EUROPEAN CO-OPERATION IN THE FIELD OF SCIENTIFIC AND TECHNICAL RESEARCH

COST

Microwave and Ultrasound Effects in Electroanalysis

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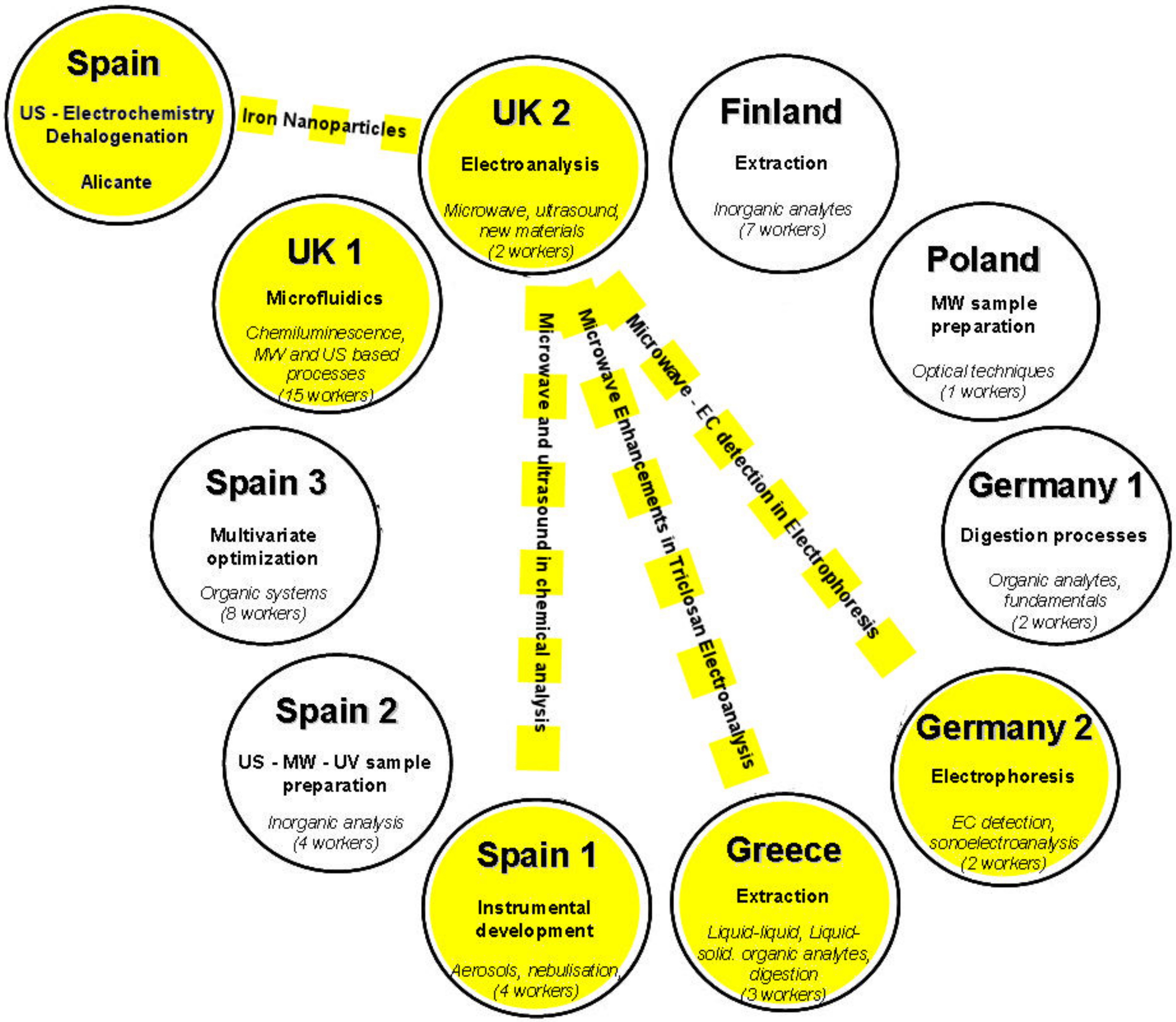
UNIVERSITY OF BATH

EUROPEAN COMMISSION
RESEARCH DIRECTORATE-GENERAL
Directorate B: European Research Area: Structural Aspects
COST

EUROPEAN CO-OPERATION IN THE FIELD OF SCIENTIFIC AND TECHNICAL RESEARCH

Proposal title: Microwaves and ultrasound activation in chemical analysis



Overview:

(A) Introduction to Power Ultrasound Applications in Electroanalysis: Iron Electrodeposition and Stripping

(B) Introduction to Microwave Enhanced Electroanalysis: Phenol Oxidation and Microwave Enhanced Electroanalysis in Aqueous Media

(C) New Reactor / Electrode Systems and Future Developments

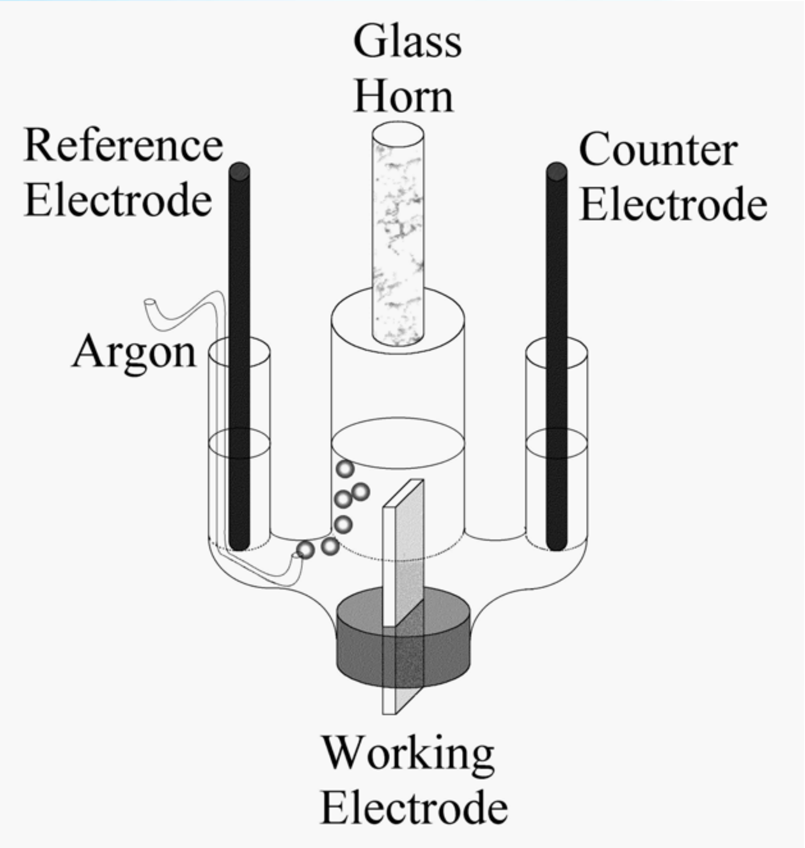
Introducing Power Ultrasound to Electrochemical Systems

Power ultrasound (20 kHz) is readily implemented with commercial horn probe systems.

In a three-electrode electrochemical cell the ultrasound intensity and the electrode-to-horn distance must be controlled.

The electrode surface experiences (i) fast mass transport and agitation, (ii) interfacial cavitation and cleaning, and (iii) erosion.

Calibration of the diffusion layer thickness provides inside into mass transport conditions (typically δ = 1 to 100 μm).

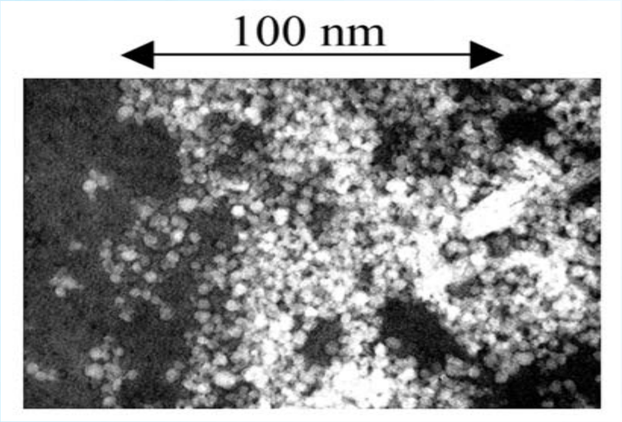


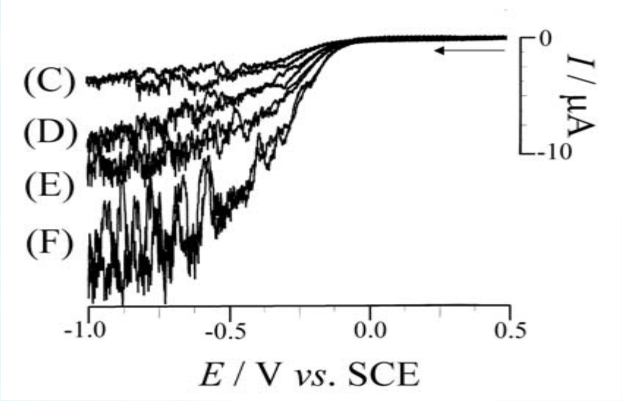
$$I_{\lim} = \frac{nFDAc}{\delta}$$

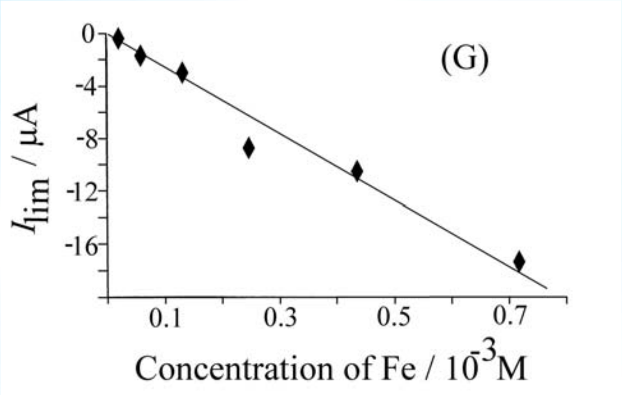
Introducing Power Ultrasound to Electrochemical Systems

Due to fast mass transport conditions in the presence of power ultrasound, very low concentrations of analyte and very slow "diffusers" can be detected.

Processes involving proteins or nanoparticle solutions (e.g. 5 nm Fe_2O_3 colloidal solution) are directly monitored







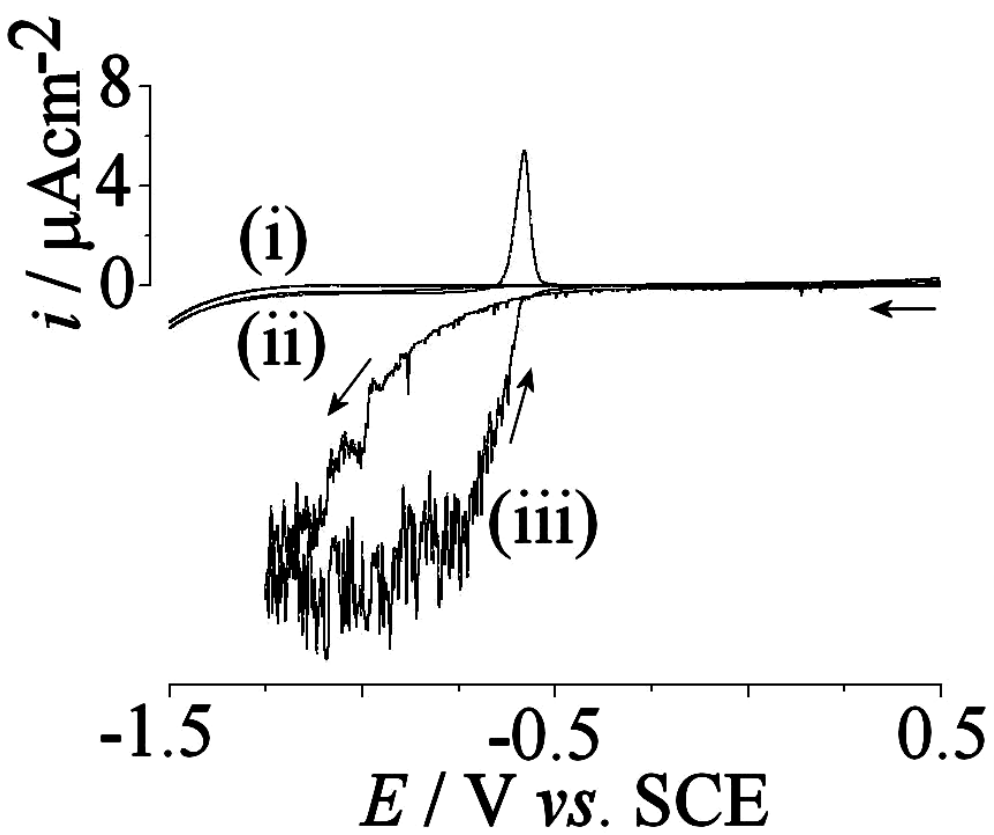
Introducing Power Ultrasound to Electrochemical Systems

The electrochemical reduction of FeF_6^{3-} in aqueous NH_4F results in a stripping peak.

Electro-deposition of iron metal onto a boron-doped diamond electrode must be occurring.

Sub-micromolar concentrations are easily observed.

