

ICP Operations Guide

A Guide for Using ICP-OES and ICP-MS

By Paul Gaines, Ph.D.





Inorganic Ventures has spent more than 30 years manufacturing inorganic certified reference materials (CRMs), specializing in creating custom blends to meet the unique needs of our customers. Our specialization in this field has enhanced the quality of our manufacturing, depth of our technical support and caliber of our customer service. Inorganic Ventures is accredited to ISO 17025 & ISO 17034 by A2LA.

The pursuit of excellence in these areas has led to the creation of the ICP Operations Guide. The purpose of this guide is to assist ICP/ICP-MS operators with the numerous tasks they encounter on a daily basis. The topics are fundamental in nature and are intended as an aid for the analyst who is completely new or somewhat new to the technique of ICP.



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by Paul R. Gaines, PhD

This guide is intended for anyone operating and preparing samples and standards for measurement using ICP (ICP hereafter refers to either ICP-MS or ICP-OES). Our last guide, *Trace Analysis: A Guide for Attaining Reliable Measurements*, focused on the task of achieving reliable trace measurements by ICP. This series will not focus on any single topic, but rather upon a multitude of day-to-day tasks required by all ICP operators. The topics will be fundamental in nature and are intended as an aid for the analyst who is completely new or somewhat new to the technique of ICP.

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MULTI-ELEMENT STANDARD BLENDS

1. Elemental and Matrix Compatibility

Nitric Acid Matrices

Most analysts prefer nitric acid (HNO_3) matrices due to the solubility of the nitrates as well as its oxidizing ability and the relative freedom from chemical and spectral interferences as compared to acids containing Cl, S, F, or P. In addition, HNO_3 is very popular in acid digestion sample preparations.

The elements that are stable/soluble and commonly diluted in aqueous/ HNO_3 are shaded in red below:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Li	Be											B	C	N		F
Na	Mg											Al	Si F	P	S	Cl (2)
K	Ca	Sc	Ti F	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge F	As	Se	Br (3)
Rb	Sr	Y	Zr F	Nb F	Mo		Ru Cl	Rh Cl	Pd	Ag (6)	Cd	In	Sn F	Sb F, T	Te (5)	I (3)
Cs	Ba	La	Hf F	Ta HF	W HF	Re	Os (1)	Ir Cl	Pt Cl	Au Cl (4)	Hg (4)	Tl	Pb	Bi		

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th		U											

- Os should never be mixed with HNO_3 due to the formation of the very volatile OsO_4 .
- Cl is oxidized to molecular Cl_2 which is volatile and adsorbs on plastic.
- Br and I are oxidized to molecular Br_2 and I_2 which adsorb onto plastic.
- Dilutions of Hg and Au in HNO_3 below 100 ppm should be stored in borosilicate glass due to Hg^{+2} adsorption on plastic.
- Not soluble above concentrations of 1000 $\mu\text{g/mL}$.
- Trace levels of HCl or Cl^- will form AgCl , which will photo-reduce to Ag^0 .

F denotes that the element can be diluted in HNO_3 if complexed with F^- .

Cl denotes that the element can be diluted in HNO_3 if complexed with Cl^- .

HF denotes that the element should have excess HF present when diluted with HNO_3 .

T denotes that the tartaric acid complex can be diluted in HNO_3 .

Hydrochloric Acid Matrices

The use of hydrochloric acid (HCl) is the next most popular acid matrix. HCl is volatile and it is corrosive to the instrument and it's electronics therefore, exposure should be kept to a minimum.

The elements that can be diluted in HCl are shaded in blue below:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Li	Be											B	C	N		F
Na	Mg											Al	Si F	P	S	Cl
K	Ca	Sc	Ti F	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge F	As	Se	Br (3)
Rb	Sr	Y	Zr F	Nb F	Mo		Ru	Rh	Pd	Ag (1)	Cd	In	Sn F	Sb F	Te (5)	I (3)
Cs	Ba	La	Hf F	Ta F	W F	Re	Os	Ir	Pt	Au	Hg (2)	Tl	Pb	Bi		

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th		U											

1. Concentrated (35%) HCl will keep up to 100 µg/mL of Ag⁺ in solution as the Ag(Cl)^{X-(X-1)} complex. For more dilute solutions, the HCl can be lowered such that 10% HCl will keep up to 10 µg/mL Ag in solution.
NOTE: The Ag(Cl)^{X-(X-1)} complex is photosensitive and will reduce to Ag⁰ when exposed to light. HNO₃ solutions of Ag⁺ are not photosensitive.
2. Parts-per-billion (ppb) dilutions of Hg⁺² in HCl are more stable to adsorption on the container walls than are dilutions in HNO₃.

F denotes that the element is more stable to hydrolysis if complexed with F⁻. In the case of Si and Ge the fluoride complex is generally considered a necessity.

Water at pH of 7

Dilutions in water at pH 7 are not as common for most elements but may be required to prevent chemical reactions of some of the compounds containing the element. Please note that solutions at pH 7 may support biological growth and therefore the long-term stability should be questioned.

Those elements that may have an advantage to being diluted in water at pH 7 are shaded in yellow below:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Li	Be											B	C	N		F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th		U											

Hydrofluoric Acid Matrices

Hydrofluoric acid (HF) requires the use of HF-resistant introduction systems. These systems are more expensive than glass, have longer washout times, and give a larger measurement precision. However, there are times when the use of HF offers a major advantage over other reagents.

Those elements where an HF matrix may be optimal are shaded in green below:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Li	Be											B	C	N (1)		F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th		U											

1. HF is used for Si_3N_4 preparations and other nitrides.

Sulfuric Acid Matrices

Sulfuric acid (H_2SO_4) is commonly used in preparations and therefore added to standards in combination with other acids.

Elements that either benefit or comfortably tolerate the presence of H_2SO_4 are shaded in orange below:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Li	Be											B	C	N		F
Na	Mg											Al	Si F	P	S	Cl (2)
K	Ca	Sc	Ti F	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge F	As	Se	Br (3)
Rb	Sr	Y	Zr F	Nb F	Mo F		Ru Cl	Rh Cl	Pd	Ag (2)	Cd	In	Sn F	Sb F, T	Te (5)	I (3)
Cs	Ba	La	Hf F	Ta HF	W HF	Re	Os (1)	Ir Cl	Pt Cl	Au Cl(1)	Hg (1)	Tl	Pb	Bi		

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th		U											

- Dilutions of Hg and Au in H_2SO_4 below 100 ppm should be stored in borosilicate glass due to adsorption on plastic.
- Trace levels of HCl or Cl^- will form AgCl, which will photoreduce to Ag^0 .

F denotes that the element can be diluted in H_2SO_4 if complexed with F^- .

Cl denotes that the element can be diluted in H_2SO_4 if complexed with Cl^- .

HF denotes that the element should have excess HF present when diluted with H_2SO_4 .

T denotes that the tartaric acid complex can be diluted in H_2SO_4 .

Phosphoric Acid Matrices

Phosphoric acid (H_3PO_4) is not commonly used in preparations since it attacks glass, quartz, porcelain, and Pt containers at elevated temperatures (greater than $100^\circ C$). However, the presence of H_3PO_4 will not adversely effect any of the elements at low $\mu g/mL$ levels and below.

2. CRM Quality Issues

There are several quality issues that are important with respect to multi-element chemical standards:

- Accuracy
- Purity
- Chemical Compatibility
- Stability
- Availability
- Documentation
- Traceability

Many of the topics above have been discussed in other publications on our site.

CRM Accuracy

The accuracy of a certified reference material (CRM) standard is dependent upon:

- The method(s) used for certification (Method Validation).
- Proper preparation of the elemental standard (a QC sample or second source sample should be analyzed against the single or multi-element blend).
- Identification and expression of all Random and Fixed Errors. (Note that uncertainty calculations will be discussed in part 3 of this series.)
- Chemical and physical stability — Container Transpiration plays an important role in chemical stability.
- Packaging and storage — Container Material Properties are important to consider.
- Absence of blunders (training, written procedures, detailed records, internal audits, etc.). Having a good quality system in place helps to prevent laboratory blunders.

Purity

Purity becomes an issue when using starting materials of single element blends to prepare multi-element blends. The degree of importance increases as the relative order of magnitude of the components increases. Known purity and hopefully very clean materials are critical in the execution of ICP-OES spectral interference studies. These studies typically involve the aspiration of a 1000 µg/mL solution of a single element while collecting the spectral regions of analytes that may be interfered with.

Inorganic Ventures' laboratory has purchased many materials claiming a purity of 5 to 6–9's. However, it's never a bad idea to confirm a manufacturer's claims. For more information regarding purity considerations, please consult the following online articles:

- Environmental Contamination
- Contamination from Reagents
- Contamination from the Analyst and Apparatus

Chemical Compatibility

It's important for the multi-element blends to be compatible with the containers in which they are prepared and stored. It's equally important that they are compatible with the introduction system of the instrument(s) used to analyze the blend and with the other analytes within the blend. Some points to consider:

- Is the matrix of the standard compatible with glass or quartz? Glass is not compatible with HF and caustic matrices.
- Are there possible reactions between the chemical components of the standard that may adversely alter the standard with time? Photo-reduction of Ag in high HCl matrices, ppt of Ag in trace Cl matrices, ppt of Pb and Ba with trace levels of sulfate or chromate, ppt of the alkaline and rare earths with F^- in HF matrices, ppt of fluorinated elements like $Sn(F)_{x-y}$ in the presence of elements that would complex with the fluoride and therefore "pull it away" from the metal stabilized as the fluoride complex, etc.
- Does the standard contain components that could form volatile compounds? A classic example is the oxidation of osmium chloride to the very volatile and toxic OsO_4 when nitric acid is added. Volatile compounds may not be lost from the standard solution but will give false high readings due to a disproportionate amount of the element making it to the plasma where the nebulization efficiency is greater due to the added mode of transport to the plasma as the vapor state.

Stability

How stable is the standard blend? When a blend is made for the first time and then remade at a later time, a comparison of the two should be made to confirm stability. If there are chemical concerns from the beginning then a fresh blend should be prepared the next analytical day for comparison.

Availability

Consider the following:

- Does the blend have to be kept away from the air (oxygen) or light?
- Must it be refrigerated or frozen?
- Is it sensitive to biological growth?
- How much time is required for preparation and how often is preparation required?
- If you purchase your standards, how quickly do you receive them?

Some of these questions may appear as if they belong in other sections but they all impact the availability of the standard in important ways. For example, blends that must be kept refrigerated or frozen cannot be used until allowed to come to room temperature. This is often the case with blends manufactured within the biological pH range of 4–10.

Documentation

Although documentation may seem less important than the above topics, it is paramount for less obvious reasons. Think about the following questions:

- Is there a potential for litigation?
- Does a customer or certifying body audit your laboratory?
- Is all the information on hand when it's needed?
- What documentation around or about your chemical standard is needed?

ISO has issued a document referred to as ISO Guide 31. This document details what the international scientific community considers to be critical to the analyst when using chemical standard solutions or CRMs.

Traceability

Is it possible that the scientific, commercial, or legal communities will scrutinize your data? If so, the issue of traceability may be more critical than you realize. Traceability has been defined as "the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties." This definition has achieved global acceptance in the metrology community.

3. Handling, Calculations, Preparation and Storage of Standards

Handling

Observing the following recommendations will save considerable time, money, and frustration:

1. Never put solution transfer devices into the standard solution. This precaution avoids possible contamination from the pipette or transfer device.
2. Always pour an aliquot from the standard solution to a suitable container for the purpose of volumetric pipette solution transfer and do not add the aliquot removed back to the original standard solution container. This precaution is intended to avoid contamination of the stock standard solution.
3. Perform volumetric pipette solution transfer at room temperature. Aqueous standard solutions stored at "lower" temperature will have a higher density. Weight solution transfers avoid this problem provided the density of the standard solution is known or the concentrations units are in wt./wt. rather than wt./volume.
4. Never use glass pipettes or transfer devices with standard solutions containing HF. Free HF attacks glass but it is sometimes considered safe to use glass when the HF is listed as trace and/or as a complex. However, many fluorinated compounds will attack glass just as readily as free HF.

- Don't trust volumetric pipette standard solution transfer. Weigh the aliquot of the standard taken. This can be easily calculated provided the density of the standard solution is known. There are too many possible pipetting errors to risk a volumetric transfer without checking the accuracy by weighing the aliquot.
- Uncap your stock standard solutions for the minimum time possible. This is to avoid transpiration concentration of the analytes as well as possible environmental contamination.
- Replace your stock standard solutions on a regular basis. Regulatory agencies recommend or require at least annual replacement. Why is this precaution taken in view of the fact that the vast majority of inorganic standard solutions are chemically stable for years? This is due to the changing concentration of the standard through container transpiration and the possibility of an operator error through general usage. A mistake may occur the first time you use the stock standard solution or it may never occur with the probability increasing with use and time. In addition, the transpiration concentration effect occurs whether the standard solution is opened / used or not and increases with use and increased vapor space (transpiration rate is proportional to the ratio of the circumference of the bottle opening to vapor space).

Calculations

The concentration units for chemical standard solutions used for ICP applications are typically expressed in $\mu\text{g/mL}$ (micrograms per milliliter) or ng/mL (nanograms per milliliter). For example, a $1000 \mu\text{g/mL}$ solution of Ca^{+2} contains 1000 micrograms of Ca^{+2} per each mL of solution and a $1 \mu\text{g/mL}$ solution of Ca^{+2} contains 1000 ng of Ca^{+2} per milliliter of solution. To convert between metric concentration units the following conversions apply:

Table 3.1: Mass portion of concentration unit where g = gram

Prefix	Scientific Notation	Decimal Equivalents	Example Units
kilo- (k)	$= 10^3$	$= 1000 \text{ g}$	kilogram (kg)
milli- (m)	$= 10^{-3}$	$= 0.001 \text{ g}$	milligram (mg)
micro- (μ)	$= 10^{-6}$	$= 0.000001 \text{ g}$	microgram (μg)
nano- (n)	$= 10^{-9}$	$= 0.000000001 \text{ g}$	nanogram (ng)
pico- (p)	$= 10^{-12}$	$= 0.000000000001 \text{ g}$	picogram (pg)

Table 3.2: Volume portion of concentration unit where L = liter

Prefix	Scientific Notation	Decimal Equivalents	Example Units
milli- (m)	$= 10^{-3}$	$= 0.001 \text{ L}$	milliliter (mL)
micro- (μ)	$= 10^{-6}$	$= 0.000001 \text{ L}$	microliter (μL)
nano- (n)	$= 10^{-9}$	$= 0.000000001 \text{ L}$	nanoliter (nL)
pico- (p)	$= 10^{-12}$	$= 0.000000000001 \text{ L}$	picoliter (pL)

The difference between ppm and $\mu\text{g/mL}$ is often confused. A common mistake is to refer to the concentration units in ppm as a short cut (parts per million) when we really mean $\mu\text{g/mL}$. One ppm is in reality equal to $1 \mu\text{g/g}$. In similar fashion ppb (parts per billion) is often equated with ng/mL . One ppb is in reality equal to 1ng/g . To convert between ppm or ppb to $\mu\text{g/mL}$ or ng/mL the density of the solution must be known. The equation for conversion between wt./wt. and wt./vol. units is:

$$(\mu\text{g/g}) (\text{density in g/mL}) = \mu\text{g/mL and/or (ng/g) (density in g/mL) = ng/mL$$

Therefore, if we have a solution that is $1000 \mu\text{g/mL Ca}^{+2}$ and know or measure the density to be 1.033g/mL then the ppm $\text{Ca}^{+2} = (1000 \mu\text{g/mL}) / (1.033 \text{g/mL}) = 968 \mu\text{g/g} = 968 \text{ppm}$.

