NANOMATERIAL-BASED MICROCHIP ENVIRONMENTAL ASSAYS

(Towards the Nano/Micro Interface)

Joe Wang
SensoChip Lab,
NMSU, Las Cruces

Why Microchips?

- **IMPROVED PERFORMANCE**
- **HIGH DEGREE OF INTEGRATION**

  Sample Cleanup (filters, extraction etc.)

  Preconcentration (beads, membranes)

  Mixing/Reactions (Derivatization)

  Separation

  Detection
- **HIGH SPEED**
- **MINIATURIZATION / PORTABILITY**
- **NEGLIGIBLE WASTE AND SAMPLE / REAGENT CONSUMPTION**
- **AUTOMATION**
- **PARALLEL ASSAYS**
- **LOW COST**

MICROCHIPS FOR ENVIRONMENTAL MONITORING

The dramatic downscaling and integration of chemical assays hold considerable promise for faster and simpler on-site monitoring of priority pollutants and make these analytical microsystems particularly attractive as ‘green analytical chemistry’ screening tools.

The amount of waste generated is reduced by ca. 4-5 orders of magnitude, in comparison, for example, to conventional liquid chromatographic assays (i.e., 10µL vs. 1L per daily use, very little ‘stuff’).

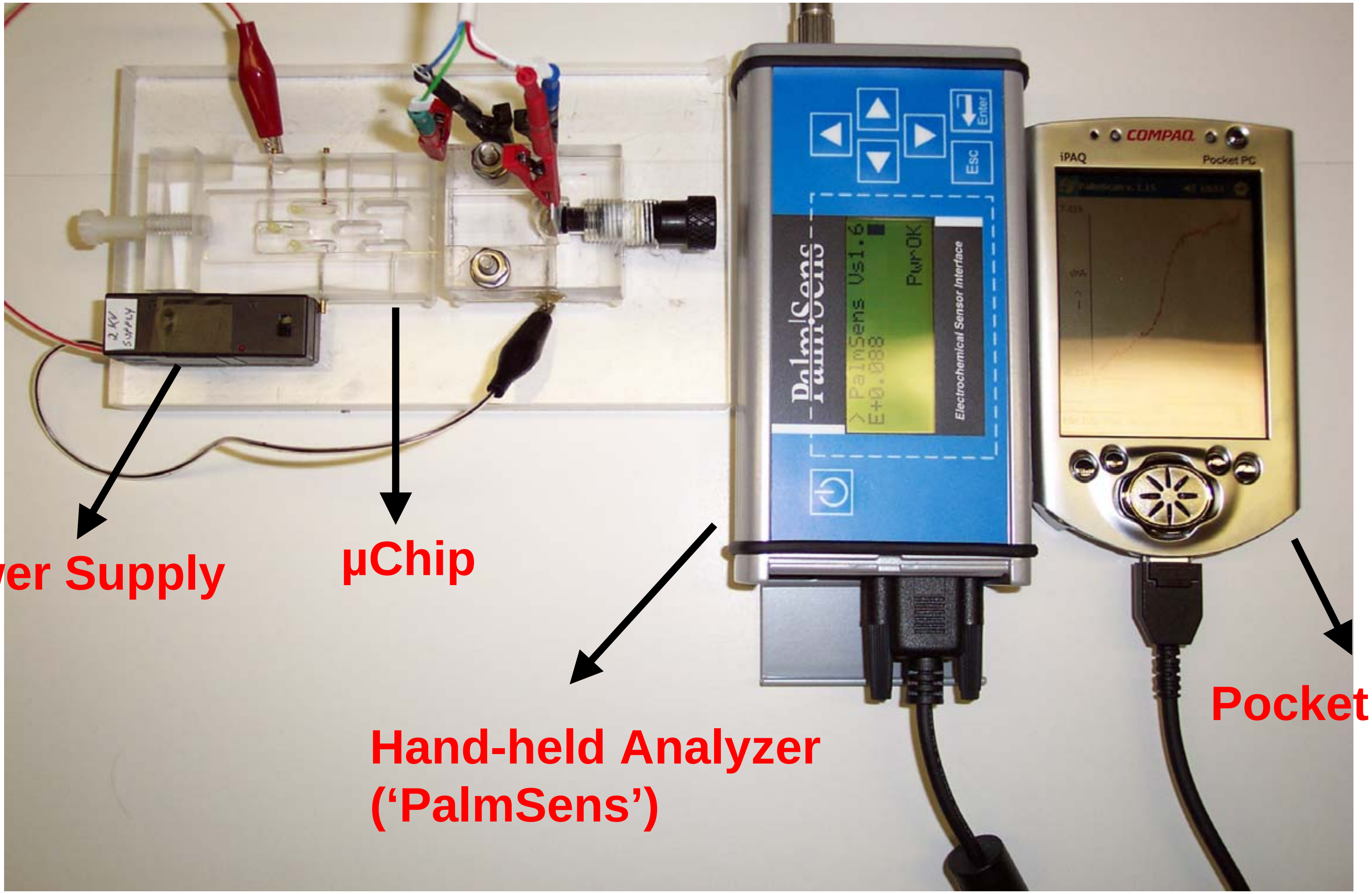
Electrochemical (EC) Detectors for Microseparation chips

- **REMARKABLY HIGH SENSITIVITY**
- **PORTABILITY (Inherent miniaturization and integration of both the detector and control instrumentation)**
- **COMPATIBITLITY WITH MICROFABRICATION TECHNOLOGIES**
- **LOW COST**
- **LOW POWER REQUIREMENTS**
- **INDEPENDENCE OF OPTICAL PATHLENGTH AND SAMPLE TURBIDITY**

Towards Self-Contained Portable Monitoring Microsystems

The inherent miniaturization and complete integration of electrochemical detection make it extremely attractive for creating truly portable (and possibly disposable) stand-alone microsystems. Optical detection systems, in contrast, are still relatively large, hence compromising the benefits of miniaturization.

NMSU 'Lab-on-a-Chip' Microsystem



Power Supply

µChip

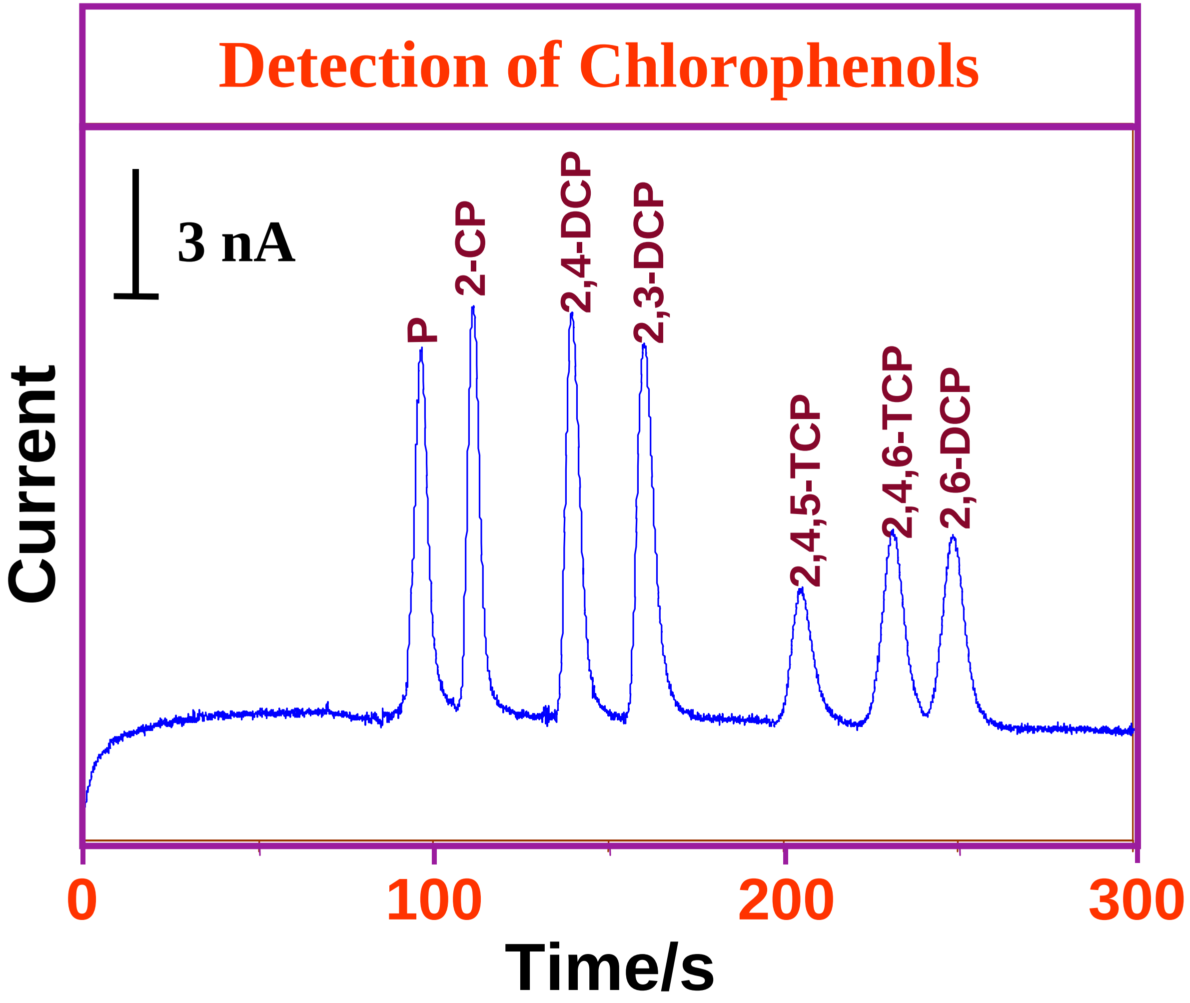
Hand-held Analyzer ('PalmSens')

Pocket PC

CE/EC MICROCHIPS: TOWARDS ENVIRONMENTAL MONITORING

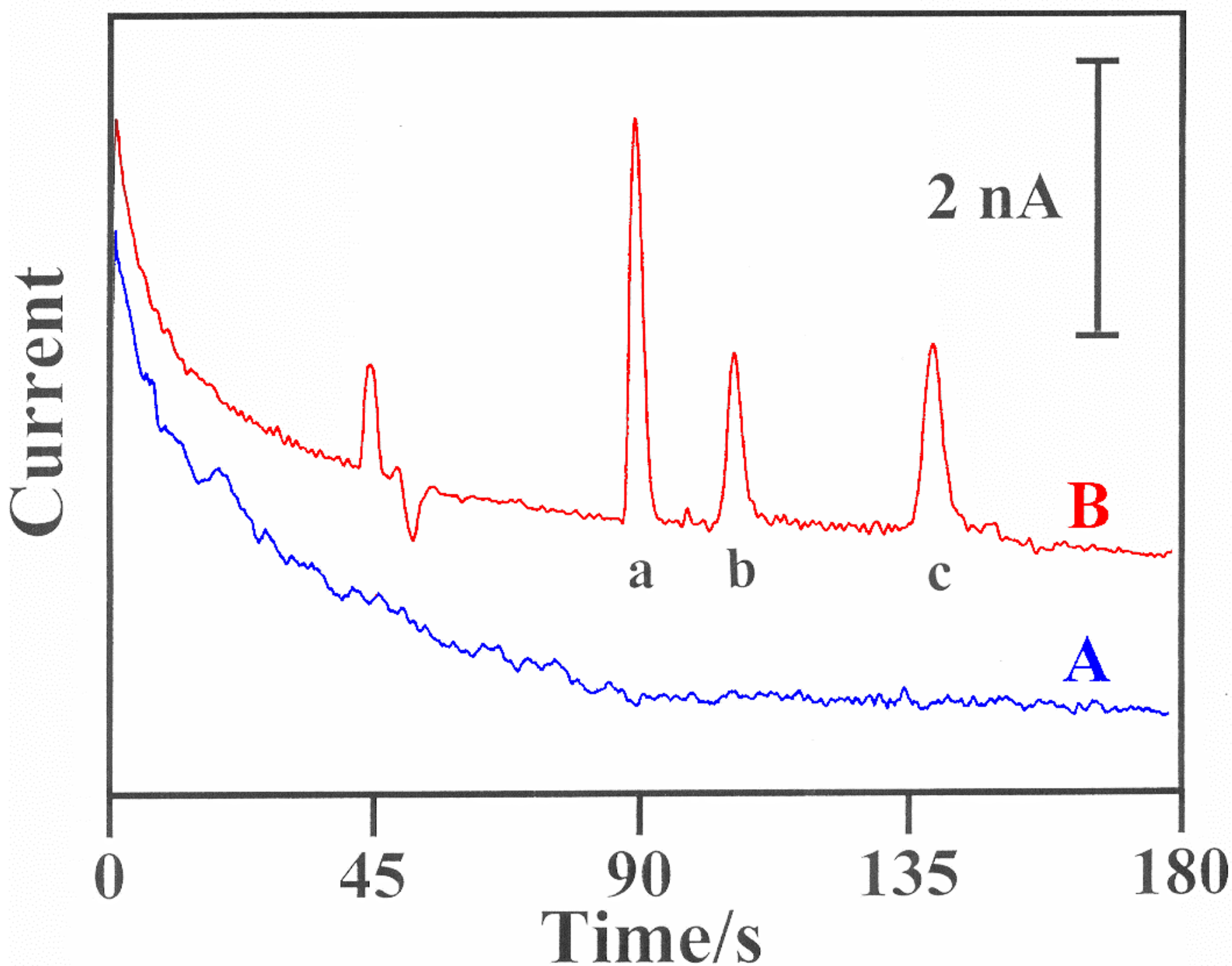
- PHENOLIC COMPOUNDS
- HYDRAZINES
- NITROAROMATIC EXPLOSIVES
- PESTICIDES AND NERVE AGENTS