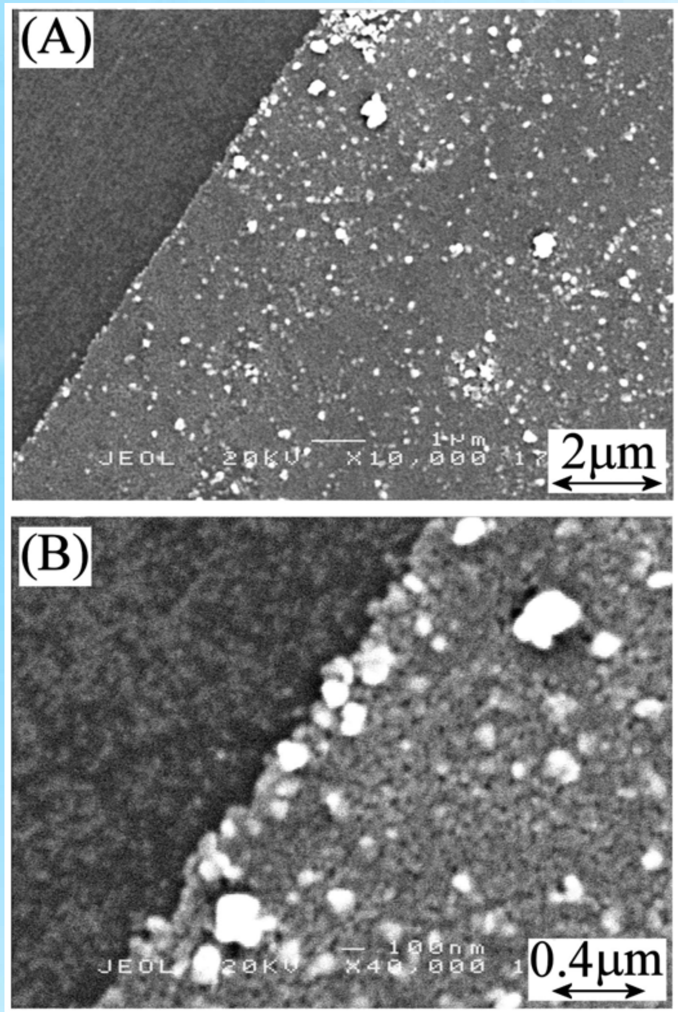
Power ultrasound increases the signal by 2 orders of magnitude.

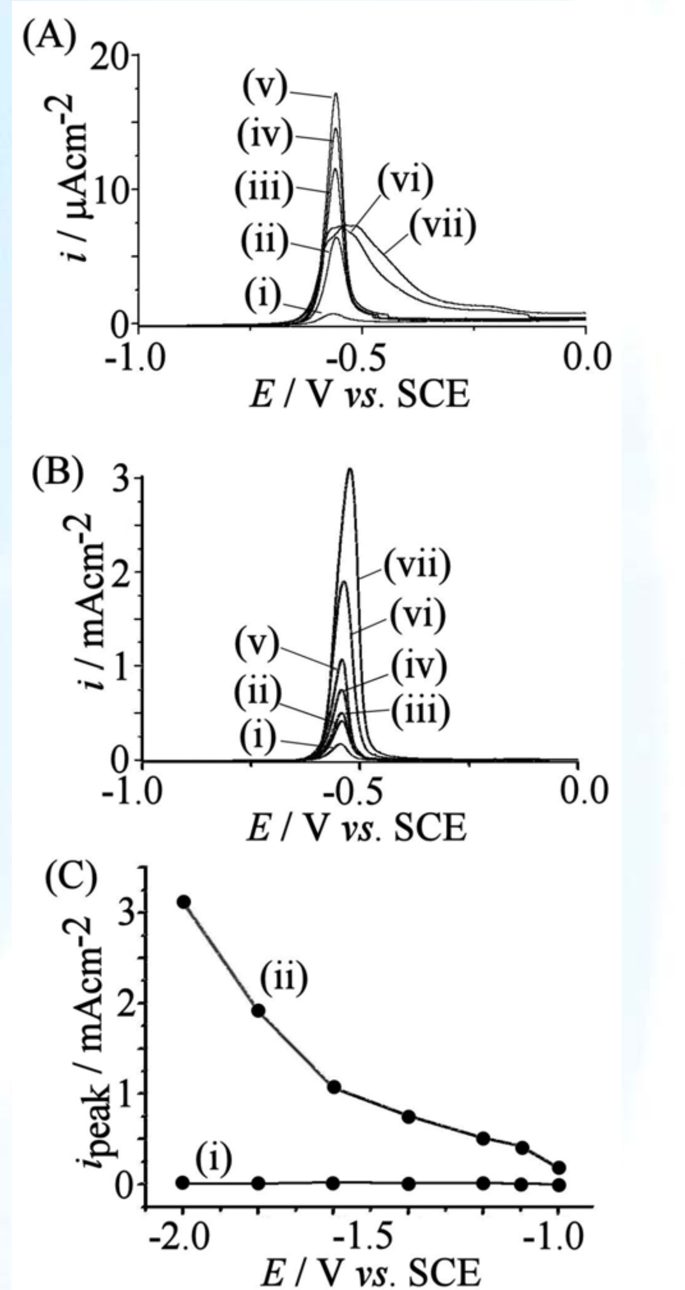


$FeF_6^{3-} + e^- \rightarrow FeF_6^{4-}$ { $\rightarrow$ Fe(s) }   catalysed by iron deposit!

Introducing Power Ultrasound to Electrochemical Systems

Iron nanoparticle deposits form as a function of concentration, time, and ultrasound power.





Introducing Power Ultrasound to Electrochemical Systems

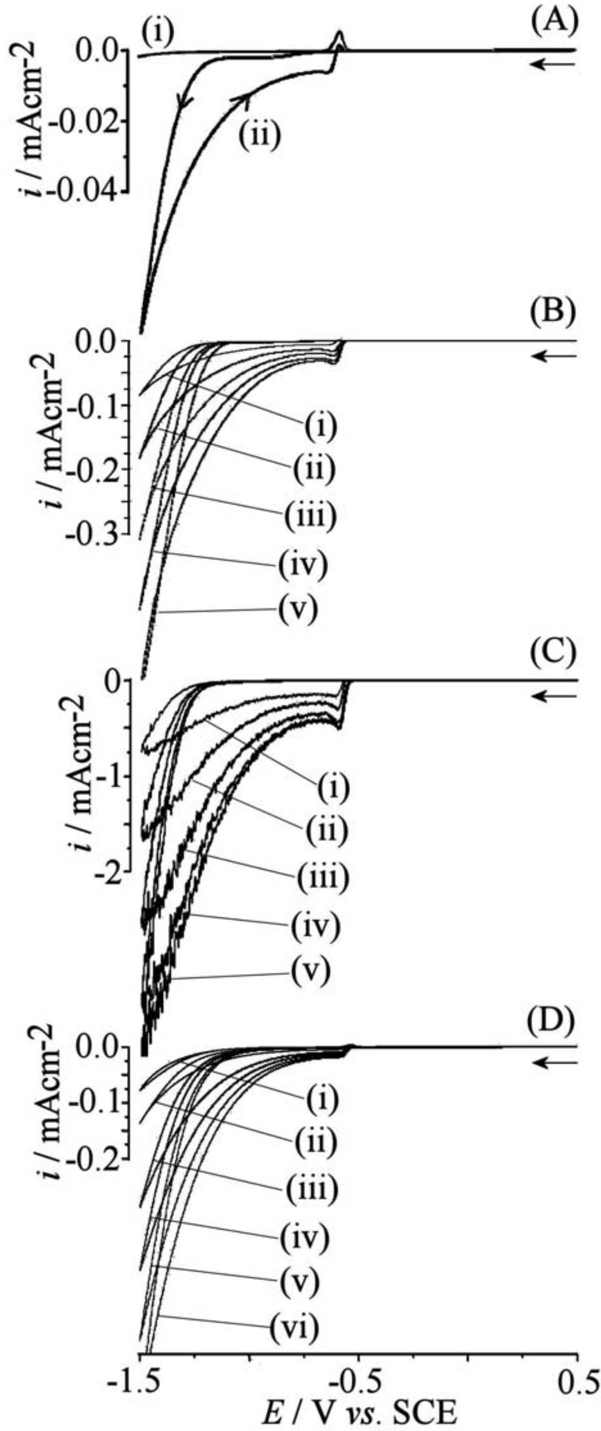
The iron nanoparticle surface is highly reactive and can be employed in dehalogentaion processes, for example for trichloroacetate (and triclorosan):

$$trichloroacetate + 2e^- + H_2O \rightarrow dichloroacetate + Cl^- + OH^-$$

$$dichloroacetate + 2e^- + H_2O \rightarrow chloroacetate + Cl^- + OH^-$$

$$chloroacetate + 2e^- + H_2O \rightarrow acetate + Cl^- + OH^-$$

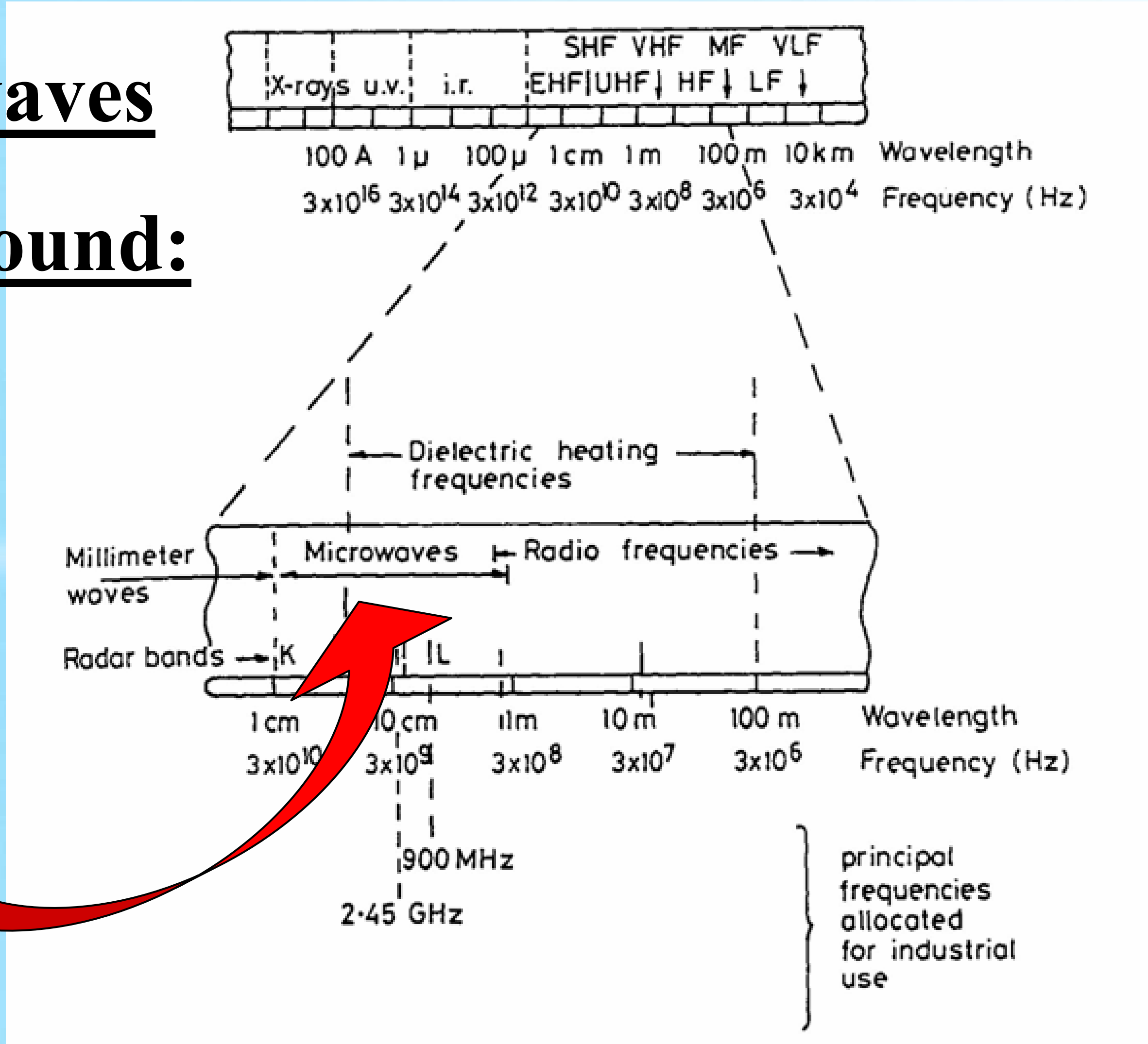
Even in the absence of intentionally added FeF_6^{3-} catalytic processes are observed due to the strong adhesion of iron oxides to boron-doped diamond.



Introduction: Why Microwaves in Electroanalysis?

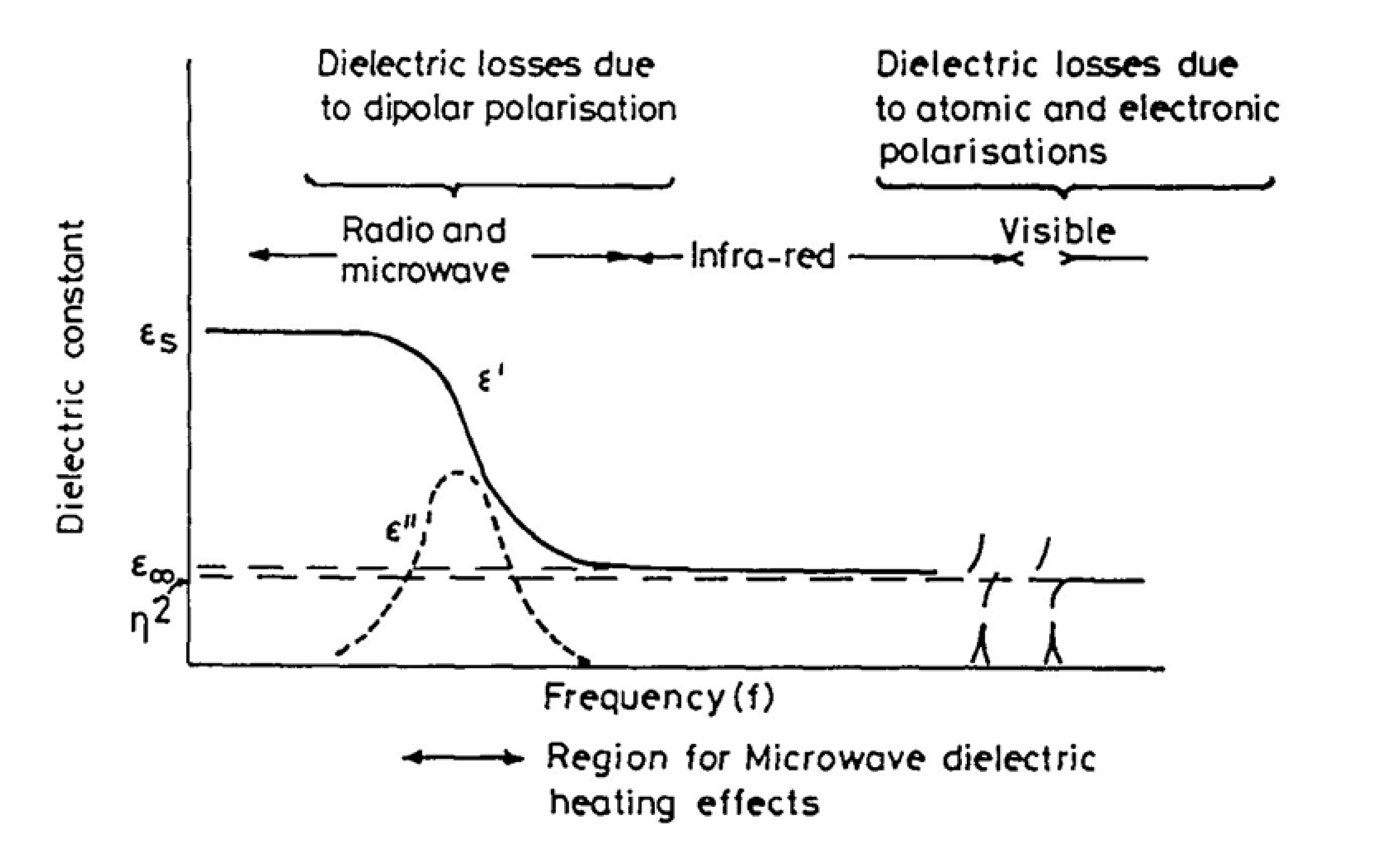
- Electrochemical processes are heterogeneous and require both mass transport and surface activation
- Focussed microwaves trigger strong local thermal effects leading to extremely high mass transport and surface activation
- Microwaves can create locally high temperature conditions affecting in situ digestion, desorption, de-complexation, and other chemical processes