When making dilutions the following equation is useful:

$$(mL_A)(C_A) = (mL_B)(C_B)$$

For example, to determine how much of a $1000 \mu\text{g/mL}$ solution of Ca^{+2} required to prepare 250mL of a $0.3 \mu\text{g/mL}$ solution of Ca^{+2} we would use the above equation as follows:

$$(mL_A)(1000 \mu\text{g/mL}) = (250 \text{mL})(0.3 \mu\text{g/mL}), (mL_A) = [(250 \text{mL})(0.3 \mu\text{g/mL})] / (1000 \mu\text{g/mL}), (mL_A) = 0.075 \text{mL} = 75 \mu\text{L}$$

Preparation

WEIGHT \neq VOLUME

Standard chemical solutions can be prepared to weight or volume. The elimination of glass volumetric flasks may be necessary to eliminate certain contamination issues with the use of borosilicate glass or to avoid chemical attack of the glass. It is often assumed that 100grams of an aqueous solution is close enough to 100mL to not make a significant difference since the density of water at room temperature is very close to 1.00 (0.998203 at 20.0°C). Diluting / preparing standard solutions by weight is much easier. Still, the above assumption should not be made. The problem is that trace metals standards are most commonly prepared in water + acid mixtures where the density of the common mineral acids is significantly greater than 1.00 . For example, a $5\% \text{v/v}$ aqueous solution of nitric acid will have a density of $\sim 1.017 \text{g/mL}$ which translates into a fixed error of $\sim 1.7\%$. Higher nitric acid levels will result in larger fixed errors. This same type of problem is true for solutions of other acids to a degree that is a function of the density and concentration of the acid in the standard solution as described by the following equation (to be used for estimation only):

$$d_s = [(100-\%) + (d_A)(\%)] / 100$$

Where:

d_s = density of final solution

$\%$ = The v/v % of a given aqueous acid solution

d_A = density of the concentrated acid used

For example, let's estimate the density of a $10\% \text{v/v}$ aqueous solution of nitric acid made using 70% concentrated nitric acid with a density of 1.42g/mL .

$$d_s = [(100-\%) + (d_A)(\%)]/100 = [(100-10) + (1.42)(10)]/100 = (90 + 14.2)/100 = 1.042 \text{g/mL}$$

ACID CONTENT

Another area of confusion is the expression of the acid content of the solution. We all agree that it is important to matrix match the standard and sample solutions to avoid a fixed error in the solution uptake rate and/or nebulization efficiency sometimes referred to as a matrix interference. If a solution is labeled as 5% HNO₃ what does this mean? If we take 5 mL of 70% concentrated nitric acid and dilute to a volume of 100 mL then this is 5% HNO₃ (v/v) where the use of 70% concentrated acid is assumed. However, nitric acid can be purchased as 40%, 65%, 70%, and > 90%. Therefore, note the concentration of the concentrated acid used if different from the "norm" as well as the method of preparation i.e. v/v or wt/wt or wt/v or v/wt. The wt. % concentrations of the common mineral acids, densities, and other information are shown in the following table:

Table 3.3: Wt. % Concentrations

Acid	Mol. Wt.	Density (g/mL)	Wt. %	Molarity
Hydrochloric	36.46	1.19	37.2	12.1
Hydrofluoric	20.0	1.18	49.0	28.9
Nitric	63.01	1.42	70.4	15.9
Perchloric	100.47	1.67	70.5	11.7
Phosphoric	97.10	1.70	85.5	14.8
Sulfuric	98.08	1.84	96.0	18.0

ACID CONTENT IN MOLARITY

It is important to know what the concentration units of the concentrated acid being used mean. Taking 70% concentrated nitric acid as an example means that 100 grams of this acid contains 70 grams of HNO₃. The concentration is expressed at 70% wt/wt or 70 wt. % HNO₃. Some analysts prefer to work in matrix acid concentrations units of Molarity (moles/liter). To calculate the Molarity of 70 wt. % nitric acid we calculate how many moles of HNO₃ are present in 1 liter of acid. Let's say that we tare a 1 liter volumetric flask and then dilute to the mark with 70.4 wt. % HNO₃. We would then measure the weight of the solution to be 1420 grams. Knowing that the solution is 70.4 wt.% would then allow us to calculate the number of grams of HNO₃ which would be (0.704)(1420g) = 999.7 grams HNO₃ per liter. Dividing the grams HNO₃ by the molecular weight of HNO₃ (63.01 g/mole) gives the moles HNO₃ / L or Molarity which is 15.9 M. The above logic explains the following equation used for calculating the Molarity of acids where the concentration of the acid is given in wt %:

$$[(\% \times d) / MW] \times 10 = \text{Molarity}$$

Where:

% = wt. % of the acid

d = density of acid (specific gravity can be used if density not available)

MW = molecular weight of acid

Using the above equation to calculate the Molarity of the 70 wt. % nitric acid we have:

$$[(70.4 \times 1.42) / 63.01] \times 10 = 15.9 \text{ M}$$

Dilutions of the concentrated acid to prepare specific volumes of specified Molarity can be made using the $(mL_A)(C_A) = (mL_B)(C_B)$ equation.

AVOIDING PRECIPITATES

In the preparation of mixtures of the elements, it is good to avoid the formation of precipitates. It is common to form precipitates when concentrates of elements that are considered compatible (see part 1 of this series) are mixed. Many precipitates are not reversible (i.e., will not go into solution upon dilution). It is therefore best to add all of the acid and most of the water to the volumetric flask or standard solution container (dilutions to weight) before adding the individual element concentrate aliquots. Mixing after each aliquot addition is strongly advised. When diluting to volume it is often found that the solution is above room temperature. Therefore allow the solution to cool to room temperature and adjust to the mark with DI water. It is best to prepare the dilution the day before needed to allow for proper volume adjustment.

Storage

The following are some considerations you may want to make before the storage of chemical standard solutions:

- Know the chemical stability of your standard. Chemical stability can be altered by changes in starting materials and preparation conditions. It is therefore advisable to perform stability studies on all standard solutions to avoid time consuming and costly delays or mistakes and to strictly adhere to preparation methodology, including order of addition for multi-component standard solutions.
- Note the temperature during storage and attempt to maintain a storage temperature at or around 20°C. Some standards are not stable for long periods at room temperature and require refrigeration or even freezing.
- Perform the stability study in the container material selected for storage. It is not advisable to use volumetric flasks as storage containers due to expense, contamination, and transpiration issues.
- Determine if the standard is photosensitive and/or store in the dark if there is a concern. This is an issue with some of the precious metals and that is a function of matrix. Photosensitivity will increase in the presence of higher energy light (sunlight as opposed to artificial light) and trace or minor amounts of organics especially if there is an extractable proton alpha to an electron withdrawing functional group such as a carbonyl group. The presence of chloride may increase instability to photo reduction. A classic example is Ag^+ in HCl solutions.
- Store the standard in containers that will not contribute to contamination of the standard. LDPE is an excellent container for most inorganic standards.
- Weigh the standard solution before storage and then just before the next use. If there is measurable transpiration the weight will decrease with time.

SAMPLE INTRODUCTION

4. Sample Introduction Systems

The most common form of ICP sample introduction is liquid. The purpose of this section is to introduce the beginner to the most popular components of liquid sample introduction systems used for the introduction of samples to ICP-OES and ICP-MS instrumentation (hereafter referred to as ICP) and to alert the reader to some common problems.

System Components

Before continuing any further, I strongly encourage you to read the following:

A Beginner's Guide to ICP-MS — Part II: The Sample-Introduction System

In the above article, author Robert Thomas gives an excellent overview of the most popular commercially available nebulizers and spray chambers. He also provides guidance and basic theory behind the available designs, as well as an overall understanding of ICP introduction systems.

The key elements of a sample introduction system start with the sipper tube and end with the torch. They are listed as follows:

- Sipper (typically plastic)
- Teflon tubing going from the sipper to the peristaltic pump tubing
- Peristaltic pump tubing
- Teflon tubing going from the peristaltic pump tubing to the nebulizer
- Spray chamber
- Torch

Troubleshooting

CONNECTION CHECKS

The main difficulty I have experienced with introduction system failure is that of connections between components. The connections are listed as follows:

1. Sipper to Teflon tubing
2. Teflon tubing to peristaltic tubing (both into and out of)
3. Teflon tubing from peristaltic pump to nebulizer
4. Nebulizer to spray chamber
5. Spray chamber to waste drain tube
6. Spray chamber to torch

If any one of these connections is not airtight, the operator will experience anything from poor precision to an inability to light the plasma. One of the many reasons I prefer concentric glass nebulizers is that they are “free flow” (i.e., the liquid will flow from the sample container to the nebulizer without assistance from the peristaltic pump). A simple check is to determine if you obtain a fine steady mist (using water as the sample) without the peristaltic pump (pressure lever released) so that free flow can occur. This can be done with the nebulizer disconnected from the spray chamber (plasma has not yet been lit) so that the mist can be easily visualized. You can also check for the appearance of any small air bubbles in the Teflon tubing, which should never be present and indicate a poor connection somewhere between and/or including the sipper and the nebulizer.

Another connection that is often taken for granted is the spray chamber drain/waste tube connection. This connection is absolutely critical. One way to test this connection is to put some water in the spray chamber using a wash bottle and determine if it drains smoothly and without leaks. Poor precision or the inability to light the plasma is a common symptom of a poor drain tube connection. During this test you should also observe the absence of water droplets in the spray chamber (assuming glass construction). A dirty spray chamber will leave water droplets and cause poor precision and carryover problems. Make sure the plasma is not lit whenever you perform this test.

SPRAY CHAMBERS

Spray chambers can be made of all glass, all plastic, and glass with plastic end caps. If you do not use HF (all plastic systems must be used with HF) and therefore have the luxury of using glass components, attempt to use a spray chamber without the plastic end cap (i.e., all glass). They are typically used with glass concentric nebulizers and use only two “O rings” to connect the nebulizer to the spray chamber. I have found that the plastic end cap may cause longer washout times, carry over problems, and is a very large connection surface where connection problems can occur. Using a glass concentric nebulizer and all glass spray chamber a precision of between 0.2 and 0.5% RSD should be observed. If an all glass system gives a precision of 1% RSD or greater, then there is most likely a connection problem or the nebulizer gas flow rate is too high (look for spitting when checking the nebulizer free flow and do not be afraid to lower the gas pressure {argon sample flow} to the nebulizer).

PERISTALTIC PUMP TUBING

Another weak link in the introduction system is the peristaltic pump tubing. When you start the day the tubing is fresh and the pressure can be set to give a steady mist when the pump is running. The problem is that the pump tubing stretches and either the pressure is not enough to drive the solution through the tubing or you over tighten and get a pulsating mist spray. This is a problem that each analyst has to be aware of and solve through experimentation. This problem is particularly troublesome for ICP-MS users because the argon flow changes as the tubing stretches. This causes a relative increase in the sensitivity of the higher atomic number elements.

Maintenance

I prefer glass components because of their ease of operation and cleaning. It is always best to start the day with a clean nebulizer, spray chamber, and torch. Cleaning the torch daily will also extend its life. There are many cleaning solutions that can be used. Some of our analysts prefer 1:1 Nitric acid/water and others prefer sulfuric acid and hydrogen peroxide. Another common cleaning solution is 1:1 HCl/nitric. All of these solutions will work depending upon the nature of the contaminants. The sulfuric/peroxide is generally a severe approach and needed only if organics such as grease, etc, are suspected.

Be advised that ultrasonic baths are great for cleaning. However, **NEVER** use them to clean a glass concentric nebulizer. Glass concentric nebulizers are cleaned by leaching and occasionally by applying a backpressure with water to remove lodged particles. The use of a cleaning wire or ultrasonic bath is a sure way to destroy the nebulizer.

In summary, when it comes to ICP introduction systems there is no substitute for experience. Relatively speaking, introduction systems are simple but they are not easy to maintain and they are challenging to operate to their maximum potential.

5. Nebulizers, Spray Chambers and Torches

There has been a tremendous activity in the area of sample introduction over the past 30 years since ICP has been commercially available. The objective of this section is to acquaint the reader with the basic options available to the ICP operator for the introduction of "liquid" samples.

Some of the considerations in selecting an introduction system include dissolved solids content, suspended solids presence, presence of HF or caustic, detection limit requirements, precision requirements, sample load requirements, sample size limitations, and operating budget. In the last section, the concentric nebulizer and all glass introduction systems were given top billing but they may not work at all for your application. The analyst is left with the task of choosing the best introduction components after taking into account the appropriate considerations.

Nebulizers

PNEUMATIC NEBULIZERS

The term "pneumatic" is defined as "of or relating to or using air or a similar gas." The word "nebulizer" is derived from the Latin "nebula" meaning mist and is defined as "an instrument for converting a liquid into a fine spray." Therefore, a pneumatic nebulizer is literally an instrument for converting a liquid into a fine spray that uses a gas as the driving force.

Some of the most popular ICP pneumatic nebulizers are:

- Concentric glass
- Concentric PFA
- Fixed Cross-Flow
- Lichte (modified)
- Micro-concentric glass
- Adjustable Cross-Flow
- High-Pressure Fixed Cross-Flow (MAK)
- Babington V-Groove (high solids)
- GMK Babington (high solids)
- Hildebrand dual grid (high solids)
- Ebdon slurry (high solids)
- Cone Spray (high solids)

The concentric and fixed cross-flow are still the most common designs. The construction of both types is described in the following article by ICP expert Robert Thomas (see Figures 5 & 6):

A Beginner's Guide to ICP-MS — Part II: The Sample-Introduction System

ICP manufacturers will give you an option as to the type of nebulizer to use depending upon your analytical requirements and the instrumental design.

Sound can be used instead of a gas as the energy source for converting a liquid to a mist. These nebulizers use an ultrasonic generator at a frequency of between 200 kHz and 10 MHz to drive a piezoelectric crystal. A pressure is produced that breaks the surface of the liquid — air interface. Ultrasonic nebulizers are more expensive and difficult to use but they will improve (lower) detection limits by about a factor of 10.