Assays of multiple contaminants in short time scales



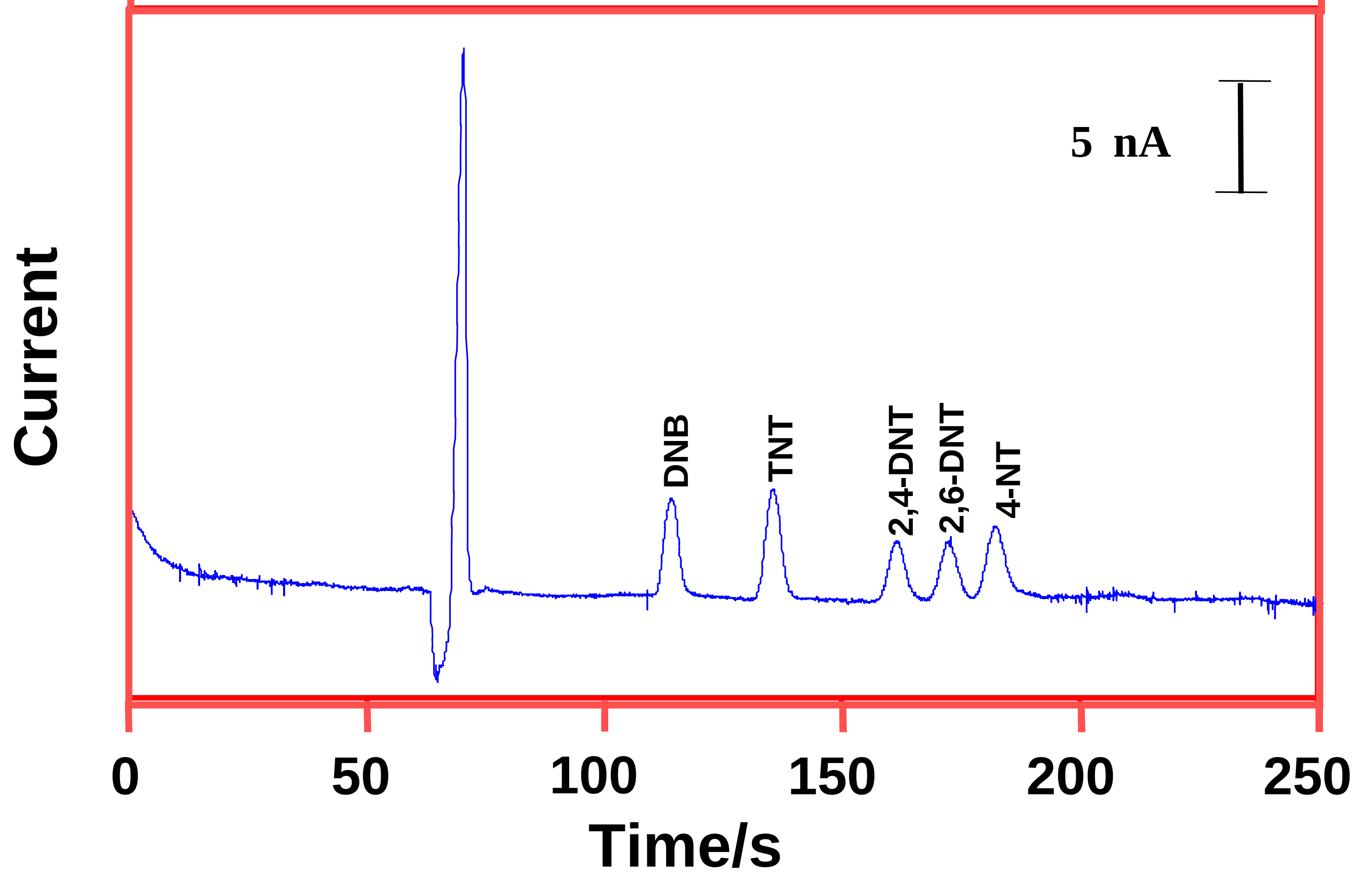
CE-Microchip with Amperometic Detector

Nerve Agent Chip



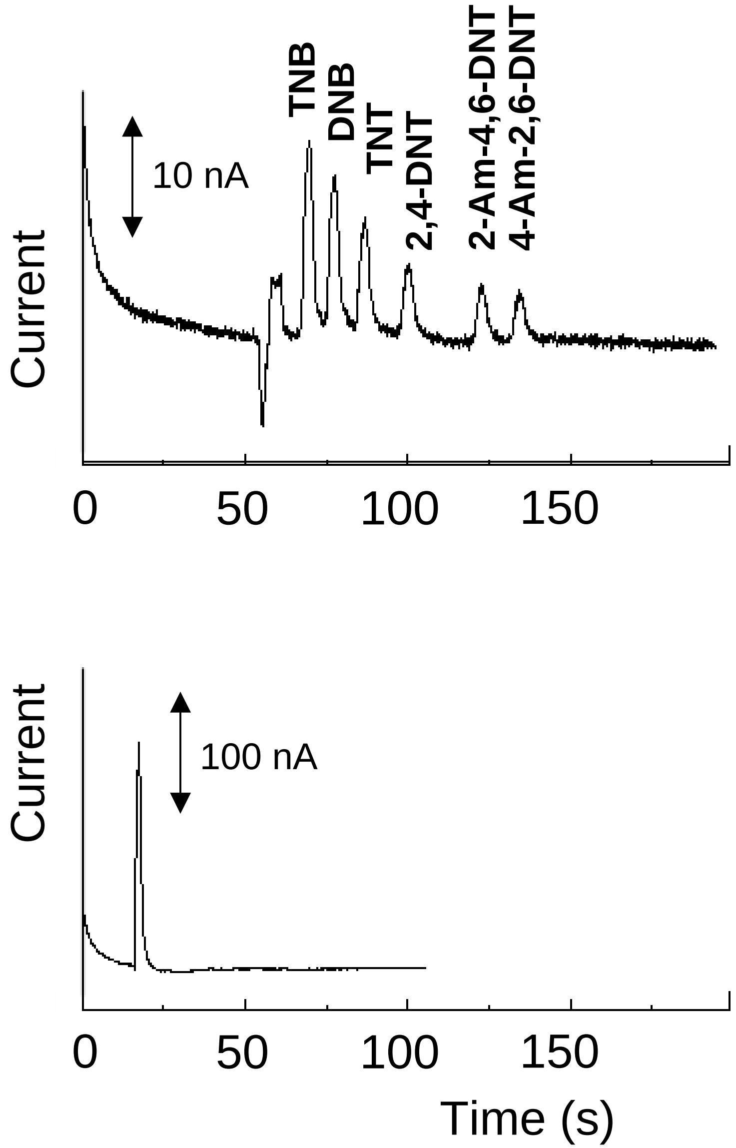
Electropherogram for river water sample before (A) and after (B) spiking with (a) paraoxon, (b) methyl parathion, and (c) fenitrothion.

