Solid-State Light Sources in Chemistry and Science: Utilizing the Benefits of Light Emitting Diodes and Laser Diodes as the Light Sources of the 21st Century in Chemical Analysis, Detection, Fluorescence Microscopy, Visualization, Photochemistry and Teaching

INNOLEC 2012, 3-5 September 2012, Brno, Czech Republic

Mirek Macka

New Stars Professor

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University of Tasmania, Hobart, Australia

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SHORT COURSE

Course Information

Course Title: Solid-State Light Sources: How to Utilize the Benefits of Light Emitting Diodes and Laser Diodes as the Light Sources of the 21st Century

Categories:
1 - Life Sciences
2 - Capillary Electrophoresis
3 - Sensors
4 - Spectroscopy
5 - Teaching Analytical Chemistry
6 - Laboratory-on-a-chip/Microfluidics

Instructor(s): Mirek Macka **Course Number:** 137

Affiliation: University of Tasmania

Course Date: 03/15/2012 - Thursday **Course Length:** 1 Day Course

Start Time: 08:30 AM **End Time:** 05:00 PM

Fee: $455 ($655 after 2/13/12) **Textbook Fee:**

Course Description

This course will give an intensive introduction to the principles, properties and practical usage of Solid-State Light Sources (SSLSs) - Light Emitting Diodes (LEDs) and Laser Diodes (LDs). The participants will gain the necessary knowledge to understand the immense potential of SSLSs and will learn how to select and use LEDs and LDs for a wide variety of applications in chemical analysis, chemistry and life sciences in general. The emphasis will be on practical issues of usage of SSLSs and examples will be given as hands-on experiments. The course participants will receive free of charge a color printed workbook based on over 350 slides.

Target Audience

A wide range of participants will benefit including scientists, engineers, students, and educators as well as those currently only considering whether they could use LEDs in their work; and those involved in teaching of instrumental analytical chemistry, physical chemistry and photochemistry.

Course Outline

- Why use SSLSs - LEDs and LDs - in chemistry and science?
- A brief history – how it came to SSLSs being hailed as "the light sources of the 21st century"?
- Fundamentals (physical principles, construction) – what you should know as a user?
- Basics of SSLSs in respect to their applications in analysis, chemistry and life sciences
- Application areas: examples will include a wide range of usage from optical detection, optical sensors, microfluidics, visualization, fluorescence microscopy, photochemistry, and teaching – attention will be paid to partic
- How to choose the right LED or LD?
- Practical issues of using SSLSs users should know of: powering, measuring optical characteristics, connecting LEDs into arrays etc
- Coupling of SSLSs to optical fibers
- Pulsed techniques: use of lock-in amplifiers and LEDs in TRF (time resolved fluorescence)
- Optical methods in chemical analysis with an emphasis on photometry and photometric detection in analytical flow-through methods (FIA, HPLC, CE), fluorimetry and optical detection methods in microfluidic chips, opti
- Fluorescence microscopy and visualization using inexpensive designs (less than $250)
- Basics of construction of simple LED-based photometers and fluorimeters
- Diode lasers for compact inexpensive LIF (Laser Induced Fluorescence) detection in on capillary and microfluidic chip formats
- LEDs as light sources for photochemistry including photopolymerisation of polymers such as porous polymer monoliths
- Other advanced and specialized methods such as heating with SSLSs, numerical modeling etc.
- Hands-on experiments: measuring emission spectra, optical power, intensity, transmittance, absorbance, pulsing LEDs and use of lock-in amplifier techniques
- Workshop on examples from participants' own specific usage, questions, discussion

Course Instructor's Biography

Mirek Macka is a New Stars Professor at the University of Tasmania, Australia. He earned his Ph.D. in Chemistry from the University of Tasmania, Australia. He has published over 140 journal papers on capillary electrophoresis, liquid chromatography, miniaturized and microfluidic chip based analysis, and use of LEDs in other areas including in photoinitiated polymerizations of porous monoliths. He has been using light emitting diodes in his research and publishing extensively for over thirteen years.

Solid-State Light Sources: How to Utilize the Benefits of Light Emitting Diodes and Laser Diodes as the Light Sources of the 21st Century

Pittcon 2012, 11-15 March 2012, Orlando, FL

Mirek Macka

New Stars Professor

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and School of Chemistry,
University of Tasmania, Hobart, Australia
http://www.utas.edu.au/chem; http://www.across.utas.edu.au
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Course Instructor

- University of Tasmania, Hobart, Australia
  - →EC/Bologna
  - Joint (cotutelle) PhD enrolments

  - ACROSS
    Australian Centre for Research on Separation Science
    http://www.across.utas.edu.au/
  - Hosting **HPLC 2013** http://hplc2013-hobart.org/

ACROSS (Australian Centre for Research on Separation Science)

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Course Participants

- Introductions
  - Where from, areas of expertise & interest
    - Level of knowledge in SSLSs

  - Quiz ☺

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Pittcon 2012

- Course history
  - Pittcon 2009
    - LEDs
      - 333 slides ☺
  - Pittcon 2012
    - Solid State Light Sources (SSLSs)
      - 380 slides


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The 2012 Short Course Program offers skill-building training for chemical professionals that will add significant value to their Pittcon experience. Many attendees have stated that participation in Short Courses is the primary factor that justifies their attendance at Pittcon year after year.

Courses range in length from one half day to two days and are taught by experienced professionals who are experts in their fields. The value of course attendance is enhanced by the opportunities to network with your peers and share your experiences in face-to-face interactions with instructors and fellow attendees.

WHY TAKE A SHORT COURSE?

- Gain valuable technical knowledge in your field
- Improve job productivity
- Obtain training in new technologies
- Provide career and professional development
- Enhance your knowledge in a particular field
- Obtain instruction by renowned professionals who are experts in their fields
- Take advantage of affordable costs compared to other venues

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Free Conference Registration – Take three (3) PAID *(does not include free)* Short Courses and receive **FREE** conference registration.

REGISTRATION FEES AND INFORMATION

All participants must sign in at the Short Course office and should bring receipts for the courses and the textbooks. Paid participants will receive links and personal passwords to download and print course notes 7-14 days before Pittcon begins. Please bring a hard copy of your Short Course notes and/or a laptop, if so desired, for note-taking. Calculators may also be useful for some courses.

Textbooks are recommended for some Short Courses. Textbook cost is not included in the course fee.

Short Course Fees	Thru 2-13-2012	After 2-13-2012

http://www.pittcon.org/short/index.php[13/09/2011 07:16:15]

INNOLEC Masaryk University Brno, 3-5 September 2012

Course schedule

- Morning
  - Intro
    - Why use SSLSs = LEDs &LDs
    - Basics
    - Usage areas
    - Coffee break 10:15-10:30
  - Practical issues
    - Choosing the right LED or LD
    - Powering, connecting LEDs into arrays
    - Measuring optical characteristics
    - Coupling of SSLSs to optical fibers
    - Lunch break 12:15-13:00

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Course schedule

- Afternoon
  - Background – what you should know
    - A brief history - ‘Alloy Road’
    - Fundamentals: Physical principles, design
    - Coffee break 14:45-15:00
  - Usage
    - Illumination, fluorescence microscopy & visualization
    - Optical analytical methods: photometry, fluorimetry
    - Photochemistry: photoinitiations, photolithography
    - Heating, other usage
  - Course evaluation, feedback, close

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Course Outline

- ‘Experiments’ summary
  - Powering LEDs
  - Protecting LEDs from wrong voltage polarity
  - Measurement of bandgap energy
  - Measurement of Planck’s constant
  - Measurement of emission spectra of LEDs
  - Peak emission wavelength and intensity shift
  - Measurements of optical power and calculation of wall-plug efficiency
  - Optical detection setups
    - Photometry
    - Fluorimetry

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Course Outline

- Course philosophy & remarks
  - Combine theory & practice
    - Background & theory
      - Focus on LEDs (NOT analytical methods, photochemistry etc.)
    - Practical aspects of use
    - Experiments
  - Different areas of LED use
  - Workshop-type course
    - **Please comment and ask questions any time**
  - The $ value

$ = 'Home-take-value'

$ Aim: $\Sigma\ (HTW_i) \geq \$455$ ☺

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Course Outline

- Course philosophy & remarks
  - **Safety in work with LEDs**
    - Only low-power LEDs safe to use shown in this course
    - Read, understand and uphold
      - Laws & regulations
      - OH&S standards – at workplace, in your lab
      - Manufacturer's recommendations
    - Caution especially in respect to
      - **Possible damage to eyesight**
        - **Laser light (e.g. green laser pointers!)**
        - **UV-light (UV-LEDs)**
        - **High light-output LEDs especially blue-violet**
      - Electricity
    - Personal protection to be used including **glasses!**

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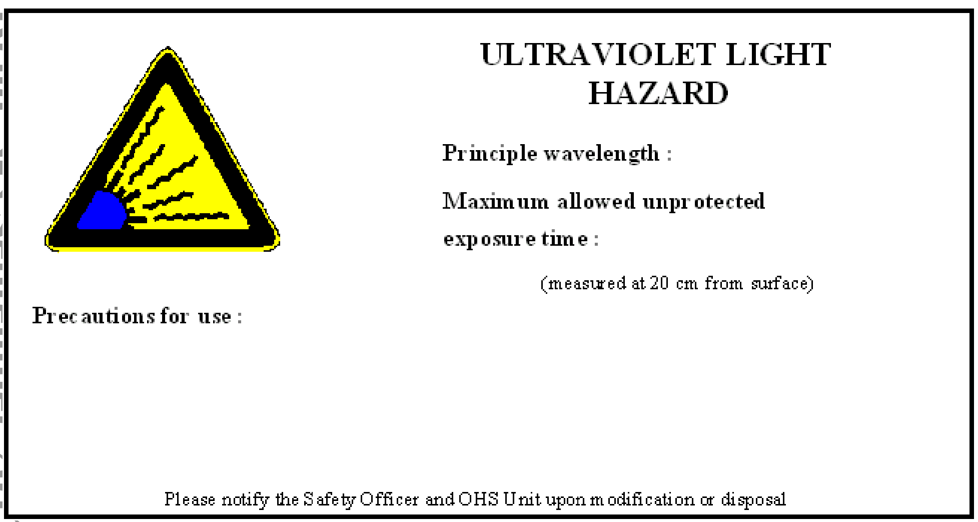
Course Outline

- Typical warning signs
  - UV LEDs, laser diodes



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Course Outline

- Many modern SSLSs are high power light sources → safety! (eye protection)
- SSLSs: LEDs *vs.* LDs


  - LEDs are 'safer' = 'easier' to use
- Power supply units are electric devices → safety!
- Always observe safety rules!!!

$ PREVENT DAMAGE & LOSS


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Course schedule

- Morning
  - Intro
    - **Why use SSLSs = LEDs &LDs**
    - Basics
    - Usage areas
    - Coffee break
  - Practical issues
    - Choosing the right LED or LD
    - Powering, connecting LEDs into arrays
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    - Coupling of SSLSs to optical fibers
    - Lunch break

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Solid State Light Sources

- ## Why SSLSs?

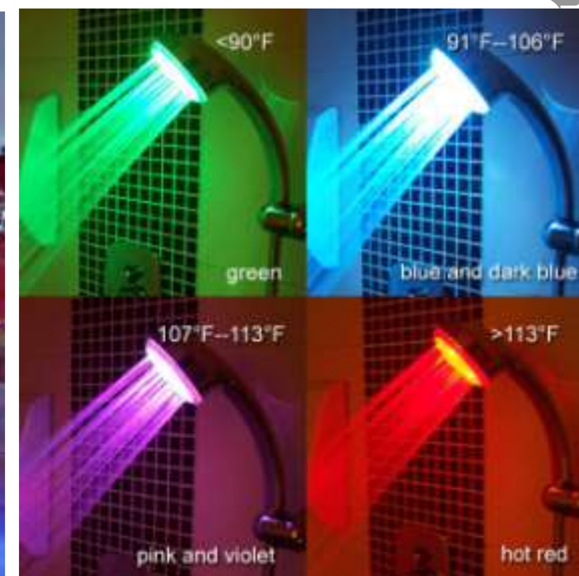
"It is expected that optics, also referred to as <u>photonics, will surpass electronics</u> in the 21st century in terms of the size of the industry reliant on it."
http://www.sfi.ie/investments-achievements/research-showcase/shedding-light-on-many-subjects/

"The world market for photonics products reached € 270 billion in 2008, of which € 55 billion was produced in Europe — a growth of nearly 30 % since 2005"
http://www.photonics21.org/download/SRA_2010.pdf

"In the next decade we will see a <u>massive transformation of the lighting industry</u> towards energy efficient Solid State Lighting (SSL)"
http://www.photonics21.org/download/olae_sra.pdf

Solid State Light Sources

- **SSLSs - 21st century light sources**
  - **LED**s, Laser Diodes (**LD**s), Superluminiscent LEDs (**SLED**s), Quantum Cascade Lasers (**QCL**s)
  - Use: Everywhere!



  - Local (Australian) example:
    - LED-solar power low-cost lamps for Africa etc.
      - http://www.barefootpower.com/
      - Award: http://www.investinaustralia.com/news/barefoot-power-wins-produ

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SSLSs: 'non-chemistry'

- They have ***many advantages*** and still a few weaknesses
- Benefits from ***large industries*** (much larger then chemistry)
  - Consumer electronics
  - Lighting
  - IT & CT
  - Automobile
  - Medical
  - Security & military

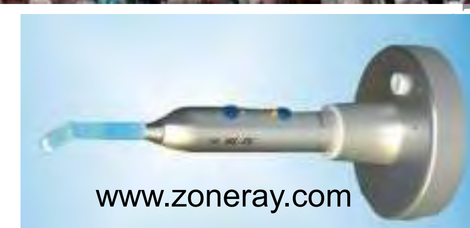


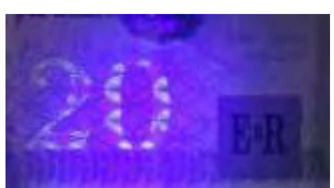






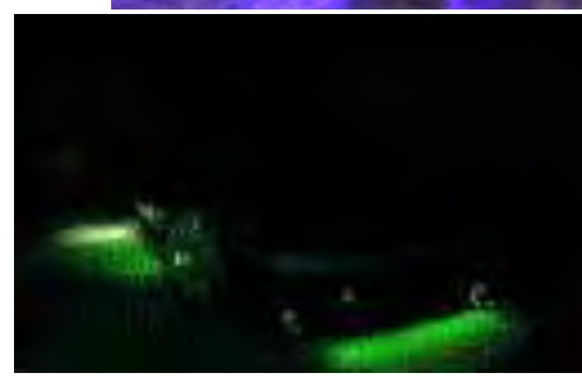





Why use LEDs?

- LEDs are everywhere!
  - Energy savings
  - ‘Cold’ light
  - Light colour/ light temperature adjustment
  - …



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LEDs are useful & cool

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LEDs are useful & cool

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LEDs are useful & cool

'Swiss army knife' element to SSLSs ☺

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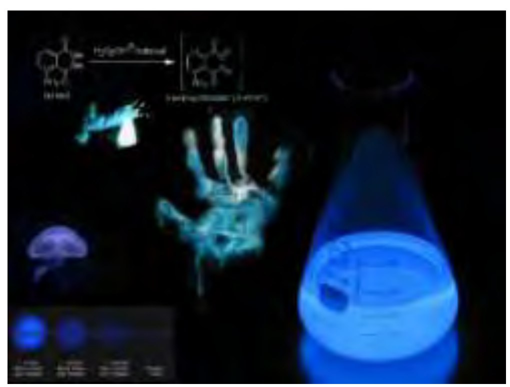
Why use LEDs?

- LEDs are one of several major modern technologies with huge socio-economic impact on global scale
  - Energy savings → LEDs as Solid State Lighting (SSL) are expected to save ~10% overall electricity consumption in the next decade in the USA alone
  - Environmental protection → Potential huge benefits
  - New functionalities → SSL allows to control emission properties to degree not possible earlier



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Why use LEDs?

- LEDs relatively new and largely underutilised
- Judging the potential of new technologies is notoriously difficult ☺
  - I think there is a **world market for** maybe **five computers**.
    - *Thomas Watson, Chairman of IBM, 1943.*
  - What the hell it **might be useful** for…?
    - *Robert Lloyd, Dept. of Advanced Computational Systems, IBM, c.a. 1968 referring to **microprocessor***
  - There is **no reason** anyone would want a **computer in their home**.
    - *Ken Olson , President, Chairman and founder of Digital Equipment Corp., 1977.*

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Why use LEDs?

- **Examples of LEDs**
- What to expect?






- Future holds many surprises
  - “Do not underestimate the power of LEDs”
  - LEDs can be utilised in countless areas!
  - LED-based instruments can be built easily and cheaply

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- Morning
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    - Why use SSLSs = LEDs &LDs
    - **Basics**
    - **Usage areas**
    - Coffee break
  - Practical issues
    - Choosing the right LED or LD
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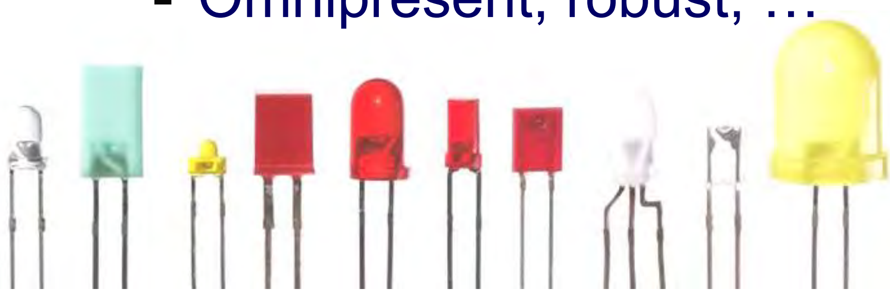
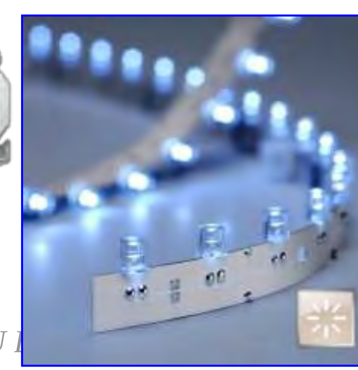
SSLSs for science?

- Why use SSLSs?
  - Conventional light sources
    - Incandescent, discharge lamps as light sources

1880 2007 ☺

  - SSLSs
    - Omnipresent, robust, …





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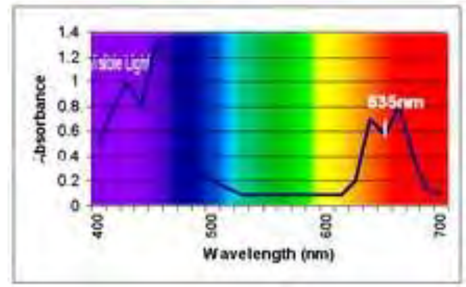
SSLSs: ‘non-analytical’

- LEDs as light sources in **many** areas
  - Plant science
    - Wavelength-selective light



  - Biotechnology
    - Green algae

  - Photochemistry
  - Photolithography – chip microfabrication
    - e. g. Breadmore MC et al.

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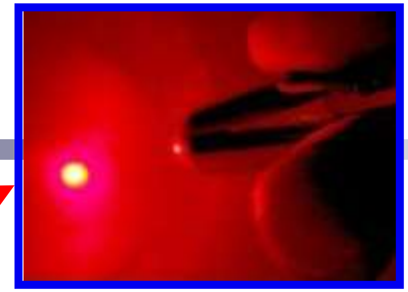
SSLSs in ‘our’ research

- LEDs, LDs, SLEDs
  - Optical detection
    - Fluorimetric
    - Photometric
      - Single-colour
      - White
  - Photoinitiated polymerisations of monoliths
  - Microphotochemistry

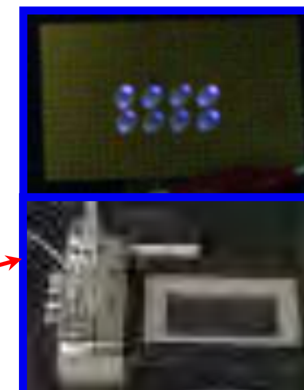


LED-IF and diode LIF

Single-colour LEDs: quasi-monochromatic light sources

White LEDs: broad spectrum light sources

Single-colour or white LEDs: photopolymerised monolith



Single-colour LEDs: photochemistry

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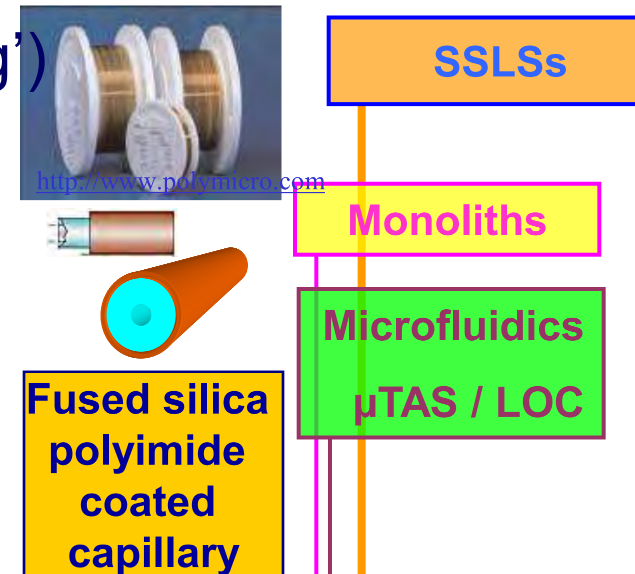
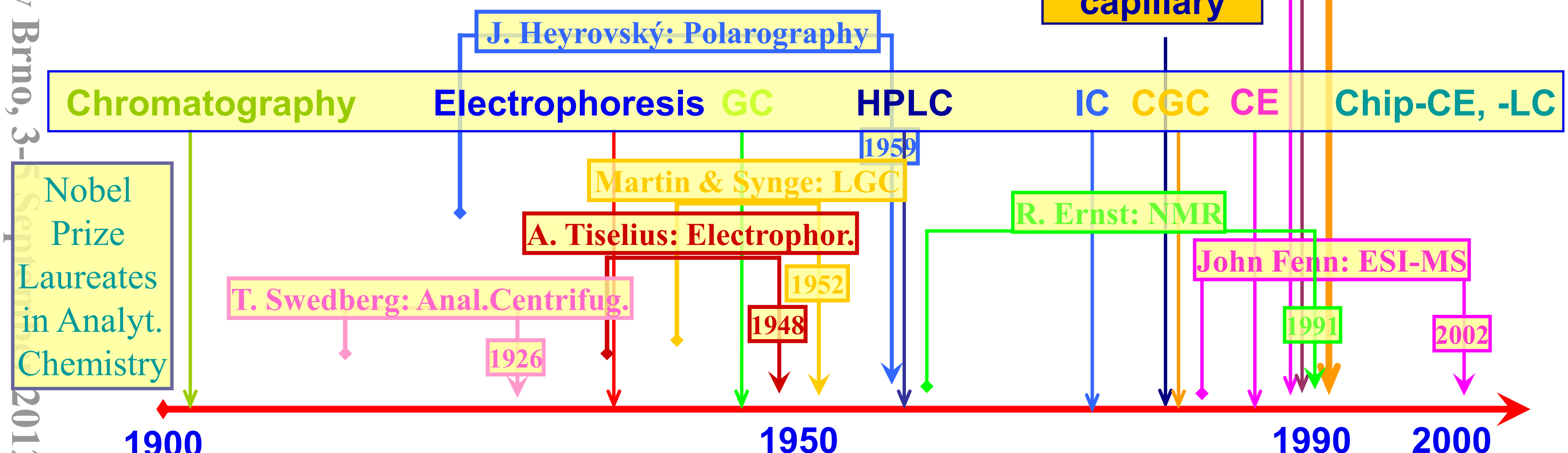
Analytical chemistry: 100 years

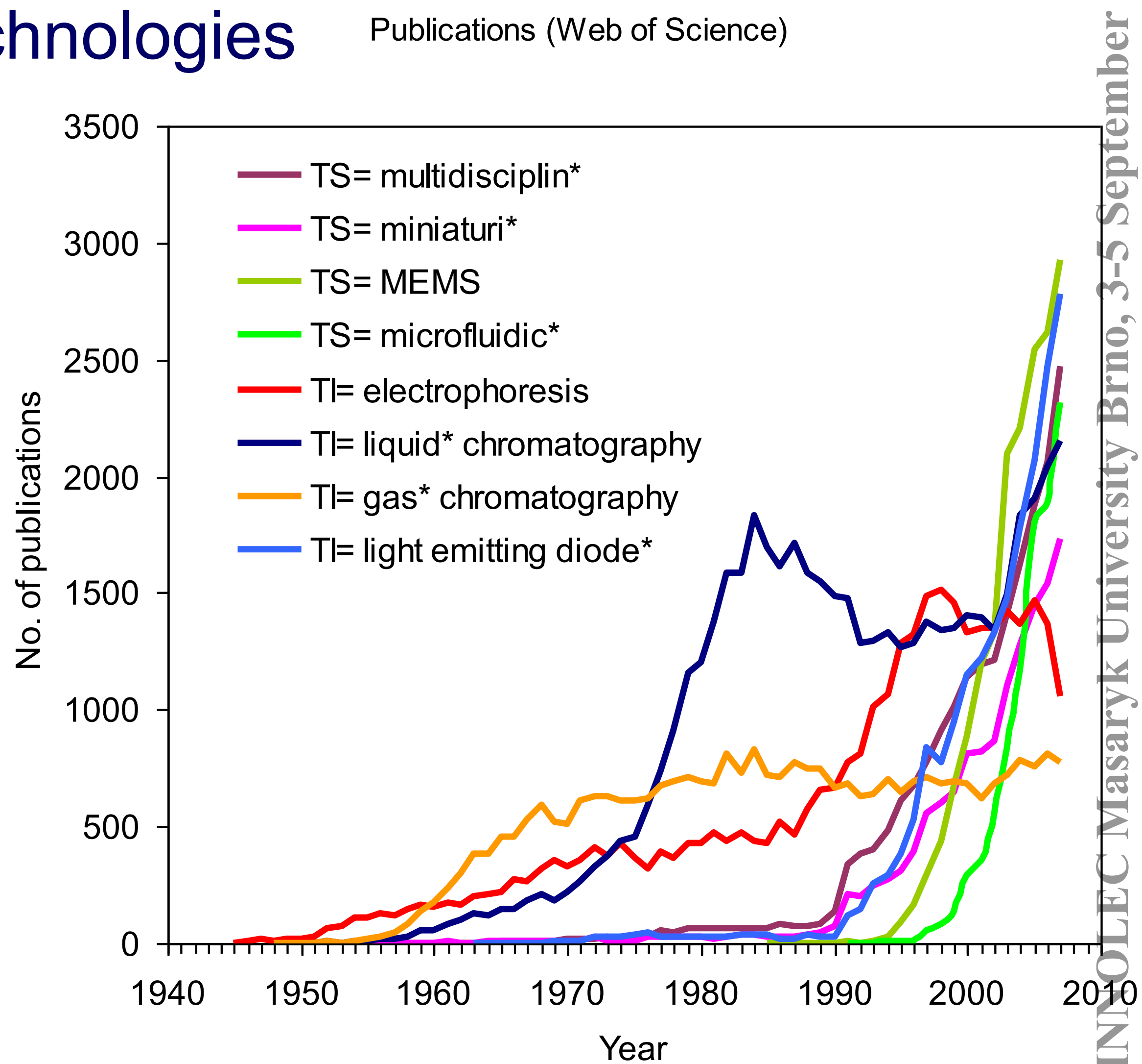
- The future?
  - Concepts & technologies ('enabling')
    - PI-coated FS capillaries (1979)
    - Microfluidics (1990s)
    - Monoliths (1990s)
    - SSLSs (1990s)





Analytical chemistry: 100 years

- What happened in the 1990s?
- New concepts & technologies in chemistry
  - Miniaturisation
  - MEMS
  - Microfluidics
  - Solid state light sources/LEDs
  - ..
  - Multidisciplinarity



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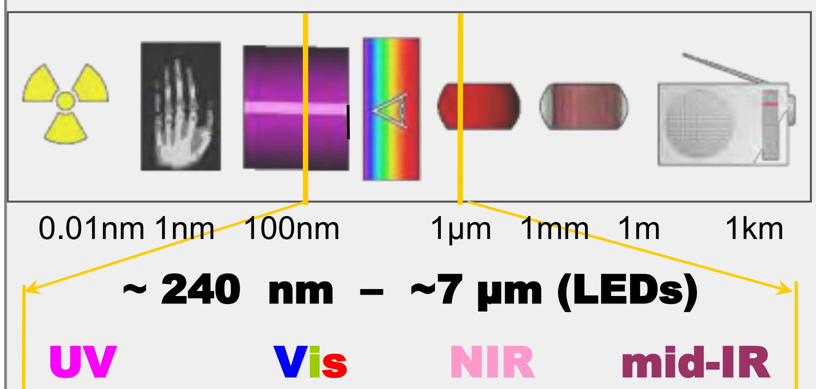
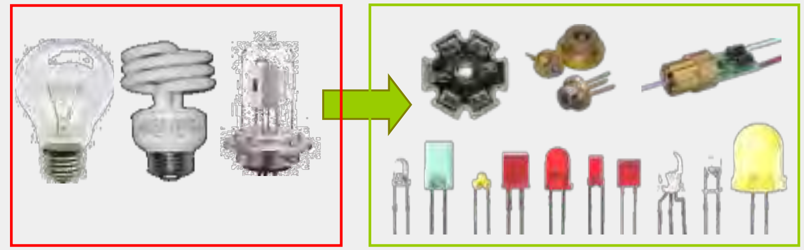
SSLSs in science

- What is available?
  - Spectral coverage
  - Properties

SSLSs spectral coverage



Traditional light sources vs SSLSs



Light sources - typical properties:

Traditional:		SSLS:
+++	Spectral coverage	- + +
(deep-UV to NIR)		(from 240 nm up)
+++	Mature well approved technology?	- + +
(up to 200 years)		(0 to ~40 years)
+ + -	Luminosity	- + -
- - -	Energy conversion, heat production	- ++
- - -	Radiative heating	+++
- - -	Miniaturisation compatible?	+++
- - -	Robustness	+++
- - -	Life time	+++
- - -	$$$	+++
- + -	Pulsed operation?	+++
- + -	Noise	+++
- + -	Future potential	+++

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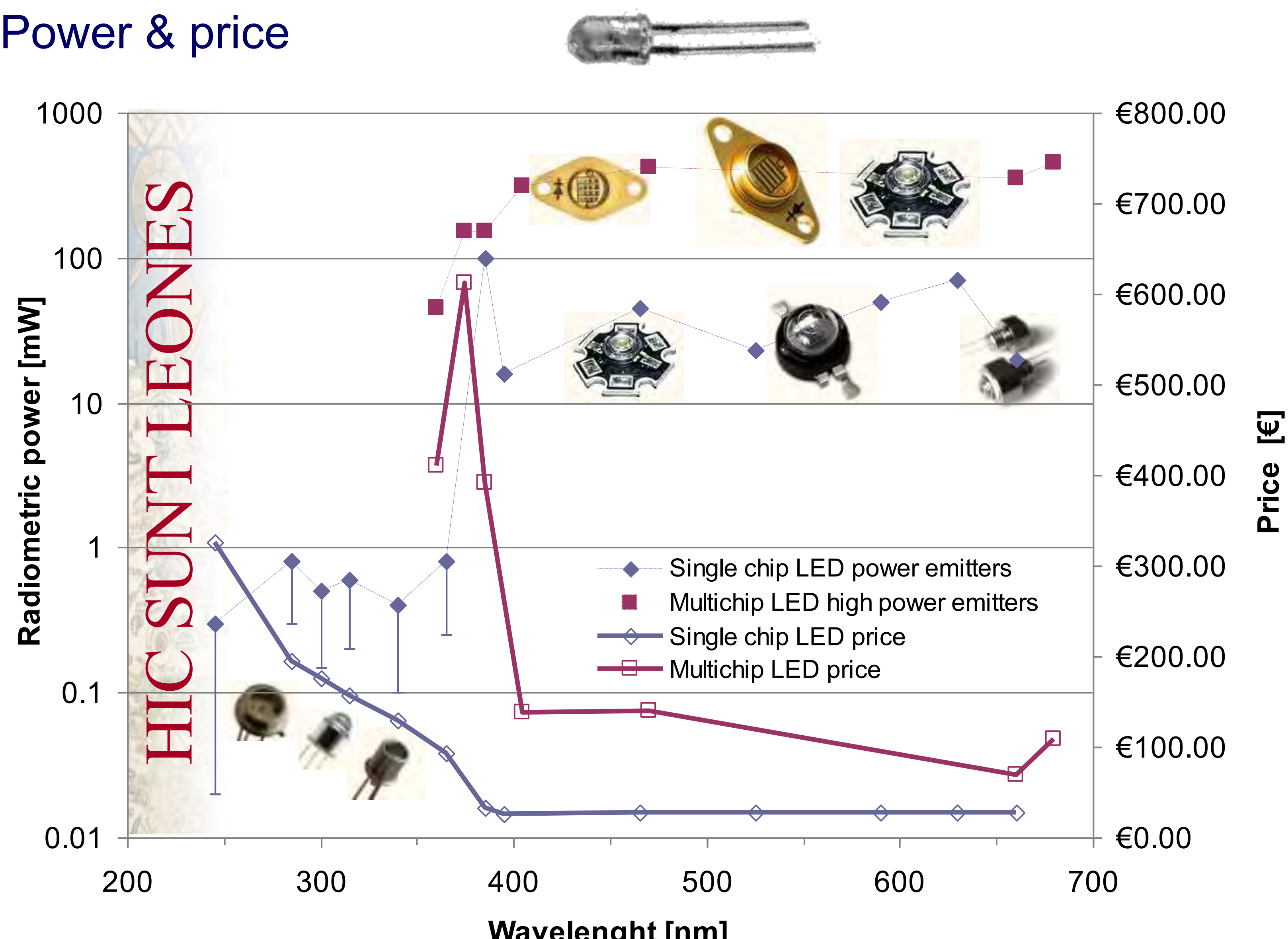
LEDs: What is available?

- Power & price



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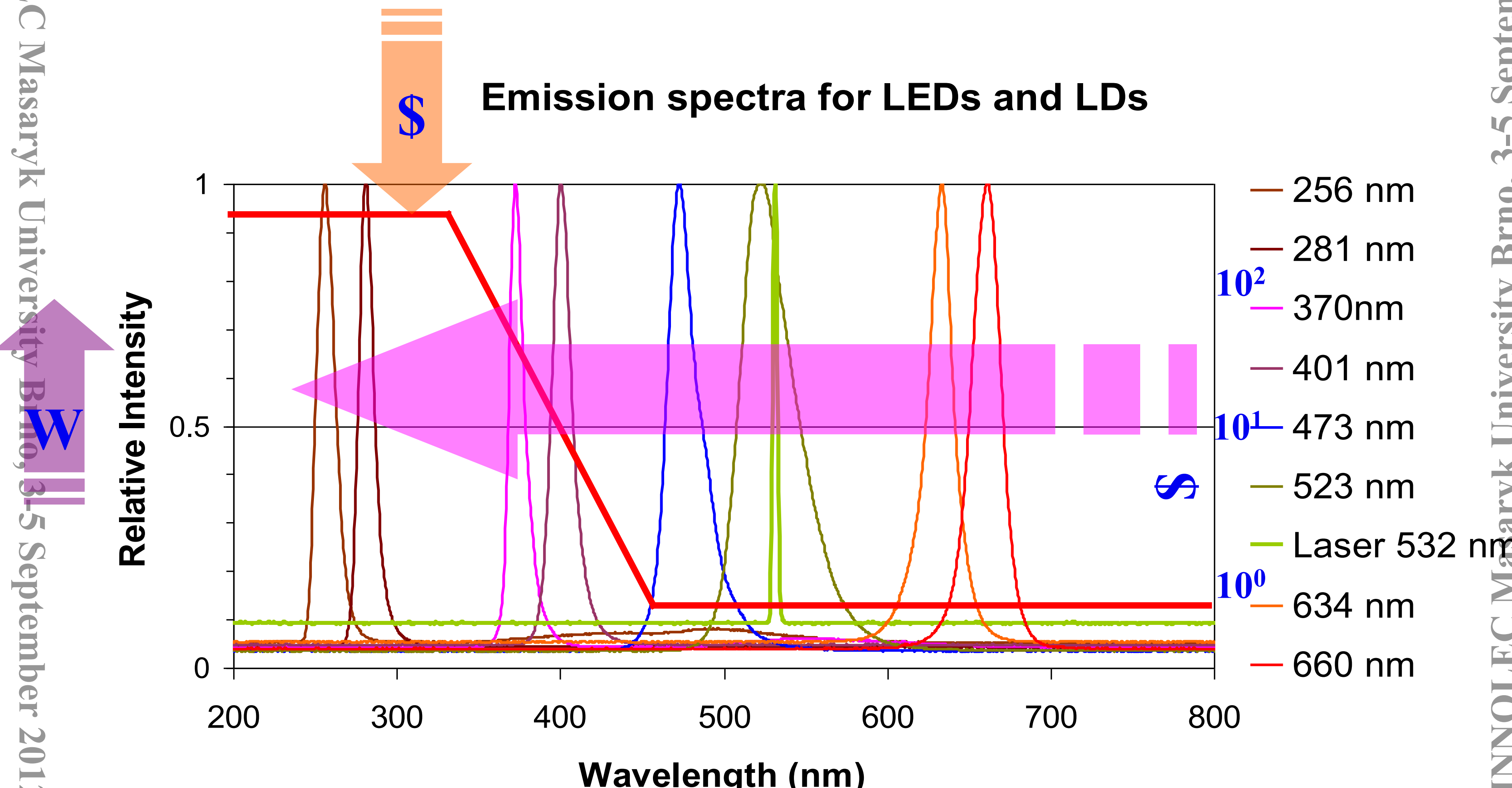
Future of SSLSs in science

- Performance/$ evolution trends
- LEDs: Spectra and prices now and into the future



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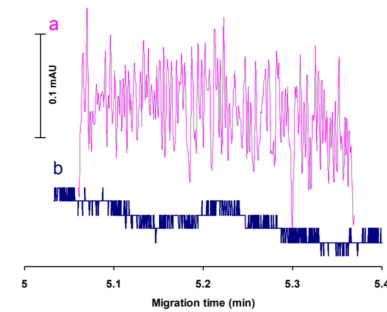
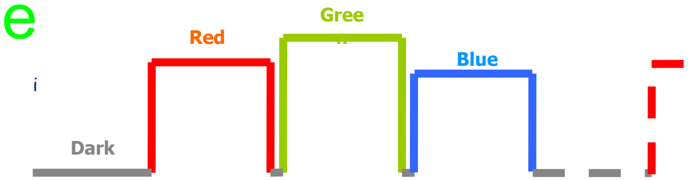
SSLSs for analytical devices?

- Advantages of LEDs
  - **Small, reliable & robust => miniaturised & portable!**
  - Low-cost: from <\$1 to ~\$50, but typically ~ \$10[1]

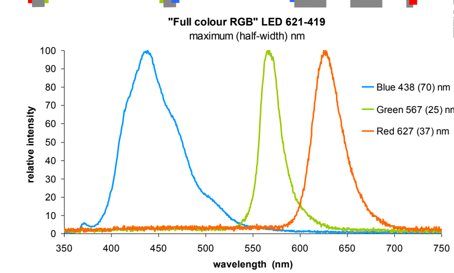
  - Long life-time: ~10^5 h & no fatal-failure
  - Very low noise → 10^{-5} AU
    - Used in various types of optical detectors (HPLC, FIA etc.)



  - Can be operated in a pulsed regime
    - Can be pulsed
      - At extremely fast rates => TRF

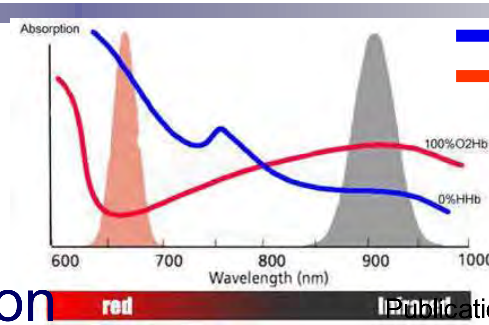


  - Single-, bi- or tri-coloured LED's available
  - Quasi-monochromatic: w(h/2) ~ 20-70 nm
  - 'Cold light'



SSLSs in analysis: history

- Blood oximeter **1972**
  - Cohen A, Wadswort N
    - Red/NIR light absorption
    - Pulsed operation
- 1990s: explosive growth
  - Analytical devices
    - FIA, LC, CE, chip
    - **1990-1995**
    - Trojanovicz
    - Cardwell & Cattrall & Scollary,
    - Huang, Dasgupta, Hauser, Yeung, Worsfold



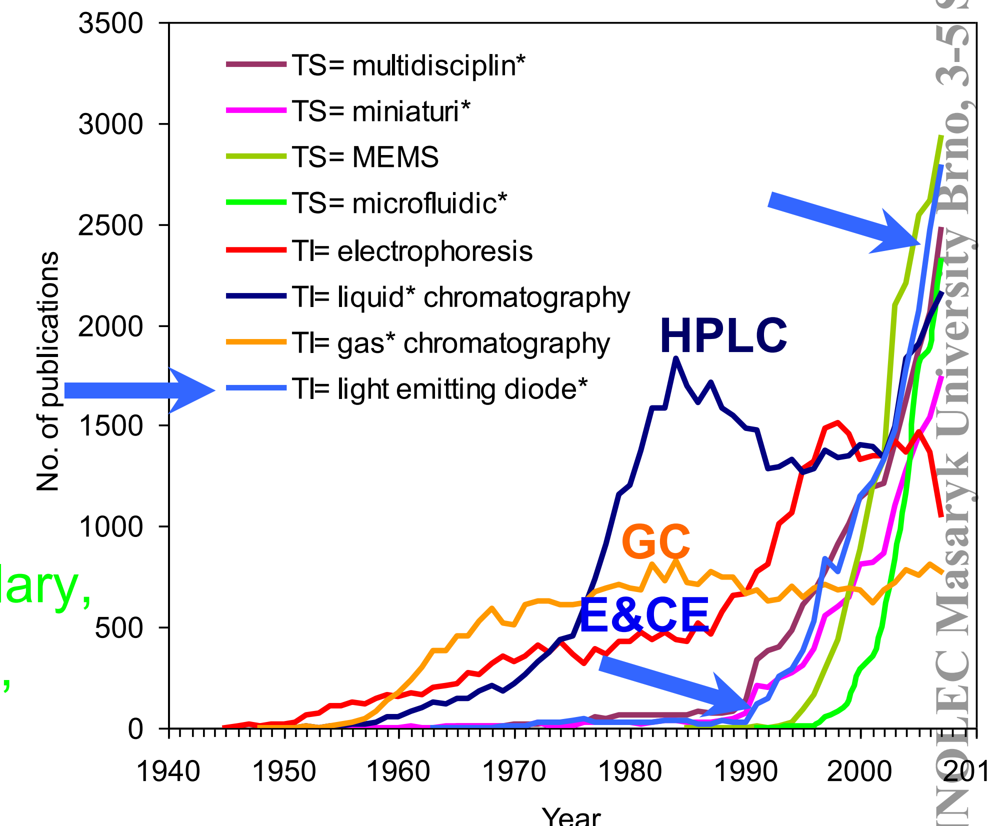
Deoxydated hemoglobin

Oxydated hemoglobin

oximeter.holisticphysio.com

www.medical-monitors.com

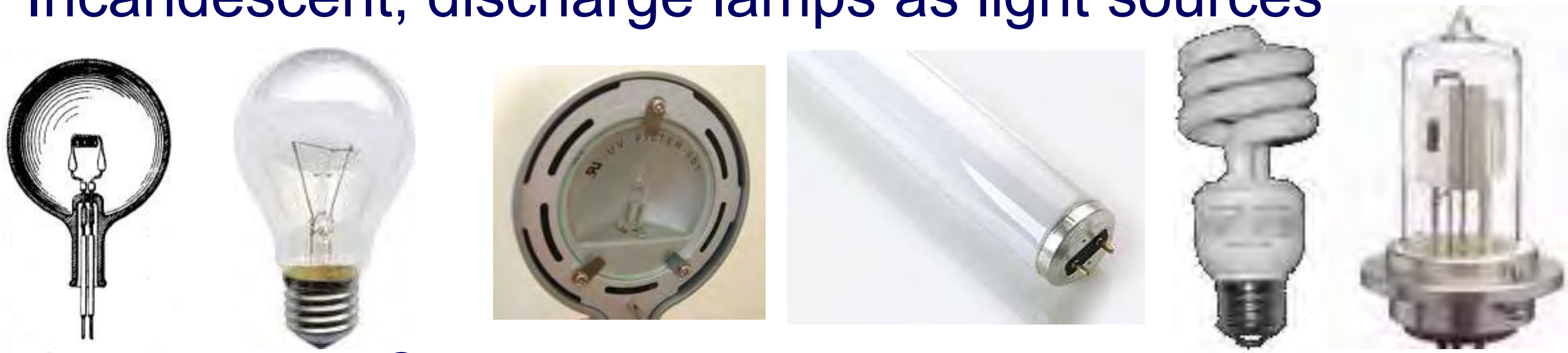
Publications (Web of Science)



Macka M., Andersson P., Haddad P.R., Linearity evaluation in absorbance detection: The use of light emitting diodes for on-capillary detection in capillary electrophoresis, Electrophoresis, 17(12), 1898-1905, 1996

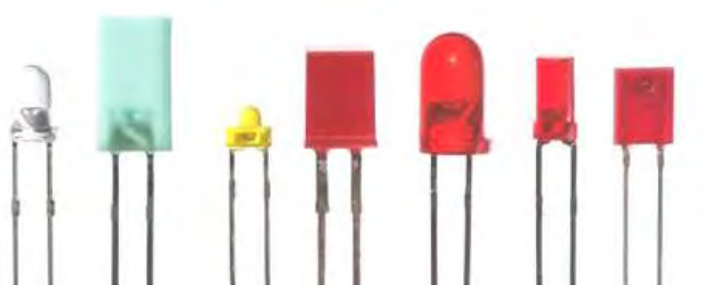
Why use LEDs?

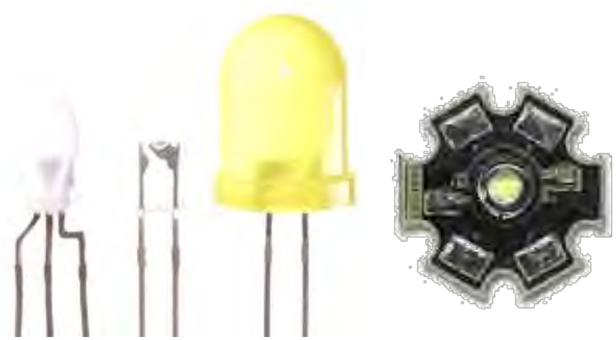
- Conventional light sources
  - Incandescent, discharge lamps as light sources



1880 2007 ☺

- LEDs
  - Omnipresent: lighting (SSL), IT, electronics, science & technology





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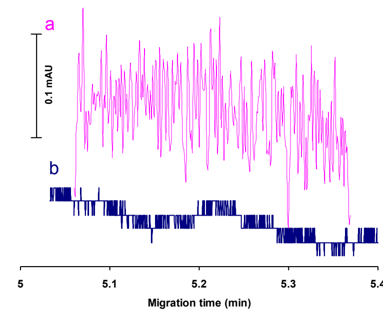
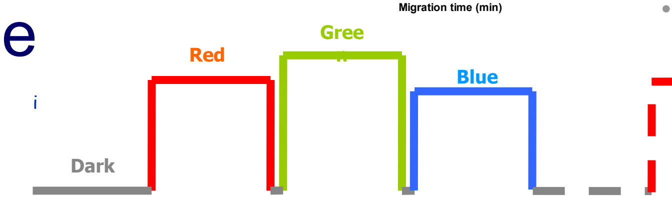
Why use LEDs?

- Advantages of LEDs
  - Small, reliable & robust → **miniaturisation compatible!**
  - **Cheap**: from <$1 to ~$50, but typically ~ $10[1]

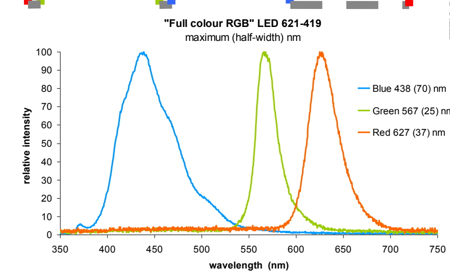
  - **Long life-time**: ~10^5 h (~11+ years)
  - Very low noise → 10^{-5} AU
    - Used in various types of optical detectors (HPLC, FIA etc.)



