TECHNICAL GUIDE

CPI INTERNATIONAL

Guide to ICP-MS & ICP-OES Calibration

Standards, calibration curves, blanks, internal standards, matrix matching, interferences, and QC considerations for elemental analysis laboratories.

This guide covers:

- How ICP-MS and ICP-OES calibration works
- Calibration standards, blanks, ICV, CCV, tuning and interference check standards
- Matrix matching, internal standards and common interferences
- How to select catalog or custom ICP standards for laboratory workflows

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Accurate Elemental Analysis Starts with Calibration

ICP-MS and ICP-OES can measure multiple elements across a wide range of concentrations, but an instrument response alone does not establish an analyte concentration.

Calibration establishes the relationship between a known analyte concentration and the analytical response produced by the instrument. That relationship allows an unknown sample response to be converted into a quantitative result.

For laboratories performing elemental analysis, reliable calibration depends on more than preparing several standards and generating a calibration curve. Analysts also need to consider:

- Calibration standard concentration
- Number and distribution of calibration levels
- Calibration blank composition
- Acid matrix
- Analyte compatibility and stability
- Internal standardization, when applicable
- Potential interferences
- Calibration verification
- Reference material quality and traceability
- Method-specific quality-control requirements

The appropriate approach ultimately depends on the analytical technique, instrument, sample matrix, analytes, expected concentrations, applicable analytical method, and laboratory quality system.

What Is ICP Calibration?

ICP calibration establishes a mathematical relationship between analyte concentration and measured instrument response using solutions containing known concentrations of the analytes being determined.

A calibration typically includes a calibration blank and one or more calibration standards. The exact calibration design is method-dependent.

In ICP-OES, the analytical response is based on element-specific optical emission. In ICP-MS, ions are separated and measured according to mass-to-charge ratio. Although the detection systems differ, both techniques require appropriate reference points to convert analytical response into quantitative concentration data.

Prepare standards	Introduce standards	Measure response	Establish calibration	Verify calibration	Monitor calibration

The verification and monitoring steps are important. An acceptable initial calibration does not establish that instrument performance will remain acceptable throughout an analytical sequence.

ICP-MS vs. ICP-OES Calibration

ICP-MS and ICP-OES share several calibration principles, but their analytical characteristics create different considerations.

Consideration	ICP-MS	ICP-OES

Measurement principle	Mass spectrometry	Optical emission spectroscopy
Calibration standards	Single- or multi-element	Single- or multi-element
Calibration blank	Commonly required	Commonly required
Internal standards	Common and required by some methods	Method/instrument dependent
Important interference considerations	Polyatomic, isobaric, doubly charged ions, matrix/physical effects	Spectral overlap, background, matrix/physical effects
Tuning/setup solutions	Important for mass calibration, sensitivity and instrument optimization	Setup/performance solutions may be used depending on instrument/method
Calibration verification	Method/quality-system dependent	Method/quality-system dependent

The applicable analytical method should determine the actual calibration procedure rather than assuming that a procedure appropriate for one ICP technique or method applies universally.

ICP Calibration Standards

What Is an ICP Calibration Standard?

An ICP calibration standard contains known concentrations of one or more elements and is used to establish the relationship between analyte concentration and instrument response.

Calibration standards may be prepared from:

- Single-element reference standards
- Multi-element reference standards
- Certified Reference Materials (CRMs)
- Reference Materials (RMs)
- Method-specific calibration mixtures
- Custom multi-element formulations

CPI provides ICP Calibration Standards, including dedicated ICP-MS Calibration Standards and ICP-OES Calibration Standards, as well as Single Element ICP Standards and custom inorganic formulations. The correct standard is determined by the method, not simply by the instrument.

Single-Element vs. Multi-Element ICP Standards

Single-Element Standards

A single-element standard contains one target element at a defined concentration and in a defined matrix. Single-element standards provide flexibility when:

- Only a few elements are required
- Analyte concentrations differ substantially
- Individual elements need to be prepared independently
- Elements cannot be combined in a stable formulation
- Methods or analyte lists change frequently

Multi-Element Standards

Multi-element standards combine several analytes into one solution. When the formulation is chemically appropriate, they can reduce pipetting, preparation time, the number of stock solutions handled, opportunities for preparation errors and laboratory waste.