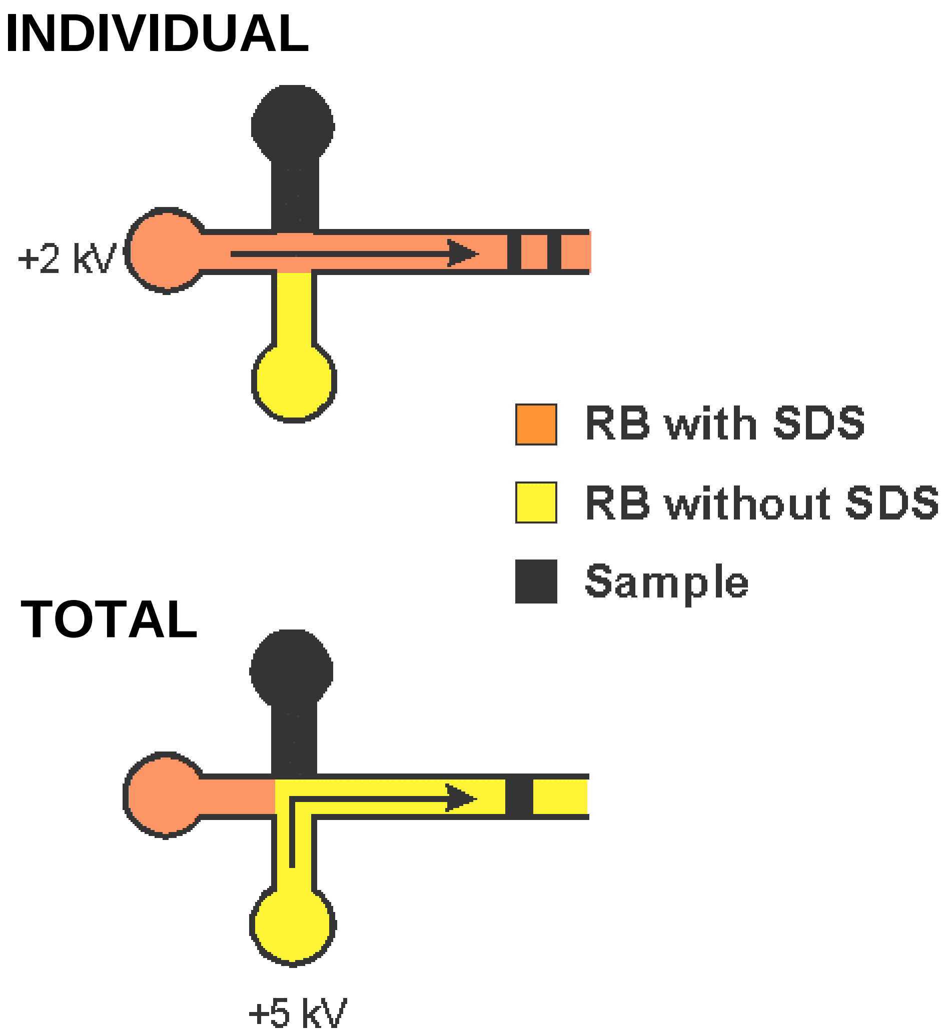
μ CZE-EC Detection of Explosives



REDUCTIVE DETECTION OF NITROAROMATIC EXPLOSIVES

MICROCHIP SWITCHING BETWEEN RAPID SCREENING AND DETAILED IDENTIFICATION





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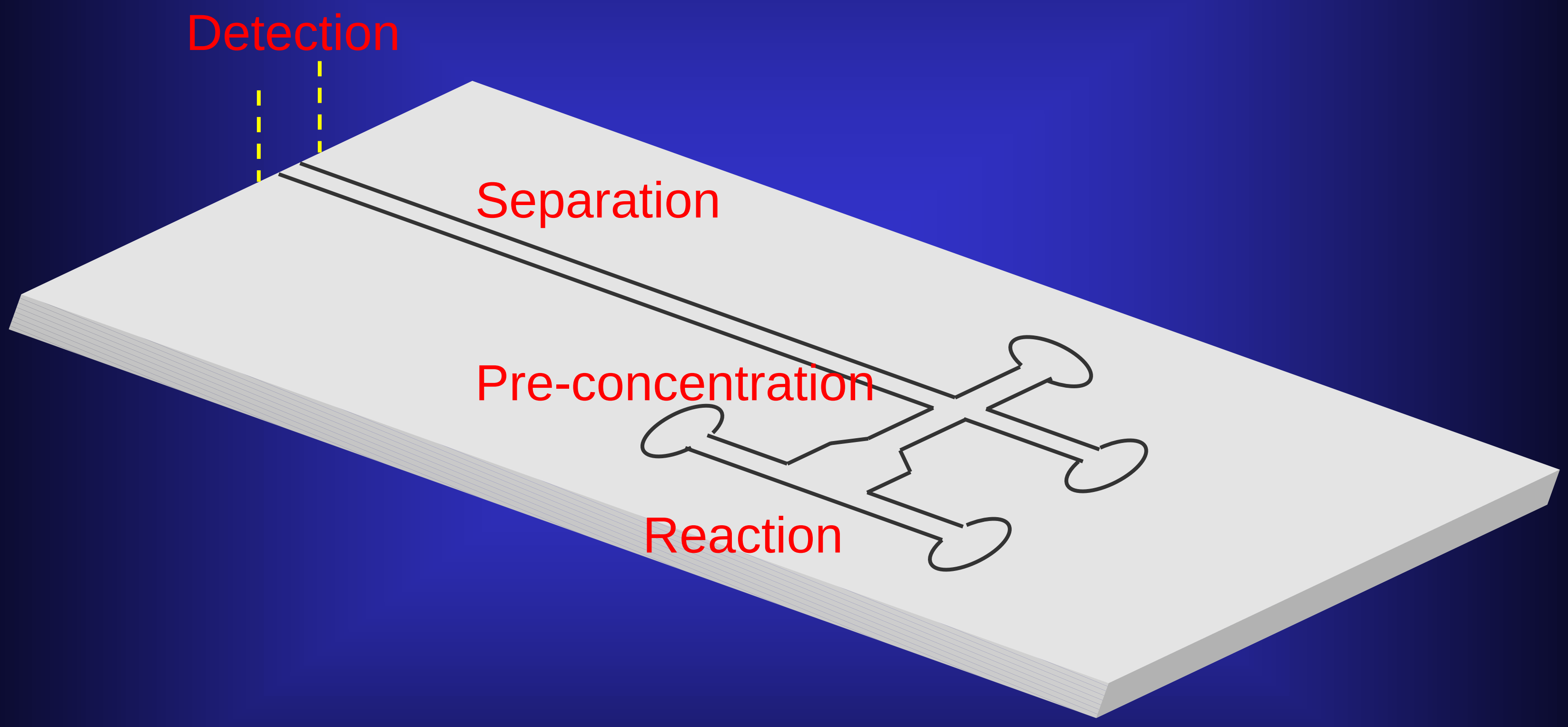
NANOMATERIAL-BASED MICROCHIP ENVIRONMENTAL ASSAYS

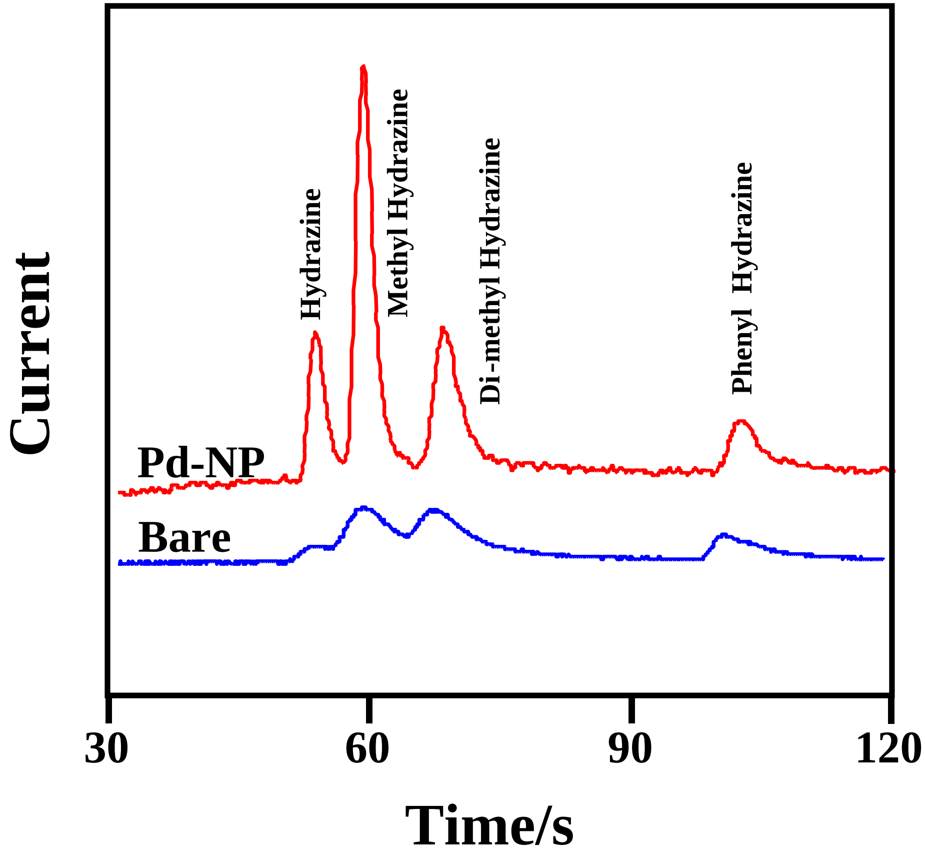
Nanotechnology is defined as the creation of functional materials, devices and systems through control of matter at the 1-100 nm scale. The use of nanomaterials in Analytical Chemistry has taken off rapidly and will surely continue to expand. The unique properties of nanoparticles, nanotubes and nanowires offer great prospects for enhancing the performance of CE microchips and for developing novel nanomaterial-based electrical detection strategies.

INTEGRATION OF MULTIPLE FUNCTIONS ON A "LAB-ON-A-CHIP" DEVICE



Nanomaterials can be used to facilitate each of these processes

μCZE-EC Chip for Hydrazine Compounds



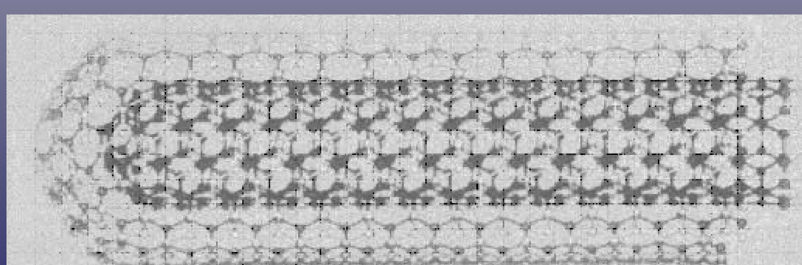
Comparison of (A) bare carbon and (B) palladium-coated Screen Printed Electrode on the response for hydrazine compounds separated on microchip.

Pd Nanoparticles for Electrocatalytic Detection

Carbon Nanotubes

- What are they?
  - Graphite sheets rolled into a cylinder to form nanometer tubes
- Preparation
  - Arc evaporation (non-catalytic)
  - Chemical Vapor Deposition (CVD)
- Multi-wall and single-wall

MWCNT

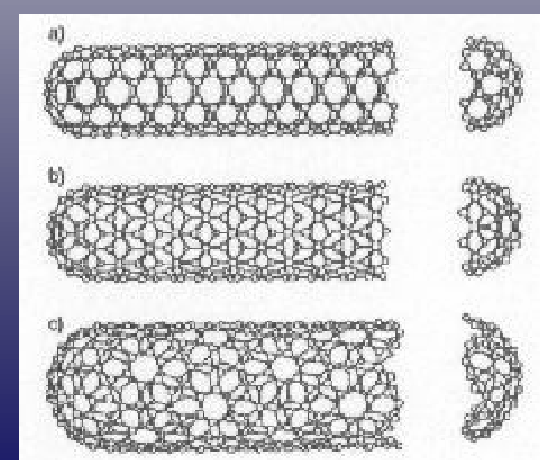


SWCNT

Armchair

Zigzag

Chiral



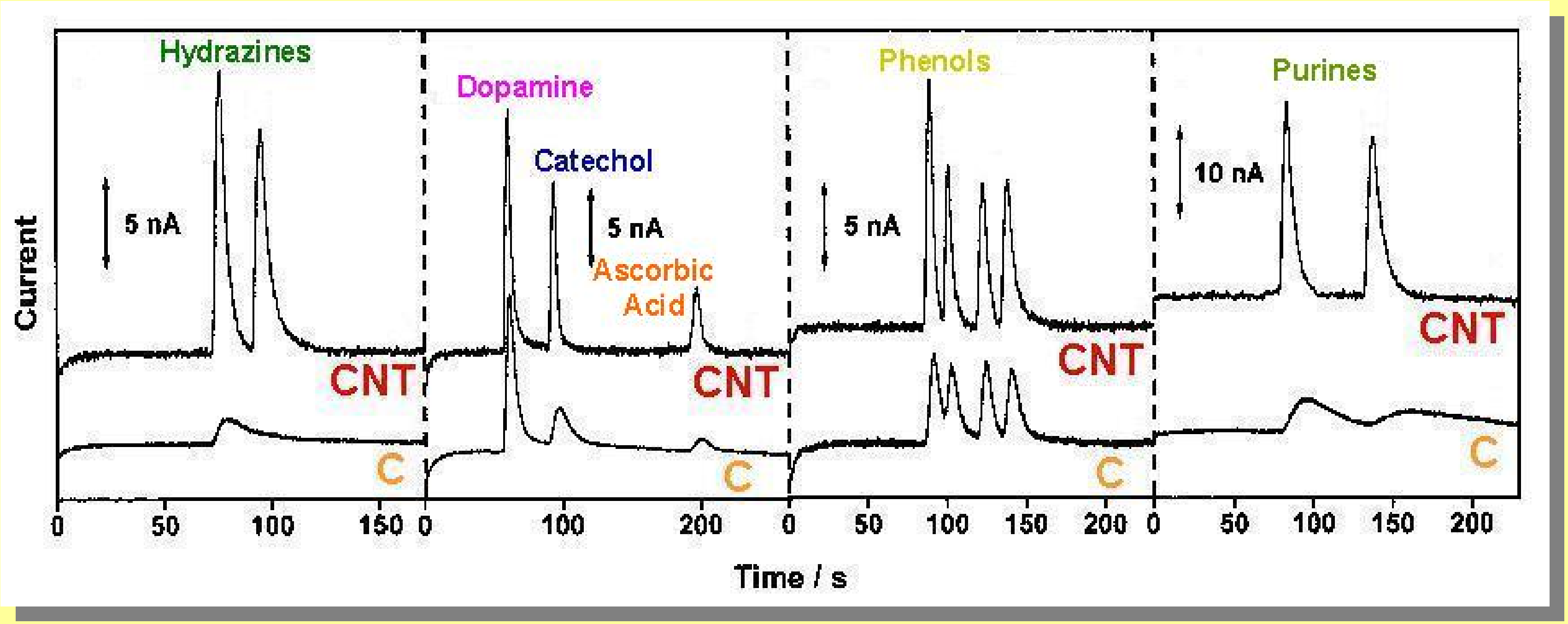
WHY CARBON NANOTUBES?

CARBON NANOTUBES POSSESS REMARKABLE ELECTRONIC, MECHANICAL AND CHEMICAL PROPERTIES WHICH MAKES THEM EXTREMELY ATTRACTIVE FOR VARIOUS SENSING DEVICES.

CARBON NANOTUBES WERE SHOWN USEFUL TO PROMOTE ELECTRON-TRANSFER REACTIONS AND IMPARTS HIGHER RESISTANCE TO SURFACE FOULING

Electropherograms at the bare and CNT-modified detectors

Enhanced performance by modifying the detector surface.



The electrocatalytic activity and resistance to surface fouling of CNT materials lead to improved sensitivity, stability and resolution compared to common carbon-electrode detectors.

