"SPECIATION" OF TRACE ELEMENTS AND TOXIC METAL ION SPECIES

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Outline

- Definition : Trace element speciation (“Species distribution”)
- Why speciation is important?
- Analytical Methods on Speciation Analysis
- Examples: Related to Use of Depleted Uranium
- Summary

"Everything is a poison, nothing is a poison, the dose alone is the poison"
P.A. Parcelus (1493-1541)

In addition:

Speciation or "species distribution" of an element can profoundly affect its toxicity.

Fear of Toxin in Tap Water Rocks California Valley

Evidence of Chromium 6 in Wells Sparks Furor, Scramble to Gauge Extent of Contamination

By RENE SANCHEZ
Washington Post Staff Writer

BURBANK, Calif.—No one tastes it, smells it or even knows how much to fear it, but a toxic chemical just featured in a popular movie has the San Fernando Valley racked with worry that its tap water has become the latest victim of Southern California's endless battle with pollution.

Chromium 6 is turning up in wells that supply water to this arid basin in metropolitan Los Angeles at levels state environmental researchers say should no longer be acceptable. There is no sign of panic in the streets, but that revelation has set off a political and scientific scramble to assess the contamination problem and decide whether it requires urgent fixing.

Nearly 200 industrial sites around the valley are being examined for evidence of the pollutant, which can cause cancer or other serious illnesses from extensive exposure. Sales of bottled water are booming and schools are sending parents reassuring letters about water safety. A nearby city, Glendale, has postponed using any well water. And the real-life inspiration for the film "Erin Brockovich," a tale of a feisty woman's heroic fight to uncover the dangers of chromium 6 in a California desert town, is back on the case.

When inhaled as dust, chromium 6 is widely considered to be a carcinogen, but scientists are still debating the dangers it may pose when ingested.

"There's significant concern," said Adam Schiff, a state senator in the valley who was elected to Congress last month. "All of us are taking a long look at the water now before we drink it down."

The furor is familiar here. This region constantly is trying to recover from its reckless or clueless environmental past. Its air and water have been pummeled for decades from byproducts of military manufacturing and runaway population growth. Last week, a study found that half of the Southern California coastline is unsafe for swimming after rainstorms because urban runoff dumps so much harmful bacteria into the ocean.

The struggle to improve the environment at times also creates as many problems as it solves. A state crackdown on chromium 6, for example, could shut wells across the valley. And that could force one of the most densely populated—and fastest-growing—parts of greater Los Angeles to scrounge once more for new sources of water at a time when soaring populations in other desert communities in the West are making it ever more scarce.

BY JUAN CARLO—VENTURA COUNTY STAR VIA ASSOCIATED PRESS

Anti-pollution activist Erin Brockovich, with lawyer and boss Edward Masry at a recent news conference, is again sounding the alarm.

"We don't currently have enough water for our growth needs," said David Beckman, a lawyer in the Los Angeles office of the Natural Resources Defense Council. "So when you start talking about taking major sources of it out of service because of contamination, it's potentially a really bad situation. But they might have to do that. Nobody here is arguing that it is good to have chromium 6 in the water."

But how much is too much? That is the fundamental question confronting state and local officials.

The debate in the valley over chromium 6 in some ways is a sign of how serious California's campaign against pollution is getting. The state has stronger rules to protect its water supply than the federal government recommends, particularly for chromium. But for the past year, a state agency that examines environmental health hazards has been calling for even tougher standards to keep the chemical out of the ground water that California cities pump and treat for human consumption.

Some officials say the step is overdue because of the risks associated with chromium 6. It is a manufacturing byproduct of chromium, which is an odorless metallic element that many industries use to make and harden steel. And it is being found in soil and water around the San Fernando Valley because long before the area became a home to movie and television studios, it was a hub for aerospace industry giants such as Lockheed Martin. The company had a large manufacturing plant in Burbank for more than 50 years.

The toxic chemical also is not just turning up in worrisome amounts around industrial wastelands. Recent county tests have shown possible contamination near schools, libraries and health clinics.

At some of those sites, water faucets and fountains are being forsaken. "Parents are asking a lot of questions," said Joan Graves, a staff member at William McKinley Elementary School. "Everyone wants more information, but it sounds like that could take awhile. Students are just bringing bottled water."

