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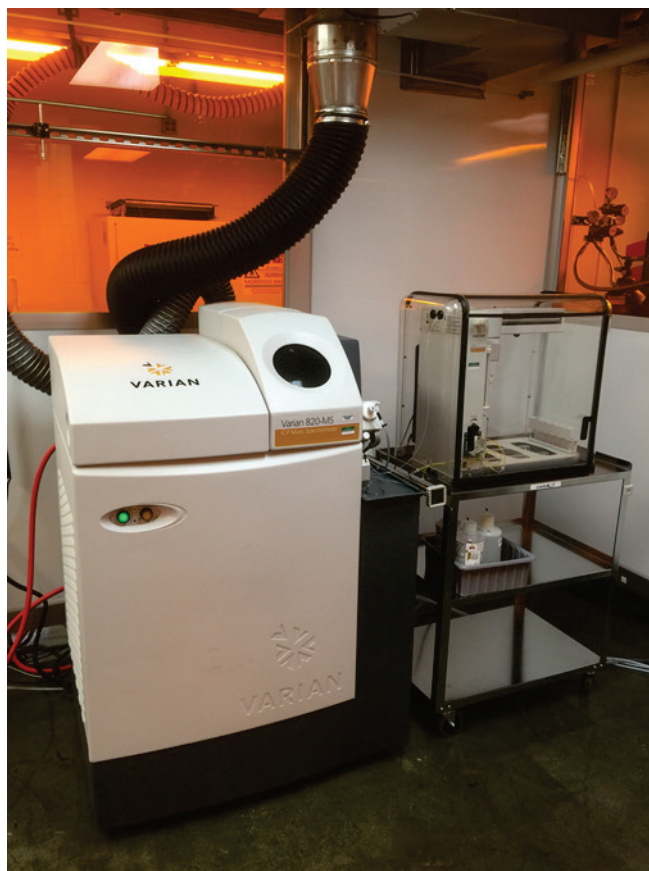
Environmental Consequences of Nanotechnologies

Determination of Metal Ion Contents in Nanomaterials Solution Using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Nano Risk SOP-P

Qihua Wu, Kathryn Kremer, Yongqing Jiang, Stephen Gibbons,
and Anthony J. Bednar

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Nano Risk SOP-P

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Device Manufacturing through Life Cycle Analysis, Risk Assessment and
Mitigation.”

Abstract

The presence of metal ions from either metal catalyst or contamination in nanomaterial solutions could directly impact the product quality, such as sensor performance. Inductively coupled plasma-mass spectrometry (ICP-MS), one of the most sensitive analytical techniques used for trace multi-element detection, has become a common tool in many laboratories for determining the metal impurities in various types of samples.

This scientific operating procedure (SOP) describes the operation and use of ICP-MS to determine trace metal concentrations in nanomaterials solutions. Procedures and recommendations of sample preparation, instrument preparation, sample analysis and results analysis are included. The procedure has been tested on a variety of carbon-based nanomaterial solutions.

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Preface

This scientific operating procedure (SOP) was developed under Task 2: “Materials process development and characterization” of project “Advancing Carbon Nanomaterials-Based Device Manufacturing through Life Cycle Analysis, Risk Assessment and Mitigation.” This program was funded by the Engineer Research and Development Center (ERDC) of the U.S. Army Corps of Engineers (USACE), contract number W912HZ-15-2-0032. The program manager was Dr. Alan J Kennedy. This work was directed by Mr. Rishi J. Patel, Senior Research Scientist at Missouri State University’s Jordan Valley Innovation Center. This task was under the direct supervision of Dr. Wu-Sheng Shih of Brewer Science, Inc. The technical monitor was Dr. Elizabeth A. Ferguson.

The work was performed by the Environmental Chemistry Branch (EP-C) of the Environmental Processes and Engineering Division (EPE), U.S. Army Engineer Research and Development Center - Environmental Research Laboratory (ERDC-EL). At the time of publication, Mr. William M. Nelson was Chief, CEERD-EP-R and Dr. Elizabeth A. Ferguson was the Technical Director for Environmental Quality and Installation. The Deputy Director of ERDC-EL was Dr. Jack E. Davis and the Director was Dr. Ilker R. Adiguzel.

