

# Mechanism of sensitivity difference between trivalent inorganic As species [As(III)] and pentavalent species [As(V)] with inductively coupled plasma spectrometry

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## Abstract

The pentavalent inorganic arsenic (As) species [As(V)] is found to be 4% more sensitive than the trivalent species [As(III)] with inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). Although there was no sensitivity difference between As(III) and As(V) with atomic absorption spectrometry (AAS), electrothermal atomization atomic absorption spectrometry (ETAAS), X-ray fluorescence (XRF), and neutron activation analysis (NAA). The calibration solutions of As(III) and As(V) were gravimetrically prepared from the unique mother standard solution of JCSS As standard solution which is certified by Japan Calibration Service System (JCSS). Since it is essential to use the calibration solutions with exactly the same concentration of As in order to accurately compare the sensitivities between As(III) and As(V). The mechanisms of this sensitivity difference between them were investigated by ICP-MS and ICP-OES, and it elucidated that the formation rates of hydride polyatomic species of As were definitively different between As(III) and As(V) species in the plasma. This phenomenon directly affected their sensitivities with ICP-MS and ICP-OES.

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**Keywords:** Arsenic species; Analytical sensitivity; ICP-MS; ICP-OES; Hydride polyatomic species

## 1. Introduction

Arsenic (As) is widely distributed in the natural environment such as ground water, river water, and sediment and in organisms such as seaweeds and fish tissues. It is well known that As is a toxic element [1–4]. The major chemical forms of As are arsenite [As(III)] and arsenate [As(V)] in environment, although organoarsenic species such as arsenobetaine, methylated As compounds, and arsenosugar compounds are mainly found in organisms. Many countries set maximum permissible concentration values for As in drinking water and food. The World Health Organization (WHO) is currently conducting the guidelines for drinking water and environmental water [5].

There are great demands to determine not only the total concentration of As in environment but also the concentration of individual chemical forms of As compounds for scientific

interests as well as for implementing regulations. In particular, the speciation determination of As(III) and As(V) is stringently required in order to measure the most toxic As compound, As(III), concentration in samples. Until now, many analytical techniques have been reported for the determination of the total concentration of As as well as the speciation determination of individual arsenic species [6]. The atomic spectrometric methods such as electrothermal atomization atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are widely employed for the determination of trace amount of As because of their high sensitivity, good precision and wide availability. Furthermore, combinations with hydride generation (HG), gas chromatography (GC) and/or liquid chromatography (LC) can be applied for speciation determination of arsenic compounds.

Creed et al. reported that the As(III) response was suppressed approximately 20% relative to As(V) standard when they were determined by ICP-OES with an ultrasonic nebulizer (USN) [7]. No response deference was observed by ICP-OES with

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a pneumatic nebulizer. They concluded that the response difference was caused by oxidation of As(III) to As(V) during the ultrasonic nebulization and desolvation process. Yu et al. reported that As(V) was about 8% more sensitive than As(III) with ICP-OES installed even with a pneumatic nebulizer [8]. The difference in sensitivity of As in atomic spectrometric analysis has been reported by other groups, too [9–12]. They also concluded that the phenomenon occurs in the injection and transportation systems and named it “desolvation effect”, “speciation effect” or “transportation effect”. Although they did not explain the mechanism resulting in the sensitivity difference between As(III) and As(V), they suggested that the sensitivity difference phenomenon occurred before the atomization step, that is, before introduction into plasma.

The authors have studied on As analysis in environmental and biological samples and have also been developing analytical techniques for total determination of As as well as speciation determination of As species [13–15]. The authors reported the sensitivity difference between As(III) and As(V) with ICP-OES and ICP-MS but not with ETAAS in 1999 [16], and informed their excitation and ionization behaviors in plasma in 2005 [17]. The calibration solutions with the exactly correct concentrations of both As(III) and As(V) are essential to discuss the sensitivity difference, so it is very important to prepare the standard solutions whose oxidation state is guaranteed. The JCSS As standard solution, which is traceable to the national standard, allows us to establish traceability of the As concentration in measurement. The concentration is characterized by titrimetry, which is one of the primary methods. Almost all the As atoms are in the trivalent oxidation state As(III) in JCSS standard, since the standard solution is made from highly pure As<sub>2</sub>O<sub>3</sub>, but JCSS does not guarantee the oxidation state of As in their standard. Thus, the authors always validated the content level of As(V) in JCSS standard solution before use, and decided that it was low

enough not to effect the experiment. On the contrary, there is no commercially available As(V) base standard solution. Standard solutions of As(V) have usually been prepared by using Na<sub>2</sub>HAsO<sub>4</sub> as a source material, however, evaluation of its purity and moisture content has rarely been carried out. Therefore, the authors used the JCSS As standard solution as a unique mother standard solution for preparation of both As(III) and As(V) calibration solutions, where As(V) standard solution was prepared by oxidizing the JCSS standard.

In this work, mechanism of sensitivity difference between As(III) and As(V) with ICP-OES and ICP-MS was investigated using the As(III) and As(V) calibration solutions prepared from the unique mother source of the standard solution. It was elucidated that the formation rates of hydride polyatomic species of As were definitively different between As(III) and As(V) species in the plasma. We propose a mechanism based on the oxidation states of atoms of this phenomenon, and define it as “the Incoherent Molecular Formation (IMF) effect”.

## 2. Experiment

### 2.1. Apparatus

An ICP-OES Optima 4300DV (Perkin-Elmer Co. Ltd., Yokohama, Japan) equipped with a concentric nebulizer and a cyclonic spray chamber was used. An ICP-MS 7500c (Agilent Co. Ltd., Tokyo, Japan) and an ICP-high resolution MS Quest Element 2 (Thermo Co. Ltd., Yokohama, Japan) equipped with a micromist nebulizer and a Scott spray chamber, and an ICP-MS ELAN DRC II (Perkin-Elmer Co. Ltd.) equipped with a micromist nebulizer and a cyclonic spray chamber were also used. Operating conditions for ICP-OES and ICP-MS are summarized in Table 1.

Table 1  
Instrument conditions of ICP-OES, ICP-MS and GFAAS

Plasma	ICP-OES	ICP-MS	
Conditions			
Incident Rf power	1.3–1.5	1.3–1.5	kW
Outer gas flow rate	Ar 15	Ar 15	1 min <sup>-1</sup>
Intermediate gas flow rate	Ar 0.2	Ar 0.9	1 min <sup>-1</sup>
Carrier gas flow rate	Ar 0.8	Ar 0.8	1 min <sup>-1</sup>
Make-up or shear gas	N <sub>2</sub> 18	Ar 0.4	1 min <sup>-1</sup>
Sampling conditions			
Nebulizer	Concentric (glass)	Micro mist (glass or PFA)	
Spray chamber	Cyclonic	Scott or cyclonic	
Sample injection	Peristaltic pumping	Peristaltic pumping natural aspirate	
GFAAS			
Wavelength	As 193.7	nm	
Lump current	380	mA	
Lump	EDL		
Slit width	0.5	nm	
Dry	130	°C	
Pyrolysis	1000	°C	
Atomize	2400	°C	
Chemical modifier	100 ppm Pd + 50 ppm Mg(NO <sub>3</sub> ) <sub>2</sub>		

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