However, instrument capability and solution chemistry are separate considerations. Potential formulation issues include:

- Precipitation
- Hydrolysis
- Adsorption
- Oxidation or reduction
- Complex formation
- Acid-matrix incompatibility
- Concentration-dependent instability

A combination that is stable at one concentration is not necessarily stable at a substantially different concentration.

Preparing ICP Calibration Standards

For routine ICP analysis, laboratories should use properly documented, commercially prepared standards in the analyte combination, concentrations and matrix required by their method. CPI supplies both ready-to-order and custom-mixed ICP standards to reduce preparation time, minimize the risk of calculation or contamination errors, and support consistent calibration.

However, a laboratory may occasionally need to prepare an interim calibration standard when its normal CPI standard is not available from its on-hand inventory and testing must proceed.

In these instances, laboratories commonly prepare working calibration standards by quantitatively diluting higher-concentration stock reference materials.

$$C_1V_1 = C_2V_2$$

C_1 = stock concentration | V_1 = stock volume | C_2 = target concentration | V_2 = final volume

For example, preparing a lower-concentration working standard from a 1,000 µg/mL stock requires calculating the appropriate volume of stock solution and quantitatively diluting it to the desired final volume.

Actual preparation requires more than performing the calculation. Analysts should also consider:

- Volumetric equipment and technique
- Diluent purity
- Acid concentration and final matrix
- Analyte stability
- Contamination control
- Number and magnitude of dilution steps
- Storage conditions
- Method requirements

At trace concentrations, contamination and preparation errors that appear insignificant at higher concentrations can become analytically important.

How Many Calibration Standards Are Required?

There is no universal number of calibration standards appropriate for every ICP method. The analytical method should specify or inform the required calibration approach. When designing a calibration, laboratories should consider:

- Applicable method requirements
- Expected sample concentration range
- Instrument response
- Required reporting limits
- Calibration model
- Calibration linearity
- Laboratory quality procedures

More calibration points are not automatically better. The calibration design needs to be appropriate for the measurement procedure and concentration range.

What Concentration Should ICP Calibration Standards Be?

There is no universal ICP calibration concentration. Calibration concentrations should be appropriate for the method and expected samples.

- Expected analyte concentrations
- Instrument working range
- Required reporting range
- Sample dilution
- Calibration model
- Method requirements
- Analyte stability
- Required QC concentrations

A concentrated reference material such as a 1,000 µg/mL single-element standard can be used to prepare substantially lower working concentrations. Alternatively, laboratories repeatedly preparing the same calibration mixture may benefit from a multi-element or custom formulation closer to routine working requirements.

Matrix Matching, Blanks and Internal Standards

Why Does Matrix Matching Matter?

The analyte concentration printed on the label is not the only characteristic of an ICP standard that matters. The matrix can influence analyte stability, sample introduction, ionization or excitation behavior and other aspects of analytical response.

Common matrices for inorganic reference standards include:

- Nitric acid
- Hydrochloric acid
- Mixed nitric/hydrochloric acid
- Matrices containing small quantities of hydrofluoric acid
- Water
- Other method-specific matrices

Whenever practical and required by the procedure, calibration solutions should be chemically appropriate for the analytical system and method. Matrix mismatch can contribute to differences between the behavior of calibration standards and samples.

Why Is Nitric Acid Commonly Used in ICP Standards?

Nitric acid is widely used in elemental analysis because it is compatible with many metals and common ICP sample-preparation workflows. However, nitric acid is not universally appropriate for every analyte or formulation.

Depending on the elements, concentration, method and stability requirements, an inorganic reference standard may instead require hydrochloric acid, mixed nitric and hydrochloric acid, small amounts of hydrofluoric acid or another appropriate matrix.

When HF-containing solutions are used, laboratories should verify that instrument components, sample-introduction components, laboratory procedures and safety controls are appropriate for hydrofluoric-acid-containing solutions.

What Is an ICP Calibration Blank?

A calibration blank contains the calibration matrix without intentionally added target analytes and provides the zero-concentration reference for calibration where specified by the method.