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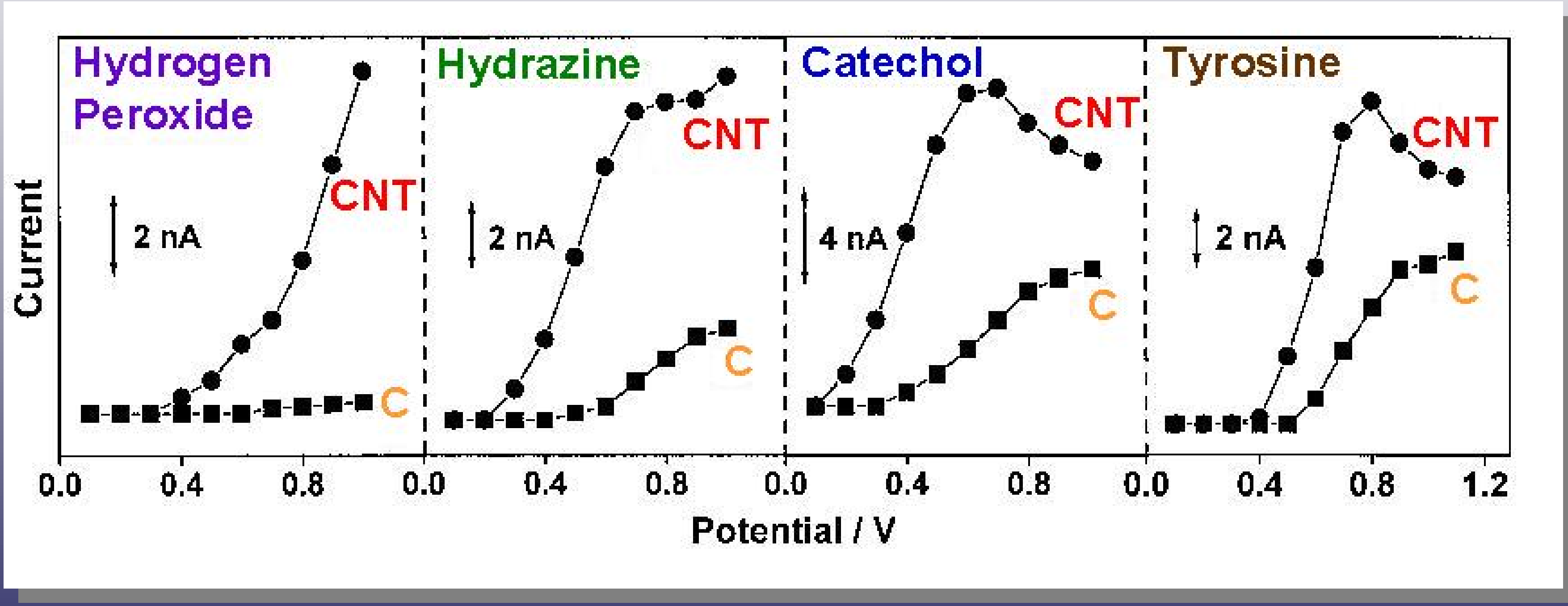
Carbon-Nanotube-based Microchip Detection

Hydrodynamic voltammograms at screen-printed carbon electrode and carbon nanotube modified (CNT) screen-printed carbon electrode



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Grant # RD-83090001-0

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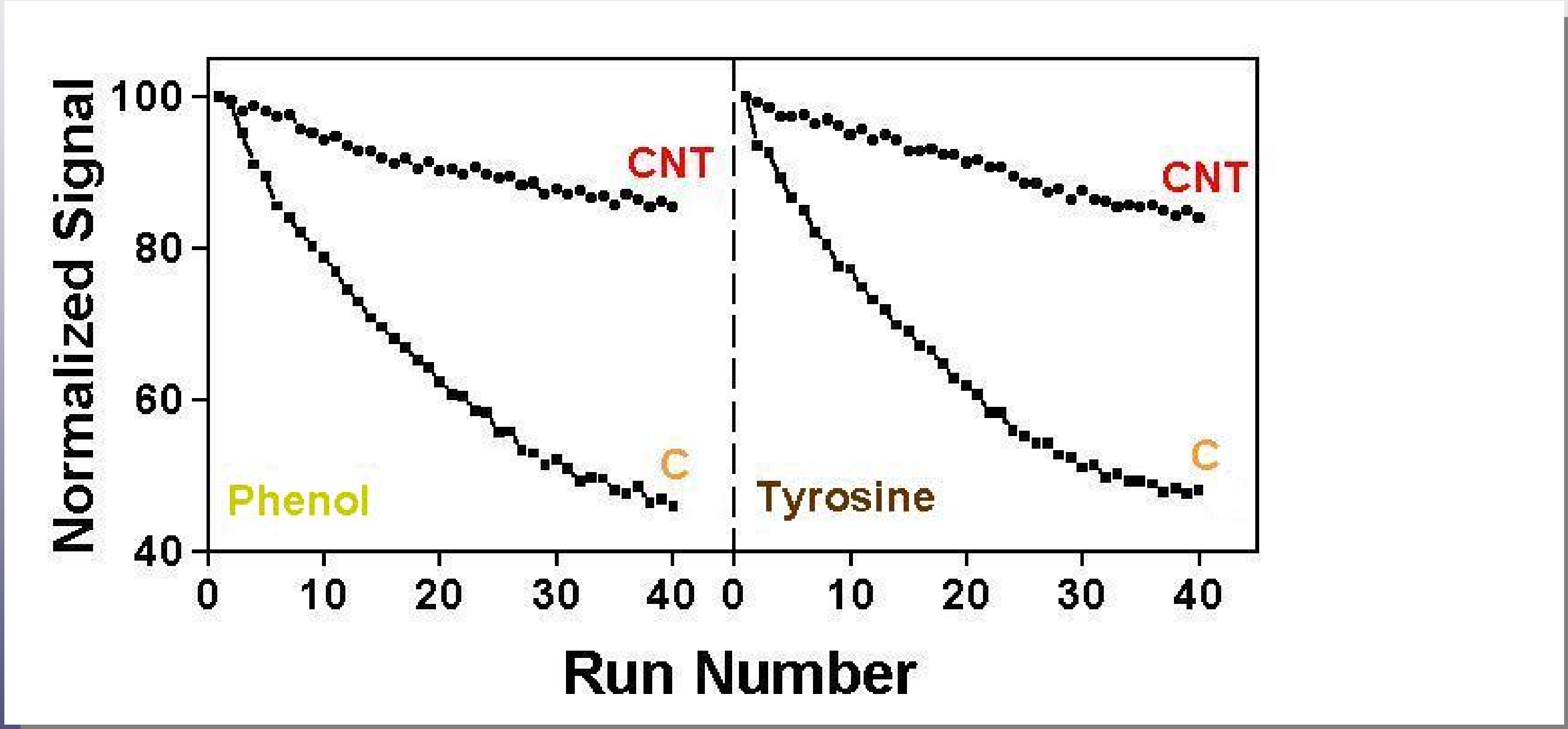
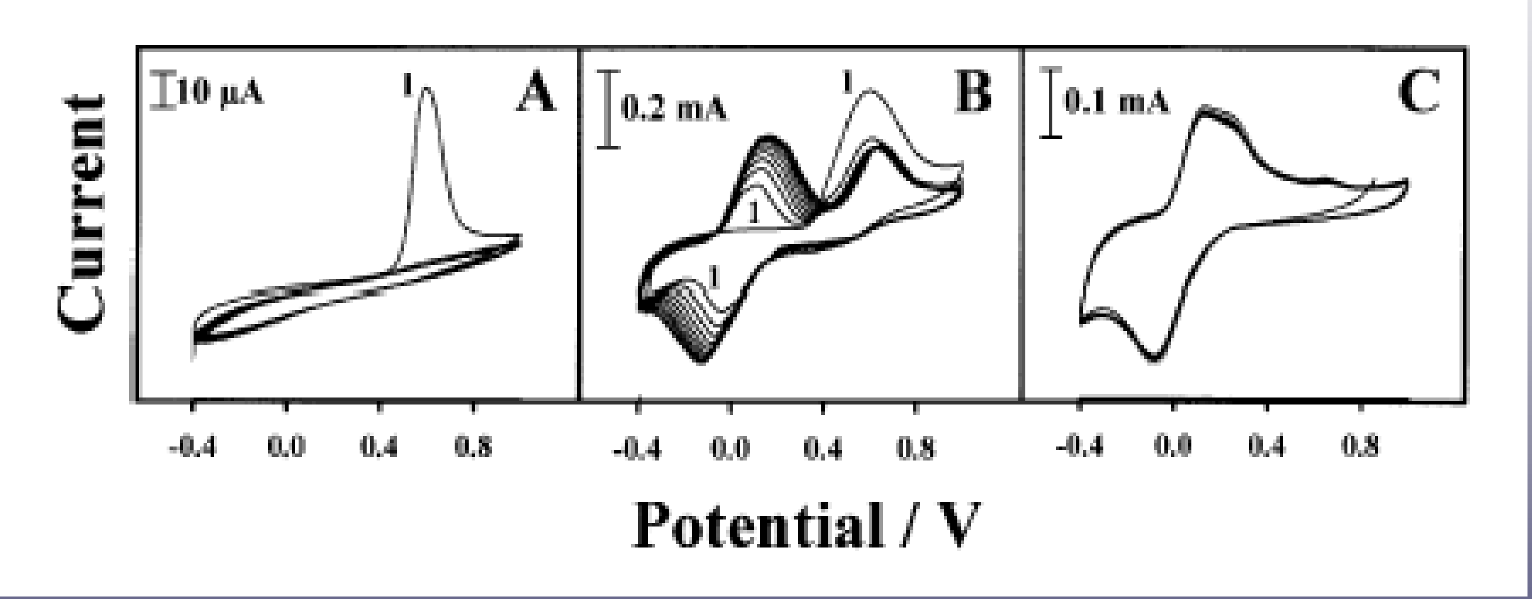
Stability of the response to phenol and tyrosine at the carbon-nanotube modified and unmodified electrodes



Minimization of Surface Fouling

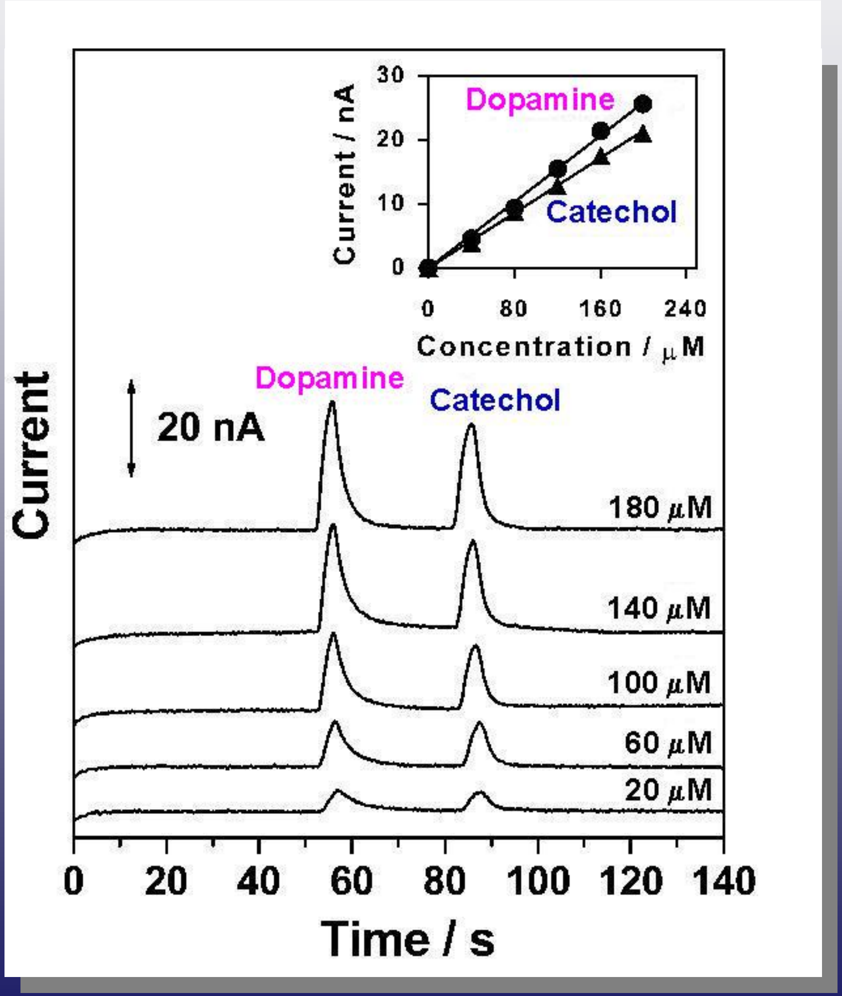
2,4-dichlorophenol

Bare GC CNT-GC CNT-GC



- CNT circumvents common surface fouling during the phenol oxidation; the redox process involves the formation of a surface-confined layer that promotes (rather than inhibits) the phenol oxidation.