  - Can be operated in a pulsed regime
    - Can be pulsed at extremely fast rates



  - Single-, bi- or tri-coloured LED's available
  - Quasi-monochromatic: FWHM ~ 20-70 nm
  - **'Cold light'**



Course schedule

- Morning
  - Intro
    - Why use SSLSs = LEDs &LDs
    - Basics
    - Usage areas
    - Coffee break
  - **Practical issues**
    - Choosing the right LED or LD
    - Powering, connecting LEDs into arrays
    - Measuring optical characteristics
    - Coupling of SSLSs to optical fibers
    - Lunch break

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Modern light sources

- Traditional light sources
  - Spectra
    - Monochromatic
    - Broad spectrum light sources
      - White: colour temperature
  - Polarisation
    - Non-polarised *vs*. polarised
  - Modulation
  - Spatial distribution
  - Heat generation
  - Life expectancy
  - Robustness
  - Energy consumption

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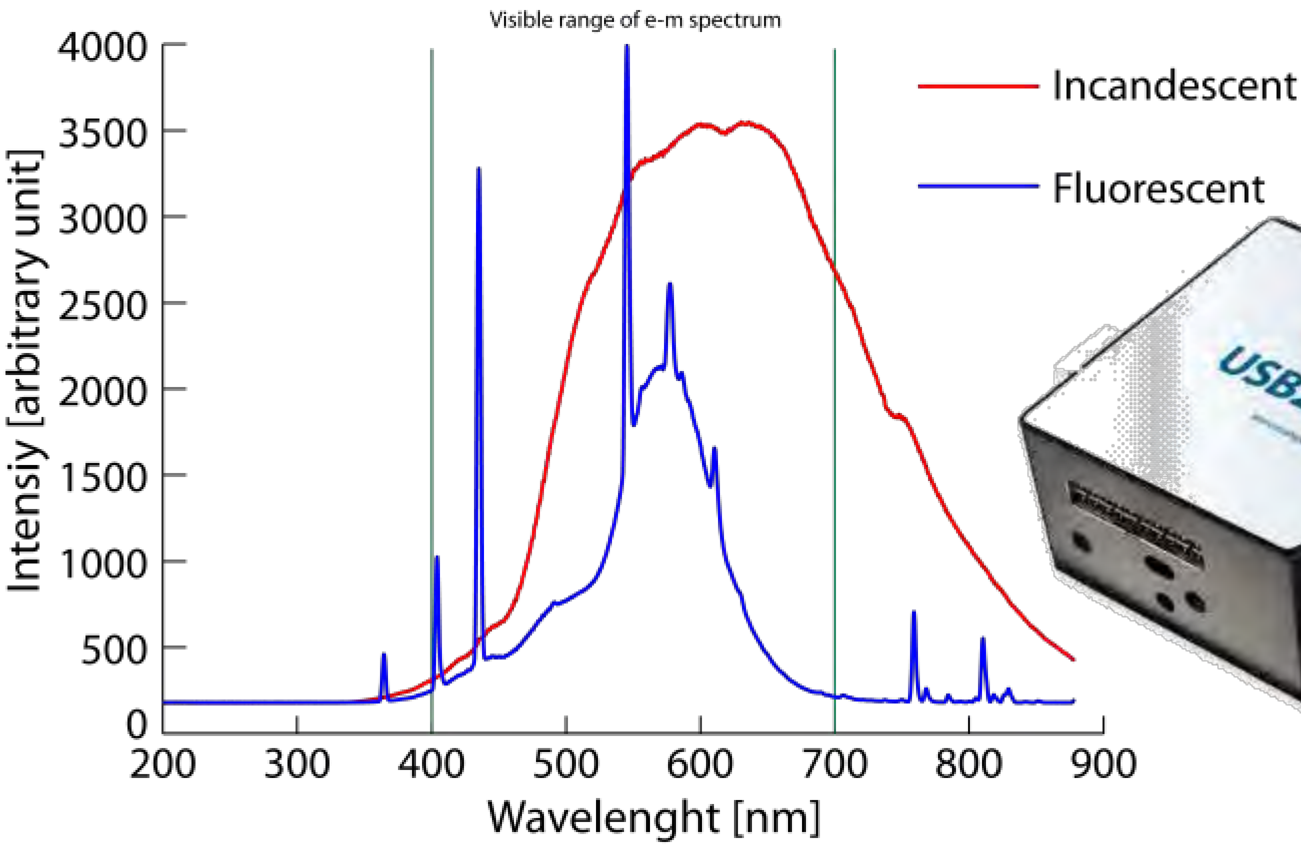
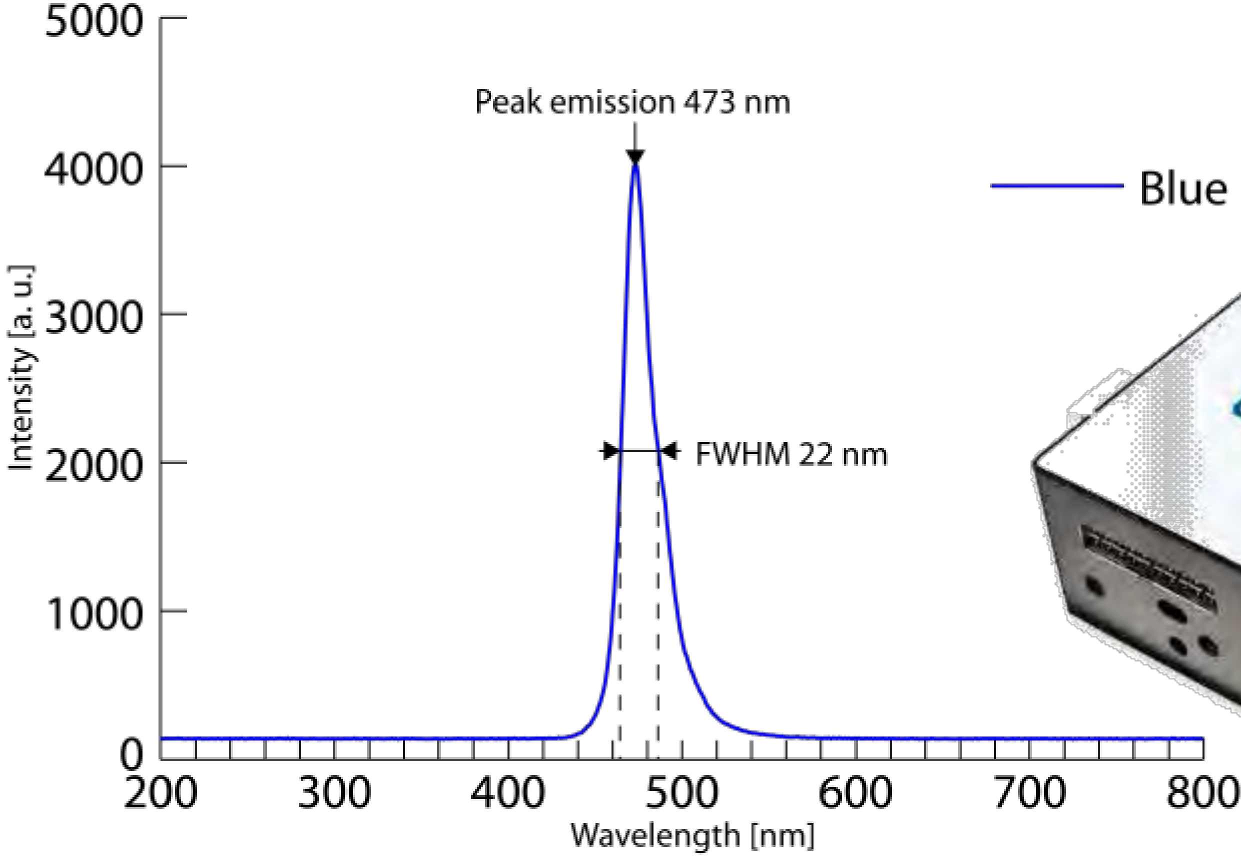
Modern light sources

- Spectra
  - Often complex, sometimes poorly defined



  - **Measurement of emission spectra**

- Measurement of LED spectra



$ Prevent wasting resources by experimenting with undefined or wrong wavelength LEDs

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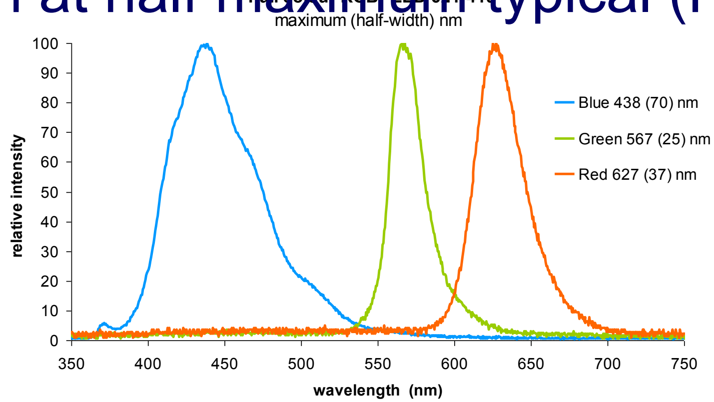
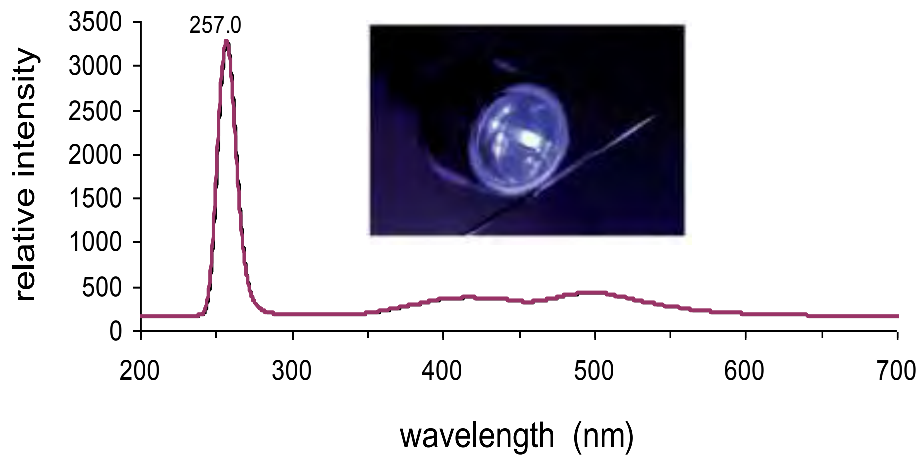
Basic principles and fundamental aspects

- LED emission spectrum
  - Quasimonochromatic
    - Full width at half maximum typical (FWHM) 20-30 nm

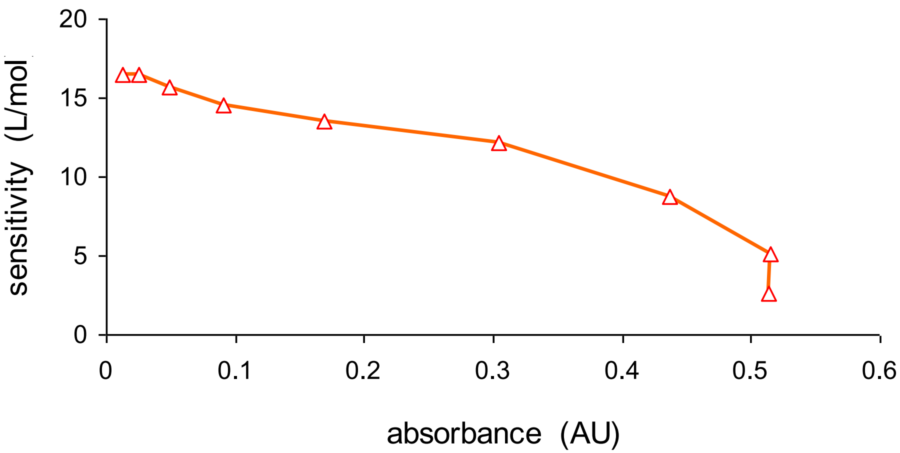


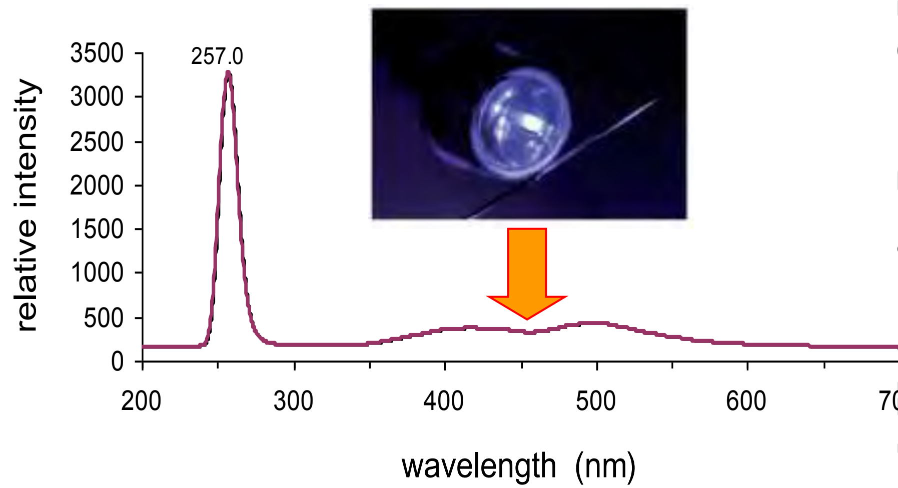
- **Beware of some undesirable parasitic emissions**



Photometric (single-detector)

- Deep-UV-LEDs: 255nm
  - Performance
    - Baseline noise N~0.1mAU
    - Poor linearity => stray light?





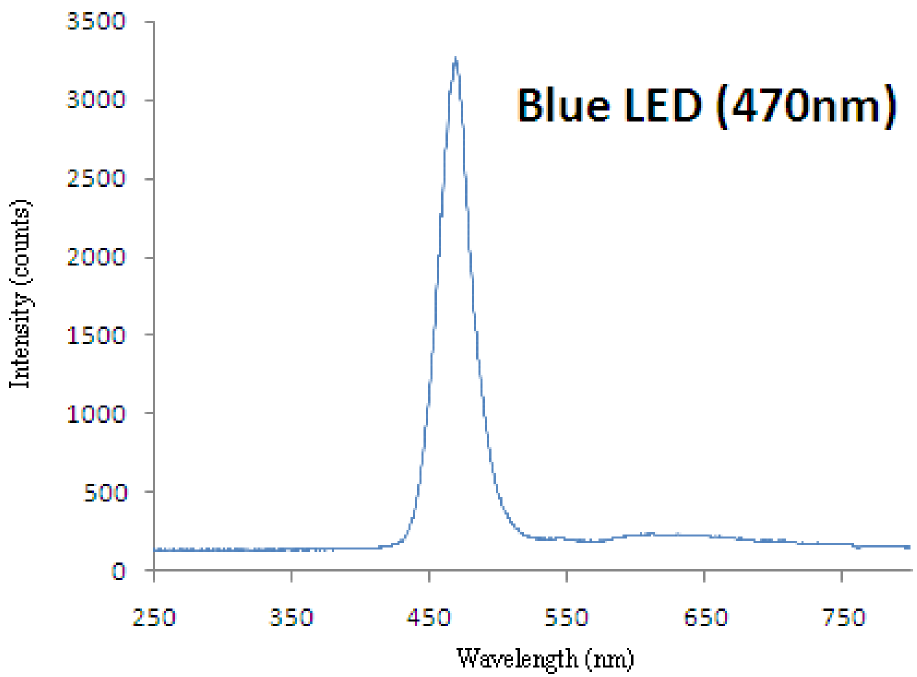
- **Need for better deep-UV-LEDs!**

✓ Lenka Krcmova, Anna Stjernlof, Sebastien Mehlen, Peter Hauser, Silvija Abele, Brett Paull, Mirek Macka, Analyst, 134, 2394 – 2396, 2009 (DOI:10.1039/ B916081G)

✓ Stefan Schmid, Mirek Macka, Peter Hauser, UV-absorbance detector for HPLC based on a light-emitting diode, Analyst, 133, 465-469, 2008 (DOI 10.1039/b715681b)

Measuring light output (mW)

- Commercial ready to use 'light meters'
- An alternative SIMPLE & INEXPENSIVE
  - 1.Measure peak wavelength of LED



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Measuring light output (mW)

- 2. Shine LED onto photodiode at max current (in dark room)
- 3. Record measured current by photodiode amplifier

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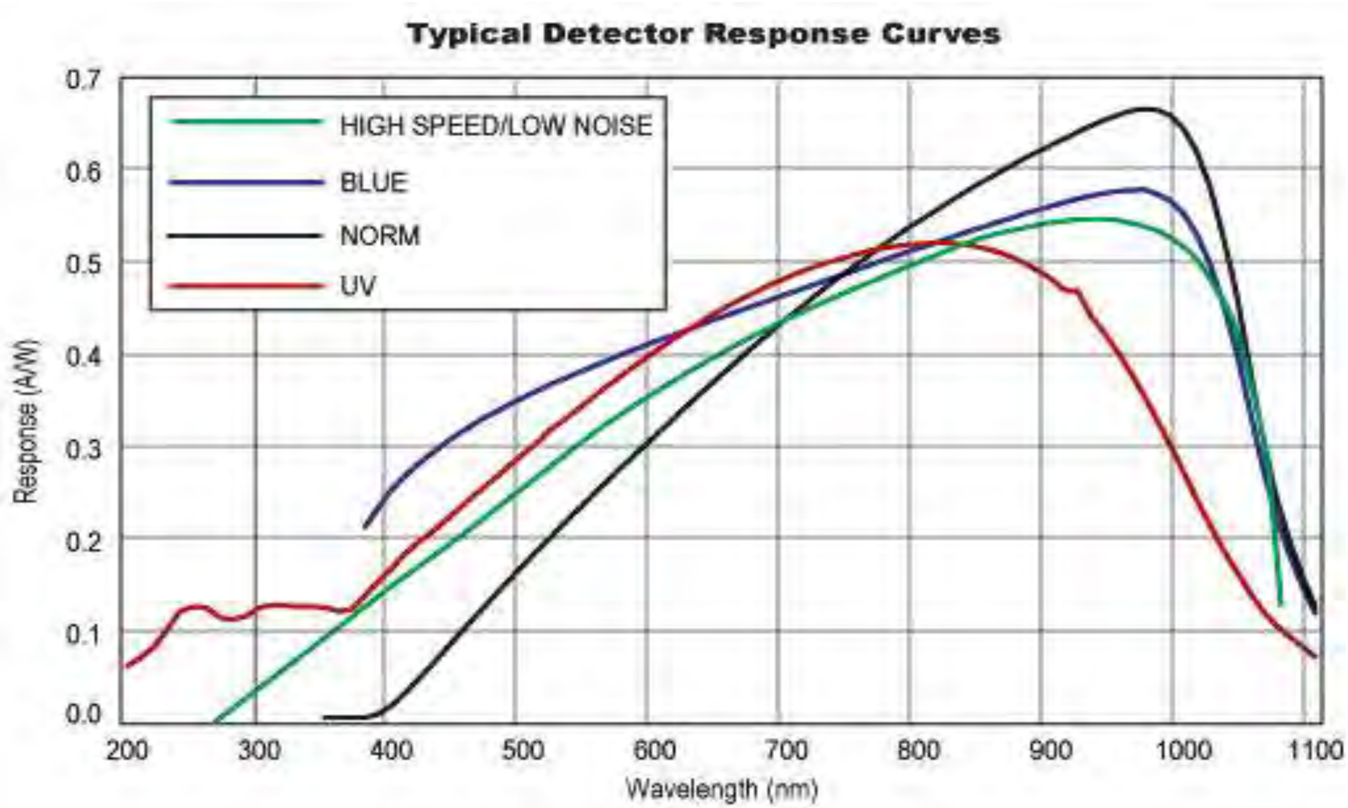
Measuring light output (mW)

- 4. Using the peak wavelength of the LED read the response as A / W (e.g. μA / μW) from the graph



- 5. Divide the measured current by the response i.e. Optical Power = Photocurrent (A) / Response (A/W)

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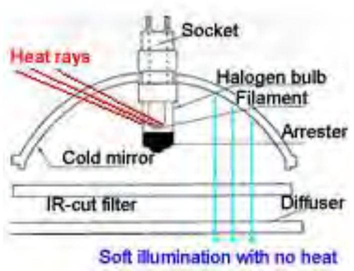
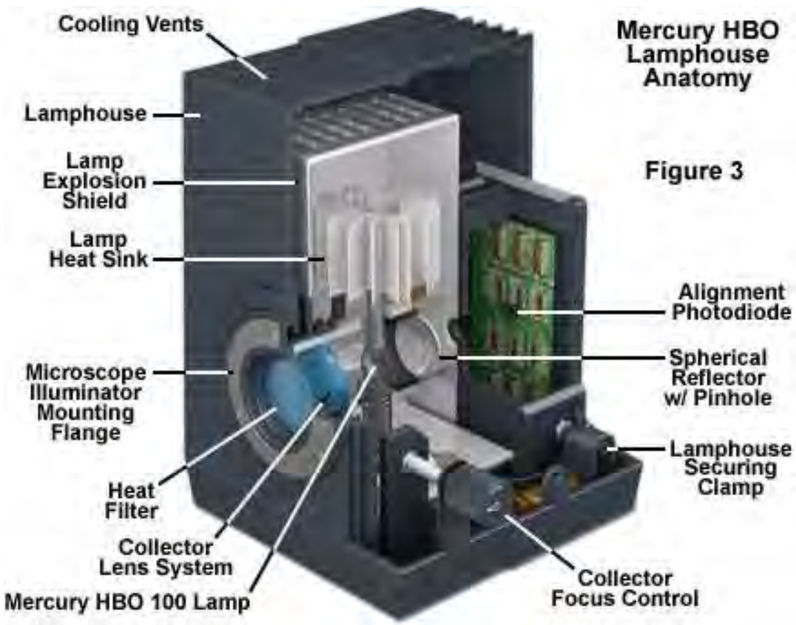
Modern light sources

- Spatial intensity and heat management
  - Incandescent, fluorescent, arc lamps are omni-directional
  - Mirrors are essential part of many lamps based on traditional light sources



http://atago-giken.co.jp/eng/index.html

www.resto-medical.com



http://zeiss-campus.magnet.fsu.edu/

$ Save on
- $ Electricity bills AND emissions!
- $ Costs of expensive traditional light sources
- $ Space

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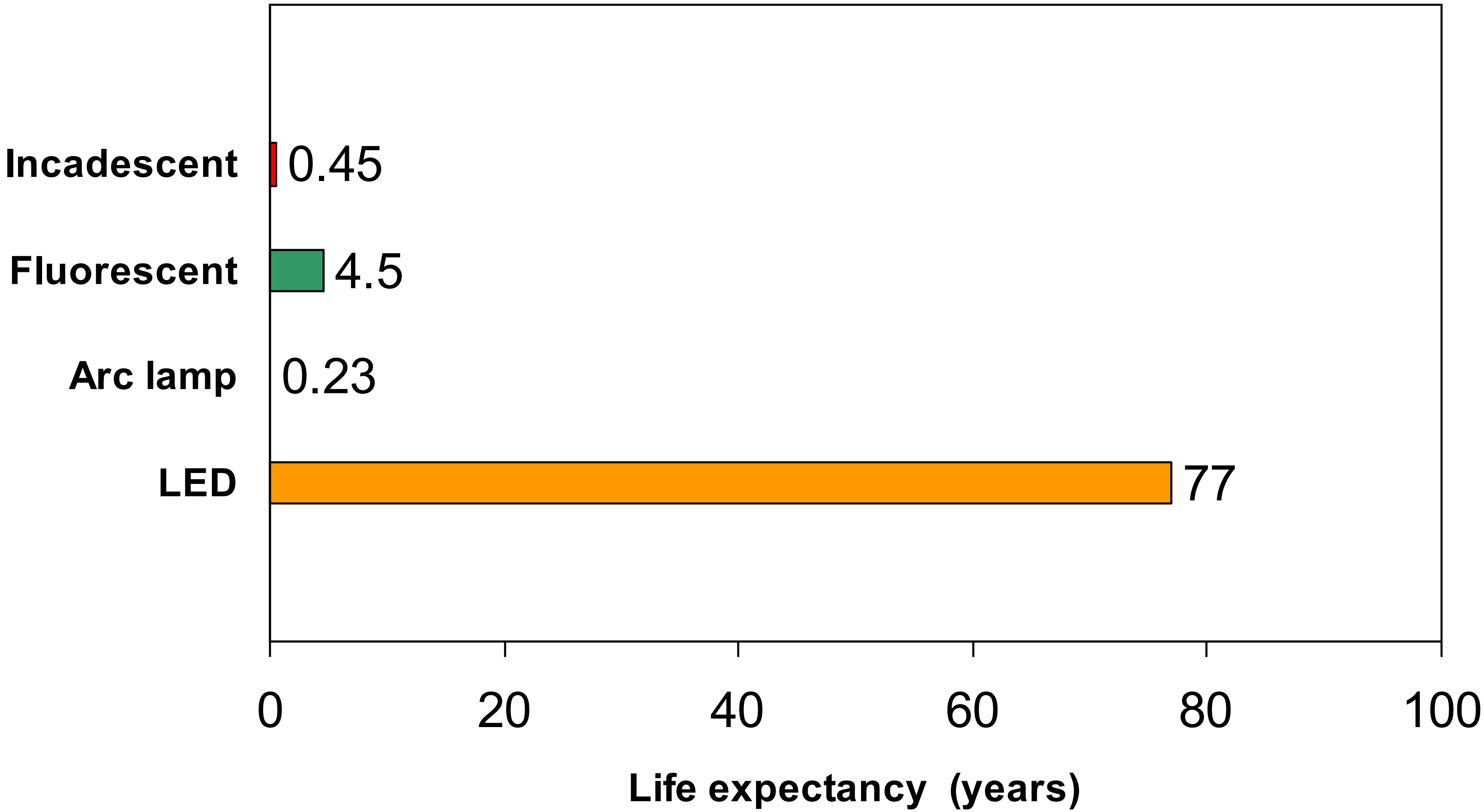
Modern light sources

- Life expectancy



$ Optimally used LED will outlive any other light source

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Modern light sources

- Typical device failure
  - Traditional light sources
    - Catastrophic – sudden and total failure
      - Failure of the whole devise
    - Fluorescent lamps are sometimes blinking before they fail
  - LEDs
    - Gradual loss of intensity
    - Devices do not fail suddenly but rather deteriorate ☺
    - Check the LED optical power
      - When new
      - If durability not known, check regularly during usage

$ Prevent losses in wasted time and resources by working with an LED that has lost a significant portion of its power

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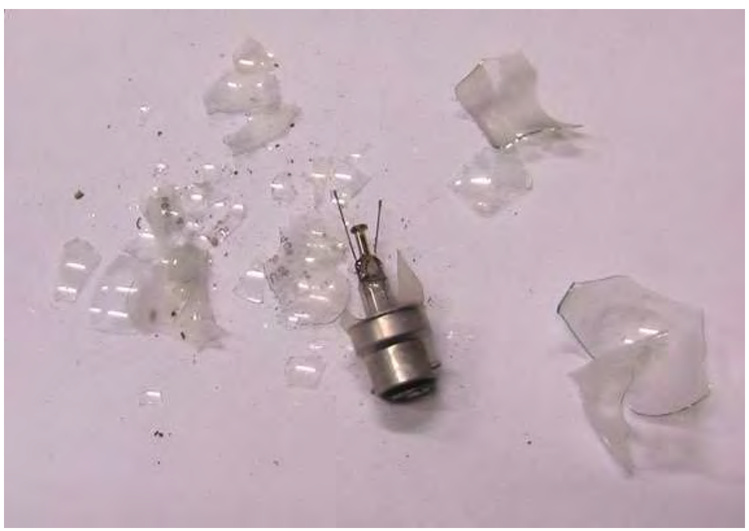
Modern light sources

- Robustness
  - Incandescent and fluorescent lamps
    - Before a fall on the floor from ca. 5 ft

… and after ...

☺



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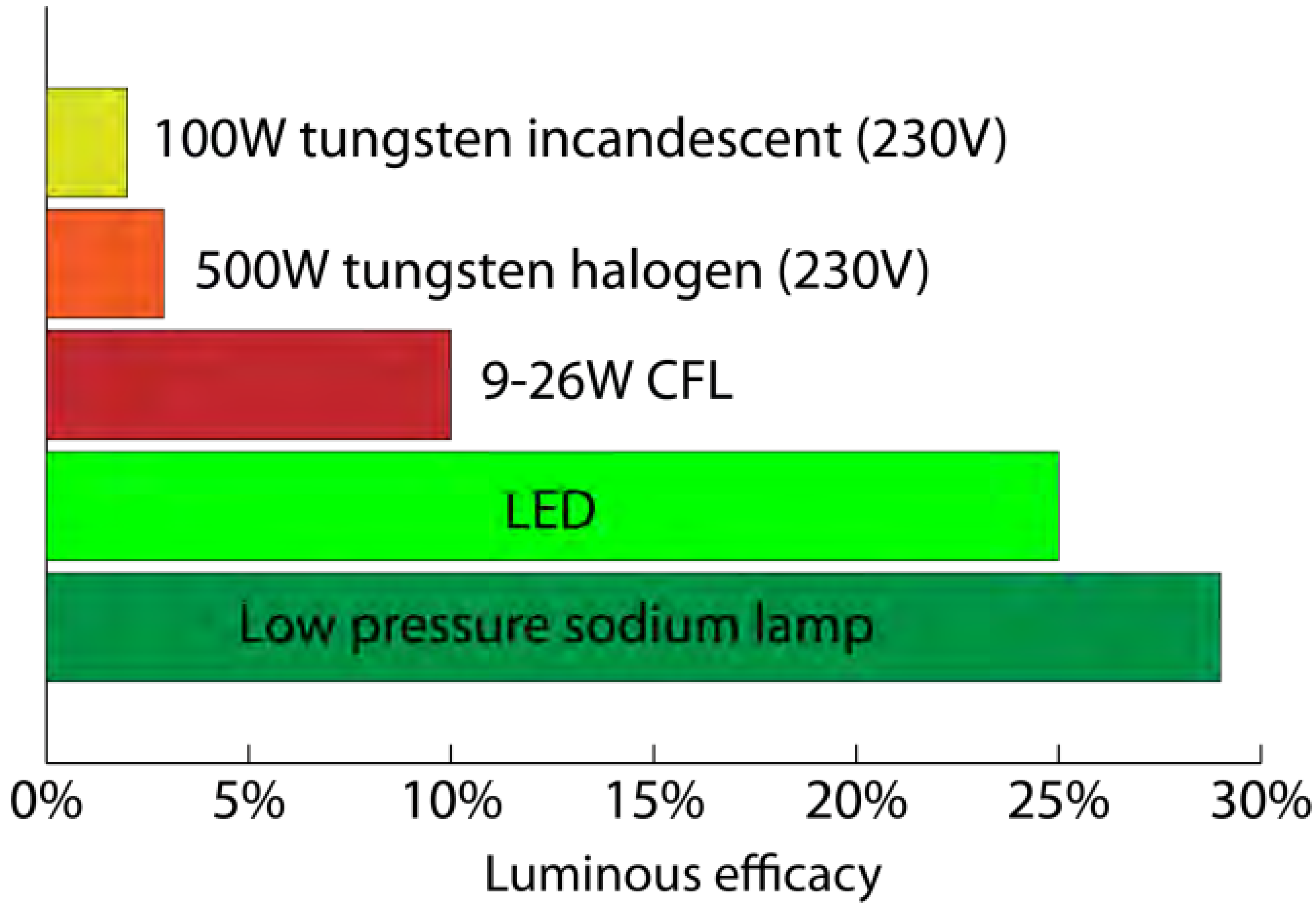
Modern light sources

- Energy consumption and maximum luminous efficacy
  - Theoretical max. luminous efficacy 683 lm/W = 100%



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LEDs in Chemistry: Outline

- Why use LEDs in chemistry and science?
- Modern light sources
- **LED – electric device driven by direct current**
- Brief history of LEDs
- Physics of LED
  - Basic principles and fundamental aspects
  - Units used in world of solid state lighting
  - Advanced aspects
- Engineering and construction of LEDs

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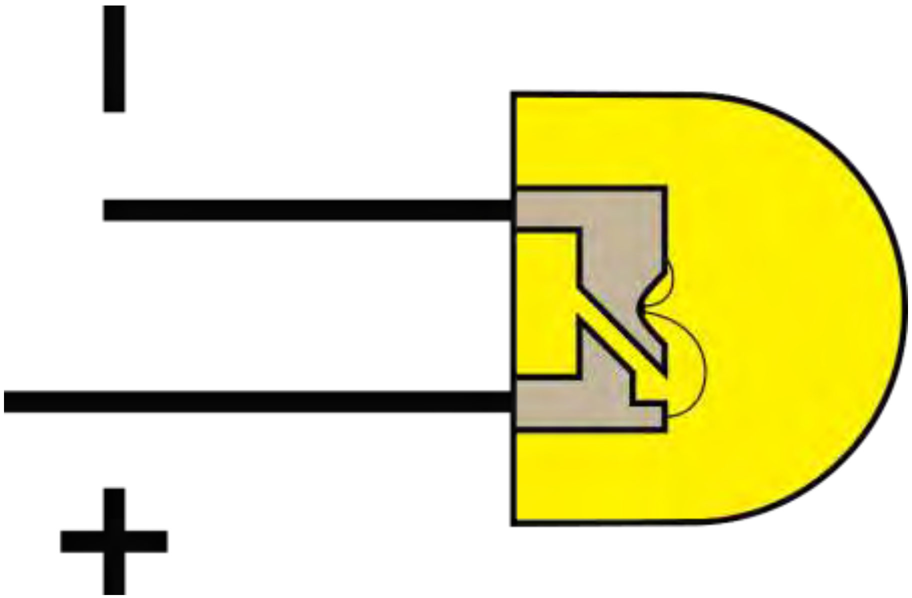
LED – electric device

- Typical LED



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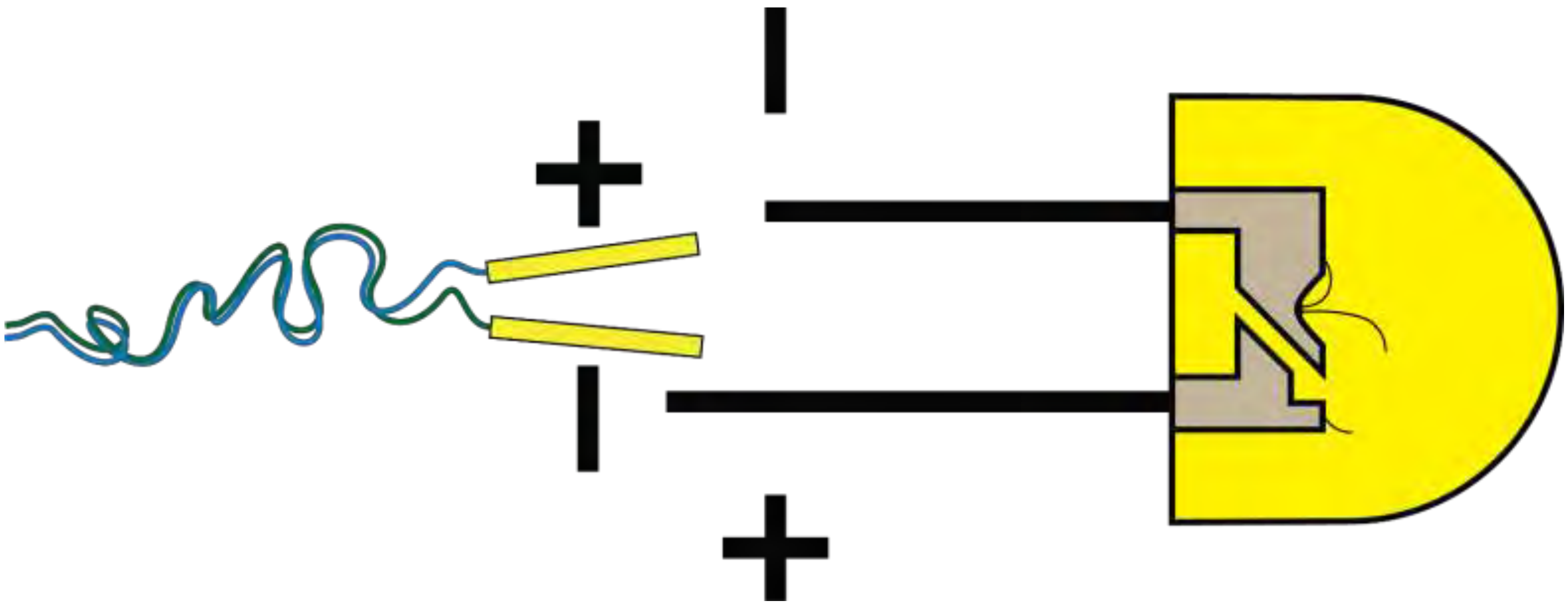
LED – electric device

- Typical mistake



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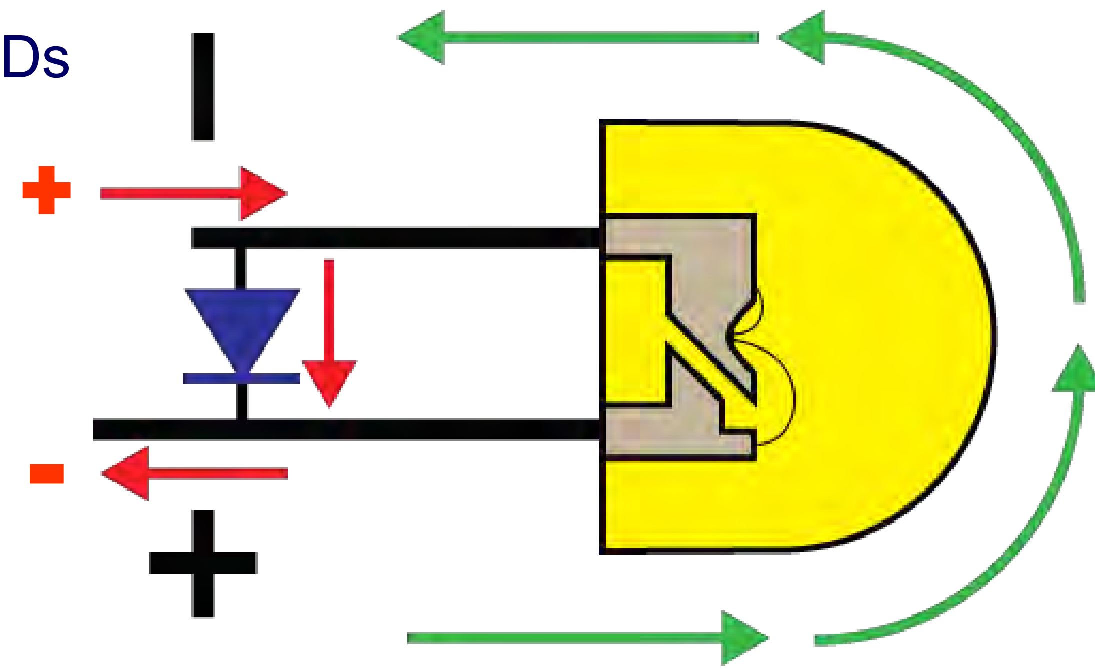
LED – electric device

- Simple solution
  - A diode connected to protect the LED (conducts wrong polarity current away from the LED)
    - Expensive UV LEDs



  - **Protection of LED from damage by a diode**

$ Prevent losses by burning expensive UV-LEDs!

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LED – electric device

- Soldering LEDs – technical remarks:
  - Heat can easily irreversibly damage LED
    - Plastic parts (bulb, base) vulnerable to heat
    - LED chip is extremely vulnerable to heat during soldering
  - Always find correct specifications for soldering e.g.
      - Example: specification for soldering a blue LED (LL-504BC2E-B4-2CC, Lucky Light Company)
    - Temperature: 260°C (500°F)
    - Max. soldering time: 5 seconds
    - Min. distance from the body: 4 mm (0.157”)

$ Prevent losses by destroying expensive UV-LEDs!

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LED – electric device

- LED power supply units
  - Stabilised
  - Best operating in constant current mode
- Power supply units for LEDs - examples:

- 500 mA Universal power supply for single LED, 10$ (www.dotlight.de)

- 700 mA Luxeon LED driver – for 6, 8, 10 or 12 Luxeon LEDs, 40$ (www.theledlight.com)

LED – electric device

- Universal power supply
  - Adjustable voltage and current
    - **Usage of power supplies in constant voltage *vs.* constant current mode**
  - Examples
    - Universal power supplier from ~$50

      - 0-18V 0-3A 89.95$ (www.multimeterwarehouse.com)

      - 0-30V 0-3A, 199$ (*www.action-electronics.com*)

      - 0-18V 0-5A, 215$ (*www.bkprecision.com*)

      - 0-20V 0-10A, 159$ (*www.abra-electronics.com*)

LED – electric device

- Operating temperature
  - Between -30°C to + 80°C (-20°F to +175°F)
- Moisture
  - Generally resistant
- Static electricity
  - Can damage LED

$ Prevent losses by destroying expensive UV-LEDs!

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LED – electric device

- Commercially available LEDs – parameters
  - Operating currents
    - "Maximum steady current" (i_{max})
      - Above i_{max} LED can be damaged irreversibly
    - Current to suit the desired light intensity but below the max. steady current i_{max}
      - Typical values of i_{max}
        - 20-30 mA for most 3-5mm LEDs
      - Larger LEDs and LED lamps
        - Cree XLamp – 140 mA
        - Luxeons – 350 mA – 1.5 A
        - Seoul Semiconductor – up to 3.2A

$ Prevent losses by burning expensive UV-LEDs!

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LED – electric device

- Operating voltages
  - Voltage above the min. threshold value
  - Typically 2.1 - 10V, 14V and 21V
    - Higher voltages for multi-chip LEDs, LED panels/arrays or LED lamps
- **Experiment**
  - **Powering LEDs**
  - **Demonstrate**
    - **Bandgap energy**

$ Power LEDs correctly → get optimal light output & prevent losses by burning expensive UV-LEDs!

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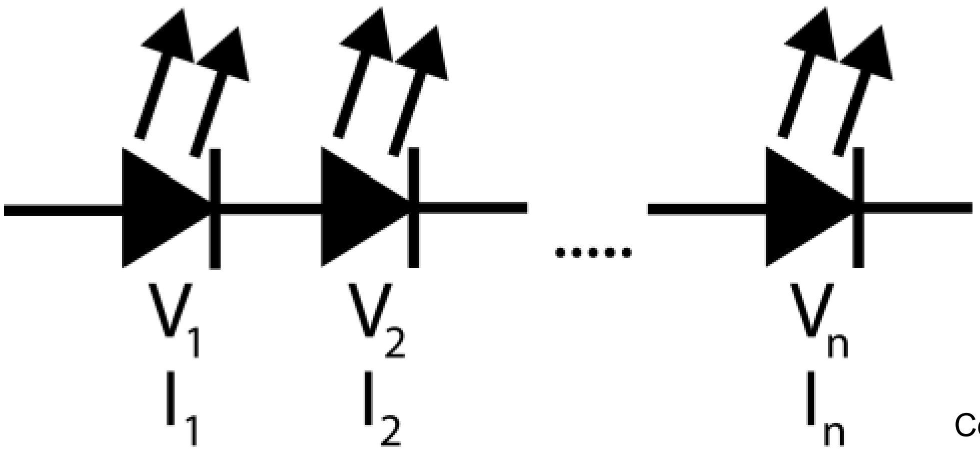
LED arrays

- LED panels and arrays
  - For increased light output multiple LEDs connected
    - Serial connection



Courtesy of prof. Y. Matsushita, Tokio Institute of Technology

$$V_{Load} = V_1 + V_2 + \ldots + V_n \qquad I_{Load} = \min\left(I_1, I_2, \ldots, I_n\right)$$

- Risk
  - If LEDs with different i_{max} are used, applied current i_{load} must not exceed the lowest i_{max} current value

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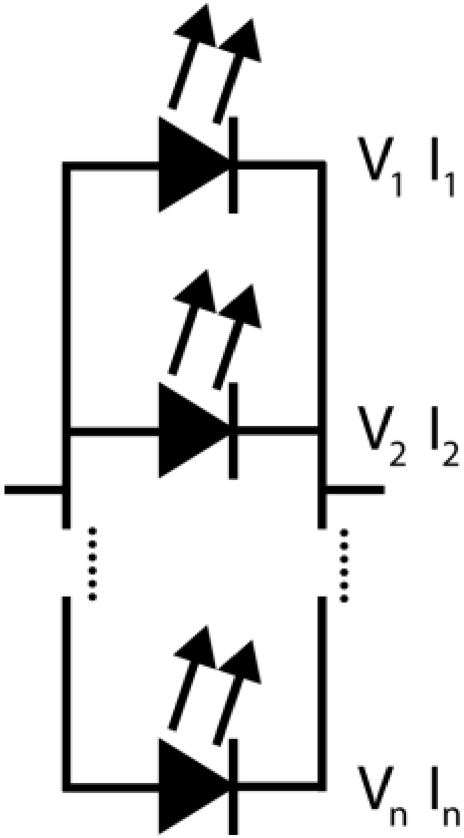
- Parallel connection



$$V_{Load} = \max(V_1, V_2, \ldots, V_n)$$

$$I_{Load} = I_1 + I_2 + \ldots + I_n$$

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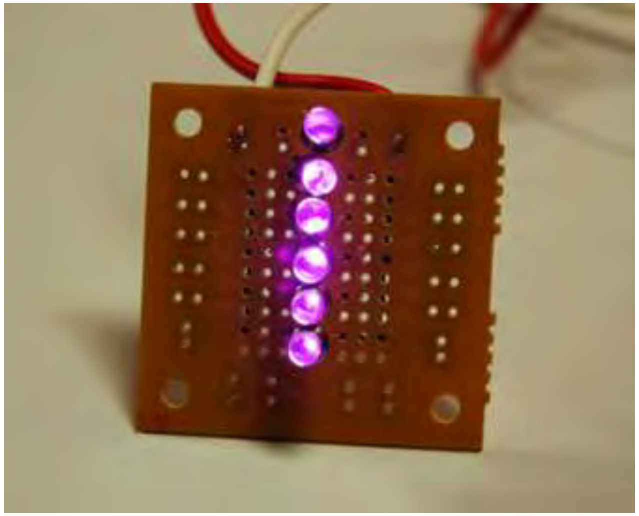
LED arrays

- Problems and risks of parallel connections of LEDs:
  - The branch with the lowest total forward voltage V_f will draw the highest current
  - This results in greater temperature increment on one branch
  - With temperature rise V_f drops
  - Positive feedback loop



Courtesy of prof. Y. Matsushita, Tokio Institute of Technology

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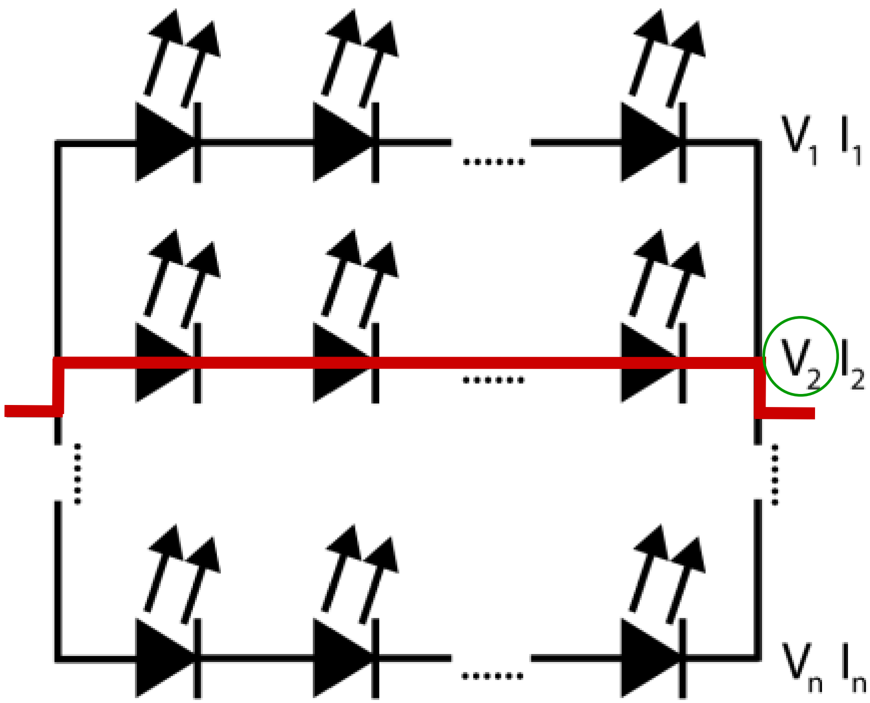
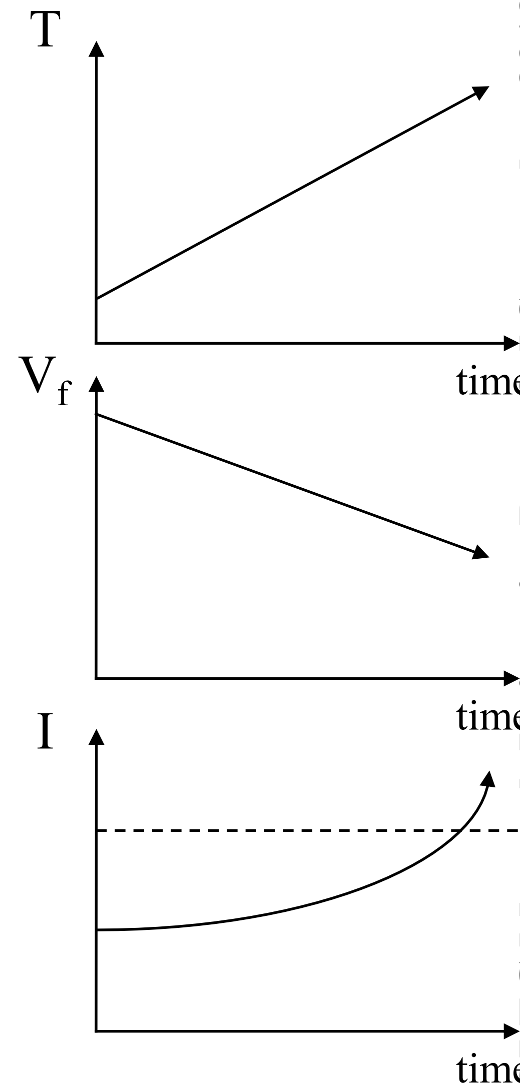
LED arrays

- To avoid problems:
  - Use same LEDs in each branch
  - Provide equal heat dissipation