Microwaves Background:



2.45 GHz

Domestic Microwave

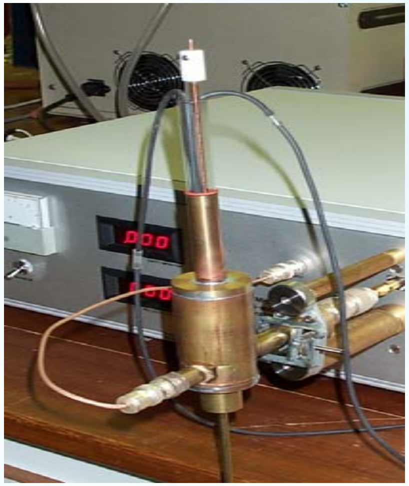

Dielectric losses due
to dipolar polarisation
Dielectric losses due
to atomic and electronic
polarisations
Radio and
microwave
Infra-red
Visible
Dielectric constant
ε_s
ε'
ε''
ε_∞
η^2
Frequency (f)
Region for Microwave dielectric
heating effects

Instrumentation for Microwave Heating in Electrochemistry:

Generation and Focusing of microwave energy:

Multi-mode System (2.45 GHz):

Based on Magnetron Source; simple technology; high power (100 W); but slow rise time; large cavity; bulky electronics



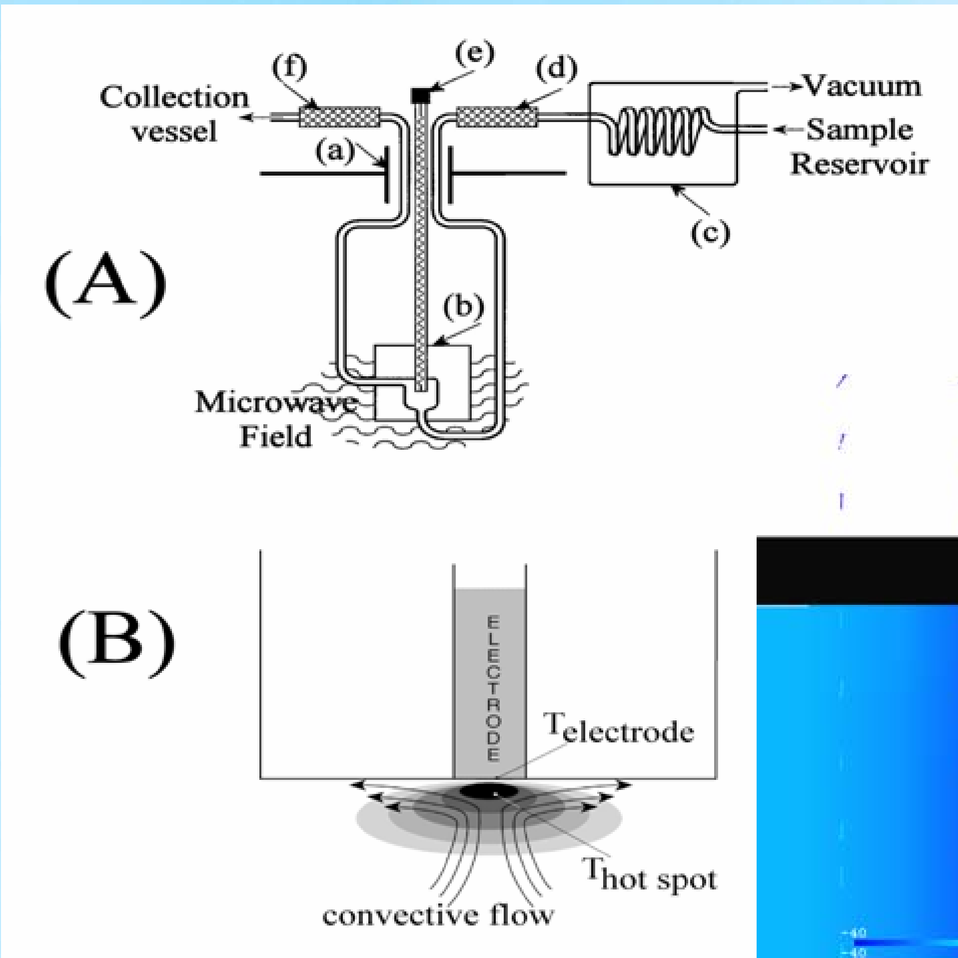
Mono-mode System (1.8 GHz):

Based on a Semiconductor Source; simple technology; modest power (40 W); extremely fast switching times; small cavity

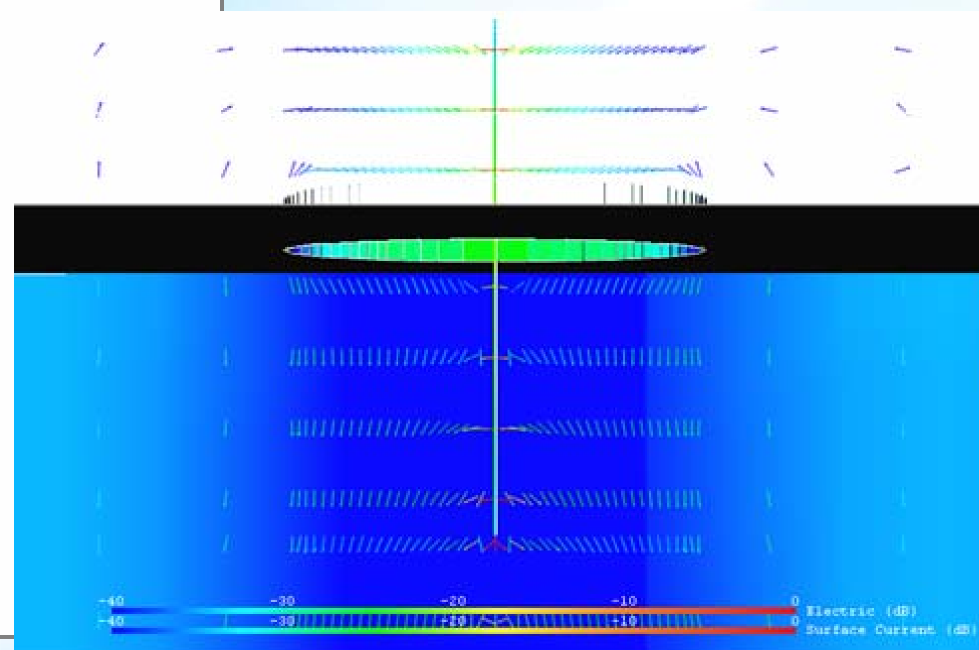
Multi-mode Stripline Systems (1-3 GHz)

Instrumentation for Microwave Heating in Electrochemistry

Electrochemical flow cell used in microwave studies

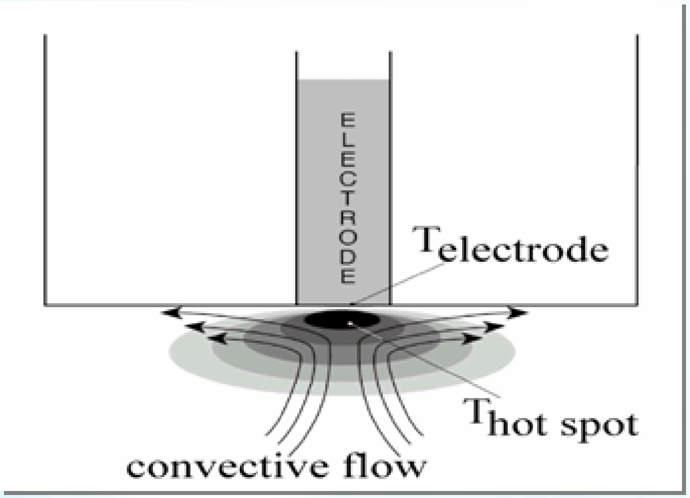


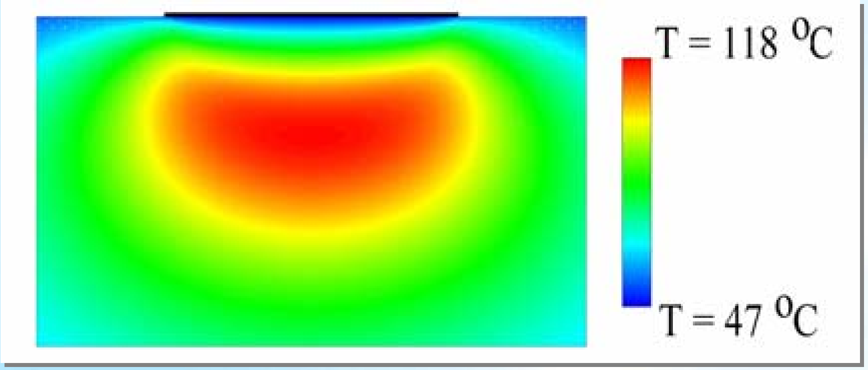
An intense microwave field is focused locally into a region at the electrode surface/solution interface



A simple model for the effect of focused Microwaves in Electrochemistry

1. Instant heating and hot spot formation (local super heating and temp gradients)
2. Convective flow
3. Extreme Temp gradients
4. Cavitation at high microwave fields



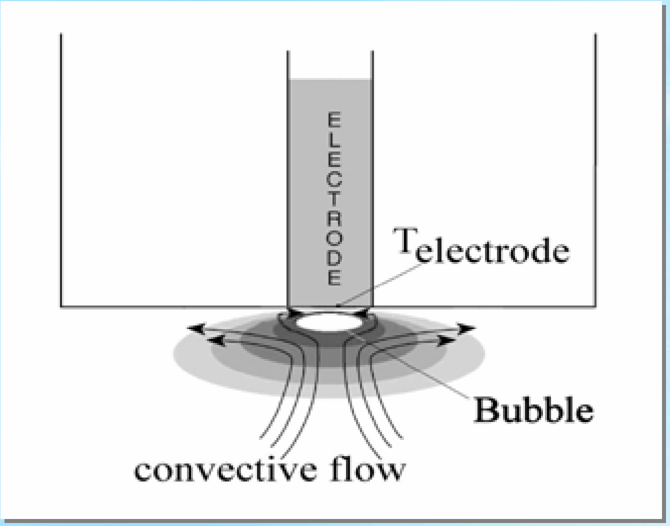


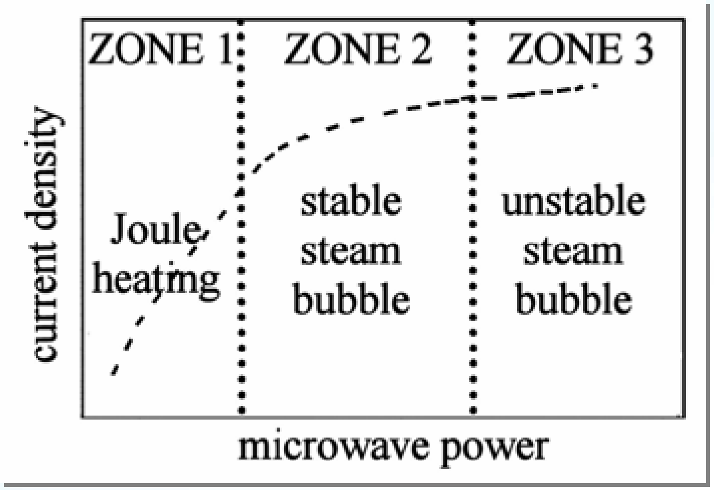
Joule Heating

Image produced based on an approximate computer model (**FIDAP**^{TM})

Extreme current enhancement in smaller electrodes can only be explained by a mechanism based on a stable vapour bubble

"JET-BOILING":