The mood is similar at the main public library in Burbank. "We don't really use the tap water," said Nancy Tidwell, a reference librarian. "But there's no way you could tell that anything is wrong with it."

At a packed hearing in the Burbank City Hall last month, a panel of scientists told lawmakers and residents that while waiting for more conclusive studies on the risks of chromium 6, the state should err on the side of caution and enact tougher protections against it seeping into the water supply.

Public anxiety over the issue is spreading in part because of the recent film "Erin Brockovich." Set in the small desert town of Hinkley, Calif., it dramatized the true story of how chromium 6 in the soil inflicted unsuspecting residents with serious illnesses. The amounts turning up around the San Fernando Valley are nowhere close to what was found in Hinkley, but they still exceed the strict new limit being proposed for the state.

Brockovich, an outspoken legal aide to local lawyer Edward Masry, is once again sounding an alarm. "People are being exposed to a poison in their water," she told a Los Angeles City Council meeting recently.

The uproar began when the state's health department conceded this fall that it could take five years to adopt a stronger standard to protect local water supplies from chemical contamination. That disclosure, reported first in the Los Angeles Times, has provoked an aggressive political attack.

California Gov. Gray Davis (D) swiftly signed legislation requiring the health department to assess the threat of chromium 6 in water in no more than a year. Last week, a coalition of legislators also urged the state to force utility companies to notify the public any time levels of chromium 6 in water exceed the new limit environmental researchers have proposed.

The state's 3,400 water systems have been asked to conduct tests for the chemical. In Los Angeles County, water also is being checked at all government facilities and the regional water board is promising to increase its inspections of suspected polluters.

But the price of purifying the water in dozens of wells, or finding new sources of water, could be steep. By some estimates, the cost in parts of the San Fernando Valley could top $50 million a year. And whether all, or any, of it is necessary to guarantee public safety is still in doubt.

Water officials are in an awkward position. Even as they endorse more investigations into chromium 6, they insist there are no reasons for residents to fear for their health when they drink tap water.

"This situation certainly bears study, and no one is brushing it off," said H. David Nahai, chairman of the Los Angeles Regional Water Quality Control Board. "But we have yet to hear from any other regulatory agency that the levels of chromium 6 in the drinking water right now are unsafe."

Nahai also suggested that rising public apprehension over pollutants could, nevertheless, be a blessing in disguise for Southern California.

"In the past, we haven't done a very good job of protecting our limited water resources," he said. "I think we've finally woken up to that."

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Trace Element Speciation: Definition

- Chemical Speciation may be defined as the determination of the various chemical (ie, oxidation/valence states) and physical (morphological state) forms of the element which together make up the total concentration of that element on a sample.

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Why Speciation?

- Chemical (oxidation/valence state) forms determines toxicity (eg, Cr^{VI} vs Cr^{III})
- Chemical forms determines the mobility of an element in the environment
- Speciation of metals: can affect the bioavailability of metals and therefore their risk.

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Speciation

Structural Aspects

- Electronic and/or Oxidation States
- Nuclear (Isotopic) Composition
- Inorganic compounds and complexes
- Organometallic compounds
- Organic and macromolecular complexes

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Trace Metal Species of Interest

- **Redox systems**
  - Se^{IV}/Se^{VI}, As^{III}/As^{V}, Sn^{II}/Sn^{IV}, Cr^{III}/Cr^{VI}
- **Alkylated forms:**
  - Methyl: Hg, Ge, Sn, Pb, As, Sb, Se
  - Ethyl: Pb, Hg
- **Bio-molecules:**
  - Organo-As, Se, Cd
  - Metalloproteins and metalloenzymes

Health Effects and Speciation Assessment of Depleted Uranium

Uranium Forms

Uranium Ore

Natural Uranium

U-234	Trace
U-235	0.71%
U-238	99.28%

Enriched Uranium

U-234	Trace
U-235	3% to >90%
U-238	<10% to 97%

Depleted Uranium

U-234	Trace
U-235	0.20%
U-238	99.8%

Uranium Exposure

- Everyone is exposed to uranium because uranium is occurs in the environment
- On Average-each of us ingest 1.9 micrograms uranium per day and inhale 0.007 micrograms uranium per day.
- Only 0.2%-5% uranium is absorbed by GI into blood.
- Uranium accumulates in Kidney and Bone.