$ Design LED array correctly to avoid damage

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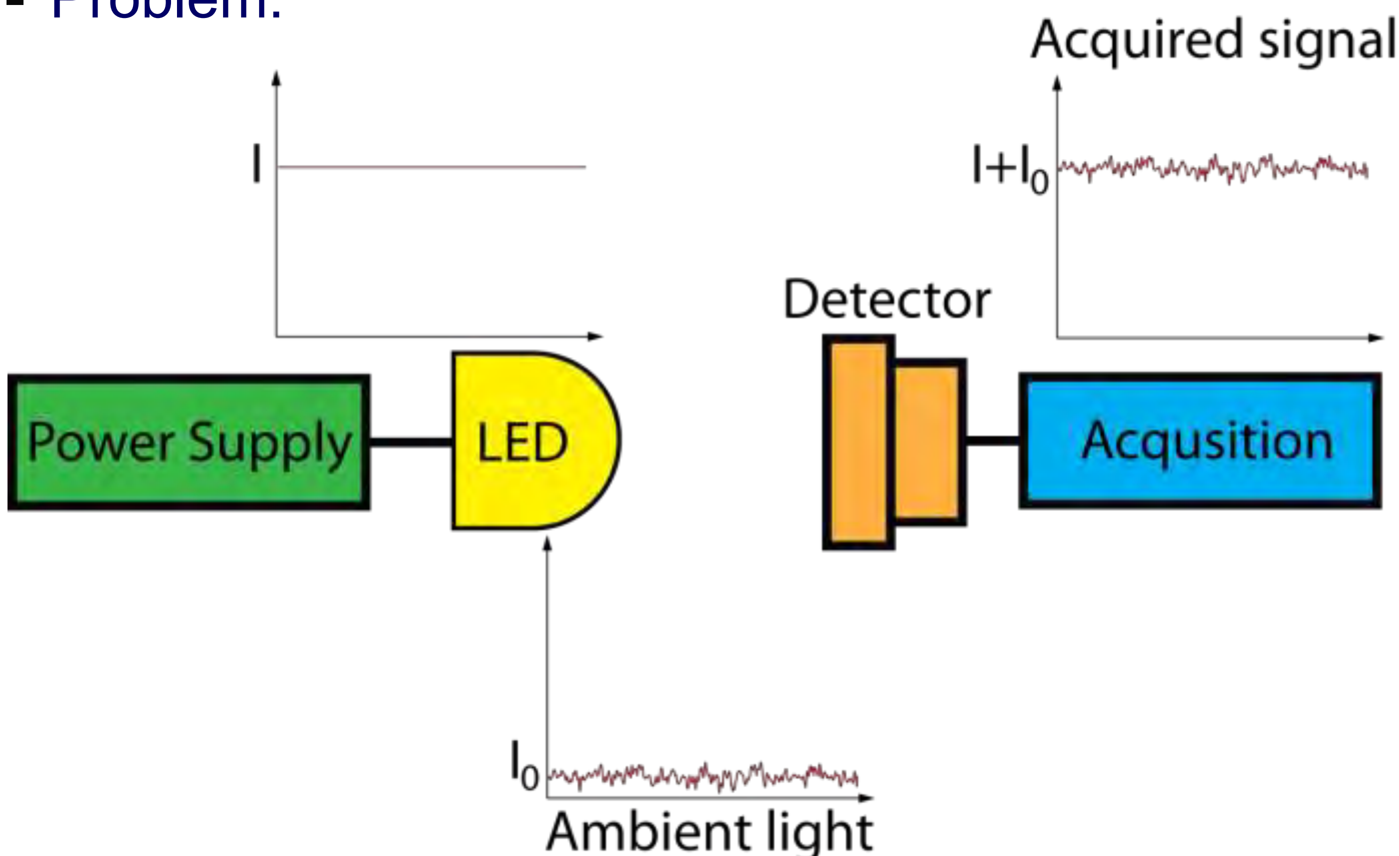
LED – electric device

- Pulsed sources – why use:
  - LED allows to work in pulse regime from ~1Hz to ~1GHz
  - kHz-range: achieve 'blindness' to ambient light
    - Problem:



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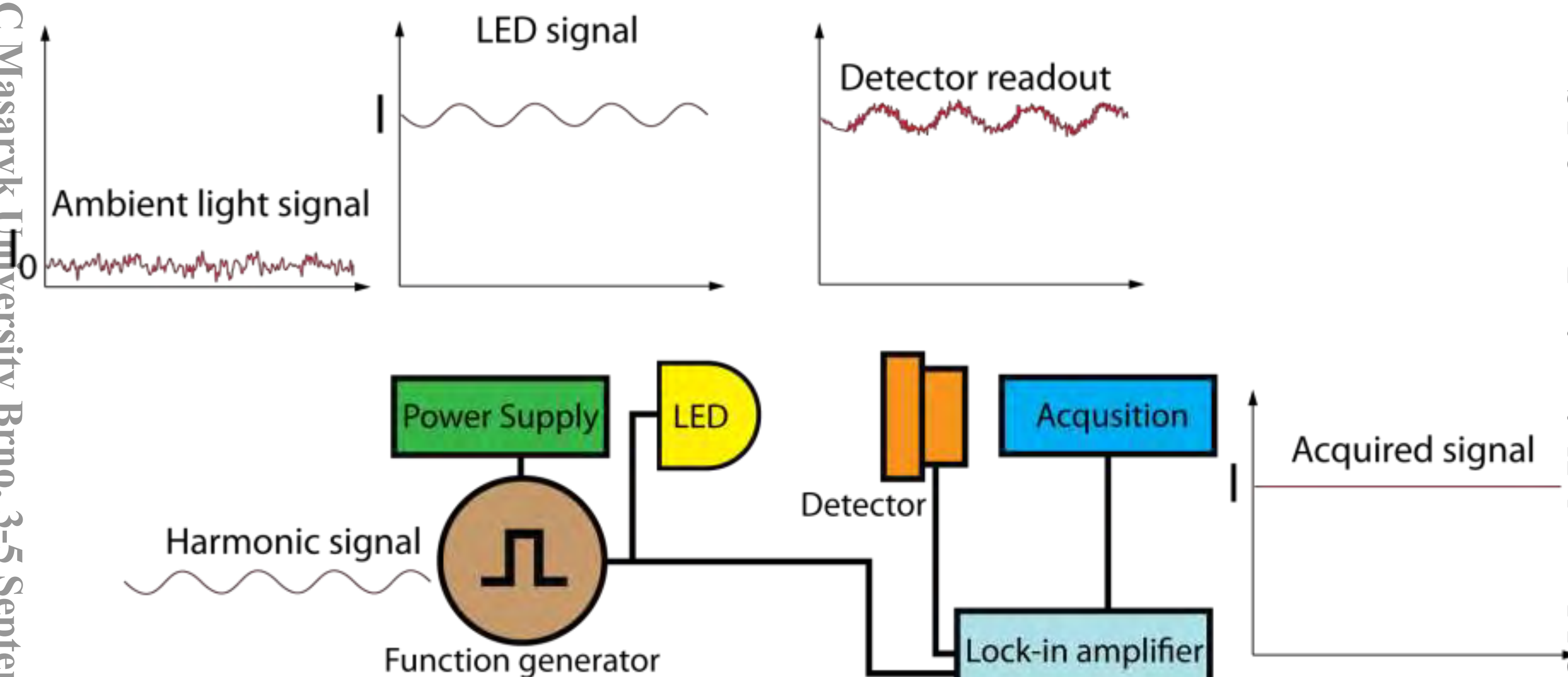
LED – electric device

- kHz-range: achieve ‘blindness’ to ambient light
  - LED + signal generator + lock-in amplifier + detector



$ LEDs can be operated in pulsed regime to achieve ‘blindness’ to ambient light or to do TRF

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Basic principles and fundamental aspects

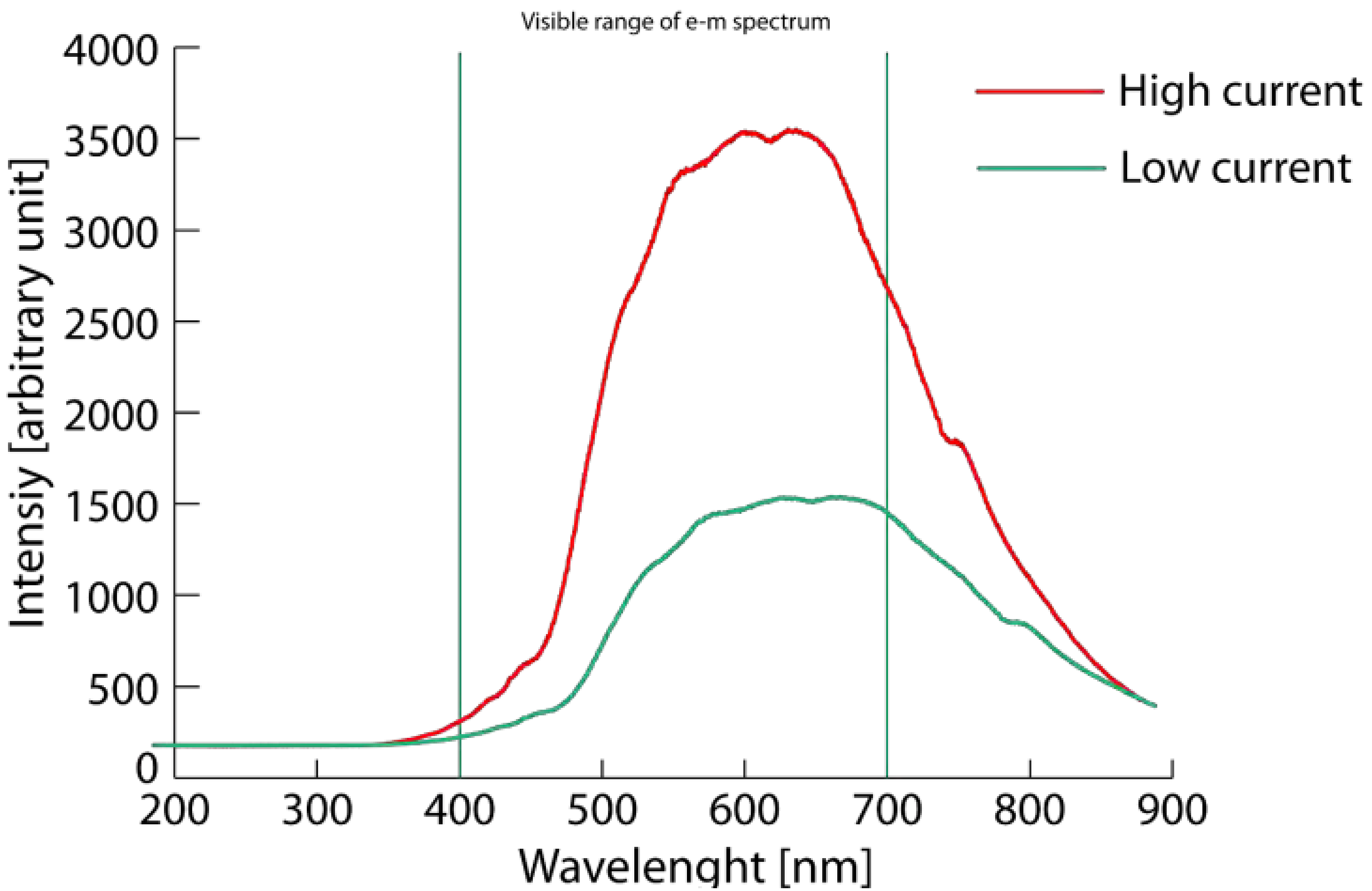
- Heating - solutions?
  - With high-power LEDs temperatures can reach ~140°C
  - Old CPU fan with radiator + aluminium plate + connector
  - High power LEDs come with built-in radiators

Phillips Luxeon Star III

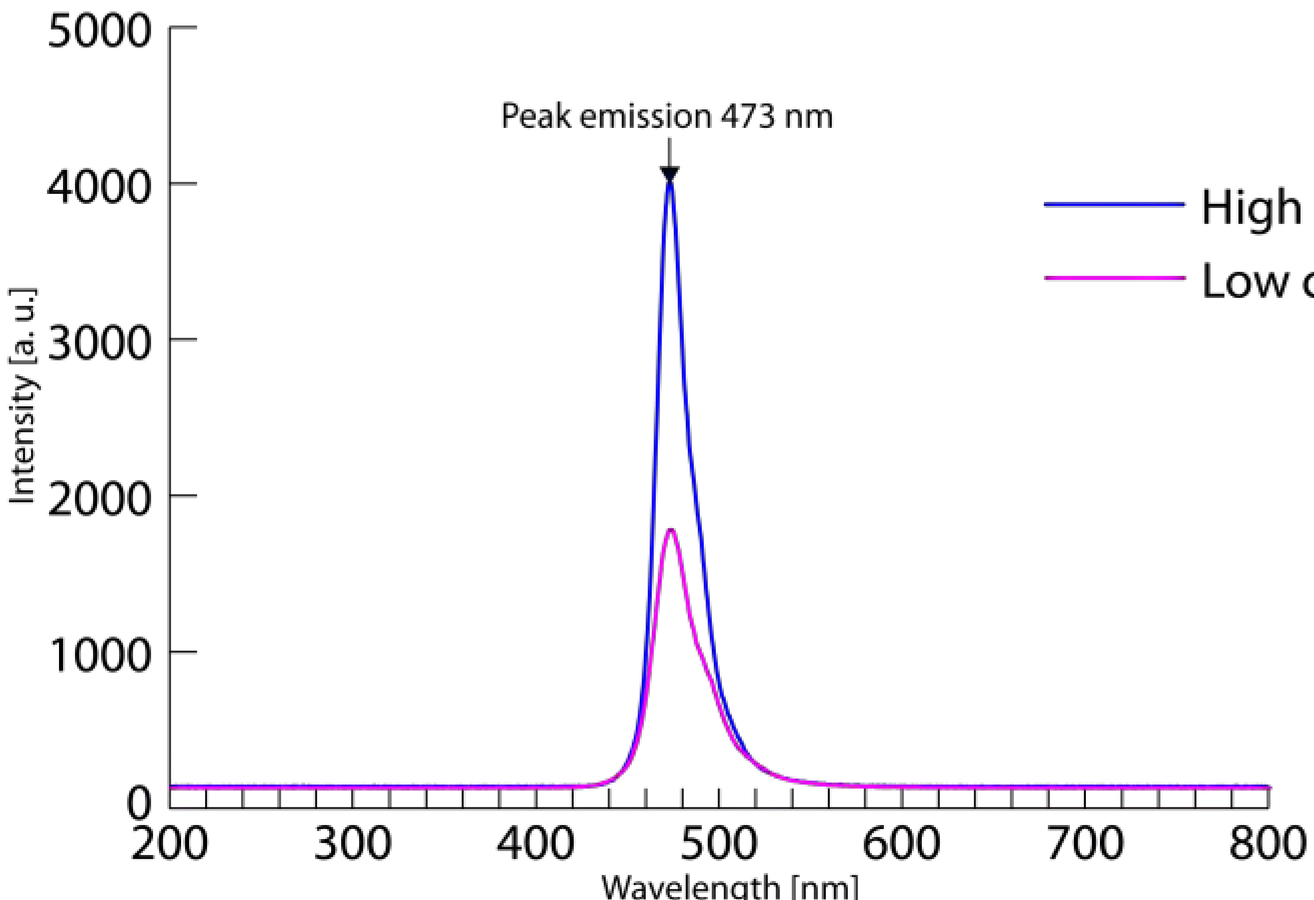
$ Temperature management possible with simple means

Basic principles and fundamental aspects

- Incandescent lamps change spectrum (colour, temperature) with current



- LED: Wavelength unchanged with increased current



- Experiment: Blue Luxeon

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LEDs in Chemistry: Outline

- Why use LEDs in chemistry and science?
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- Brief history of LEDs
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  - **Units used in world of solid state lighting**
  - Advanced aspects
- Engineering and construction of LEDs

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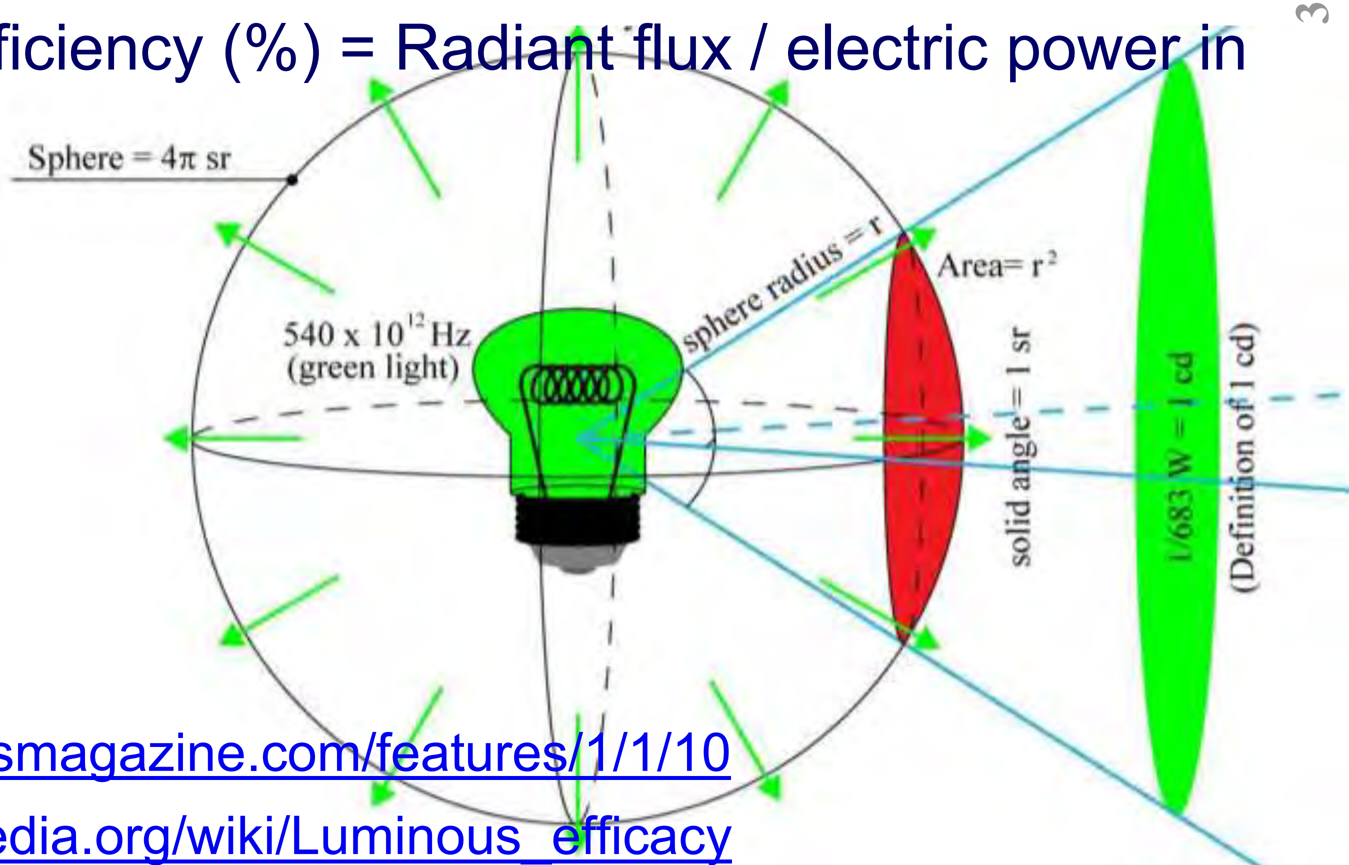
Units

- Various units used
  - Luminosity = luminous intensity [cd] (= lm / sr)
  - Luminous flux [lm] (= cd x sr)
  - Radiant flux (power) [W]
  - Wall-plug efficiency (%) = Radiant flux / electric power in



  - http://www.ledsmagazine.com/features/1/1/10
  - http://en.wikipedia.org/wiki/Luminous_efficacy

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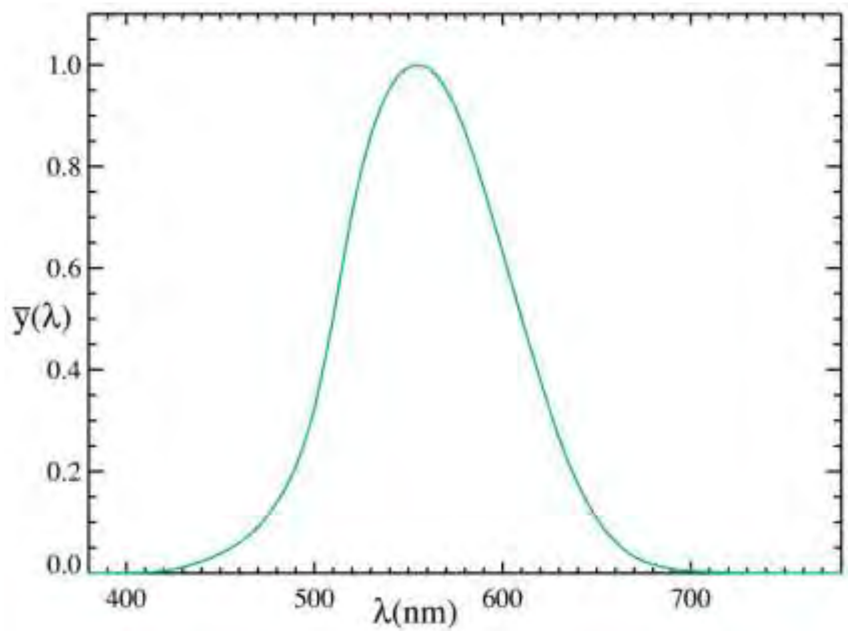
Units

- 1 candela [cd] – unit of luminous intensity – defined as: *In a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian*

$$I_v(\lambda)[cd] = 683.002\,\bar{y}(\lambda) I(\lambda)\left[\frac{W}{sr}\right]$$

Standard luminosity function (photopic)



www.wikipedia.org

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Units

- 1 lumen [lm] – unit of luminous flux – perceived power of light – defined as: *Luminous flux of light produced by a light source that emits one candela of luminous intensity over a solid angle of one steradian*

- Luminous flux is NOT equal to radiant flux (optical power) [W]

- Luminous efficacy – [lm/W] – how good is light source
  - Theoretical possible maximum 683 lm/W
  - Best LEDs (white) 169 lm/W
  - Low pressure sodium lamp ~200 lm/W

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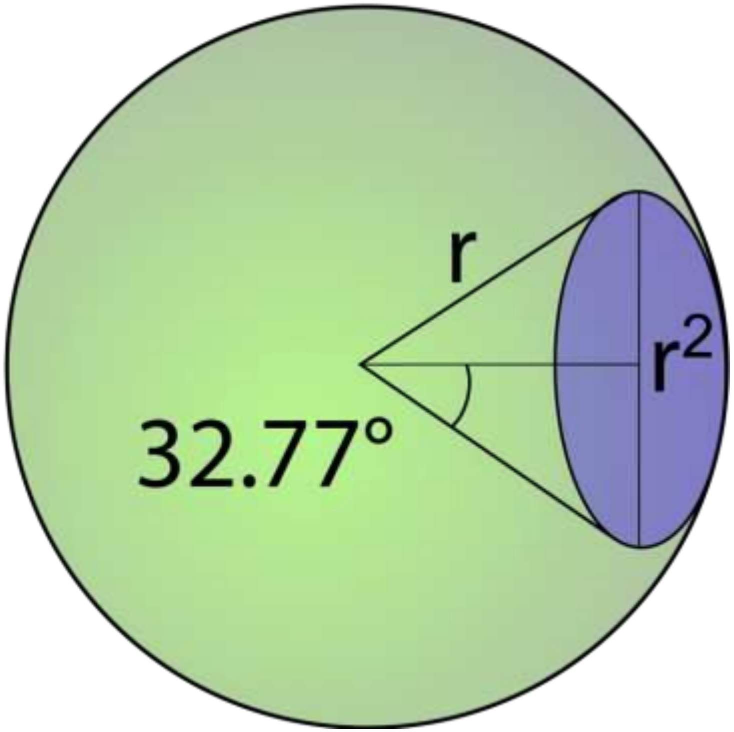
Units

- 1 steradian [sr] – unit of solid angle, defined as: *the solid angle subtended at the centre of a sphere of radius r by a portion of the surface of the sphere having an area r^2*



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Units

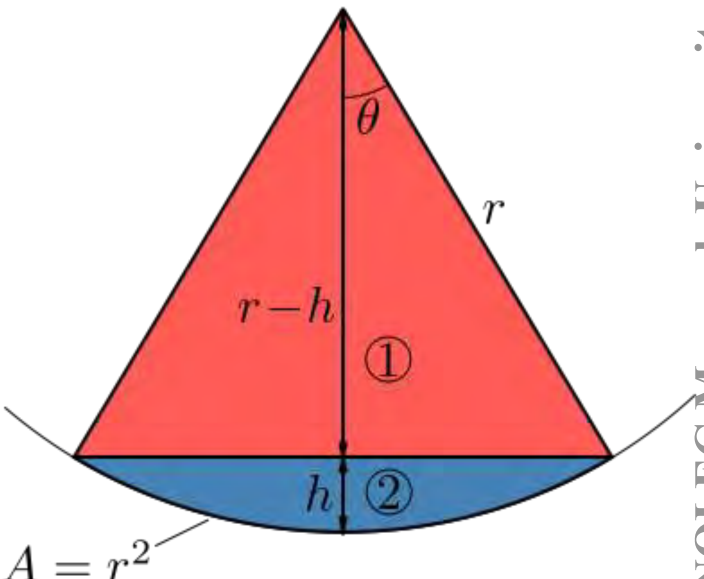
- Problem with conversion from steradians to degrees – nonlinearity

$$\Omega = \frac{S}{r^2}$$

$$\cos\theta = \frac{r-h}{h} \rightarrow h$$

$$r - h = \cos\theta \cdot r$$

$$h = r(1-\cos\theta)$$



www.wikipedia.org

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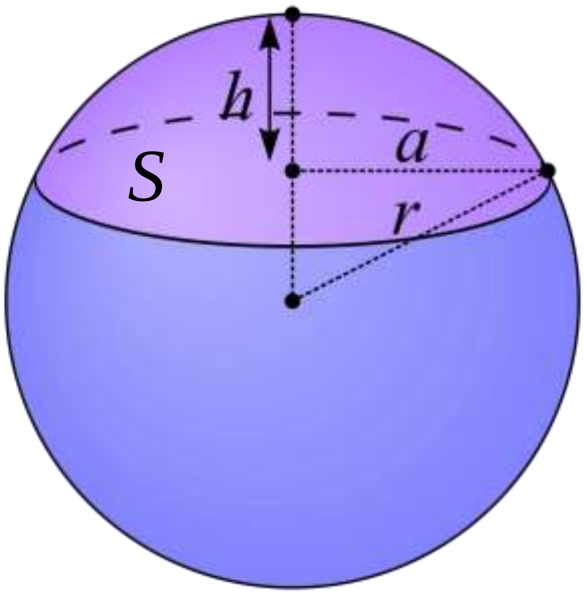
Units

$$S = 2\pi \cdot rh$$



www.wikipedia.org

$$\Omega = \frac{2\pi rh}{r^2} = \frac{2\pi r \cdot r(1-\cos\theta)}{r^2}$$

$$\underline{\Omega = 2\pi(1-\cos\theta)}$$

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Units

- Conversion of degrees into steradians

Degrees	Steradians [sr]
10	0.0954
15	0.2141
20	0.3789
25	0.5886
30	0.8417
45	1.8403
60	3.1459 (π)
90	6.2832 (2π)
120	9.4247 (3π)
135	10.7261
180	12.5664 (4π)

  - http://www.rutronik.com/index.php?id=754

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Units

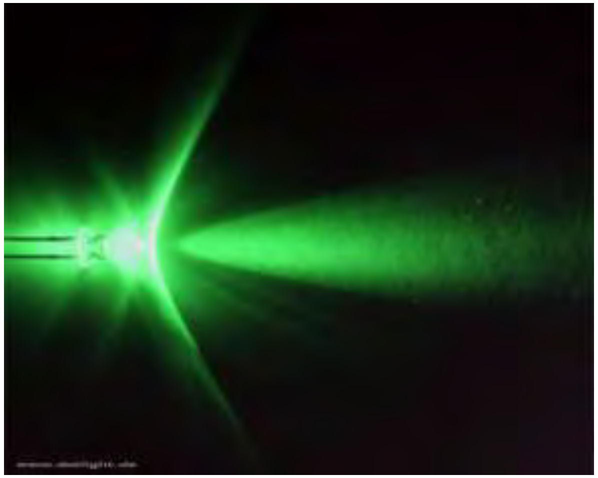
- „Ultra-bright” LEDs
  - red (630 nm) – 15800 mcd, 10°
  - yellow (592 nm) – 7000 mcd, 20°
  - green (520 nm) – 22000 mcd, 15°
  - blue (470 nm) – 12000 mcd, 18°
  - white – 22000 mcd, 15°
- „High power” LEDs
  - Luxeon Star 3W green – flux: typical 64 lm, 140°
  - Seoul Z-LED P4 green – flux: typical 70 lm / max: 160 lm, 130°

How to compare them?

Units

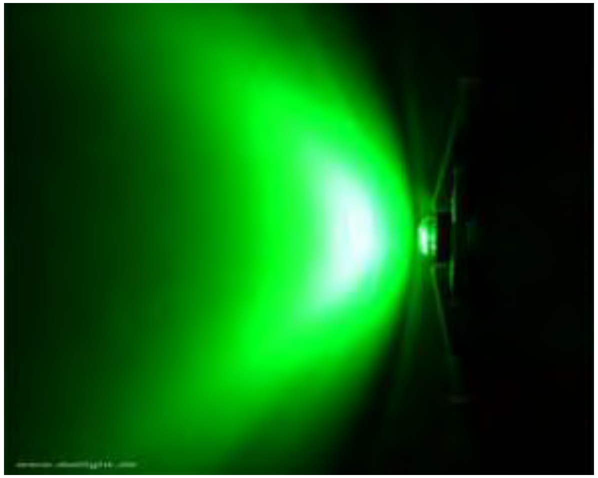
1. Calculate solid angle [sr]
2. Luminosity [cd] x solid angle [sr] = flux [lm]
   - Both luminosity and flux are perceived value – therefore not correction for luminosity function is needed

- Example: 5mm: 520 nm, 22000 mcd, 15° and Luxeon: 3W, 530 nm, 64 lm, 140°



www.dotlight.de

VS.



www.dotlight.de

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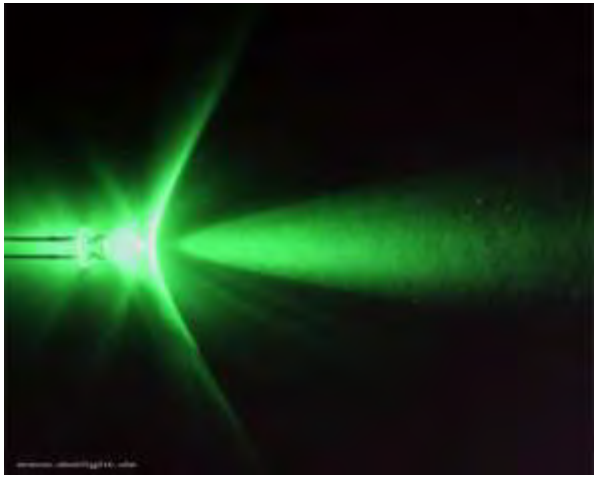
Units

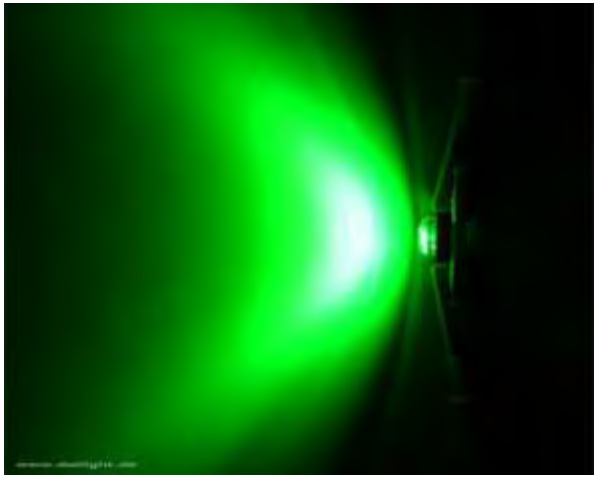
- 15° → 0.2141 sr
- 22 cd x 0.2141 sr = 4.71 lm

  some information, but... not very useful
- 140° → 11.1 sr
- 64lm / 11.1 sr = 5765 mcd
- 22000 mcd vs. 5765 mcd



= 4x*

*In terms of luminosity



- http://www.rutronik.com/index.php?id=754

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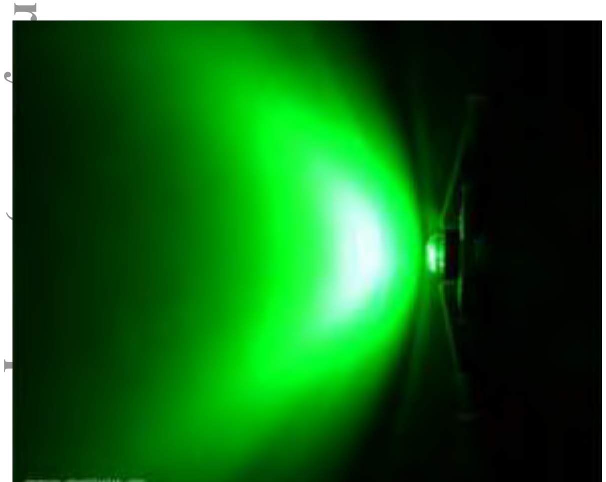
Units

- LEDs with high flux not necessarily have high luminosity
- It is necessary to take into account emission pattern
  - Large illumination cone – lower luminosity
  - Application of optics can have tremendous impact:
    - LED with 5700 mcd with 10° external collimating optics goes up to 600,000 mcd!! (manufacturer data)



+

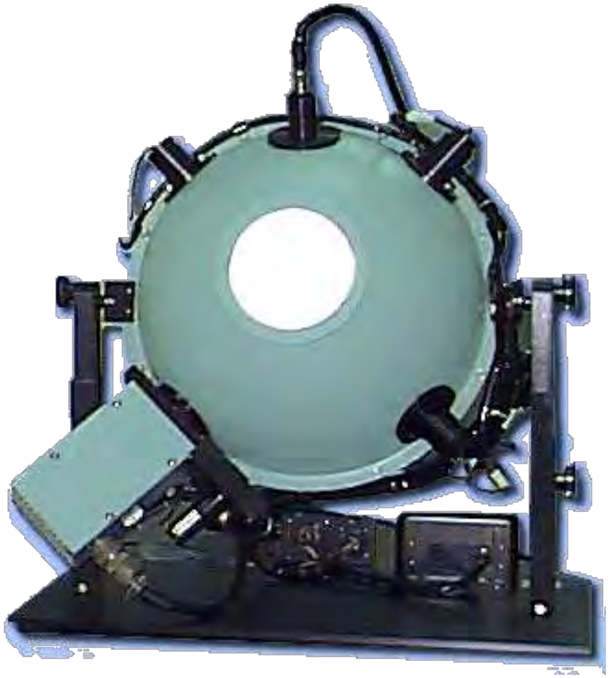
www.dotlight.de

= Luminosity x100

$ Narrow down emission pattern for higher luminosity

Units

- Wall-plug efficiency (WPE) – how much current power is transformed into light power? – estimation of radiant flux
  - Spectroradiometer with integrating sphere



www.electro-optical.com

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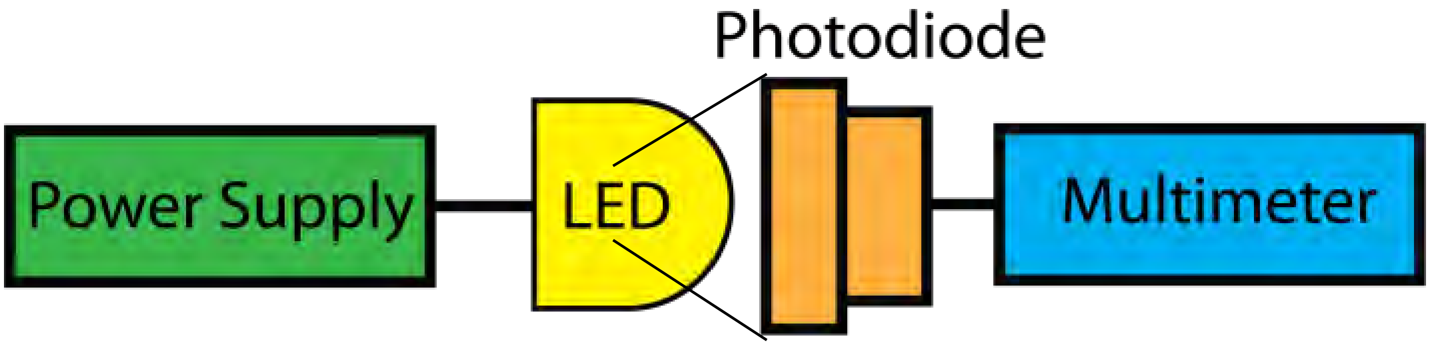
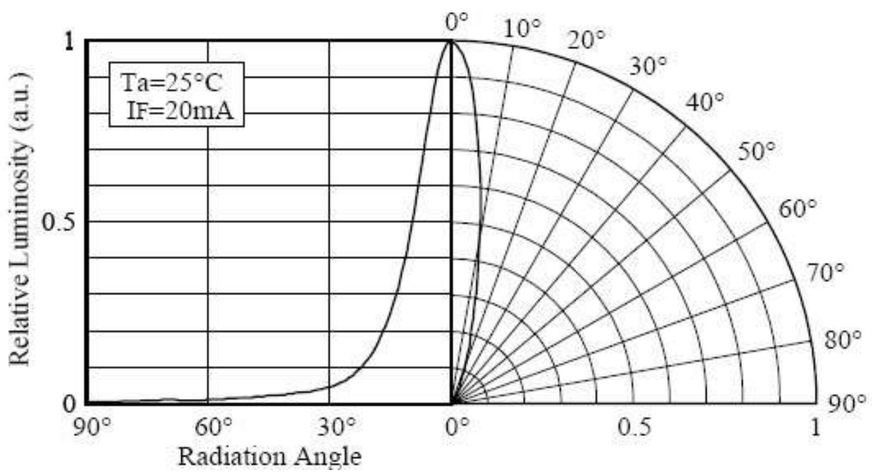
Units

- A simple & inexpensive method
  - Measurement with a photodiode and A-meter





Nichia Corp.

$ Can be measured with inexpensive equipment

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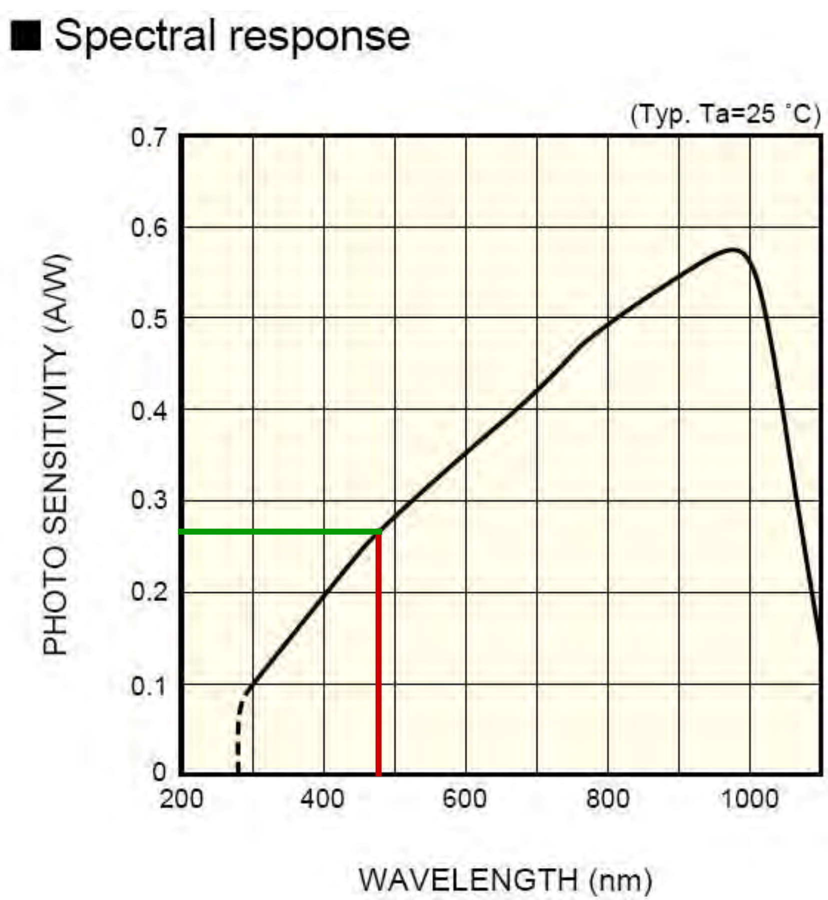
Units

- Datasheet of used photodiode
  - Spectral response curve
- Measured current at the photodiode
- Photosensitivity from graph [A/W]
- Known Amps → Watts

$$\frac{photocurrent}{photosensitivity} = power$$



$ Measure optical power and WPE simply & cheaply

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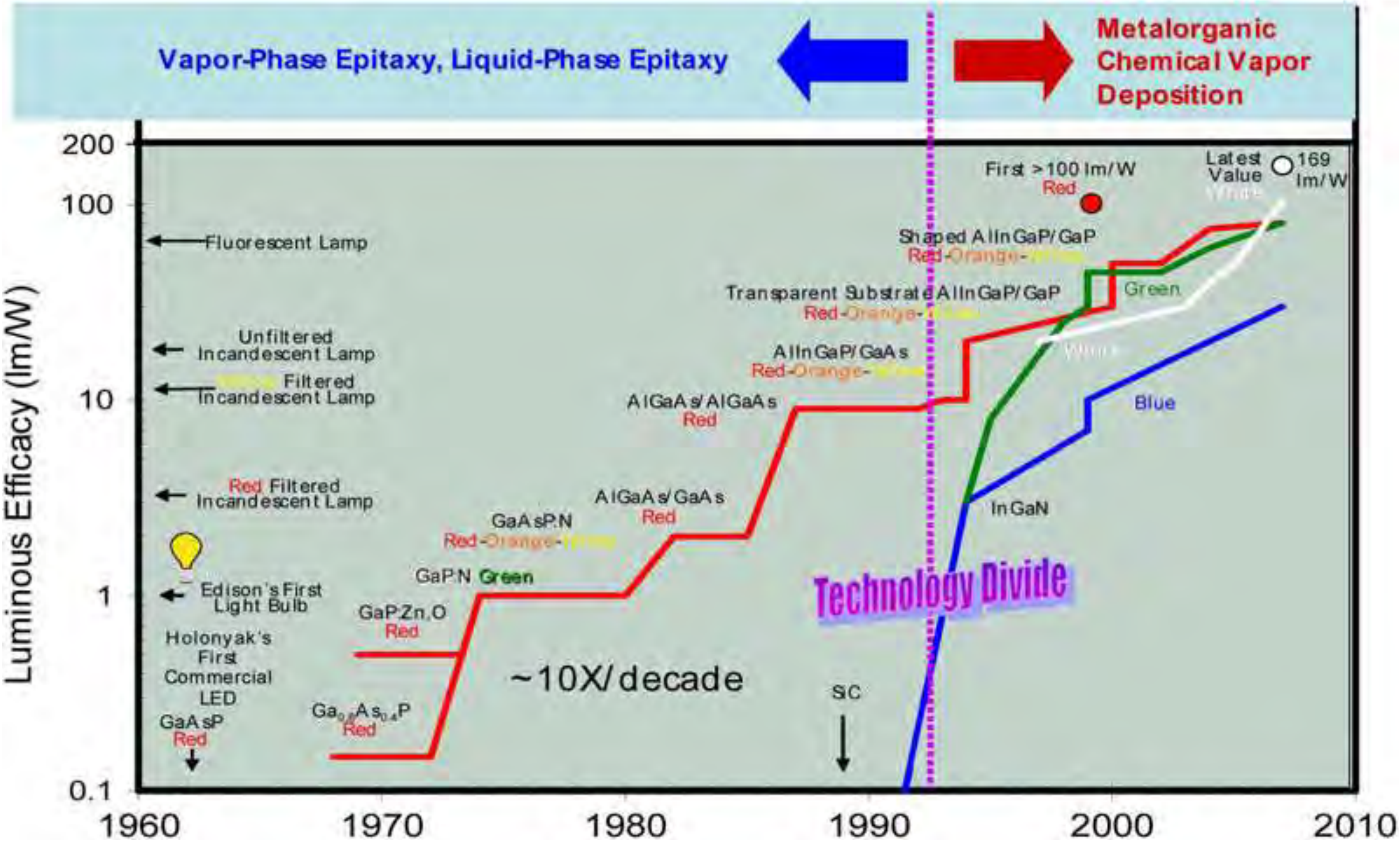
- Luminous efficacy – evolution



Dupuis, R. D., Krames, M. R., *Journal of Lightwave Technology*, 2008, 26

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LEDs in Chemistry: Outline

- **Properties of LEDs in respect to their applications in chemistry**
  - **Practical considerations of usage of LEDs**
- Applications I
  - Optical methods in chemical analysis
    - Photometry and photometric detection
    - Fluorometry
  - LEDs for sensors

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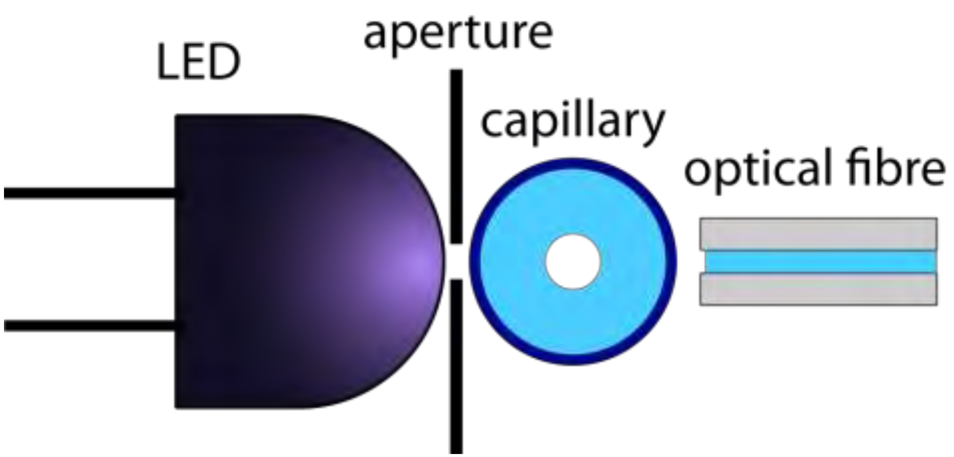
Practical considerations

- Small size compatible with miniaturised detectors and chips
  - Coupling of LEDs to the detector/chip
    - Heating
    - Size
    - Power consumption



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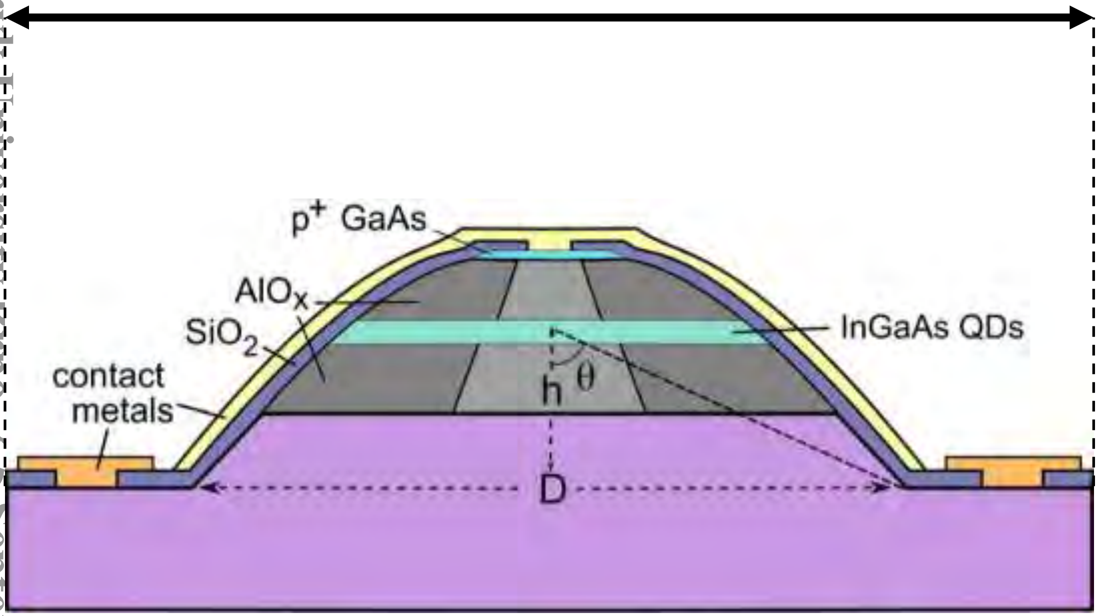
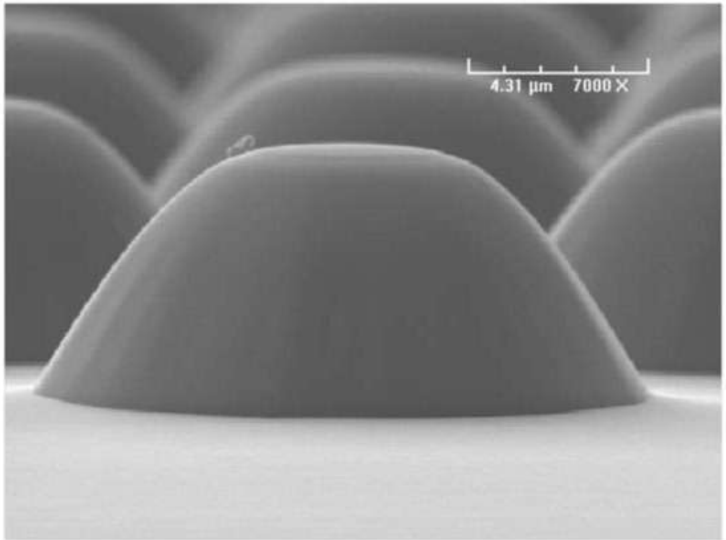
Practical considerations

