Risk e Learning

Metals – Analytical Techniques

June 11, 2003
2:00 – 4:00 pm EDT

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University of Cincinnati

SUPERFUND
BASIC RESEARCH PROGRAM

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Introduction

- Metals analysis at Superfund sites can be done off-site, on-site, in-situ or ex-situ
- The selection will depend on cost factors, data reliability needed, the elements to be analyzed and available technologies
- We will focus here on on-site analysis procedures

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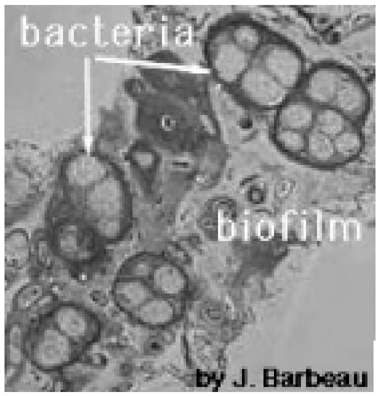
What are Biofilms?



•Biofilms are colonies of microbial cells encased in an organic polymeric matrix and attached to a surface.

•Allows for mixed microbial communities, concentration of nutrients, protection from antibiotics and from desiccation, etc.

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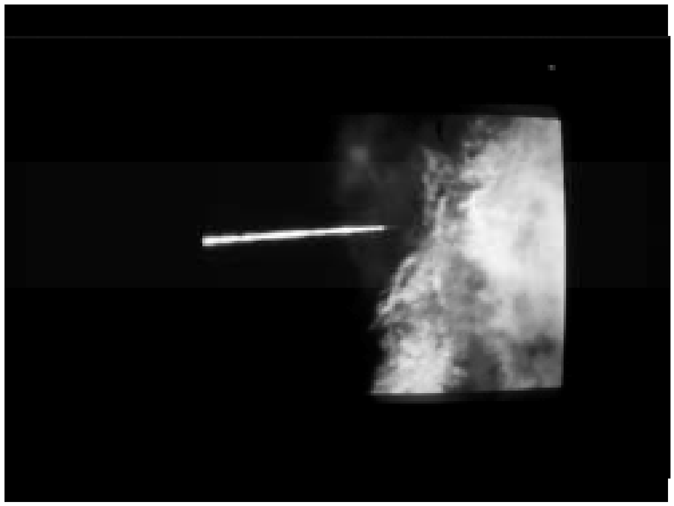
Microelectrode Approaching Biofilm



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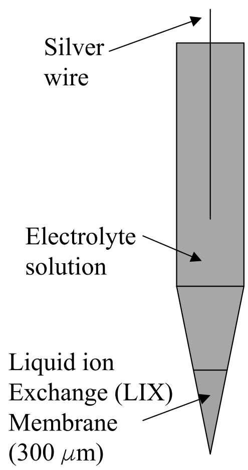
Ion Selective Microelectrodes



- pH, ammonium, potassium, phosphorus and nitrate microelectrodes are neutral carrier based liquid membrane ion selective microelectrodes.
- Sulfide microelectrode is a solid state ion selective microelectrode with fixed sensing layer at the tip.
- ISE microelectrodes could also be developed for many heavy metals

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Microelectrode Analytical System

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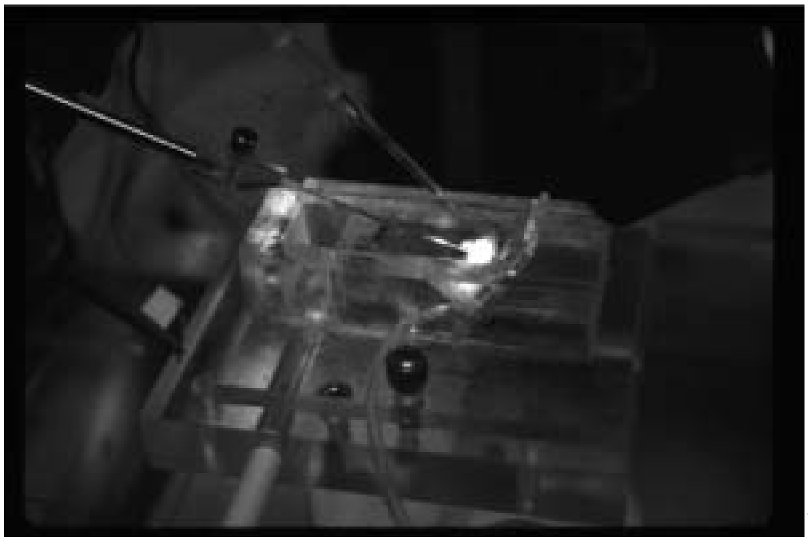
Microelectrode Flow Cell



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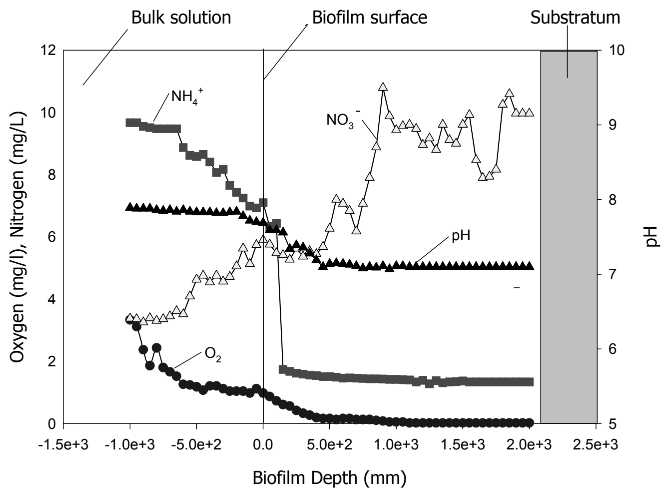
Microprofiles in an Aerobic/Anaerobic Biofilm