The Commander of ERDC was COL Ivan P. Beckman and the Director was Dr. David W. Pittman.

Acronyms and Abbreviations

CNT	Carbon Nanotube
CPS	Counts Per Second
DoD	Department of Defense
DIW	Deionized Water
ERDC	Engineer Research and Development Center
FFF	Field Flow Fractionation
HNO ₃	nitric acid
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer
µg/l	microgram per liter
µl	microliter
ml	milliliter
mm	millimetre
ng/l	nanogram per liter
MALDI	Matrix Assisted Laser Desorption Ionization
NIST	National Institute of Standards and Technology
NP	nanoparticle
OD	Optical Density
QA	Quality Assurance
QC	Quality Control
SOP	Scientific Operating Procedure
SP-ICP-MS	Single-Particle Inductively Coupled Plasma-Mass Spectrometry
TS	Tuning Solution
USACE	U.S. Army Corps of Engineers
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet-Spectroscopy

Unit Conversion Factors

Multiply	By	To Obtain
degrees Fahrenheit	$(F-32)/1.8$	degrees Celsius
horsepower (550 foot-pounds force per second)	745.6999	watts
microns	1.0 E-06	meters
mils	0.0254	millimeters
pounds (force) per square inch	6.894757	kilopascals

1 Introduction

This Scientific operating procedure (SOP) describes how to determine the metal ion concentrations of nanomaterials in solution using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS).

Metal impurities in nanomaterials, especially carbon-based nanomaterials are undesirable for many applications. For instance, they may have a negative influence on the electrical properties of processed sensors or other electronic devices. Major sources of metal impurities include metal catalysts used for synthesis of nanomaterials (e.g., carbon nanotubes [CNT]) and contamination from the environment or during the manufacturing process. Typically, concentrations of these metal impurities in samples are extremely low, which demands trace elements analysis at levels of $\mu\text{g/l}$ or even ng/l .

1.1 Background

ICP-MS is a type of mass spectrometry that detects trace amounts of elements (mostly metals) on non-interfered isotopes. Since the 1980s, ICP-MS has evolved to become a powerful technique for multi-elemental trace analysis on a wide variety of sample matrices (Beauchemin 2010; Montaser 1998; Gray and Date 1983; Pröfrock and Prange 2012).

In ICP-MS, samples are ionized by inductively coupled plasma and a mass spectrometer is used as a detector. Compared with other popular ionization techniques of mass spectrometry, such as electrospray or matrix assisted laser desorption ionization (MALDI), ICP-MS utilizes a high-temperature plasma discharge as the source for mainly positively charged ions (Montaser 1998). This high-temperature process generally leads to a complete fragmentation and decomposition of sample molecules that yield only the detectable atomic metals for extremely low background noises. Thus, ICP-MS is particularly suitable for handling liquid samples with appropriate sample introduction technique (e.g., flow injection). In addition, isotope ratio information can be obtained by ICP-MS for those elements that have multiple stable isotopes and can be used in isotope dilution analysis (Rodríguez-González et al. 2005). Overall, ICP-MS provides high sensitivity (ng/l range), wide linearity range, and specificity for the accurate detection of metals and their isotopes.

ICP-MS has been intensively used for the determination of trace elements (mostly metals) in a variety of samples (EPA 1998; Vanhoe 1993). It has been published by the United States Environmental Protection Agency (USEPA) for the determination of trace elements in water and wastes (EPA 1998). ICP-MS has also been used for the determination of trace and ultra-trace elements in biological materials. Results are given of the analysis of human serum and of several biological reference materials (bovine liver, milk powder, wheat flour, and pig kidney) (Vanhoe 1993).

Recently, single-particle ICP-MS (SP-ICP-MS) has been reported for the detection of individual nanoparticles (Mitrano et al. 2012; Pace et al. 2011; Laborda et al. 2011). SP-ICP-MS enables simultaneous determination of nanoparticle concentration and size at a very low level (Mitrano et al. 2012). Field flow fractionation (FFF) has also been applied with ICP-MS for a broad range of environmental (Hassellöv et al. 2008), biological (Reschiglian et al. 2005; Roda et al. 2009), and nanoparticle measurements (Hassellöv et al. 2008; Williams et al. 2010; Baalousha et al. 2011; Bouby et al. 2008).