- LEDs can be the smallest light sources ever constructed
  - Micro LEDs with diameter ~15 μm

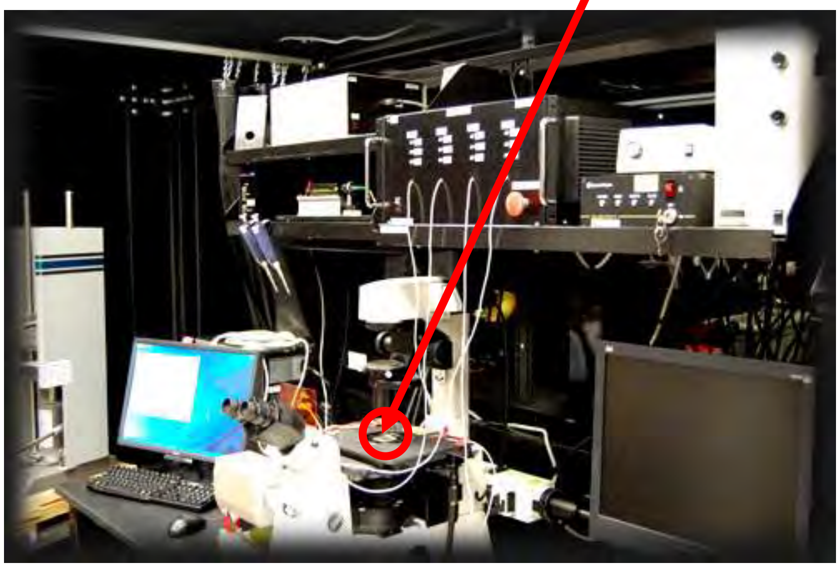




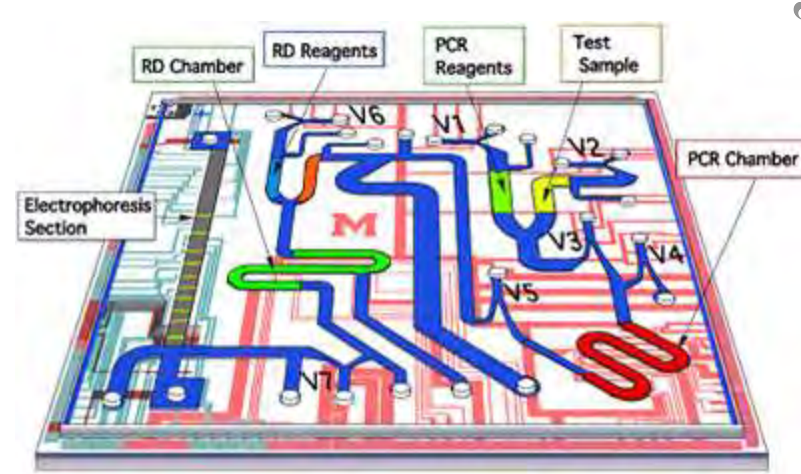
Tanriseven, S., Maaskant, P., Corbett, B. *Applied Physics Letters* **92**, 123501 (2008)

Practical considerations

- Miniaturisation of light sources is one of crucial factors for changing “chip-in-lab” into “lab-on-chip”



www.martytornil.com



www3.niaid.nih.gov

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Practical considerations

- Visible range LEDs are cheap
  - Monochromatic in 400-700 nm range – form 0.24 to 2$
  - White 1-5$ (www.superbrightleds.com, www.led1.de)
  - UV-LEDs – highly dependant on emitted wavelength (www.roithner-laser.com)
    - 400 nm – 1-5$
    - 340-360 – 100-200$
    - 270 nm – 200-300$
    - 255 nm – 400$
  - With lifetime expectancy ~10^5 working hours it may not be expensive after all

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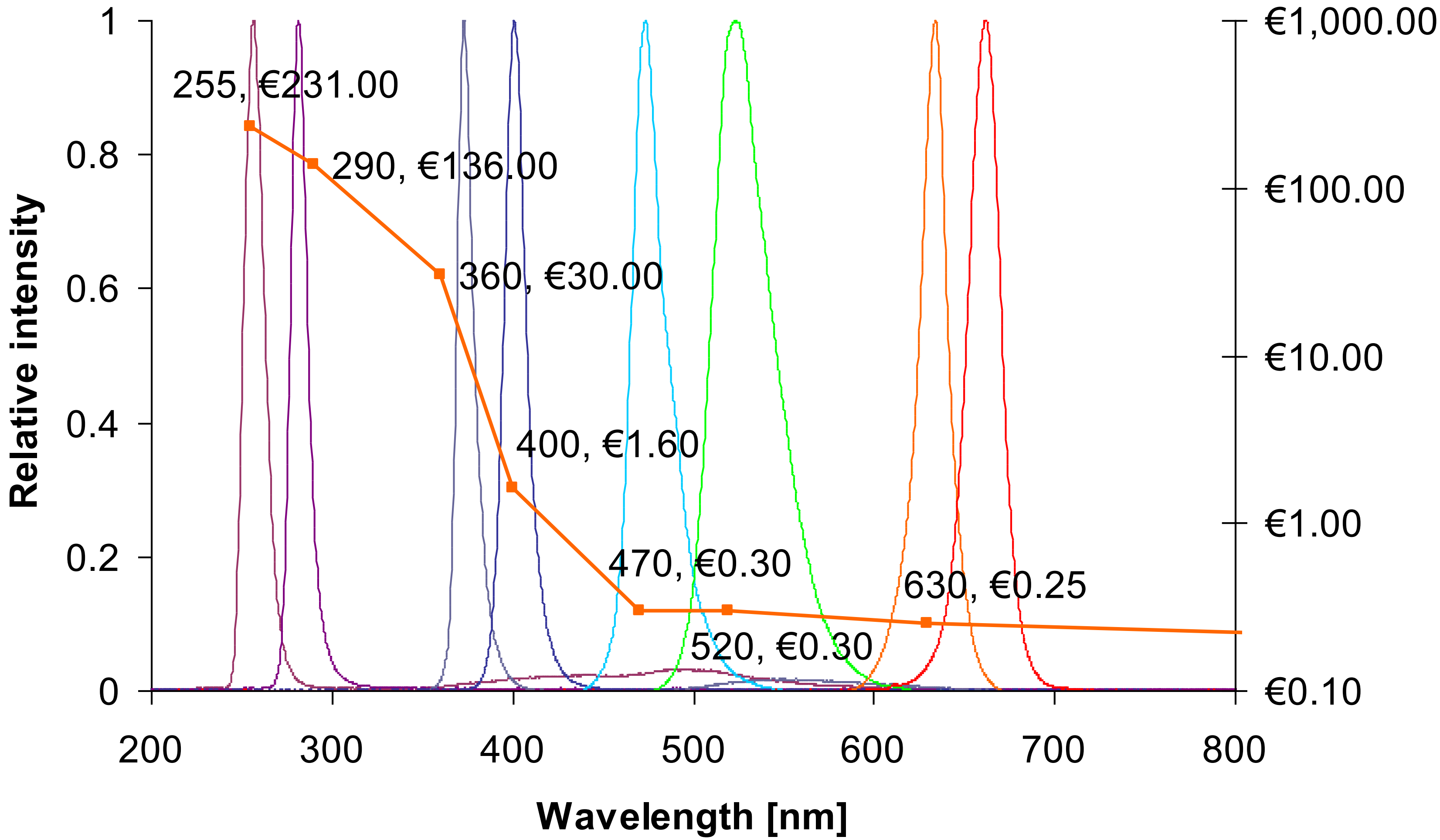
Practical considerations

- Price *vs.* wavelength



$ Know that today deep-UV-LED = expensive LED

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Practical considerations

- Suppliers of SSLSs: LEDs, Laser Diodes, SLEDs
  - Roithner Lasertechnik, Austria (www.roithner-laser.com)
  - LED Supply, USA (www.ledsupply.com)
  - Super Bright LEDs, USA (www.superbrightleds.com)
  - Dotlight, Germany (www.dotlight.de)
  - RS Electronics, USA (www.rselectronics.com)

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Practical considerations

- Suppliers of SSLSs: LEDs, Laser Diodes, SLEDs
  - Power Technology, USA (www.powertechnology.com/)

  - THELEDSTORE http://www.theledstore.com.au
    - Authorized Distributor for
      - LedEngin Inc **www.LedEngin.com**
      - illumitex Inc **www.illumitex.com**
      - Cutter Electronics Pty Ltd **www.cutter.com.au**

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Practical considerations

- High-power LEDs
  - Single chip x multiple chip
  - UV
    - Example:
      365nm 40W (electrical power) multiple chip (12-die)
      - $770 (May 2012)
      - 10 W/cm^2
      - http://www.farnell.com/datasheets/1339334.pdf

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Practical considerations

- UV-LED torches
  - 395 nm

    - http://au.element14.com/night-searcher/nsnuvled395/torch-led-uv/dp/1823957?Ntt=1823957&CMP=i-55c5-00001402
  - 365 nm, 395 nm
    - 5W (electrical input)
      - http://www.farnell.com/datasheets/606066.pdf

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Practical considerations

- High power low cost lasers
  - http://www.wickedlasers.com/

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Practical considerations

- Suppliers of SSLSs: LEDs, Laser Diodes, SLEDs

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Practical considerations

- Long life expectancy in the order of 10^5 working hours
- Wavelength stability
  - Not an issue (changes with temperature small)
- Intensity stability
  - Temperature of junction in LED is a key factor
  - Current will play a role
  - Spatial/geometrical stability
    - Shaping of emitting chip in LED for low spatial fluctuations
    - LED emission pattern does not change in time

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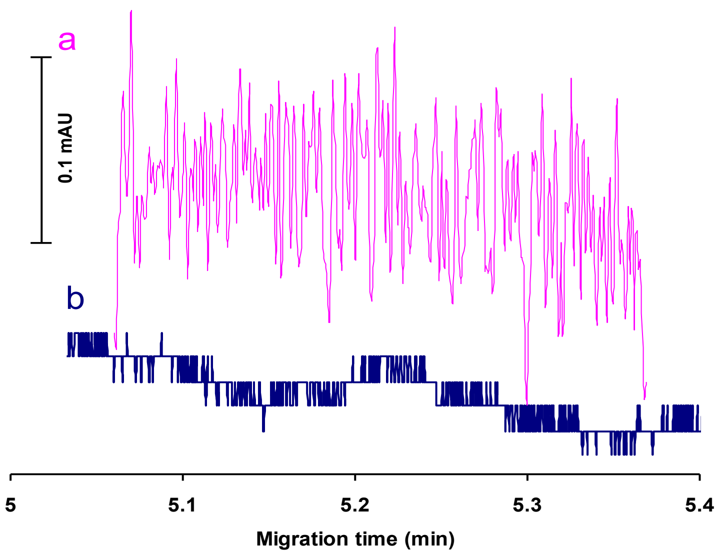
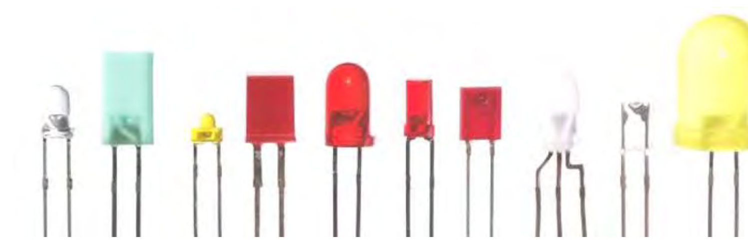
Practical considerations

- Short-term (noise) vs. long-term (fluctuations, drift)
  - Approx. up to 1 order of magnitude gained by switching from D_2-lamp to LED in visible region
  - Frequency filtering (additionally)





Absorbance baseline noise

- Deuterium lamp
- LED

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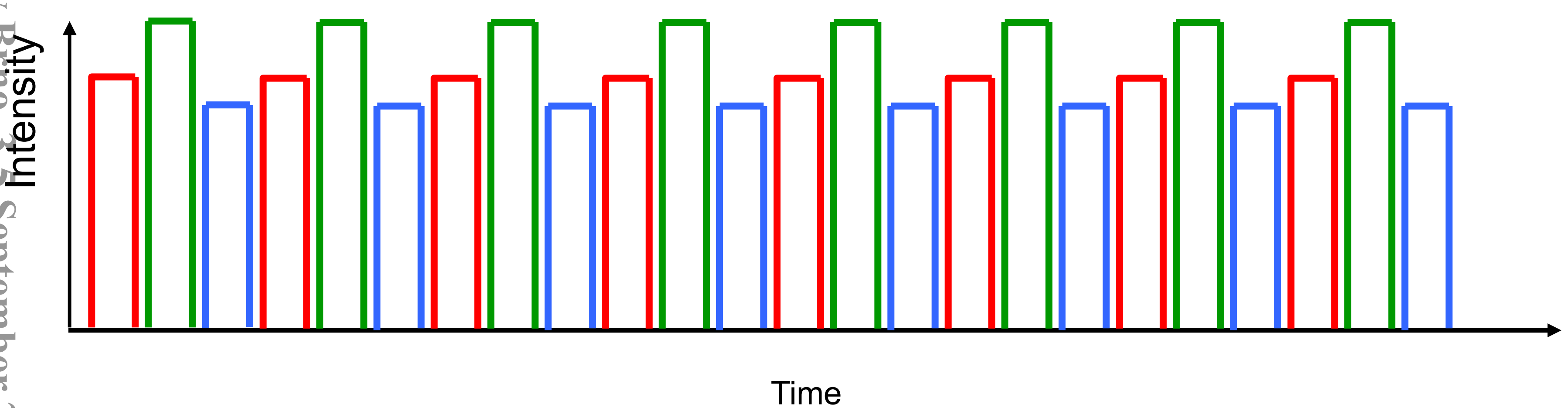
Practical considerations

- Can be pulsed at extremely fast frequencies
  - Source light can be ‘electronically chopped’
    - Allows several wavelength to be measured on time-shared basis simultaneously



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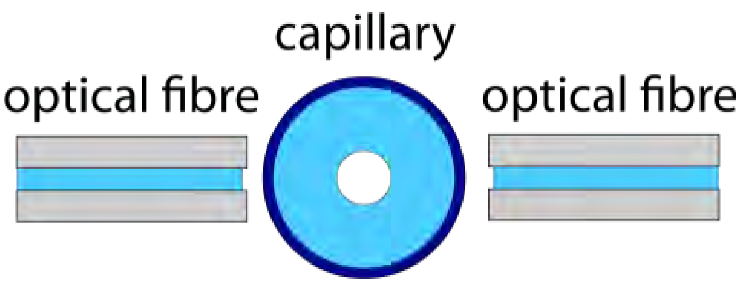
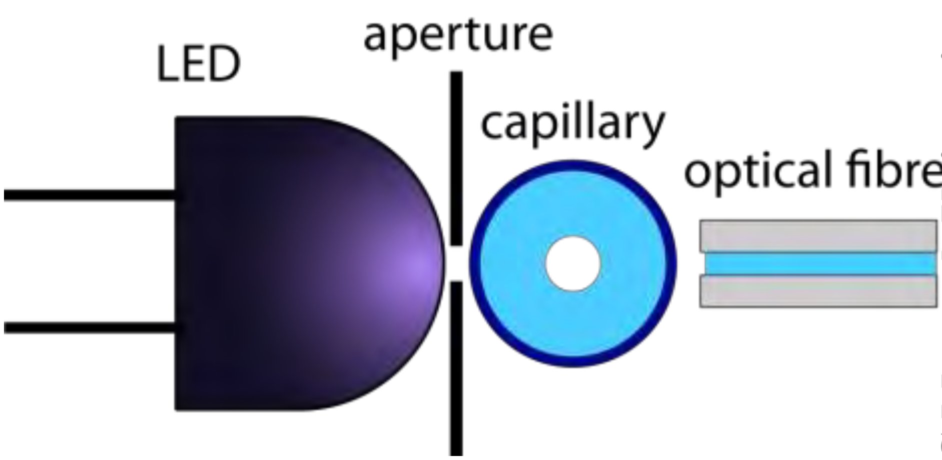
Practical considerations

- Optical fibres
  - Coupling to LEDs if used as light source
  - LEDs can be installed right on capillary (or chip) in a on-capillary cell (or on-chip setup)
  - Use of optical interface/setup





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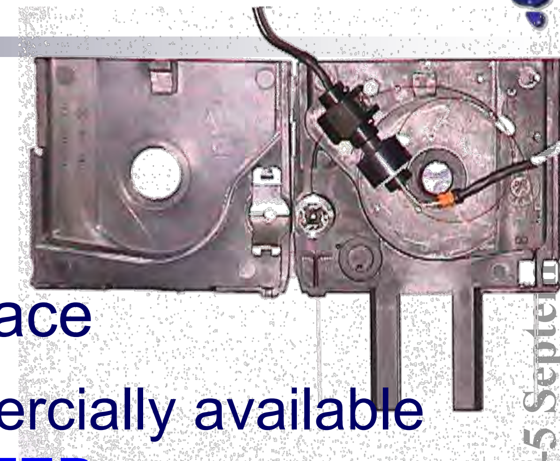
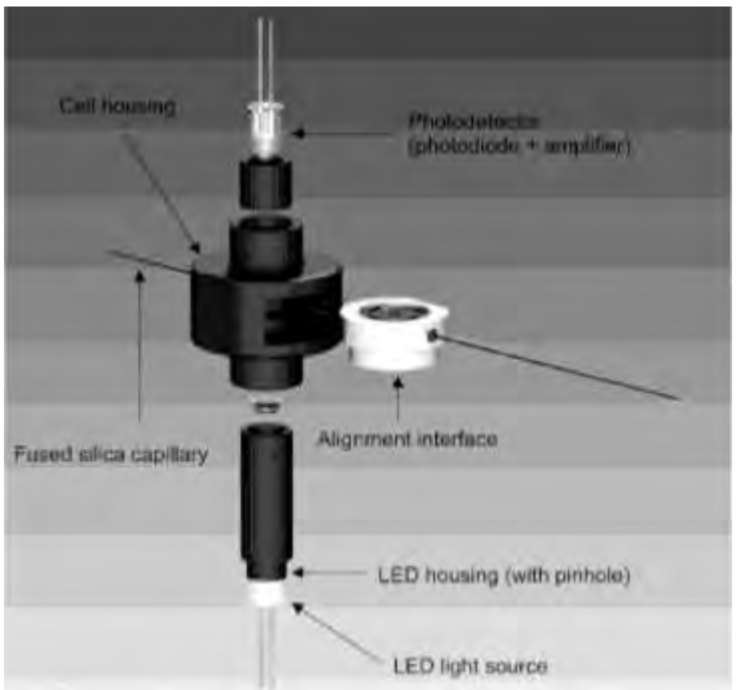
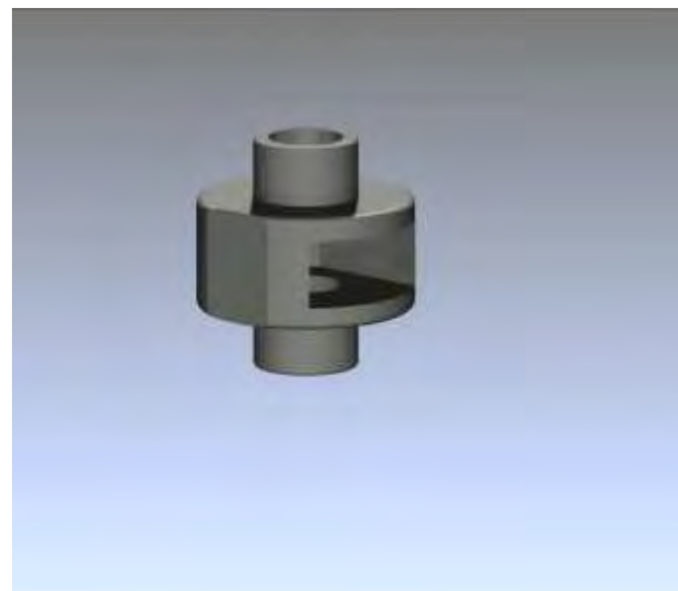
Practical considerations

- On-capillary photometric detection
  - Optical interface from Agilent CE
  - Can be in-house designed optical interface
    - Design is needed – easier to use commercially available



ANIMATED





Johns, C., et al. *Journal of Chromatography A* **2001**, *927*, 237-241

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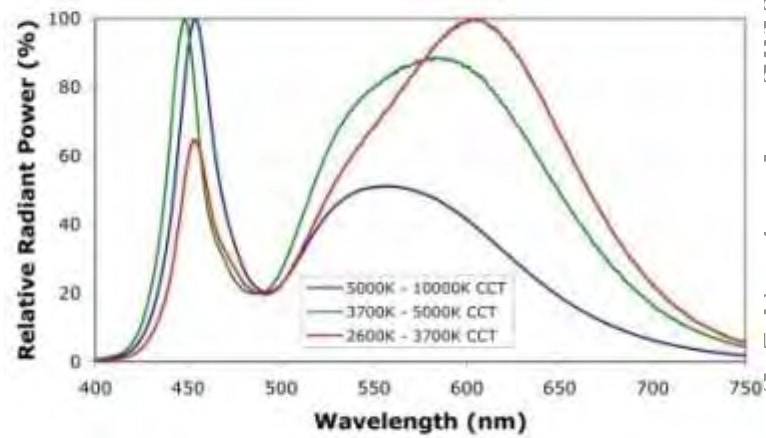
Practical considerations

- Negligible heat generation
  - Monochromatic UV-vis LEDs do not radiate in IR
  - White LEDs do not exceed 800 nm



  - LEDs are dissipating heat in convective manner
    - Operating temperature of 5 mm LED does not exceed 70-80 °C (160-175 °F)
    - Temperatures of high-power LEDs (like Luxeons) can reach 140-150 °C (285-300 °F)
      - LEDs are not supposed to work at such high temperatures – these are threshold values for irreversible damage
    - Typical 100W incandescent bulb have outside bulb temperature in the range of 200-260 °C (400-550 °F)

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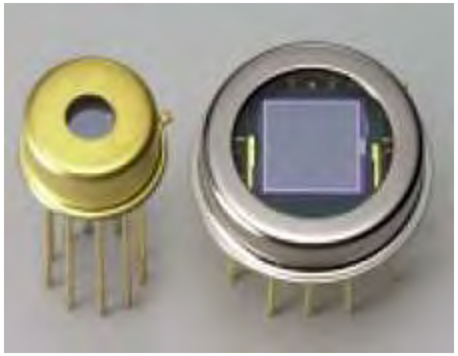
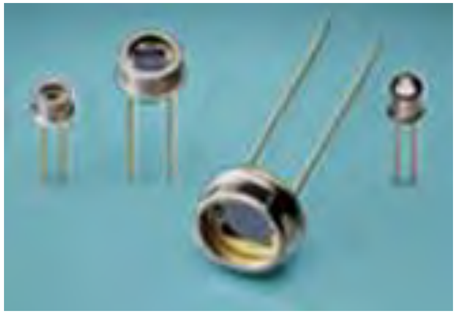
Detectors for LEDs

- Silicon photodiodes
  - Most commonly used photodetector
  - Good sensitivity
  - Price range ~$25-450
  - Wide range of sizes available
    - ~0.2-613 mm^2 (www.edmundoptics.com)
  - Two types:
    - Without preamplifier
    - With integrated preamplifier
  - Wavelength range
    - Standard: vis-NIR
    - UV: ~190-1100 nm



www.edmundoptics.com



www.hamamatsu.com

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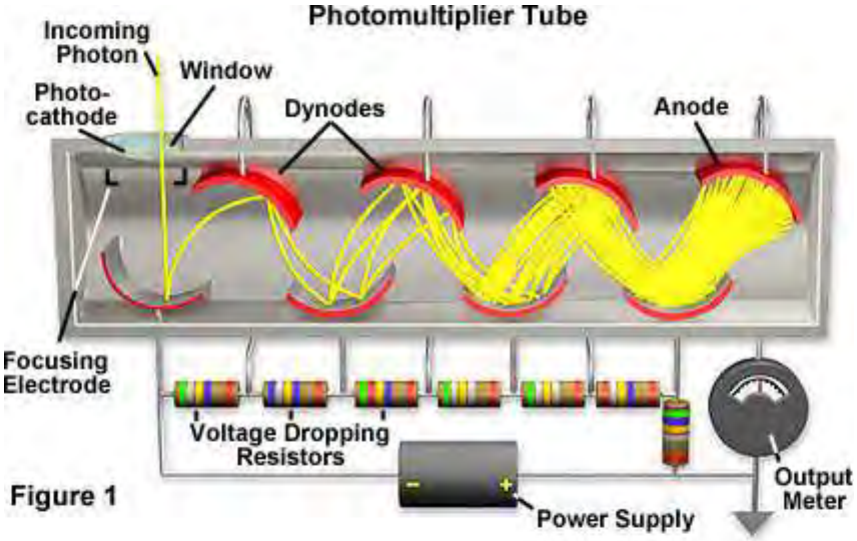
Detectors for LEDs

- Low light detection
  - Avalanche photodiode
    - Gain c.a. 100 times
    - ~ $ 150-1500

www.globalspec.com

  - Photomultiplier
    - Gain of 10^7 times and higher
    - Requirement of external amplifier (often)
    - ~ $450-2500+
    - www.newport.com
    - www.hamamatsu.com



micro.magnet.fsu.edu

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Data acquisition systems

- Data aquisition systems
  - eDAQ eCORDER
    - Multichanel data aquisition
    - Separate aquisition channels
    - Arythmetic operations
    - ~ $ 3,000
  - Picologger ADC-16
    - Simple yet accurate (16-bit)
    - Compact design
    - Up to 8 channels
    - ~ $230

www.edaq.com

www.picotech.com

$ A wide range of inexpensive products available

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Course schedule

- Afternoon
  - Background – what you should know
    - **A brief history - 'Alloy Road'**
    - Fundamentals: Physical principles, design
    - Coffee break
  - Usage
    - Illumination, fluorescence microscopy & visualization
    - Optical analytical methods: photometry, fluorimetry
    - Photochemistry: photoinitiations, photolithography
    - Heating, other usage
  - Course evaluation, feedback, close

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Brief history of LEDs

- LED – 4^{th} generation light source
  - 1^{st} – fuel combustion (wood, wax, oil)
  - 2^{nd} – incandescent (tungsten bulb)
  - 3^{rd} – fluorescent (fluorescent tube)
  - 4^{th} – solid-state light sources (SSL) - LED

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Brief history of LEDs

- Incandescent laps
- 100 years of evolution
  - 1802: Sir Humphrey Davy
    - First experiments with passing current through platinum filament
  - 1879: Thomas A. Edison
    - First commercially successful incandescent lamp
  - 1910: William D. Coolidge
    - Tungsten filament

Wikipedia.org

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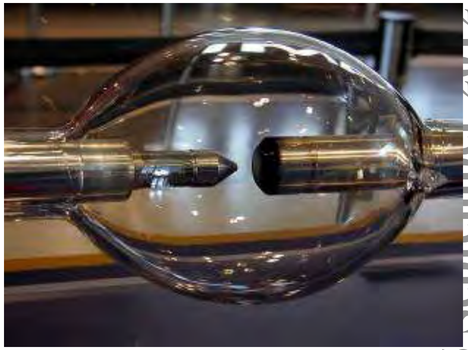
Brief history of LEDs

- Arc lamps
  - 1809: Sir Humphrey Davy
    - Carbon arc lamp (demonstrated in 1810)



- Fluorescent lamps
  - 1857: Heinrich Geissler
    - Demonstration of gas discharge tube
  - 1901: Peter C. Hewitt
    - Mercury vapour lamp, precursor of modern CFL
  - 1926: Jacques Risler
    - Fluorescent coating in glass tube

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Brief history of LEDs

- LEDs
  - 1907: Henry Joseph Round
    - First documented observation of electroluminescence

- 1927: Oleg Losew
  - First known publication

- 1940: Russel Ohl
  - Discovery of p-n junction and photovoltaic effect

Brief history of LEDs

- 1933-1939: Eugene Wigner and Frederick Seitz
    - Quantum theory of solids, basic theory of metals and semiconductors, band structure

- 1947: John Bardeen, Walter Brattain, William Shockley
    - First explanation of electron-hole recombination, physical theory of p-n junction, development of transistor

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Brief history of LEDs

- 1951: Kurt Lehovec
  - First correct explanation using band theory of electroluminescence due to band to band recombination
- 1951: Heinrich Welker
  - First identification of III-V semiconductors
- 1952: J. R. Hayner and H. Briggs
  - First reported electroluminescence from germanium

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Brief history of LEDs

- 1957: Leo Esaki
  - Identification of the process of carrier tunnelling in bipolar transistors – basis for tunnel diode

- 1962: Robert N. Hall
  - First semiconductor laser device (infrared, GaAs) on 16 September 1962

Brief history of LEDs

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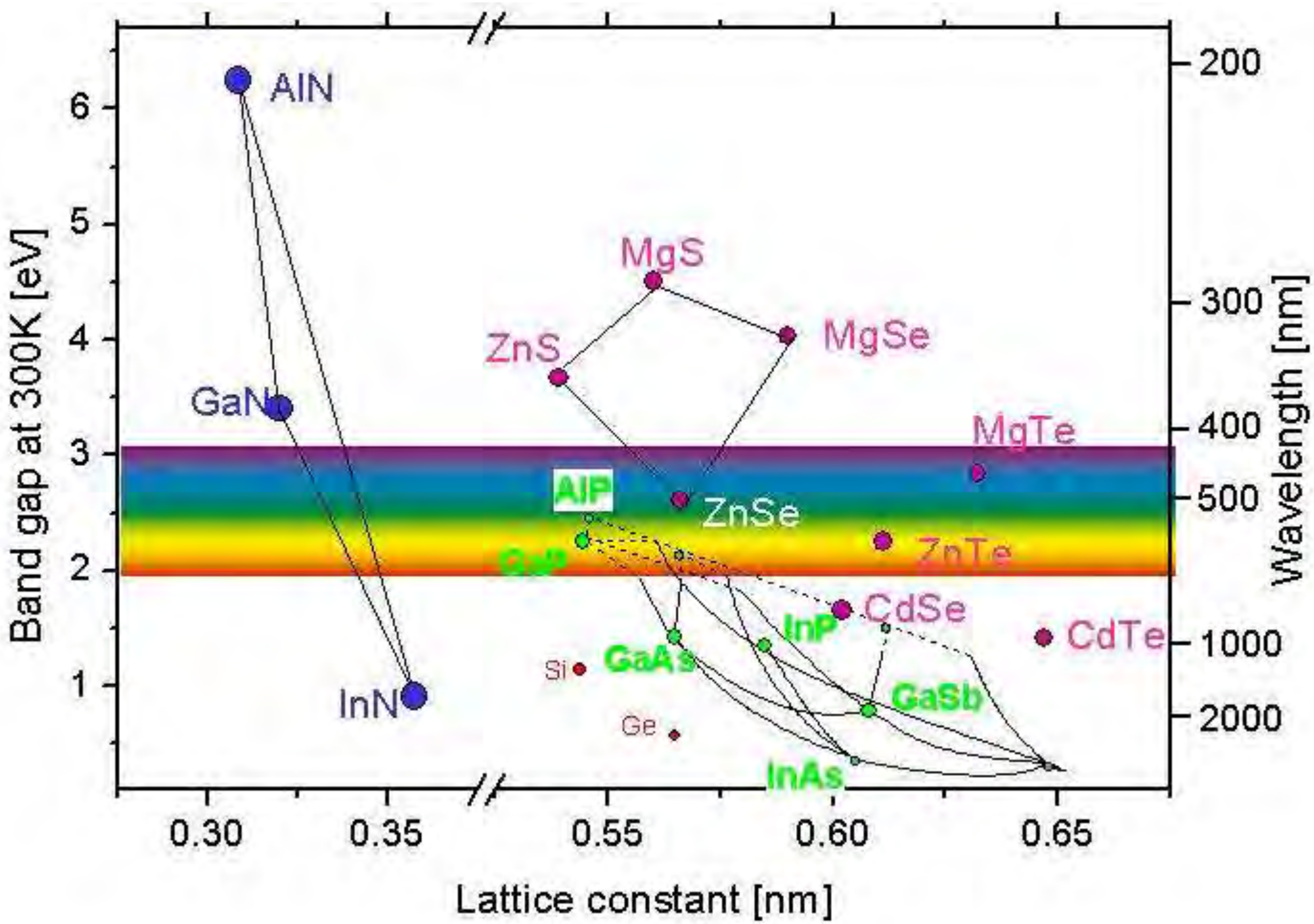
- 6 October 1962: Nick Holonyak, Jr „father of LED"
  - First created visible emission form semiconductor at 710 nm laser diode (6 October 1962)
- 1962:
  - World first diode emitting visible (red) light GaAs/GaAsP (260 $)

$ Know brief background & history of LED

$ Value for teaching

Brief history of LEDs

- The „Alloy Road”



www-opto.e-technik.uni-ulm.de

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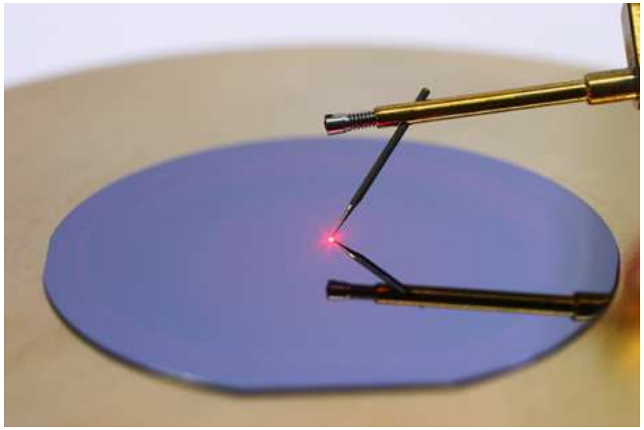
Brief history of LEDs

- The „Alloy Road"



  - ~1956: studies on Ge-Si alloy
    - First semiconductor alloy
  - 1960-1962: $GaAs_{1-x}P_x$
    - First ternary semiconductor
  - 1962-1963: Heterojunction layer – $GaAs_{1-x}P_x$/ $GaAs_{1-y}P_y$
    - The beginning of „Alloy Road" – N. Holonyak
  - 1970: AlGaAs/GaAs, Z. Alferov (U.S.S.R.)
    - First room temperature operating solid state laser (300K)

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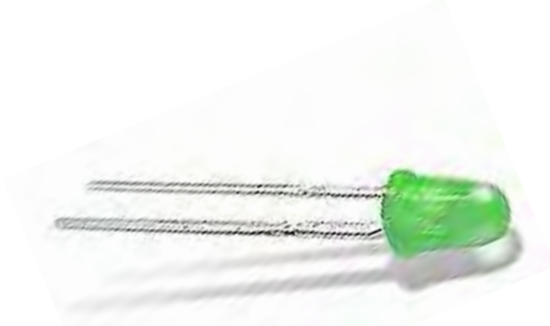
Brief history of LEDs

- The „Alloy Road”
  - 1968: First green LED
  - 1970s:
    - Rapid growth of ternary alloys GaAsP, AlGaAs, InGaAs, InAlAs, InGaP, AlAsP, etc.
  - 1970: N. Holonyak - GaAlAsP/GaAsP
    - First quaternary alloy – high degree of freedom in lattice matching and bandgap energy
  - 1970: M. Crawford - GaAsP:N
    - High performance LEDs: amber, yellow-green and green



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Brief history of LEDs

- 1969: H.P. Maruska, J. Pankove
  - First solid state source of blue light: structure MIS (metal-insulator-semiconductor), GaN (*n*-type)

- 1991: M. Haase
  - World first blue laser (ZnSe/CdZnSe) – theoretical success but short lifetime and toxic
- 1992: I. Akasaki
  - First working blue diode (p-n), GaN

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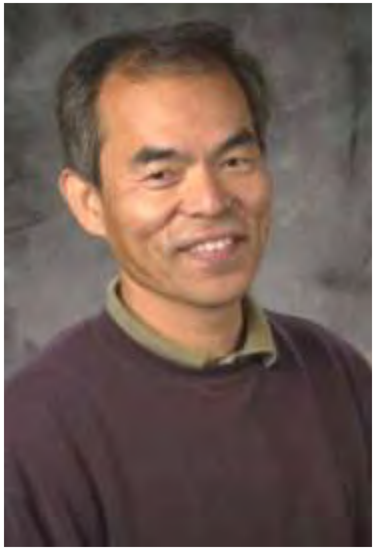
Brief history of LEDs



- 1993: Shuji Nakamura
  - High luminosity blue diode (p-n) GaN, >1cd
- It was the high-brightness blue LED that opened the way to SSL

$ Know brief background & history of LED
  $ Value for teaching

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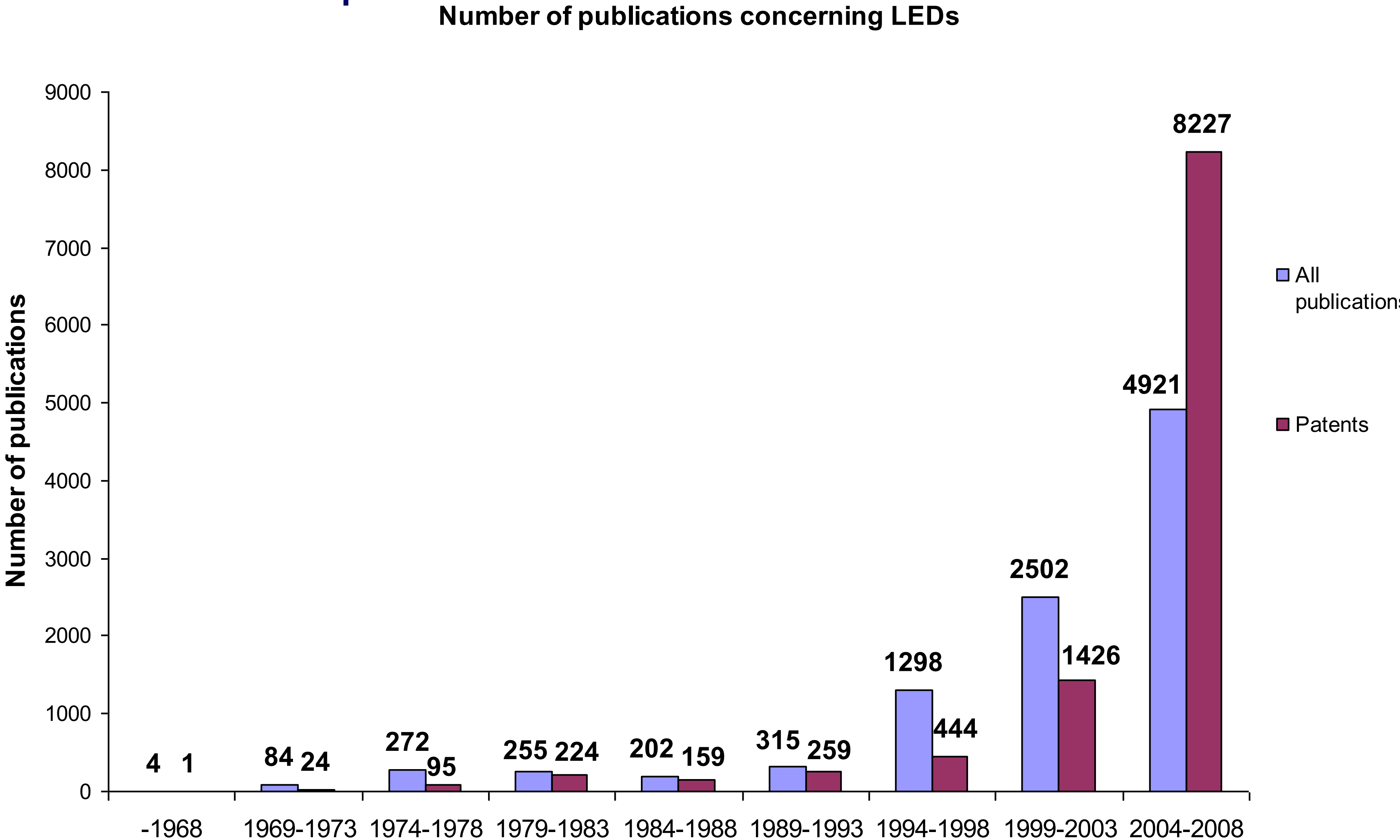
Brief history of LEDs

- Numbers of publications for LEDs



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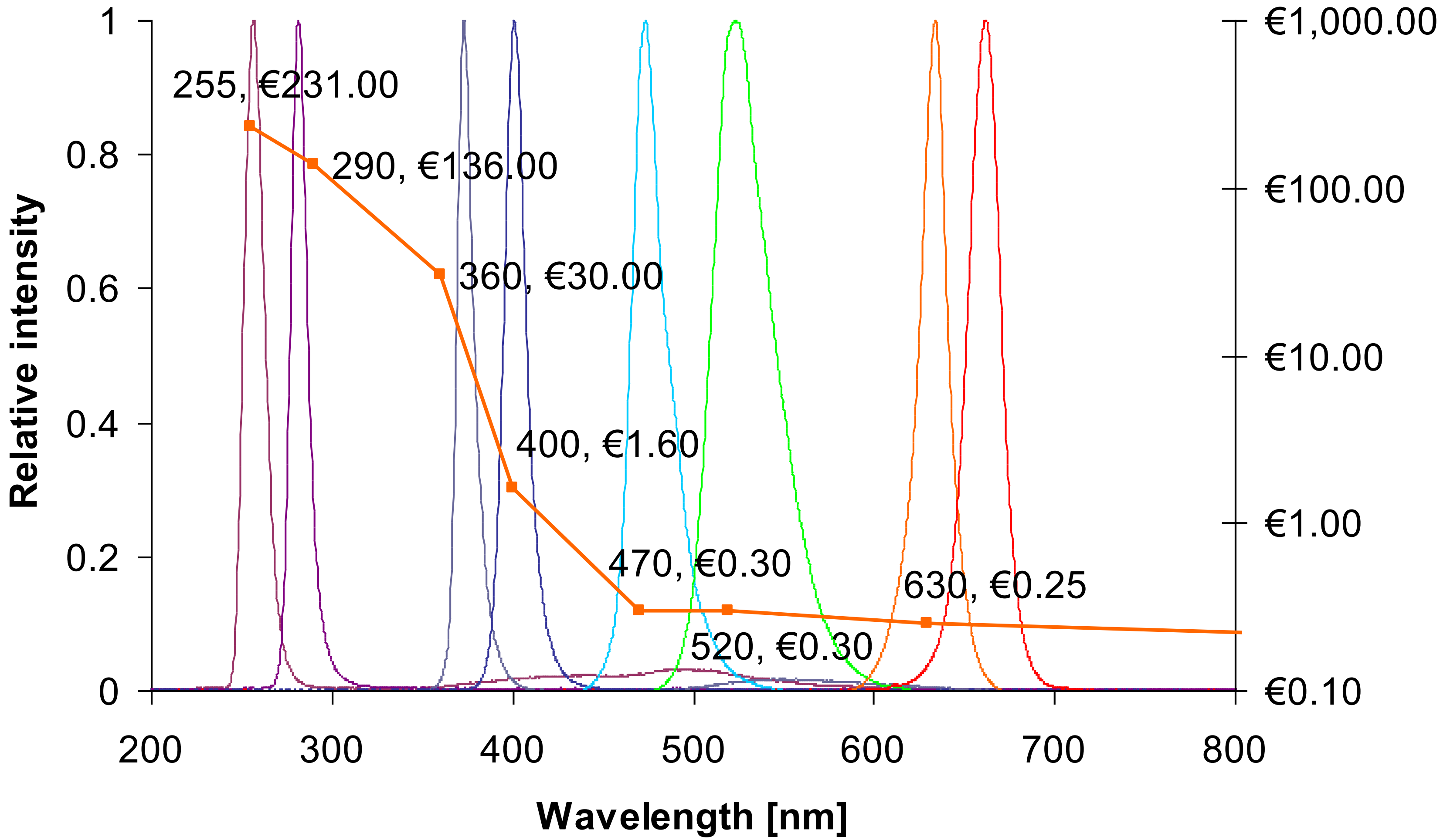
Brief history of LEDs

- Price *vs.* wavelength



$ Know that today deep-UV-LED = expensive LED

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LEDs in Chemistry: Outline

- Why use LEDs in chemistry and science?
- Modern light sources
- LED – electric device driven by direct current
- Brief history of LEDs
- **Physics of LED**
  - **Basic principles and fundamental aspects**
  - Units used in world of solid state lighting
  - Advanced aspects
- Engineering and construction of LEDs

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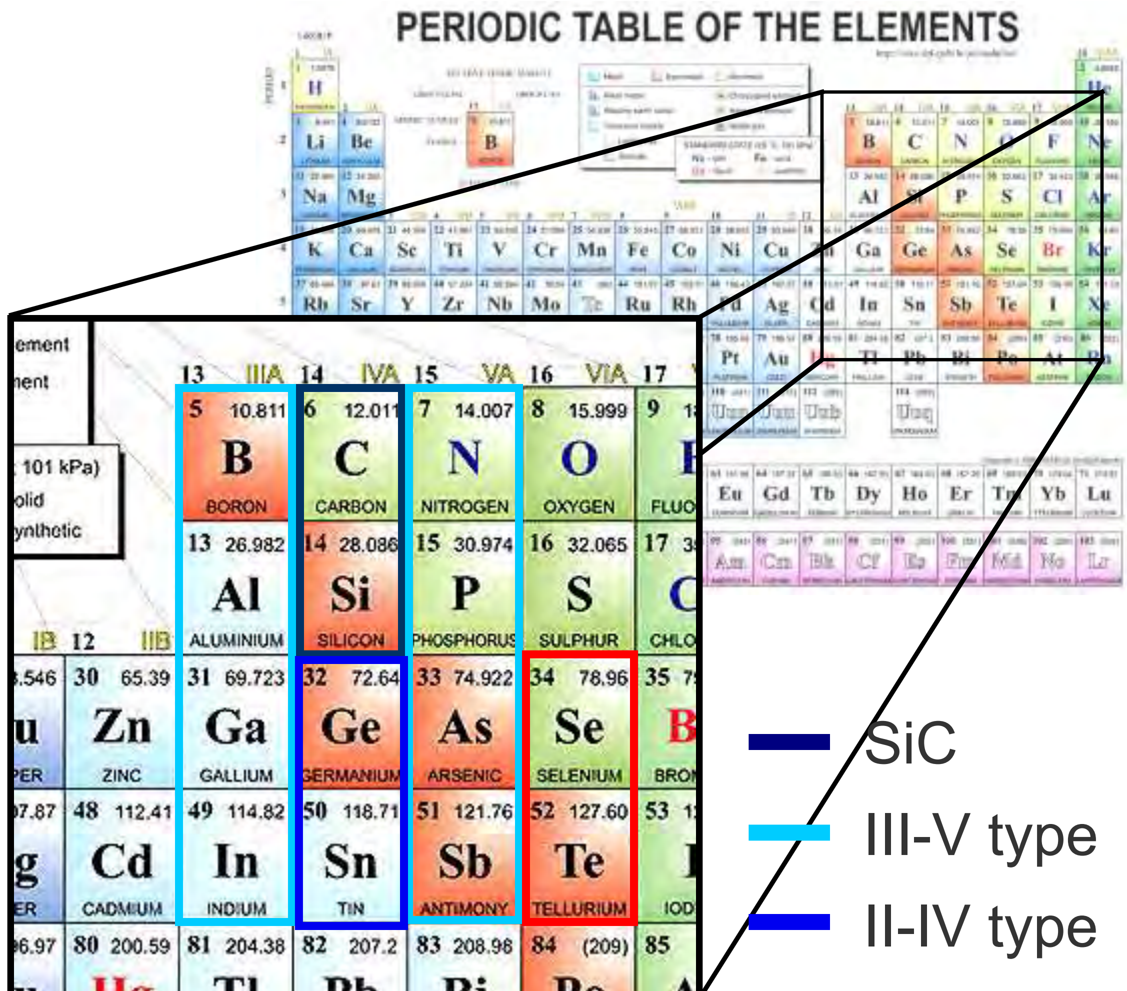
Physics of LEDs

- Semiconductors – materials with unique feature that allow us to construct diodes