Spray Chambers

The basic designs that have remained over the years are the Scott double-pass and the Cyclonic. To review the designs of these two components, see Figures 8 & 9 in Robert Thomas' article:

A Beginner's Guide to ICP-MS — Part II: The Sample-Introduction System

The Cyclonic design is relatively new but is very popular. The purpose of the spray chamber is to remove droplets produced by the nebulizer that are $> 8\mu\text{m}$ in diameter. Considerations include the wash-in-time, washout time, stability, and sensitivity. The drainage characteristics are important in part due to pressure changes that may occur during drainage. It is important that the drainage process be smooth and continuous. The analyst may observe faster washout times with the Cyclonic design. The chamber material of construction as well as the sample matrix and the chemistry of the element will influence the washout time. In addition, the analyst may observe faster washout times with glass construction than with polymers. This is due in part to the better wetting ability of the glass (lack of beading). Both designs are excellent and the analysts may wish to experiment with each to determine which yields the best performance for their specific analyses.

Torches

The two basic torch designs are the Greenfield and Fassel torches. The Greenfield torch requires higher gas flows and RF powers. The Greenfield torch is more rugged (less likely to extinguish due to misalignment and introduction of air) whereas the Fassel torch requires less Ar and power. Both designs produce similar detection limits.

Some nebulizer designs work better with one torch design over another. Before experimenting with torches, it is best to contact your instrument manufacturer to determine the torch design recommended for your instrument as well as any design specifications, operating conditions, and dimensions that must be observed.

CONSIDERATIONS

The following are some questions you may want to consider, whether you are looking to purchase a new ICP or already have one or more existing units:

- What torch design is used and what are the power and Ar gas flow requirements? (It may be helpful to calculate/determine your annual Ar expense).
- What nebulizer and spray chamber designs are available and can they be obtained from alternate suppliers?
- Are there specific nebulizer designs that cannot be used with the recommended torch/spray chamber?
- What are the costs of the individual introduction system components and what are the upkeep costs over a year of operation?
- What is the lifetime of the torch and what is the most common reason for failure?
- How tolerant is the system to slight changes in torch alignment?
- How tolerant is the system to air coming from the nebulizer and will it extinguish after a few seconds?
- How tolerant is the system to the introduction of organic solvents?
- What is the lowest boiling point solvent that can be introduced?
- How tolerant is the system to the torch building up coke for aromatic and aliphatic non-polar solvents?
- What is the most precise nebulizer that can be used with your ICP and what precision should be obtained?
- What are the detection limits for your analytes of interest? Are you achieving the detection limits required for your application?
- When looking for lower detection limits have you considered axial view ICP? Ultrasonic nebulizers? Both?
- Do your analytical solution samples contain high levels of dissolved solids? Do they contain any suspended solids?
- Do you experience nebulizer salting out or plugging?
- Which high solids nebulizer is recommended for your current or potential ICP and what is the precision to be expected? How rugged is it and what does it cost?
- How difficult is it to connect an ultrasonic nebulizer?
- Can either the Scott or Cyclonic spray chamber designs be used?
- What are the washout times for Hg, B, Y, and Cu in nitric acid? In HCl?
- Are corrosion resistant/HF resistant introduction systems available? What do they cost? How easy are they to switch in and out?
- When analyzing for Si in trace HF, how much of a Si, B, Na, and, Al background signal do you get?
- If the introduction system contains glass, how much HF can be tolerated before signals from Si are observed? What about before damage occurs?

6. Compatibility and Precision Issues

Solutions Containing HF

The presence of HF causes the vast majority of compatibility problems between the sample matrix and the introduction system components. If you are preparing samples containing one or more of the following elements, then you are likely using HF in your sample preparation:

HF elements: Ti, Zr, Hf, Nb, Ta, Mo, W, Si, Ge, Sn, Sb

WHEN HF ATTACKS

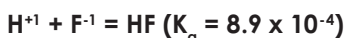
The introduction of solutions containing HF should be of concern to the instrument operator, especially if he/she is determining Si, B, or Na. When glass or quartz is exposed to HF, they are attacked to a degree depending upon the concentration of the HF and the type of glass or quartz. It is the HF molecule that does the attacking; not the fluoride anion (F^{-1}). There is absolutely no attack by neutral solutions of F^{-1} upon any form of glass or quartz (note that there is water solubility of amorphous and crystalline forms of silica that is a function of the surface area, impurities, and structure).

The HF attack is enhanced by the presence of a strong acid, such as HNO_3 or HCl , by:

- Increasing the relative amount of HF through a shift in the equilibrium of equation 6.1 below and;
- By adsorbing as the hydronium ion on the solid silica surface where it behaves as a catalyst (i.e., the reaction of HF with a solid silicate can be described by two equations that work in parallel).

In addition, the crystalline form of the silicate influences the rate of attack. The net result being that quartz is not attacked as readily as glass. *(This is a generalization — please note that there are four “production types” of quartz in addition to natural quartz where different solubility and contamination characteristics can be expected from each. It may be more appropriate to think of glass as amorphous silica and quartz as structured or better yet crystalline silica).*

EQUATION 6.1:



It follows that solutions containing HF that are neutralized with a base to eliminate HF will not attack silicates provided that the HO^{-1} concentration is not too high (i.e., the pH is not above 8). This is why organic amines such as triethanol amine are so good at eliminating HF attack simply through neutralization of the HF as opposed to $NaOH$, which will attack silicates if high enough in concentration.

There is a general misunderstanding that the addition of boric acid will eliminate HF attack, allowing the analyst to use glass introduction components. It is common practice to react HF with boric acid (typically, 1 gram of boric acid is added for every 1 mL of 49% HF) to form the mono-fluoroboric acid. Unfortunately, fluoroboric acid will attack glass (including concentric nebulizers) and the attack of silicates,

in general, is not greatly altered. The formation of the fluoroboric acid will diminish the tendency to form insoluble fluorides such as CaF_2 which is why it was originally added.

GLASS INTRODUCTION SYSTEMS

Glass introduction systems are generally preferred by analysts because they are less expensive, have shorter washout times, and give better precision than plastic. This is why many analysts opt to use all-glass introductions provided the HF content is < 100 ppm. Quartz is less reactive than glass and is sometimes used if the analyst is concerned with making low level B measurements in a trace HF matrix.

Our laboratory uses a Type C glass concentric nebulizer at an Ar flow of ~ 0.75 L/min, a pressure of 30-35 PSI, and a sample introduction rate of 0.7 mL/min. The spray chamber is an all glass cyclonic and the torch is made of quartz. A typical measurement precision is between 0.2 and 0.5 % RSD and the washout times are excellent for all elements, including B and Hg (Hg takes ~ 75 seconds of rinse with 10 % (v/v) HNO_3). Trace levels of HF are easily tolerated even when elements such as Si and B are measured.

RECOMMENDATIONS

HF concentrations ≥ 0.1 % will attack both glass and quartz and cause considerable problems for the analyst attempting to determine Si, B, or Na. It is necessary to either switch to an HF-resistant introduction system or neutralize the HF with a base. Our laboratory introduces 1000 to 20000 $\mu\text{g/mL}$ solutions of all the "HF" elements using the neutralization (triethanol amine) option with the addition of H_4EDTA when required for chemical stabilization, while other laboratories get excellent results using the HF-resistant (plastic) introduction systems. The PFA concentric nebulizer is popular with a PFA or PEEK spray chamber and Al_2O_3 (inner tube) torch. I would suggest checking with your instrument manufacturer for power supply and gas flow compatibility before investing in an HF resistant system.

High Dissolved Solids

For conventional fixed cross-flow and concentric nebulizers, high dissolved solids may be a problem. The problem lies in the "salting out" of the matrix component(s) in the nebulizer. This occurs in the nebulizer at the point where the solution goes from a liquid to a mist, resulting in a temperature drop and reduced solubility. If the solution component is well below its solubility limit then a conventional nebulizer will not experience salting out. Therefore, the question is: "What is 'high'?"

The answer is relative to the solubility of the matrix. If you are aspirating a 0.7 % solution of B as boric acid then salting out will occur. A 4 % solution of Cu as the nitrate or chloride will not salt out. Salting out is indicated by poor precision and a gradual loss of signal. The analyst has several options — he/she can:

1. Dilute the sample.
2. Humidify the sample Ar stream.
3. Use one of the high solids or high pressure concentric nebulizers mentioned in part 5 of this series.
4. Increase the solubility of the culprit.

Our laboratory uses option 1 or 4 in order to retain the excellent characteristics of the type C concentric glass nebulizer. The addition of TEA is made to high boric acid solutions. This greatly increases the boric acid solubility and eliminates salting out. Other matrices are best dealt with through dilution, where the highest concentration of the matrix metal that can be tolerated by a type C concentric — in our experience — is 10000 ppm.

Suspended Solids

Samples containing suspended solids may cause a problem with the conventional fixed cross-flow or concentric nebulizers depending upon particle size. Solids that will pass through a 0.3 μm filter will not plug these nebulizers and will behave as if they are in solution with respect to the entire sample introduction process. Particles $> 10 \mu\text{m}$ will not aspirate normally and may cause plugging. Many sample types have particulate that is easily visible to the naked eye and will cause difficulty with the cross-flow and concentric nebulizers. The Babington V-Groove, GMK Babington, Hildebrand dual grid, Ebdon slurry, Cone Spray, and Noordermer V-groove nebulizers are all popular choices. Other options include filtration to remove the solids and chemical treatments such as fusion, ashing, or acid digestion to dissolve the solids.

Closing Remarks

HF, high dissolved solids, and suspended solids are the most common compatibility issues facing the ICP analyst. The ways around these problems are often expensive, time consuming, and result in lowered detection limits, longer wash out times, and poorer precision. In extreme cases, alternate analytical measurement techniques are required. It is always best to consult with your instrument's manufacturer before switching introduction components outside the realm of those recommended/ supplied by the manufacturer.

PERFORMANCE CHARACTERISTICS

7. Linearity and Detection Limits

Defining ICP Performance Characteristics

The following steps are intended as a practical guide for the determination of an ICP's performance characteristics:

1. Read the operating manual and familiarize yourself with the software, key instrumental parameters and preferred settings before the instrument is installed.

Most instruments are supplied with optimization and wavelength or mass calibration standards that will be used during set-up by the service technician and are intended for use on a regular basis by the operator. Discuss the optimization process with the manufacturer as well as the preferred settings for the key instrumental parameters.

The remaining steps assume that the operator fully understands and is able to perform the optimization process that has been defined by the manufacturer as well as the spectral limitations of the instrument.

2. Select the lines to be studied for each element ("lines" is used in this document to mean either wavelength or mass).

Line selection is based upon spectral interference issues, detection limit requirements and working range requirements. Select as many lines as possible within practicality for each element. The greater the number of lines, the greater the flexibility.

3. Prepare single element standards over the anticipated working range for each element. The range of standards depends upon the analytical requirements. The following ranges are suggestions only:
 - Radial view ICP-OES: 0.0, 1, 10, 100, and 1000 $\mu\text{g/mL}$
 - Axial view ICP-OES: 0.0, 0.1, 1, 10, and 100 $\mu\text{g/mL}$
 - Quadrupole (R~ 300) mass filtered ICP-MS: 0, 1, 10, 100, and 1000 ng/mL

This step is important because these data can be used to determine instrument detection limits (IDL), linear working ranges, and spectral characteristics such as background equivalent concentrations (BEC) and spectral interferences. With most modern (if not all) instruments, the spectra obtained for each element at each concentration can be saved for review later. In addition, the software will calculate the IDL and BEC plus the linear regression of each line will establish the linear working range. All of this is typically done for the operator by the software that comes with the instrument. If at all possible, attempt to:

- Use single element standards that have the trace metals impurities reported on the certificate of analysis. Most chemical standards manufacturers provide this information with their single element standards. These data are important in identifying direct spectral overlap interferences and in not identifying an impurity as an interference of this type.
 - Store all spectra on computer and collect the spectra for all lines of interest on each and every solution. This means that if you are interested in possibly using up to 6 lines for roughly 72 elements, then each solution spectrum totaling $72 \times 6 = \sim 432$ lines per solution and $\sim 432 \times 5 = 2160$ spectra for each element need to be stored for future reference. Most ICP-MS applications would require far fewer data to be collected due to the reduced number of lines available and/or feasible.
 - Wash blank acid solution through the instrument for several minutes "between elements" and always analyze a blank at the beginning of each element concentration series. Look for the presence of the prior element analyzed to confirm that it has been completely washed out of the introduction system.
4. Having the data available on a desktop computer is convenient and allows the analyst to construct potential spectra by calling up the element and the anticipated concentration for each element in the analytical sample. Having several lines available makes the job of line selection easy as well as the estimation of the line's sensitivity and linearity. Constructing these composite spectra from pure single element solutions eliminates confusion as to the identity of the line. The following example is intended to illustrate the process:

Figure 7.1:

Spectra of pure 100 ppm Fe and Ni solutions, 0.1 ppm Cr and a water blank at the 205.552 nm Cr wavelength

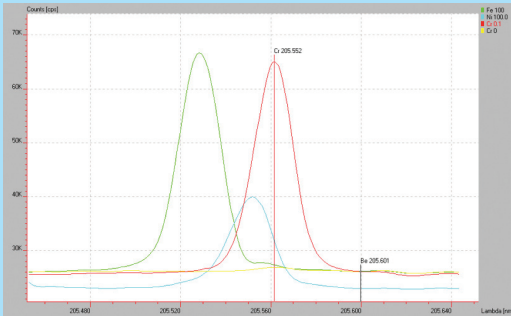
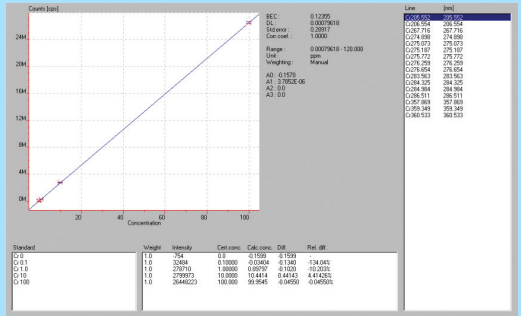


Figure 7.2:

IDL, BEC and regression data for the 205.552 nm Cr line



EXAMPLES OF SPECTRA

FYI: All spectra were obtained using a concentric glass nebulizer with no problems around salting out or plugging.

The following example is for an application where a submitter has been obtaining minor levels (0.1 to 1.0 %) of Cr in an alloy containing roughly equal amounts of Fe and Ni. The laboratory where this alloy is analyzed uses a procedure where 0.2 grams of the sample is dissolved in 5 mL of a 1:1 HNO₃ / HCl mixture and diluted to 1000 mL with DI water. The analyst is informed that a limit of detection (LOD = 3SD₀) of 1 ppm Cr based upon the original sample and the ability to quantify the Cr to within ±10 % relative at the 10 ppm level is an absolute minimum requirement.

The submitter then asks the analyst the usual question, "I need the results tomorrow — can you do it?" The analyst does a quick calculation and determines that using the most sensitive Cr line and the current procedure, the lowest possible detection limit is 4 ppm and a more realistic estimation would be ~ 4 times the IDL or ~ 16 ppm. The analyst then pulls up the following spectra, instrument detection limits, and linear regression data which were obtained on their radial view instrument about four years ago when installed using pure single element solutions as described above.