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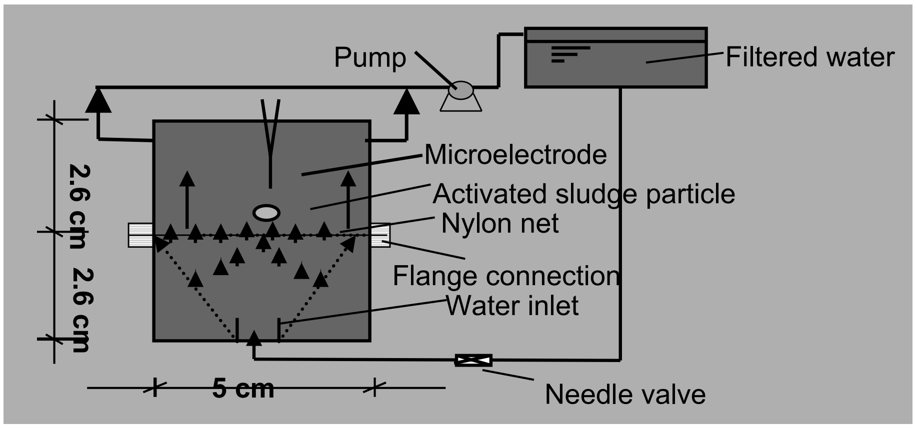
Chamber for Micro-profile Measurements in Activated Sludge Floc



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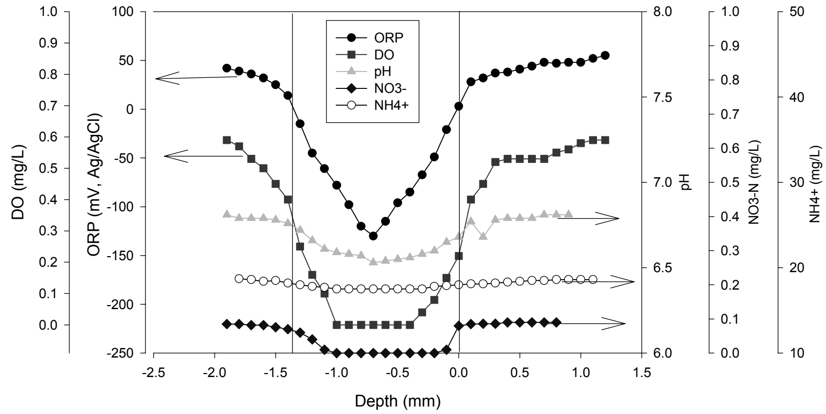
Microprofiles in an Activated Sludge Floc Particle



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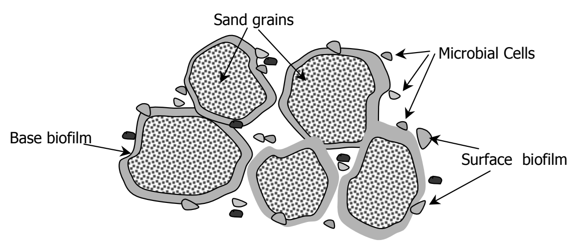
Soil Biofilms



•Continuous surface films (5-15 μm in thickness)
• Variety of aggregate structures (5-30 μm in diameter)
• EPS, extracellular polymeric substances, which protrude from the surface film and form bridges to adjacent sand grains

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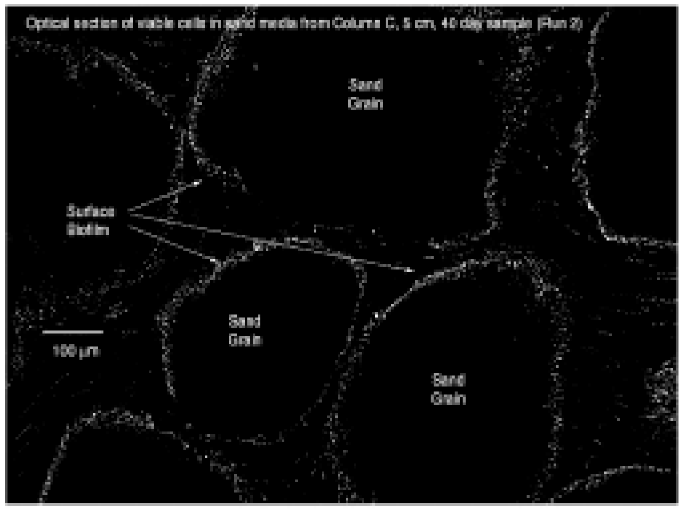
CLSM Image of Soil Biofilms



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New Generation of Microelectrodes

- Currently available microelectrodes are very fragile, have a short life and usually must be used in a lab under controlled conditions
- Need a new type of microelectrode that is more robust and environmentally-friendly
- We are developing a new kind of microelectrode that is intimately connected to a microelectronic circuit for amplifying, processing and transmitting microelectrode signals

