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## USE OF INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY, ICP-MS, IN ENTOMOLOGY

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### ABSTRACT

Applications of the inductively coupled plasma-mass spectroscopy (ICP-MS) in various fields with emphasis on entomology are reviewed. Examples of the using a broad spectrum of ICP-MS in entomology including ecotoxicology, physiology, disease treatments, bioremediation, bioindication, homeostasis, and immune system, and determining and removing environmental contaminations are discussed and summarized.

**Keywords:** Application, entomology, ICP-MS, inductively coupled plasma, mass spectrometry.

### INTRODUCTION

Inductively coupled plasma-mass spectroscopy (ICP-MS) was created in the late 1980's to incorporate the easy sample introgression and rapid analysis with the exact and very low exploration limits of a mass spectrometer. ICP-MS is able to measuring the trace multi elements, often at the part per trillion levels. The instrument has been applied widely in a number of different fields including drinking water, wastewater, natural water systems, geology, soil science, mining, food sciences and medicine over the years (Sadeghi, 1999; Worley and Kvech, 2000; Wang *et al.*, 2010).

Inductively coupled plasma-mass spectroscopy is a method of breaking chemical samples down to their component atoms and ions. Peripheral plasma has a neutral state that is formed by atoms in the equilibrium between the neutral state (1-2%) and electrons ( $10^{18} \text{ cm}^{-3}$ ) and is considered as the fourth state of matter. ICP was made upon the same principles exploited in the atomic emission spectrometry. Samples are broken up to neutral elements in the high temperature argon plasma and assayed based on their mass to charge ratios. It have four main processes, including sample loading and aerosol production, ionization, mass discrimination, and the detection phase (Worley and Kvech, 2000; Sadeghi,

2011). One of the great advantages of ICP-MS that typically was used for measuring many trace and ultra-trace metals and some nonmetals at extremely low detection limits for wide range of elements from  $^6\text{Li}$  to  $^{238}\text{U}$ . Many elements can be detected down to part per quadrillion levels while most can be assayed at part per trillion levels (Worley and Kvech, 2000).

Principles with very detailed knowledge and all sequence of processes including instrument description and theory, sample introduction, argon plasma, sample ionization, mass spectrometer (MS), detector and detection limits are described and well-illustrated (Worley and Kvech, 2000). In this paper, applications of ICP-MS in various fields with emphasis on entomology are discussed and reviewed. Examples of the use of a broad spectrum of ICP-MS in entomology including ecotoxicology, physiology, disease treatments, bioremediation, bioindication, homeostasis, immune system, and determining and removing environmental contaminations are summarized.

### MATERIAL AND METHODS

#### ICP-MS APPLICATIONS

**General Application of ICP-MS:** ICP-MS is typically used for measure the many trace and ultra-trace metals, and some nonmetals in various fields for wide range of elements from  $^6\text{Li}$  to  $^{238}\text{U}$  that are: Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, Ba, Hf, Ta, W, Re, Tl, Pb, Th, U and rare earth elements (Sadeghi, 2011).

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The most popular its applications are in the field of animal and plant biological sciences (Truong *et al.*, 2010; Mao *et al.*, 2010; Tang *et al.*, 2010; Garcia *et al.*, 2010), environmental sciences (Inouye *et al.*, 2007; Eeva and Penttinen *et al.*, 2009; Vermeulen *et al.*, 2009), geological sciences (Martínez-Fernández *et al.*, 2011; Malsy and Klemmb, 2010; Stafilov *et al.*, 2010; Silva *et al.*, 2010; Jamshidi *et al.*, 2010), archaeology (Thornton *et al.*, 2002), immunology (Goenaga-Infante *et al.*, 2010), diets and dietary nutritional supplements (Ghaedi *et al.*, 2007), public health sciences (Lewen, 2010; Groessl *et al.*, 2010; Qin *et al.*, 2010), forensic medicine (Roeterdink *et al.*, 2004; Ma *et al.*, 2010), industry, toxicology studies (Boulassel *et al.*, 2010; Yoshimura *et al.*, 2010; Judy *et al.*, 2010; Hariri *et al.*, 2010), studies of metabolism, cancer researches (Hanada *et al.*, 1998; Lunoe *et al.*, 2010; Faucher *et al.*, 2010; Zhou *et al.*, 2010), chemistry (Ryan *et al.*, 2011; Hansen *et al.*, 2010; Banerjee *et al.*, 2010; Judd *et al.*, 2010; Berg *et al.*, 2010), bacteriology (Sun *et al.*, 2010; Galiová *et al.*, 2010; Hansen *et al.*, 2010) and construction (Bassioni *et al.*, 2010).