The 205.552 nm Cr line was found to be the most sensitive of the 16 Cr lines originally characterized with an IDL of 4.0 ppm = [(0.0008 µg/mL Cr IDL) x 1000] / 0.2 based upon original sample size and dilution as described above. However, the spectrum of a 0.1 ppm Cr standard shows significant interference from both Ni and Fe at a concentration of 100 ppm making the line useless at low ppm Cr levels (**see Figures 7.1 and 7.2**).

The analyst then begins the relatively simple process of identifying a Cr line with the most sensitivity that is spectrally clean. **Figures 7.3 and 7.4** show the line identified using the same scan data shown for the 205 Cr line. The 267.716 nm Cr line looks clean at the current dilution factors and has an IDL of 0.0016 µg/mL Cr which increases the detection limit to somewhere between 8 to 32 ppm.

Figure 7.3:

Spectra of pure 100 ppm Fe and Ni solutions, 0.1 ppm Cr and a water blank at the 267.716 nm Cr wavelength

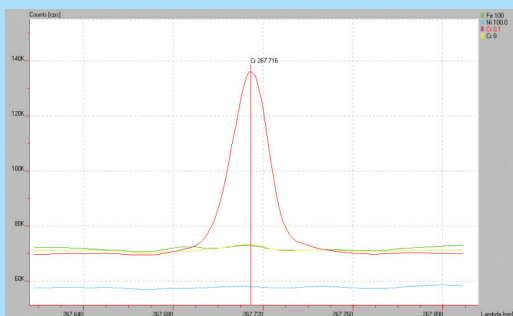
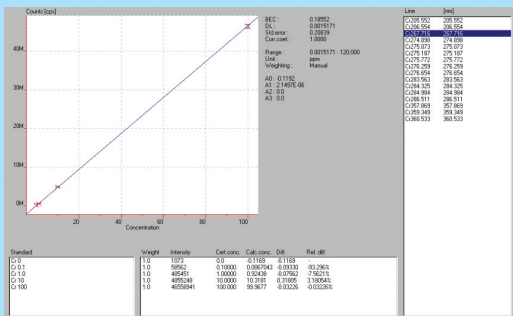


Figure 7.4:

IDL, BEC and regression data for the 267.716 nm Cr line



The good news is that the 267.716 line looks spectrally clean and the possibility of increasing the sample size while lowering the final volume by a factor of 100 is possible (i.e., 2 grams sample up to 100 mL using 20 mL of 1:1 HCl/HNO₃). The concentrations of the Fe and Ni in the final solution would be ~ 10,000 µg/mL each. This capability was confirmed when 40,000 µg/mL solutions of both Fe and Ni were scanned as shown in **Figure 7.5**. These spectral data indicate a realistic detection of << 1 ppm Cr.

Figure 7.5:

Spectra of pure 40,000 ppm Fe and Ni solutions, 0.1 ppm Cr and a water blank at the 267.716 nm Cr wavelength

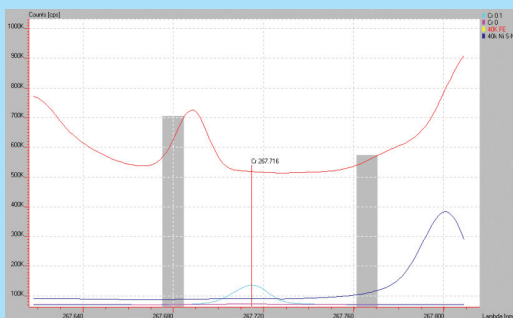
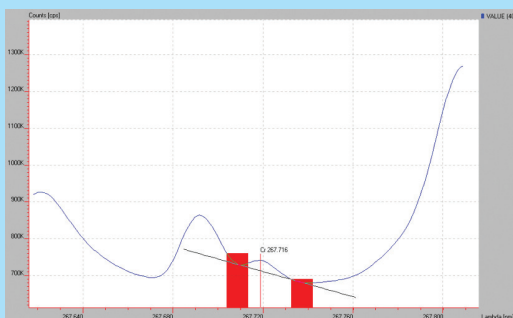


Figure 7.6:

Simulated spectrum of a solution produced from 2 grams 100 mL solution of a 50/50 wt. % Ni/Fe alloy containing 1.25 ppm Cr at the 267.716 nm Cr wavelength



The spectra in **Figure 7.5** were used to artificially produce **Figure 7.6** which approximates signals that would be measured for a Fe/Ni alloy where 2 grams to 100 mL dilution were made on a sample containing 1.25 ppm Cr. The entire investigation was performed using spectra that had been stored on computer (i.e., the analyst can literally provide an answer as to project feasibility while speaking on the phone with the client).

The above process is not intended to take the place of method validation, but rather to arm the analyst with sufficient data to make intelligent choices during the initial stages of method development.

Confirm Basic Performance Criteria

This section discusses performance criteria confirmation during the method validation process. Please note that the validation process is more detailed and specific.

The method must “fit the purpose” as agreed upon between the client and the analyst. In the case of trace analysis, the following criteria are typically evaluated as part of the method development process:

- **Specificity** involves the process of line selection and confirmation that interferences for the ICP-OES or ICP-MS measurement process are not significant. A comparison of results obtained using a straight calibration curve (without internal standardization or the technique of standard additions) will give information concerning matrix effects, drift, stability, and the factors that influence the stability. The various types of spectral interferences encountered using ICP-MS and ICP-OES (see above links) should be explored.
- **Accuracy or Bias** can be best established through the analysis of a certified reference material (CRM, or SRM if obtained from NIST). If a CRM is not available, then a comparison to data obtained by an independent validated method is the next best approach. If an alternate method is not available, then an inter-laboratory comparison, whereby the laboratories involved are accredited (ISO 17025 with the analysis on the scope of accreditation) is a third choice. The last resort is an attempt to establish accuracy through spike recovery experiments and/or the use of standard additions.
- **Repeatability** (single laboratory precision) can be initially based upon one homogeneous sample and is measured by the laboratory developing the method. The repeatability is expressed as standard deviation.
- **Limit of Detection (LOD)** is a criterion that can be difficult to establish. The detection limit of the method is defined as $3 \cdot SD_0$, where SD_0 is the value of the standard deviation as the concentration of the analyte approaches 0. The value of SD_0 can be obtained by extrapolation from a plot of standard deviation (y axis) versus concentration (x axis) where three concentrations are analyzed ~ 11 times each that are at the low, mid, and high regions of interest. This determination should be made using a matrix that matches the sample matrix.
- **Sensitivity** or $\Delta C = 2 (2)^{1/2} SD_c$, where SD_c is the standard deviation at the mid point of the region of interest. This represents the minimum difference in two samples of concentration C that can be distinguished at the 95% confidence level.
- **Limit of Quantitation (LOQ)** is defined as $10 SD_0$ and will have an uncertainty of ~ 30% at the 95% confidence level.
- **Linearity or Range** is a property that is between the limit of quantitation and the point where a plot of concentration versus response goes non-linear.

8. Spectral Interference: Types, Avoidance and Correction

Types of Spectral Interference: ICP-OES

As noted in part 7 of this guide, the collection of spectra at different concentrations on all elements and lines available will save a lot of time in the line selection process.

Avoidance: ICP-OES

Several modern ICP instruments have the capability of avoiding the spectral interference by going to another line. Many instruments can make measurements simultaneously on several lines for 70+ elements in the same time it used to take to make a measurement on a single line/element combination. If you have the opportunity, I would strongly encourage the avoidance approach over attempting to make correction on a direct spectral overlap or wing overlap interference. Background corrections are another manner and can be routinely dealt with.

Figure 8.1:

Spectrum of 6% Ca solution vs. nitric acid blank

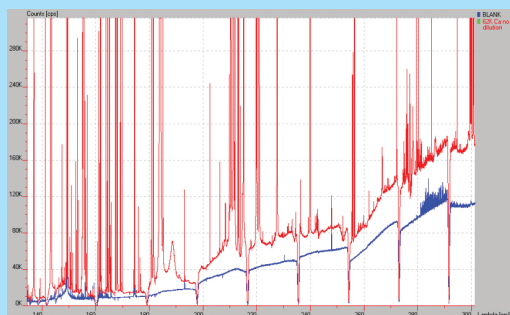
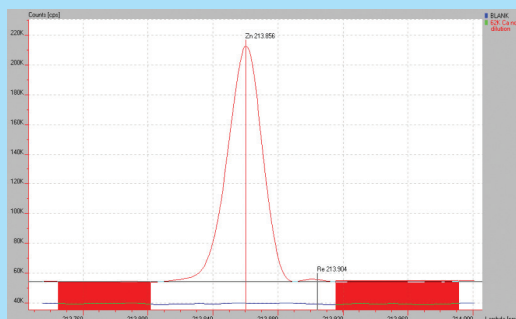


Figure 8.2:

Flat background correction



Correction: ICP-OES

Examples are provided below for background interference and spectral overlap.

BACKGROUND INTERFERENCE

Background radiation is a potential source of error that requires correction. The source of the background radiation is from a combination of sources that cannot be easily controlled by the operator. **Figure 8.1** shows the spectra for a highly concentrated Ca sample as compared to a nitric acid blank.

The background radiation intensity for the nitric acid blank is ~ 110,000 counts at 300 nm whereas the background radiation for the Ca containing solution is ~ 170,000 counts at the same wavelength. Although background radiation can be lowered somewhat by adjusting instrumental parameters, it cannot be eliminated and corrections are typically necessary. It can be seen that the highly concentrated

Ca matrix contributes some to the background radiation but there are greater contributions from other sources independent of the sample matrix.

It can be argued that matrix-matched standards and samples will eliminate the need for background correction where the analyst only has to measure the peak intensity. It would follow that the precision of the measurement would be better (lower) and for some instruments the measurement time will be shorter. However, the problems with matrix matching are obvious and may offset any advantage gained when you don't make them.

The correction for background radiation is typically made by first selecting background points or regions and then a correction mode or algorithm. The "algorithm" or "correction mode" depends upon the curvature of the background, as is illustrated below.

Figure 8.2 shows a flat background where correction was made on both sides of the line. In this case the instrument allows for the selection of background regions thereby improving the accuracy of the estimated background radiation. If the instrument only allows for selection of background points then intensities are taken at set wavelengths, averaged and subtracted from the peak intensity. For flat backgrounds the distance of each point from the peak intensity is not important provided there is no interference from other lines in that vicinity. **Figure 8.2** demonstrates that care was taken to avoid the Re line on the long wavelength side of the Zn 213.856 nm line and that a straight line that accurately determines the background intensity in the peak area is obtained.

Figure 8.3:
Sloping background correction

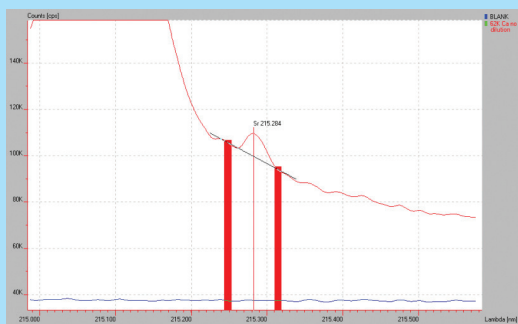


Figure 8.4:
Curved background correction

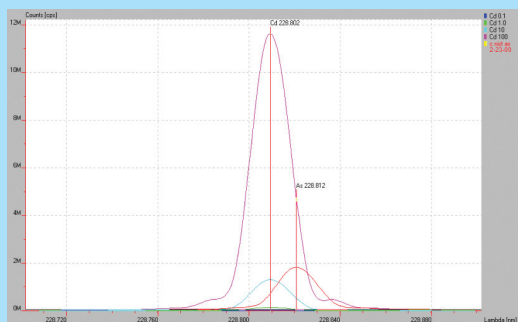
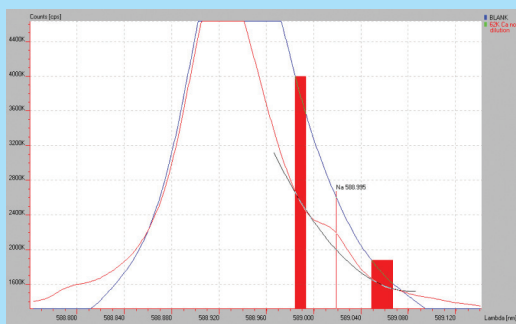


Figure 8.5:
Spectra for 100 $\mu\text{g/mL}$ As and 0.1, 1.0, 10, and 100 $\mu\text{g/mL}$ Cd

Figure 8.3 shows a sloping but linear background. If the instrument only allows for selection of background points then intensities are taken at set wavelengths, averaged and subtracted from the peak intensity. Here, background points must be taken equal distance from the peak center in order to make an accurate correction. Again, a linear fit was used.

Curved backgrounds are encountered when the analytical line is near a high intensity line, as is the case shown in **Figure 8.4**. In this case an algorithm estimating a curve (parabola) was used. For some instruments, depending upon design and software, this type of correction can be very difficult. This is a case where the 589.592 nm Na line would allow for the easier linear correction without loss in sensitivity.

SPECTRAL OVERLAP

For purposes of demonstration the interference of the As 228.812 nm line upon the Cd 228.802 nm line will be used. In this example, the analyst is attempting to determine the feasibility of measuring Cd in the 0.05 to 100 µg/mL range with 100 µg/mL As present. The analyst would like to have both elements present in the calibrations samples as well as make accurate Cd determinations in unknown samples. The analyst would also like to estimate the detection limit for Cd under these conditions.

As discussed in part 7 of this guide, spectra collected at the time of the establishment of a given instrument in the laboratory can save significant time later. In this case, we will be using spectra collected just after the instrument was installed. It is true that the instrument has aged and its performance characteristics may be different (better or worse), but the analyst can still call upon the aid of these data to gain some insight into the feasibility of making a given determination. Consequently, **Figure 8.5** shows the spectra for solutions containing 0.1, 1.0, 10 and 100 µg/mL Cd along with the spectrum of a 100 µg/mL As solution.

Table 8.1 contains intensity data collected from **Figure 8.5**. This table shows:

- (A) the concentration of Cd;
- (B) the relative concentration of As to Cd;
- (C) the net intensity of the corresponding Cd concentration with no As present;
- (D) the estimated standard deviation of measurement of Cd;
- (E) the net intensity of 100 ppm As at the 228.802 nm wavelength;
- (F) the estimated standard deviation for measurement of As;
- (G) the estimated standard deviation of the combined signals for As at 100 ppm and Cd at the concentrations given;
- (H) the uncorrected relative error for measuring Cd 228.802 nm with 100 ppm As present, and;
- (I) the best-case relative errors for correcting the Cd intensity to account for 100 ppm As.