It is important to distinguish a calibration blank from other blanks used in an analytical workflow:

- Calibration blanks
- Method blanks
- Reagent blanks
- Rinse blanks
- Field blanks

They do not necessarily serve the same purpose. Using precise terminology matters because each blank is intended to answer a different analytical question.

What Are Internal Standards in ICP-MS?

An internal standard is an element introduced at a controlled concentration to help monitor and compensate for changes affecting analytical response. Internal standardization is particularly important in ICP-MS.

Potential changes can arise from sample introduction, nebulization, matrix effects, instrument drift, signal suppression or enhancement and physical differences between samples and standards.

Internal standards should be selected carefully. Factors can include:

- Mass proximity to the analyte
- Ionization characteristics
- Potential spectral or polyatomic interferences
- Natural presence in the sample
- Matrix compatibility
- Required concentration
- Instrument configuration
- Analytical method

Method-specific requirements take precedence over generic selection rules. EPA Method 200.8, for example, requires internal standardization for analyses performed under that method and specifies that internal standards be present at identical levels in samples, standards and blanks.

Calibration Does Not Eliminate Interferences

ICP-MS Interferences

ICP-MS can be affected by:

- Polyatomic interferences
- Isobaric interferences
- Oxide species
- Doubly charged ions
- Matrix-induced signal effects
- Physical/sample-introduction effects

The appropriate correction strategy depends on the analyte, isotope, matrix, instrument and method. Approaches can include alternative isotope selection, internal standardization, matrix matching, sample dilution, mathematical correction, collision/reaction cell techniques, sample preparation and interference check solutions.

ICP-OES Interferences

ICP-OES can be affected by:

- Spectral overlap
- Background emission
- Matrix effects
- Physical interferences
- Chemical effects

Appropriate wavelength selection, background correction, matrix control, interference correction, sample preparation and QC materials can help evaluate or address these effects.

An acceptable calibration therefore demonstrates only one component of analytical performance.

ICV, CCV, Second-Source Standards and QC

What Is Initial Calibration Verification?

After calibration, a laboratory may need to demonstrate that the calibration is producing acceptable results. An Initial Calibration Verification (ICV) Standard is used after initial calibration to independently evaluate calibration performance.

When an applicable method or quality program requires an independent source, the ICV should be obtained or prepared accordingly.

Calibration standards	Establish calibration.
ICV	Evaluates the established calibration.

The exact concentration, acceptance criteria, source requirements and frequency must follow the applicable analytical method and laboratory quality program. CPI offers Initial Calibration Verification (ICV) Standards for ICP analytical workflows.

What Is Continuing Calibration Verification?

Calibration performance can change during an analytical sequence. A Continuing Calibration Verification (CCV) Standard is analyzed periodically to evaluate whether the established calibration continues to meet the applicable acceptance requirements.

Standard	Primary Analytical Question	Typical Role
ICV	Did the initial calibration produce acceptable results?	Verification following calibration
CCV	Has calibration remained acceptable?	Periodic verification during an analytical sequence

Both are calibration-verification materials, but they are not interchangeable simply because they may contain similar analytes. Their intended function and method requirements determine how they should be used.

What Is a Second-Source Standard?

A second-source standard is obtained or prepared independently from the material used to establish calibration when the applicable procedure requires an independent source.

Whether an ICV, calibration verification solution or other QC material must come from a second source depends on the applicable method and quality system. Laboratories should verify the actual source requirement rather than assuming every ICV or CCV must, or need not, be independent.

What Are Interference Check Standards?

An Interference Check Standard contains analytes and/or potential interfering elements at defined concentrations to evaluate the effect of interferences on analytical measurement.

These standards answer a different question from calibration verification. Calibration verification asks whether the established calibration is performing acceptably. Interference evaluation asks whether the analytical system can accurately determine the target analyte in the presence of potential interference.

What Are ICP Tuning and Setup Solutions?

Instrument optimization occurs before or alongside calibration. ICP Tuning and Setup Solutions can support functions such as instrument optimization, mass calibration, resolution checks, sensitivity evaluation, stability checks and performance verification.

A tuning solution should not automatically be treated as a calibration standard, ICV, CCV or interference standard. Each serves a different analytical function.