- This is NOT a semiconductor

- These ARE



SiC

III-V type

II-IV type

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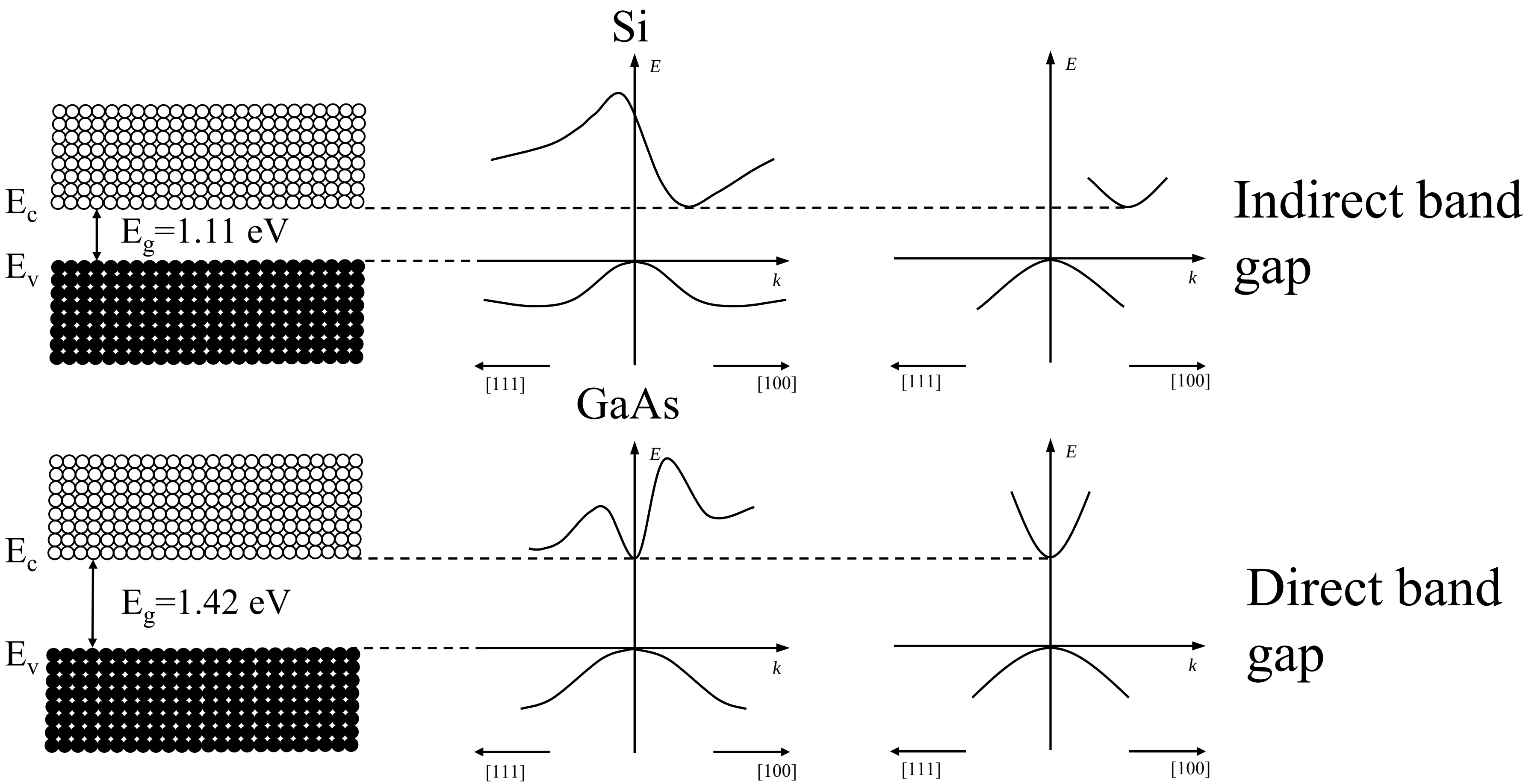
- Band gap, direct/indirect gap, parabolic approximation
  - T = 0K + Pauli exclusion principle



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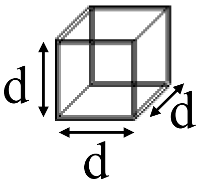
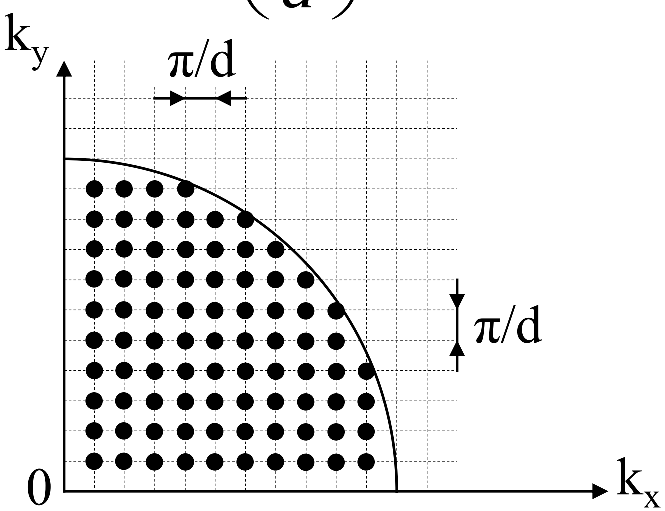
- Density of electronic states



$$\vec{k} = \frac{\pi}{d}(q_i)$$

$$N = 2\frac{\frac{1}{8}\cdot\frac{4}{3}\pi k^3}{\left(\frac{\pi}{d}\right)^3} = \frac{k^3 d^3}{3\pi^2}$$



- Boundary conditions for electron wave function
- N – number of states with wave vector < k, (2 – spin)
- Dots – only possible places for electrons

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Physics of LEDs

$$n = \frac{N}{d^3} = \frac{k^3}{3\pi^2}$$

- n – state density per volume unit

$$\rho(k)dk = \frac{dn}{dk}dk \Rightarrow \rho(k) = \frac{k^2}{\pi^2}$$

- ρ(k) – state density per volume unit per wave vector unit; k^2 depends on E

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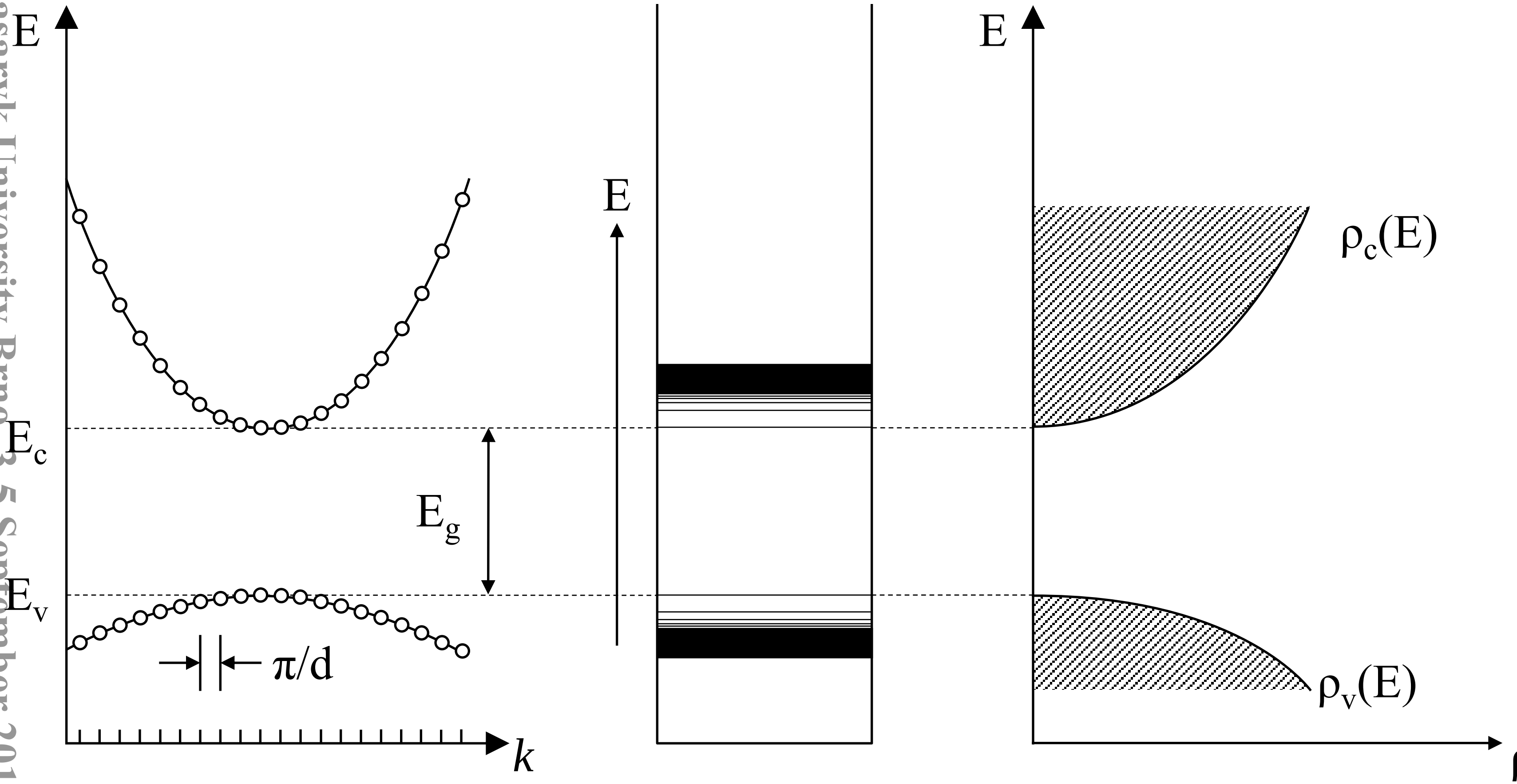
Physics of LEDs

$$\rho_c(E) = \frac{(2m_c)^{3/2}}{2\pi^2\hbar^3}\sqrt{(E - E_c)}$$

$$\rho_v(E) = \frac{(2m_v)^{3/2}}{2\pi^2\hbar^3}\sqrt{(E_v - E)}$$



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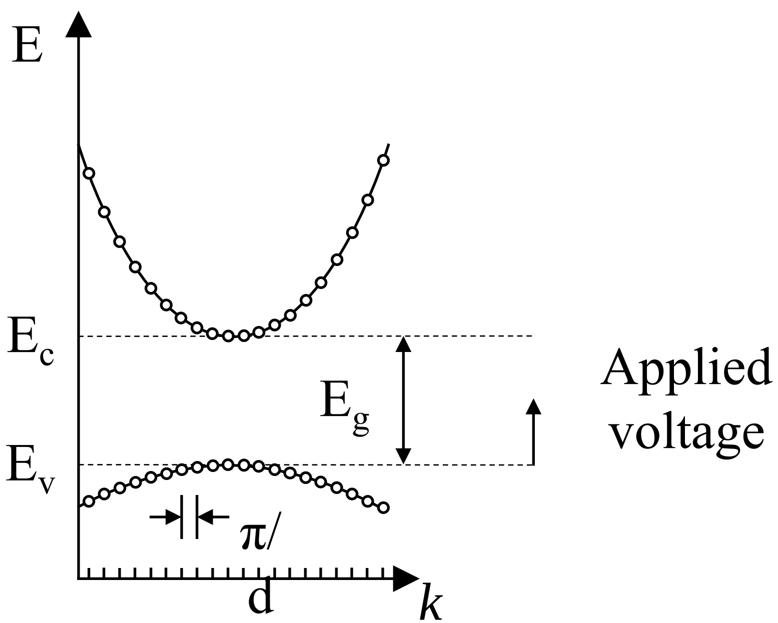
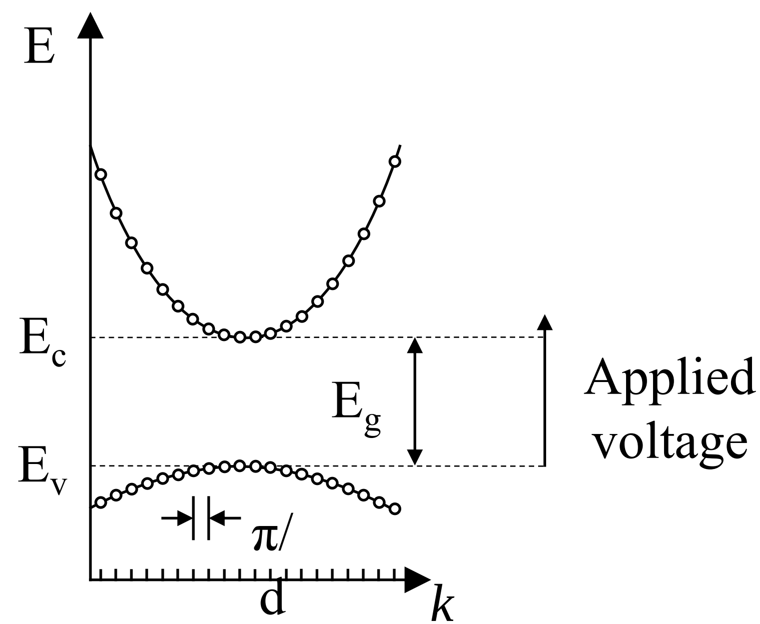
Physics of LEDs

- Measurement of bandgap energy
  - Continuous increment of applied voltage from 0 to 10 V
  - At low voltage diode is closed (below bangap energy), no current is passing though – no light is emitted
  - At high voltage diode is open (above bangap energy), current passes – light is emitted





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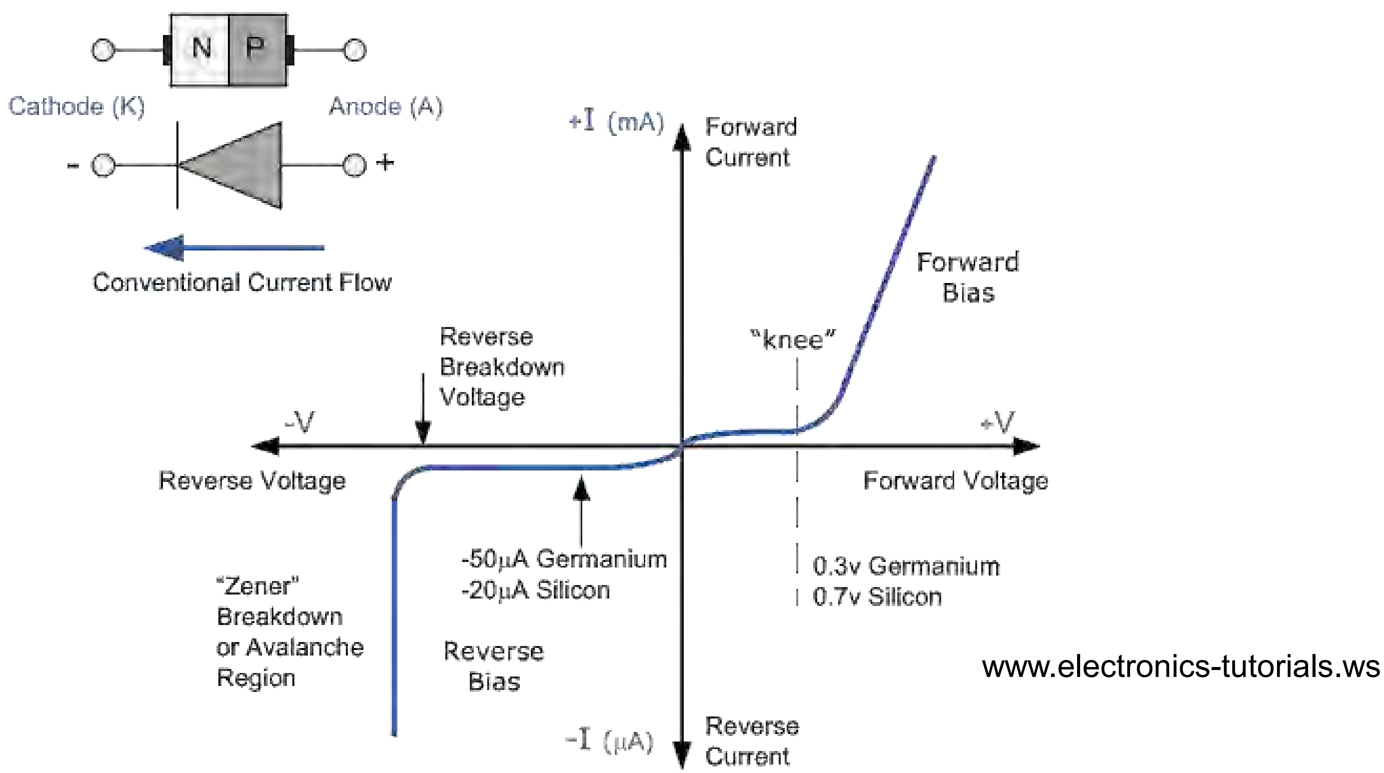
Physics of LEDs

- Bandbap energy – Electron Volts, voltage – Volts ....?
  - 1 eV is energy which is gained by (unbound) electron when it accelerates through a potential of 1 Volt
  - Applying 1V potential gives energy of 1 eV to carriers in a diode



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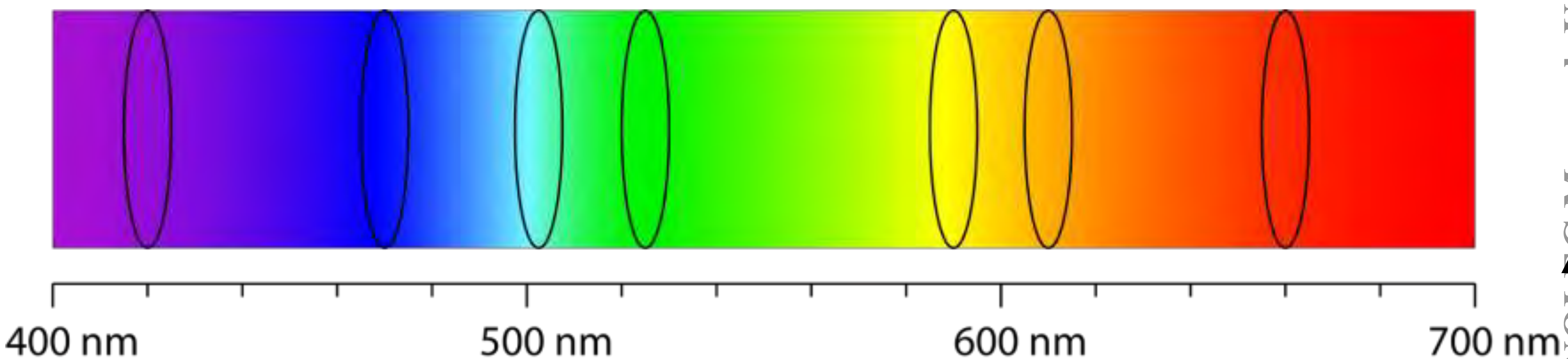
Physics of LEDs

- LED test module – 8 LEDs (eDAQ)
  - Violet, blue, aqua, green, yellow, orange, red, IR

Courtesy of eDAQ corp.



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Physics of LEDs

- Increasing voltage form 0 to 10V, separately for each LED, monitoring current and notifying voltage when diode opens (LED starts to emit light)

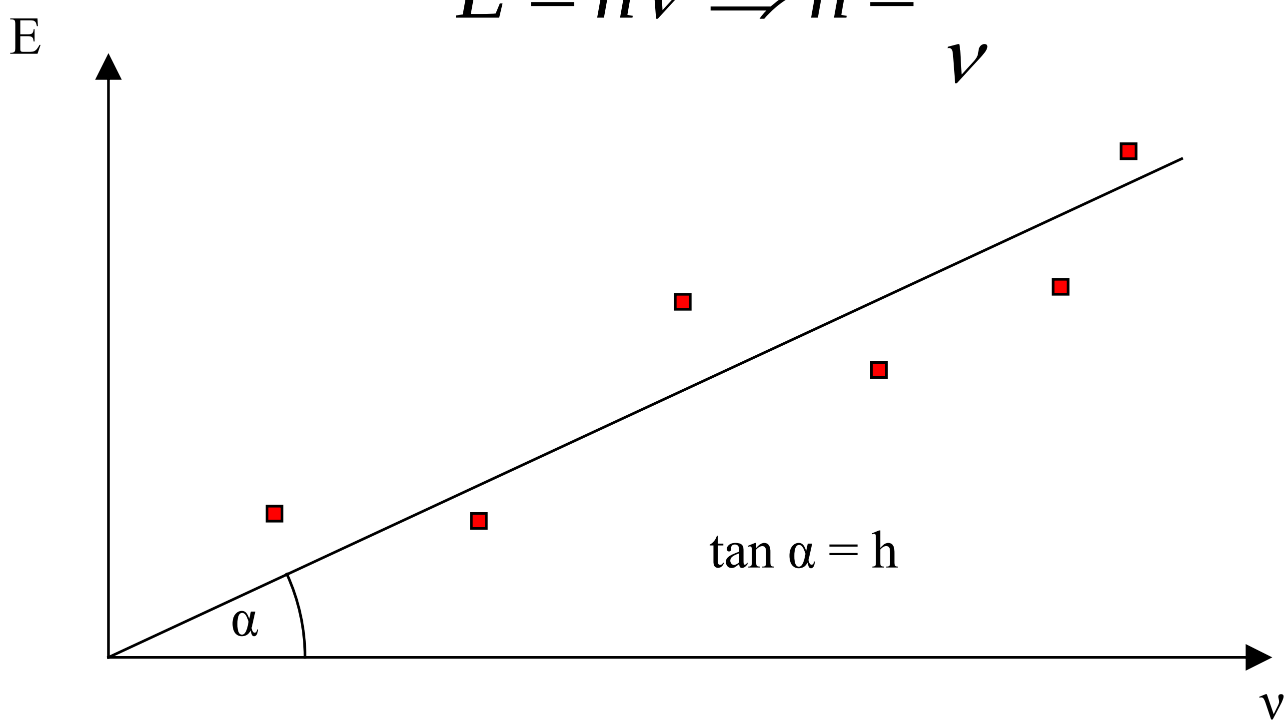
Courtesy of eDAQ corp.

$ Understanding that different LED colour → different bandgap energy → different threshold voltage

Physics of LEDs

- Step 2 from bandgap energy to Planck constant
  - What will be needed?
  - Bandgap energy and frequency

$$E = h\nu \Rightarrow h = \frac{E}{\nu}$$



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Physics of LEDs

- Wavelength – frequency

$$\lambda = \frac{c}{\nu}$$

- Wavelength at maxmum intensity taken as reference

Color	Wavelength [nm]	Frequency [Hz]	Energy [eV]
Violet	420 nm	7.1428e+14 Hz	2.5363
Blue	470 nm	6.3830e+14 Hz	2.4931
Aqua	505 nm	5.9406e+14 Hz	2.2191
Green	525 nm	5.7143e+14 Hz	2.4506
Yellow	590 nm	5.0847e+14 Hz	1.6053
Orange	610 nm	4.9180e+14 Hz	1.6025
Red	660 nm	4.5455e+14 Hz	1.4603
Infra red	940 nm	3.1915e+14 Hz	0.8609

Courtesy of eDAQ Sydney.

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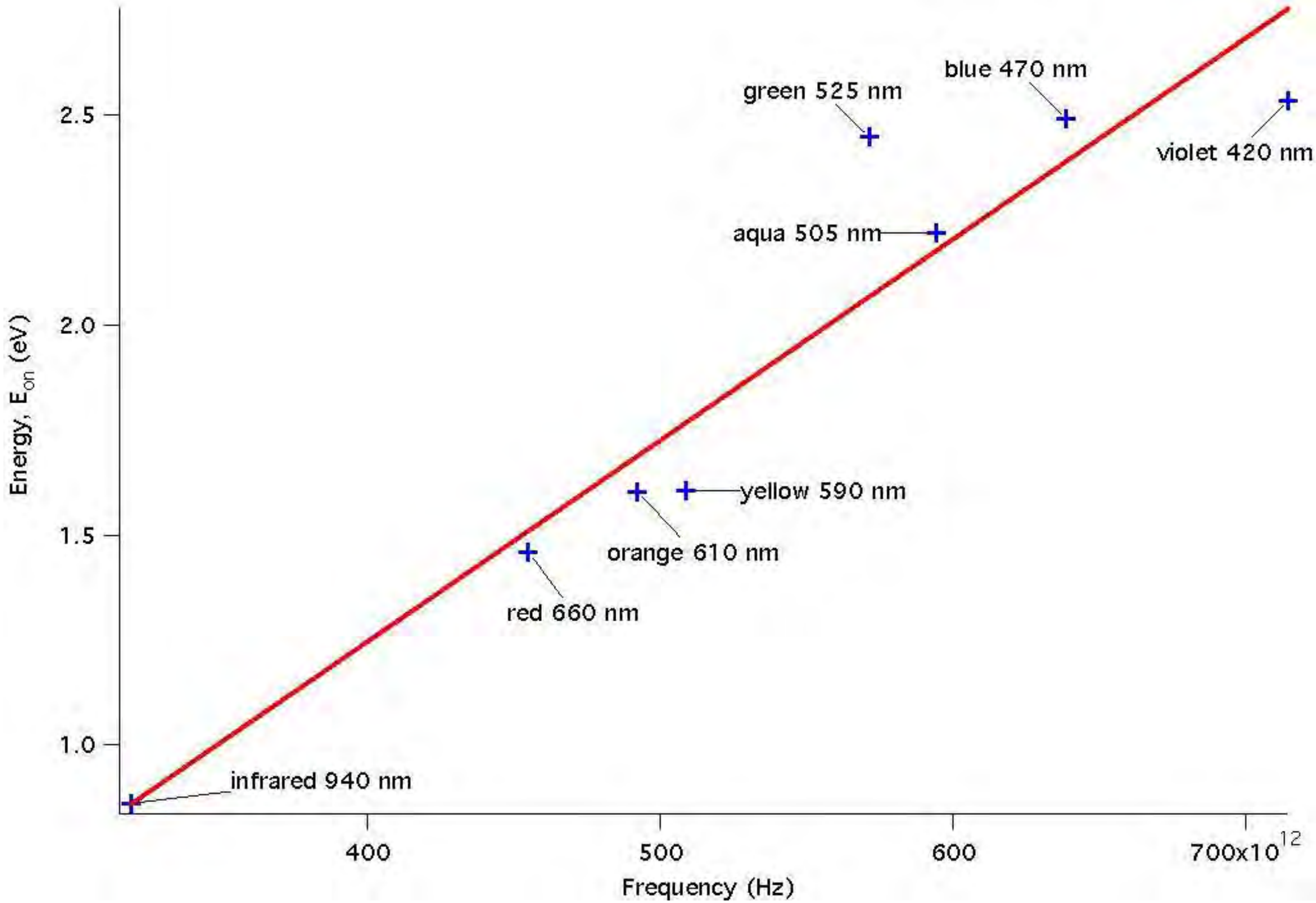
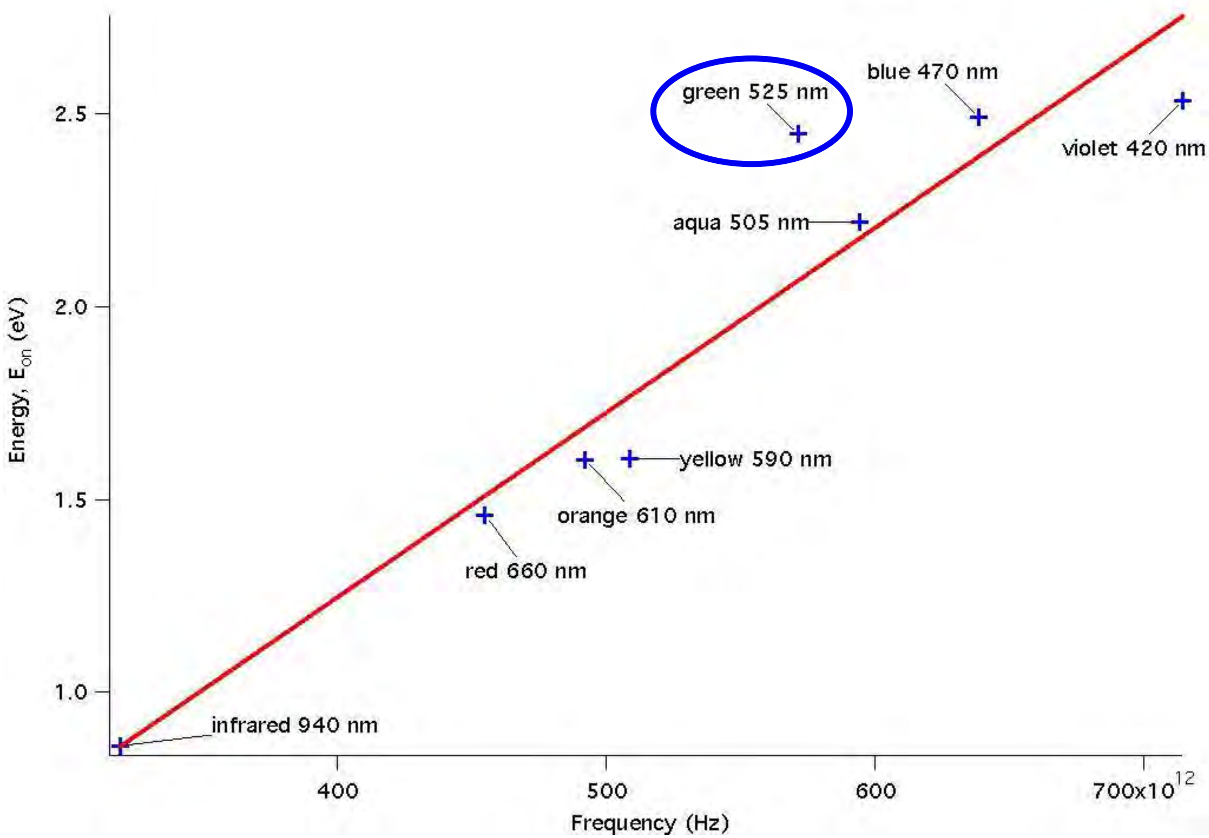
Physics of LEDs



Courtesy of eDAQ corp.

Physics of LEDs

- Results and discussion
  - Slope 4.8 ± 0.6 x10^{-15} [eV·s] (7.7 ± 1.0 × 10^{-34} J·s)
  - 1 eV =1,602 176 53 × 10^{-19} J



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Physics of LEDs

- Slope = $4.6 \pm 0.4 \times 10^{-15}$ [eV·s] ($7.4 \pm 0.6 \times 10^{-34}$ J·s)
  - Tabulated value Planck constant is 6.626×10^{-34} J·s
- Simple experiment – surprisingly good results!
- Remarks:
  - Maximum intensity wavelength is not precisely bandgap transition
  - Mismatch of bandgap has also an influence

$ LEDs can be used for teaching experiments with excellent results

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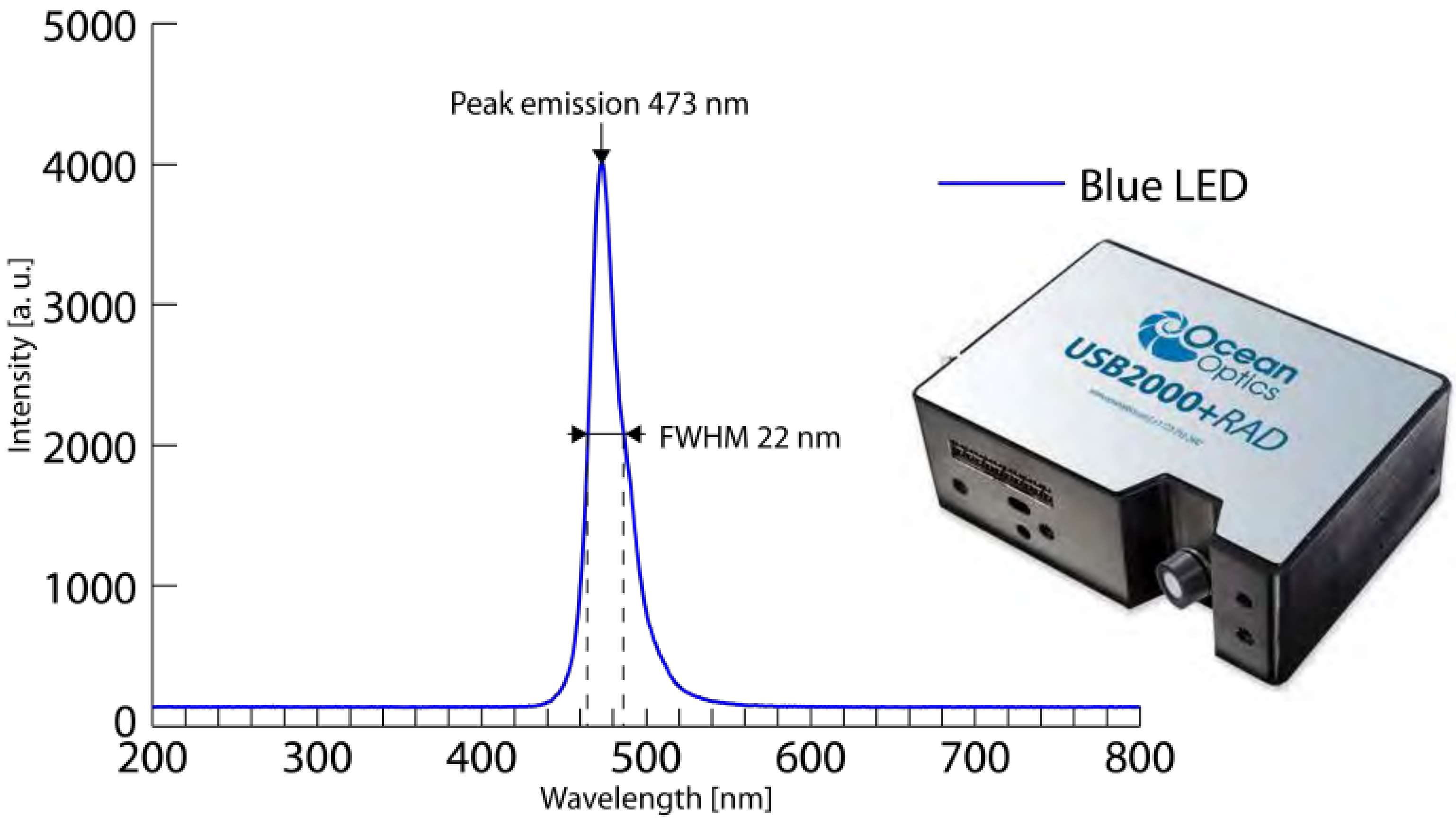
Physics of LEDs

- Measurement of LED spectra



$ Prevent wasting resources by experimenting with undefined or wrong wavelength LEDs

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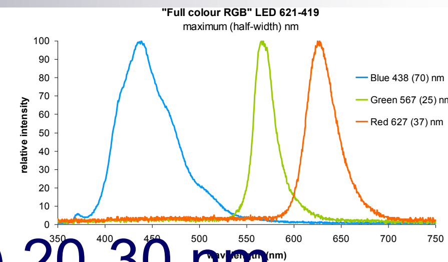
Basic principles and fundamental aspects



- LED emission spectrum
  - Quasimonochromatic
    - Full width at half maximum typical (FWHM) 20-30 nm
    - **Beware of some undesirable parasitic emissions**
  - No infrared radiation – no radiative heating
    - Small quantities of chemical samples (typically aqueous solutions) can be illuminated without risk of evaporation or ignition
    - Boiling points:
      - Acetone 53.5 °C (134 °F)
      - Acetonitrile 82 °C (179.5 °F)
      - Methanol 64.7 °C (148.4 °F)
      - Ethanol 78.4 °C (173 °F)

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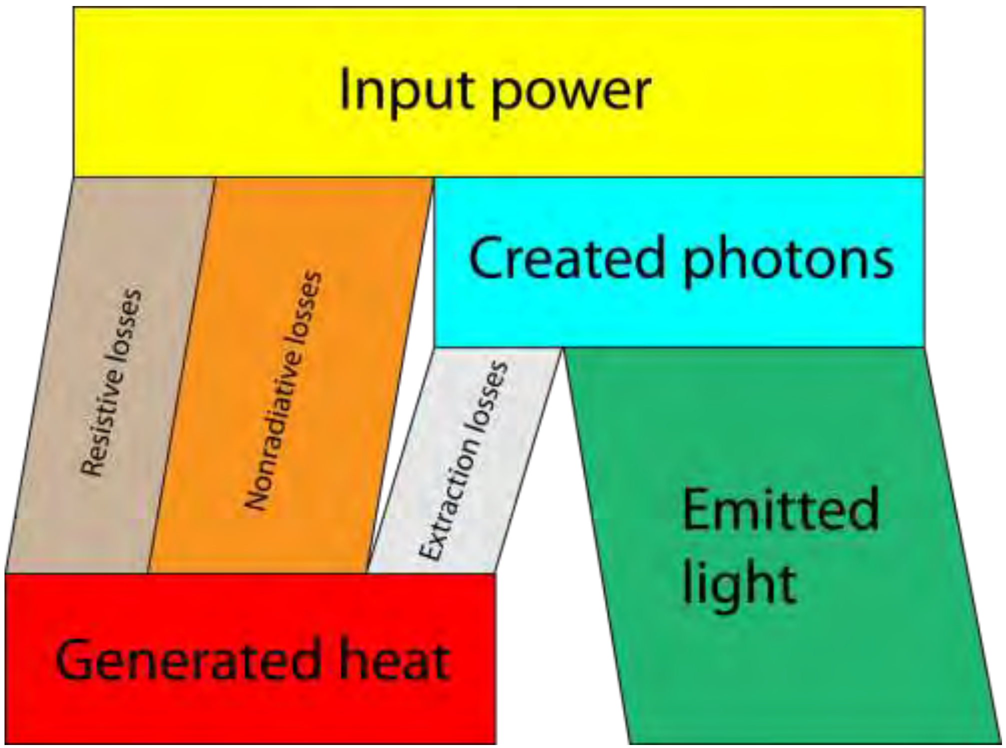
Basic principles and fundamental aspects

- Convective heating
  - Grows with frequency
  - Resistive losses, non-radiative transitions and photon absorption



after M. Krames *et al.*, Journ. Techn. 2007, 3, 160-175

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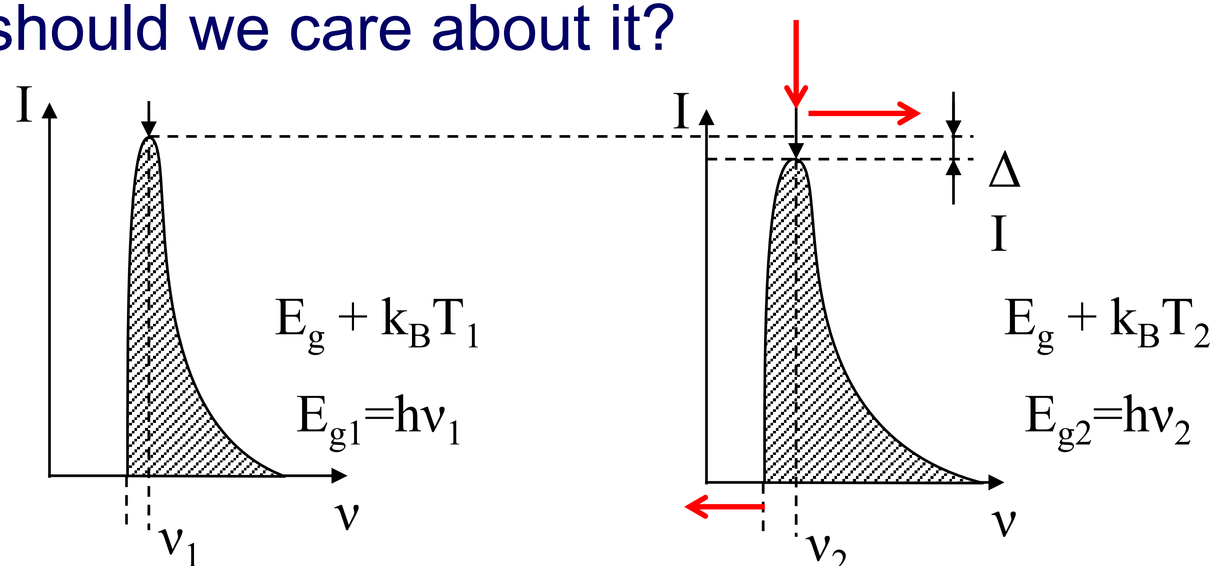
Basic principles and fundamental aspects

- Heating
  - LED bulbs get hot especially for UV and high power LEDs
  - Why should we care about it?



- Bandgap energy lowers – peak wavelength increases and spectrum broadens
  - “..before they go they all turn yellow..”

$ Overheating causes changes of spectrum and intensity

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LEDs in Chemistry: Outline

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  - **Advanced aspects**
- Engineering and construction of LEDs

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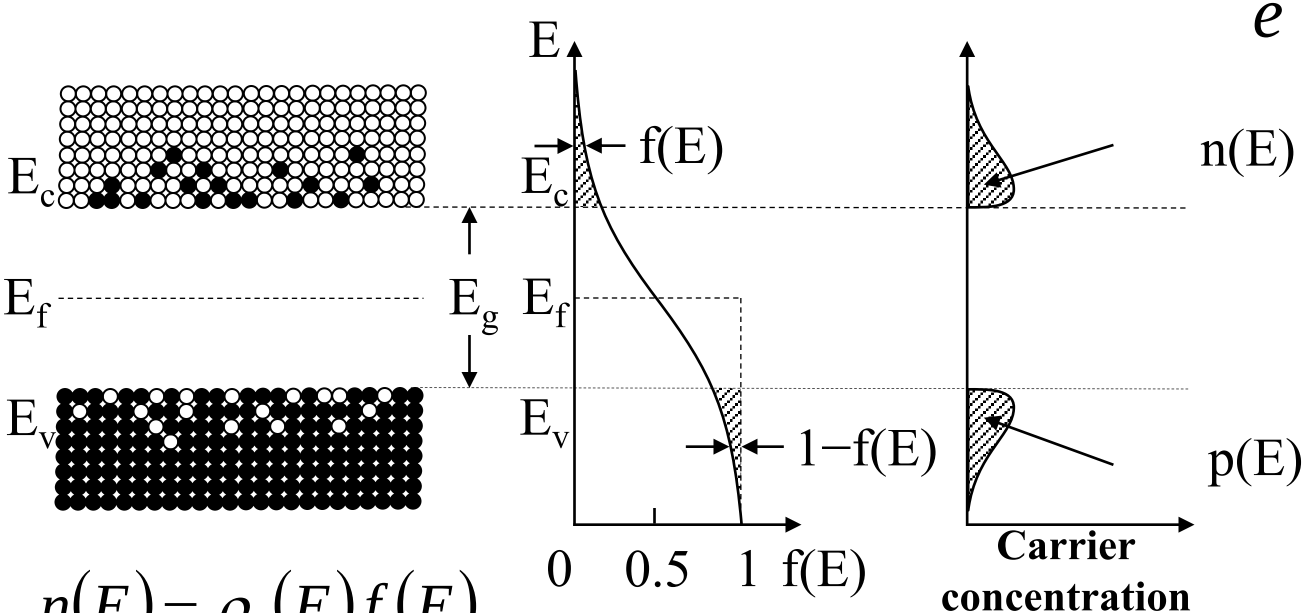
Physics of LEDs

- LED emission – advanced physics considerations
  - Carrier density (thermodynamic equilibrum)
  - Fermi-Dirac distibution

$$f(E) = \frac{1}{e^{-(E-E_f)/kT} + 1}$$



T > 0K

$$n = \int_{E_c}^{\infty} n(E)\,dE$$

$$p = \int_{-\infty}^{E_v} p(E)\,dE$$

$$n(E) = \rho_c(E) f(E)$$

$$p(E) = \rho_v(E) f(E)$$

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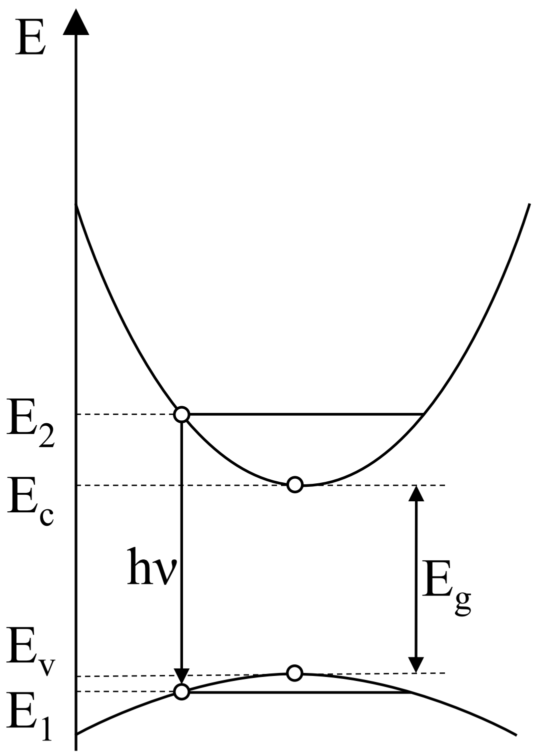
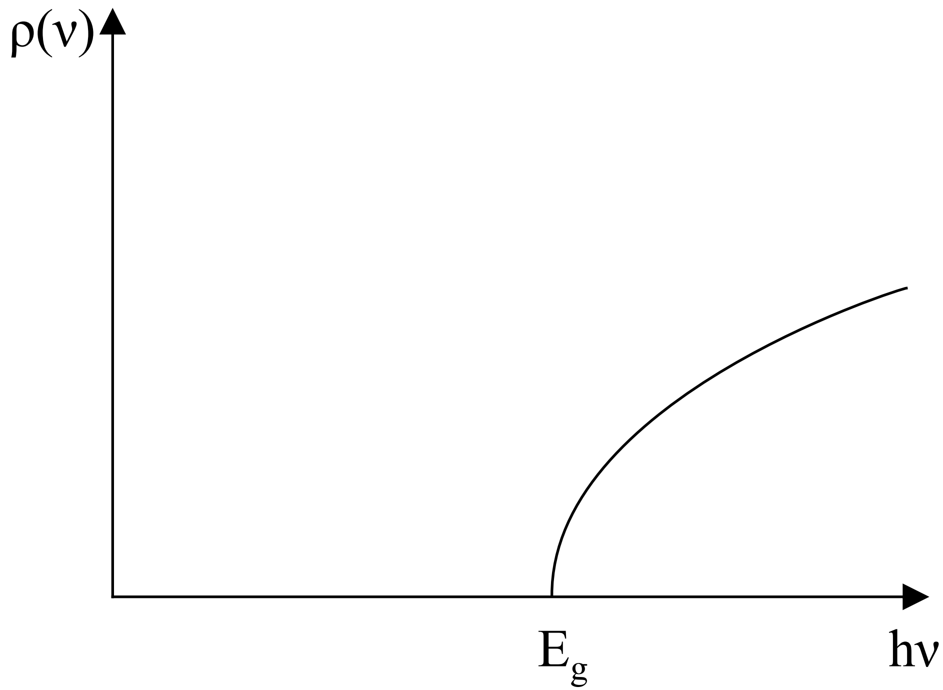
Physics of LEDs

- Wavelength of emitted light and bandgap energy
  - State density available for radiation at frequency ν





$$E_2 - E_1 = h\nu \geq E_g$$

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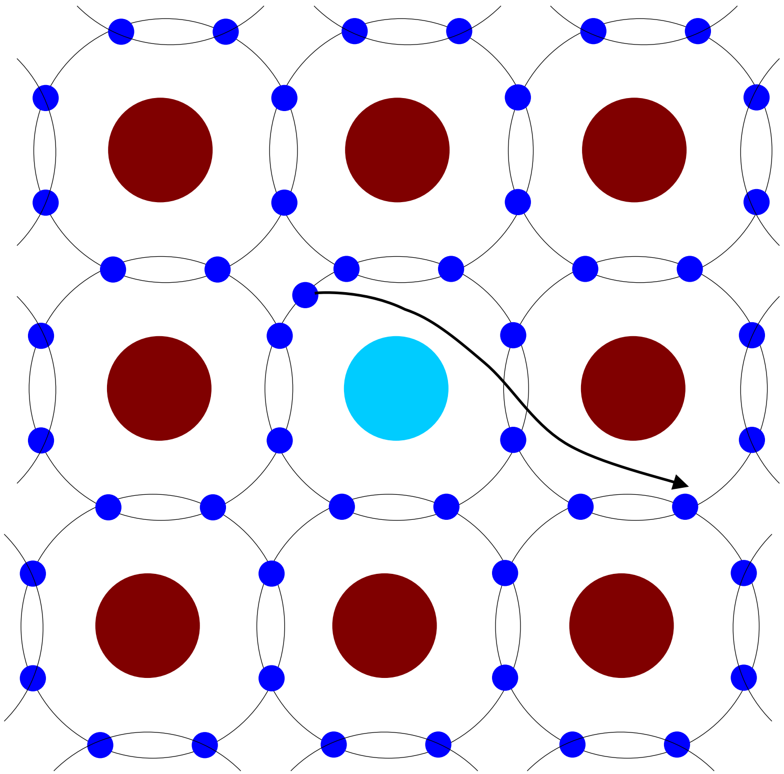
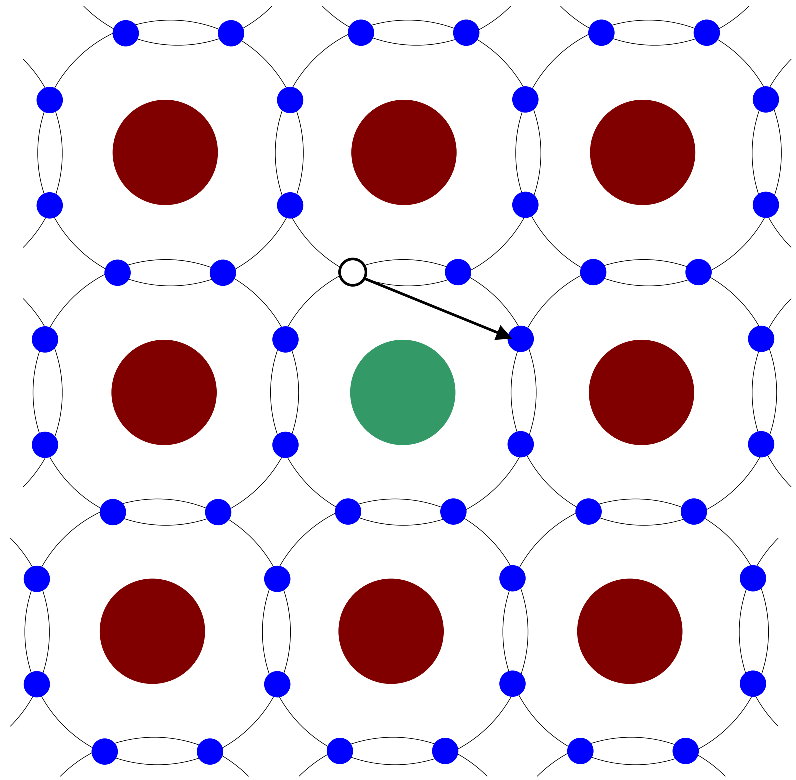
- Doped semiconductors