Table 8.1:
Estimated Errors of As on Cd 228.802 nm line

Conc. Cd ppm	Rel conc. As/Cd	Cd 228.802 net intensity	Estimated SD on clean Cd line	100 ppm As net intensity at 228.802	Estimated SD on 100 ppm As at 228.802	Estimated SD of 100 ppm As + corr. Cd conc at 228.802	Uncorrected Relative Error (%)	Best-Case Corrected Relative Error (%)
A	B	C	D	E	F	G	H	I
0.1	1000	13913	132	672850	6729	6730	5100	51.0
1	100	124410	1244	672850	6729	6843	541	5.5
10	10	1242401	12424	672850	6729	14129	54	1.1
100	1	11196655	111967	672850	6729	112169	6	1.0

It was assumed that the precision (expressed above as standard deviation) of measuring the intensity of the As or Cd contributions at 228.802 nm is 1%. In addition, it was assumed that the best-case precision for making a correction is calculated using the following equation:

$$SD_{\text{correction}} = [(SD_{\text{CdI}})^2 + (SD_{\text{AsI}})^2]^{1/2}$$

where:

$SD_{\text{correction}}$ = standard deviation of the corrected Cd intensity;

SD_{CdI} = standard deviation of the Cd intensity at 228.802 nm;

SD_{AsI} = standard deviation of the As intensity at 228.802 nm

We can see from the above assumptions that a very optimistic view was taken in making this assessment. If we assume that a best-case detection limit for Cd at 228.802 nm in the presence of 100 ppm As would be $2 \times SD_{\text{correction}}$, then the calculated detection limit is 0.1 ppm. In reality, the detection limit would be closer to .5 ppm. The detection limit for the Cd 228.802 nm line is 0.004 ppm (spectrally clean) showing roughly a 100-fold loss. Furthermore, the lower limit of quantitation has been increased from 0.04 ppm (10 x the DL) to somewhere between 1 and more realistically 5 ppm Cd. **Figure 8.6** illustrates the situation with the spectra of 1 and 10 ppm Cd solutions with and without 100 ppm As present.

Correcting for the interference of As upon Cd would require that (1) the As concentration in the solution be measured and that (2) the analyst already have measured the counts/ppm As at the 228.802 nm line (sometimes called correction coefficient). This information allows for a correction by subtracting the calculated intensity contribution of As upon the 228.802 nm Cd line, thereby making the correction. This approach further assumes that slight changes in the instrumental operating parameters and conditions will influence both the analyte (Cd) and the interfering element (As) equally (i.e., an assumption many analysts are not willing to make).

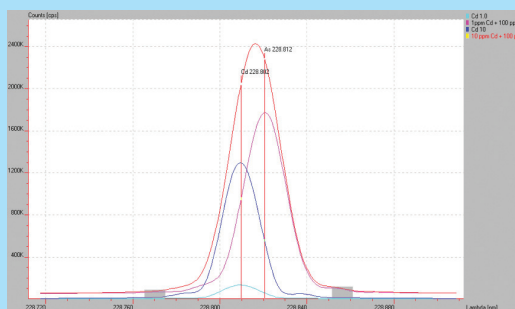


Figure 8.6:
1 and 10 ppm Cd with and without
100 ppm As

The problems associated with direct spectral overlap make it difficult for the analyst to perform quantitative measurements. Each case should be reviewed. If a spectral correction is found to be necessary, the reader is advised to consult their operating manual where a defined procedure will be outlined using the instrument's software.

Avoidance: ICP-MS

The following are possible avoidance pathways:

- The use of high resolution ICP-MS.
- Matrix alteration through elimination - for example, elimination of S, and halogen containing reagents such as Cl.
- The use of reaction and or collision cells to remove molecular interfering ions.
- Cool plasma to reduce background interferences.
- Separation of analyte(s) - for example the use of chromatography or solvent extraction, etc.
- The use of alternate ICP discharges such as He, mixed gas (He-Ar, N₂-Ar, etc.).
- Low-Pressure ICP discharges.

These approaches are just examples of some of the approaches that have been taken to avoid interferences. For a given application, it is suggested that a literature search be performed in an attempt to benefit from the vast amount of research that has been conducted in this area. In addition, instrument manufacturers are constantly revising and updating their instrumentation and software in an attempt to take advantage of new technologies. Thus, consulting with the manufacturer may help when interferences are encountered.

The fact is that the mass spectra of elements are much less detailed than in optical emission spectroscopy. Most elements have fewer than seven isotopes and many have only one (monoisotopic). When interference is encountered, it may be possible to go to another isotope even if it is less abundant. The difficulty in obtaining low detection limits in ICP-MS with interference correction is a function of the relative signal intensities and measurement precision as illustrated above for ICP-OES. If a correction cannot be avoided, many analysts seek alternate techniques rather than run the risk of reporting unreliable data.

9. Key Instrument Parameters

The performance characteristics of an ICP is a function of a variety of instrumental parameters. Current instrumentation has many parameters that are fixed by the manufacturer and all instrumentation will come with recommended settings for those parameters that are not. The purpose of this section is to point out the key parameters that will require adjustment on a regular basis. This discussion will be limited to the introduction of the analyte as a nebulized solution and Ar as the plasma gas.

Gas Flow Rates

There are three gas flow rates for the common torch designs. The outer gas flow is sometimes referred to as the coolant or plasma gas flow; the middle or intermediate gas flow is sometimes referred to as the auxiliary gas flow; and the central gas flow is referred to as the sample or nebulizer gas flow. When working with aqueous solutions, the outer and intermediate gas flows do not have a great impact upon the performance characteristics and the values suggested by the manufacturer should be used for common applications. However, the sample gas flow rate will vary between nebulizers of the same design and require adjustment on a regular basis.

SAMPLE AR GAS FLOW FOR ICP-OES

Assuming sample solution is not significantly limited, the main consideration when adjusting the sample Ar gas flow is that of precision. Increasing the sample Ar gas flow does not necessarily increase the emission intensity. The objective in setting this flow rate is to obtain the best detection limit. Noisy signals will typically result from higher flow rates that will serve to degrade the stability of the plasma, increase the short-term measurement precision and consequently give poorer detection limits.

The following considerations should prove helpful:

- Nebulizers of the same type (design) will not necessarily give optimum performance at the same Ar flow rates.
- Each new nebulizer should be optimized.
- Determining the standard deviation of a dilute solution of a common analyte at different Ar flow settings is a simple way of determining the optimum flow setting for a given nebulizer.
- Use the Ar flow that gives the lowest standard deviation i.e. best precision.
- Most nebulizers come in a box or container that can be labeled with the optimum Ar flow determined for your instrument.
- Regularly check each nebulizer to confirm that the Ar flow rate is indeed optimal. Partial plugging, chipping, corrosion, matrix deposition, or an ailing mass flow controller are possible causes for a change in the optimum setting or an inability to reproduce the same precision as when the nebulizer was new.

Applied Power for ICP-OES

The second key parameter that the operator may wish to vary is the applied power. Higher applied power will increase the net signal intensity but not necessarily improve the detection limit.

The following information may prove useful:

- The net signal intensity will increase as the applied power is increased.
- The background signal intensity will increase as the applied power is increased.
- In the early days of ICP there was a lot of discussion about optimum power settings and observation heights (for radial view). Over the years manufacturers have determined the optimum power and observation height settings. Therefore, first try using the settings recommended by the manufacturer.
- If changes in applied power are made then determine the effect upon the detection limits of the analytes of interest.
- Higher net signal intensities will not necessarily result in lower (better) detection limits.

IMPORTANT: Sample Ar Gas Flow cannot be separated from Applied Power and Sampling Depth for ICP-MS.

The sample Ar gas flow for ICP-MS systems is a parameter that is more complex than with ICP-OES instrumentation. Assuming the goal is to obtain the maximum signal intensity, the Ar gas flow is closely related to the applied power and sampling depth. There is not a single set of optimum power, sampling depth, and sample Ar flow settings. For example, a higher applied power will increase the signal intensity but change the optimum sampling depth and sample Ar flow. However, the higher sample Ar flow rates required at high power bring about some degradation in other performance characteristics. If the applied power is constant for every method, then the optimum sampling depth will change as the sample Ar is changed. The consideration of MO (metal oxide) formation and different sensitivities at different mass ranges must also be made with increased sample Ar flow.

Here are some final observations that may prove useful:

- Higher applied power will require higher sample Ar flow to achieve optimum sensitivity.
- Increased sample Ar flow will shift the ion zone in the direction of the sampler cone orifice.
- As applied power is increased, the ion zone will shift away from the sampler cone orifice.
- At a constant applied power and sampling depth, MO formation will increase with higher sample Ar flow rates.
- At a constant applied power and sampling depth, M^{+2} formation will increase with higher sample Ar flow rates.
- Deposition on the sampler cone will increase with higher sample Ar flow rates.
- At a constant applied power and sampling depth, an increased sample Ar flow will boost the sensitivity of the lighter masses relative to the heavy masses.

- Determine the effect that changes in applied power, sample Ar flow, sampling depth, and peristaltic pump speed make on your particular model instrument using a suite of elements covering the mass range. A mixture of Mg, Rh, Ce, and U should suffice where the CeO and Ce⁺² masses are measured as well.

The above observations may seem confusing, but in reality they give the operator a degree of flexibility that the ICP-OES operator does not have in that you can optimize the instrument for selected mass ranges. For example, we know that a higher applied power will increase the signal intensity. We also know that there is an optimum gas flow for each nebulizer. Therefore, if an applied power of 1.35 kW is selected and we know that our nebulizer performs best at an Ar gas flow of 1.0 L/min then the next step is to adjust the sampling depth to give the optimum signal while aspirating a solution containing a combination of light, mid-range, and heavy elements such as Mg, Rh, Ce, and U. If the double ion or MO signals are higher than desirable, a reduction in the peristaltic pump tubing diameter or pumping speed should lower these signals. These initial adjustments will take a lot of time and patience but they are well worth the effort. As the operator makes adjustments in these key parameters, a pattern will begin to unfold allowing the operator to optimize the instrument for selected mass ranges.

It is suggested that new ICP-MS operators take the time to determine the trends when changes in applied power, sample Ar flow, sampling depth and peristaltic pump speed are made.

CALIBRATION TECHNIQUES

10. Calibration Curves

Both the accuracy and precision of ICP measurements is dependent, in part, upon the calibration technique used. This section is focused upon errors (both fixed and random) that can be introduced through the use of different calibration techniques using accurate calibration standards, samples that have been prepared accurately to within defined error limits, and an instrument that has been "set-up" correctly using a procedure programmed where there are no spectral/mass interferences that include background correction. You may believe that if the above errors have been confined to within acceptable and known limits that there is nothing else to worry about. Unfortunately, this is not the case.

The most common calibration technique options for ICP measurements are calibration curve and standard additions. In addition, the option of using internal standardization is available for the calibration curve technique and the ability of matrix matching may also be available. ICP-MS has the added option of using an internal standard that is an enhanced isotope of the element being measured (i.e., isotope dilution ICP-MS). This discussion will be limited to the above approaches, to the introduction of the analyte as a nebulized solution, and to the use of Ar as the plasma gas.

Basic Considerations

Before reading ahead, it may be helpful to restate the assumptions made above and make some additional considerations:

- ICP is a “Comparative Method” where the measurement of an unknown sample is based upon chemical standards, i.e., the measurement is a comparison process.
- It is not assumed that the calibration standards and samples have identical matrices.
- It is assumed that the calibration is linear. This means that the standard and sample elemental concentrations give an instrumental response that is described by the equation for a straight line.
- It is assumed that the analyst has prepared the chemical standards accurately to within defined error limits (i.e., the uncertainty of the prepared standard solution is known and has been calculated).
- It is assumed that the stability of the standards, however and by whoever prepared, is known and are only used within these defined limits of time, matrix, concentration, temperature/humidity, and container material(s).
- The uncertainty of the measurement of an unknown can only be worse (greater) than the uncertainty of the calibration.
- It is assumed that there are no spectral/mass interferences. This of course is an area of great concern and effort on the part of the analyst. This assumption is made to allow us to focus completely upon the potential errors involved with the calibration process.
- It is assumed that the sample prepared for analysis involves no positive or negative contamination errors and no sampling errors. It is therefore assumed that the uncertainty in preparation can be described by the random and known sampling, weighing and volume dilution errors. Again, this is an assumption that is often not the case but is made to allow us to focus completely upon the potential errors involved with the calibration process.

Calibrations Standards

ICP is a matrix-dependent technique. Based upon the above assumptions and the fact that ICP is a comparative method, the prime concern is the availability and use of appropriate calibration standards. The problem analysts face is that ICP (ICP-OES and ICP-MS) is extremely matrix-dependent. Therefore, the ideal situation is that the matrices of the standards and samples be identical.

RECOMMENDATIONS

This section lists several recommendations. Discussions relating to these recommendations are provided in the next section for the reader who would like more detail.

Recommendation A — Match the acid content of your calibration standards and samples in both the type of acid used and the concentration of the acid.

Recommendation B — Match the elemental matrix components of your calibration standards and samples to the greatest extent possible. In this situation, the analyst who knows the composition of the sample has this capability.

Recommendation C — With unknown sample matrices, matching is not possible and is most accurately dealt with using the technique of standard additions. However, this approach is slow as compared to the calibration curve technique with the use of internal standardization.

Recommendation D — The use of internal standardization is very effective in many cases but may introduce — or not correct for — all errors. This statement does not apply to isotope dilution ICP-MS that is considered to be a primary analytical technique.

Recommendation E — Chemical calibration is an approximation at best. The analytical chemist must be constantly aware of the possibility of bias introduced by the nature of the standards used, which may be the major source of bias in the analytical data. Appropriate reference materials should be used to evaluate this and other aspects of the measurement process.

DISCUSSIONS

Discussion (A and B) — The matrix will influence the nebulization efficiency, which is proportional to the signal intensity. Nebulization efficiency is the percent of solution that reaches the plasma. Therefore, if the nebulization efficiency is 1%, then 99% of the solution is going to waste and 1% is making it to the plasma. Typically, nebulized solution “mist particles” that are greater in diameter than 8 microns will go to waste. If a matrix component changes the efficiency from 1.0% to 0.8%, then a relative drop of ~ 20% would be expected from this effect alone. The droplet size distribution of a pneumatic nebulizer is governed by the physical properties of the solution as well as the volume flow rates of liquid (influenced by peristaltic pump speed and tubing diameter) and gas (sample Ar flow rate). The physical properties claimed to influence the droplet size distribution are the surface tension, viscosity, and density.

See: *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*; Montaser, A., Golightly, D. W., Eds.; VCH Publishers: New York, 1992 — page 703 for more detail and additional references on this topic.

For the ICP analyst, the most common matrix component that will alter the physical properties of a solution is the acid content. This is not to say that other differences such as the presence of trace organics (added intentionally or not) should not be considered. However, the identity and concentration(s) of one or more acids is an issue that virtually all ICP analysts have to decide upon. The ICP analyst is most commonly involved in the preparation of samples where one or more inorganic mineral acids are required to bring about dissolution of the sample and/or to maintain solution stability of the analyte(s) of interest. The acids most commonly used are HNO_3 , HCl , HF , HClO_4 , H_2SO_4 , and H_3PO_4 and are listed in the order of best to worst.

The effect of acid matrix upon nebulization efficiency is such that a change in acid content from 5 to 10% v/v will cause a decrease in efficiency of 10 to 35% depending upon the acid used, nebulizer design and liquid and gas flow rates. Matching the matrix to within 1% relative is necessary for the most accurate (we use the term “assay”) work (i.e., a 5% HNO_3 acid solution would be made to $5.00 \pm 0.05\%$).