A Practical ICP Calibration and QC Workflow

Step	Analytical Question	Possible Materials
1. Prepare/optimize	Is the instrument ready to perform the analysis?	Tuning, setup, performance check solutions
2. Establish calibration	What relationship exists between analyte concentration and instrument response?	Calibration blank, calibration standards

3. Verify initial calibration	Is the calibration producing acceptable results?	ICV or method-specific verification solution
4. Analyze QC and samples	Is the analytical procedure performing acceptably?	Method blank, LCS, matrix spike, duplicate, interference checks
5. Monitor calibration	Has calibration remained acceptable during the sequence?	CCV, calibration blank, method-specific checks

The exact sequence, terminology, frequency, concentrations and acceptance limits must follow the applicable analytical method.

Reference Materials, CRMs and Metrological Traceability

Calibration is only as defensible as the reference system supporting it.

A Reference Material (RM) is a material sufficiently homogeneous and stable with respect to specified properties and established as fit for its intended use in measurement.

A Certified Reference Material (CRM) carries additional metrological documentation. NIST defines a CRM as a reference material characterized through a metrologically valid procedure and accompanied by a certificate providing the specified property value, associated uncertainty and a statement of metrological traceability.

Metrological traceability concerns the relationship between a measurement result and an appropriate reference through a documented, unbroken chain of calibrations, with each step contributing to measurement uncertainty.

When selecting reference materials, laboratories should evaluate:

- Intended use
- Certified values where required
- Measurement uncertainty
- Metrological traceability
- Matrix
- Concentration
- Stability and homogeneity
- Certificate documentation
- Applicable accreditation and scope

CPI offers Peak Performance™ CRMs produced in an ISO 17034-accredited facility, as well as high-quality RMs manufactured and tested in ISO/IEC 17025-accredited laboratories.

Important terminology: Accreditation applies to the relevant organization, facility, laboratory and scope, not to an individual product.

When Does a Custom ICP Standard Make Sense?

Commercial catalog standards work well when their formulation matches the analytical requirement. But laboratories performing the same method repeatedly may find themselves combining multiple individual stock standards for every preparation.

A custom standard can be useful when the laboratory requires a defined combination of:

- Analytes
- Individual analyte concentrations
- Matrix
- Volume
- Packaging
- Certification requirements
- Analytical application

The analytical chemistry still determines whether the requested formulation is appropriate and stable. When a suitable formulation can be produced, a custom multi-

element standard can reduce routine pipetting, preparation time, the number of individual standards handled, opportunities for dilution errors, opportunities for transcription errors and excess material or waste.

CPI custom inorganic standards allow laboratories to specify the concentration, matrix, analyte combination and volume their analytical workflow requires.

How to Select ICP Calibration Standards

Before purchasing or preparing a calibration standard, answer these questions.

Selection Question	Why It Matters
1. Which analytical method are you running?	Start with the method, not the catalog.
2. Which technique are you using?	ICP-MS and ICP-OES can have different calibration, interference, internal-standard and performance requirements.
3. Which elements are being measured?	Determine the required analytes and whether they can be combined appropriately.
4. What concentrations are required?	Consider calibration range, expected samples, reporting requirements, dilution and instrument response.
5. What matrix is appropriate?	Match the analytical chemistry and method requirements as closely as appropriate.
6. Is a CRM required?	Determine the reference-material and documentation requirements of the method and laboratory quality system.
7. What QC materials are required?	Identify ICV, CCV, interference, tuning, blank and other method-specific requirements separately.
8. Is an independent source required?	Verify rather than assume.
9. Will the same formulation be prepared repeatedly?	If so, determine whether an appropriate custom multi-element formulation could simplify routine preparation.

Common ICP Calibration Problems

Calibration curve is nonlinear

Potential causes can include inappropriate calibration range, standard-preparation error, contamination, incorrect background correction, detector or signal limitations, interferences, matrix effects or instrument instability.

Calibration blank is too high

Investigate potential contamination from reagents, water, labware, pipettes, sample-introduction components, previous high-concentration samples and the laboratory environment.

ICV fails but calibration looks acceptable

Potential areas to investigate include calibration-standard preparation, ICV preparation, incorrect concentration, matrix mismatch, contamination, interference, instrument drift and differences between calibration and verification sources.