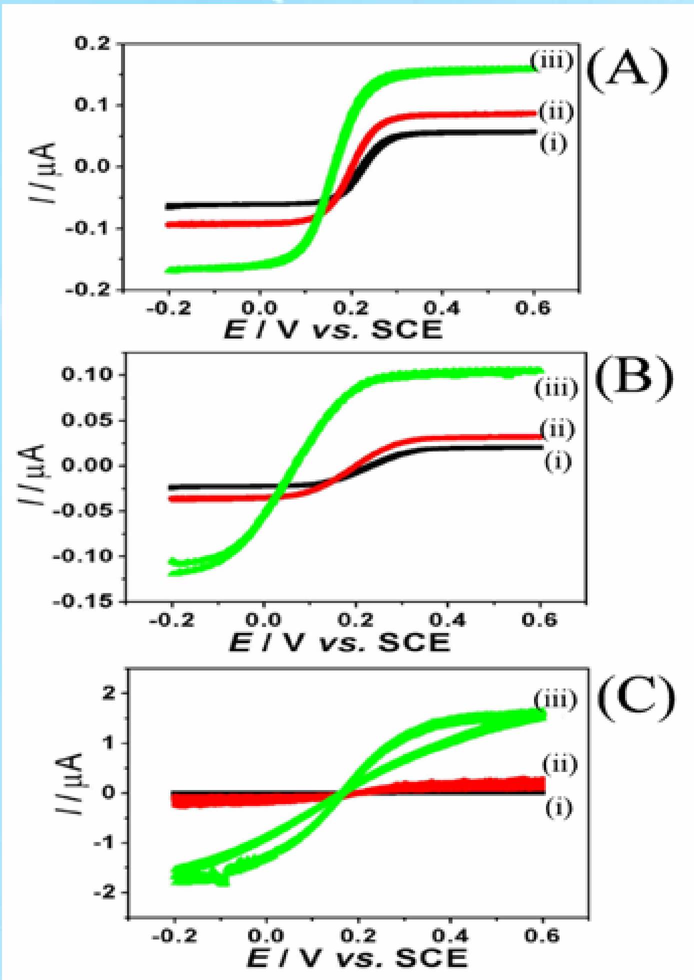




- Initially convective flow towards electrode
- Switch to jet-flow away from the electrode

The Effect of Microwaves on Mass Transport at Metal Electrodes

$Fe(CN)_6^{3-}(aq) \quad + \quad e^- \quad \rightarrow \quad Fe(CN)_6^{4-}(aq)$



100 µm Pt microelectrode

50 µm Pt microelectrode

25 µm Pt microelectrode

Capillary Electrophoresis with Microwave-Enhanced Electrochemical Detection

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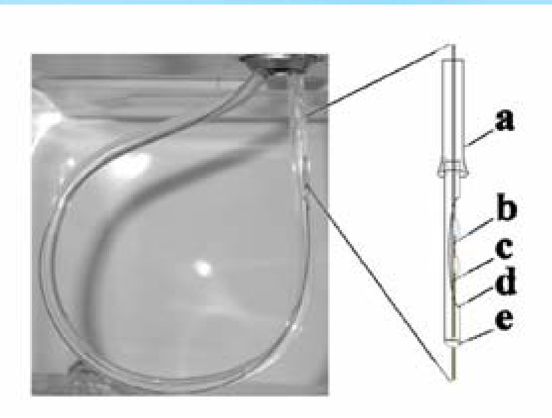
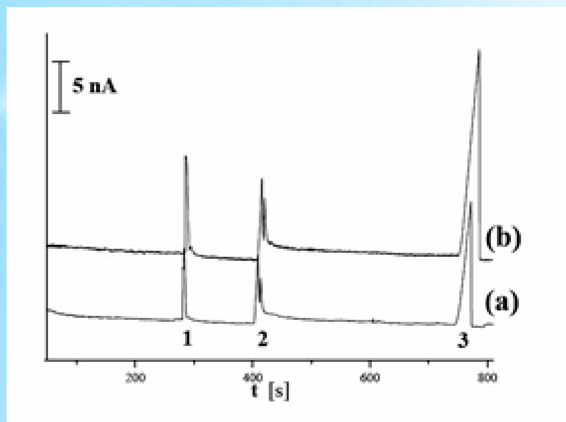
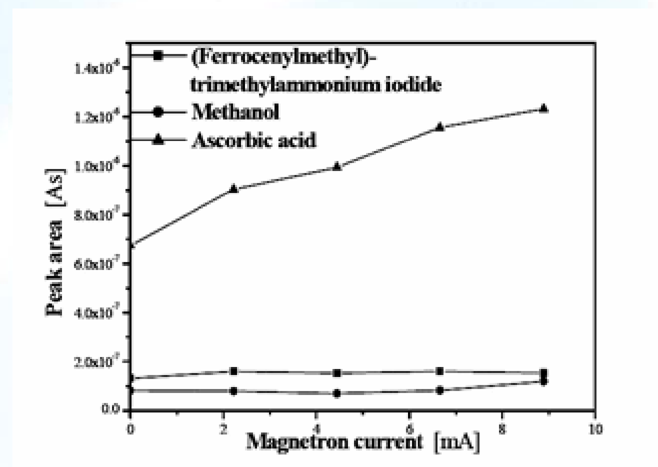
[b] *Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK; E-mail: F.Marken@Bath.ac.uk*



Detector electrodes are the point of microwave energy focussing.



Analysis for cationic, neutral, and anionic system shows purely kinetic microwave effects for ascorbic acid.

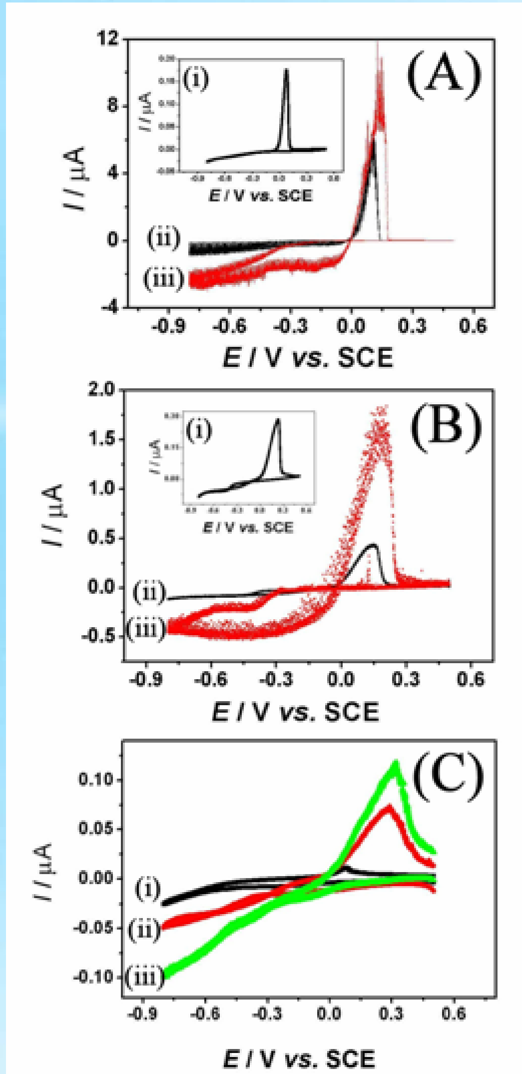


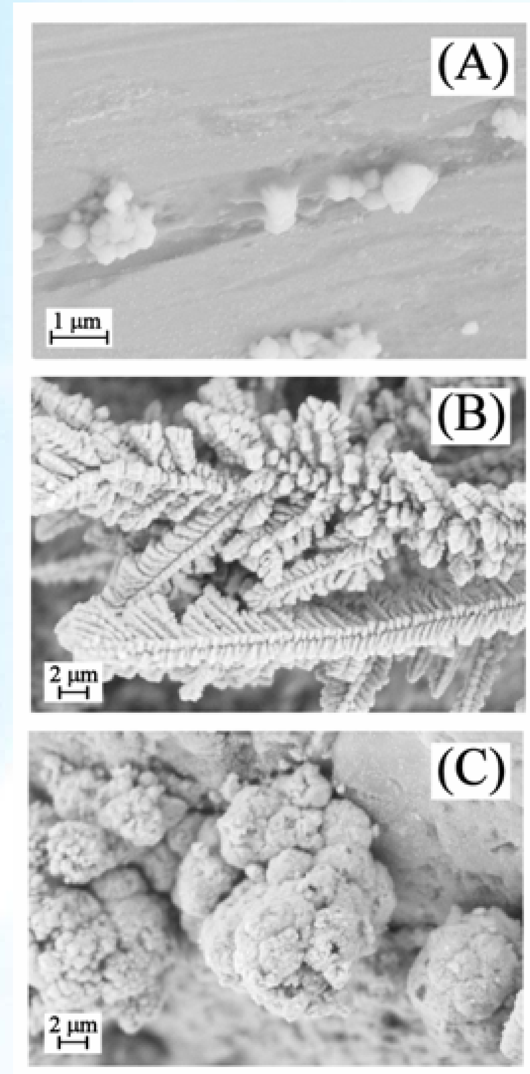
The Effect of microwaves on the Electrochemical Deposition of Copper:

25 μm diameter platinum:

50 μm diameter gold:

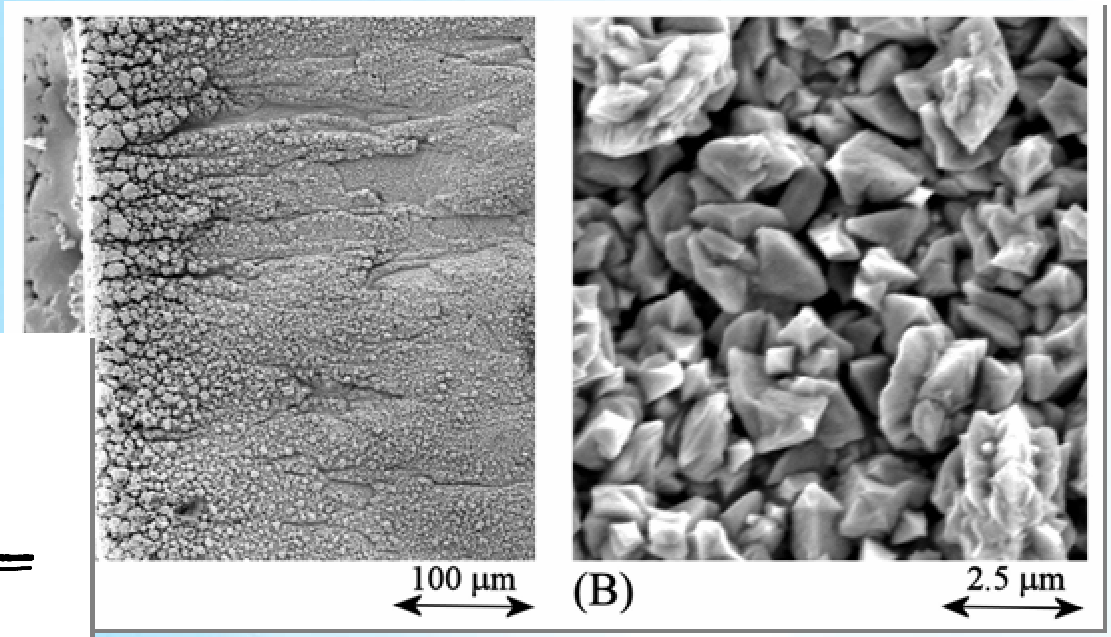
33 μm diameter glassy carbon:

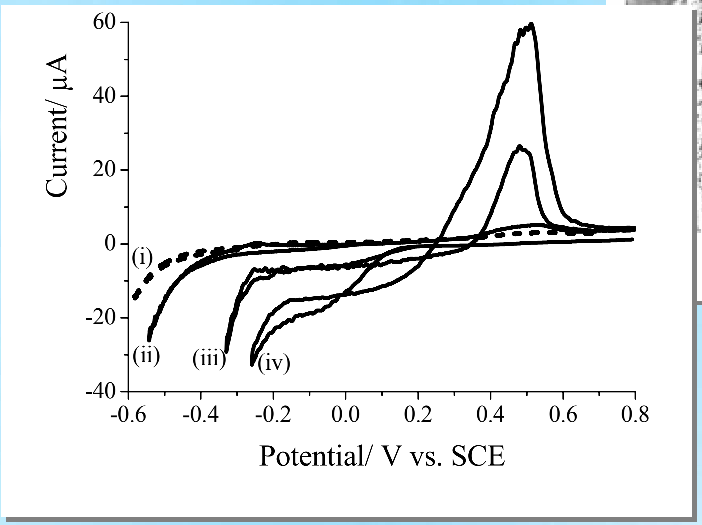




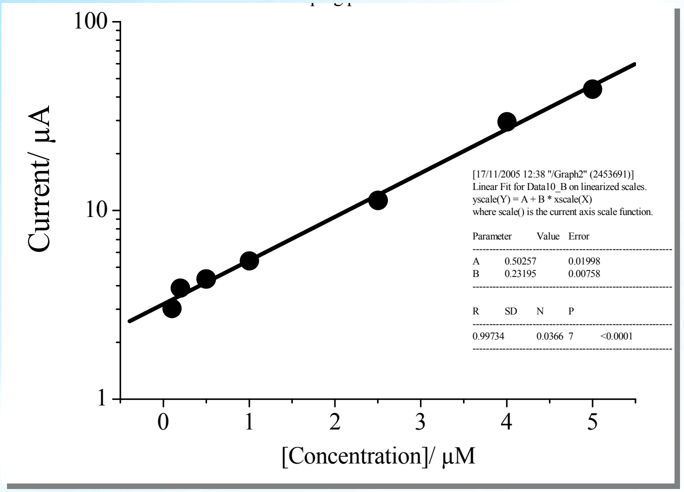
The Effect of microwaves on the Electrochemical Deposition and Stripping of Palladium at Boron-Doped Diamond:

Fast deposition generating high surface area film deposits:

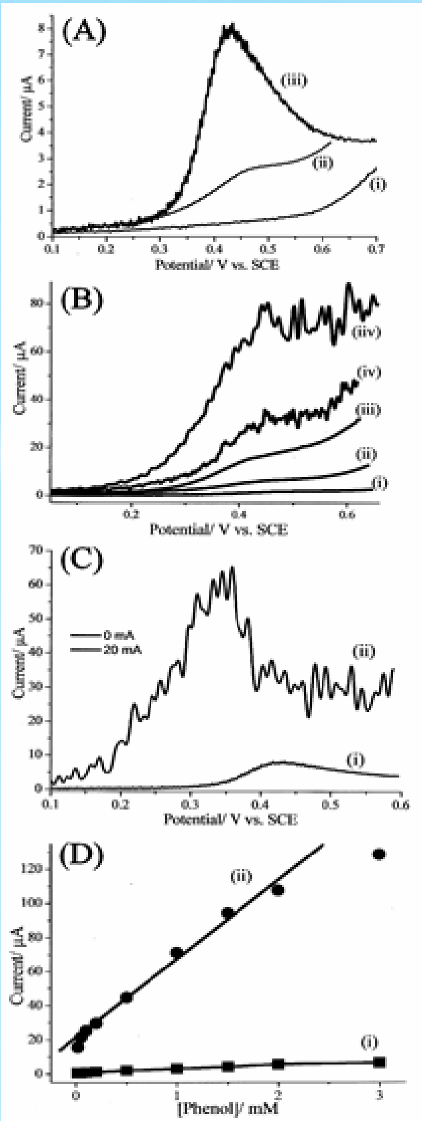


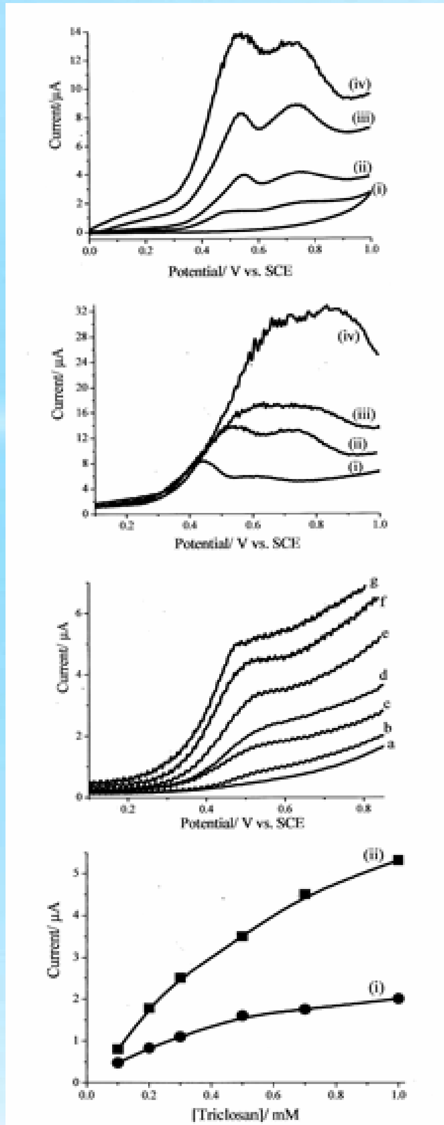


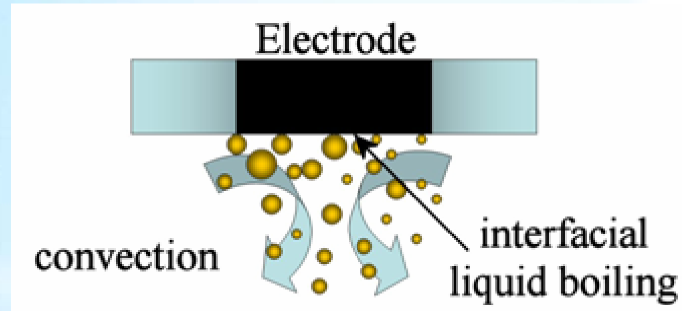
Lowered detection limits:



Phenol and Triclosan Oxidation in Aqueous Media:



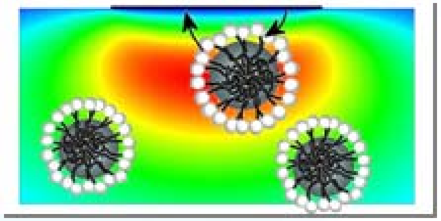


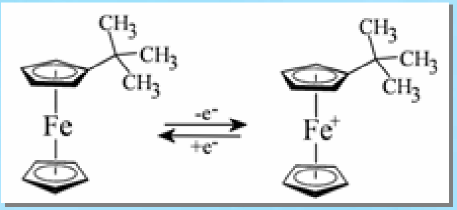


The oxidation of phenol in alkaline aqueous solution occurs as a one or four electron process depending on concentration and conditions.

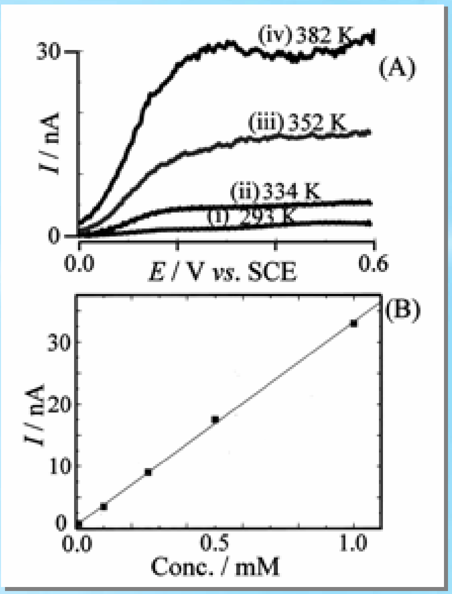
The oxidation of triclosan is a one electron process and leads to blocking even under high microwave power conditions.

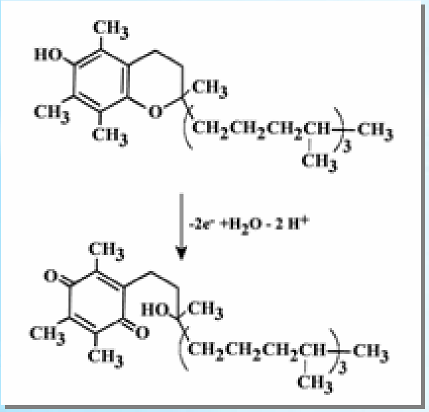
Electroanalysis in Emulsions:

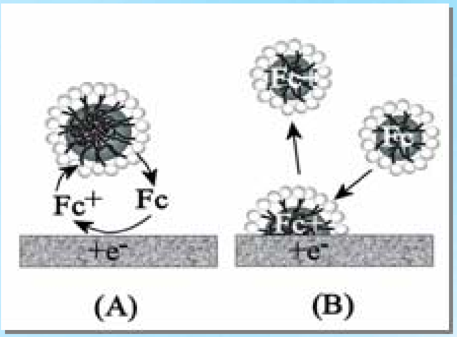




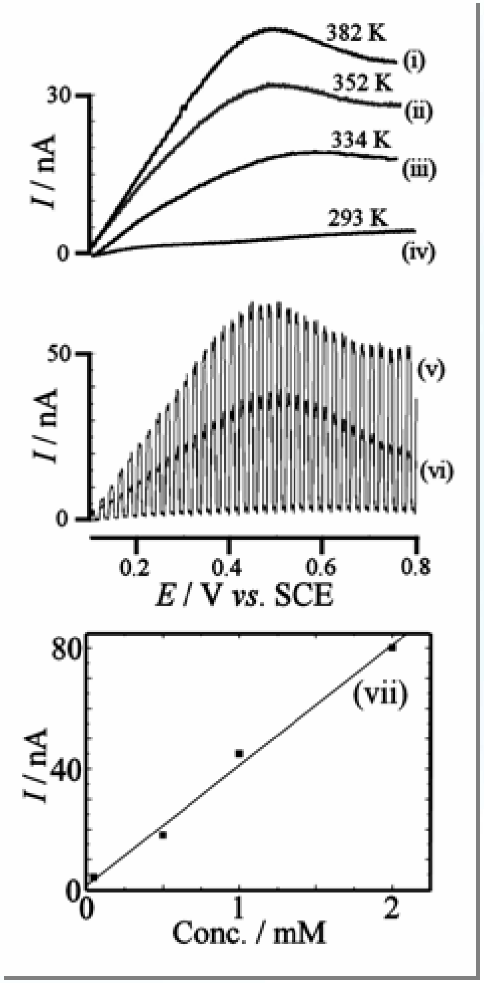
The **tert-butylferrocene** oxidation becomes facile (diffusion controlled) with microwave activation.



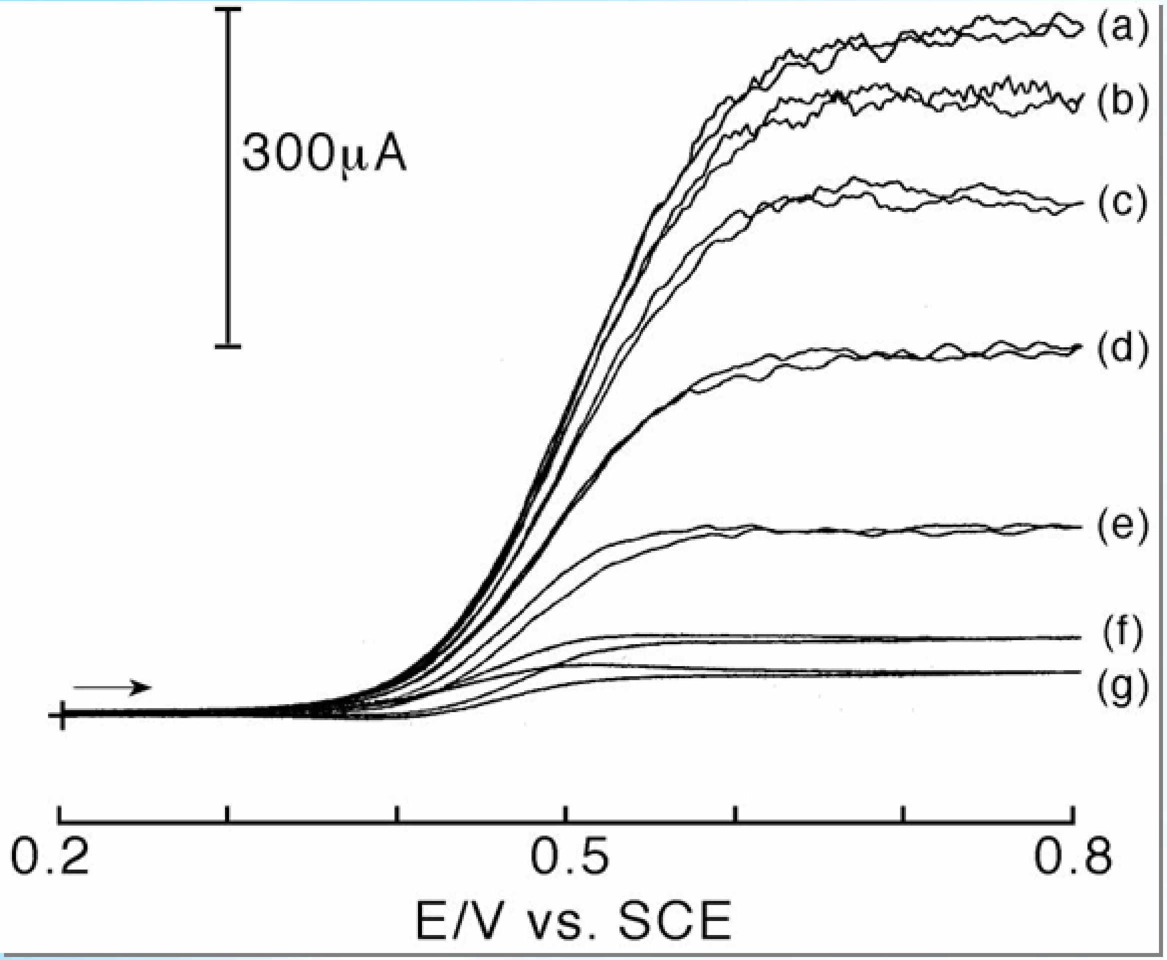




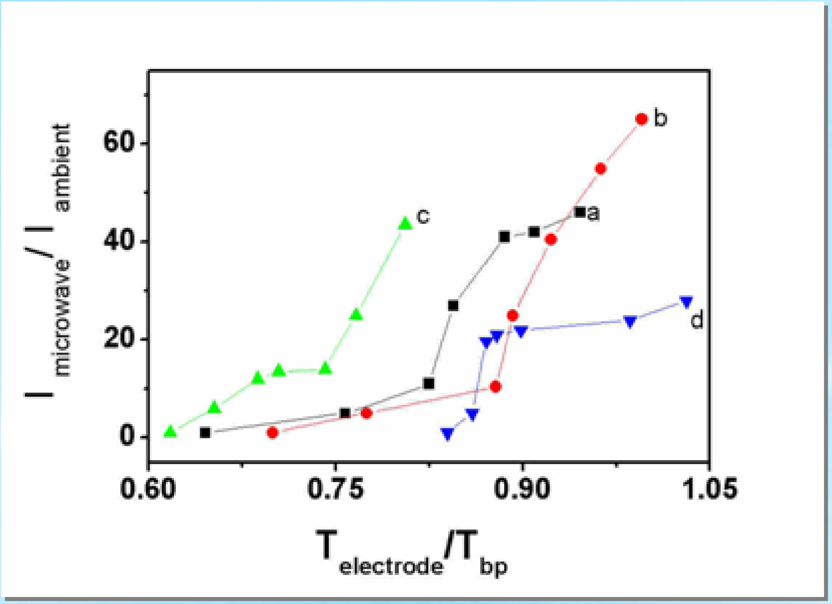
Even extremely water-insoluble **vitamin E** can be oxidised with a current proportional to the emulsion concentration.