Calibration data for mixtures containing increasing levels of dopamine and catechol



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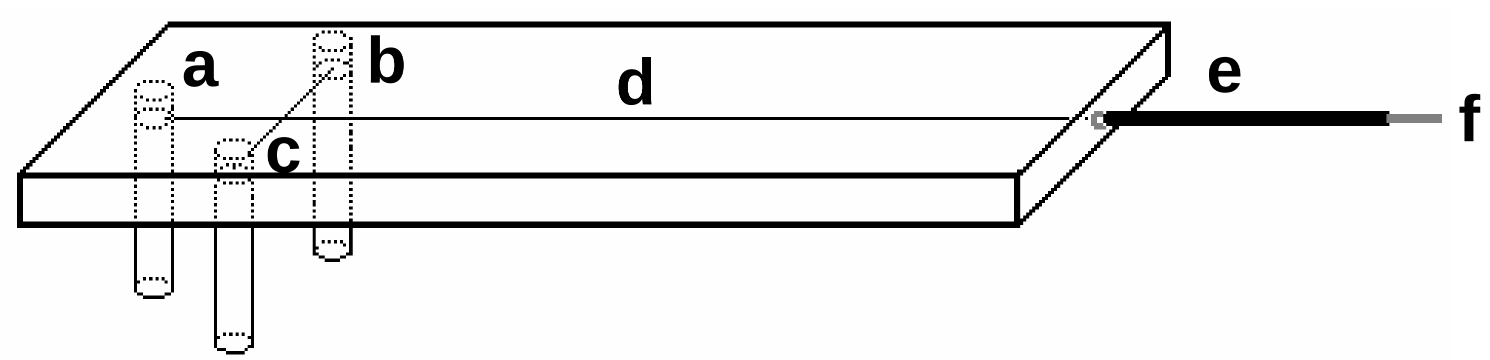
Carbon Nanotube/Copper Composite Electrode for Capillary Electrophoresis Microchip



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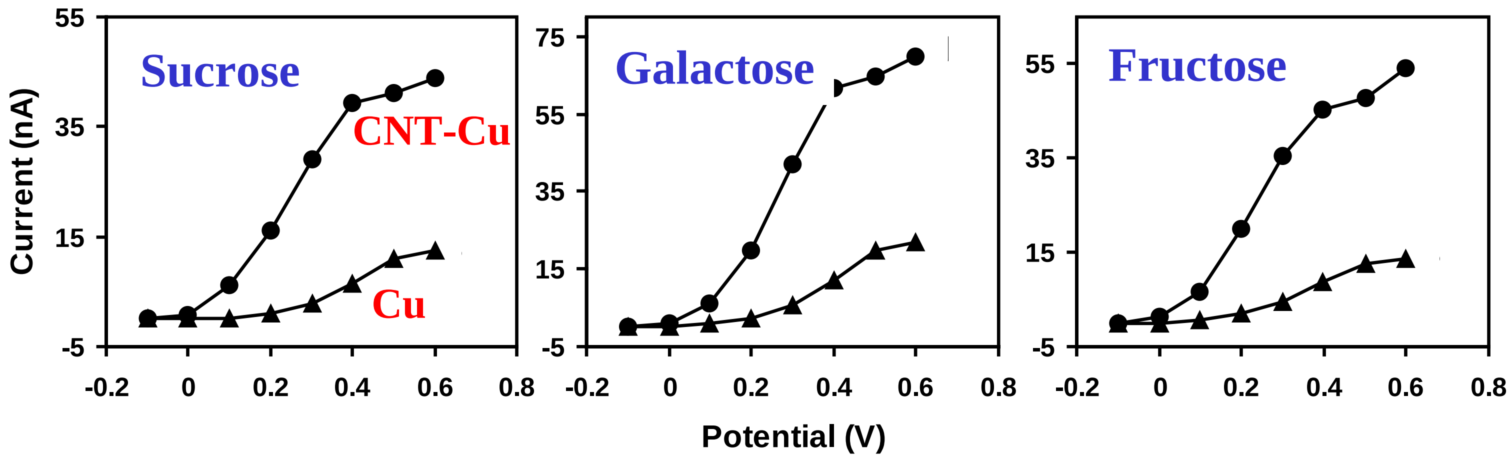
CE Microchip with a CNT/Cu Amperom. Detector

Coupling of CNT with metal NP catalysts: Cu/CNT composites



Hydrodynamic voltammograms for different sugars

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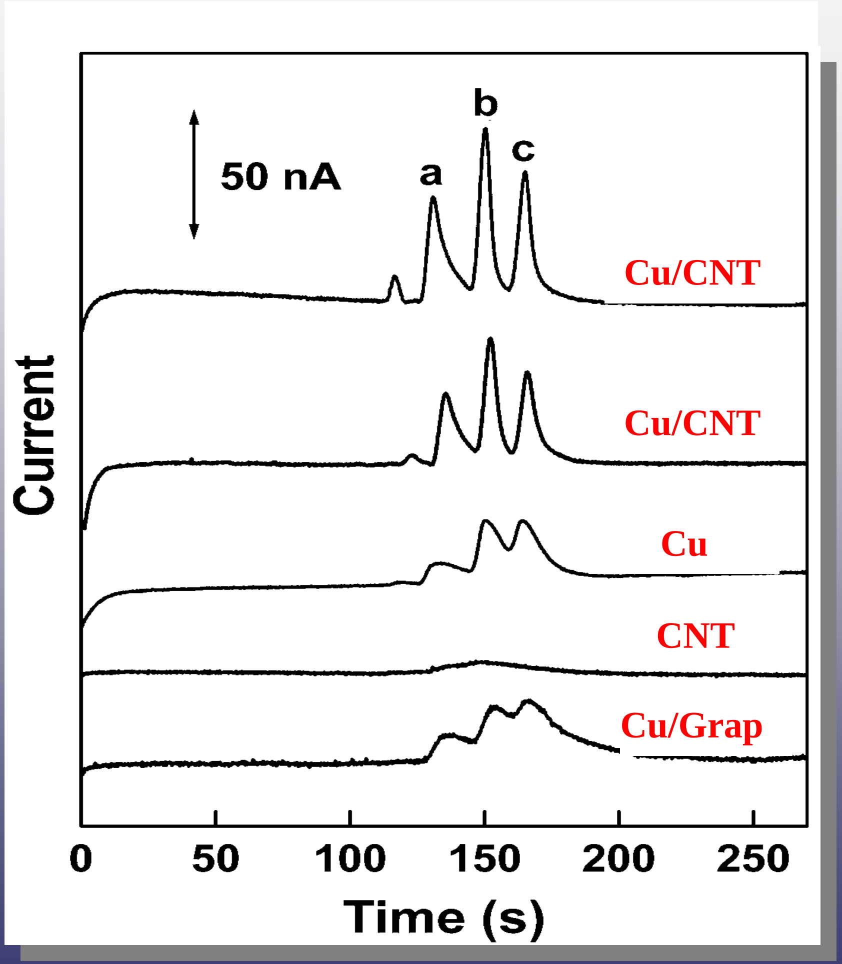
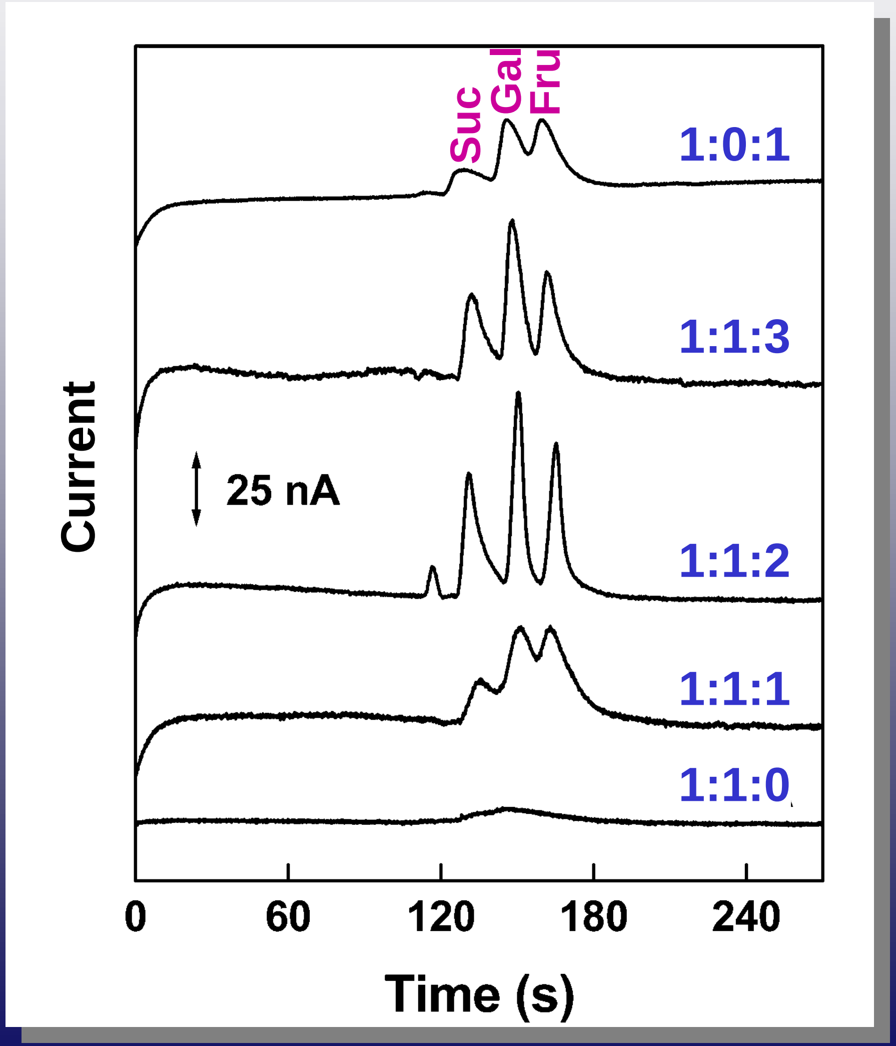
CE Microchip with a CNT/Cu Amperom. Detector



Electropherograms for a mixture containing 0.5 mM sucrose (a), galatose (b), and fructose (c)

Effect of Composition (Oil:CNT:Cu): Synergitic Effect:

Response at different paste formulations



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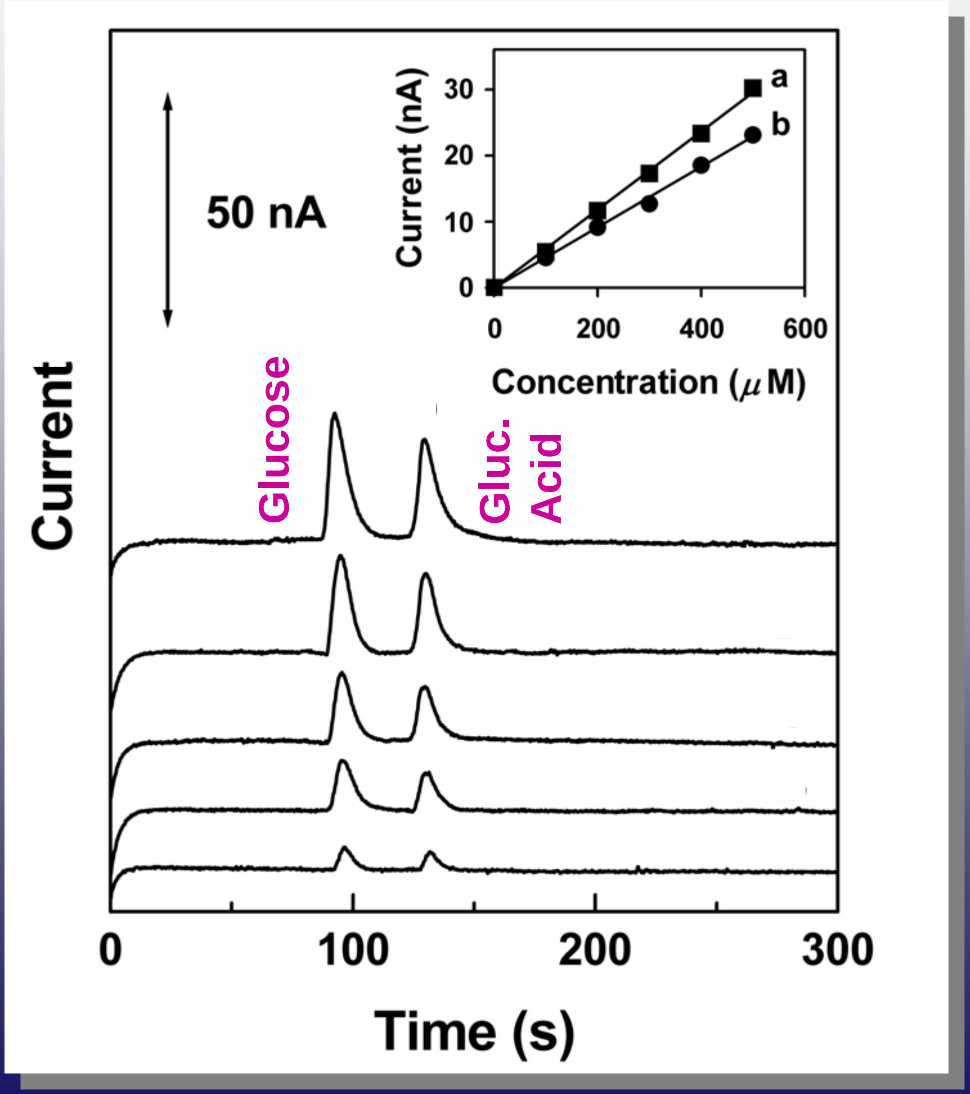
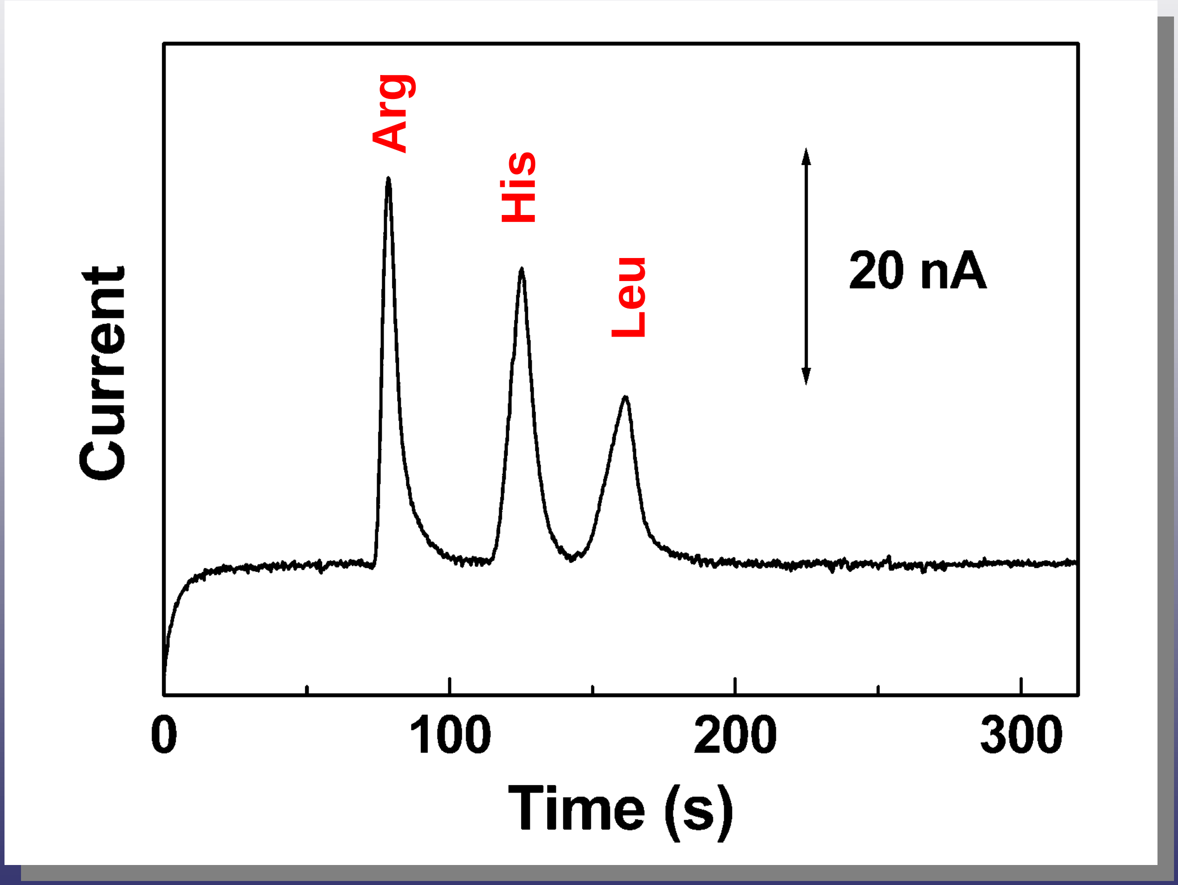
Analytical Performance:
Calibration Study



Carbon Nanotube/Copper Composite Electrode for the Detection of Amino Acids



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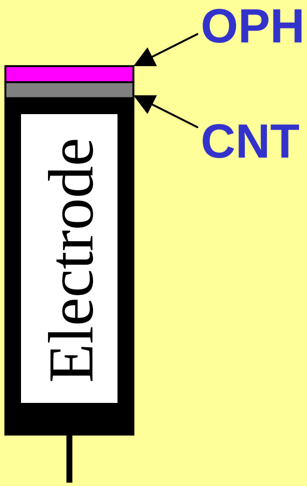
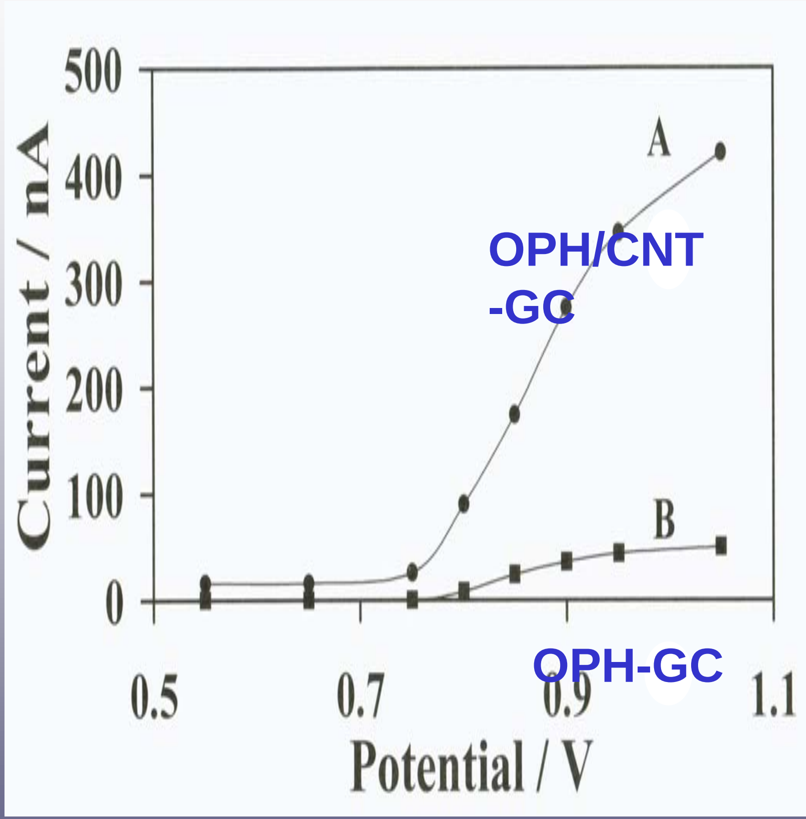
CNT FOR ENHANCED BIOSENSING OF OP PESTICIDES THROUGH CATALYTIC DETECTION OF THE p-NITROPHENOL PRODUCT

- Organophosphorus compounds
  - neurotoxic



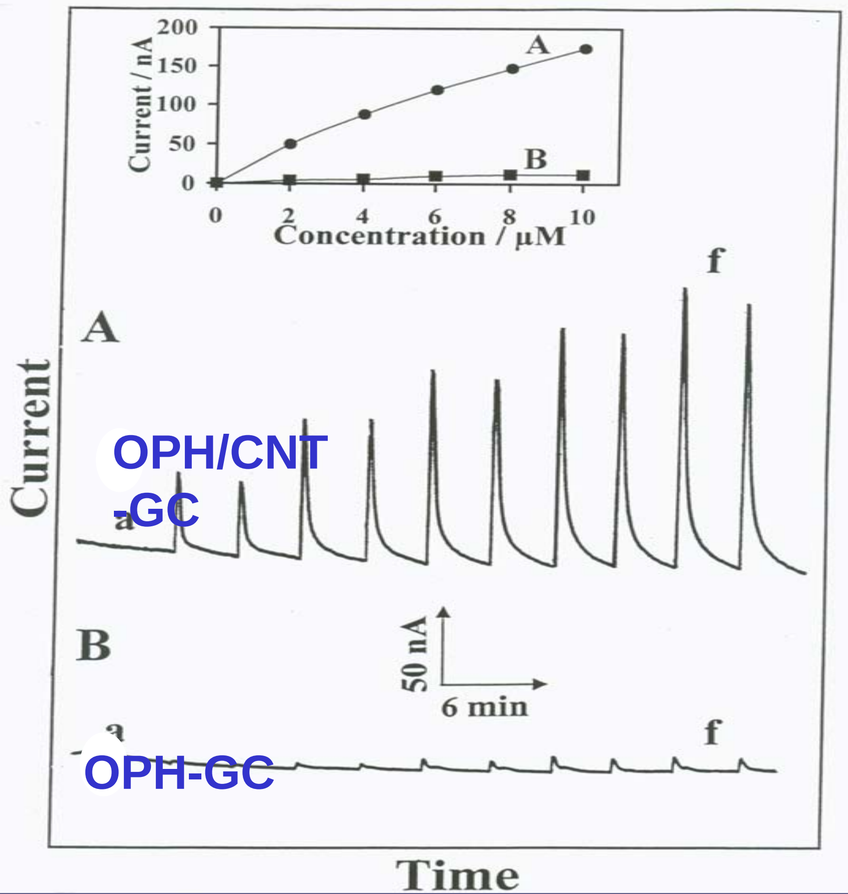
<u>Optimized condition</u>: 5mg CNT; 0.5% Nafion; 48 IU/µL OPH

Pesticides



HDV for 10 μM paraoxon

Potential: +0.85 V



Calibration for 2 μM paraoxon

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Gold Nanoparticle-Enhanced Microchip Capillary Electrophoresis

Martin Pumera,[†] Joseph Wang,[*,†] Eli Grushka,[*,‡] and Ronen Polsky[†]

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88003, and Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel

We describe here the use of gold nanoparticles in conjunction with chip-based capillary electrophoresis to improve the selectivities between solutes and to increase the efficiency of the separation. We coated the microchannel wall of a microfluidic device with a layer of poly(diallyldimethylammonium chloride) (PDADMAC) and then collected on it citrate-stabilized gold nanoparticles. The resolutions and the plate numbers of the solutes were doubled in the presence of the gold nanoparticles. Such selectivity improvements reflect changes in the observed mobility accrued from interactions of solutes with the particle surface. The electrochemical detection and the quantitation of the solutes were not effected by the PDADMAC and the gold nanoparticles.

particles in conventional CE systems.[1–12] For example, Huber and coworkers[13] as well as Rodriguez and Colon[9,10] used polymer-based nanoparticles to coat fused-silica capillaries for use in CE. Fujimoto and Muranaka[11] used commercially available silica gel nanoparticles as a run buffer additive in CE. Neiman et al.[12] recently reported on the use of colloidal gold nanoparticles dispersed in the run buffer for capillary electrophoretic separations. To the best of our knowledge, nanoparticles have not been used in microchip CE systems. In the following sections we extend the use of gold-based nanoparticles to chip-based capillary electrophoresis devices and demonstrate that the presence of such nanoparticles in the microchannels acts as a selectivity modifier by changing both the apparent electrophoretic mobilities of the solutes and the electroosmotic mobility.