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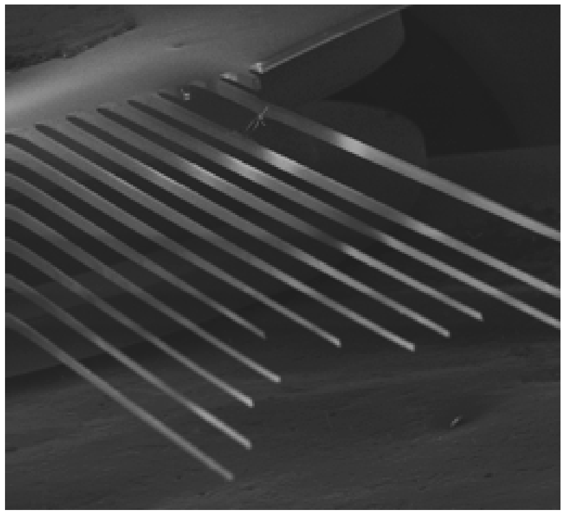
SEM of Array of Solid Glass Probes



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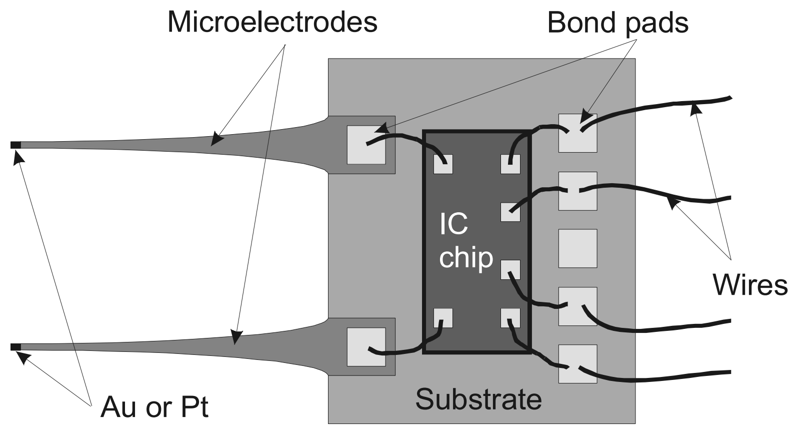
Proposed Microelectrode Sensor Package



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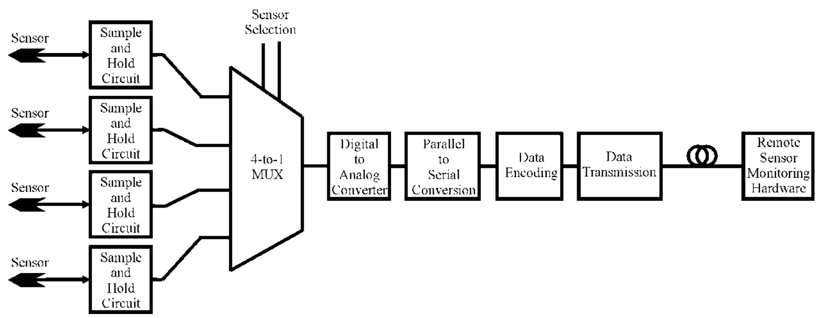
Sensor Component with an Array of 4 Sensors Multiplexed to a Single Signal Processing Chip



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In-Situ Metal Analysis in Soils

- Traditionally, soil characterization at hazardous waste sites requires drilling for soil cores followed by off-site analysis
- Process is slow and costly
- Need processes that are:
  - Cost effective
  - Rapid
  - Have sufficient spatial resolution
  - Provide field screening sensitivity

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On-Site Metal Analysis Approaches

- Laser-Induced Breakdown Spectroscopy (LIBS)
- X-ray Fluorescence (XRF)
- Electrochemical Techniques
  - Microelectrodes
  - Ultramicroelectrode Arrays
  - Voltammetry
- MEMS

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LIBS Approach

- Originally developed for use in ore analysis, but now being evaluated for in-situ field screening of contaminants in soil
- USACE WES procedure utilizes a cone penetrometer containing a fiber-optic laser sensor
- Laser-Induced Breakdown Spectroscopy utilizes a pulsed laser that rapidly heats (~5000 K) and ablates the soil forming a plasma. The emission spectrum can be analyzed to indicate which atomic species are present.

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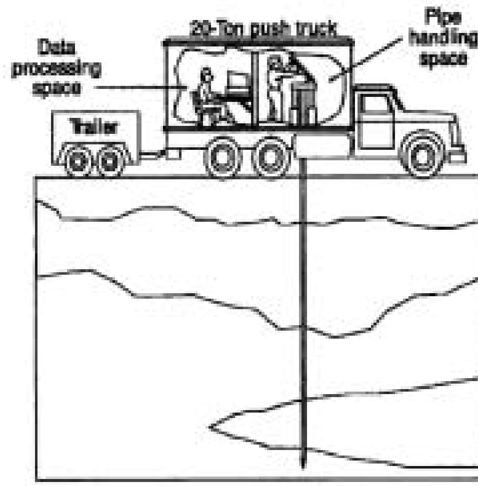
LIBS Penetrometer System



(Miles and Cortes, 1998)