1.2 Objectives

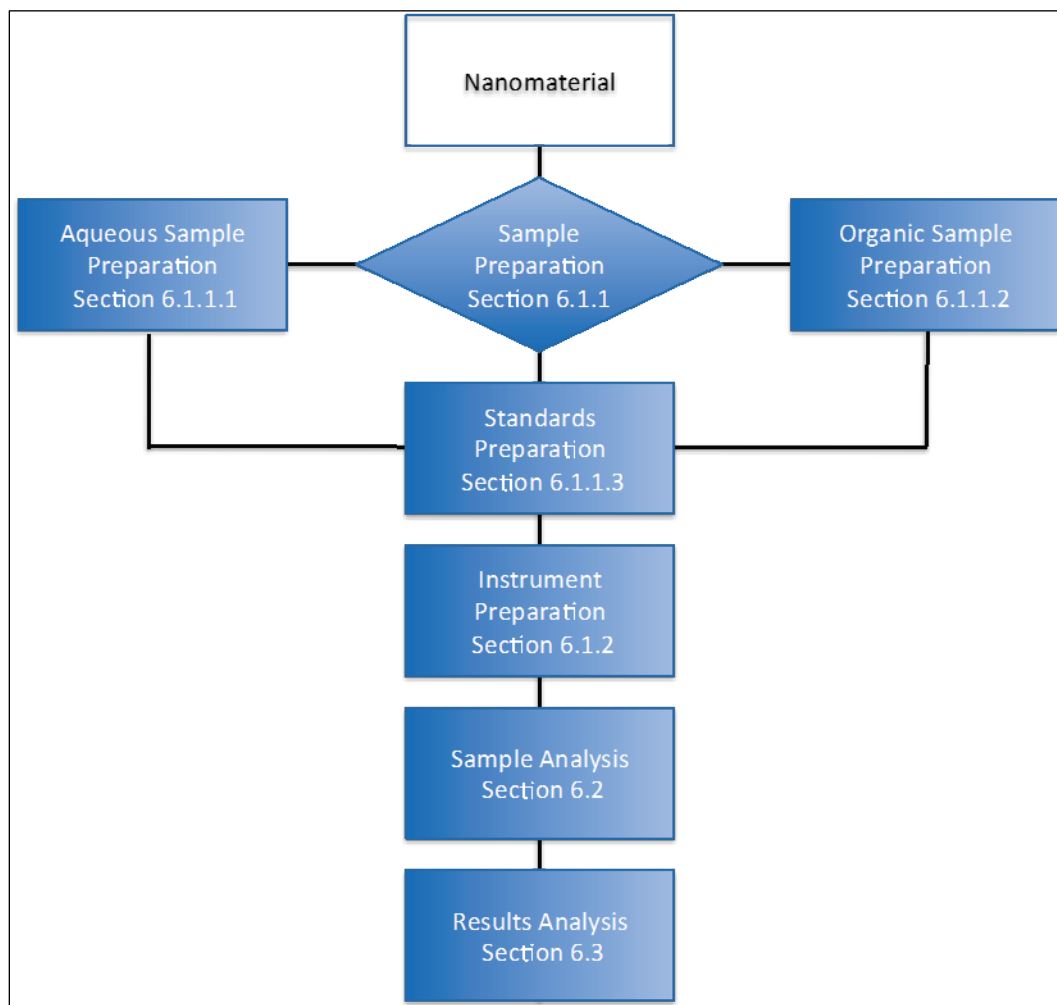
The objective of this SOP is to define the operating procedure for measuring metal ions concentrations of carbon-based nanomaterials in solution by using ICP-MS.

1.3 Scope

This procedure applies to most nanomaterials solutions produced, including carbon-based nanomaterials solutions, raw materials, intermediates, final products, and experimental solutions. Based on the properties of samples, sample pretreatment may apply. The operation procedure of a Varian 820 ICP-MS with the Agilent SPS 3 auto-sampler is included as an example.

The general outline of the procedure is illustrated in Figure 1.

Figure 1. Outline of determination of metal ions concentrations in nanomaterial by ICP-MS.