IMPROVED MICROCHIP SEPARATIONS BY ADDING GOLD NANOPARTICLES TO RUN BUFFER

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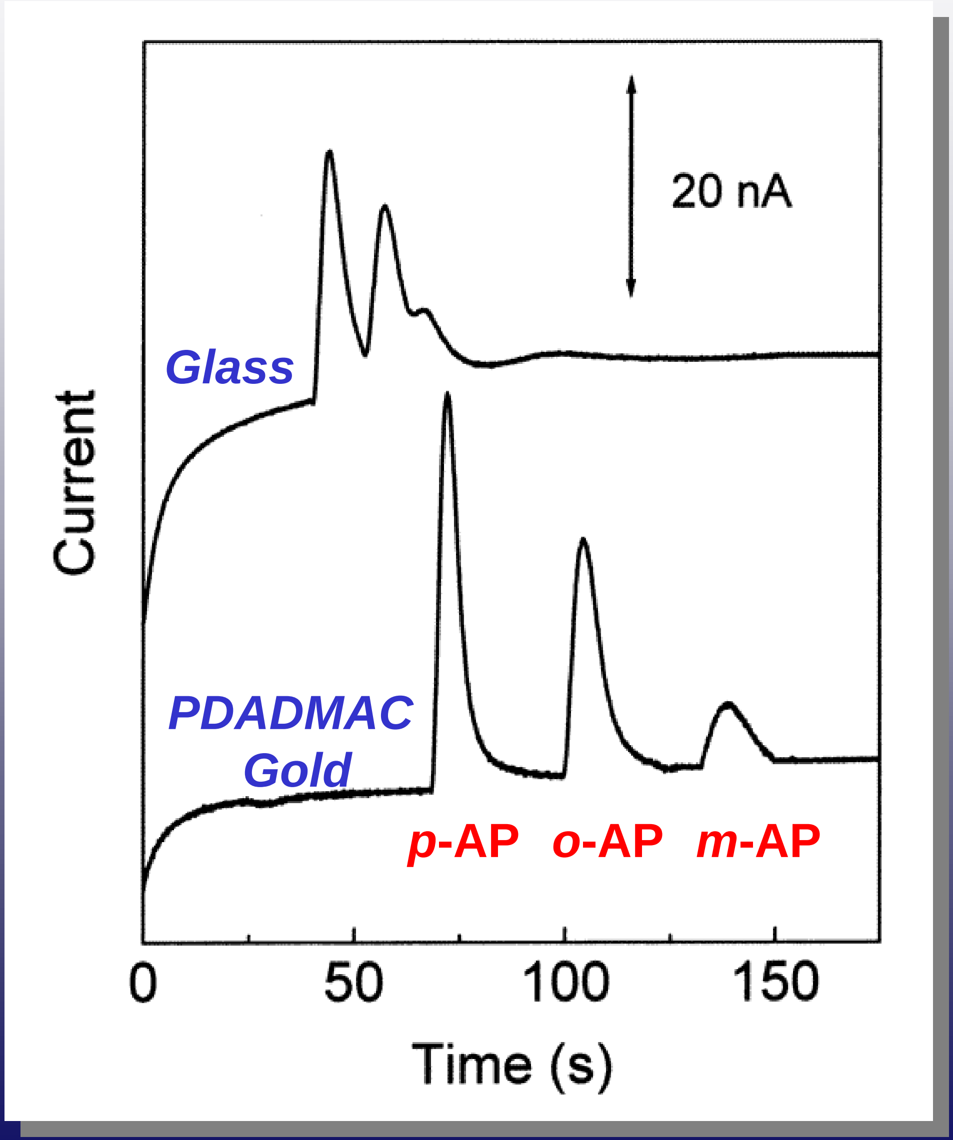
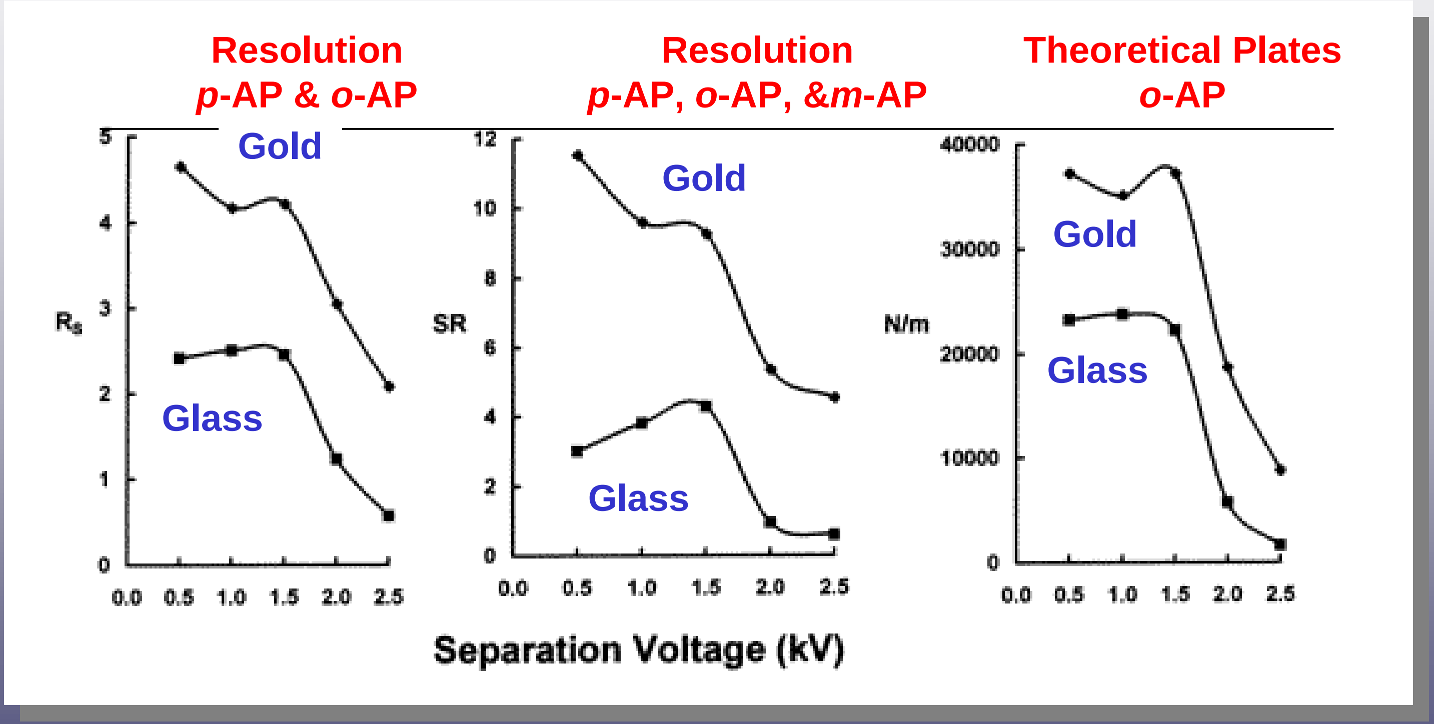
Gold Nanoparticle-Enhanced Separation of Aminophenols



Gold Nanoparticle-Enhanced Separation of Aminophenols

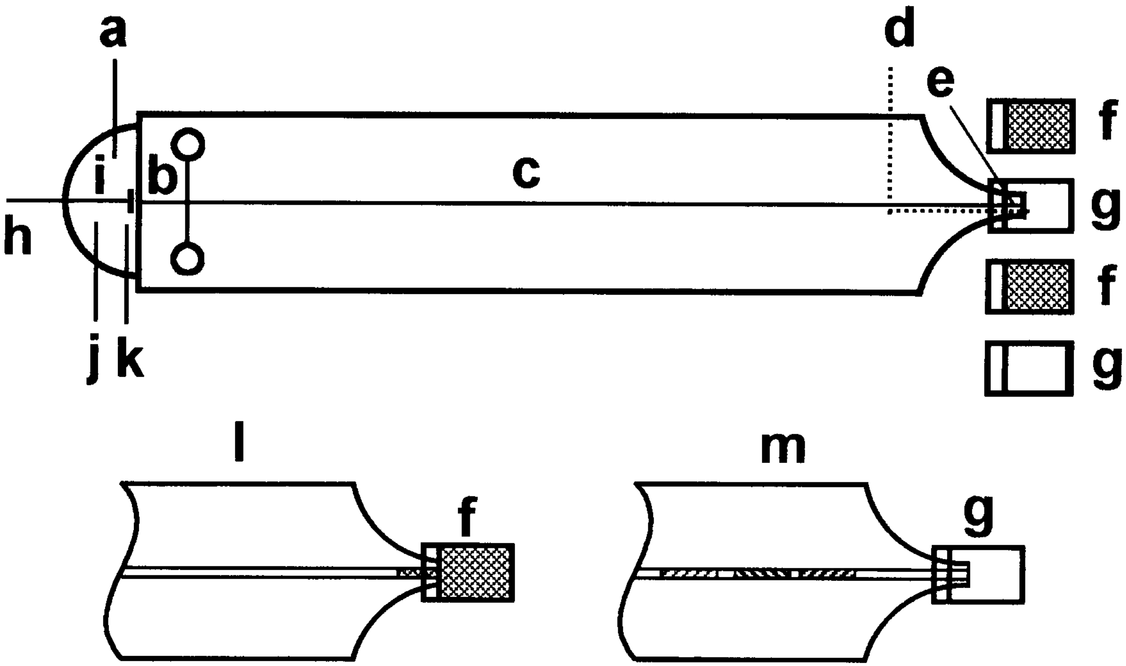


Effect of Gold Nanoparticles on Separation Efficiency

(Doubling the Resolution and Plate Number)

Sharp Microchip for Fast and Simple Sample Introduction for CE Microsystems:

Towards 'World-to-Chip' Interface



Facilitates convenient electrokinetic loading of samples directly into the separation microchannel

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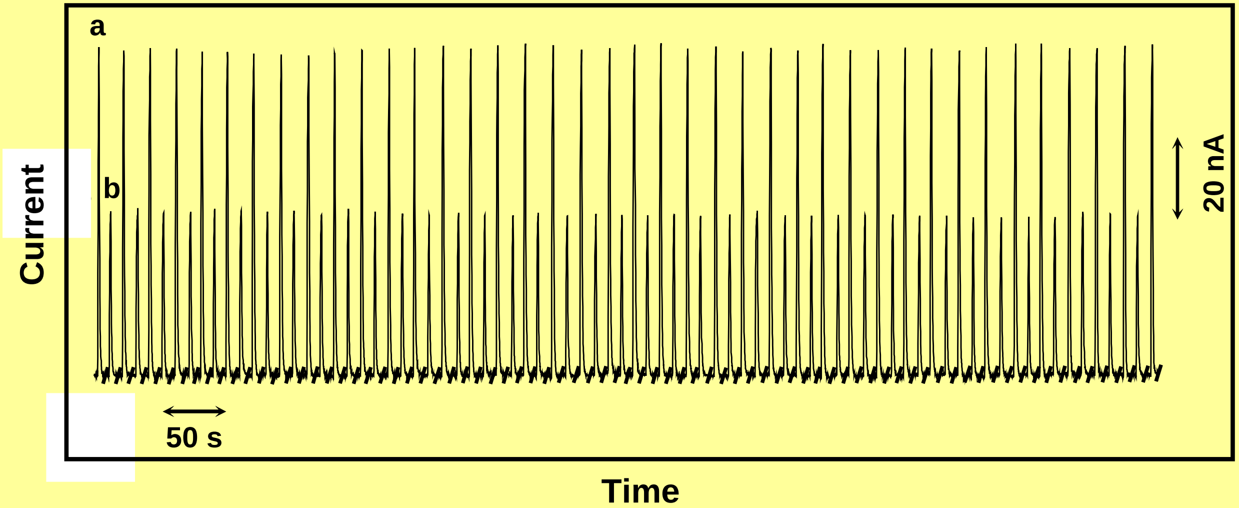
Sharp Microchip for Fast and Simple Sample Introduction for CE Microsystems



Electropherograms for 80 alternative injections of 10 (a) and 5 (b) ppm TNT solutions.