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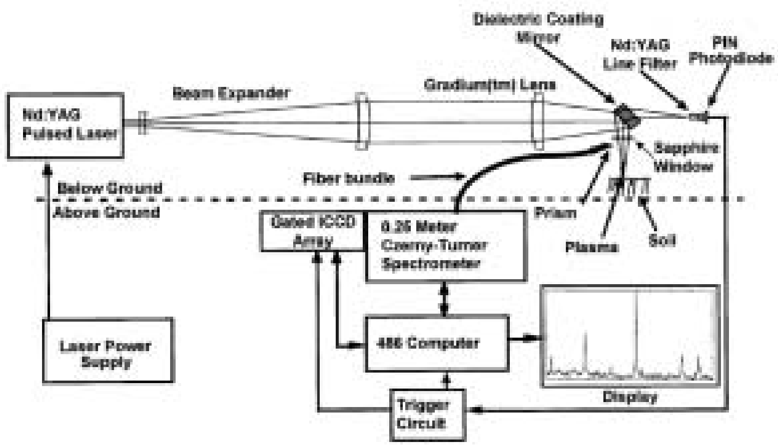
Block Diagram of WES LIBS System



(Miles and Cortes, 1998)

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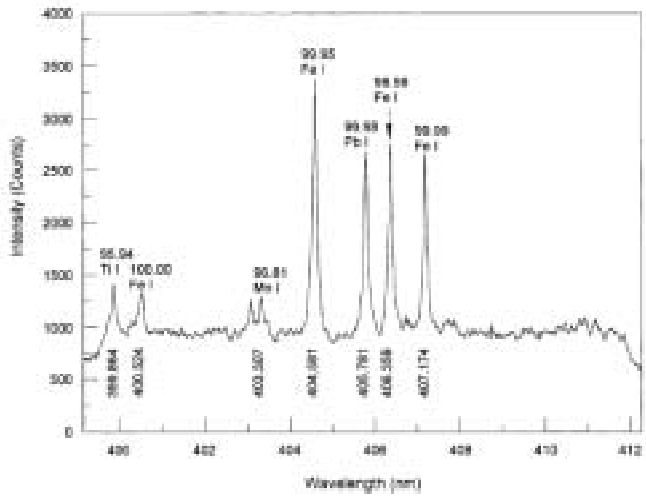
Representative LIBS Spectra Output



(Miles and Cortes, 1998)

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X-ray Fluorescence Approach

- Field portable x-ray fluorescence instruments are widely used by USEPA for analysis of metals in soils and sediments
- Determine concentration of desired metals in as little as 30 seconds
- Can be coupled with a cone penetrometer to eliminate need for drilling

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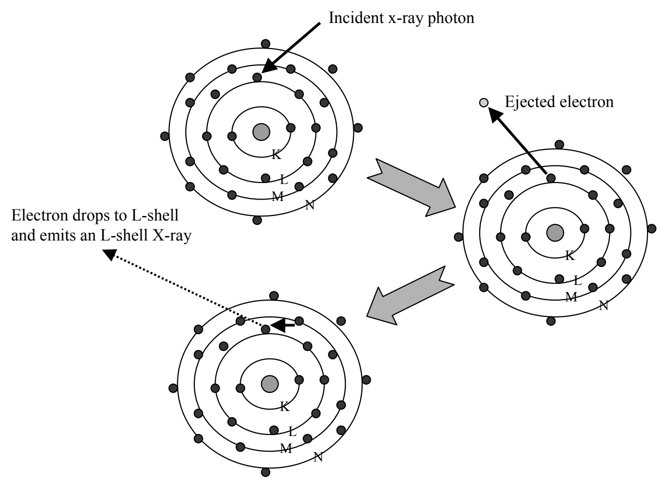
Mechanism for X-Ray Fluorescence



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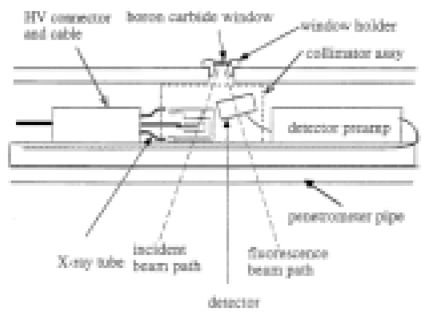
XRF Analysis

- Each element produces a fluorescence x-ray at a unique frequency or energy that can be detected.
- By counting the total number of x-rays that are detected at a given frequency during a given amount of time, the concentration can be determined.
- Analysis is rapid and low cost
- Typical minimum detection limits are 100 – 300 mg/kg

In-Situ vs. Ex-Situ XRF Analysis

- Most XRF analyses done on-site are done ex-situ on excavated soil samples
- Studies are underway to place a XRF in a cone penetrometer to measure metals in soils in-situ



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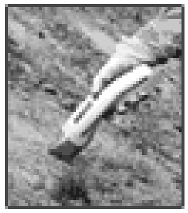
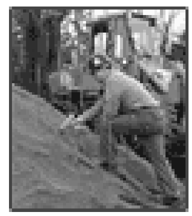
On-Site Testing with XRF



New Niton 7000 XRF

Old Niton 7000 XRF



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Comparison of Lead Concentrations using Field XRF and Laboratory XRF