**Using ICP-MS for quantification of proteins and biomolecules:** An increasing trend of applications would have been exist for ICP-MS in the speciation analysis which regularly utilize in chromatography with elemental selective detectors. For example, ICP-MS may be incorporated with size exclusion chromatography and quantitative preparative native continuous polyacrylamide gel electrophoresis for recognizing and quantifying the native metal cofactor of proteins in the biofluids. Also the phosphorylation condition of the proteins can be identified and analyzed (Yoshimura *et al.*, 2010; Qiao *et al.*, 2010; Engelhard, 2010; Leufroy *et al.*, 2011; Milliard *et al.*, 2011; Chen *et al.*, 2011). However, the insect sensitivity level and insecticide resistance mechanisms can be determined by bioassay methods (Nasirian *et al.*, 2006a-f; Nasirian, 2007; Nasirian, 2008; Nasirian, 2010), but integrated ICP-MS with a variety methods of chromatography can be used for determination of pesticide residues.

**Applications of ICP-MS in Entomology:** Inductively coupled plasma-mass spectroscopy has been used in various entomology branches such as ecotoxicology, bioremediation, physiology, treatment of diseases, hemostasis, immune system, forensic medicine and environmental pollution studies or in any its subject related.

Many studies have been showed that ICP-MS has a

various application in the entomology. For example, lead through human activity has been a dangerous environmental neurotoxin, recognized to affect activity levels, attention and both sensory and cognitive function in children. Lead study would be simplified by having an animal model such as *Drosophila melanogaster* that could be administrated easily and quickly. Human will be expected from further studies with *Drosophila melanogaster* to realize better how lead affects the developing nervous system, and thus ultimately its effects on children (Hirsch *et al.*, 2003).

Bee venom has pharmacological properties used in treatment of arthritis, rheumatism, pain, cancerous tumors, and skin diseases. However, in a study metals of honeybee venom were determined due to human contamination (Kokot and Matysiak, 2008). Also, Royal jelly from *Apis mellifera*, whose demonstrates homeostatic adjustment as mammalian and human breast milk, is a highly active natural biological matter and is probably one of the most interesting raw substances in the natural product chemistry. Trace elements perform a key role in the biomedical activities affiliated with royal jelly, as these elements have a multitude of known and unknown biological functions (Stocker *et al.*, 2005).

The common treatment of human visceral leishmaniasis requires the use of pentavalent antimony (SbV) which its mechanism of action is unknown because of the limited information available about intracellular antimony metabolism and about the genes that adjust these processes. Here, flow injection ICP-MS, flow injection hydride generation ICP-MS, and ion chromatography ICP-MS were applied to assay antimony (Ulrich *et al.*, 2000; Shaked-Mishan *et al.*, 2001; Miekeley *et al.*, 2002; Neves *et al.*, 2009; Séby *et al.*, 2012).

Concern about the environmental pollution effects on the immune function in both humans and wildlife is increasing and practically nothing is known about this impact on terrestrial invertebrates, even though they are known to easily accumulate contaminants. The effect of industrial heavy metal pollution on *Formica aquilonia* immune defense, were investigated. The *Formica aquilonia* encapsulation response was increased in moderate whereas suppressed in high heavy metal levels suggesting higher risk for infections in heavily contaminated areas (Sorvari *et al.*, 2007). Environmental pollution from heavy metals has become a matter of great concern in many countries. Heavy metal contents

in the mineralised dental tissues are indicators of the contact of their mineral phase to heavy metals during the time of the dental tissue formation and tooth development. Teeth whose accurately reflect the environmental or dietary contact of animals and humans to heavy metals have been used as bioindicators. The bank vole (*Clethrionomys glareolus*) teeth heavy metal content was investigated as a contact

indicator of environmental contamination (Gdula-Argasińska *et al.*, 2004).

#### RESULTS AND DISCUSSION

Examples of the use of a broad spectrum of ICP-MS in entomology including ecotoxicology, physiology, disease treatments, determining and removing environmental contaminations, homeostasis, and immune system are summarized in tables 1-4.

Table 1. Selected recent and specific examples to illustrate the range of applications of ICP-MS in ecotoxicology studies related to entomology