- type n P(V) → Si(IV)



- type p In(III) → Si(IV)



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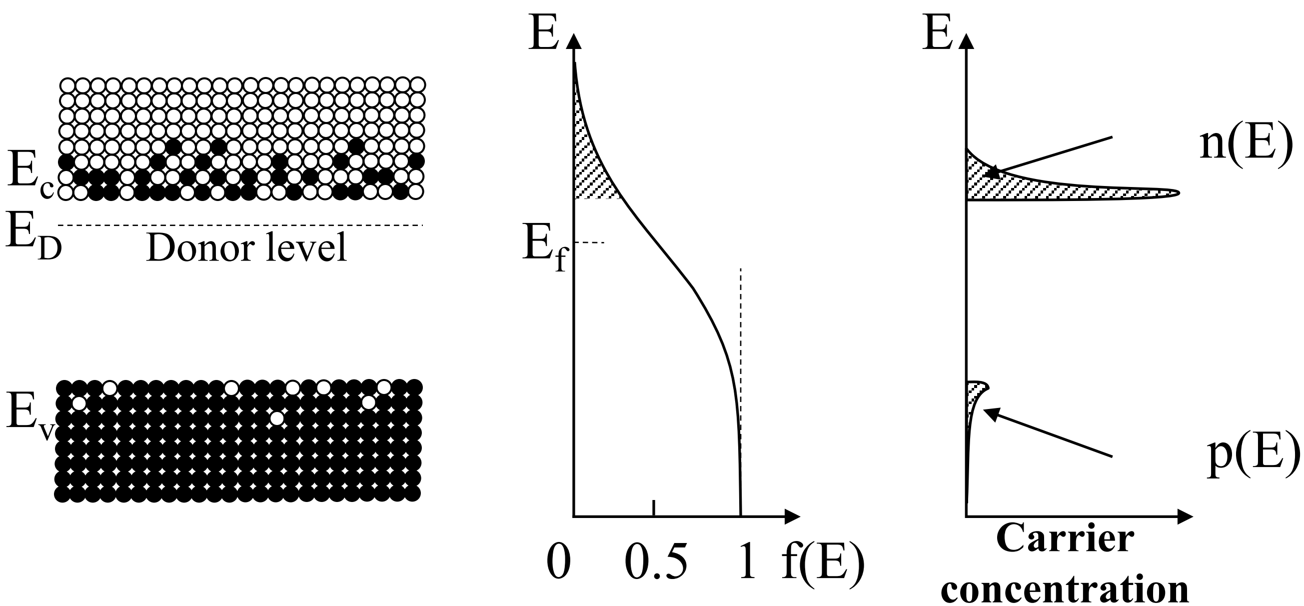
Physics of LEDs

- Doped semiconductors – type n
  - Majority carriers – electrons
  - Minority carriers – holes



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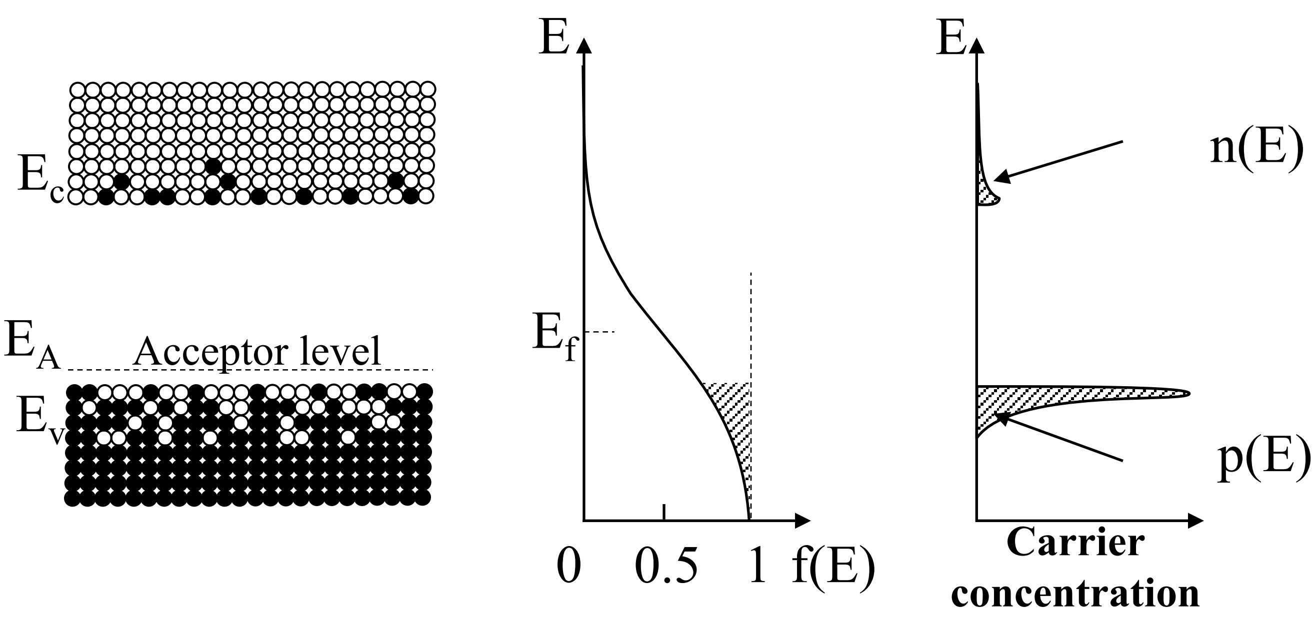
Physics of LEDs

- Doped semiconductors – type p
  - Majority carriers – holes
  - Minority carriers – electrons



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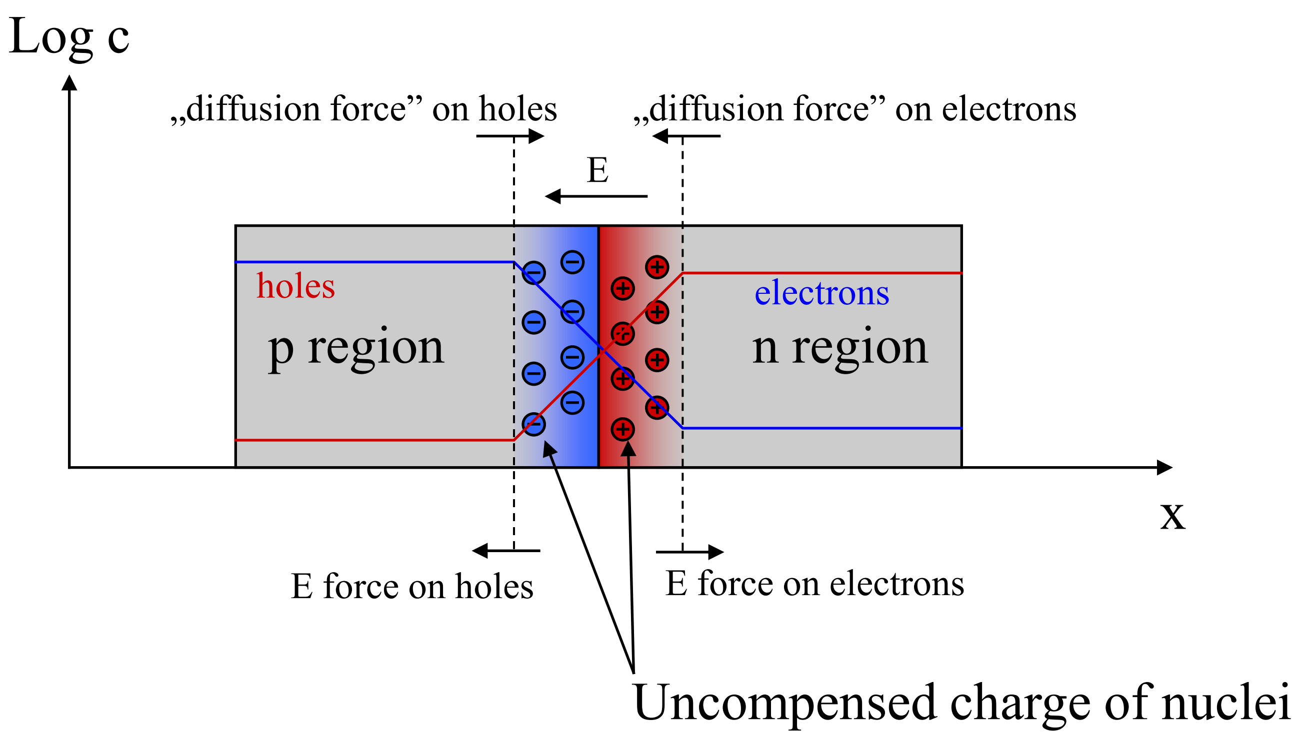
- P-n junction – principle of LED
  - Depletion zone
  - Thermal equilibrum with no voltage applied



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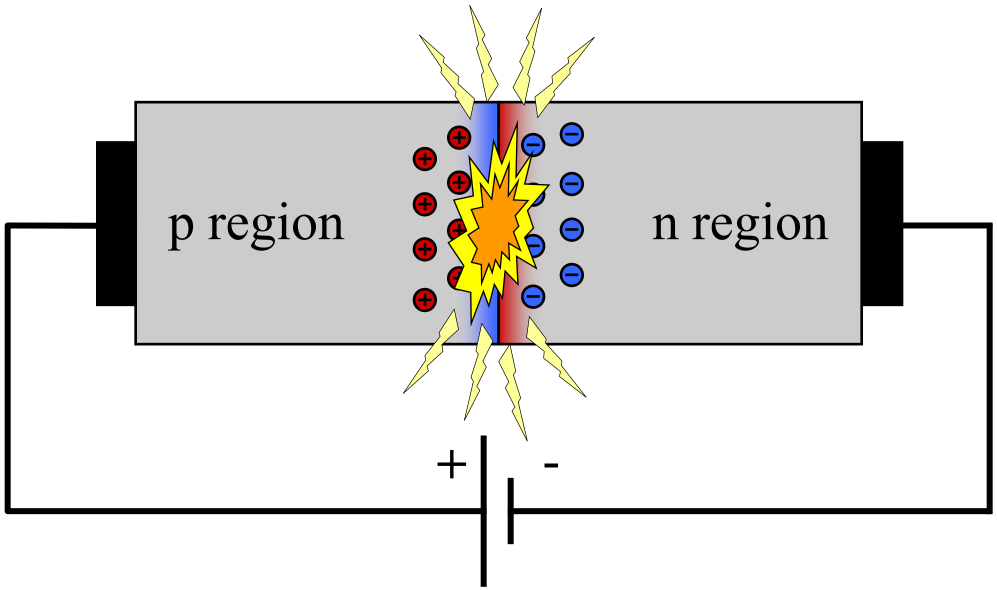
Physics of LEDs

- P-n junction in forward bias
  - Injection of charge carriers
  - Radiative recombination
  - Optical transition only on direct band gap



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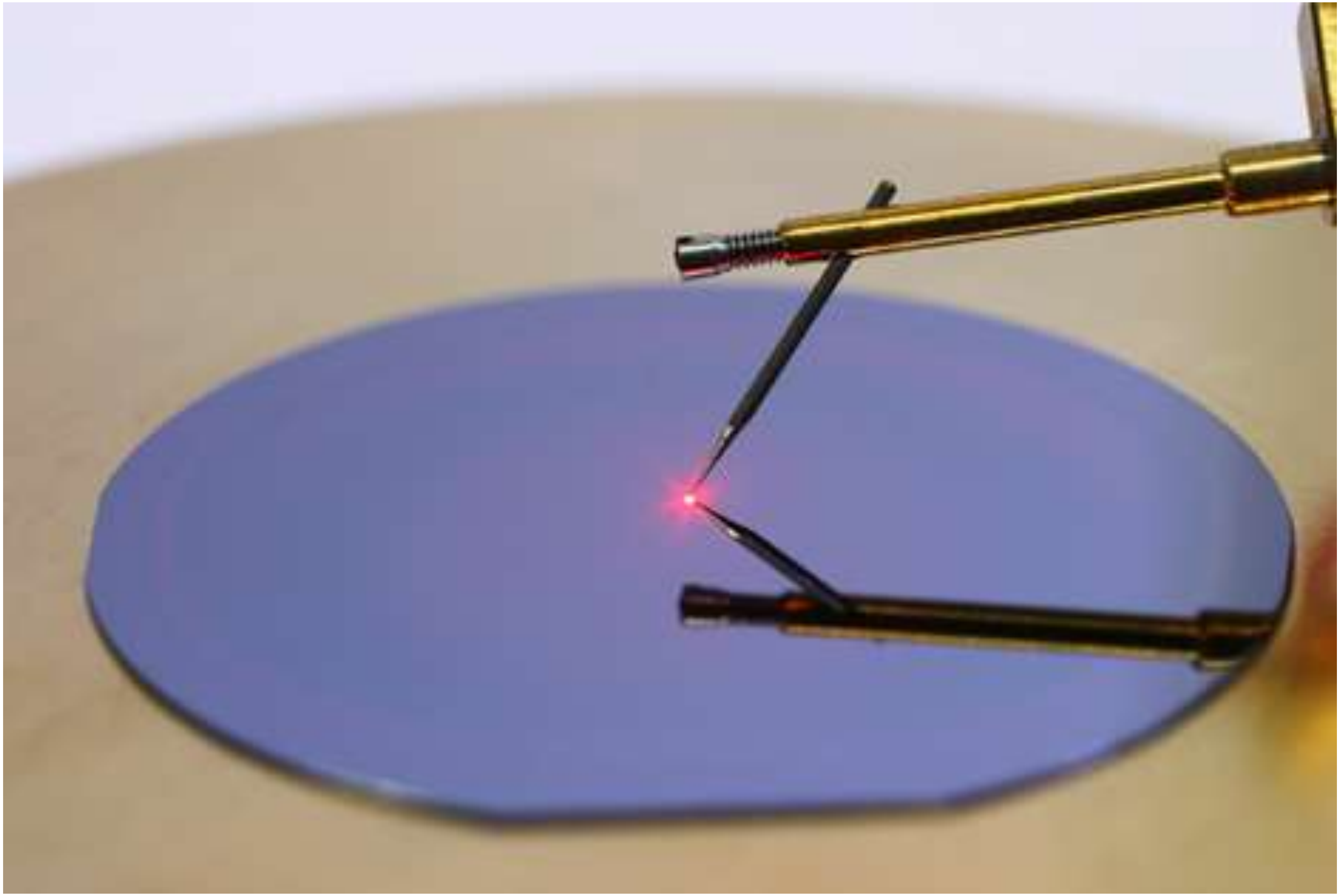
Physics of LEDs



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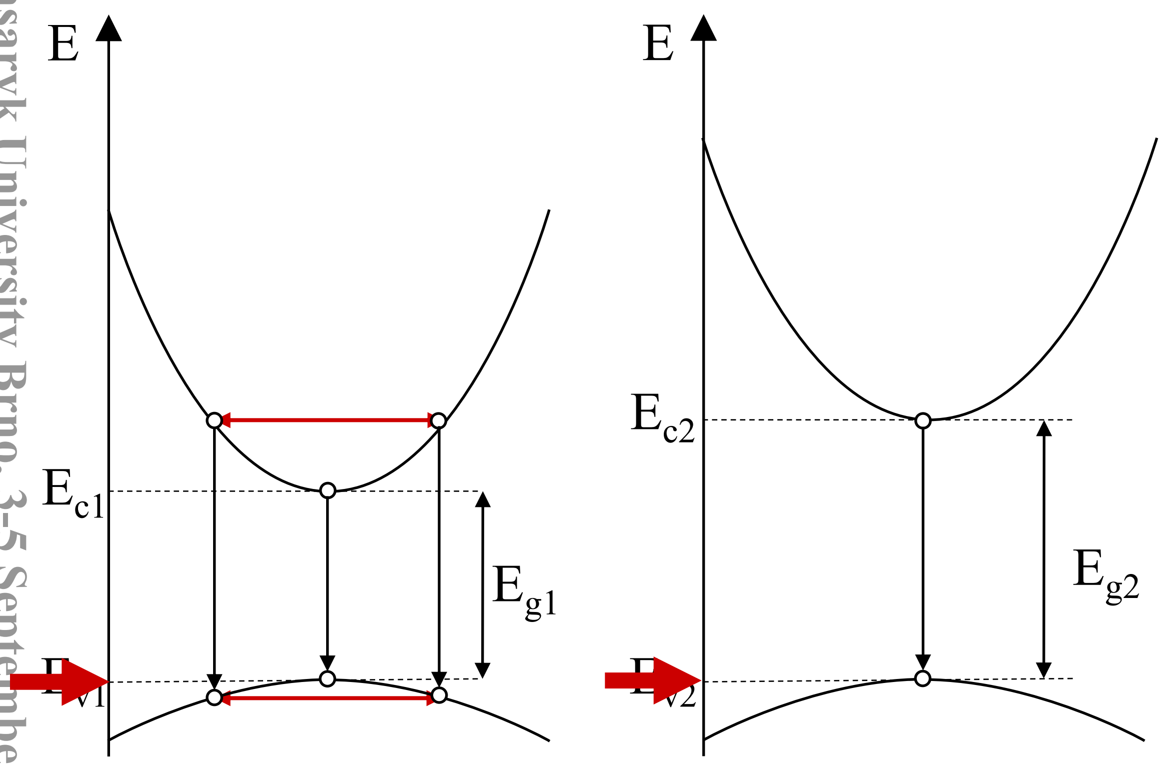
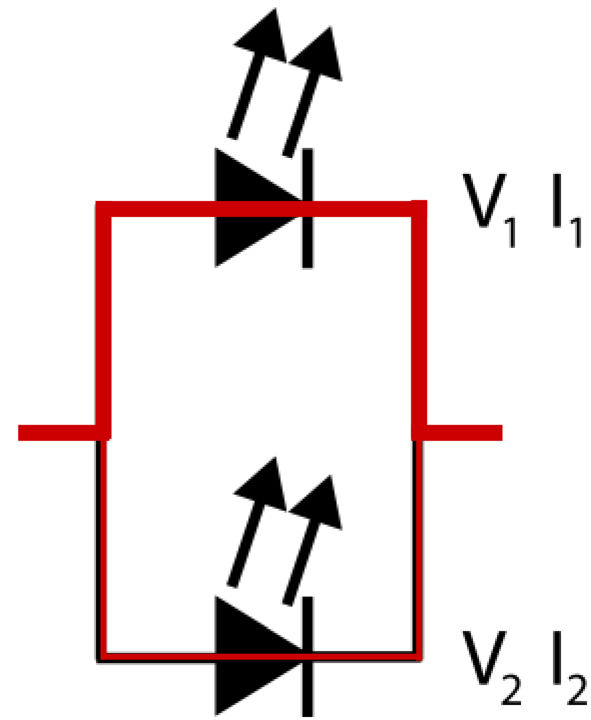
Physics of LEDs

- Physical mechanism for burning LEDS in parallel connection

$$V_1 < V_2$$





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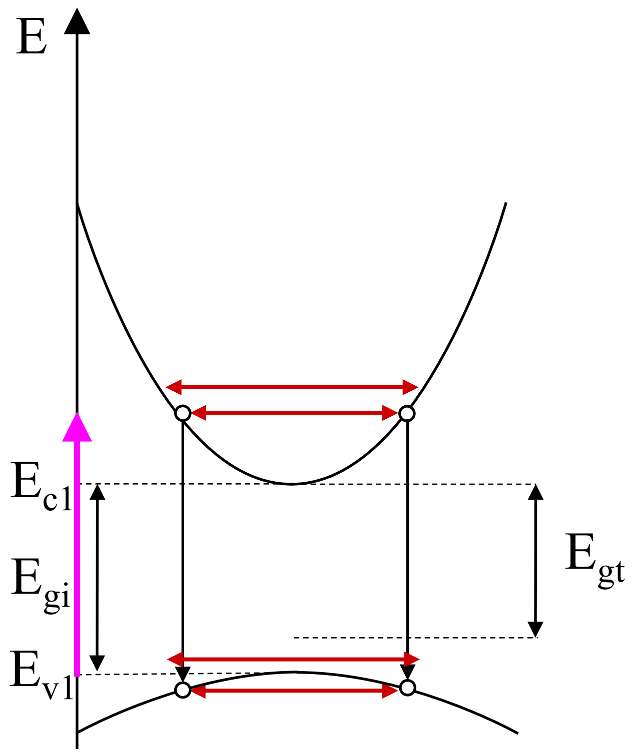
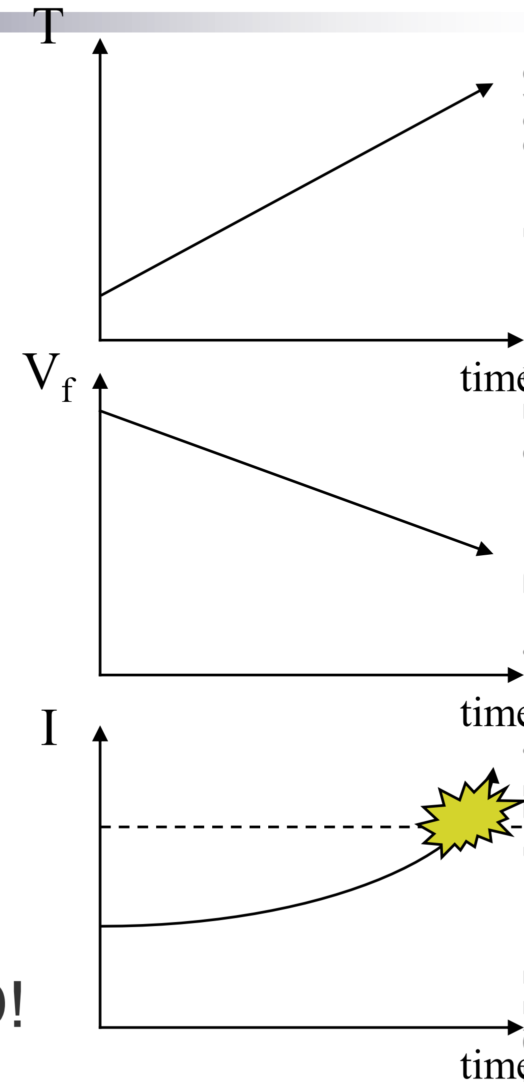
Physics of LEDs

- Positive feedback loop – thermal effect





- Prevent overheating that can kill your LED!
  - Uphold the max. steady current (i_{max})
  - Be cautious with soldering and exposure to heat

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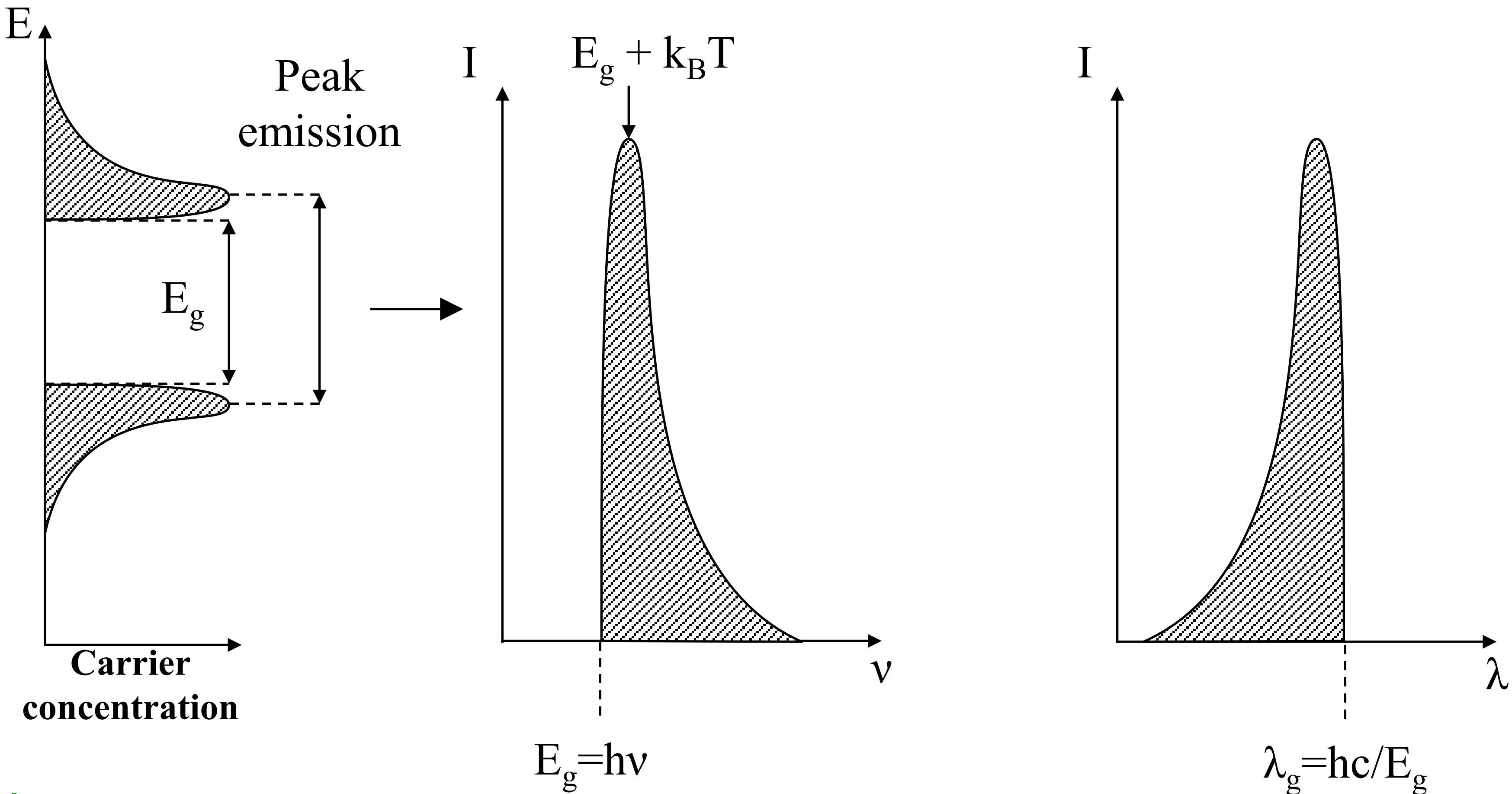
Physics of LEDs

- Spectra of LEDs - shape



$ Understanding that maximum emission is not precisely bangap transition

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- **Engineering and construction of LEDs**

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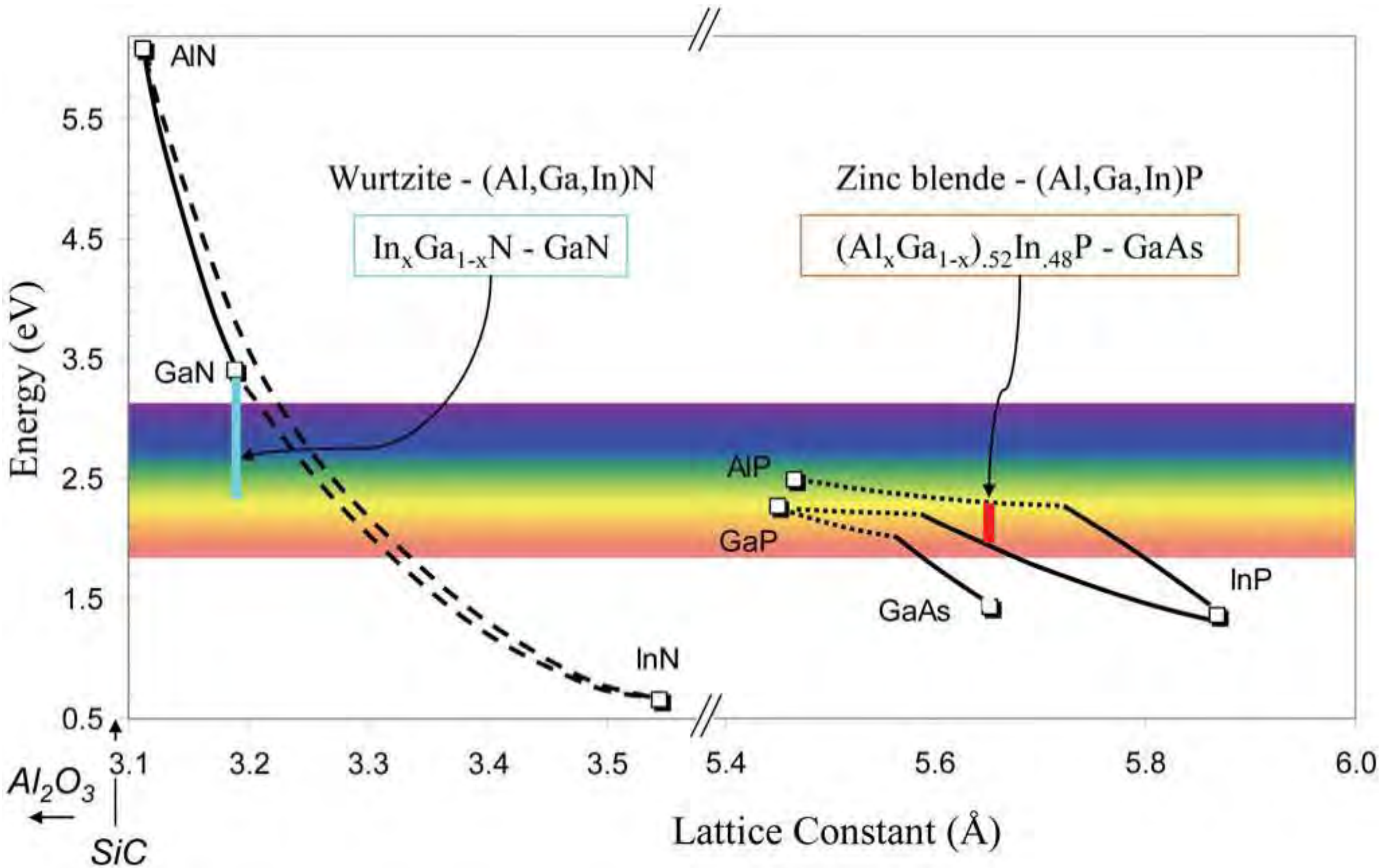
Today's part of „Alloy Road"



Krames, M. R., *et al.* Journ. Disp. Techn. 2007, 3, 160

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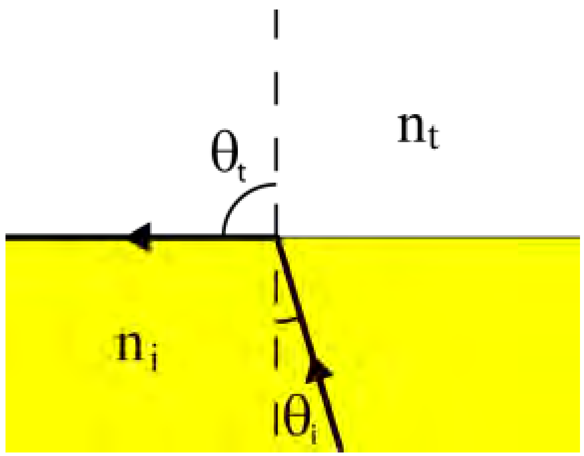
Engineering and construction of LED

- Semiconductors
  - High refractive index
    - Air n = 1
    - GaN n = 2.4 → 24.6° = 0.57 sr → 4.54%
    - GaP n = 3.3 → 17.6° = 0.29 sr → 2.34%
    - InGaN n = 3.5 → 16.6° = 0.26 sr → 2.08%



$$\frac{n_i}{n_t} = \frac{\sin\theta_t}{\sin\theta_i}$$

$ Extracting photons from LED chip is crucial for luminosity and heating

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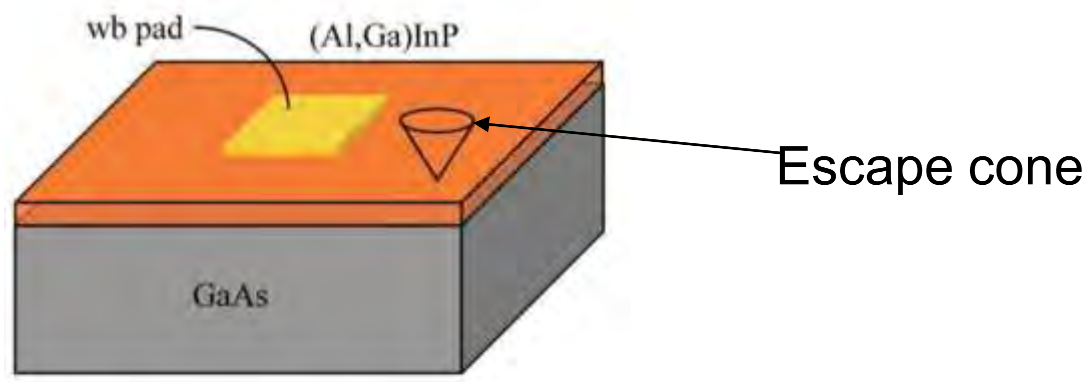
Engineering and construction of LED

- Conventional chip (CC)
- **Experiment: LED chip imaging with a microscope**
  - Historically first extraction method was thin epitaxial layers on absorbing substrate (AS) (GaAs)



Krames, M. R., *et al.* Journ. Disp. Techn. 2007, 3, 162

  - Layer thickness much lower than chip width
  - The lowest extraction rate ~4%

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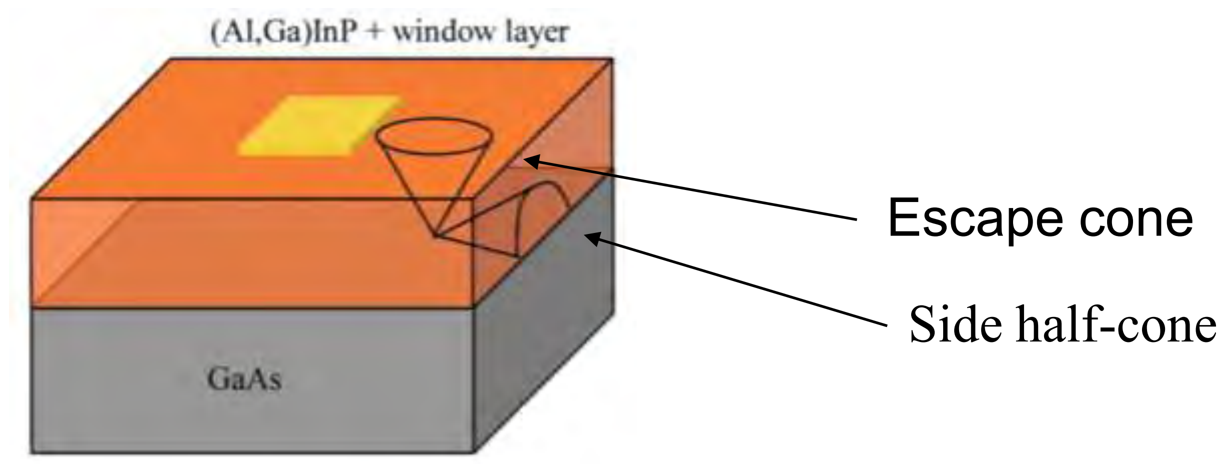
Engineering and construction of LED

- Thick epitaxial layers on AS (GaAs)



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- Epitaxial layer thick enough that some light can escape through sides of chip
- Extraction rate ~12% (x3 improvement)

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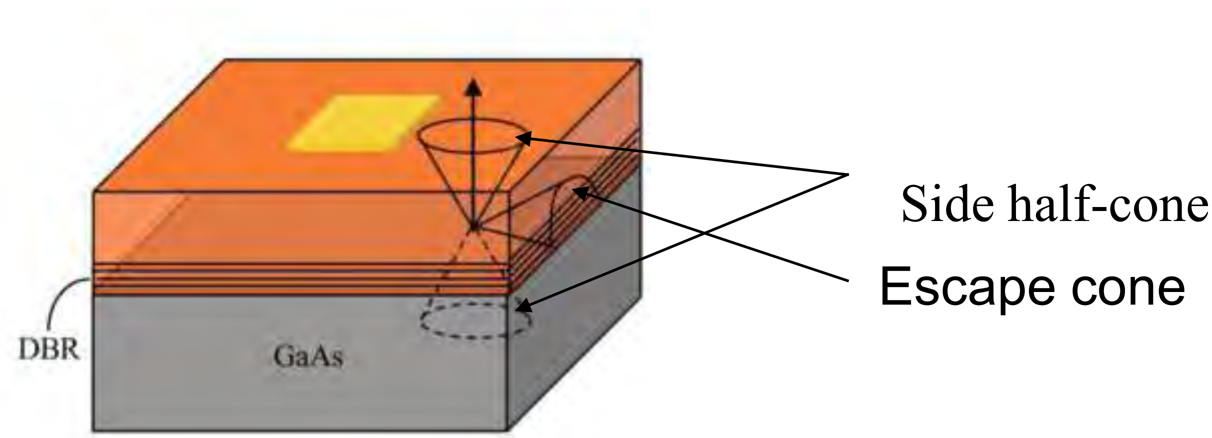
Engineering and construction of LED

- Distributed Bragg Reflector (DBR) added epitaxially to thick AS type chip
  - DBR is a multilayer structure of two dielectrics with varying refractive indices giving highly reflective surface



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- "Bottom cone" added
- Extraction rate ~16%

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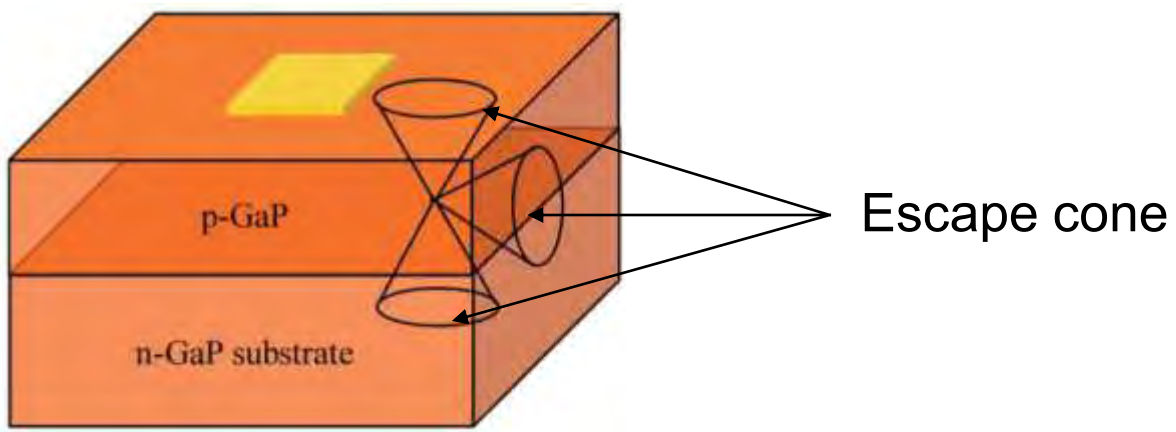
Engineering and construction of LED

- Thick transparent substrate chip – removal of GaAs i. e. with selective wet etching



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- All cones are available
- Light can escape at 3rd or further pass
- Depending on reflectivity of bottom metallization extraction rate ~20-24%

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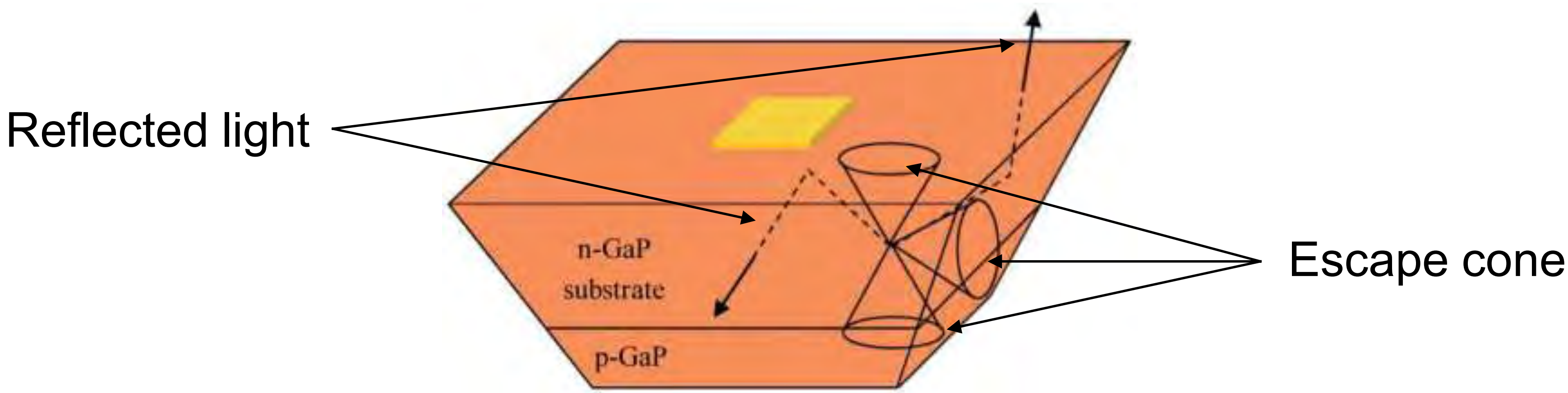
Engineering and construction of LED

- Chip with non-rectangular geometry



Krames, M. R., *et al*. Journ. Disp. Techn. 2007, 3, 162

- Shaping chip to increase chance of total internal reflection on walls to direct light into escape cone
- Different attempts (like compound parabolic concentrator)
- Truncated-inverted-pyramid (TIP)
- Extraction efficiency up to 60%

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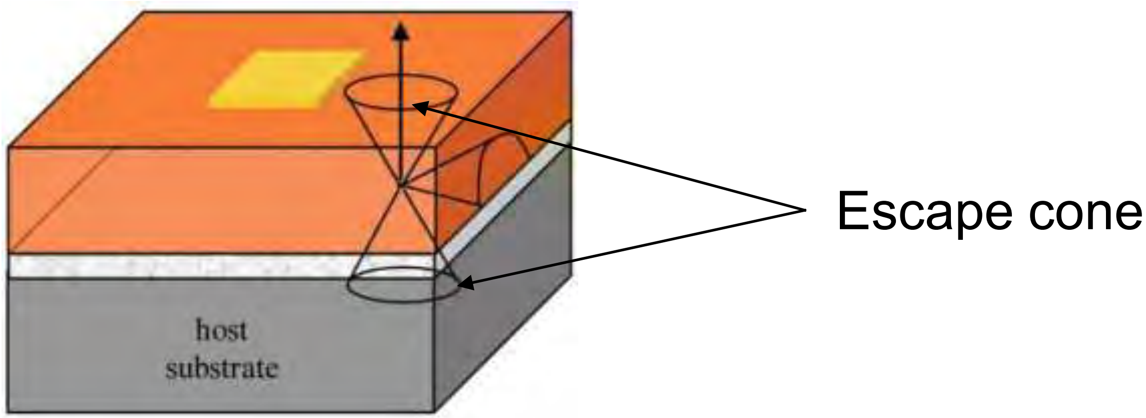
Engineering and construction of LED

- "Reflective substrate" – metallized layer between semiconductors



Krames, M. R., *et al.* Journ. Disp. Techn. 2007, 3, 162

- Significant benefit – dominant extraction through top surface
- Extraction efficiency up to 50%
  - Extraction efficiency still below TIP structure even when combined with chip shaping

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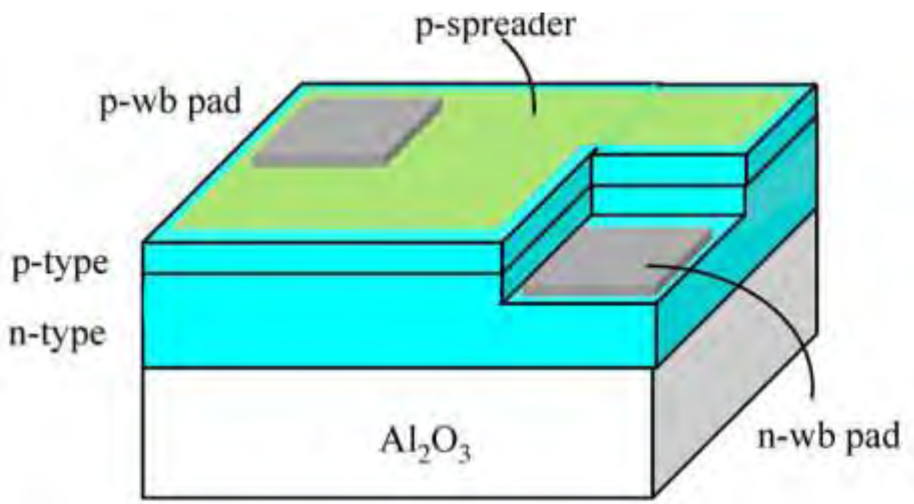
Engineering and construction of LED

- Conventional chip technology (CC)
  - Conventional chips required semitransparent layer of spreader to improve current distribution in chip
  - Poor thermal conduction of sapphire (Al_2O_3) created another barrier



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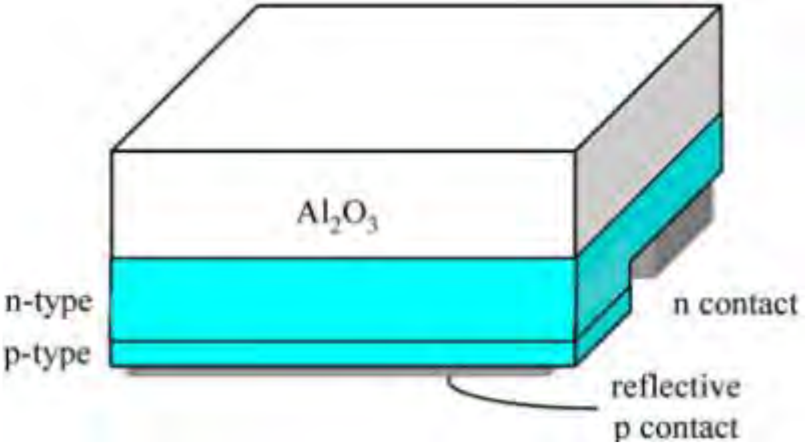
Engineering and construction of LED

- Flip-chip technology (FC)
  - Highly reflective (typically Ag) contact is added as p-contact
  - Wirebond free



Krames, M. R., *et al*. Journ. Disp. Techn. 2007, 3, 164

  - InGaN has anisotropic light emission (~$1+\cos^2\theta$) what plays additional role in FC LEDs
  - FC technology give extraction rate above 50%

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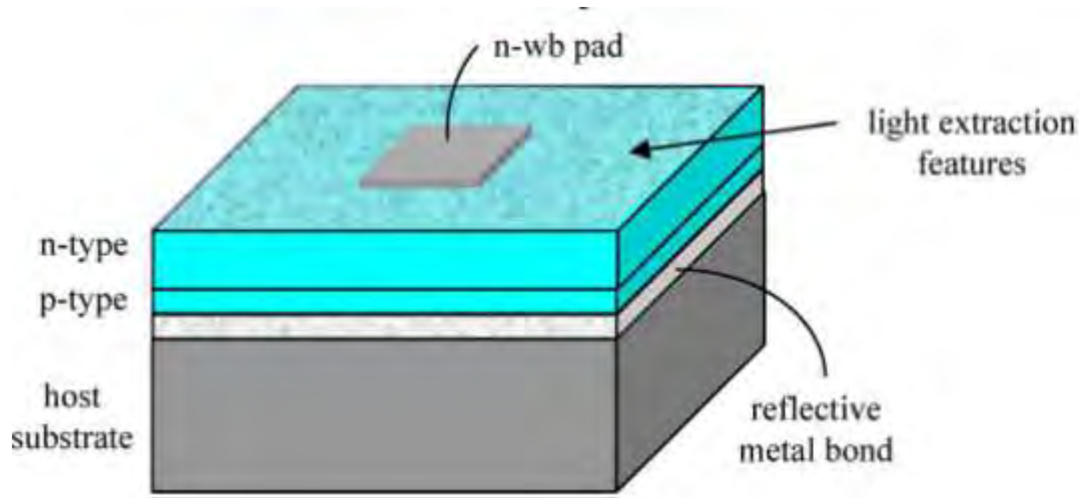
Engineering and construction of LED

- Vertical thin-film (VTF)



Krames, M. R., *et al*. Journ. Disp. Techn. 2007, 3, 164

- Method similar to reflective substrate
- Removal of substrate typically with excimer laser ablation
- Extraction efficiency ~75%

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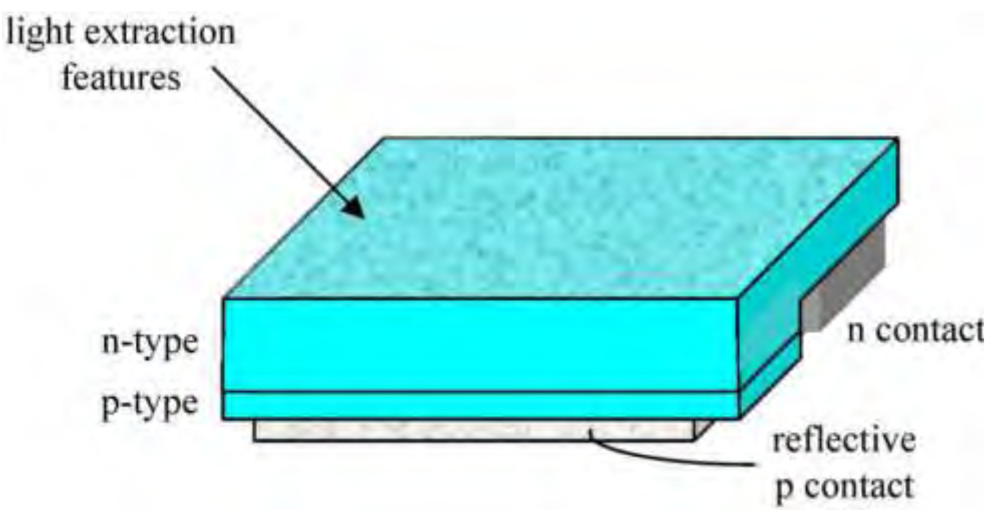
Engineering and construction of LED

- Thin-film flip-chip (TFFC)



Krames, M. R., *et al*. Journ. Disp. Techn. 2007, 3, 164

- Sapphire substrate is completely removed from chip
- Photo-electrochemical etching is applied for further extraction efficiency increase (both TFFC and VTF)
- Extraction efficiency exceeding 80%

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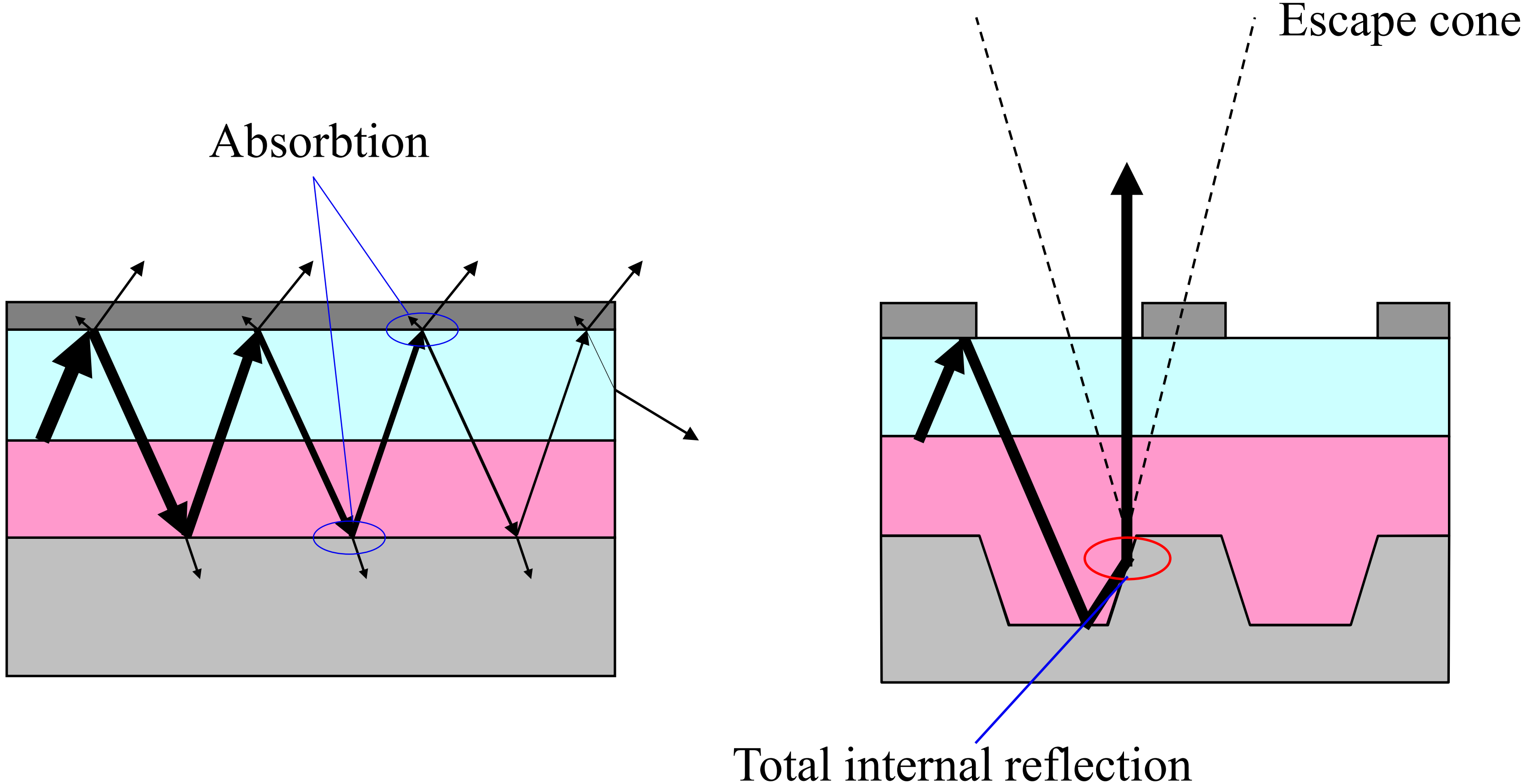
Engineering and construction of LED

- Chip texturing
  - By etching top and/or bottom chip surface ,more rays can be directed in escape cone



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Course schedule

- Afternoon
  - Background – what you should know
    - A brief history - 'Alloy Road'
    - Fundamentals: Physical principles, design
    - Coffee break
  - **Usage**
    - Illumination, fluorescence microscopy & visualization
    - Optical analytical methods: photometry, fluorimetry
    - Photochemistry: photoinitiations, photolithography
    - Heating, other usage
  - Course evaluation, feedback, close

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LEDs in Chemistry: Outline

- LEDs properties in respect to their applications in chemistry
  - Practical considerations of usage of LEDs
- Applications I
  - Optical methods in chemical analysis
    - Photometry and photometric detection
    - Fluorometry
  - LEDs for sensors

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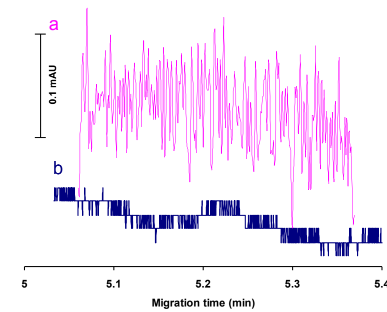
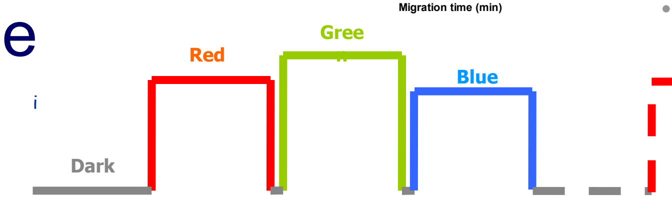
Why use LEDs?