Testing Method	Correlation (r^2)	Slope
In situ	0.81	0.86
Bagged	0.87	0.98
Ground	0.91	0.91
Sieved	0.93	0.95

n = 119
Sample range = 10 – 31,000 ppm Pb

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Electrochemical Techniques

- Microelectrodes
- Microelectrode Arrays
- Stripping Voltammetry Microelectrodes
- MEMS

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Microelectrodes for Metals

- We have developed microelectrodes for measurement of potassium and sodium in groundwater, based on liquid ion exchange, in addition to those constituents listed earlier
- USDA has developed a microelectrode for Cd in soil pore water next to plant roots
- Other researchers are developing chemical ion-selective microsensors for Pb, Cd, Zn and Fe
- Common drawbacks are their fragility and short lifetime

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Microelectrode Arrays

- Consist of microlithographically fabricated microelectrode array sensors
- Sensor consists of patterned thin film materials such as iridium, platinum, gold and carbon on silicon wafers
- Can detect many metals at trace concentrations (ppt to ppb)

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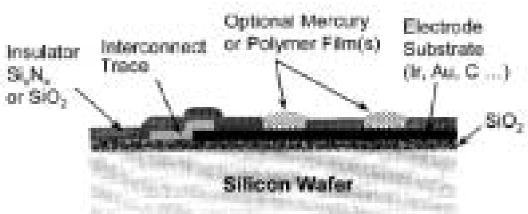
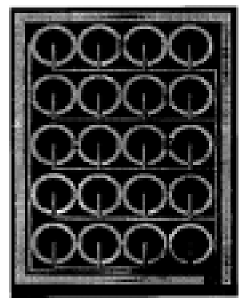
Typical Microelectrode Array

- Arrays are typically fabricated on 10 cm silicon wafers and divided into individual sensor chips



Cross-section



Typical array with microelectrode
Surrounded by a reference electrode

Feeney and Kounaves, 2000

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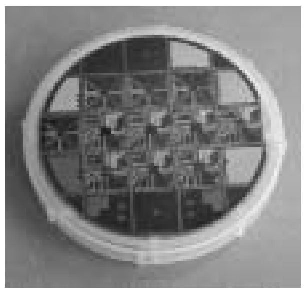
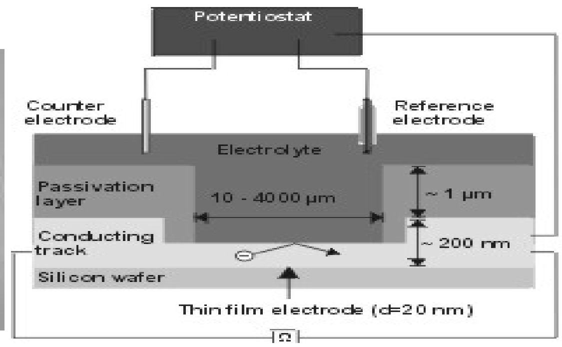
German Microelectrode Array Design





Courtesy Forschungzentrum Julich

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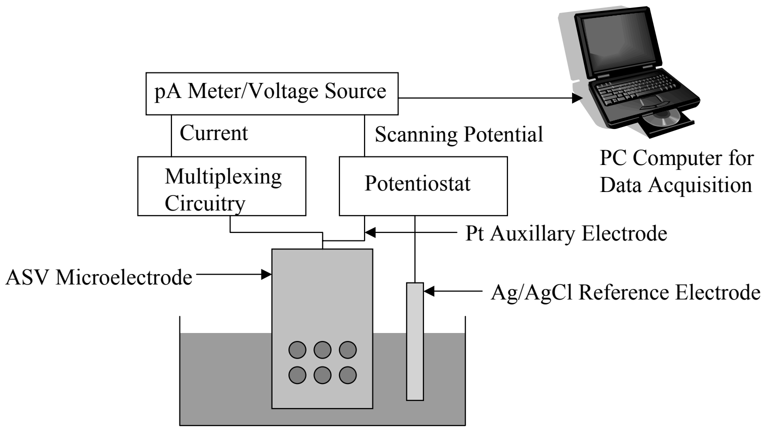
Stripping Voltammetry Microelectrodes

- Based on the anodic stripping voltammetry (ASV) technique
- This is a preconcentration technique where the metal ion of interest is electrochemically deposited, by applying a negative potential, into a thin film on mercury which has been deposited on the electrode
- After preconcentration, the potential is scanned from the applied negative potential to a more positive one
- The metals are stripped from the electrode, providing a current signal in the form of a peak at a redox potential characteristic of the metal and proportional to its concentration in solution

Typical ASV Microelectrode



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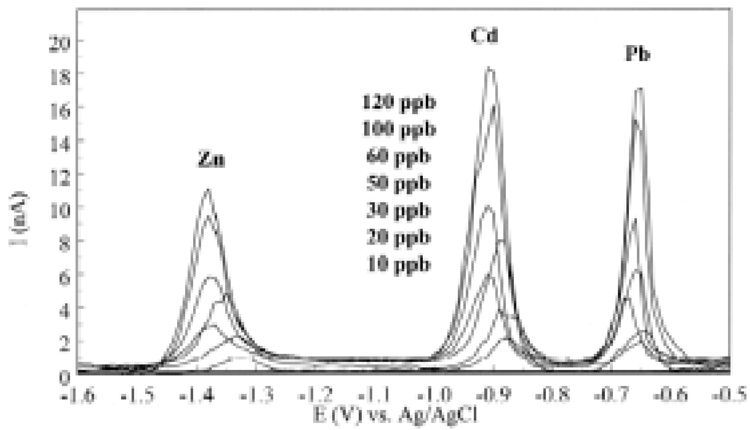
Typical ASV Microarray Output