2 Terminology

2.1 Related documents

- ASTM JAI12967 *The Use of Microwave Digestion and ICP to Determine Elements in Petroleum Samples* (Hwang et al. 2005).
- US EPA Test Method 200.8: *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry* (Long and Martin 1989).
- US EPA Test Method 1638: *Determination of Trace Elements in Ambient by Inductively Coupled Plasma-Mass Spectrometry* (1996).
- Instrument operation manual provided by instrument manufacturers (for example, Varian 820 ICP-MS operation manual).

2.2 Definitions

- Optical density: The measure of ultraviolet-spectroscopy (UV-Vis) absorbance of a nanomaterial solution. Specifically, the absorbance is measured at a wavelength of 550 nm. The dilution factor needs to be taken into account in the calculation when a sample is diluted before measurement.
- Dilution factor (also known as dilution ratio): The total number of unit volumes in which the sample is diluted. The dilution factor can be calculated by total volume of final solution divided by the volume of sample added.

3 Materials and Apparatus

3.1 Materials

- Nanomaterial samples (solid or liquid)
- DI water (DIW)
- Nitric acid (Optima grade, available from various vendors)
- National Institute of Standards and Technology (NIST)-traceable calibration standards for elements of interest that are available from various vendors. (e.g., IV-ICPMS-71A and IV-ICPMS-71B from Inorganic Ventures)
- Element tune solution that is available from various vendors. (e.g., VAR-TS-MS from Inorganic Ventures)
- Certified internal standard that is available from various vendors. (e.g., 6020 ISS from Inorganic Ventures)
- High-purity supplier gas (argon and helium, >99.99%)
- Calibrated automated pipettes that are available from various vendors, typical range 100 μ l to 10 ml
- Pipette tips that are available from various vendors, typical range is 100 μ l to 10 ml
- Sample preparation container (polypropylene is suggested)
- Sample container for analysis (varies depending on auto-sampler type)
- Water chiller with temperature control and measurement capabilities

3.2 Apparatus

- ICP-MS instrument equipped with auto-sampler that has the capability of accurately detecting elements of interests in the low μ g/l or even ng/l range (e.g., Varian 820 ICP-MS with Agilent SPS 3 auto-sampler). The instrument parameters may be different based on the type of instrument and nature of samples.
- Microwave digester with controllable powers (approximately 400 to 1200 Watts), temperature and pressure controls (e.g., CEM Mars 5 micro-wave digester).

4 Procedure

4.1 Experiment preparation

Samples submitted for ICP-MS are normally low ion level concentrations ($\mu\text{g/l}$ or even ng/l). To avoid possible contamination, use trace-metal-clean materials and wear clean, powder-free gloves when directly handling samples and the analytical apparatus.

4.1.1 Specimen preparation

4.1.1.1 Aqueous sample preparation

Aqueous samples can either be analyzed directly or may be diluted. Typically, DI water or 1% HNO_3 should be used for sample dilution. Samples need to be well mixed before injection for ICP-MS analysis.

For carbon nanomaterials in aqueous solution, the desired dilution factor can be determined by the optical density (OD) of the sample. A diluted sample with an OD around two (or around 50 mg/l) is suggested for direct metal concentration detection by ICP-MS.

4.1.1.2 Organic sample preparation

Typically samples in organic solvents or mixture cannot be directly injected into an ICP-MS that is running an aqueous system. Acid digestion or microwave-assisted acid digestion is needed for those samples. Refer to ASTM JAI12967 (Hwang et al. 2005) for digestion procedure. Once the sample is successfully digested, it can be analyzed directly or with the proper dilution (see Section 4.1.1.1).

4.1.1.3 Calibration standards preparation

Calibration standards need to be analyzed for quantification of metal ions concentration in samples. These standards should to be prepared and analyzed prior to sample analysis. A set of calibration standards should have at least five (preferably seven) different concentrations, which contain the linearity range of the method and include the estimated metal ions concentration of samples. Calibration standards should be prepared in dilute acid, generally in 1% HNO_3 .

Also, internal standards should be prepared to ensure the accuracy of the results. Internal standards should be prepared in the same medium as that of calibration standards, generally in 1% HNO₃.