- Advantages of LEDs - many unique properties ☺
  - Small, reliable & robust → **miniaturisation compatible!**
  - **Cheap**: from <$1 to ~$50, but typically ~ $10[1]

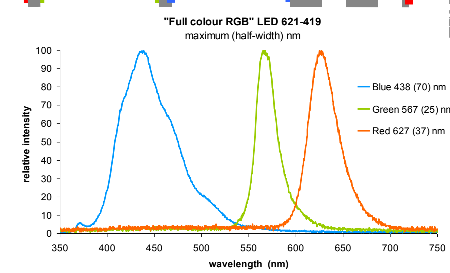
  - **Long life-time**: ~10^5 h (~11+ years)
  - Very low noise → 10^{-5} AU
    - Used in various types of optical detectors (HPLC, FIA etc.)



  - Can be operated in a pulsed regime
    - Can be pulsed at extremely fast rates



  - Single-, bi- or tri-coloured LED's available
  - Quasi-monochromatic: FWHM ~ 20-70 nm
  - **'Cold light'**



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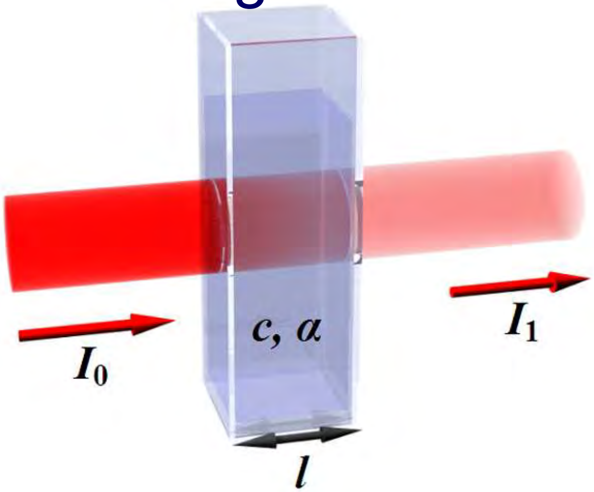
- Photometry
  - Measures light attenuation at one wavelength or as a function of wavelength
    - ***T*** (transmittance, 0-1 = 0-100%), ***A*** (absorbance, 0 - +∞)
    - ***T*** , ***A*** are absolute values



    - Small changes of light intensity on a high base level must be measured
      - Stable levels of light needed
      - High levels of light are detected → photodiodes

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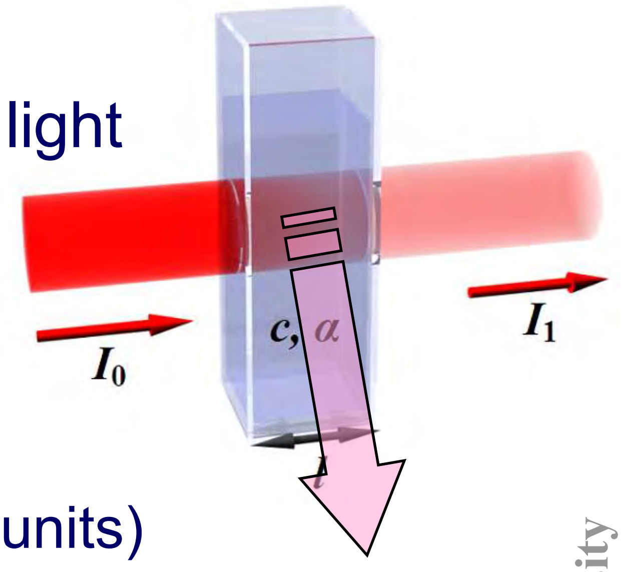
- Fluorometry (= Fluorimetry)
  - Measures relative intensity of emitted light at one wavelength or as a function of wavelength



    - *I* (relative emission intensity, arbitrary units)
    - Small changes of light intensity on a low base level must be measured
      - Most crucial is a high light source power – directional
      - Narrow emission spectrum (short-pass or band filter)
      - Stable levels of light needed
      - High levels of light are detected → photodiodes

Optical methods in chemical analysis

- Refractometry
  - Measures RI either as an absolute value or relatively to a reference
  - Schlieren optics visualisation & detection
- Low-angle laser light scattering (LALLS)
  - Measures light scattered from a sample, depends on particle size
- Other
  - Optical coherence tomography
  - Measures light scattered from a sample

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LEDs in Chemistry: Outline

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- Applications I
  - Optical methods in chemical analysis
    - Photometry and photometric detection
    - Fluorometry
  - LEDs for sensors

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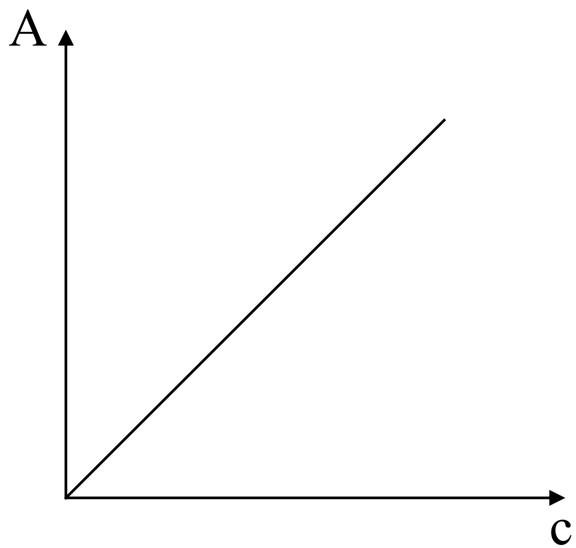
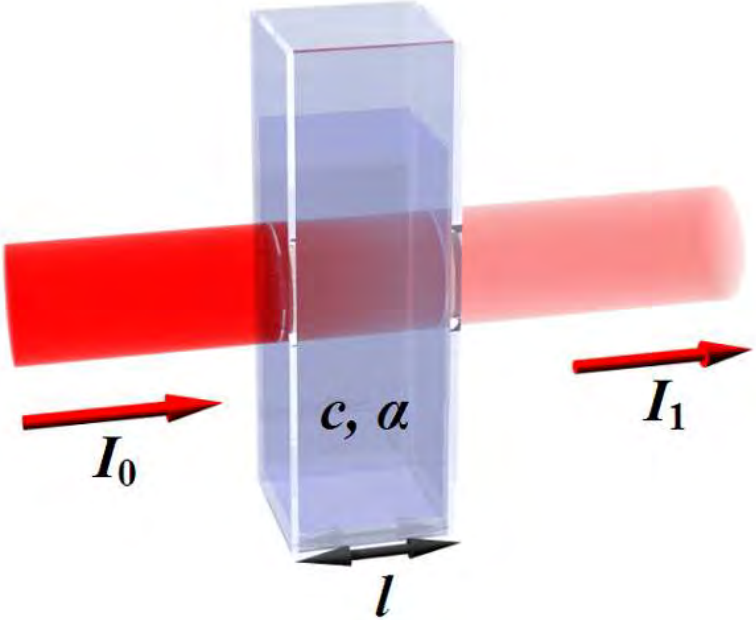
Photometry and photometric detection

- Lambert-Beer's law

$$T = \frac{I}{I_0} = 10^{-A}$$

$$A = \varepsilon l c$$





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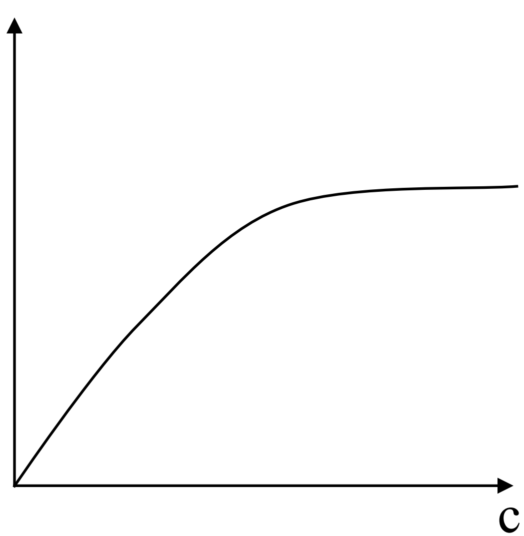
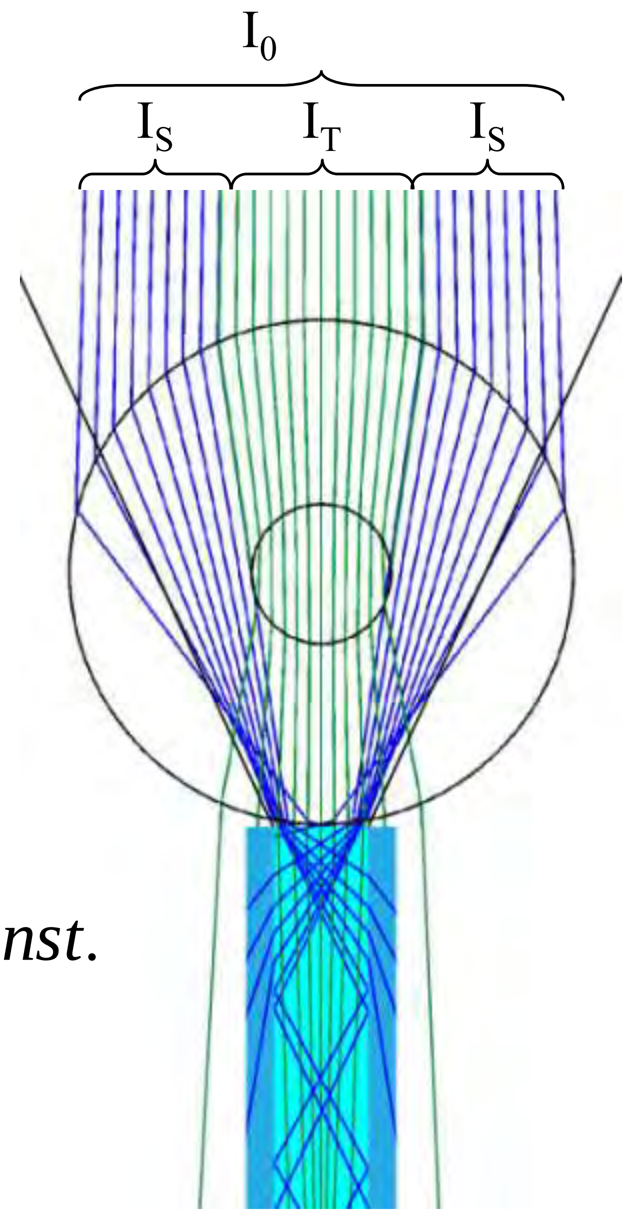
Photometry and photometric detection

- Lambert-Beer's law with stray light
  - Cell with cylindrical symmetry
  - Stray light

$$A = -\log\left(\frac{I_T + I_S}{I_0}\right)$$



$$\underset{I_T \to 0}{A} \to -\log\left(\frac{I_S}{I_0}\right) = const.$$



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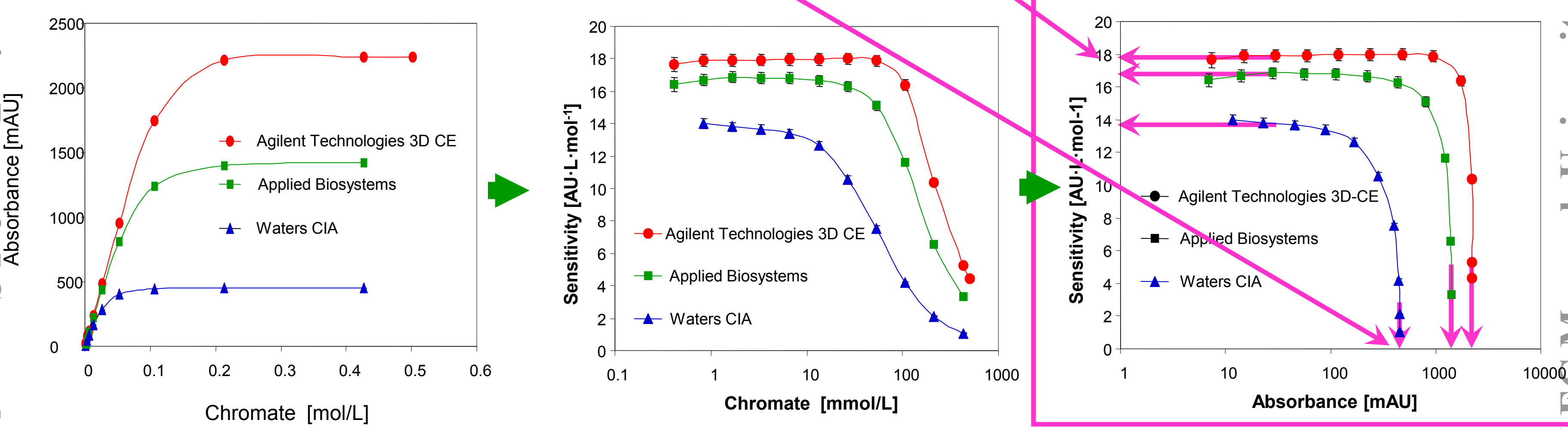
Photometry and photometric detection

- Quality of detection optical setup easily checked: Sensitivity vs. absorbance graph
  - Effective pathlength
  - Stray light %
    - Linearity evaluation



Johns C., Macka M., Haddad P.R., King M., Paull B., Practical Method for Evaluation of Linearity and Effective Pathlength of On-Capillary Photometric Detectors in Capillary Electrophoresis, *J. Chromatogr. A, 927(1-2),* 237-241, 2001

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Photometry and photometric detection

- Photometry
  - CCD or DA
    - Fibre optics

$ A wide range of ~k$-range priced products available

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LEDs for photometry

- Why LEDs?
  - Small, reliable & robust
  - Cheap: from <$1 to ~$50, but typically $10[1]
  - Long life-time: ~10^5 h
  - Quasi-monochromatic: FWHM ~ 20-70 nm
  - Very low noise
    - Used in various types of optical detectors (HPLC, FIA etc.)
  - Can be operated in a pulsed regime
    - Can be pulsed at extremely fast rates ~MHz - ANIMATED

  - Single-, bi- or tri-coloured LED's available

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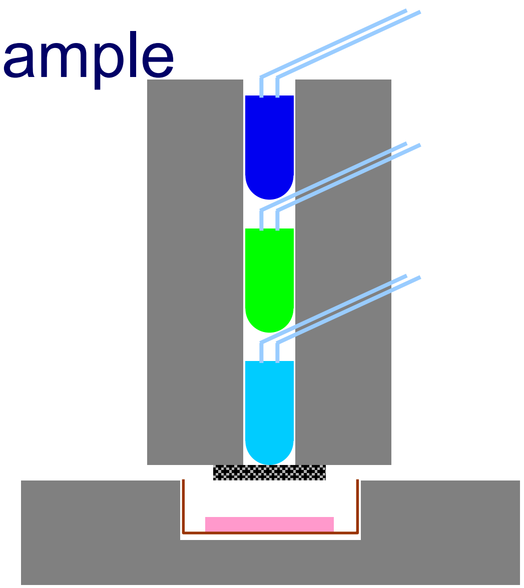
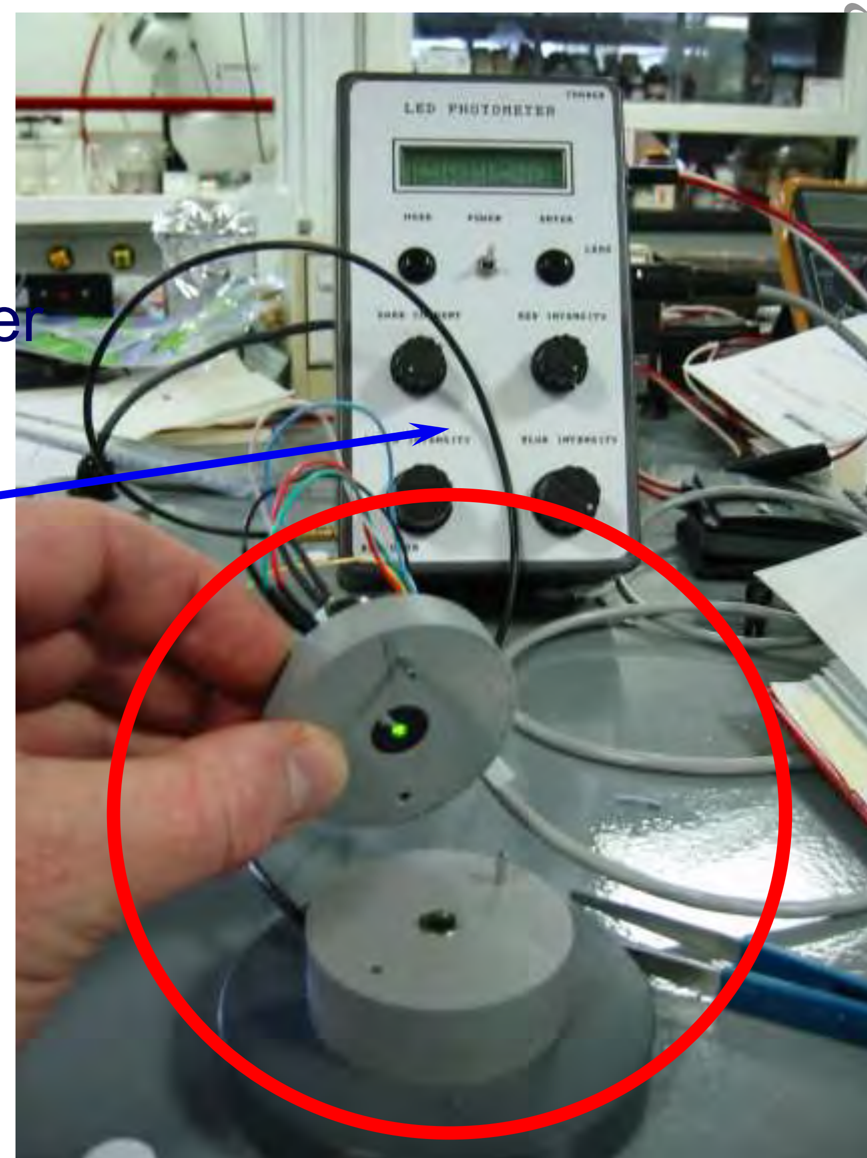
Photometry and photometric detection

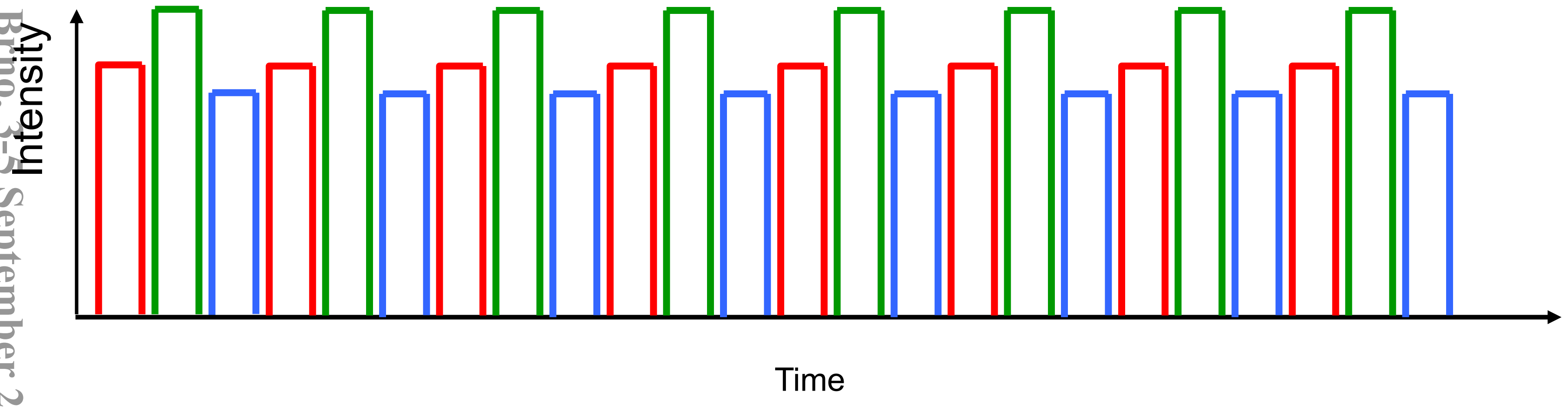
- ‘Electronically chopped’ LED photometer
- Photometer design
  - LED’s fitted in a plastic holder
  - Silicon photodiode detector
  - Electronics
  - Sample





Photometry and photometric detection

- Can be pulsed at extremely fast frequencies
  - Source light can be 'electronically chopped'
    - Using a PIC processor programmed in PIC-Basic Pro
    - Amount of instructions and calculations executed each cycle equal to 7 pages of source code



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Photometry and photometric detection

- Photometer design
  - Pulsed operation
  - Usage of pseudo-reference wavelength

  - $A = A_{Sig} - A_{ref}$, usually $I_{Sig} < I_{Ref}$
  - To compensate for blank absorbance due to scattered light

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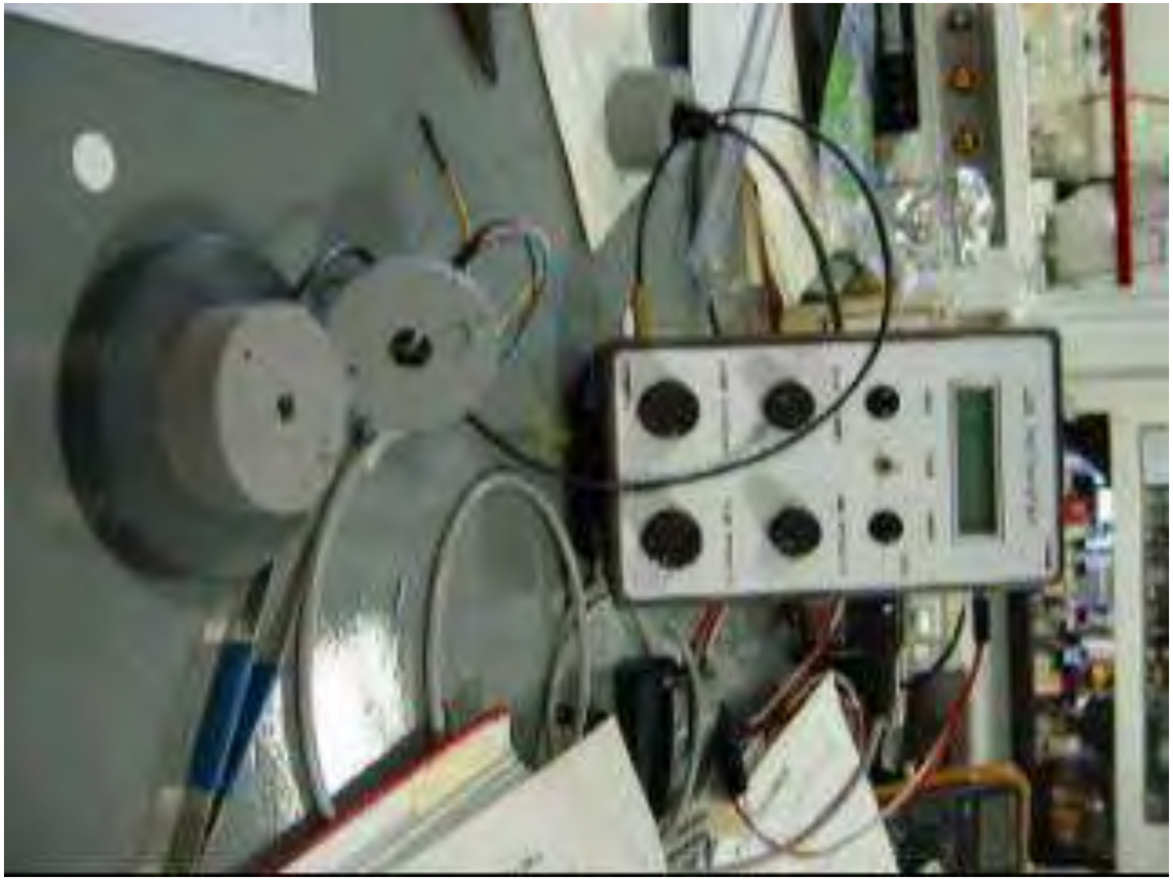
Photometry and photometric detection

- LED Photometer - VIDEO



$ An LED photometer can be constructed very cheaply

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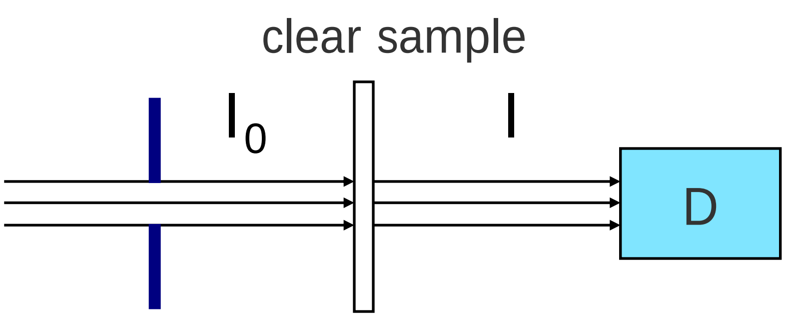
Photometry and photometric detection

- Transmittance photometry
- Measures through the body of the sample
  - Interaction with sample does change path of light
  - Photon can be only absorbed (no scattering)
  - Lambert-Beer's law



$$T = I/I_0$$
$$A = -\log T$$
$$A = -\log I/I_0$$

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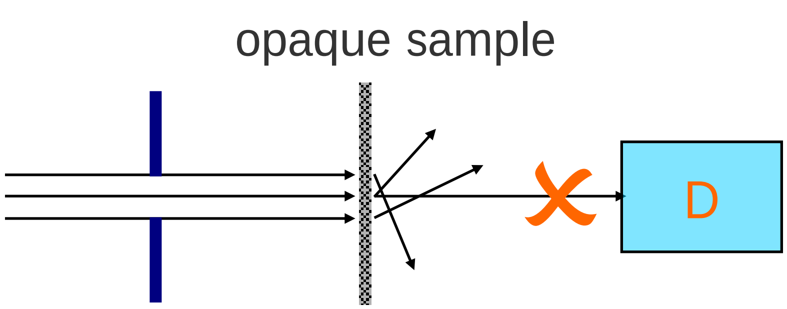
Photometry and photometric detection

- When it does not work for translucent samples in 'classical' photometers and why?
  - When the sample is NOT optically clear
    - Turbid
    - Translucent
  - The portion of light that reaches the detector will be too small



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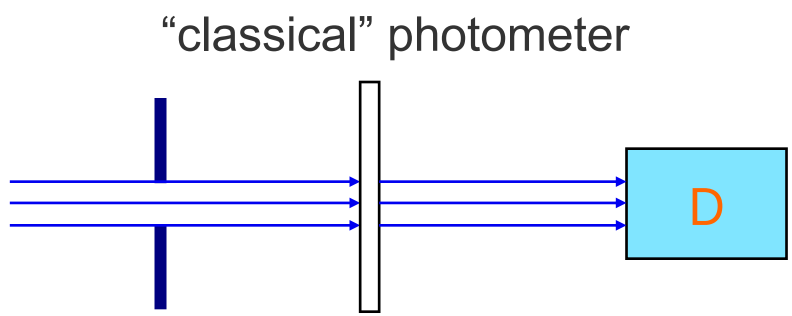
Photometry and photometric detection

- ‘Electronically chopped’ LED photometer
  - Test system
    - Absorbance measurements of diffuse samples



- ‘Pocket’ photometer to measure colour intensity of test stripes & papers
- Work in transmittance / absorbance mode rather than reflectance - advantages
- Chemistry & applications: SPE/detection - environmental, NASA program

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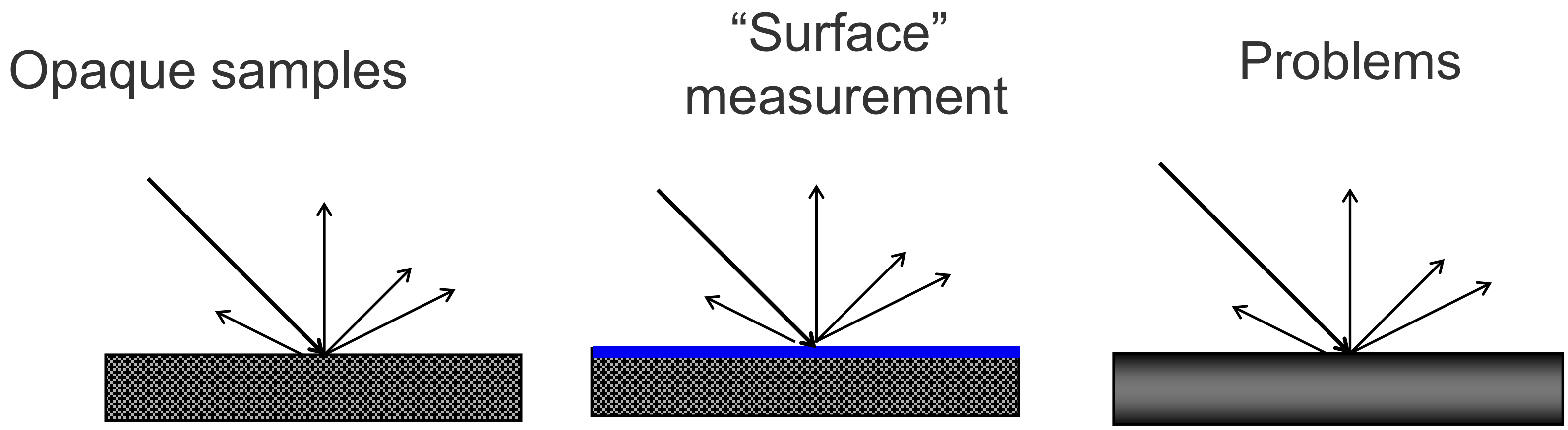
Photometry and photometric detection

- Opaque samples - DRS
- How are opaque samples measured?
- Diffuse Reflectance Spectrophotometry (DRS)



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Photometry and photometric detection

- Opaque samples - DRS
- Kubelka-Munk theory of reflectance
  - Kubelka-Munk function
    - Relates the observed reflected light intensity to the sample concentration

$$\frac{(1-R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s}$$

R – reflectance
k – absorption coefficient
A – absorbance
c – concentration
s – scattering coefficient

- What is the limitation?
  - Only light reflected from the surface of the sample is measured

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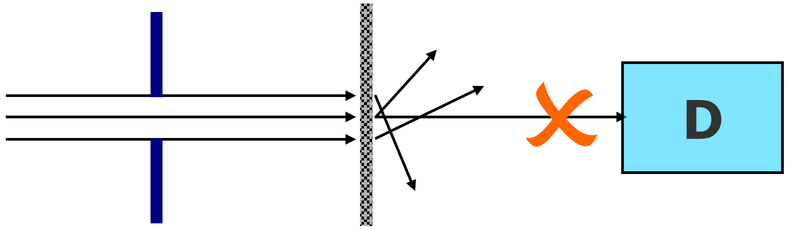
Photometry and photometric detection

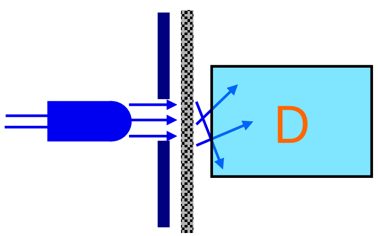
- How to make it work?
- Collect a larger portion of the transmitted light
- Instead of:

“classical” transmittance photometer



- A new optical scheme using - LED’s

LED photometer



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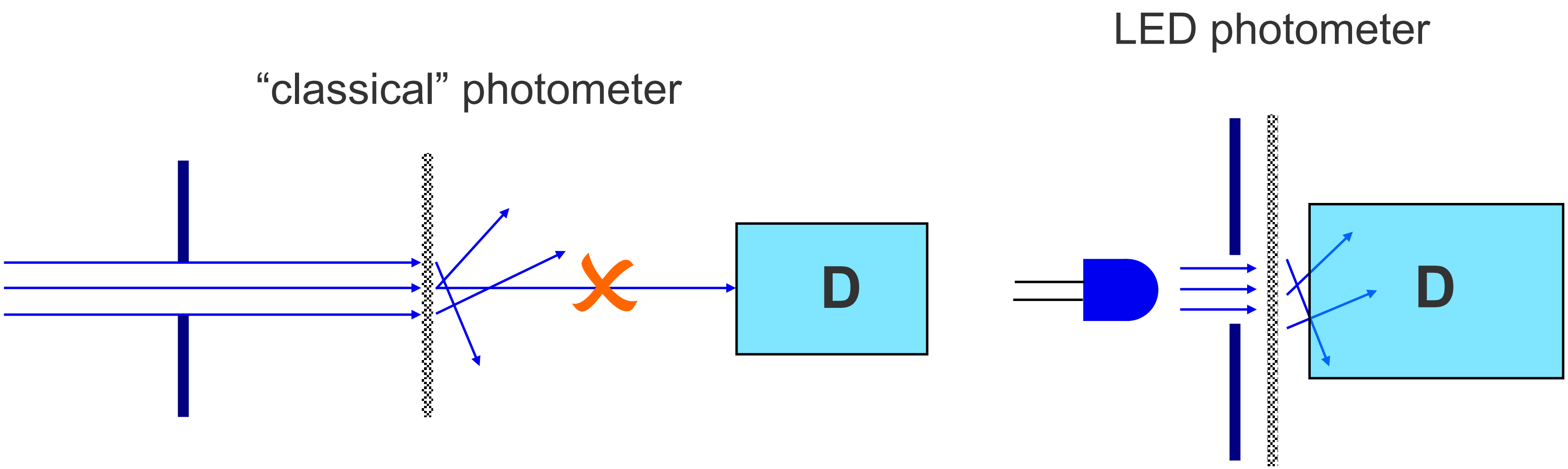
Photometry and photometric detection

- ‘Electronically chopped’ LED photometer
  - Test system
    - Absorbance measurements of diffuse samples

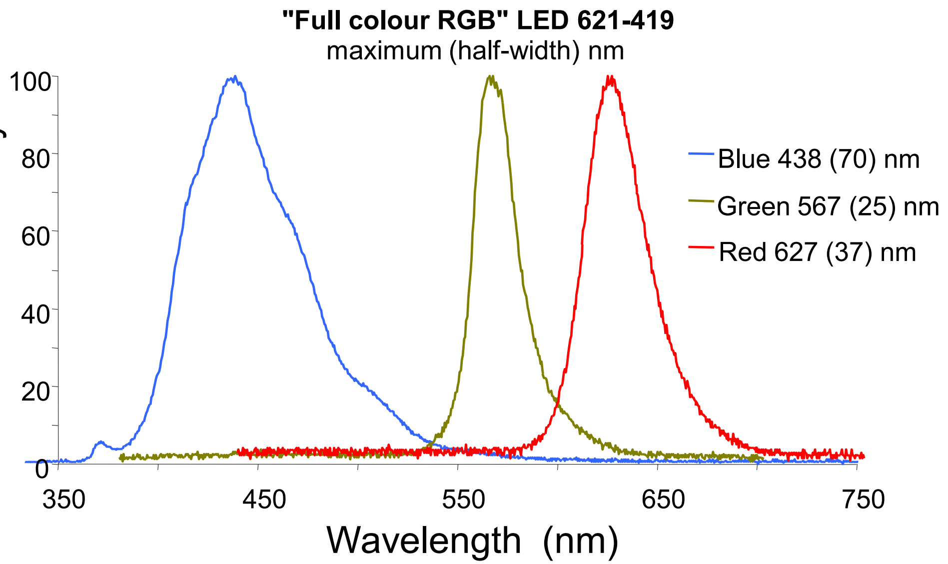


A_{bkg} ~ 2-3 AU

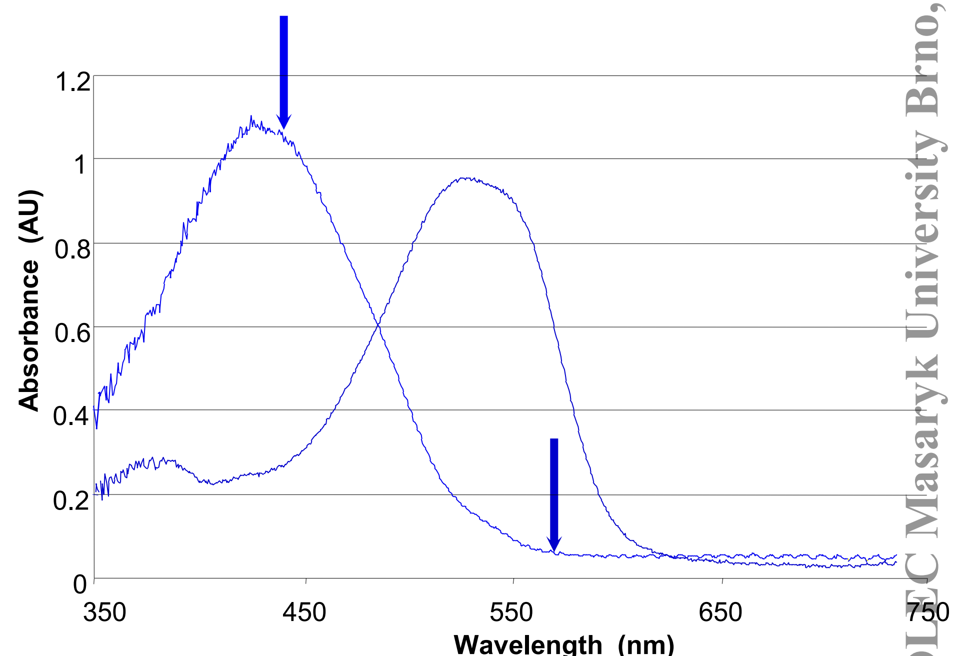
A_{bkg} ~ 0.7 AU

$ LED photometer can measure high A background samples e.g. translucent indicator papers etc.

Physical testing - linearity graphs



- Precision:
  RSD = **2.2%** (B, A=0.7AU), **2.8%** (G, A=0.07AU)



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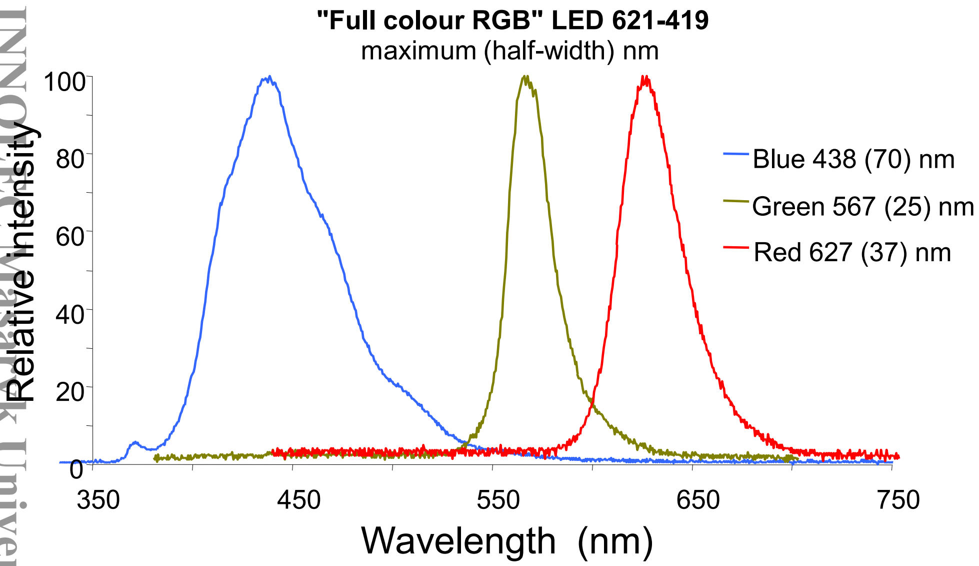
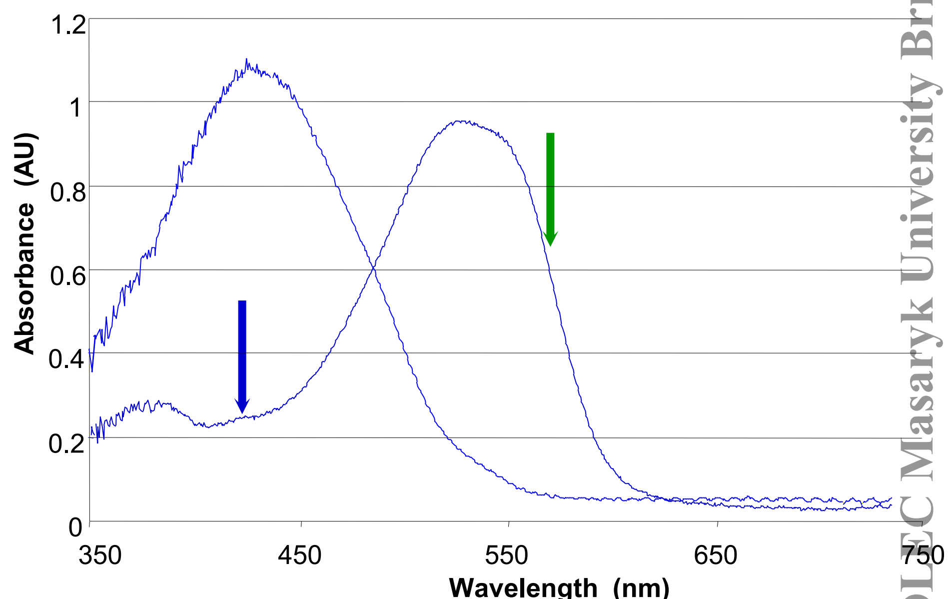
Physical testing - linearity graphs



- Precision:
  RSD = **1.6%** (B, A=0.4AU), **0.9%** (G, A=0.3AU)



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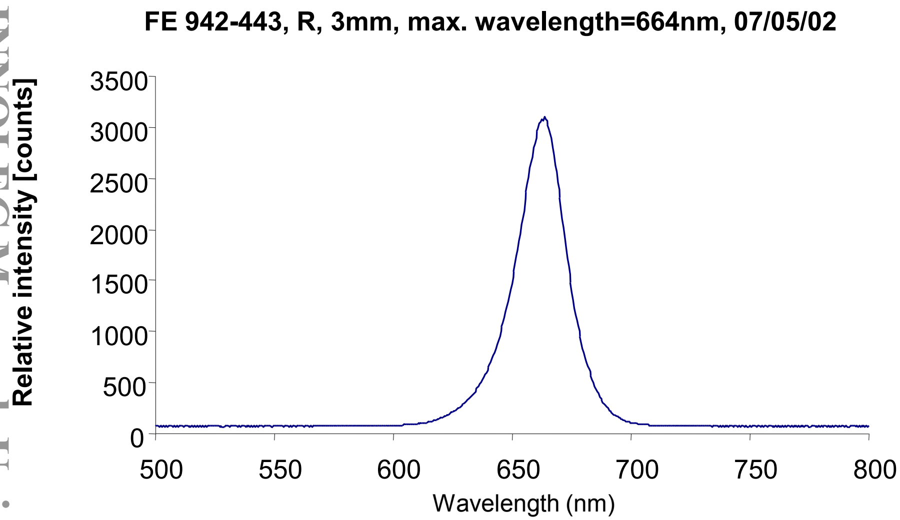
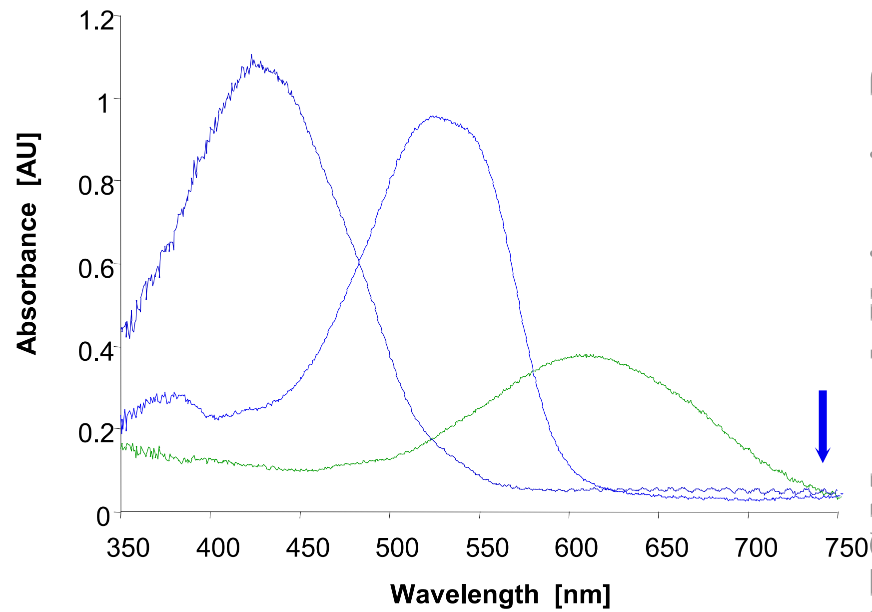
Physical testing - linearity graphs



- Typical precision for physical tests **RSD <3%**



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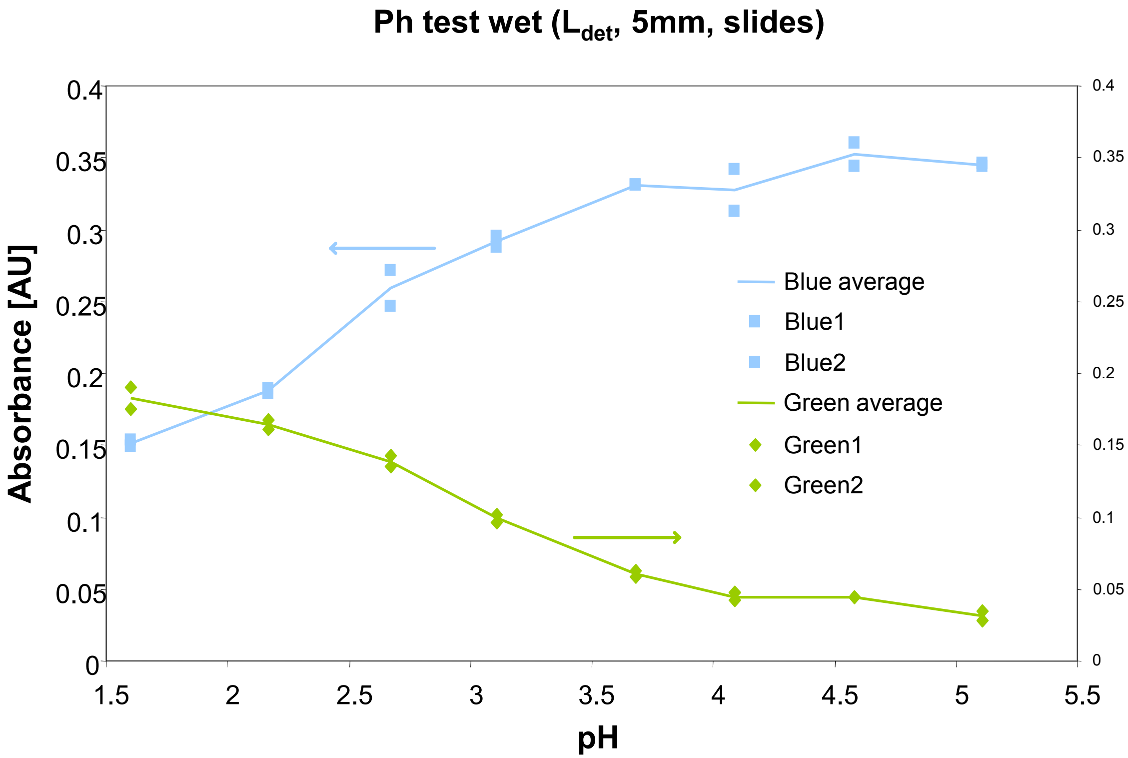
- pH paper
  - Universal (yellow)



<u>Conditions</u>:

Membrane: pH paper universal 0-14 (Toyo Roshi Kaisha) measured wet

LEDs: 'RGB' 3-colour 438/567/627 nm 5 mm i.d.