Saban et al., 1999

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MEMS - Mercury Droplet Microelectrode Sensor on Lab-on-a-Chip

- Being developed at the University of Cincinnati
- Mercury droplet is uniformly generated and controlled from an on-chip mercury reservoir by thermopneumatic actuation and the surface tension effect of the mercury droplet
- Metals are detected by square wave anodic stripping voltammetry (SWASV)

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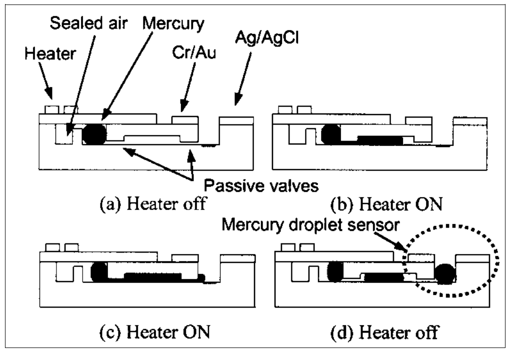
Principle of Mercury Droplet Electrode Generation



(a) Structure for mercury droplet electrode
(b) Mercury is driven in channel when heater is on
(c) Mercury goes into cavity passing through a passive valve
(d) Mercury slug breaks at passive valve due to surface tension and mercury in cavity touches Au/Pt layer to form a mercury droplet electrode

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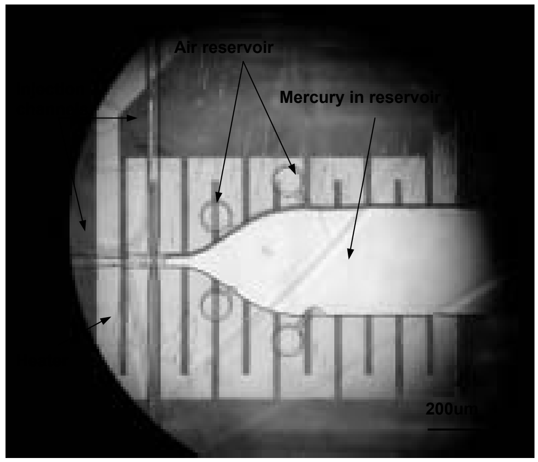
Microphotograph of MEMS Device



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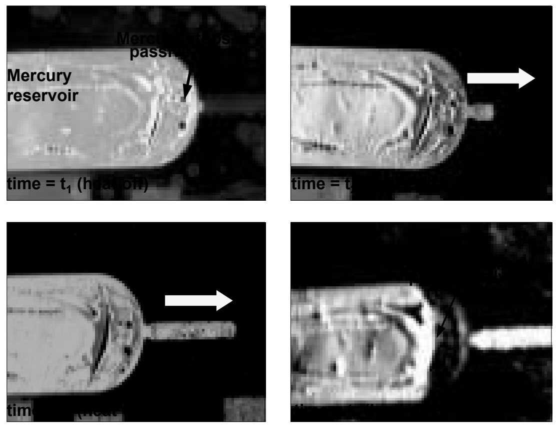
Mercury Droplet Formation



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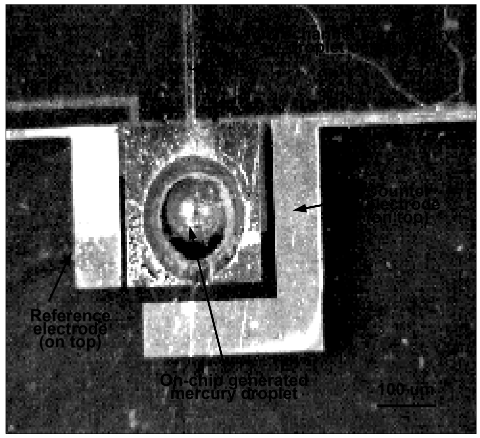
Microphotograph of Mercury Droplet and Lab-on-a Chip System



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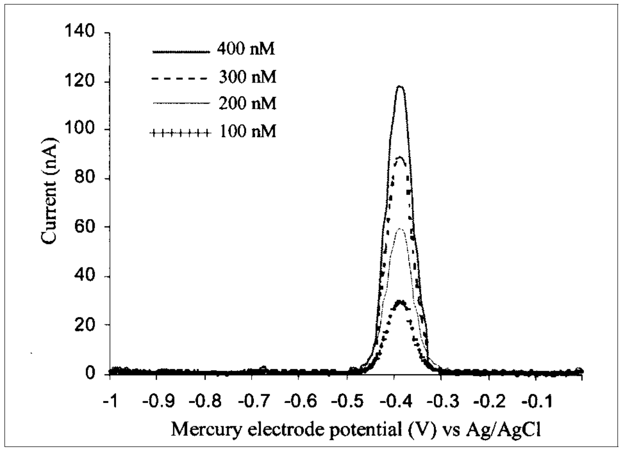
ASV for PB^{2+}

(30 second preconcentration)