The Oxidation of Ferrocene in Organic Solvents (DMF) at variable Microwave Power

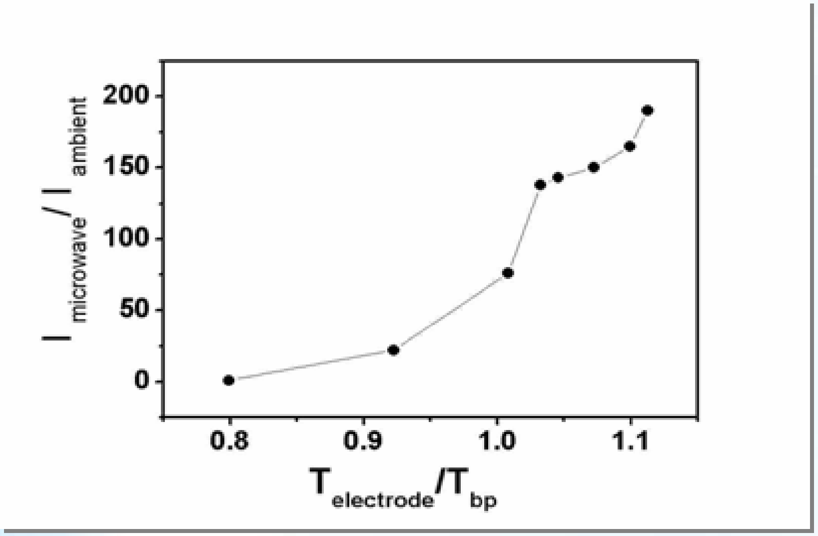


High Temperature Electrochemistry in Organic Liquids:

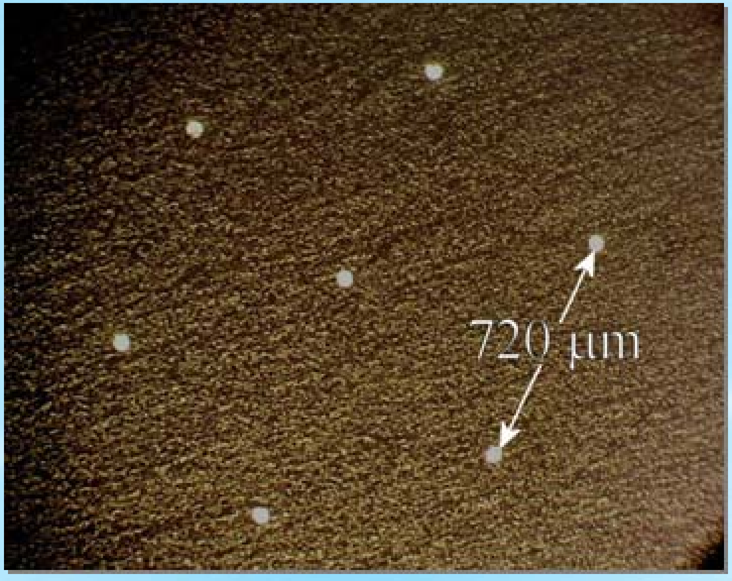


Plot of the microwave enhanced current divided by the steady state current under ambient condition as a function of $T_{electrode}/T_{bp}$ for the oxidation of 2 mM ferrocene (0.1 M NBu_4PF_6) at different microwave power settings at a 25 µm diameter platinum disk electrode in (a) DMSO, (b) DMF, (c) formamide, and (d) acetonitrile. T_{bp} corresponds to the thermo-dynamic boiling point of the solvents.

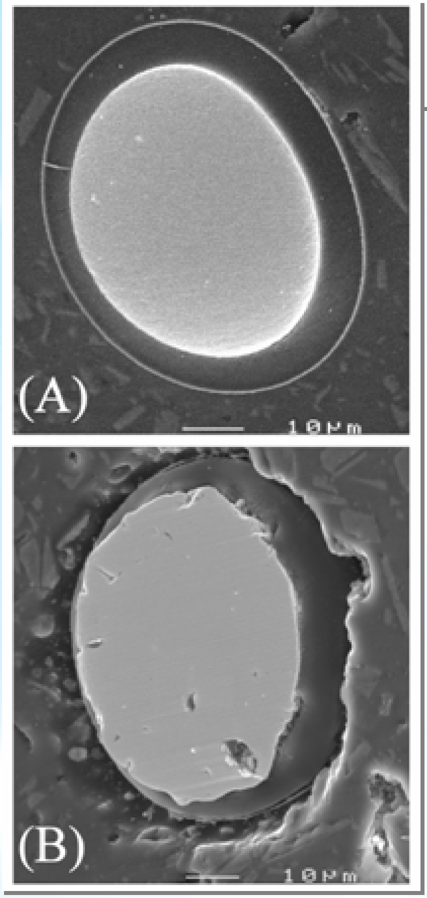
Plot of the microwave enhanced current divided by the steady state current under ambient condition as a function of $T_{electrode}/T_{bp}$ for water.

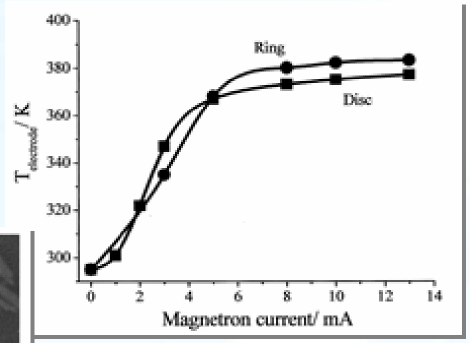


New Reactors and New Electrodes:



Arrays of electrodes show independent effects and therefore several electrodes can be placed into one reactor system.





Ring-disc electrodes allow generator-collector experiments and both electrodes show temperature and mass transport effects when operated in the presence of microwaves.

Summary:

- Effects Occur only in solution in the Vicinity of the Electrode (due to microwave self-focusing)
- No Special Electrochemical Instrumentation required
- Well-Defined MW Field Characteristics
- Very High Energy Available at Low Microwave Power
- Very Short High Energy Pulses can be applied
- New Types of Electrode Processes Possible under 'Hot Spot' Conditions (Emulsions, etc.)
- Coupling of microwave activation to other methods such as CE-ED is possible

Acknowledgements:

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Professor Richard G. Compton and Dr. Barry A. Coles (Oxford)

Severin Harvey and Dr. Danny O'Hare (London)

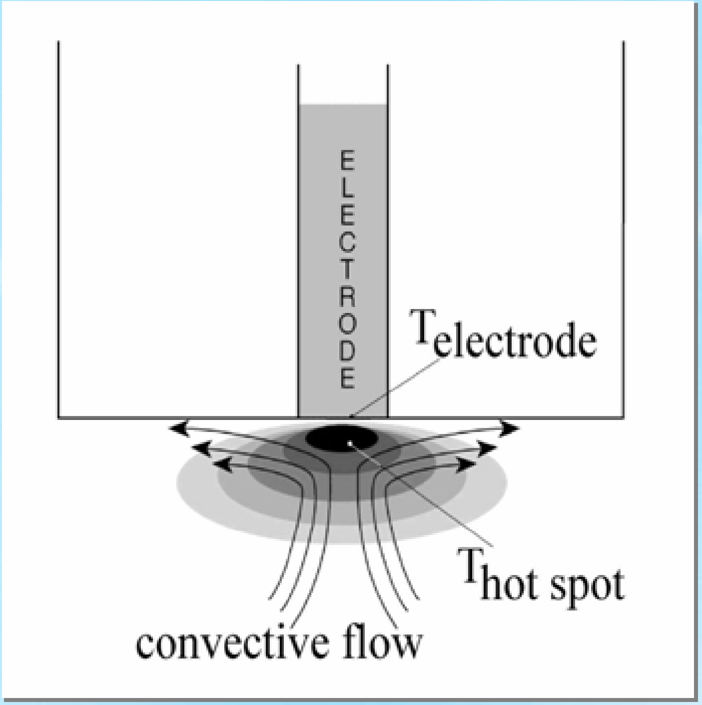
EPSRC

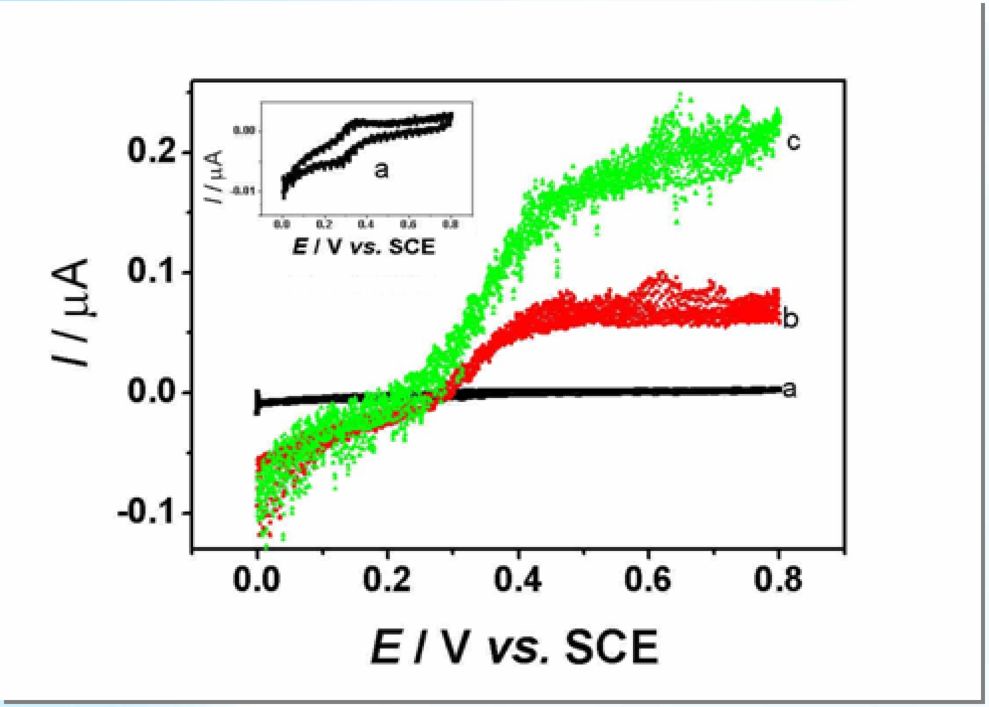
The British Council

The Royal Society

Pyro-Electrochemistry in Ionic Liquids:

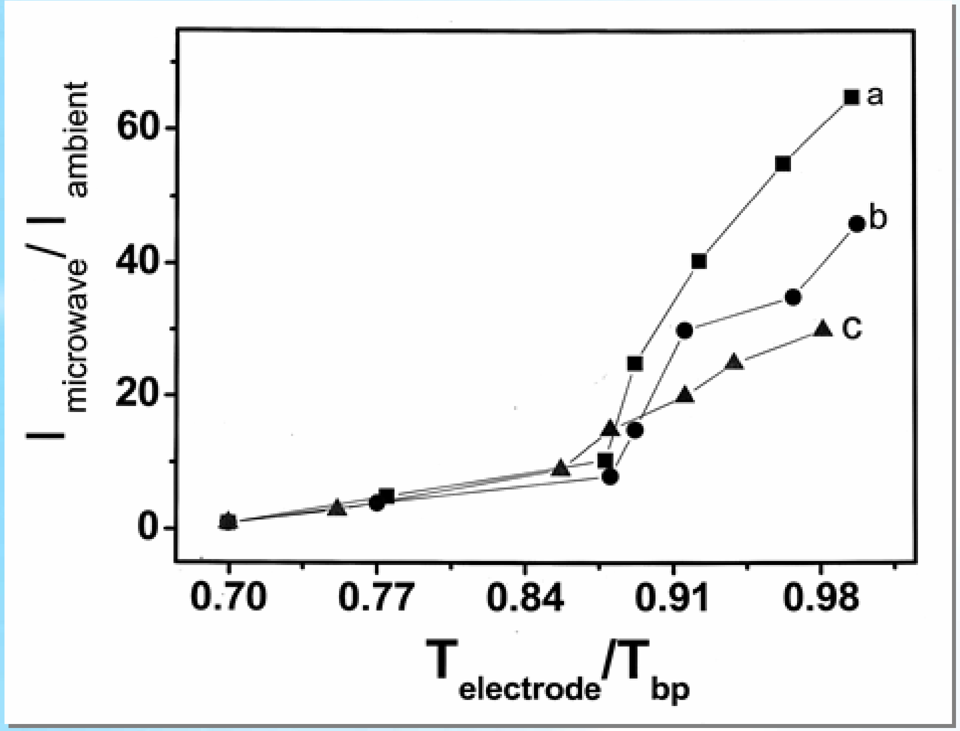
Temperature of higher than 400°C can be reached locally in a non-volatile ionic liquid, here $BMIM^+PF_6^-$



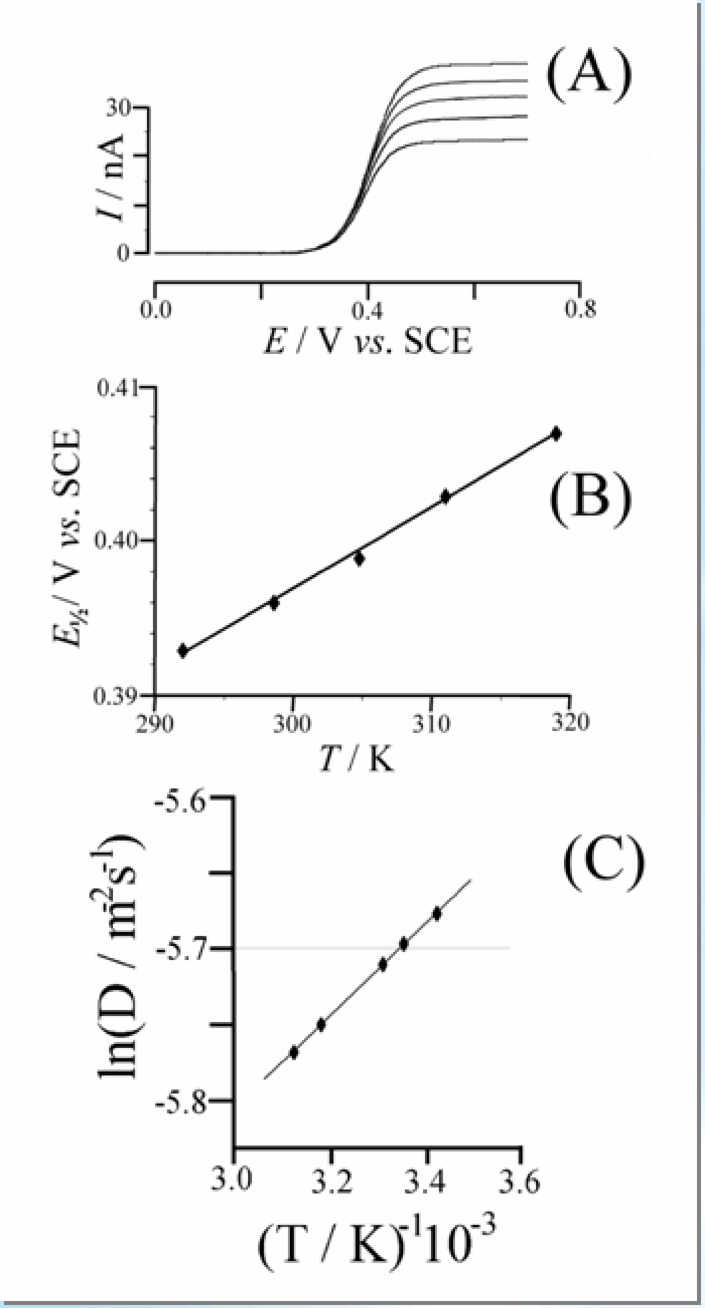


Mass Transport Effect Modest (ca. 40-fold) probably due to the absence of a vapour bubble.