CCV fails during the run

A failed CCV can indicate that calibration performance has changed. Possible contributors include instrument drift, sample deposition, nebulizer or injector problems, matrix buildup, changes in sensitivity, standard degradation or contamination and preparation errors.

The applicable analytical method should determine which samples are affected and what corrective action is required.

Frequently Asked Questions About ICP Calibration

What is ICP calibration?

ICP calibration establishes the relationship between known analyte concentrations and instrument response so that concentrations in unknown samples can be determined quantitatively.

Are ICP-MS and ICP-OES calibrated the same way?

They share basic calibration principles, but instrument operation, interferences, internal-standard requirements, detection systems and method-specific procedures differ.

What standards are used for ICP calibration?

Laboratories may use single-element or multi-element reference materials, CRMs, RMs, method-specific standards and custom formulations depending on the analytical requirements.

What concentration should an ICP calibration standard be?

There is no universal concentration. It depends on the method, expected sample concentrations, instrument response, calibration range, dilution procedure and reporting requirements.

Can one multi-element standard contain every ICP analyte?

Not necessarily. Element compatibility, concentration, acid matrix, oxidation state and long-term stability must be considered.

What is the difference between an ICV and CCV?

An ICV evaluates the initial calibration after it has been established. A CCV monitors whether calibration remains acceptable during an analytical sequence.

Does an ICV need to come from a second source?

Not universally. Independent-source requirements depend on the analytical method and laboratory quality program.

Why are internal standards used in ICP-MS?

Internal standards help monitor and correct for changes in analytical response caused by factors such as instrument drift and physical or matrix-related effects.

Why does the acid matrix of an ICP standard matter?

Matrix composition can affect analyte stability and analytical response. Standards should use a matrix appropriate for the analytes, method, samples and instrument.

Is an ICP tuning solution the same as a calibration standard?

No. A tuning/setup solution is used to evaluate or optimize aspects of instrument performance. Calibration standards establish the concentration-response relationship.

Is a CRM the same as an ICP calibration standard?

Not necessarily. “Calibration standard” describes analytical function; “CRM” describes the metrological characterization and documentation of a reference material. A CRM may be used as a calibration standard when appropriate.

Build Calibration Around the Method

Reliable ICP analysis does not begin with the instrument. It begins with an analytical procedure supported by appropriate reference materials.

Calibration standards establish the concentration-response relationship. Internal standards can help compensate for changes in response. ICV and CCV materials evaluate calibration performance. Interference standards help investigate measurement bias. Tuning and setup solutions evaluate instrument performance.

Each material answers a different analytical question. Selecting them should therefore begin with:

Method	Technique	Analytes	Concentration	Matrix	Calibration	QC	Documentation

CPI International provides ICP Calibration Standards, ICP-MS Calibration Standards, ICP-OES Calibration Standards, ICP Quality Control Standards, ICP Tuning and Setup Solutions, Single Element ICP Standards and Custom Inorganic Standards for analytical laboratories.

CPI's Peak Performance™ standards use high-purity starting materials with NIST traceability, with available single- and multi-element formulations and custom options designed around laboratory analytical requirements.

Explore CPI ICP Calibration Standards for ICP-MS and ICP-OES workflows.

Standardize Your Standards.

Technical Source Notes

Use these sources to verify method-specific and metrology-specific claims before publication. CPI product/category claims should be verified against current CPI product documentation and Odoo category data.

Source	Use	URL
EPA Method 200.8	Determination of trace elements in waters and wastes by ICP-MS	https://www.epa.gov/esam/epa-method-2008-determination-tra...
EPA Method 200.7	Determination of metals and trace elements in water and wastes by ICP-AES/ICP-OES	https://www.epa.gov/esam/method-2007-determination-metals-...
NIST Metrological Traceability	Traceability terminology and claims	https://www.nist.gov/metrology/metrological-traceability
NIST SRM Definitions	Reference material and certified reference material definitions	https://www.nist.gov/srm/srm-definitions
ISO 17034:2016	Competence of reference material producers	https://www.iso.org/standard/29357.html
ISO/IEC 17025	Testing and calibration laboratory competence	https://www.iso.org/ISO-IEC-17025-testing-and-calibration-...