What is DU?

Definition:

- DU is a byproduct from the enrichment process to make nuclear fuel or weapons grade uranium.
- Environmental uranium contains 99.28% ^{238}U, 0.72% ^{235}U and 0.0058% ^{234}U.
- Depleted Uranium-NRC defines DU as uranium containing less than 0.711% ^{235}U.
- DU contains ~99.8% ^{238}U, 0.2% ^{235}U and 0.002 ^{234}U.

Properties:

- Dense (19 g/cm3) – high inertia
- DU is 50% less radioactive than environmental uranium.
- DU has radiologic and chemical toxicity properties.

DU vs Tungsten

Use:

- DU used as armor and ammunitions in military applications (alloy – titanium)
- DU is used commercially by chemical companies and as counterweights in aircrafts.

Target Organs

- Lung (insoluble)
- Kidney (soluble)
- Liver and bone (soluble)
- Skin
- Ongoing research suggests other potential target organs

Known Health Effects

- The kidney is the target organ for soluble forms of depleted uranium;
- More insoluble forms may remain in the lungs for longer periods;
- Health risk depends upon the depleted uranium intake and chemical.

DU Analysis
Sample Preparation

- Type of sample: 24hr urine collection
- Ash 10 ml urine by dry ashing at 450 degrees and heating on hot plate after additions of 1 ml nitric acid and 0.5 ml hydrogen peroxide.
- Ashing repeated until samples are a white ash
- Sample reconstituted with 10 ml of 1M or 1 % nitric acid
- Sample analyzed by DRC-ICP-MS

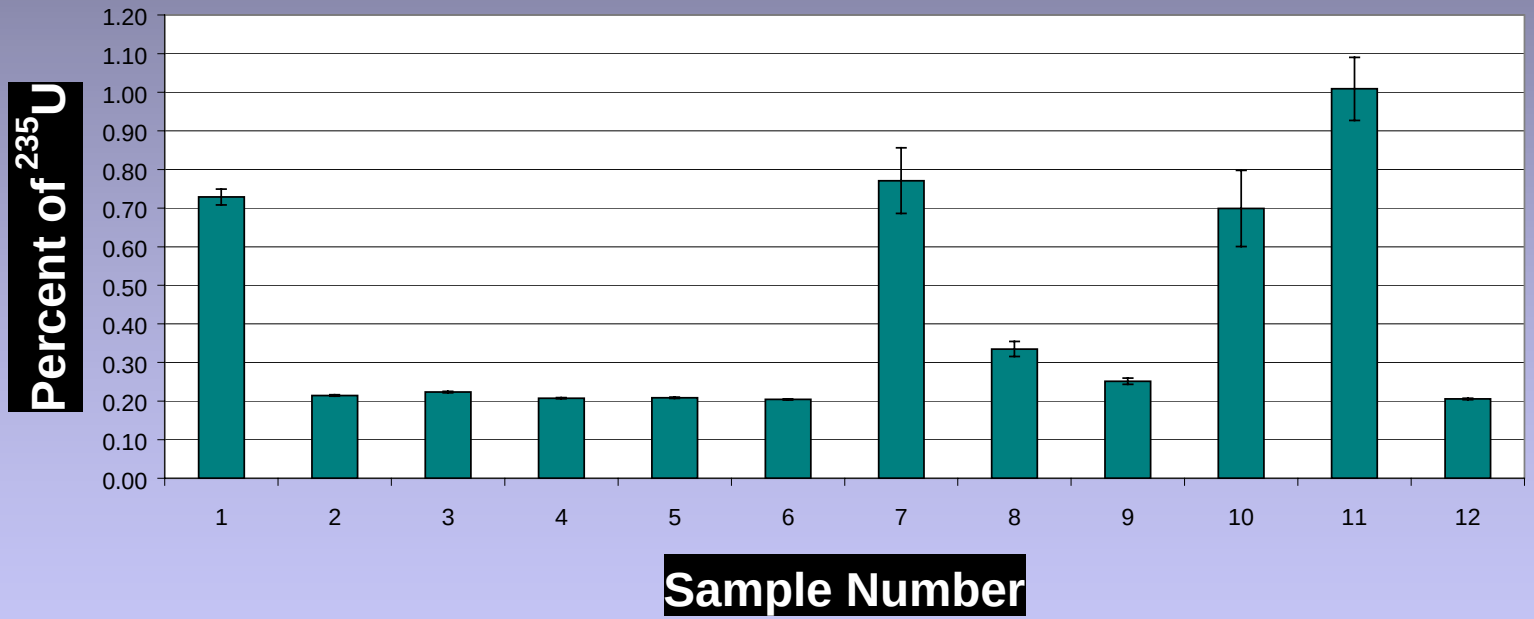
DRC-ICP-MS = “Dynamic Reaction Cell”-Inductively Coupled Plasma-Mass Spectrometry