Effect of the Supporting Electrolyte on the Current Enhancement



Plot of the microwave enhanced current divided by the steady state current under ambient condition as a function of $T_{electrode}/T_{bp}$ for the oxidation of 2 mM ferrocene at different microwave power settings at a 25 μm diameter platinum disk electrode in DMF at different supporting electrolyte concentrations (0.1, 0.05 and 0.01 M NBu_4PF_6).



Important Parameters:

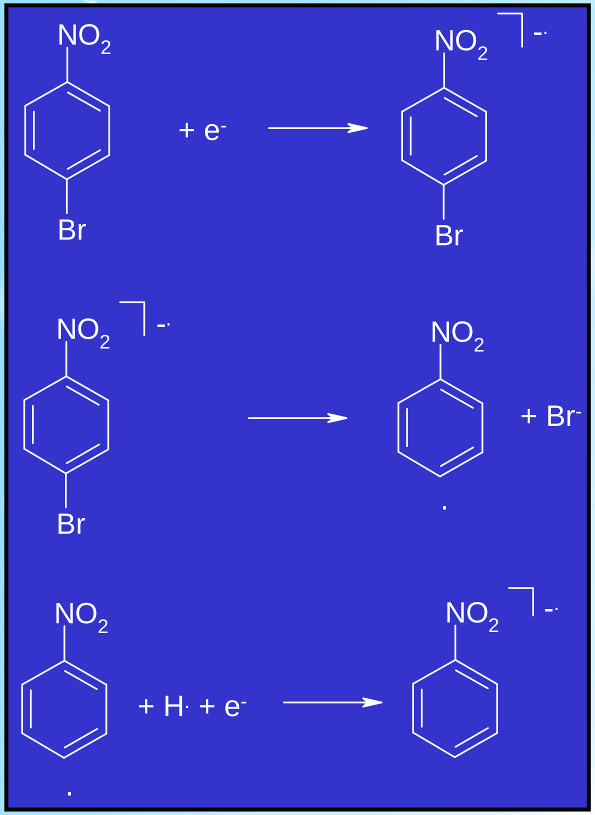
-The half wave potential

-The Tomĕs criterion

$$E_{3/4} - E_{1/4} = \frac{RT}{nF} 2.22$$

-The limiting current

Kinetic Parameters for Microwave Activated Processes in Organic Solvents: ECE Processes

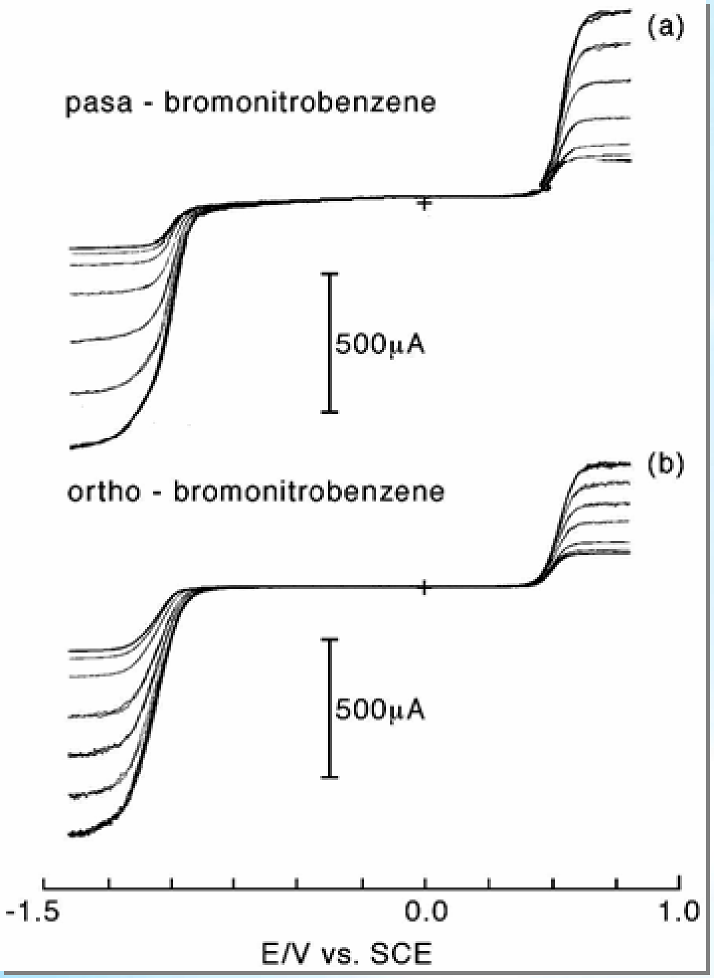


Electron Transfer

Chemical Step

Electron Transfer

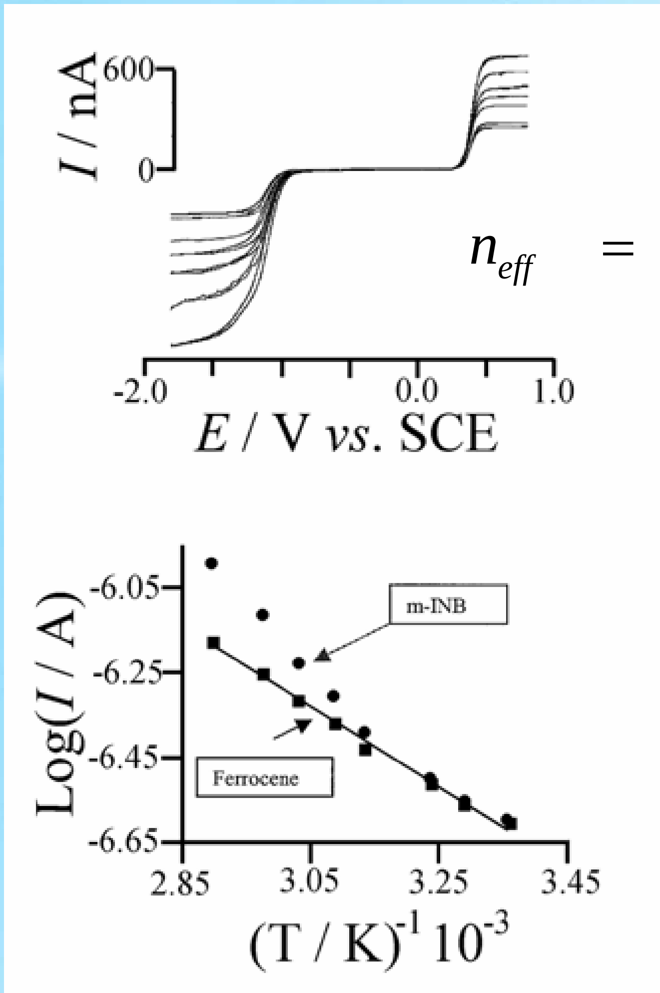
The Reduction of *para*- and *ortho*-bromo-nitrobenzene:



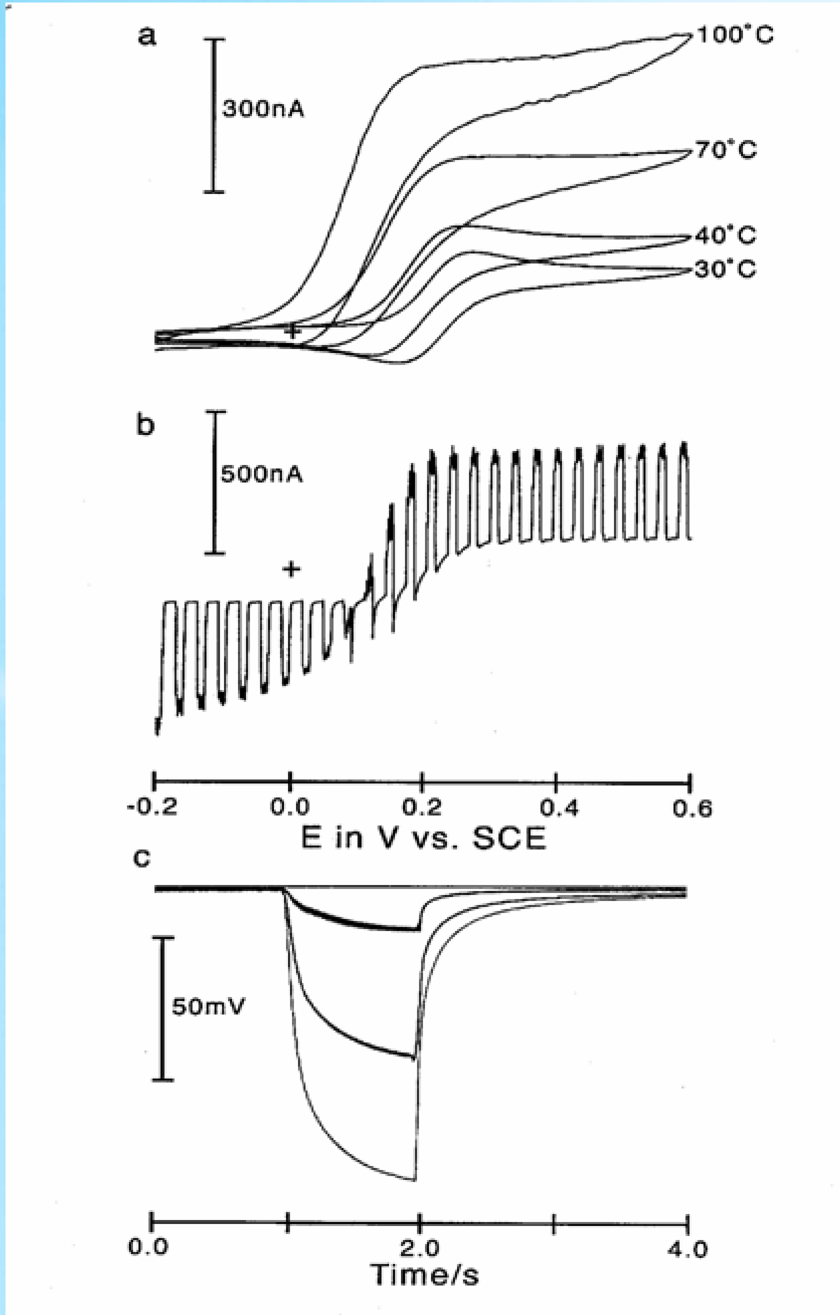
Always **one** electron transferred

Always **two** electrons transferred

The Reduction of *meta*-Iodo-nitrobenzene



$$n_{eff} = \frac{I_{\lim}}{I_{\lim}^{0}} = 2 - \frac{\tanh\sqrt{\delta^2 k / D}}{\sqrt{\delta^2 k / D}}$$

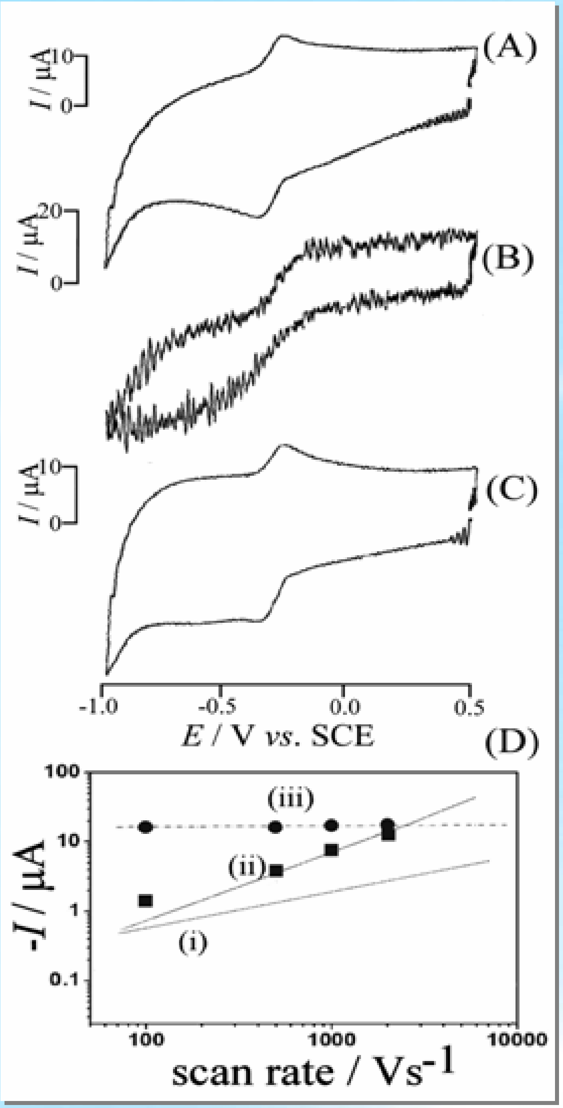


High Temperature Cyclic Voltammetry

Temperature Transient Voltammetry

Chronopotentio-metric Temperature Measurement

High Scan Rate Voltammetry under Microwave Radiation for the Reduction of $Ru(NH_3)_6^{3+}$



$Ru(NH_3)_6^{3+}(aq) + e^- \rightarrow Ru(NH_3)_6^{2+}(aq)$

25 µm diameter Pt microelectrode

Scan rate = 1000 V s^{-1}

9 mM $Ru(NH_3)_6^{3+}$ in 1 M KCl

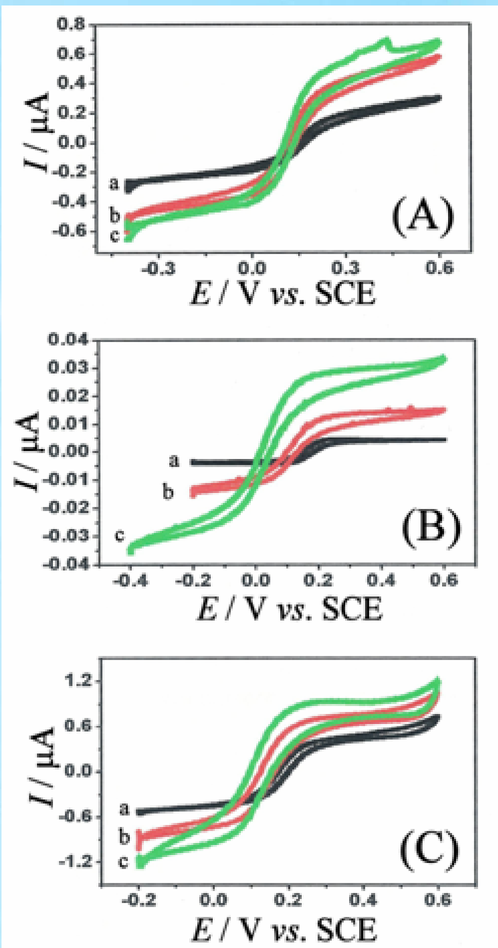
Voltammetry under sub-millisecond time domains in presence of microwaves gives concentration dependent limiting currents.