4.1.2 Instrument preparation

This section provides a general guide of ICP-MS instrument preparation practice for the analysis of trace metal concentration in nanomaterials. The operation of Varian 820 ICP-MS with Agilent SPS 3 auto-sampler is demonstrated as the example.

4.1.2.1 General preparation

Check that the argon pressure (110 psi) and helium pressure (40 psi) are within the appropriate ranges. Insufficient gas may cause failure of the plasma to ignite. Turn on the chiller and set water temperature to 20°C. The glassware, including the nebulizer, spray chamber, sheath gas port, and torch (varies depends on the instrument), should be clean and aligned in the appropriate positions. The glassware may need to be removed for cleaning or replacement as necessary.

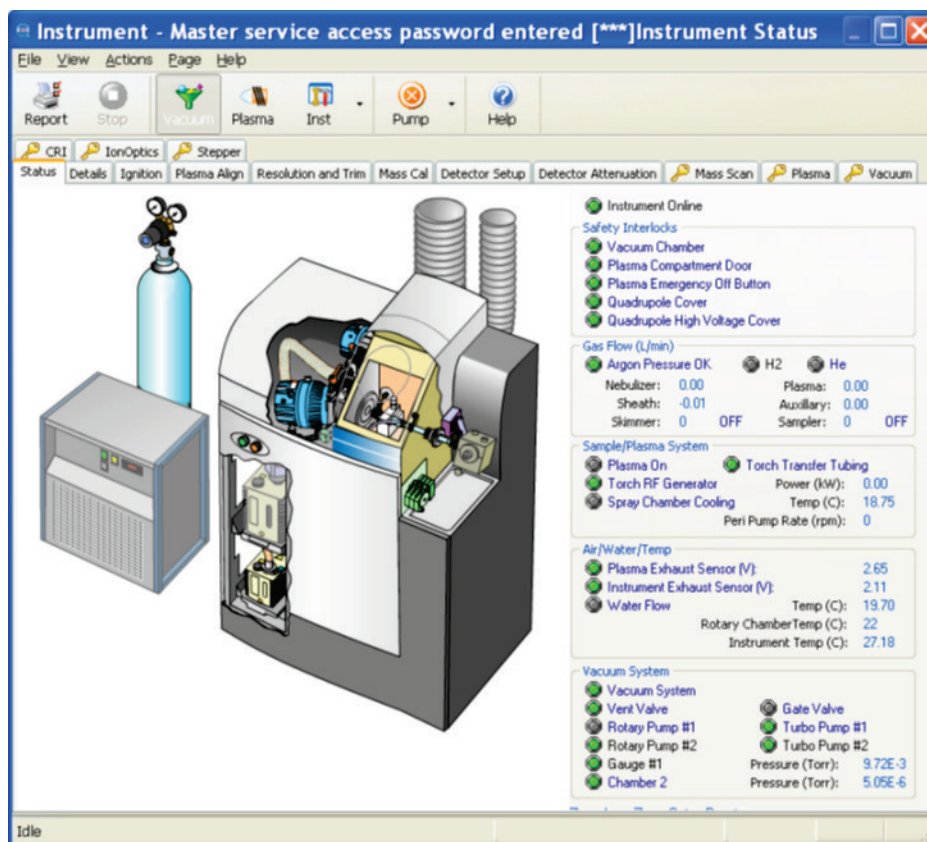
If an auto-sampler is equipped, inspect the pump tubing and lock the tensioners in place. The tubing must be replaced after it has been stressed beyond its elastic limit and remains flat. Replace the auto-sampler rinse solution and sample DI water with fresh DI water. Replace the tuning solution, DI water, and nitric acid (blank) prior to sample measurement.

4.1.2.2 Instrument start-up

Switch on the computer and start the instrument software. Open the Instrument Setup dialog box (Figure 2). Ensure vacuum is on and the appropriate pressures are reached. If the vacuum is off, start the vacuum and wait for proper vacuum to be reached (the light on the instrument status panel will turn green). It may take several hours to reach the appropriate pressures.