Goal for Uranium Isotopic Analysis

- Analysis of urine samples that contain 50 ng/L or greater of total uranium.
- Isotopic speciation by ICP-MS provides a sensitive, accurate, and fast method to determine “source of exposure” (environmental vs DU);

Determination of the Isotopic Composition of Uranium in Urine by Inductively Coupled Plasma Mass Spectrometry

Health Physics, January 2000, Volume 78, Number 1



Detection Limits

- Detection limits of 0.01 PPT
- Because of uranium 235 low abundance ideal limit of detection in samples is 5PPT DU and 1.5 PPT in Natural uranium (NU)
- Because of matrix effects in biological samples actual detection limits in urines samples will be 10 PPT DU and 3 PPT NU

HPLC-DRC-ICP-MS
Isotopic Uranium Analysis

Sample Concentration	Measured % ^{235}U (Urine)	Certified % ^{235}U (STD)
#1 – 51.8 ng/L	0.28 ± 0.10	0.26 ± 0.01
#2 – 54.2 ng/L	0.54 ± 0.04	0.49 ± 0.02
#3 – 55.3 ng/L	0.63 ± 0.04	0.62 ± 0.01
#4 – 55.7 ng/L	0.70 ± 0.14	0.72 ± 0.01
#5 – 99.1 ng/L	0.28 ±0.01	0.26 ± 0.01

ANALYTICAL TECHNIQUES IN TRACE ELEMENT SPECIATION

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Modern Methods of Analysis

(Chemical Speciation and Modes of Occurrence)

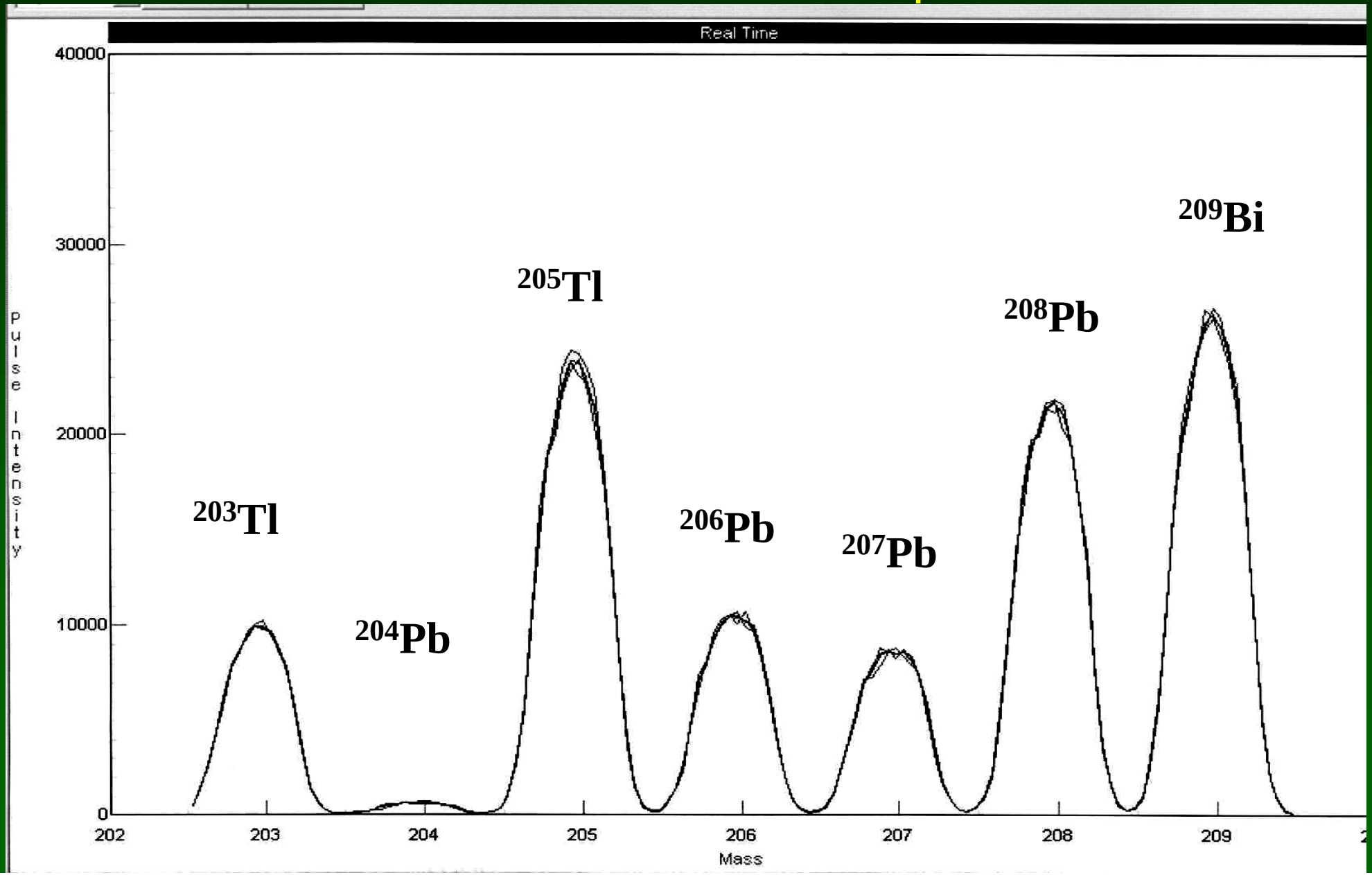
Speciation Studies:

- **Inductively Coupled Plasma & MS (ICP-MS)**
- **High-Resolution HPLC-ICP-MS (with DRC technology)**
- **Extended X-ray Analysis Fine Structure (XAFS)**
- **Electron microprobe**

Chemical Analysis

- **Instrumental Neutron Activation Analysis (NAA)**
- **X-ray fluorescence (XRF)**
- **Atomic Absorption Spectroscopy**

ICP-MS : Scan of Isotopes



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Applications of ICP-MS to *Blood-Lead Determination*

- **Measurement of Isotope Ratios**
  - ^{208}Pb:^{206}Pb, and **^{206}Pb:^{207}Pb**
  - Potential for Pb source identification
  - Isotope Dilution Measurements (IDMS)
  - Plasma Pb measurements possible

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Applications of ICP-MS to Arsenic Speciation

- **Accurate analysis of inorganic, organic and biological (liver) metabolites**
  - Fast, accurate and sensitive technique for As speciation
  - Detection limits of 1-5 ppt (with DRC technology)
  - Analysis of a wide range of specimens: tissues, fluids, hair, and geo-environmental samples.

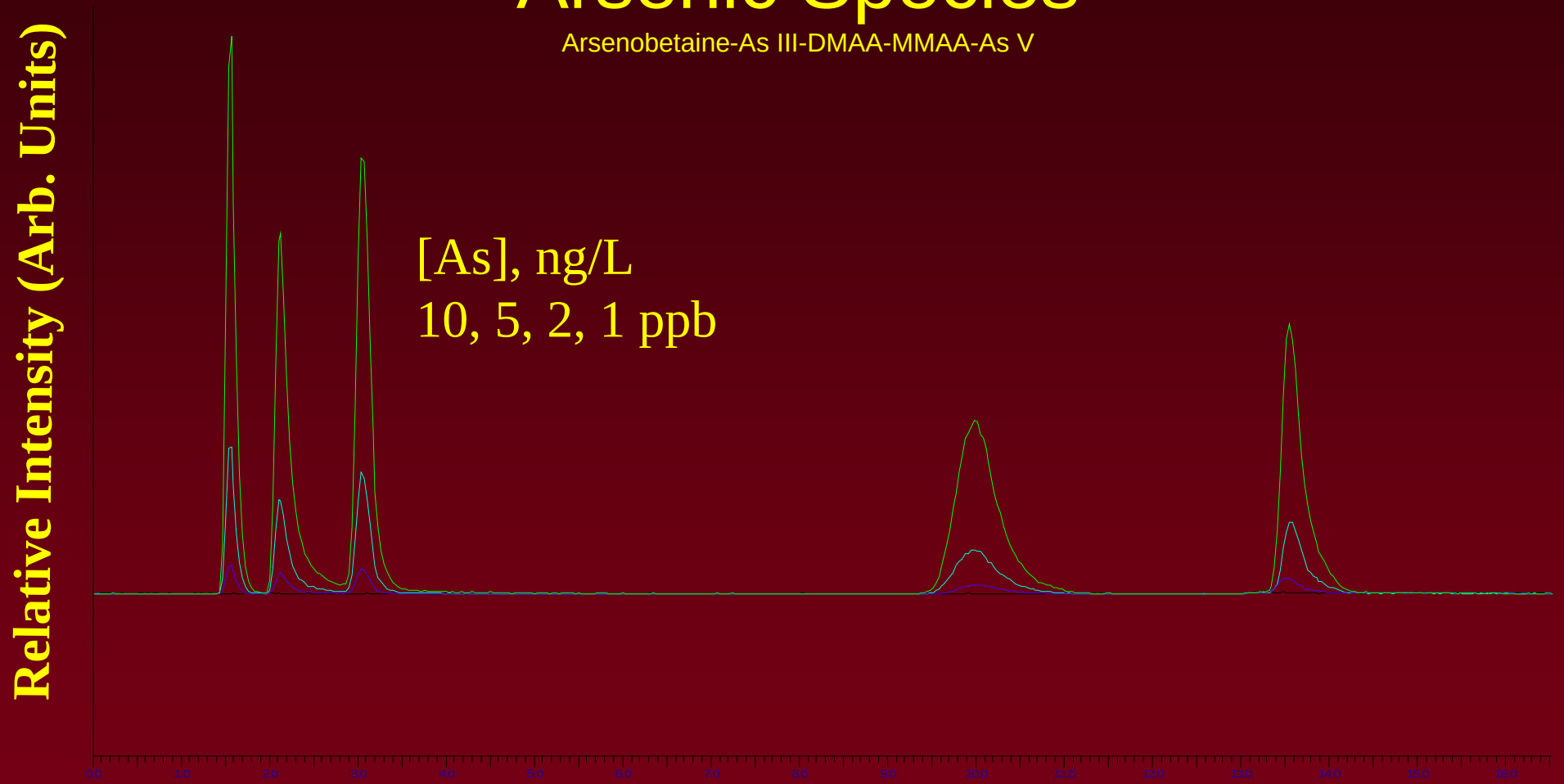
Method for the Speciation of As in Biological Materials

- Column- Hamilton PRP X-100
- Buffer A - 20 mM NH_4HCO_3 , pH 8.5
- Buffer B - 20 mM NH_4PO_4, pH 7.5
- Gradient