The matrix will influence the plasma temperature, which is related to the signal intensity for ICP-OES. The other effect matrix components have on the ICP cannot be explained by a change in nebulization efficiency. The effect is one where the matrix components give the appearance of taking power away from the plasma (lowering the temperature of the plasma). It has been reported that this effect is related to the excitation potential of the line and that the effect increases as the excitation potential increases. A similar effect would be seen by decreasing the applied RF power or by increasing the sample (nebulizer) Ar flow rate since both result in a reduction of the plasma temperature. Therefore different lines of the same element would be affected differently according to their excitation potentials. In addition, when choosing an internal standard element it follows that the excitation potentials of the internal standard and analyte lines should be as close as possible, unless the calibration standards and samples are matrix matched. For more information and additional references, see:

Inductively Coupled Plasmas in Analytical Atomic Spectrometry; Montaser, A., Golightly, D. W., Eds.; VCH Publishers: New York, 1992 — pages 279–281.

ICP-MS suffers from nonspectral matrix effects. The effect most commonly encountered is referred to as "quenching" and is thought to be due to defocusing of the ion optics by space charge effects. Generally, as the concentration of the "matrix element(s)" increases, the analyte signal will be suppressed. Quenching increases in effect as the matrix element absolute concentration increases, the matrix element mass increases and the analyte mass decreases. This effect is absolute in nature and not a function of the relative concentrations of the matrix elements and analyte elements. Therefore, when sensitivity allows, it can be diluted out. It is also greater in effect as the RF power is lowered. The effect is such that an element matrix concentration of 100 ppm can severely suppress a "cool plasma" (RF power W ~ 800) and has little effect at normal power (an RF power of ~ 1300 W). For more information and additional references, see:

Inductively Coupled Plasma Mass Spectrometry; Mantaser, A., Ed.; Wiley-VCH: New York, 1998 — page 543.

11. Standard Addition Techniques, Internal Standardization and Isotope Dilutions

Matrix effects are arguably the subtlest danger to the ICP-OES analyst. Slight differences in the matrix can cause a considerable systematic error. The most common calibration technique options for ICP measurements are calibration curve and standard additions.

Standard Additions

The technique of standard additions is used when the matrix is quite variable and/or when an internal standard that corrects for plasma related effects couldn't be found. This technique is also useful in confirming the ability of an internal standard calibration curve technique to correct for both nebulizer and plasma related effects (see part 10 of this series for more on nebulizer and plasma related matrix effects).

The following considerations may prove useful in performing the technique of standard additions:

- Split the analytical (sample) solution accurately. For example, if the final sample solution is made to 100.00 grams, then remove exactly 50.00 grams of solution to a separate clean container for spiking.
- The technique of standard additions requires a linear response. It is therefore important to work within the linear working range for each analyte.
- It is beneficial to perform a quick semi-quantitative analysis of the unknown to estimate analyte levels so that the analyst can spike the unknown solution with a concentrate of the analyte(s) of interest to levels of between $2x_u$ and $3x_u$ where x_u represents the unknown concentration(s) of the analyte(s) of interest.
- Many analysts prefer to make more than one spiked level (i.e., $2x_u$, $3x_u$, $4x_u$, and $5x_u$). As with all techniques, a primary concern is in making an accurate spiked addition. For ICP, an additional concern is drift. The objective is to make an accurate measurement. Rather than making multiple spiked additions where drift is given more ground to introduce error, it is suggested that the analyst measure the sample along with a single spiked sample several times to account for drift. A reasonable measurement sequence would be:

blank -> sample -> blank -> spiked sample -> blank -> sample -> blank -> spiked sample -> blank -> sample -> blank

where an average of all measurements is taken for the final calculation. The above analysis sequence assumes linear drift that should be confirmed before acceptance of the data.

- Attempt to keep the spiking volumes low. For example, a spike of 100 μL to a 50.00 gram sample aliquot represents a 0.2% relative error. If larger spiking aliquots are required then an equal volume of 18 M Ω water should be added to the unspiked sample portion to cancel out volume dilution errors.
- The technique of standard additions assumes that the instrumental response is described by the equation of a straight line with x,y coordinates of 0,0 as follows:

$$(1) \quad Y_1 = mx_u$$

where Y_1 = intensity of the sample, m = slope, and x_u = concentration of the unknown analyte

When a spike addition is made the equation becomes:

$$(2) \quad Y_k = m(x_u + x_s) = mx_u + mx_s$$

Where x_s = the concentration contribution from the spike addition to the analyte concentration and Y_k = intensity for the spiked sample

- Note that the above equation (1) relating intensity (Y) to concentration (x) requires that the intensity is zero at an analyte concentration of zero. It is therefore necessary that the signal intensities be background corrected.
- The analyte concentration is determined as follows:

Subtract the intensity of the unspiked from the spiked sample solution and divide this by the concentration of the analyte spike to calculate the slope (m)

$$Y_k - Y_1 = mx_u + mx_s - mx_u = mx_s$$

$$(Y_k - Y_1) / x_s = m$$

Substitute the value for m into equation (1) along with the intensity (Y_1) to calculate the unknown analyte concentration (x_u)

The technique of standard additions offers the best possible solution to matrix interference through plasma related effects. The technique requires an accurate background correction of the analytical signal intensities and does not account for instrument drift. For unknown matrices, it may well be the fastest approach. When using standard additions on unknown matrices, it is possible to have severe spectral and background correction problems. It is cautioned here that at least two spectral lines should be used and the spectral region carefully scanned and studied.

Internal Standardization

The calibration curve technique is the most popular calibration technique. If the sample matrices are known and consistent then matrix matching the calibration standards to the samples is an excellent option. Even when matrix matching is an option, many analysts still use an internal standard. It is suggested that the analyst consider the following questions before using an internal standard:

1. Is the internal standard (IS) element compatible with your matrix? (Avoid using rare earths in fluoride matrices.)
2. Are there any possible spectral interferences upon the IS line?
3. Is the concentration of the IS sufficient to give a good signal to noise ratio?
4. Can your sample possibly contain the IS element as a natural component?
5. Is the IS clean? Are the trace impurities reported on the certificate of analysis?
6. Is your method of addition of the IS very precise? Is the same amount added precisely to all standards, blanks, and samples?
7. Do you always use the same lot of IS for the standards and samples? (Using the same lot is very important.)
8. If your plasma temperature were to go up or down, is the IS likely to follow the same pattern of intensity change as the analyte? This is where many IS problems occur (i.e., — an IS with the same plasma / temperature behavior as the analyte is difficult [at best] to find for each analyte while avoiding other issues listed above).

As discussed in the last part of this series, the matrix can influence the plasma as well as the nebulizer. Internal standardization is very effective in correcting for nebulizer related effects and may be effective for correcting plasma related effects. It is obviously important that the matrix effect influence both the internal standard to the same extent as the analyte. This should be the case for nebulizer related effects but it may not be so for plasma related effects where the matrix influence is related to the excitation potential of the emission line (as discussed in Part 10). It may be difficult to find an internal standard that has a similar excitation potential as the analyte in measurements where several analytes are involved. The analyst is advised to confirm that the matrix influences the internal standard and analyte signal intensities proportionately.

Isotope Dilution Mass Spectrometry

As discussed in part 10, ICP-MS suffers from matrix related effects upon the nebulizer and the signal intensity (quenching). In addition, even slight deposition on the sampler cone will cause drifting. Due in part to drifting, analysts have chosen to use the calibration curve technique with internal standardization over the technique of standard additions. Although the standard additions technique should work well in theory, the drifting associated with ICP-MS is too pronounced. The use of a ratio technique such as internal standardization is a reasonable compromise with the understanding that the internal standard is not influenced to exactly the same degree as the analyte signal. This is due to mass dependence. The internal standards commonly used are only used over relatively narrow mass ranges making the use of multiple internal standard elements required for broad mass range applications. The most common internal standard elements listed from low to high mass are ^6Li (isotope 6 enriched), Sc, Y, In, Tb and Bi.

ICP-MS has the unique capability of using an enriched isotope of the element of interest as the internal standard. This technique, which is known as isotope dilution mass spectrometry (IDMS), has been known for nearly 50 years¹. IDMS is made possible through the availability of enriched stable isotopes of most of the elements from the National Isotope Development Center (U.S.A.). IDMS is therefore not applicable to monoisotopic elements.

The IDMS technique involves the addition of a known amount of an enriched isotope of the element of interest to the sample. This addition is made prior to sample preparation during which the spiked addition of the enhanced isotope is "equilibrated" with the sample. By measuring the isotope ratio of the sample and sample + spike isotope addition and knowing the isotopic ratio of the enhanced addition, the sample concentration can be calculated. The entire measurement is based upon ratio measurements of one isotope of the element to another. Drift, quenching and other related matrix effects do not present an interference with IDMS. This technique is considered a definitive² method and is well suited and established for the certification of certified reference materials.

IDMS is free from matrix effects (physical interference) but it is not interference-free in that mass interference must still be dealt with (isobaric, MO^+ , M^{++} , etc.) in addition to correction of the signal intensity for detector dead time and mass bias interference.

To view an example of an IDMS method, reference EPA Method 6800.

1. Hintenberger, H, *Electromagnetically Enriched Isotopes and Mass Spectrometry, Proceedings Conference, Harwell, (1955): pg 177; Butterworths Scientific Publications, London.*
2. *Definitive is defined as, "A method of exceptional scientific status, which is sufficiently accurate to stand alone in the determination of a given property for the Certification of a Reference Material. Such a method must have a firm theoretical foundation so that systematic error is negligible relative to the intended use. Analyte masses (amounts) or concentrations must be measured directly in terms of the base units of measurements, or indirectly related through sound theoretical equations. Definitive methods, together with Certified Reference Materials, are primary means for transferring accuracy -- i.e., establishing traceability.*

Traceability is defined as, "The property of a result or measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons."

PROBLEM ELEMENTS

12. Common Problems with Hg, Au, Si, Os and Na

This part of our ICP Operations guide provides some suggestions when attempting to work with mercury, gold, silicon, osmium, or sodium.

Mercury (Hg)

In March of 2003, the EPA published a bulletin describing the use of Au to stabilize Hg solutions: Mercury Preservation Techniques. When working at the ppb level we have found that using HCl rather than nitric acid will maintain the stability of Hg⁺² solutions in plastic (LDPE) containers.

The stability of mercury-containing solutions has been a topic of concern for all trace analysts performing Hg determinations. Our in-house stability studies have yielded the following conclusions.

Mercury Stability

1. Hg is stable in glass (only borosilicate glass studied) in 5% nitric acid at room temperature at all concentrations studied (0.05 to 1000 µg/mL) for 4 years.
2. Hg is stable in glass (only borosilicate glass studied) in 5% nitric acid at 4°C at 0.05 µg/mL for 14 months.
3. Hg is stable in in LDPE (only borosilicate glass studied) in 5–10% nitric acid at room temperature at at concentrations greater than 200 µg/mL for 4 years.
4. Hg is stable in 10% v/v HCl in at room temperature at all concentrations studied (0.1 to 1000 µg/mL) for at least 4 years.
5. Hg is stable in LDPE in 5% v/v HNO₃ / 1% v/v HCl at 0.1 and 1 µg/mL with other elements for at least 3 years.
6. Hg is stable in LDPE in 2% v/v HNO₃ / 1ppm AuCl₃ at concentrations between 0.001 and 0.1 µg/mL for no more than 12 months.

Mercury Instability

1. Hg is not stable in multi-element blends containing Sb as the tartrate.
2. Hg standards at 0.1, 1.0, 5, 10 and 100 µg/mL were studied in LDPE and it was found that Hg is lost. The loss at 100 µg/mL is relatively small.
3. Hg loses up to 1 µg/mL Hg in LDPE over time. Therefore, Hg standards <200 µg/mL should be packaged in borosilicate glass with an acid concentration of at least 5% v/v HNO₃.
4. The most dramatic result of Hg loss:
In a comparison of 5 µg/mL Hg standards in 5% nitric acid stored at room temperature in glass and LDPE over a period of ~2.5 years, it was found that the glass was stable. The LDPE container lost greater than 99% of the Hg indicating amounts of Hg >1 µg/mL can be lost in LDPE with time.

Another problem with Hg is loss during sample preparation. When performing acid digestions, the use of closed vessel digestion or the use of condensers should be considered. Ashing should be avoided. Only use validated sample preparation procedures.

Here are some additional suggestions when working with mercury:

- The presence of reducing agents in the solution may reduce Hg to the metal causing false high results due to the volatility of the element where the introduction system delivers more Hg to the plasma as a result.
- The use of plastic introduction systems will cause unusually long washout times. Glass is preferred and the use of HCl rather than nitric acid will reduce the washout time.
- The use of nitric acid matrices for ppb Hg determinations by ICP-MS should only be attempted when using Au as a stabilizing agent.

Gold (Au)

The chemical stability of Au is very similar to that of Hg. The following suggestions may be helpful:

- Nitric acid solutions of Au at the low ppm and ppb levels are not stable. Use HCl matrices.
- Do not use Pt crucibles when ashing samples containing Au. Au will alloy with the Pt.
- When measuring Au in the presence of significantly greater amounts of Pt using ICP-MS, be aware of the resolving capability of your instrument.

Silicon (Si)

The following suggestions are advised when working with silicon:

- Si is a common contaminant. In addition to the obvious use of laboratory glassware, common sources of contamination include silicon oil/grease, plastics containing catalyst residue, and air particulates.

- Si^0 is easily dissolved using an equal mixture of $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$. SiO_2 is readily soluble in either HF or NaOH. Regardless of the mode of dissolution, solutions should be stored in plastics known to contain no catalyst residues or that have been leached with dilute HF for 48 hours.
- Exercise caution when heating solutions containing Si and HF. Si may be lost as the volatile H_2SiF_6 when heated. When water is present H_2SiF_6 will not form. If you wish to remove Si from the sample then add sulfuric acid and heat in a Pt crucible.
- Silicon dioxide is soluble in caustic media. When acidified it is stable at low ppm levels but will slowly polymerize and precipitate out of solution. Common preparations involve sodium carbonate fusions in Pt crucibles and dissolution of the fuseate with HCl — make sure the ppm level of Si upon dilution is low ppm and the solution is not allowed to sit for extended periods.
- HF (even low ppm levels of HF) containing samples should not be put through glass or quartz introduction systems when Si, B, Na, or Al are analytes of interest.

Osmium (Os)

Keep the following in mind when working with osmium:

- Os should not be exposed to any oxidizing agents to avoid the formation of OsO_4 . The tetroxide is very volatile and toxic.
- A common mistake is to dilute Os containing solutions with solutions containing nitric acid. Tetroxide formation is slow but will cause false high readings due to the increased amount of the gaseous tetroxide reaching the plasma.
- Only work with Os in HCl containing solutions and use a separate waste container. Check with your safety coordinator or manager before using and attempting to dispose of Os.
- Use glass introduction systems if at all possible when measuring Os. The washout times from plastic introduction systems are longer.