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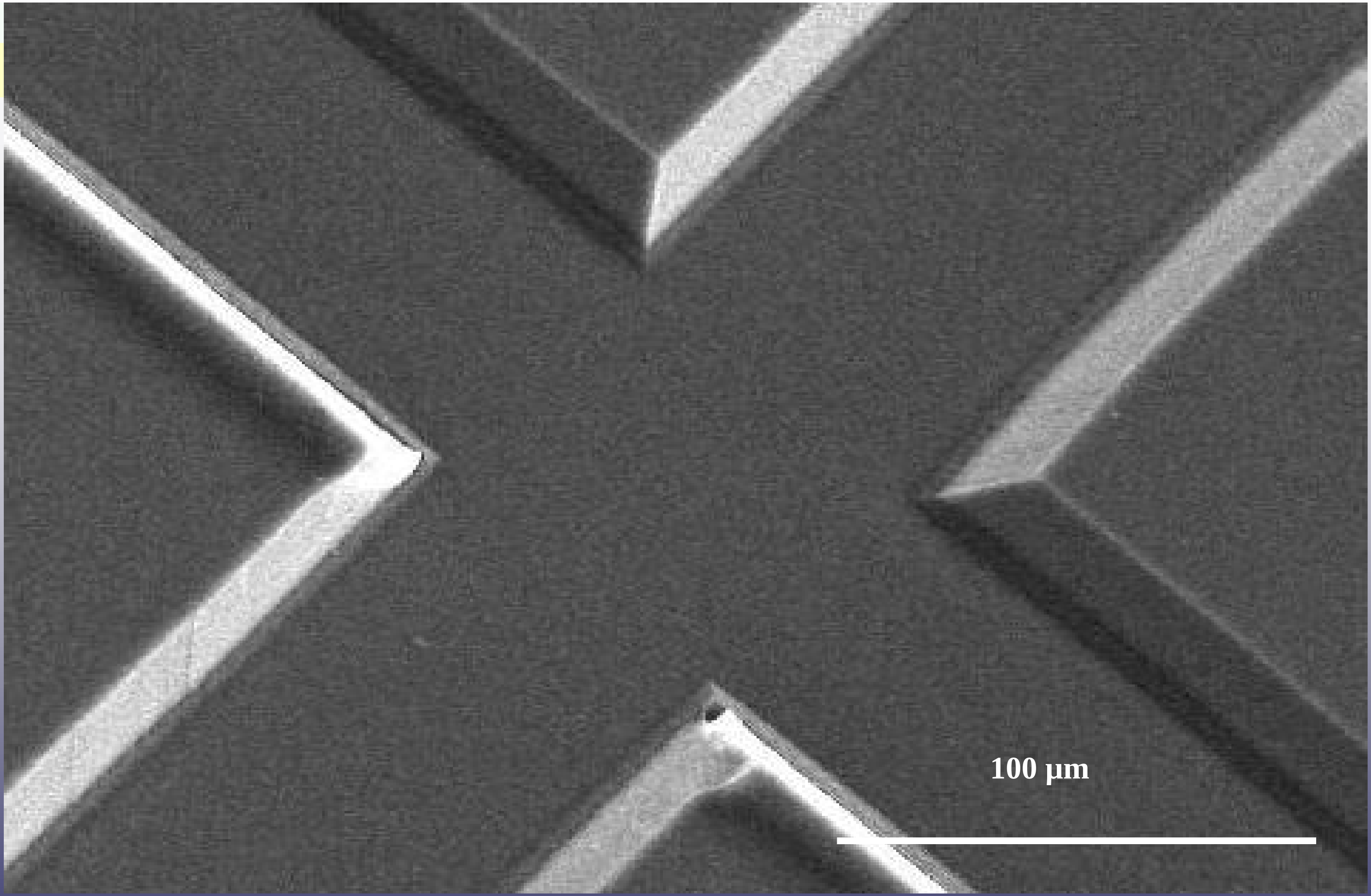
Towards Low-Cost (Disposable?) Microchips



A typical section of a polymer microchip produced at NMSU

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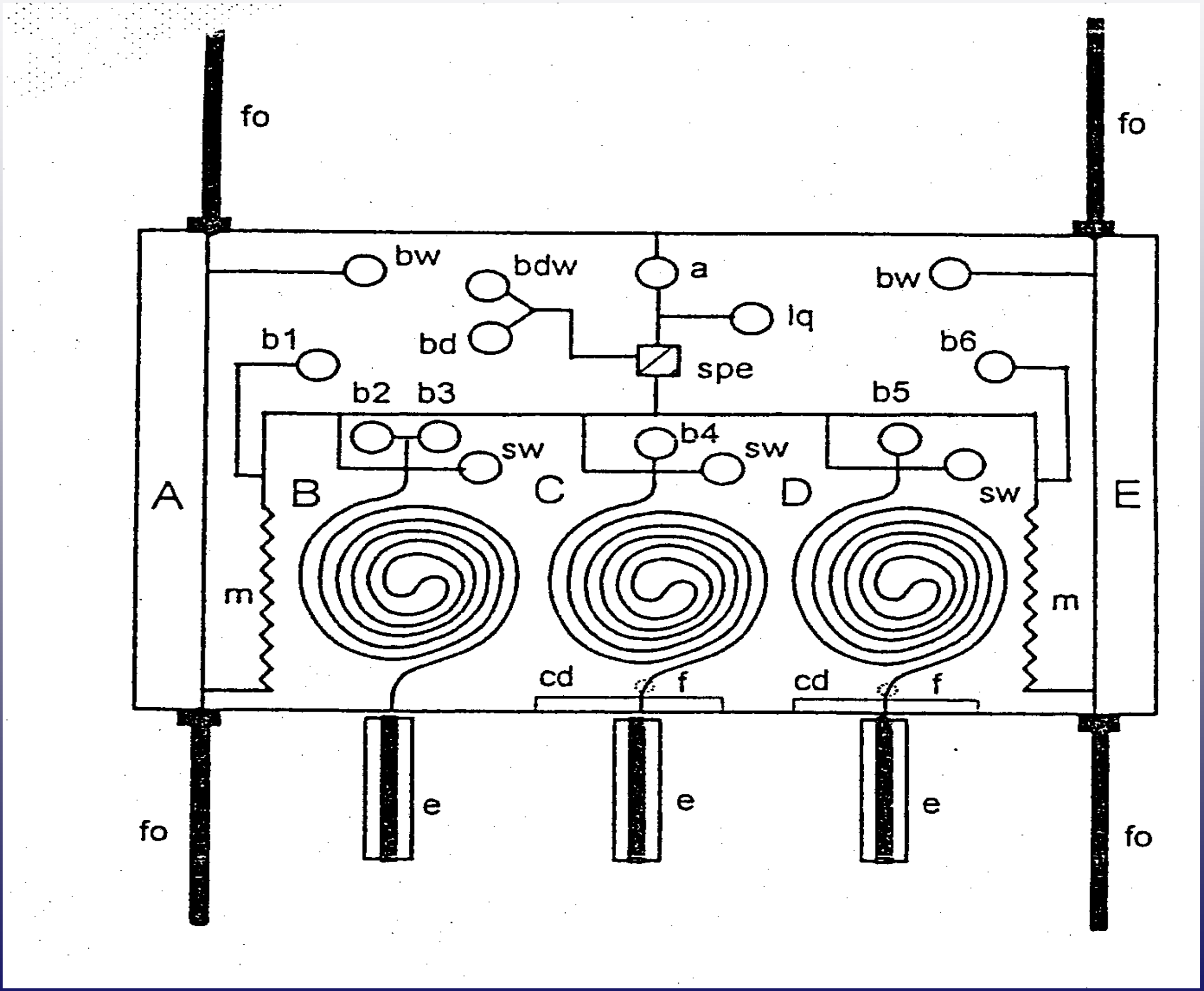
MULTI-CHANNEL MICROCHIP FOR PARALLEL ASSAYS OF MAJOR CONTAMINANTS



CONCLUSIONS

Nanomaterials, such as nanotubes or nanoparticles offer great promise for enhancing the performance of microchip devices.

Such nanomaterials-based microchip devices are expected to have a major impact upon environmental monitoring and security surveillance.

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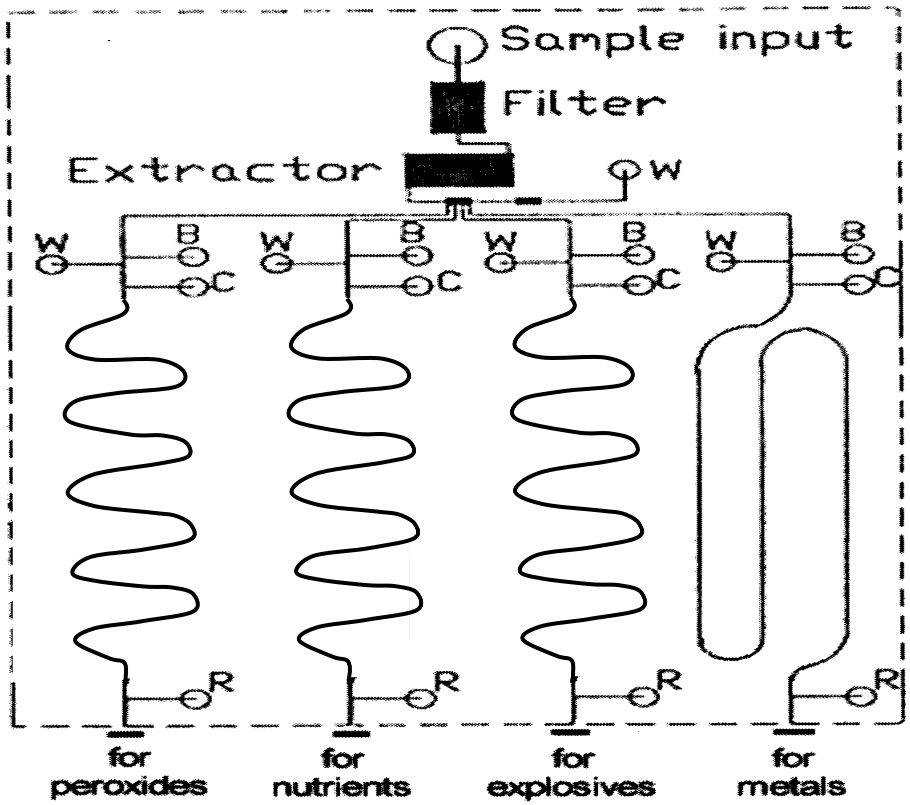
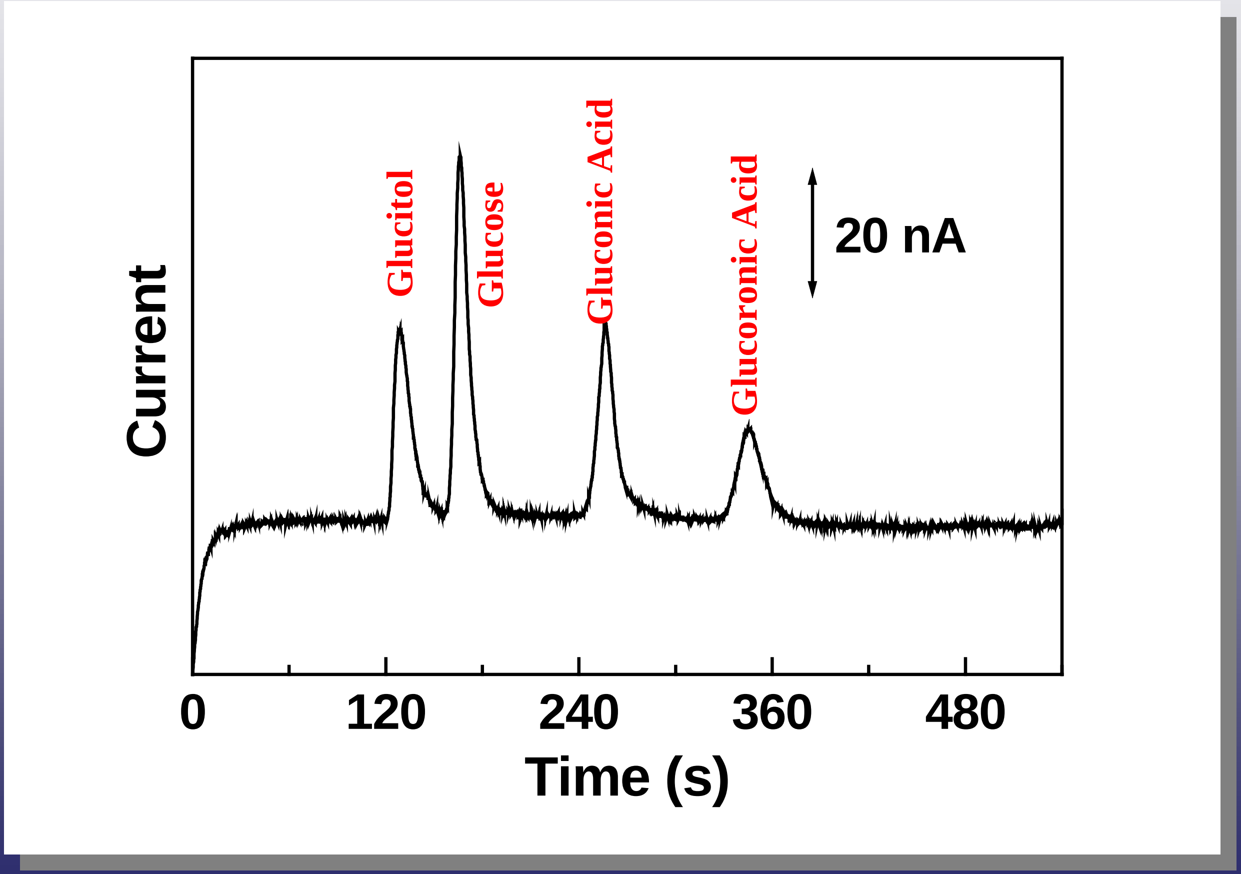
THANK YOU !!!

MULTICHANNEL CHIP FOR PARALLEL ENVIRONMENTAL ASSAYS



Carbon Nanotube/Copper Composite Electrode for the Detection of Glucose Family



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