Step	Time (min)	A	B
1	6	100%0%	
2	4	0%	100%
3	8	100%0%	

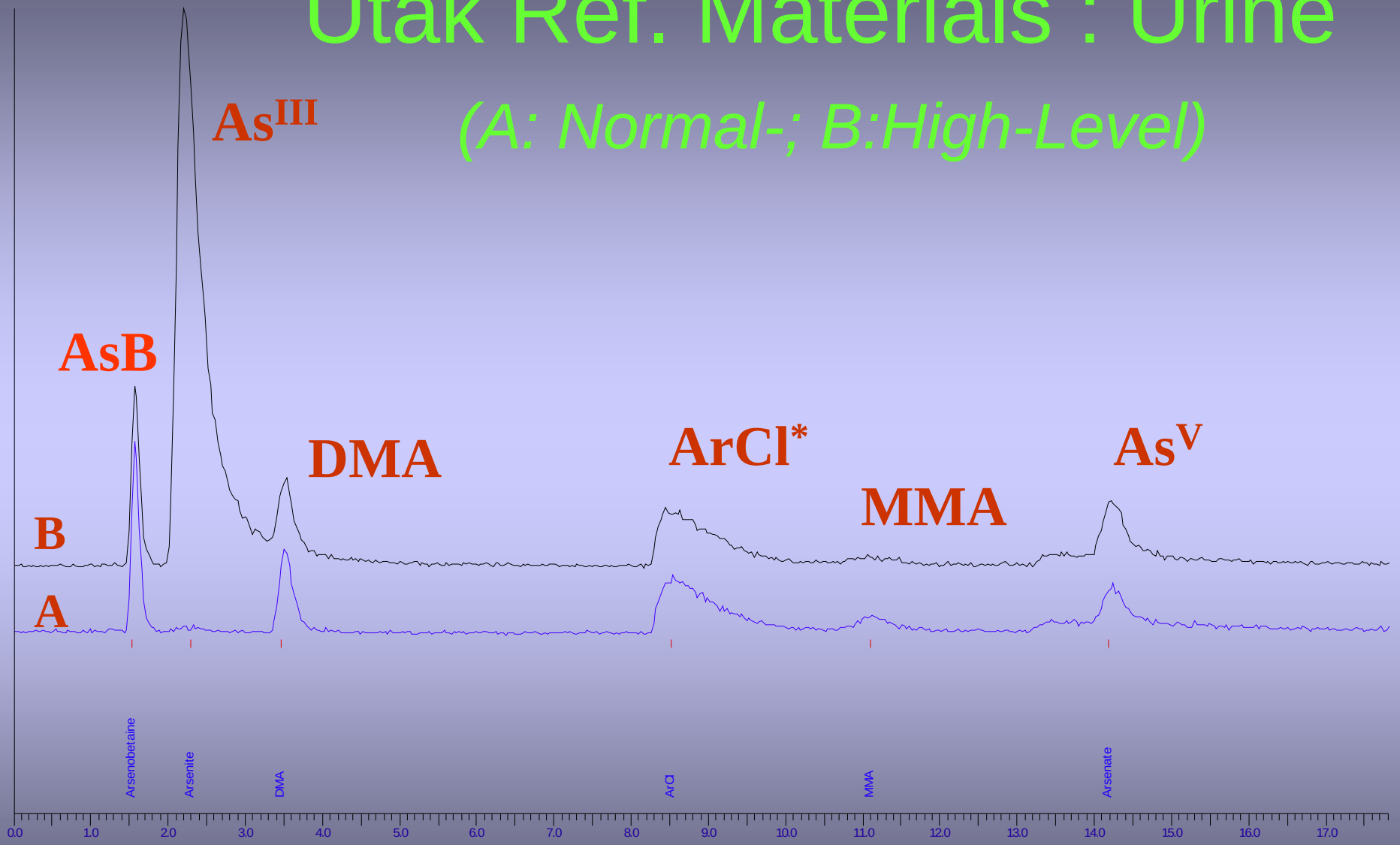
Standards
Arsenic Species

Arsenobetaine-As III-DMAA-MMAA-As V



Utak Ref. Materials : Urine

(A: Normal-; B:High-Level)



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Speciation:Certified Reference Materials

Certified Reference Materials Available:

- MeHg in marine matrices and sediments
- Organo-Sn in solution & sediments
- Trimethyl-Pb in solution and urban dust
- Cr^{III}/Cr^{VI} in solution

Produce by:

NIST (USA); NIES (Japan); IAEA (Germany);
NRCC (Canada); SM&T Programme/EU

Summary: Challenges and the Future in Trace Element Speciation

- Maintaining the integrity species and their distribution in the sample during the sampling, preparation, and analysis steps
- Availability of certified standard reference materials
- Validation of analytical methods and identification of unknowns

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Information Sites on Trace Element Speciation

- **Commission of the European Community**
  - **Web Site: http://www.speciation21.plymouth.ac.uk**
  - **NewsLetter**
  - **Int. Working Group on Medical Geology: home.swipnet.se/medicalgeology**
- **International Conferences:**
  - **7th International Symposium on Metal Ions in Biology and Medicine; May 6-10, 2002; St. Petersburg, Russia.**
  - **International Conference on Trace Element Speciation in Environmental, Biomedical and Nutritional Sciences. May 7-10, 2004; Munich, Germany.**
  - **Int. Conference on Environmental Toxicology and Medical Geology; San Juan, PR-USA. May 2003.**