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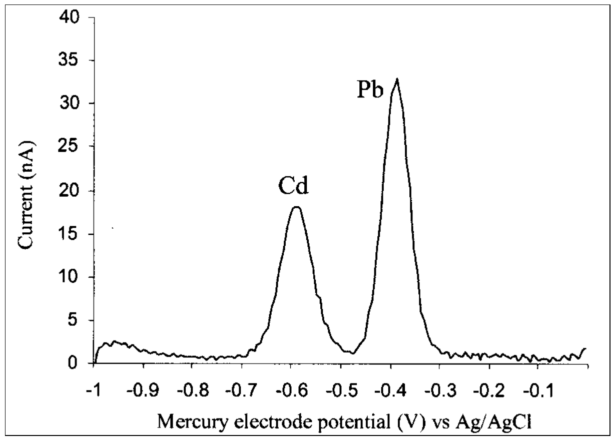
Cd^{2+} and Pb^{2+} by MEMS
(100 nm each)



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Summary

- On-site analysis of metals in soils or groundwater is now becoming routine at relatively low cost
- This can sometimes be done both ex-situ or in-situ
- XRF and LIBS procedures are the most mature of the technologies available, but microelectrodes, microelectrode arrays and MEMS devices will soon be commercially available at low cost

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Unique Environmental Chemistry Solutions to Superfund Problems

Tammy Jones-Lepp
Environmental Chemistry Branch
Environmental Sciences Division
National Exposure Research Laboratory
Las Vegas, Nevada

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Introduction

Many of ORD's research projects relate to broad scientific themes, such as biological and chemical indicators or computational toxicology. Others are discrete studies resulting from requests by clients or contacts with collaborators (in a number of scientific disciplines). This presentation presents a montage of recent "grass roots" research efforts that the Environmental Chemistry Branch (ECB) at ORD-Las Vegas has conducted in response to real-world analytical chemistry problems of the Regions, the States, and Tribal Authorities.

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Environmental Chemistry Branch
ORD/NERL-ESD – Las Vegas, NV

- **Who are we?**
  - 15 Research Scientists – Chemists and Environmental Scientists with a wide variety of skills and expertise
- **What do we do?**
  - We develop and apply new analytical tools to improve monitoring for a variety of media (water, soils, sediments, biological tissue) and analytes (organics, organometallics, inorganics) by making improvements to sample preparation, sample cleanup, and analyte identification, speciation, and quantification.
- **How do we do this?**
  - **By evaluating and developing analytical tools such as:**

  High resolution mass spectrometry • ion trap mass spectrometry • quadrupole mass spectrometry • inductively coupled plasma mass spectrometry • vacuum distillation • liquid chromatography • gas chromatography • atomic emission detection • gel permeation chromatography • direct mercury analyzer • pre-enrichment for trace analysis •chemical modeling

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ECB Mission Statement

We provide chemical answers to
environmental exposure
and risk problems.

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Overview

- "Environmental Forensics"
- Volatile organics – Vacuum distillation
- Organometallic speciation:
  - organoarsenics
  - organotins
- Mercury
- Low-level detection of pesticides
- Pharmaceuticals (some are RCRA-waste listed)

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Environmental Forensics

- Environmental forensics is the non-target identification of *unanticipated* compounds in environmental samples. At Superfund sites, this approach can allow more accurate risk assessments, identify potential causative agents of human health or environmental effects, and link contamination to responsible parties.
- A newly developed high resolution mass spectrometric software technique, *ion composition elucidation* [ICE], is used in ECB's environmental forensic investigations. ICE often allows the identification of unknown chemical contaminants under non-ideal circumstances.

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Breakout box for slide 3

ICE-man cometh

- Region 2/State of New Jersey – Increased incidence of childhood cancers at Tom's River, NJ. Help requested – ICE applied – identifications of unknown contaminants reported to State of New Jersey – toxicological tests are now being performed by the state.
- Region 3 – Bad smelling water in nearby town. A tar-like substance is removed from a nearby site and sent to the laboratory - ICE applied – identification made – tar-like substance linked to bad smelling water - source is found for chemical contaminants.
- Region 4 – Well water samples from nearby town are contaminated with unknown contaminants – increasing illness – ICE applied – identifications made – risk assessments underway.
- Region 9 – Superfund site needs cleanup – ICE applied – identifications made – Potentially Responsible Parties (PRPs) can be traced and levied to pay for cleanups.

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Vacuum distillation

- Vacuum distillation is a method developed and patented at ECB for the extraction of volatile organic contaminants from any solid or liquid matrix, including those not possible with purge and trap. It is simpler and faster than conventional methods, and the method self-incorporates quality assurance and controls in each extraction.
- Region 2 requested assistance in identifying whether vinyl chloride (known human carcinogen) was present in milk samples. Vacuum distillation was applied to detecting volatile organic solutes.
- This study led to a wider survey of milk from Nevada, Arizona, Utah, and California for the fuel additive MTBE and other volatile organics.

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Organometallic Speciation – Part I - organoarsenics

- Development and application of high performance liquid chromatography, and capillary electrophoresis, coupled to inductively coupled plasma/mass spectrometry (ICP/MS) to provide arsenic speciation.
- The mobility and toxicity of arsenic and other elemental contaminants at Superfund sites vary among the different chemical forms. Accurate risk assessments and cost-effective clean-ups depend on ability to measure individual species. Total-element concentrations that are typically measured do not provide sufficient information.

