. (by clicking ***Calibrate>>Convert to Calibration Method)***

Trace Elements in Water (NIST SRM 1643)

Sample Preparation

None needed (already acidified)

Quantitative Analysis

Create a sequence using the ASX-500 Autosampler.

1 Make the standard solutions for the calibration curve as follows:
Standard solutions --- blank, 10, 50 and 100 ppb mixed solution
Analytes --- Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, and Pb
Internal standard elements --- Sc (for Al, V, Cr, Mn, Co, Ni, Cu, Zn and As),
In (for Cd) and Ho (for Pb)

2 Set up the method and the sequence.
Set the acquisition parameters as follows:
Measurement mass number and integration time --- Select as appropriate
Peak Pattern --- Full Quant (3 points/mass)
Repetition --- 3

NOTE

Using both interference equations and internal standard correction, at first raw counts are corrected by the interference equation, and then the internal standard correction is performed. Therefore, ISTD selection for masses used in the interference equation (the masses in parentheses) is not necessary in the calibration table.

Remember, background subtraction subtracts the raw data, before ISTD correction, so it cannot be used for quantitation, since it would subtract the ISTD counts from the sample. Always use blank subtraction for subtracting a reagent blank during quantitation. This method only makes the subtraction after the ISTD correction has been applied to both blank and sample.

3 Analyze the standard solutions and sample, and then generate the quantitative results.

Refer to the *Agilent 7500 ICP-MS ChemStation Operator's Manual* for more detail.

4

Analysis of Semiconductor Samples

Analysis of Semiconductor Samples

Since ICP-MS allows ppt or sub-ppt level elemental analysis, it has been commonly used in the semiconductor industry to determine ultra trace levels of impurities in chemicals and semiconductor devices. In this chapter, the analysis of semiconductor samples is described.

General Considerations

Environment

In semiconductor devices, contamination deteriorates performance: alkali and alkali-earth elements reduce breakdown voltage, transition metals reduce the lifetime of the carrier causing higher dark current, doping elements cause a shift in the device operating point and particles cause short circuits. Therefore, this contamination has to be controlled in the semiconductor industry. However, these contaminants exist everywhere in the atmosphere and special attention has to be paid to prevent airborne contamination of the various chemical and semiconductor device samples to be analyzed by ICP-MS. The best way to avoid such contamination is to install the ICP-MS in a clean room.

The Agilent 7500 is designed for clean room use. The rotary pumps can be installed outside the clean room while the instrument itself is installed inside the clean room. All cooling air flows from outside to inside and is vented through the ventilation duct at the top of the Agilent 7500, which prevents introduction of particles from the instrument into the clean room.

The cleanliness of a clean room is expressed by its class number. Class 1000 means that the number of particles bigger than 0.5 µm is 1000 per cubic foot. The normal environment is worse than class 1,000,000. To get better cleanliness, the floor of the clean room must have a grating to allow air to flow down. Installing the Agilent 7500 in a class 1000 clean room is recommended.

For the sample and standard solution preparation facility, better cleanliness will be required: a class 100 clean room with a clean draft.

Cleaning of the Sample Introduction System

To analyze ultra trace levels, the sample introduction devices must be cleaned carefully.

- **Sampling and Skimmer Cones**

There are two types of interfaces for the Agilent 7500.
Ni interfaces are used for this application; the typical Ni background at m/z 60 is about 50 ppt.
Pt interfaces are better for this application because of their inertness. Pt interfaces can be used for higher concentration of acids. The background of Pt is negligible, but a small amount of Ni is present as an impurity in Pt.

Sample memory can arise from the interface on which an oxide of an element deposits. This is the most common memory effect, which occurs for refractory elements. Oxides of Ca, Al, Si, U, Th, and REEs are typical. To remove this memory, soak in 5% HNO_3 for about 10 minutes. Mechanical cleaning by using sand paper or alumina powder will be required when the deposition can not be removed by soaking in acid.
Interfaces for semiconductor samples should be maintained and used separately from those for environmental samples.

- **Sample Introduction Devices**

The sample introduction devices for semiconductor application should not be used for other applications. For cleaning glassware such as the spray chamber, torch and concentric nebulizer, aqua regia is the best solution. Soaking in 5% HNO_3 overnight is convenient for routine cleaning. Etching the glass surface by a 0.1% HF solution for five minutes is commonly used by glass manufacturers to clean glass and can be applied here. A sonicator must not be used for this glassware.

For cleaning the babington nebulizer and crossflow nebulizer, higher concentrations of acid and aqua regia should not be used, only 5% HNO_3 or 5% HCl maximum. The endcap and polypropylene spray chamber can be cleaned in the same way as the glassware, and an ultrasonic bath can be used. The peristaltic pump tube used for the sample should be cleaned by about 5% acid. Higher concentrations of acid deteriorate the tube. If ultra trace level analysis is required, self-aspiration is preferred.

The ShieldTorch System

The ShieldTorch system is an extremely powerful device for semiconductor applications. The shield plate can be used all the time - it is not necessary to remove it for the analysis of elements requiring normal plasma conditions. More specifically, for the analysis of semiconductor samples, cool plasma conditions give better detection limits for Li, Na, Mg, Al, K, Ca, Cr, Fe and Cu. For analysis of **K, Ca, Cr and Fe**, the recommended mass is **m/z 39, 40, 52 and 56**, respectively.

CAUTION m/z 40 must be used only under cool plasma conditions.