Ensure all tubes of the auto-sampler pump are connected and test the pump. If no leaking is observed, ignite the plasma by controlling the software or from the instrument control panel. Watch the plasma for excessive arcing and use emergency shutdown to turn off the plasma if arcing occurs. Wait until the cone is cooled before another trial of igniting the plasma.

Figure 2. Example ICP-MS instrument setup page.



4.1.2.3 Instrument preparation

Plasma alignment should be completed before running any standard sample. Open the Instrument Setup screen to start running the tuning solution for plasma alignment. Allow the tuning solution (TS) to be run for at least 20 minutes (for the 1200 s) or as the manufacturer recommends. Periodically check the tuning solution readings to ensure the values of TS elements are as expected. This is to ensure the proper function of the plasma.

Torch alignment is generally recommended if the glassware has been moved, replaced, or realigned. Open the Instrument Setup screen to start running the tuning solution for torch alignment. Record the horizontal and vertical torch positions (in millimeter [mm]) in an appropriate lab notebook and accept the new values of torch positions.

Mass calibration needs to be performed after preventative maintenance or instrument repair. The tuning solution is tested in most instances. A voltage scan should be performed on a monthly basis, depending on the

usage of the instrument. The detector voltage will be scanned as a function of total counts of tuning solution to determine the ideal voltage.

4.2 Sample analysis

Sample analysis on a Varian 820 ICP-MS with Agilent SPS 3 auto-sampler is demonstrated as an example.

4.2.1 Running calibration standards

Create a new file tab for data storage with appropriate operators, date, and sample information. Prepare fresh calibration standards and internal standard solutions for analysis following Section 6.1.1.3. Place the appropriate calibration standards into the auto-sampler rack with the blank (same solution used for preparing standards). Analyze results of calibration standards and check each concentration as well as correlation coefficients to ensure the proper function of the instrument.

4.2.2 Running samples

When calibration standards are tested and quality control samples are passed, samples can be analyzed. Follow Section 4.1.1 for sample preparation. Add samples to the auto-sampler rack and record the positions with correlated sample name. When running a large amount of samples, check the calibration standard or quality control samples between every six to ten samples. The USEPA also recommends performing duplicated runs for at least 20% of samples.

5 Reporting

5.1 Analysis of results

Most instruments provide data analyzing software, which can automatically process data if the correct sample types are defined (standard and unknown). In most cases, the raw data will be the detector signal in counts per second (CPS) of each individual ion and isotope.

The calibration standards should be analyzed first to create a fresh calibration curve. Once concentrations of calibration standards are given, the software should generate the calibration curve for each ion and isotope. The CPS will be plotted against the known concentration and the correlation coefficient will be calculated. A correlation coefficient greater than 0.999 indicates good linearity. If internal standards are also analyzed, one can choose whether use or not use the internal standard (IS) for calibration curve and sample analysis. The answer depends on the metal ions of interest and the sample matrices. Typically, it is recommended to use IS for result analysis to minimize the influence of differences between the sample matrix and calibration standards.

5.2 Key results provided

Basic information should be included in the report such as sample name, operator, test date, and method name. Key results should be the final concentration of each individual ion/isotope analyzed in samples, as well as sample preparation method, especially dilution factors for the calculation of concentrations in original samples.

Quality Control (QC) sample results and correlation coefficient may also be reported if necessary to ensure data quality.

5.3 Quality Assurance/Quality Control (QA/QC) concerns

All calibration standards values should be within the $\pm 5\%$ range. QC samples with known amounts of standards spiked into sample matrices should have recoveries of approximately 80% to 120%. The definition and procedure of QC samples can be found from USEPA method 6020A (1998). Duplicated runs of samples should have percent difference or standard deviation less than 10%.

6 Summary

ICP-MS has been one of the most sensitive analytical techniques used for trace multi-element detection in the areas of both scientific research and industrial applications. This SOP describes the use of ICP-MS to determine metal ions concentrations in nanomaterials solutions. General procedure and considerations of specimen preparation, instrument preparation, sample testing and results analysis are included. This SOP also includes the operation procedure of a Varian 820 ICP-MS with the Agilent SPS 3 auto-sampler as an example. The SOP can be used as a guidance for tests such as metal ions quantification and impurity identification for most nanomaterials solutions including raw materials, intermediates, final products, and experimental solutions.

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