Sodium (Na)

The single most common problem with Na is contamination. Sodium is literally everywhere. Thousands of tons of salt are transferred from the ocean to the air in the form of sub-micron particulates and can travel for hundreds of miles inland. For more information on contamination, please refer to the following sections of our Trace Analysis series: Environmental Contamination, Contamination from Reagents, Contamination from the Analysis and Apparatus, and Na elemental data.

13. Common Problems with Ag, As, S, Ba, Pb and Cr

This part of our ICP Operations guide provides some suggestions that you may find useful when attempting to work with silver, arsenic, sulfur, barium, lead, or chromium.

Silver (Ag)

Ag forms more insoluble salts than any other metal, although Pb and Hg are not far behind.

Table 13.1

Solubility of common silver salts at room temp. (~22C°)

Salt	Solubility in g./100g. H ₂ O
Acetate	1.04
Arsenate	0.085
Arsenite	0.00115
Borate	0.905
Bromate	0.196
Bromide	0.014
Carbonate	0.105
Chloride	0.0154
Chromate	0.00256
Cyanide	0.022
Ferricyanide	0.066
Fluoride	172
Iodate	0.00503
Iodide	0.028
Nitrate	216
Oxalate	0.00378
Oxide	0.00248
Phosphate	0.064
Sulfate	0.83
Sulfide	0.0174
Tartrate	0.0201
Thiocyanate	0.025

- The use of nitric acid and/or HF is preferred for preparation of samples for Ag analysis. Solutions of Ag in either acid are stable for extended periods.
- Trace levels of HCl or Cl⁻¹ must be eliminated otherwise a fixed error due to AgCl precipitation will result.
- If the sample preparation requires the use of HCl, attempt to keep the HCl content high (10% v/v) in an attempt to keep the Ag in solution as the AgCl_x^{1-x} anionic chloride complex. In addition, the concentration of Ag should be ≤10 µg/mL Ag. In short, keep the HCl concentration high and the Ag concentration low.
- Solutions containing suspended AgCl and/or the AgCl_x^{1-x} anionic chloride complex are photosensitive. The Ag⁺¹ will undergo photo-reduction to the metal (Ag⁰). When intentionally working in HCl minimize exposure to light.
- Many analysts experience low Ag recoveries when working in HNO₃ media. The problem is due to trace chloride contamination. Although analysts are aware of the problems with precipitation as the chloride, they are puzzled because no AgCl is observed. However, the metal has already photo-reduced onto the container walls.

Arsenic (As)

- Avoid using dry ashing for sample preparation. Loss during sample preparation as the volatile oxide (As_2O_3 bp 460°C) or chloride (AsCl_3 bp 130°C) can be avoided by performing closed vessel digestions (EPA Methods 3051 and 3052), acid digestions under reflux conditions or by caustic fusion using either sodium carbonate or sodium peroxide/sodium carbonate fluxes.
- Approach ICP-OES and ICP-MS determinations with caution. ICP-OES suffers from poor sensitivity and spectral interference issues and ICP-MS from the $^{40}\text{Ar}^{35}\text{Cl}$ mass interference (other interferences include $^{59}\text{Co}^{16}\text{O}$, $^{36}\text{Ar}^{38}\text{Ar}^1\text{H}$, $^{38}\text{Ar}^{37}\text{Cl}$, $^{36}\text{Ar}^{39}\text{K}$, $^{150}\text{Nd}^{2+}$, and $^{150}\text{Sm}^{2+}$) on the monoisotopic ^{75}As . The use of atomic absorption using either the hydride generation or the graphite furnace techniques is very popular, although the use of "reaction cells" that appear to eliminate the $^{40}\text{Ar}^{35}\text{Cl}$ interference in ICP-MS is an option worth exploring.

Sulfur (S)

Conventionally, sulfur measurements are made using combustion techniques coupled with measurement of the SO_2 combustion gas by infrared, micro-coulometric, or titrimetric (iodometric) techniques. Since 1974, techniques involving ion chromatography (speciation) and X-ray fluorescence have become very popular. More recently, ICP-OES has become a viable measurement technique for sulfur due to the availability of affordable radial view instrumentation with measurement capability in the vacuum UV spectral region and the relative freedom of spectral interferences. Popular emission lines with IDLs measured in our laboratory are shown in Table 13.2:

Table 13.2
Common Sulfur Emission Lines

Line	IDL (radial)	Line	IDL (radial)
142.503	.04 $\mu\text{g}/\text{mL}$	166.668	.02 $\mu\text{g}/\text{mL}$
143.328	.04 $\mu\text{g}/\text{mL}$	180.734	.07 $\mu\text{g}/\text{mL}$
147.399	.05 $\mu\text{g}/\text{mL}$	182.040	.03 $\mu\text{g}/\text{mL}$

The following tips may prove useful in the preparation and solution chemistry of samples for sulfur analysis using ICP-OES:

- Loss during sample preparation is a significant issue. Preparations using closed vessel systems are recommended. Parr bomb fusions, Schöniger Flask combustions, and closed vessel microwave digestions should be considered depending upon the sample matrix, sulfur compound type(s), sulfur levels and sample size requirements needed to make quantitative measurements.
- Preparations including sulfate, Ba and Pb should be avoided. The molecular form of the sulfur may have compatibility issues with other chemical species in the sample solution preparation. Sulfate (SO_4^{2-}) sulfur is a common molecular form resulting from oxidative sample preparations. Even though the preparation

promises to deliver sulfite (SO_3^{2-}) sulfur this species quickly air oxidizes in aqueous solution to the sulfate form. Sulfate readily precipitates with solutions containing Pb or Ba.

- Water soluble samples known to contain sulfur as sulfate, sulfite or low molecular weight water soluble sulfonic acids (RSO_3H) may need no sample preparation but samples known to contain sulfur in other forms such as sulfides (S^{2-}), elemental (S^0), polysulfides (S_n^{2-}), thiols (RSH), organic sulfides and disulfides (R-S-R and R-S-S-R), thioesters (R-CO-SR) etc. should undergo oxidative sample preparation to avoid possible compatibility issues with other solution components. In addition, the addition of acid to sulfide containing samples will emit H_2S .

Barium (Ba)

Of the four acids most commonly used in sample preparations, Ba will form precipitates with HF and H_2SO_4 . In addition, the solubility of BaHPO_4 and BaCrO_4 are 0.01 and 0.001 g/100 g H_2O respectively. Solutions that are neutral or alkaline will ppt. BaCO_3 (solubility 0.0024g/100g H_2O).

- Samples containing Ba and sulfur compounds may form BaSO_4 in oxidative decompositions. I know of no simple way to dissolve this precipitate. Since small amounts of barium sulfate do not readily coagulate the precipitate can easily go unnoticed. Attempts to dissolve barium sulfate have seemingly focused upon the use of EDTA (K_f 7.86) and DTPA (K_f 8.78). However, the pH of the solution, which must be ~ 5 , can lead to precipitation and/or adsorption problems with other analytes and the dissolution rate is slow.
- Avoid combinations of Ba^{+2} with SO_4^{2-} , CrO_4^{2-} or F^- in acidic media.
- Avoid raising the pH of sample solutions containing Ba^{+2} to 7 or greater to avoid loss as the carbonate or hydrogen phosphate.

Lead (Pb)

Lead has a number of chemical compatibility issues. In trace analyses the analyst typically does not experience serious problems unless attempting to combine Pb with sulfate or chromate. Other chemical components to avoid are the halogens (Cl, F, Br, and I), thiosulfate, arsenate, and sulfide to name the most common. However, the major problem with trace Pb analysis is contamination from the apparatus and atmosphere. Pb is used in industry in plumbing (pipes), solder, gasoline (significantly curtailed), drying agent for oils, glass, plumber's cement, covering of steel to prevent rust, as a pigment in paint (significantly curtailed), hair dye and as a pigment in plastics.

- Environmental contamination from airborne particulates is still a major concern in certain regions/laboratories depending upon location and age. When tetraethyl lead was widely used as an octane booster it was impossible to avoid environmental contamination in an open digestion apparatus. Open digestions in hoods where large volumes of air pass over the apparatus are of most concern. Closed container digestions or clean rooms / hoods are suggested to avoid this source of contamination.

- Avoid the use of any type of glass in sample preparations for Pb. Use quartz or fused silica and perform a sufficient number of blanks to define the degree of contamination.
- Avoid the use of any plastic with an inorganic pigment. Here Pb is only one of many concerns.
- Teflon containers should be carefully leached with dilute nitric acid before use and blanks performed to confirm freedom from Pb contamination. Be particularly suspicious of Teflon that has been used in sample preparations where Pb was a major, minor or trace component.

Chromium (Cr)

The major difficulty that I have experienced with Cr is that it often exists in forms that are difficult to put into solution. Chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$), chromic oxide, pigments, stainless steel and ferro-chrome all present a challenge but the hexavalent chromium oxides are the most difficult. If the oxide has been ignited (pigments) the refractory nature is such that an analyst confronted with the task of bringing about solution will never forget the experience. The most common approach is to perform a fusion. Fusions that have been used include but are not limited to potassium and sodium bisulfate, carbonate (sodium or potassium), sodium peroxide, $\text{NaOH} / \text{KNO}_3$, and $\text{NaOH} / \text{Na}_2\text{O}_2$. In addition, the fusion will not be complete unless the chrome is finely divided and mixed with the flux.

- Know your sample to the fullest extent possible. The possible chemical forms of Cr should influence the sample preparation technique employed.
- If your sample is an inorganic pigment containing Cr then you know that you have an extremely refractory material to dissolve.
- If you are unfamiliar with your sample type a literature search is strongly suggested.
- Method validation using a CRM containing Cr in the suspected or known chemical form(s) is vital. The importance of CRMs prepared from "real world" materials is critical (i.e., synthetic CRMs are likely to contain easily dissolved compounds).
- Avoid mixing water-soluble hexavalent chrome with Ba or Pb to avoid loss of Cr, Pb and Ba as the insoluble chromates.

BASIC CALCULATIONS

14. Accuracy, Precision, Mean and Standard Deviation

There are certain basic concepts in analytical chemistry that are helpful to the analyst when treating analytical data. This section will address accuracy, precision, mean, and deviation as related to chemical measurements in the general field of analytical chemistry.

Accuracy

In analytical chemistry, the term “accuracy” is used in relation to a chemical measurement. The International Vocabulary of Basic and General Terms in Metrology (VIM) defines accuracy of measurement as ... “closeness of the agreement between the result of a measurement and a true value.” The VIM reminds us that accuracy is a “qualitative concept” and that a true value is indeterminate by nature. In theory, a true value is that value that would be obtained by a perfect measurement. Since there is no perfect measurement in analytical chemistry, we can never know the true value.

Our inability to perform perfect measurements and thereby determine true values does not mean that we have to give up the concept of accuracy. However, we must add the reality of error to our understanding. For example, let's call a measurement we make X_i and give the symbol μ for the true value. We can then define the error in relation to the true value and the measured value according to the following equation:

$$\text{error} = X_i - \mu \quad (14.1)$$

We often speak of accuracy in qualitative terms such as “good,” “expected,” “poor,” and so on. However, we have the ability to make quantitative measurements. We therefore have the ability to make quantitative estimates of the error of a given measurement. Since we can estimate the error, we can also estimate the accuracy of a measurement. In addition, we can define error as the difference between the measured result and the true value as shown in equation 14.1 above. However, we cannot use equation 14.1 to calculate the exact error because we can never determine the true value. We can, however, estimate the error with the introduction of the “conventional true value” which is more appropriately called either the assigned value, the best estimate of a true value, the conventional value, or the reference value. Therefore, the error can be estimated using equation 14.1 and the conventional true value.

Errors in analytical chemistry are classified as systematic (determinate) and random (indeterminate). The VIM definitions of error, systematic error, and random error follow:

- **Error** — the result of a measurement minus a true value of the measurand.
- **Systematic Error** — the mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions, minus a true value of the measurand.
- **Random Error** — the result of a measurement minus the mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions.

A **systematic error** is caused by a defect in the analytical method or by an improperly functioning instrument or analyst. A procedure that suffers from a systematic error is always going to give a mean value that is different from the true value. The term "bias" is sometimes used when defining and describing a systematic error. The measured value is described as being biased high or low when a systematic error is present and the calculated uncertainty of the measured value is sufficiently small to see a definite difference when a comparison of the measured value to the conventional true value is made.

Some analysts prefer the term "determinate" instead of systematic because it is more descriptive in stating that this type of error can be determined. A systematic error can be estimated, but it cannot be known with certainty because the true value cannot be known. Systematic errors can therefore be avoided, i.e., they are determinate. Sources of systematic errors include spectral interferences, chemical standards, volumetric ware, and analytical balances where an improper calibration or use will result in a systematic error, i.e., a dirty glass pipette will always deliver less than the intended volume of liquid and a chemical standard that has an assigned value that is different from the true value will always bias the measurements either high or low and so on. The possibilities seem to be endless.

Random errors are unavoidable. They are unavoidable due to the fact that every physical measurement has limitation, i.e., some uncertainty. Using the utmost of care, the analyst can only obtain a weight to the uncertainty of the balance or deliver a volume to the uncertainty of the glass pipette. For example, most four-place analytical balances are accurate to ± 0.0001 grams. Therefore, with care, an analyst can measure a 1.0000 gram weight (true value) to an accuracy of ± 0.0001 grams where a value of 1.0001 to 0.999 grams would be within the random error of measurement. If the analyst touches the weight with their finger and obtains a weight of 1.0005 grams, the total error = $1.0005 - 1.0000 = 0.0005$ grams and the random and systematic errors could be estimated to be 0.0001 and 0.0004 grams respectively. Note that the systematic error could be as great as 0.0006 grams, taking into account the uncertainty of the measurement.

A truly random error is just as likely to be positive as negative, making the average of several measurements more reliable than any single measurement. Hence, taking several measurements of the 1.0000 gram weight with the added weight of the fingerprint, the analyst would eventually report the weight of the fingerprint as 0.0005 grams where the random error is still 0.0001 grams and the systematic error is 0.0005 grams. However, random errors set a limit upon accuracy no matter how many replicates are made.

Precision

The term precision is used in describing the agreement of a set of results among themselves. Precision is usually expressed in terms of the deviation of a set of results from the arithmetic mean of the set (mean and standard deviation to be discussed later in this section). The student of analytical chemistry is taught — correctly — that good precision does not mean good accuracy. However, It sounds reasonable to assume otherwise.

Why doesn't good precision mean we have good accuracy? We know from our discussion of error that there are systematic and random errors. We also know that the total error is the sum of the systematic error and random error. Since truly random error is just as likely to be negative as positive, we can reason that a measurement that has only random error is accurate to within the precision of measurement and the more precise the measurement, the better idea we have of the true value, i.e., there is no bias in the data. In the case of random error only, good precision indicates good accuracy.

Now lets add the possibility of systematic error. We know that systematic error will produce a bias in the data from the true value. This bias will be negative or positive depending upon the type and there may be several systematic errors at work. Many systematic errors can be repeated to a high degree of precision. Therefore, it follows that systematic errors prevent us from making the conclusion that good precision means good accuracy. When we go about the task of determining the accuracy of a method, we are focusing upon the identification and elimination of systematic errors. Don't be misled by the statement that "good precision is an indication of good accuracy." Too many systematic errors can be repeated to a high degree of precision for this statement to be true.