Heavy metal	Arthropod	Measure	Reference
Lead	<i>Drosophila melanogaster</i> (Tephritidae)	Behavioral (courtship, fecundity, locomotor activity) effects of chronic exposure	Hirsch <i>et al.</i> , 2003
Cadmium	Wolfspiders ( <i>Pardosa saltans</i> : Lycosidae)	Effects of experimental exposure on metallothionein-like protein levels from polluted and reference populations	Eraly <i>et al.</i> , 2010
Cadmium, lambda-cyhalothrin	<i>Daphnia magna</i> (Daphniidae)	Binary mixtures of toxic substances: pharmacological versus ecotoxicological modes of action	Barata <i>et al.</i> , 2007
Zinc	<i>Daphnia magna</i> (Daphniidae)	Bioaccumulation by waterborne and dietary exposure	Balcaen <i>et al.</i> , 2008
Mg, K, Na, Zn, Fe, Al, Cu, Sr, Ba, Mn, Ti, Se, Mo, Ag, Cd, Co, Li, Ce	<i>Oxidus gracilis</i> (Polydesmida: Paradoxosomatidae)	Distribution and relation to environmental habitats	Nakamura and Taira, 2005
Cadmium, copper, lambda-cyhalothrin, deltamethrin	<i>Daphnia magna</i> (Daphniidae)	Toxicity of binary mixtures of metals and pyrethroid insecticides, implications for multi-substance risks assessment	Barata <i>et al.</i> , 2006
Cr, Co, Fe, Mg, Mn, Ni, Se, Na, Zn	Tobacco budworm ( <i>Heliothis virescens</i> : Lepidoptera: Noctuidae)	Uptake of dietary micronutrients from artificial diets	Popham and Shelby, 2006
Na, K, Mg, Ca, Cu, Zn	<i>Bombyx mori</i> (Bombycidae)	Effect of metallic ions on silk formation	Zhou <i>et al.</i> , 2005
Arsenic	<i>Stenopsyche marmorata</i> (Trichoptera: Stenopsychidae)	Rapid determination of arsenic species	Miyashita <i>et al.</i> , 2009
Arsenic	<i>Cherax destructor</i> (Parastacidae)	Arsenic speciation	Williams <i>et al.</i> , 2009
Arsenic	Terrestrial invertebrates	Arsenic speciation	Moriarty <i>et al.</i> , 2009
Arsenic	<i>Mya arenaria</i>	Speciation analysis	Yang <i>et al.</i> , 2009
Cd, Cu, Zn	<i>Penaeus semisulcatus</i> (Penaeidae), <i>Penaeus merguensis</i> (Penaeidae)	Distribution of trace elements in tissues of two shrimp species from the Persian Gulf and roles of metallothionein in their redistribution	Pourang and Dennis, 2005

In addition to the application of inductive coupled plasma-mass spectrometry in the various sciences, the use of this method of analysis can be used to determine most trace and ultra-trace metals, and some nonmetals, tracking of elements in biological samples and various studies that will be done on arthropods or related subjects to entomology such as ecotoxicology, physiology, disease treatments, determining and removing environmental contaminations, homeostasis, and immune system. Based on principles, ICP-MS

device is similar to the atomic emission spectroscopy method that can be used as a prominent, efficient, and very special tool in the process of various samples analysis. Inductively coupled plasma-mass spectroscopy can be coupled with devices such as mass spectrometers, chromatography, or polyacrylamide gel electrophoresis for identifying and quantifying of the native metal cofactor of proteins and their phosphorylation in biofluids, determination of pesticides residues, etc.

Table 2. Selected recent and specific examples to illustrate the range of applications of ICP-MS in physiology and bioindication studies related to entomology.

Heavy metals	Arthropod	Measure	Reference
Iron	<i>Aedes aegypti</i> larvae	Regulation of cell ferritin	Geiser <i>et al.</i> , 2007
Iron	<i>Aedes aegypti</i> larvae	Secreted ferritin: mosquito defense against iron overload	Geiser <i>et al.</i> , 2006
Cu, Zn	<i>Drosophila melanogaster</i>	Metallothioneins (MTO): the second member of a <i>Drosophila</i> dual copper-thionein system	Domenech <i>et al.</i> , 2003
Ferrihemeprotein nitrophorin-7	<i>Rhodnius prolixus</i> (Reduviidae)	Overexpression in <i>Escherichia coli</i> (Enterobacteriaceae) and functional reconstitution of the liposome binding ferriheme protein nitrophorin-7	Knipp <i>et al.</i> , 2007
Bioindication			
Finnish Cu-Ni smelter	Oribatid mites ( <i>Chamobates cuspidatus</i> : Oribatidae)	Leg deformities of oribatid mites as an indicator of environmental pollution	Eeva and Penttinen, 2009
As, Cd, Cu, Pb, Zn	Earthworms, beetles and woodlice	Habitat type-based bioaccumulation and risk assessment of metal and As contamination	Vermeulen <i>et al.</i> , 2009
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	<i>Paramoera walkeri</i> (Eusiridae, Amphipoda)	Baseline metal concentrations	Palmer <i>et al.</i> , 2006
Cd, Cu, Zn, Pb, As	Red swamp crayfish ( <i>Procambarus clarkia</i> : Cambaridae)	Indicator of the bioavailability of heavy metals in environmental monitoring in the River Guadiamar (SW, Spain)	Alcorlo <i>et al.</i> , 2006
As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb, Zn	Insects	Heavy metal contamination survey	Nasirian, 2013

Table 3. Selected recent and specific examples to illustrate the range of applications of ICP-MS in human treatment disease studies related to entomology.