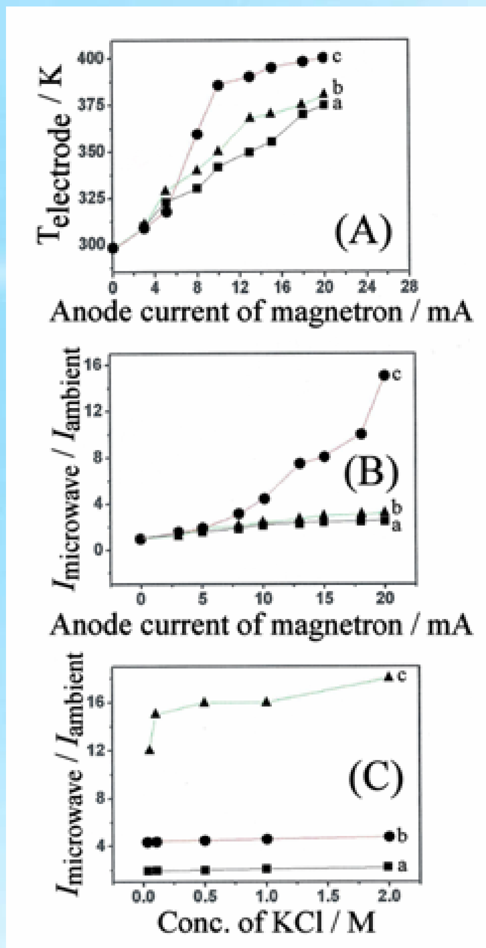
Possible Applications of Microwaves:

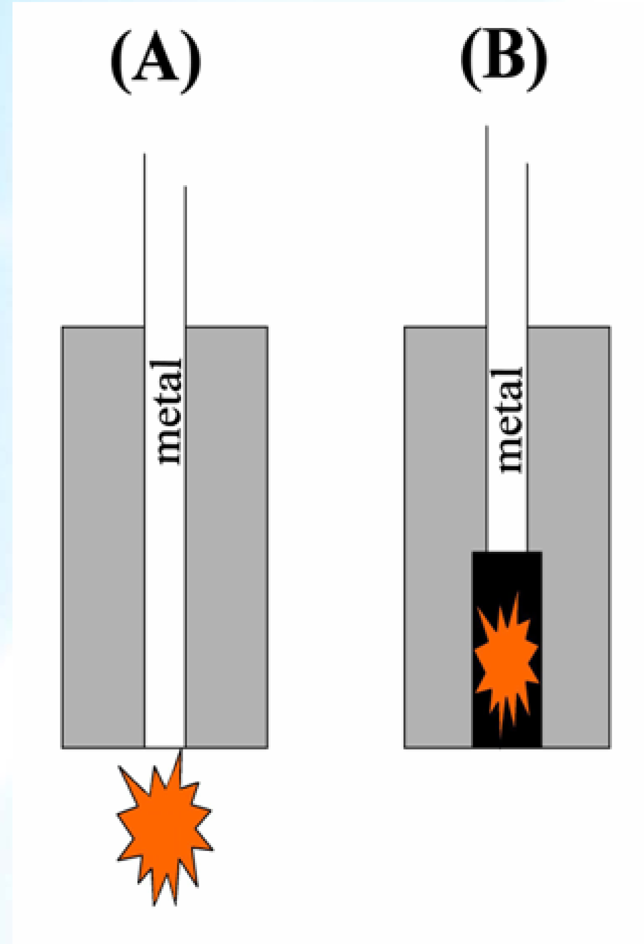
- ✓ **Microwave Enhanced Electroanalysis** for in situ Sample Mineralisation and Liberation/Decomplexation e.g. in Emulsions
- ✓ **Microwave Enhanced Electroanalysis** for high speed determination of low concentrations of heavy metals
- ✓ **Electroanalysis based on Modified Electrodes** for example with accumulation/extraction and thermal release
- ✓ **New Types of Electrode Processes** with ‘heat shock’ pathway e.g. amino acid analysis based on thermal formation of redox intermediates/ thermal discrimination
- ✓ **Small Scale Electrosynthesis** for example with array electrodes thermally enhanced processes (organic/inorganic)

Carbon Electrodes for Microwave Enhanced Electrochemistry:

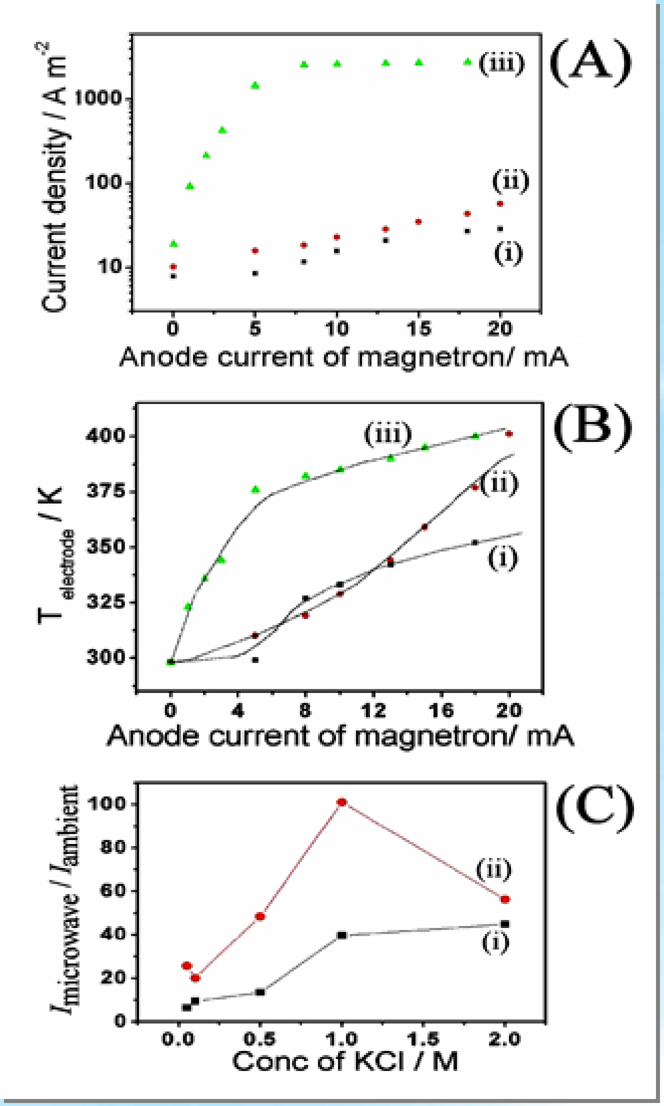
Arrays of carbon microelectrodes, a 33 micron diameter glassy carbon electrode, a boron-doped diamond electrode







The Effect of Microwave power on Current and Electrode Temperature:

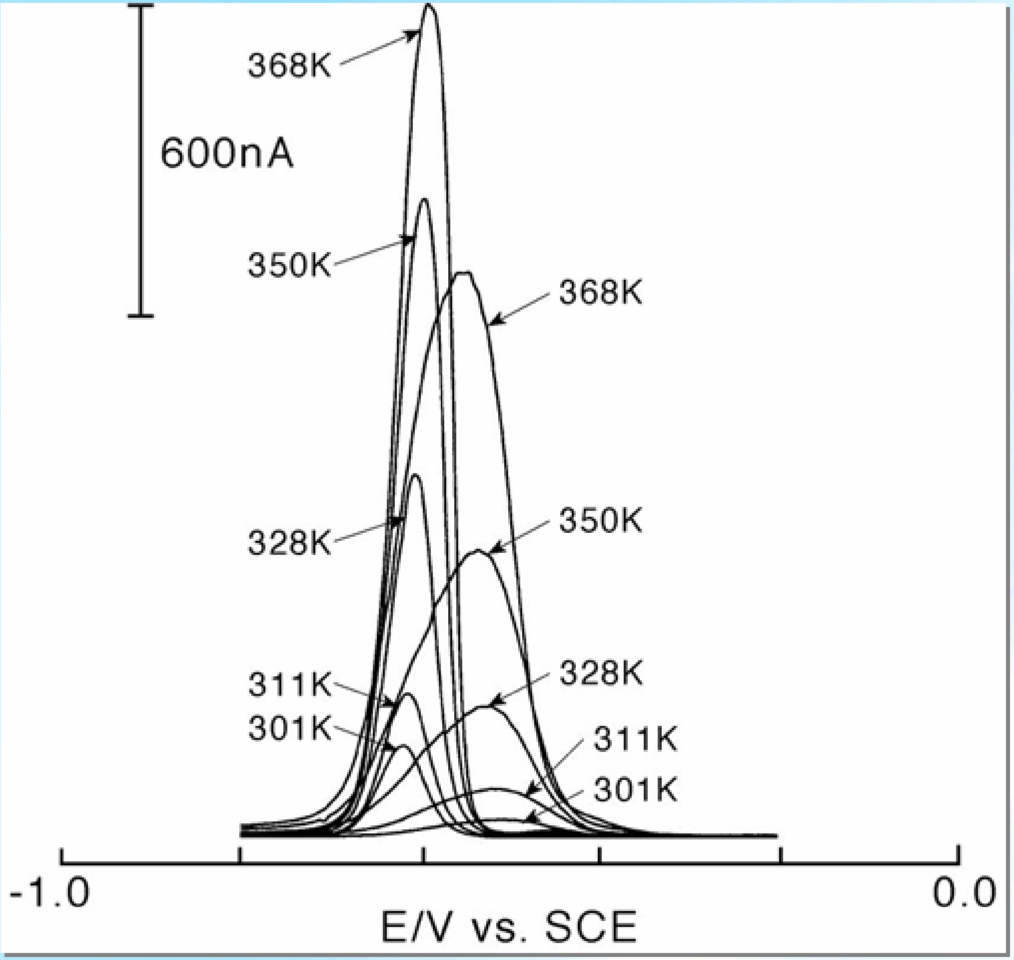


Increase of current with microwave power (extreme currents at small electrodes)

Increase of temperature with microwave power (local super-heating at small electrodes)

The Effect of Supporting electrolyte concentration on the current enhancement (dielectric loss ε'' increases with electrolyte concentration)

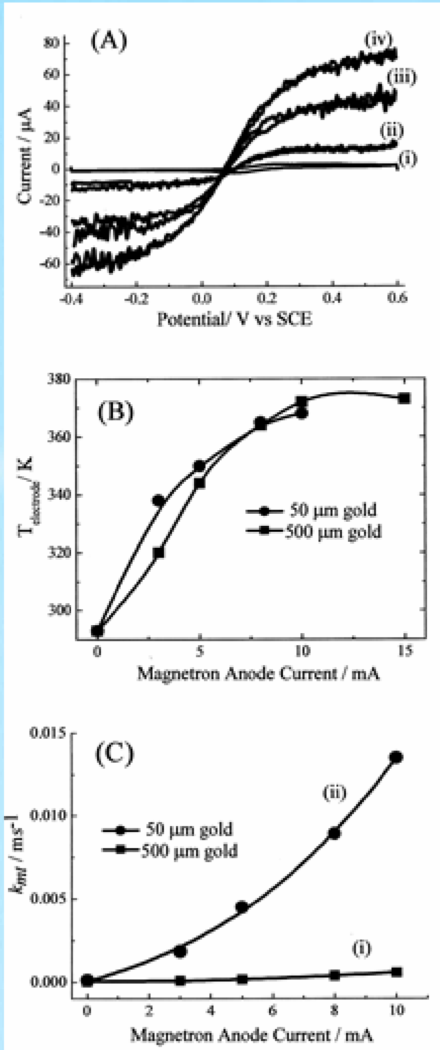
Square Wave Voltammetric Analytical Detection of Cd^{2+} / Triton-X



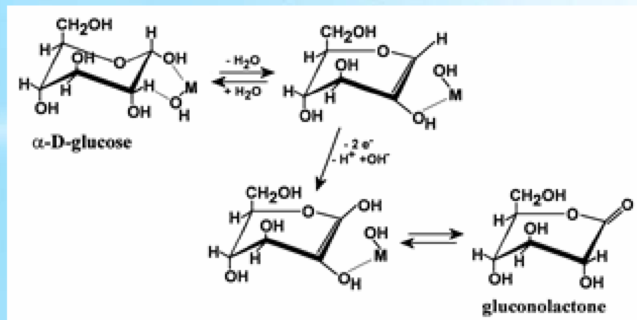
Measurements are faster and higher currents are detected.

Measurements in difficult matrices (e.g. with Triton-X) become possible.

Glucose Oxidation in Alkaline Media:



Ferrocyanide calibration defines the temperature at the electrode surface and the mass transport.



The oxidation of D-glucose occurs as a surface catalytic process. Rate data at 50 μm and 500 μm diameter electrodes are different.