The VIM uses the terms "repeatability" and "reproducibility" instead of the more general term "precision." The following definitions and notes are taken directly from the VIM:

- **Repeatability** (of results of measurements) — the closeness of the agreement between the results of successive measurements of the same measure and carried out under the same conditions of measurement.

Additional Notes:

1. *These conditions are called repeatability conditions.*
2. *Repeatability conditions include the same measurement procedure, the same observer, the same measuring instrument, used under the same conditions, the same location, and repetition over a short period of time.*

- **Reproducibility** (of results of measurement) — the closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement.

Additional Notes:

1. *A valid statement of reproducibility requires specification of the conditions changed.*
2. *The changed conditions may include principle of measurement, method of measurement, observer, measuring instrument, reference standard, location, conditions of use, and time.*

When discussing the precision of measurement data, it is helpful for the analyst to define how the data are collected and to use the term “repeatability” when applicable. It is equally important to specify the conditions used for the collection of “reproducibility” data.

Mean

The definition of mean is, “an average of n numbers computed by adding some function of the numbers and dividing by some function of n .” The central tendency of a set of measurement results is typically found by calculating the arithmetic mean (\bar{x}) and less commonly the median or geometric mean. The mean is an estimate of the true value as long as there is no systematic error. In the absence of systematic error, the mean approaches the true value (μ) as the number of measurements (n) increases. The frequency distribution of the measurements approximates a bell-shaped curve that is symmetrical around the mean. The arithmetic mean is calculated using the following equation:

$$\bar{X} = (X_1 + X_2 + \dots + X_n) / n \quad (14.2)$$

Typically, insufficient data are collected to determine if the data are evenly distributed. Most analysts rely upon quality control data obtained along with the sample data to indicate the accuracy of the procedural execution, i.e., the absence of systematic error(s). The analysis of at least one QC sample with the unknown sample(s) is strongly recommended.

Even when the QC sample is in control it is still important to inspect the data for outliers. There is a third type of error typically referred to as a “blunder.” This is an error that is made unintentionally. A blunder does not fall in the systematic or random error categories. It is a mistake that went unnoticed, such as a transcription error or a spilled solution. For limited data sets ($n = 3$ to 10), the range ($X_n - X_1$), where X_n is the largest value and X_1 is the smallest value, is a good estimate of the precision and a useful value in data inspection. In the situation where a limited data set has a suspicious outlier and the QC sample is in control, the analyst should calculate the range of the data and determine if it is significantly larger than would be expected based upon the QC data. If an explanation cannot be found for an outlier (other than it appears too high or low), there is a convenient test that can be used for the rejection of possible outliers from limited data sets. This is the Q test.

The Q test is commonly conducted at the 90% confidence level but the following **Table 14.3** includes the 96% and 99% levels as well for your convenience. At the 90% confidence level, the analyst can reject a result with 90% confidence that an outlier is significantly different from the other results in the data set. The Q test involves dividing the difference between the outlier and its nearest value in the set by the range, which gives a quotient $-Q$. The range is always calculated by including the outlier, which is automatically the largest or smallest value in the data set. If the quotient is greater than the rejection quotient, $Q_{0.90}$, then the outlier can be rejected.

Table 14.3: The Q Test

n	Q0.90	Q0.96	Q0.99
3	0.94	0.98	0.99
4	0.76	0.85	0.93
5	0.64	0.73	0.82
6	0.56	0.64	0.74
7	0.51	0.59	0.68
8	0.47	0.64	0.53
9	0.44	0.51	0.60
10	0.41	0.48	0.57

EXAMPLE: This example will test four results in a data set — 1004, 1005, 1001, and 981.

- The range is calculated: $1005 - 981 = 24$.
- The difference between the questionable result (981) and its nearest neighbor is calculated: $1001 - 981 = 20$.
- The quotient is calculated: $20/24 = 0.83$.
- The calculated quotient is compared to the Q0.90 value of 0.76 for $n=4$ (from table 14.3 above) and found to be greater.
- The questionable result (981) is rejected.

Standard Deviation

A useful and commonly used measure of precision is the experimental standard deviation defined by the VIM as... "for a series of n measurements of the same measurand, the quantity s characterizing the dispersion of the results and given by the formula:

$$s = [\sum (x_i - \bar{x})^2 / (n-1)]^{1/2} \quad (14.4)$$

x_i being the result of the i -th measurement and \bar{x} being the arithmetic mean of the n results considered.

The above definition is for estimating the standard deviation for n values of a sample of a population and is always calculated using $n-1$. The standard deviation of a population is symbolized as s and is calculated using n . Unless the entire population is examined, s cannot be known and is estimated from samples randomly selected from it. For example, an analyst may make four measurements upon a given production lot of material (population). The standard deviation of the set ($n=4$) of measurements would be estimated using $(n-1)$. If this analysis was repeated several times to produce several sample sets (four each) of data, it would be expected that each set of measurements would have a different mean and a different estimate of the standard deviation.

The experimental standard deviations of the mean for each set is calculated using the following expression:

$$s / (n)^{1/2} \quad (14.5)$$

Using the above example, where values of 1004, 1005, and 1001 were considered acceptable for the calculation of the mean and the experimental standard deviation the mean would be 1003, the experimental standard deviation would be 2 and the standard deviation of the mean would be 1.

15. Significant Figures and Uncertainty

Significant Figures

When working with analytical data it is important to be certain that you are using and reporting the correct number of significant figures. The number of significant figures is dependent upon the uncertainty of the measurement or process of establishing a given reported value. In a given number, the figures reported, i.e. significant figures, are those digits that are certain and the first uncertain digit. It is confusing to the reader to see data or values reported without the uncertainty reported with that value.

EXAMPLE

A sample is measured using ICP-OES and reported to contain 0.00131 ppm of Fe. This value implies with certainty that the sample contains 0.0013 ppm Fe and that there is uncertainty in the last digit (the 1). However, we know how difficult it is to make trace measurements to 3 significant figures and may be more than a little suspicious. If the value is reported as 0.00131 ± 0.00006 ppm Fe this indicates that there was an estimation of the uncertainty. A statement of how the uncertainty was determined would add much more value to the data in allowing the user to make judgments as to the validity of the data reported with respect to the number of significant figures reported.

EXAMPLES

- You purchase a standard solution that is certified to contain $10,000 \pm 3$ ppm boron prepared by weight using a 5-place analytical balance. This number contains 5 significant figures. However, the atomic weight of boron is 10.811 ± 5 . It is, therefore, difficult to believe the data reported in consideration of this fact alone.
- The number 0.000013 ± 0.000002 contains two significant figures. The zeros to the left of the number are never significant. Scientific notation makes life easier for the reader and reporting the number as $1.3 \times 10^{-5} \pm 0.2 \times 10^{-5}$ is preferred in some circles.
- A number reported as 10,300 is considered to have five significant figures. Reporting it as 1.03×10^4 implies only three significant figures, meaning an uncertainty of ± 100 . Reporting an uncertainty of 0.05×10^4 does not leave the impression that the uncertainty is $\pm 0.01 \times 10^4$, i.e., ± 100 .

- A number reported as $10,300 \pm 50$ containing four significant figures. If the number is reported as $10,300 \pm 53$, the number of significant figures is still 4 and the number reported this way is acceptable, but the 3 in the 53 is not significant.

Mathematical calculations require a good understanding of significant figures. In multiplication and division, the number with the least number of significant figures determines the number of significant figures in the result. With addition and subtraction, it is the least number of figures to the left or right of the decimal point that determines the number of significant figures.

EXAMPLE

- The number 1.4589 (five significant figures) is multiplied by 1.2 (two significant figures). The product, which is equal to 1.75068, would be reported as 1.8 (two significant figures).
- The number 1.4589 (five significant figures) is divided by 1.2 (two significant figures). The dividend, which is equal to 1.21575, would be reported as 1.2 (two significant figures).
- The addition of 5.789 (four significant figures) to 105 (three significant figures) would be reported as 111.

Uncertainty

The International Vocabulary of Basic and General Terms in Metrology (VIM) defines uncertainty as:

"A parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand."

NOTE 1: The parameter may be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.

NOTE 2: Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results or series of measurements and can be characterized by standard deviations. The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information. The ISO Guide refers to these different cases as Type A and Type B estimations respectively.

There are numerous publications concerning uncertainty calculations. I am concerned that many presentations on the topic are written in a language that may be difficult for the beginner to easily grasp. However, there is a clear and complete guide that I highly recommend.

RECOMMENDED READING

Whether you're a beginner or an experienced student of the subject, I strongly encourage you to read *Quantifying Uncertainty in Analytical Measurement*, published by Eurachem.

Of the numerous volumes of publications on this topic I have seen over the years, this one stands out above all others. It is quite thorough, written in an understandable manner and it includes several good examples.

16. Traceability

To imply reliability, chemical standard manufacturers use the term traceability, but it is not always clear exactly what that means.

Traceability has been defined as “the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.”

This definition has achieved global acceptance in the metrology community. This section will discuss traceability as it is related to chemical measurement standards.

Background

In order to compare results from different laboratories with confidence, the metrology community agrees that there must be a way whereby each laboratory can establish a chain of calibrations leading to a single primary national or international standard. The formalization of this concept dates back to the Convention du Metre, signed by seventeen countries in 1875. All length measurements are ultimately made in comparison to the international prototype meter located in Paris. Formally a diplomatic organization, the General Conference of Weights and Measures (CGPM) was created by the Metre Convention. The name International System of Units (SI) was given to the system by the eleventh CGPM in 1960. At the fourteenth CGPM in 1971, the current version of the SI was completed by adding the mole as base unit for amount of substance, bringing the total number of base units to seven (see Table 16.1).

Table 16.1: SI Base Units

Base Quantity	Name	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

Achieving traceability to the SI for physical measurements (length, mass, etc.) is therefore established through an unbroken chain of comparisons with a stated uncertainty.

More recently, the concept of traceability of chemical measurements has been addressed. Establishing the required unbroken chain of comparisons is much more difficult to establish than for physical measurements, which can be related directly to the SI base units. There has not always been agreement about which comparisons are needed to satisfy the traceability requirements of chemical measurements with a principle difficulty being the dependence on the selectivity of the analytical procedure. However, it is generally agreed that one way in which a laboratory can establish traceability in chemical measurements is through the use of certified reference materials (CRMs).

Terms and Explanations

Traceability has been defined as “the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.” This definition has achieved global acceptance in the metrology community.

ISO (International Organization for Standardization) is a federation of national standards bodies from more than one hundred countries whose mission is to promote activities related to standardization in order to facilitate international exchange of goods and services and to develop co-operation among its members in the areas of intellectual, scientific, technological, and economic activity (REMCO 1995). The ISO functions through its technical committees, subcommittees and working groups to produce international agreements that are published as international “technical” standards.

Standards is a term surrounded by ambiguity. The word “standard” can either be defined as a written specification (i.e. “technical standard”) or a chemical reference material intended to define the concentrations of specified components (i.e. “measurement standard”). This guide uses the latter definition.

REMCO is ISO’s Committee on Reference Materials. It was established in 1975 to carry out and encourage a broad international effort for harmonization and promotion of certified reference materials (CRMs) and their applications. REMCO task groups have produced a number of ISO Guides establishing definitions of reference materials and setting forth internationally agreed “technical” standards for the production, certification, and use of reference materials. The primary ISO accreditations dealing with certified reference material manufacturers are clarified in our guide, ISO 17034, 17025, and 9001 Explained.

NIST (National Institute of Standards and Technology) is “responsible for developing, maintaining, and disseminating national standards — realizations of the SI — for the basic measurement quantities, and for many derived measurement quantities. NIST is also responsible for assessing the measurement uncertainties associated with the values assigned to these measurement standards.” As such, the concept of measurement traceability is central to NIST’s mission.

SRM (Standard Reference Material) is a federally registered trademark of NIST and the US Federal Government. This term describes the certified reference materials distributed specifically by NIST.

Discussion

Traceability to the SI can be achieved through NIST's SRM program. NIST has developed a very comprehensive line of SRMs in a wide variety of matrices. Their organization functions as the path to achieving traceability. Laboratories can purchase SRMs from NIST in the process of method validation and calibration. In addition, chemical standards for use in calibration and method validation are produced commercially. Most, if not all, of the commercial manufacturers claim traceability.

The definition of traceability requires that a statement of uncertainty be made with each comparison in the chain. If a laboratory chooses to purchase standards from a commercial supplier rather than from NIST directly, it should be with the understanding that the stated uncertainty cannot be smaller than the uncertainty of the SRM used by the commercial manufacturer for comparison. This is due to the fact that the comparison process has a standard uncertainty that must be added onto the standard uncertainty of the NIST SRM, which is used in making the comparison.

EXAMPLE: A commercial supplier certifies a 10,000 $\mu\text{g/mL}$ (nominal value) solution of Cu and determines that the standard deviation of all systematic and random errors in their certification process is 25 $\mu\text{g/mL}$. In addition the NIST SRM used for comparison has a certified value of $10,000 \pm 30 \mu\text{g/mL}$ Cu. NIST uses a coverage factor of 2 in reporting the uncertainty. Therefore the standard deviation of the SRM is 15 $\mu\text{g/mL}$. The reported uncertainty of the CRM produced by the commercial supplier would then be calculated taking into account the standard deviation of their production process and the standard deviation of the NIST SRM. The reported uncertainty, using a coverage factor of 2, is calculated taking the square root of the sum of the squares, i.e., $((25)^2 + (15)^2)^{1/2} \times 2 = 58 \mu\text{g/mL}$.

A chemical standard obtained from a commercial supplier that claims traceability to a specified NIST SRM should have the following information on the certificate of analysis to support a claim of traceability (the following is cited from the NIST website):

"To support a claim, the provider of a measurement result or value of a standard must document the measurement process or system used to establish the claim and provide a description of the chain of comparisons that were used to establish a connection to a particular stated reference. There are several common elements to all valid statements or claims of traceability:

- A clearly defined particular quantity that has been measured.
- A complete description of the measurement system or working standard used to perform the measurement.
- A stated measurement result or value, with a documented uncertainty.
- A complete specification of the stated reference at the time that it was compared to the measurement system or working standard.
- An 'internal measurement assurance' program for establishing the status of the measurement system or working standard at all times pertinent to the claim of traceability."

An internal measurement assurance program can be simple or complex, depending on the level of uncertainty at issue and what is necessary to demonstrate its credibility. The user of a measurement result is responsible for determining what is adequate to meet his or her own needs.

It is the responsibility of the end user of a "measurement" standard to assess the validity of a claim of traceability. Likewise, it is the responsibility of the standard manufacturer to provide the necessary information on the Certificate of Analysis that the user assesses. This mutual interest shared by both parties establishes a greater sense of trust in the quality of the standard.

1. *International Standard Organization VIM, 2nd ed., definition 6.10, 1993.*



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