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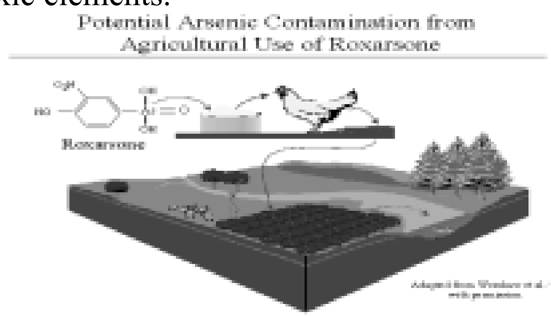
This isn’t your mother’s Henny Penny fairy tale

- Region 3 – Delmarva Peninsula – More chickens (and poultry farms) than people. Many dietary arsenical feed additives are fed to chickens to enhance growth. Run-off from farm waste ponds and application of chicken manure leads to stream contamination. ECB collaborated with USGS to assist Region 3 evaluate risk from factory-farm run-off. Development and transfer to Regional users of speciation methods for arsenic and other toxic elements.



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Organometallic Speciation – Part II - organotins

- A unique methodology using micro-liquid chromatography coupled to electrospray/ion trap mass spectrometer was developed for detecting and speciating organotins.
- Organotin compounds can elicit a wide range of endocrine- and nervous-system effects, depending on the nature and number of alkyl groups bonded to the tin atom. Organotin compounds show a wide variety of adverse health effects in many species, including imposex in mollusks, neural degeneration in fetal rat cell cultures, and induction of diabetes in hamsters

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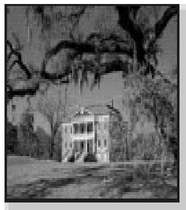

A Tale of Two Rivers

- A six mile stretch of a beautiful South Carolina river became sick – a massive fish kill was experienced. State of South Carolina officials needed confirmation that an organotin factory upstream might be responsible. Water and fish samples were collected. Using state-of-the art methodology, organotins were detected in all of the samples. Data was provided to state of SC and Region 4.
- Case goes to court – three company employees plead guilty, they are sentenced, the factory is shut down, and fines are levied to help pay clean-up costs.

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Mercury Analysis

- A new method for the rapid detection of mercury in tissue was developed using an automatic mercury analyzer (Milestone Inc., Monroe, CT) based on *combustion* atomic absorption spectrometry (AAS)
- This technique provides results statistically equivalent to conventional cold-vapor AAS. In short, total Hg is determined by AAS after tissue combustion and pre-concentration by amalgamation with gold
- It is well documented that mercury (Hg) biomagnifies within the aquatic food chain and consumption of fish contaminated with Hg can cause poisoning in both humans and wildlife. Fish populations themselves can also be adversely affected by Hg within their tissues.

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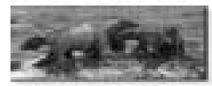
What do dietary surveys of Alaskan Tribes, inspection of fish for NOAA, and hair-collection in Washington State all have in common?

--Mercury--



- Tribal authorities, the state of Alaska, and National Institute of Environmental Health Sciences (NIEHS) requested help for mercury dietary studies. Study underway to look at mercury content in indigenous food sources (fish, sea-going mammals) using a recently developed method that determines mercury directly in solid matrices.
- NOAA's National Seafood Inspection Laboratory in Mississippi requested help to determine mercury levels in Gulf of Mexico fish. Measurement-validation reports and technical advice were provided.
- Collaborations with Washington State and Region 10 to assess the mercury exposure to an Asian-American community in the Puget Sound area. Hair-collection and analysis protocols, study-design suggestions, and data are being provided for risk assessments.

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Low-level detection of pesticides for long-term monitoring of Superfund sites

- The ability to do ambient monitoring for true contaminant backgrounds was recently listed as an OERR (Superfund) need.
- State-of-the art extraction and detection methodologies are being developed and applied to detecting possible spray drift into the Sierra Nevada.

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What? Your frogs are disappearing!

- Millions of tons of pesticides are used in the San Joaquin Valley of California every year. How much is transported by winds into the nearby southern Sierra Nevada? Could this be a cause for the disappearance of the mountain yellow-legged frog in much of the area?
- ECB, working closely with EPA Biologists, is conducting a comprehensive survey to help Region 9, the National Park Service, and the state of California understand the impact of pesticide contamination in the alpine lakes of the southern Sierra Nevada mountains. This data will better help our clients decide if steps need to be taken to protect these sensitive ecosystems.

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Protecting your Environment with Environmental Forensic Chemistry

http://www.epa.gov/nerlesd1/chemistry/anal-env-chem.htm

ECB expertise: mass spectrometry, ICE, high resolution mass spectrometry, gas chromatography/mass spectrometry, unique MS sample introduction techniques, volatile organic methodologies, vacuum distillation, mass spectral interpretation, separation techniques, sample preparation and cleanup techniques, ground-water migration, mercury methodologies, inorganic methodologies, organic methodologies, PPCPs† , arsenic speciation, organotin speciation, computational toxicology

† http://www.epa.gov/nerlesd1/chemistry/pharma/index.htm

Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded this research. The actual presentation has not been peer reviewed by EPA.

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Thank You

After viewing the links to additional resources, please complete our online feedback form.

Thank You

Links to Additional Resources

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