Heavy metal	Arthropod, disease treatment/ agent	Measure	Reference
Microelements (Al, Co, Cu, Zn, Mn, Mo, B, V, Sr, Ni); Macro-elements (Ca, Mg, K, Na); Toxic metals (As, Ba, Pb, Cd, Sb, Cr)	Honeybee ( <i>Apis mellifera</i> : Apidae)	Determination of metals in honeybee venom	Kokot and Matysiak, 2008
Cisplatin	<i>Drosophila melanogaster</i>	DNA adducts induced by cisplatin and their correlation with genotoxic damage	García <i>et al.</i> , 2008
Iron	<i>Trypanosoma brucei brucei</i>	Purification and kinetic characterization of recombinant alternative oxidase	Kido <i>et al.</i> , 2010
Antimony	Treatment of leishmaniasis	Speciation of antimony in injectable drugs used for leishmaniasis treatment	Seby <i>et al.</i> , 2012
Antimony	Treatment of leishmaniasis	Antimony in plasma and skin of patients with cutaneous leishmaniasis-relationship with side effects	Neves <i>et al.</i> , 2009
Antimony	Treatment of leishmaniasis	Monitoring of total antimony and its species in biological samples from patients	Miekeley <i>et al.</i> , 2002
Antimony	Treatment of leishmaniasis	Speciation of antimony (III) and antimony (V) in cell extracts	Ulrich <i>et al.</i> , 2000
Antimony	<i>Leishmania donovani</i>	Novel Intracellular SbV reducing activity correlates with antimony susceptibility	Shaked- Mishan <i>et al.</i> , 2001

Table 4. Selected recent and specific examples to illustrate the range of applications of ICP-MS in miscellaneous studies related to entomology.

Heavy metals	Organism	Measure	Reference
<b>Bioremediation</b>			
Selenium	<i>Cotesia marginiventris</i> (Hymenoptera: Braconidae), parasitizing the beet armyworm ( <i>Spodoptera exigua</i> : Noctuidae), feeding on alfalfa ( <i>Medicago sativa</i> )	Biotransformations in an insect ecosystem: effects of insects on phytoremediation	Vickerman <i>et al.</i> , 2004
<b>Hemostasis</b>			
Al, Ba, Sr, Bi, Cd, Hg, Pb, Sn, Te, Tl, W, Sb, Cr, Ni, Ti, V, Co, Mo, P, S, Ca, Mg, K, Na, Zn, Fe, Cu, Mn	Royal jelly from <i>Apis mellifera</i>	Trace and mineral elements in royal jelly and homeostatic effects	Stocker <i>et al.</i> , 2005

<b>Insect immune system</b>			
As, Cd, Cu, Ni, Pb	Free-living wood ant ( <i>Formica aquilonia</i> : Hymenoptera: Formicidae)	Immune response disturbance	Sorvari <i>et al.</i> , 2007
Metalloprotein	<i>Ostrinia furnacalis</i> (Lepidoptera: Pyralidae) larvae	Purification and characterization of hemolymph prophenoloxidase	Feng <i>et al.</i> , 2008
<b>Forensic medicine</b>			
Pb, Ba, Sb	Forensically important blowfly <i>Calliphora dubia</i> (Diptera: Calliphoridae)	Extraction of gunshot residues from the larvae	Roeterdink <i>et al.</i> , 2004
<b>Environmental pollution</b>			
Lead	Western fence lizards ( <i>Sceloporus occidentalis</i> : Phrynosomatidae), <i>Acheta domestica</i> (Gryllidae), <i>Tenebrio molitor</i> (Tenebrionidae) larvae, <i>Porcellio scaber</i> (Porcellionidae)	Assessment of lead uptake in reptilian prey species	Inouye <i>et al.</i> , 2007
Selenium, arsenic, copper, cadmium	Eastern mosquitofish ( <i>Gambusia holbrooki</i> : Poeciliidae)	Respiratory and reproductive characteristics	Staub <i>et al.</i> , 2004
Mn, Cd, Pb	Bank vole ( <i>Clethrionomys glareolus</i> : Cricetidae)	Heavy metal of teeth as an indicator of environmental pollution	Gdula-Argasińska <i>et al.</i> , 2004
<b>Bioindication</b>			
As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb, Zn	<i>Gambusia affinis</i> (Poeciliidae)	Heavy metal bioconcentration	Nasirian <i>et al.</i> , 2013

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