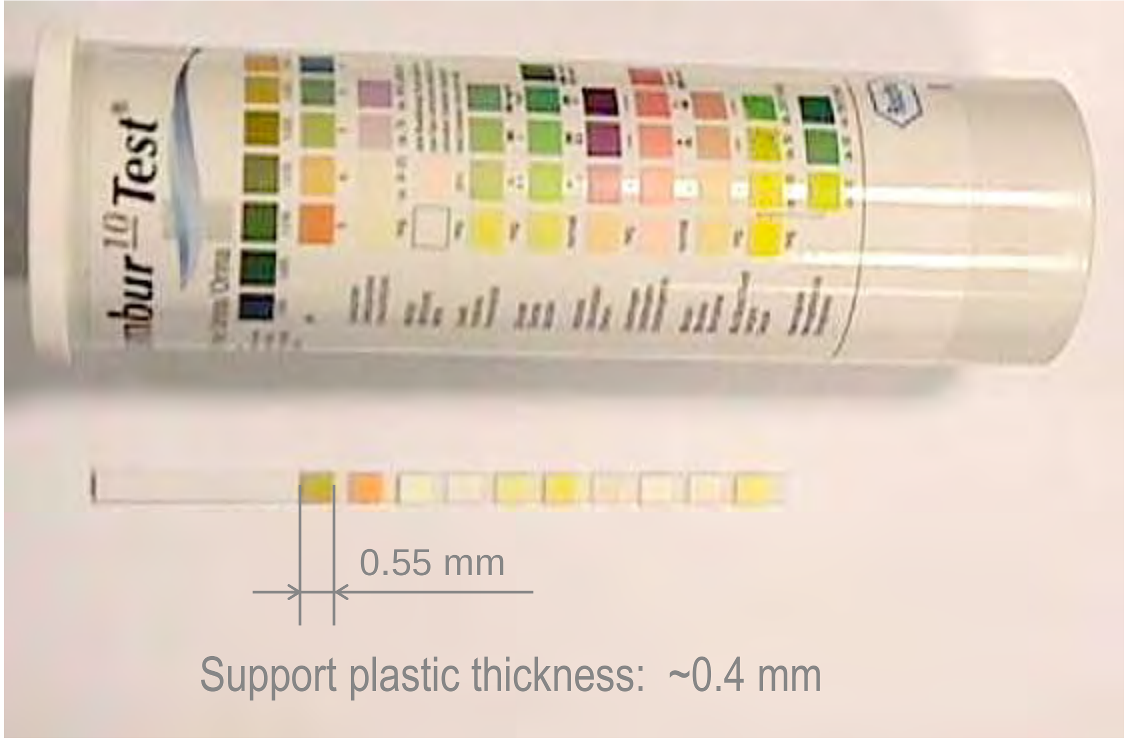
Detector: 5x5mm

Repeats: n = 2

- Precision limited by leaching out of the dyes

Applications - urine test strip

- Combur 10 (Roche)
  - Specific gravity
  - pH
  - Leukocytes
  - Nitrite
  - Protein
  - Glucose
  - Ketones
  - Urobilinogen
  - Bilirubin
  - Blood



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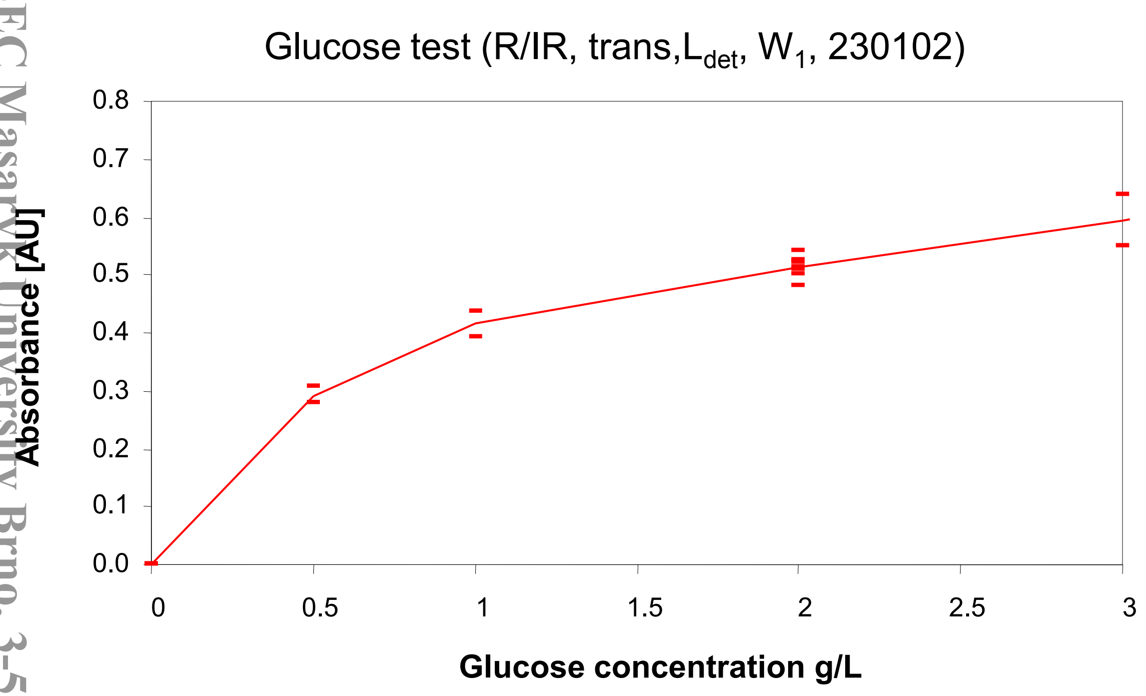
Applications - urine test strip

- Combur 10 (Roche)
  - Specific gravity
  - pH
  - Leukocytes
  - Nitrite
  - Protein
  - Glucose
  - Ketones
  - Urobilinogen
  - Bilirubin
  - Blood

Applications - urine test strip

- Glucose



Conditions:

Membrane: Combur10

LEDs: **Red 667nm** (Signal)
IR 875nm (Reference)
3 mm i.d.

Detector: 10x10mm

Repeats: n = 2 or 6

- Precision: RSD = **3.7%** (2 g/L)

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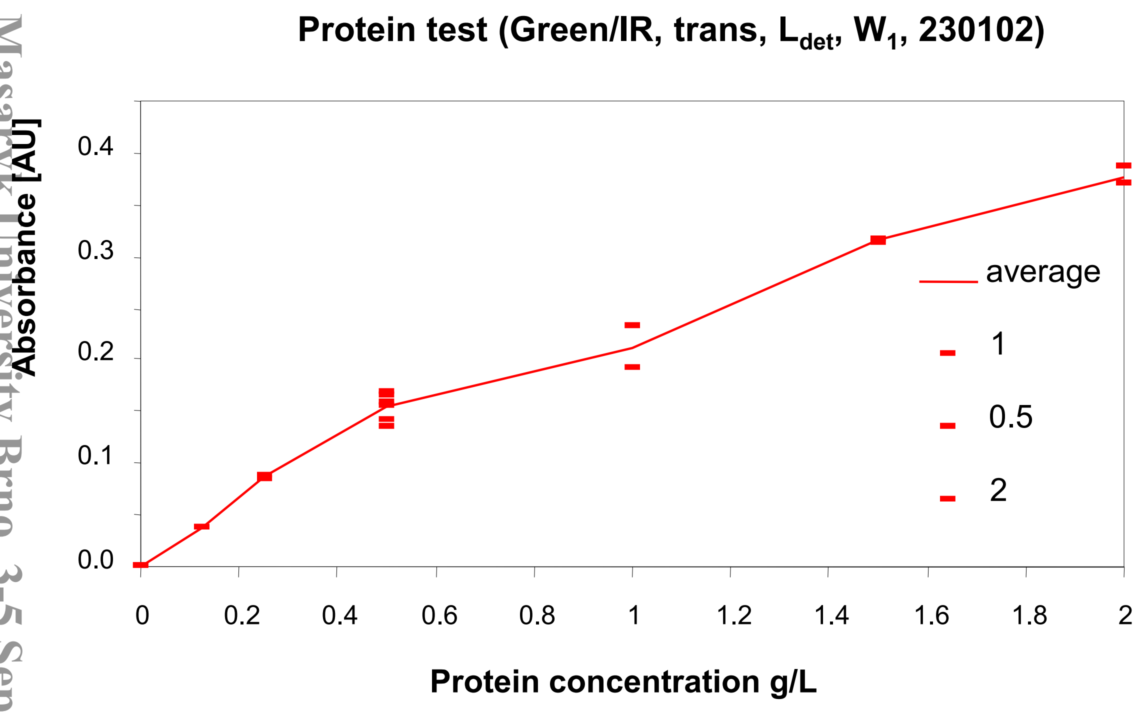
Applications - urine test strip

- Protein



Conditions:

Membrane: Combur10

LEDs: Green 581nm (Signal)
IR 875nm (Reference)
3 mm i.d.

Detector: 10x10mm

Repeats: n = 2 or 6

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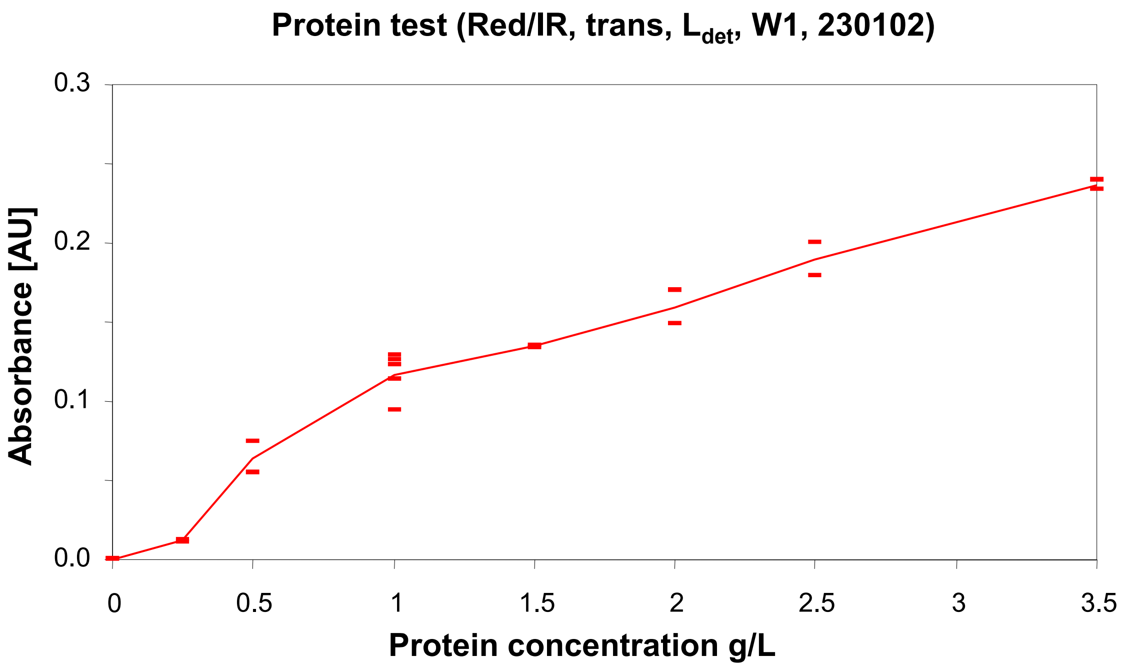
Applications - urine test strip

- Protein



Conditions:

Membrane: Combur10

LEDs: **Red 667nm** (Signal) **IR 875nm** (Reference) 3 mm i.d.

Detector: 10x10mm

Repeats: n = 2 or 6

- Precision: RSD = **8.8% - 10.4%** (0.5 or 1.0 g/L)

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Applications - Merckoquant strips

- Cu

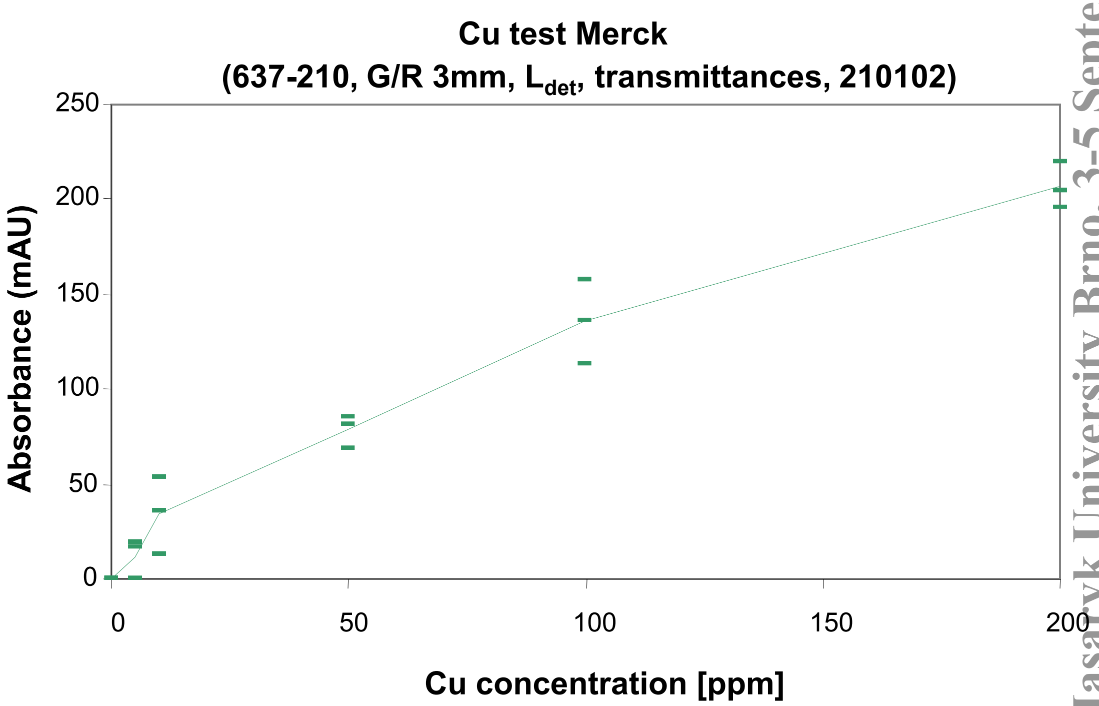
Conditions:

Membrane: Merckoquant

LEDs: **Green 574 nm** (Signal)
Red 694 nm (reference)
3 mm i.d.

Detector: 10x10mm

Repeats: n = 2



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Applications - Merckoquant strips

- NO_3^-

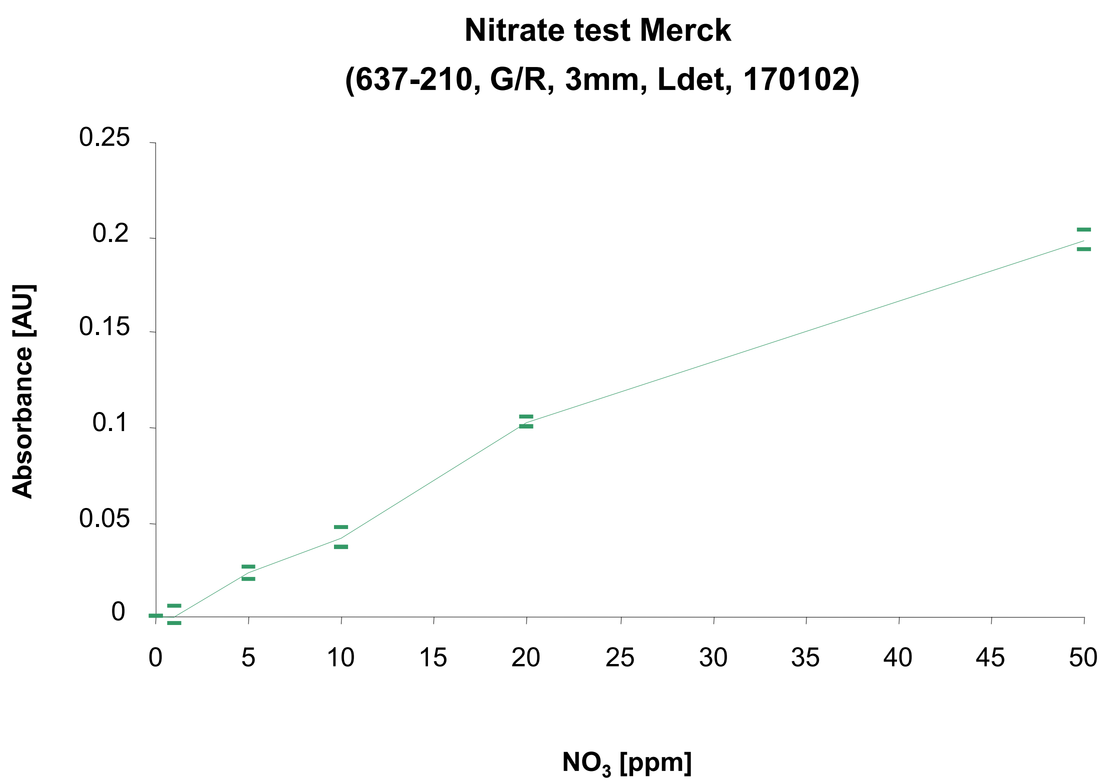
<u>Conditions</u>:

Membrane: Merckoquant

LEDs: **Green 574 nm (Signal)**
Red 694 nm (Reference)
3 mm i.d.

Detector: 10x10mm

Repeats: n = 2 or 6



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Applications - Merckoquant strips

- Cr^{VI}

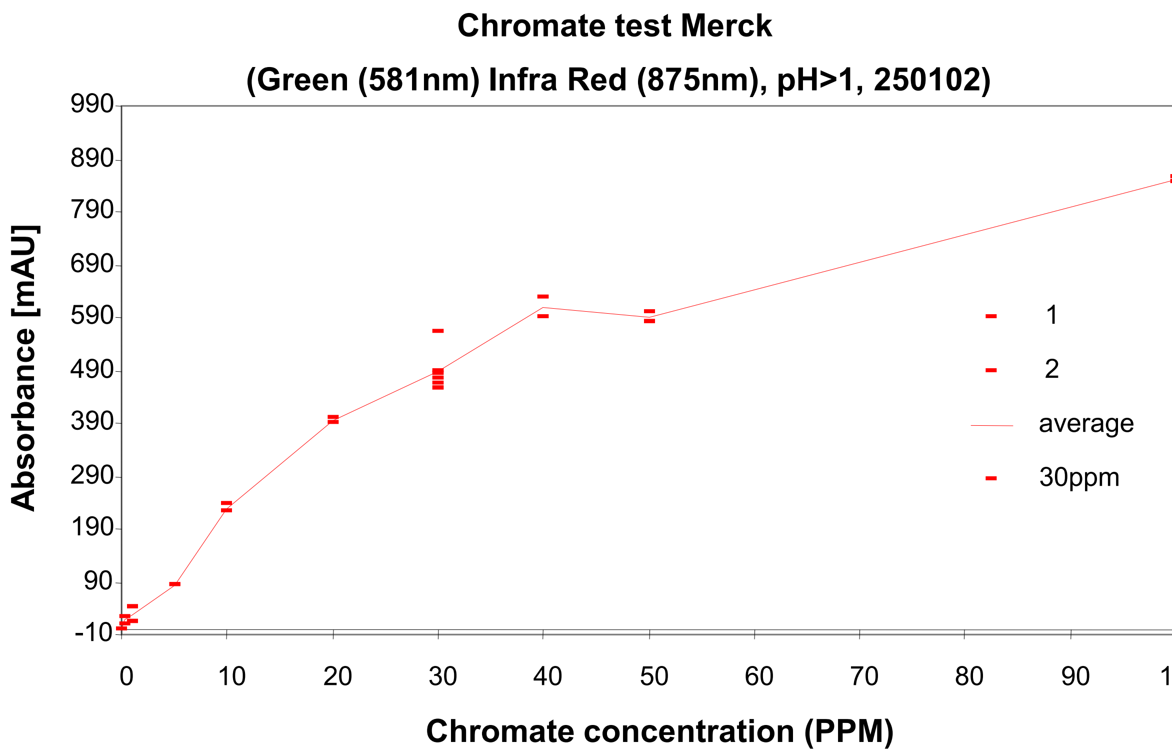
Conditions:

Membrane: Merckoquant

LEDs: **Green 581 nm (Signal)**
IR 875 nm (Reference)
3 mm i.d.

Detector: 10x10mm

Repeats: n = 2 or 6



- Precision: RSD = **7.9%** (30 ppm Cr^{IV})

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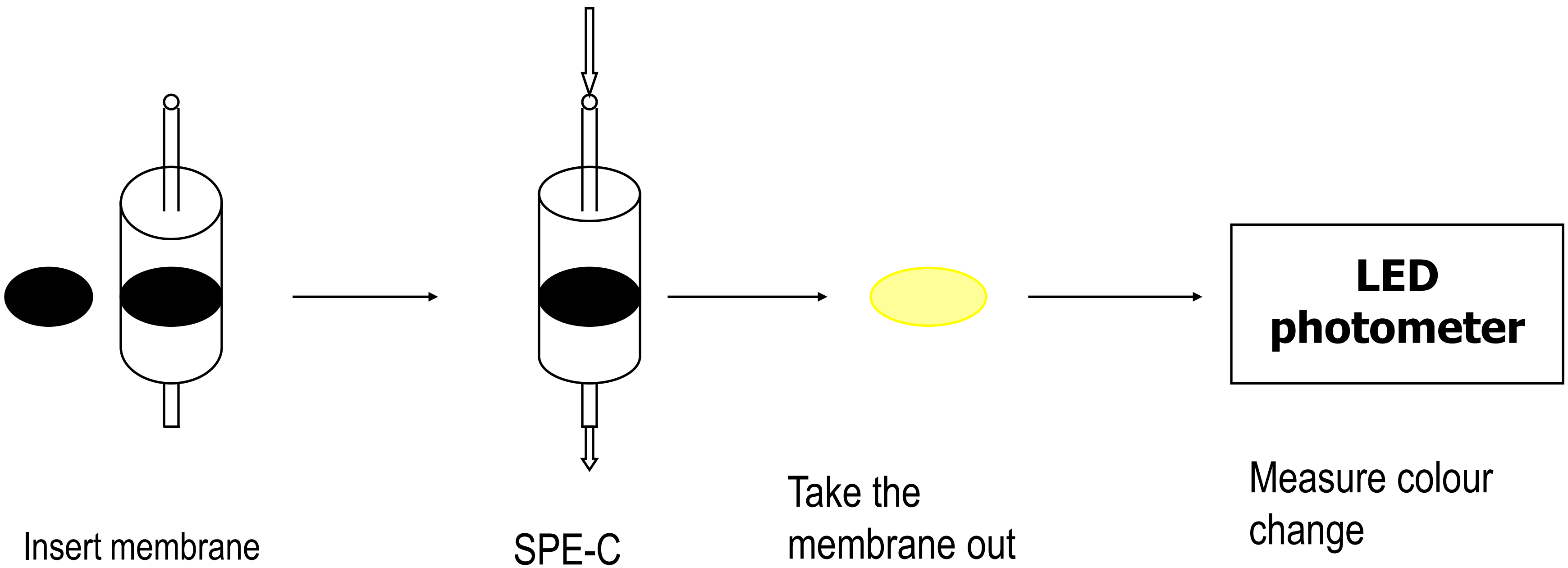
Applications - SPE-C*

- Solid phase extraction - colorimetry (SPE-C)*
  - Measurement of trace concentrations of analytes
    - I_2 in water on spacecraft (0.1-5 ppm US NASA)
    - SPE onto a C-18 membrane impregnated with PVP



*Matteo P. Arena, Marc D. Porter, J.S.Fritz, Rapid, specific determination of Iodine and Iodide by combined solid phase extraction/diffuse reflectance spectroscopy, Anal. Chem., 2002, *74*, 185-190

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Method - Iodine Determination

- Results - Calibration graph

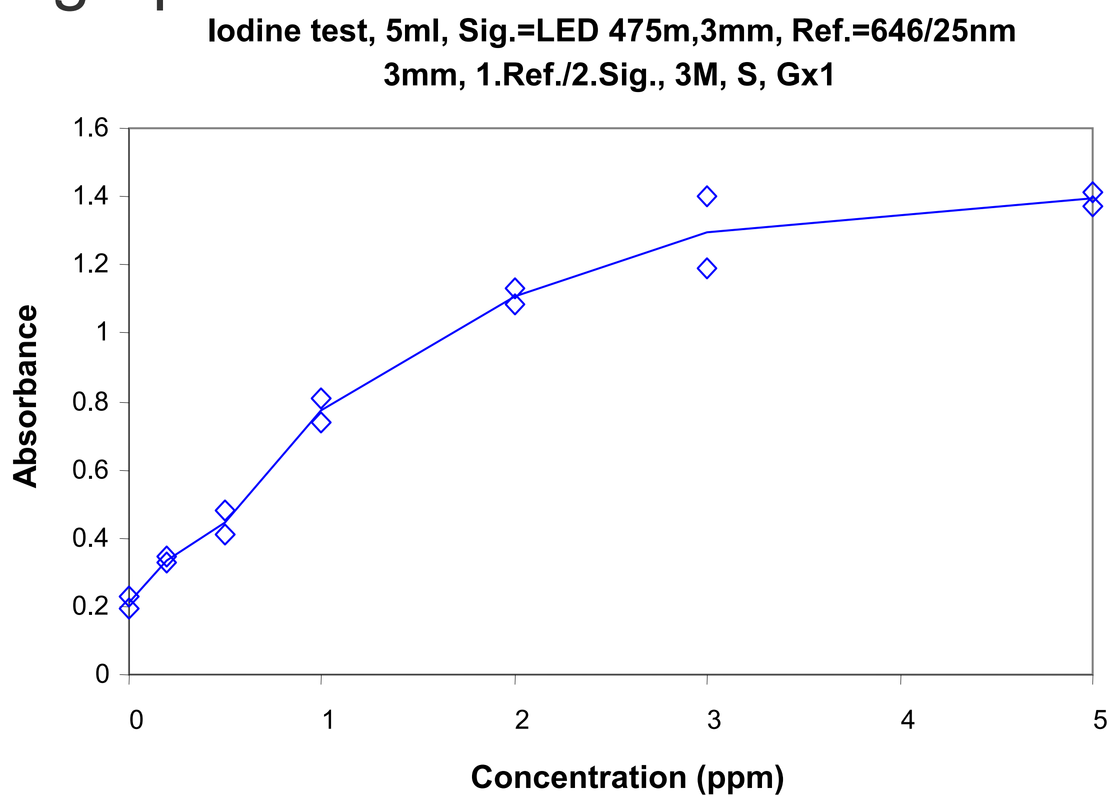
<u>Conditions</u>:

Membrane: 3M PTFE-C18 membrane PVP impregnated

LEDs: **Blue 475 nm** **(Signal)** **Red 646** nm (Reference) 3 mm i.d.

Detector: 5x5mm

Repeats: n = 2 (or 6 for RSD)



- Precision: RSD = **7%** (0.5 ppm, n=6)
- LOD: 0.48 ppm
- R2 = 0.988 (0-1 ppm)

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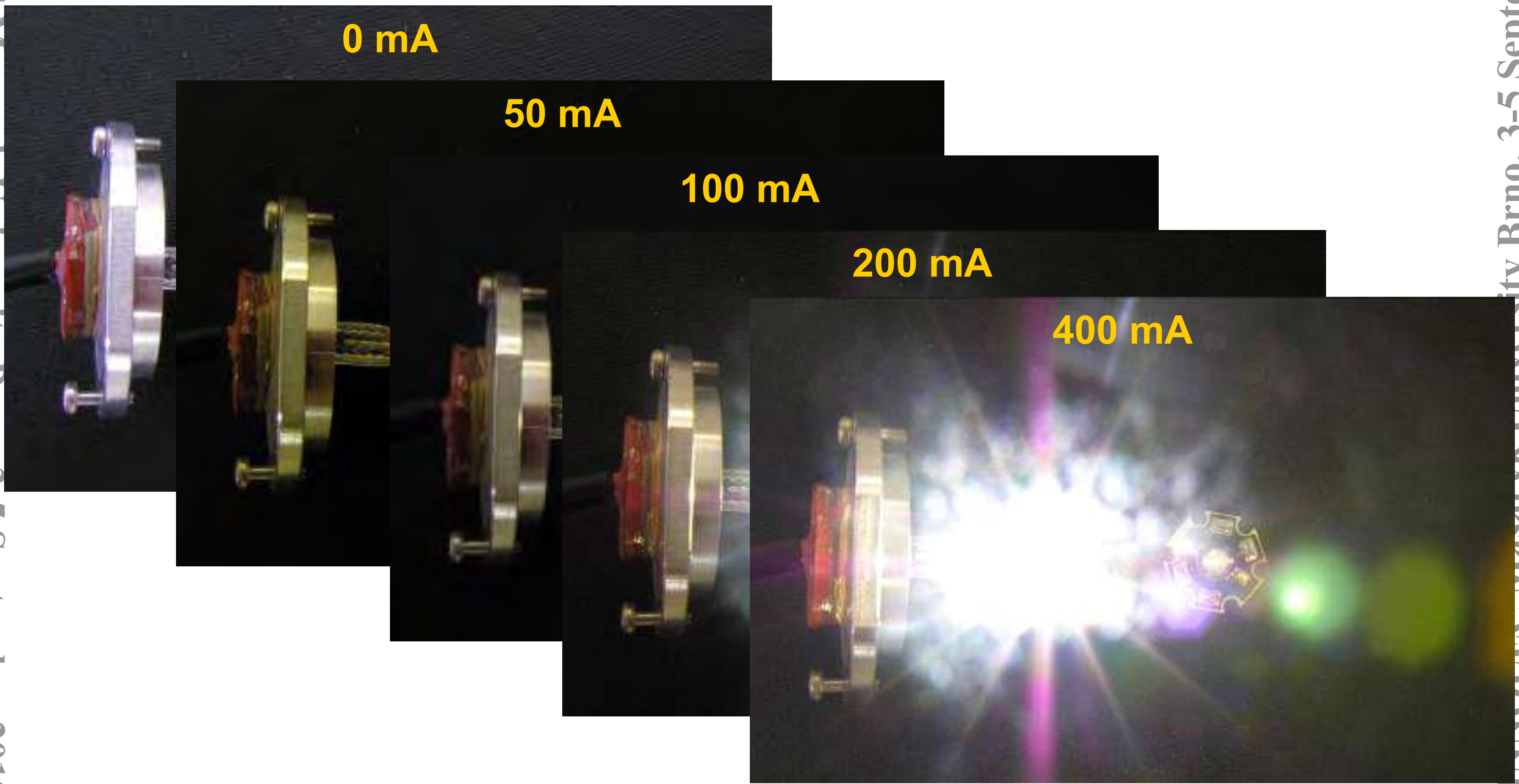
Photometric detection for CE

- White LED as a broad-spectrum light source for a DAD
  - Luxeon LED powered to currents of 0-400 mA.



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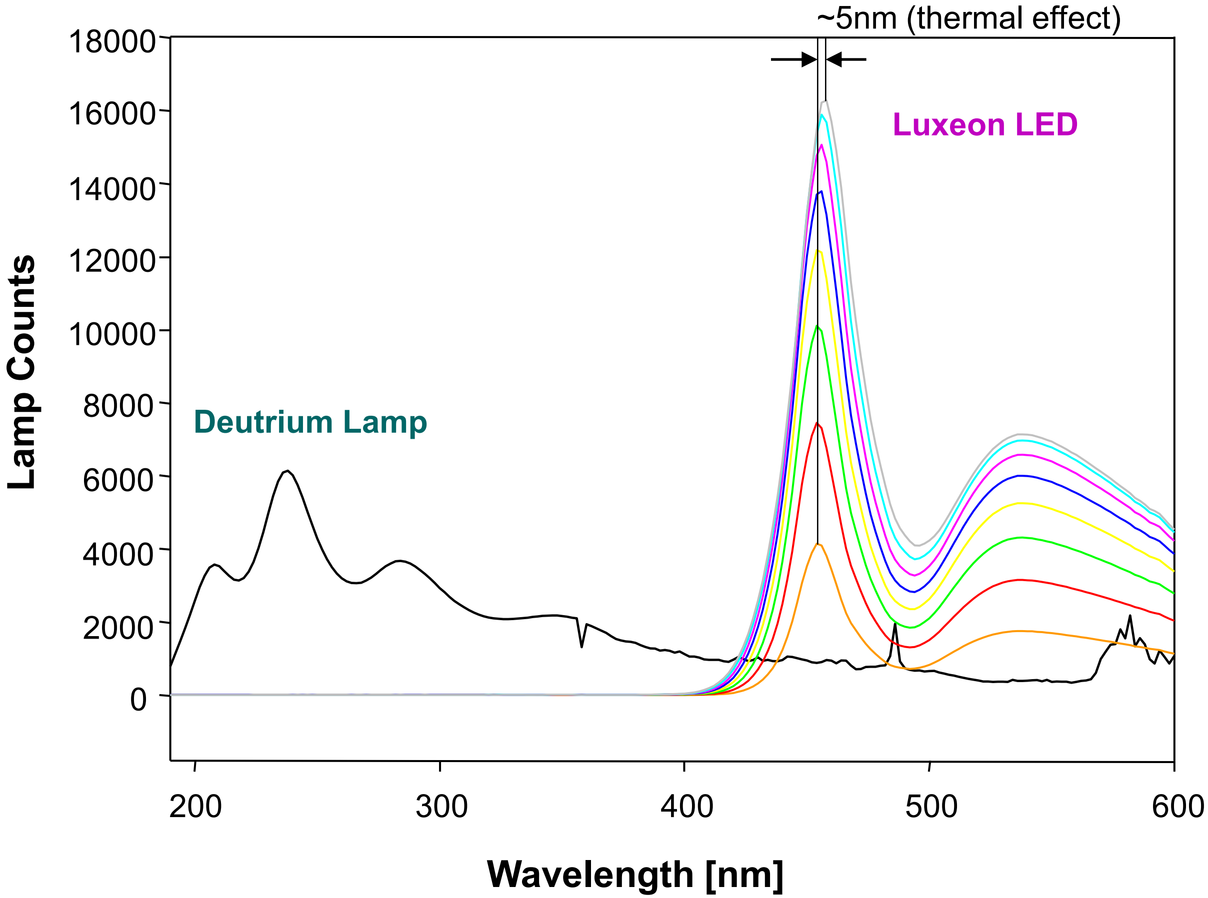
Photometric detection for CE

- Spectra
  - Luxeon powered with different currents (colour)
  - Deuterium lamp (black)



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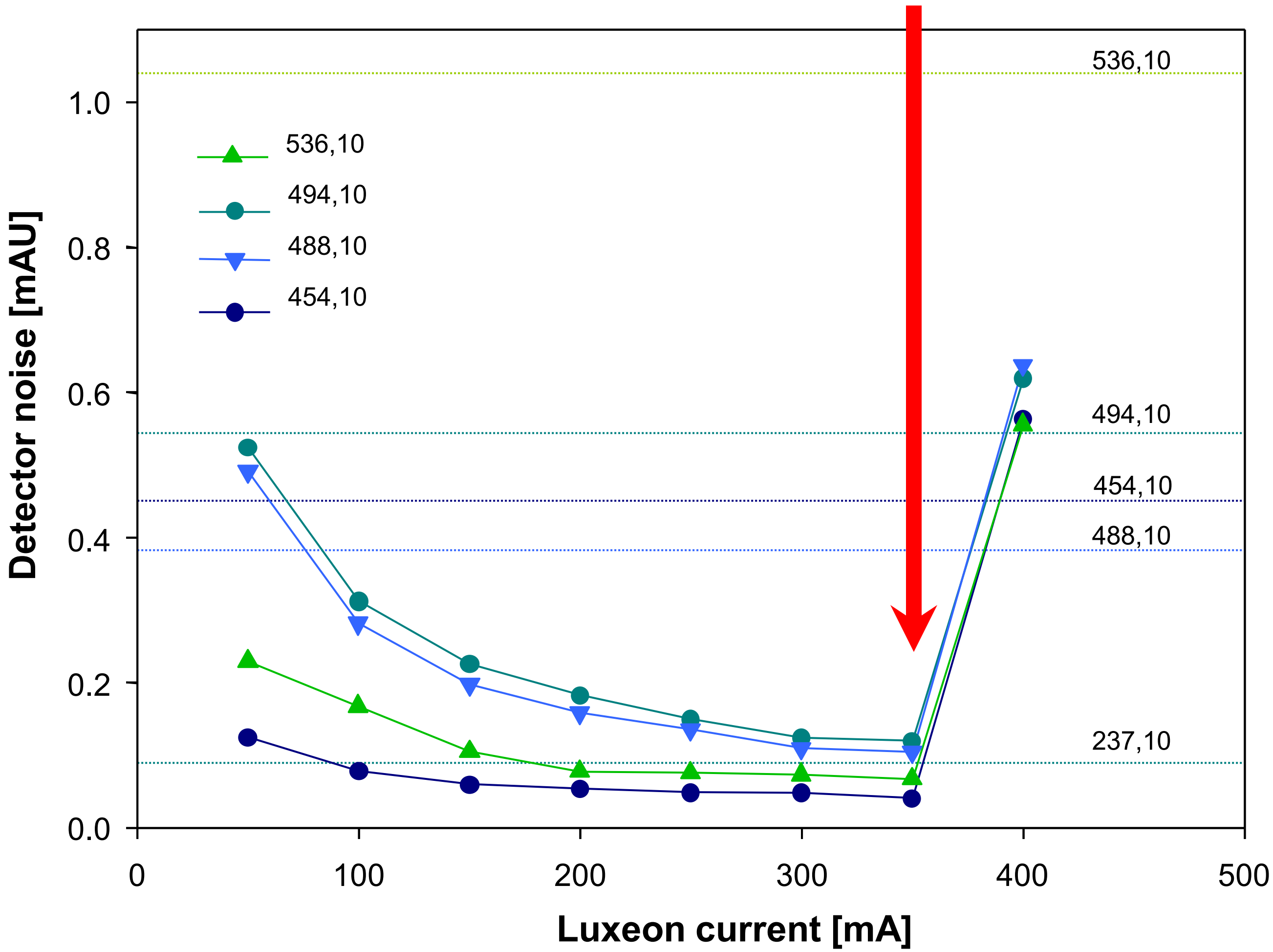
Photometric detection for CE

- Noise
  - Can go up when a certain power is exceeded



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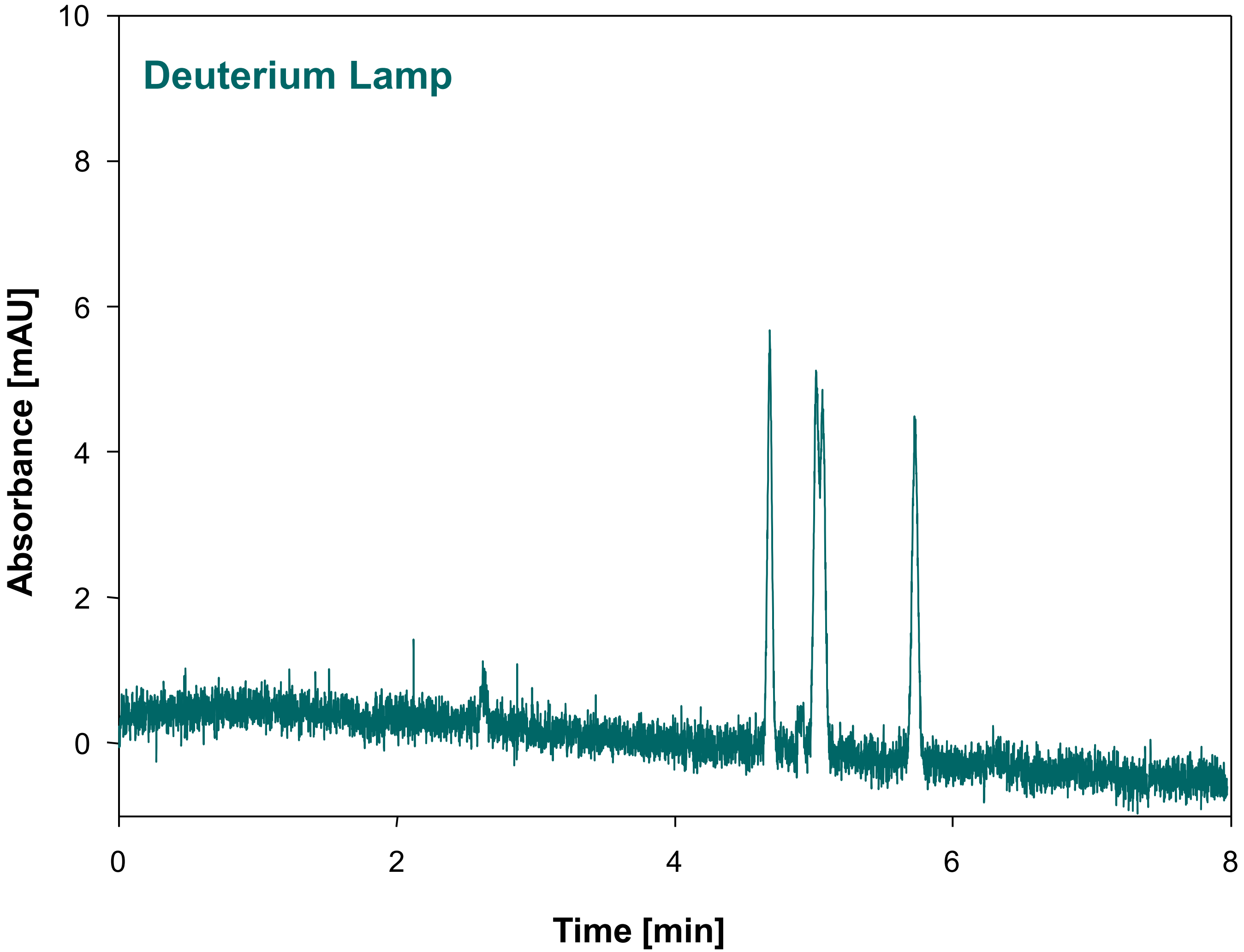
Photometric detection for CE

- Demonstration of use in CE



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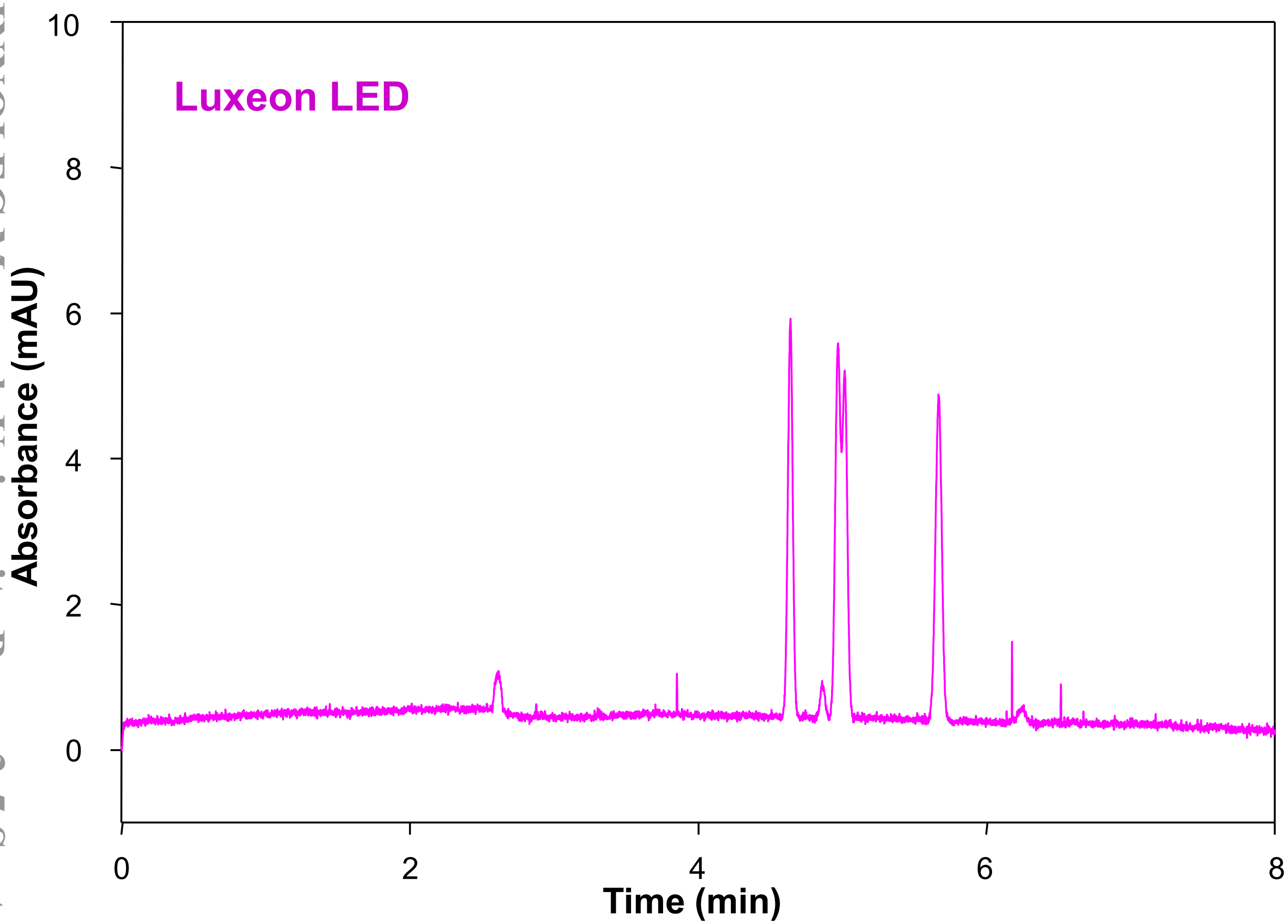
Photometric detection for CE



- LED performs better
  - Lower noise

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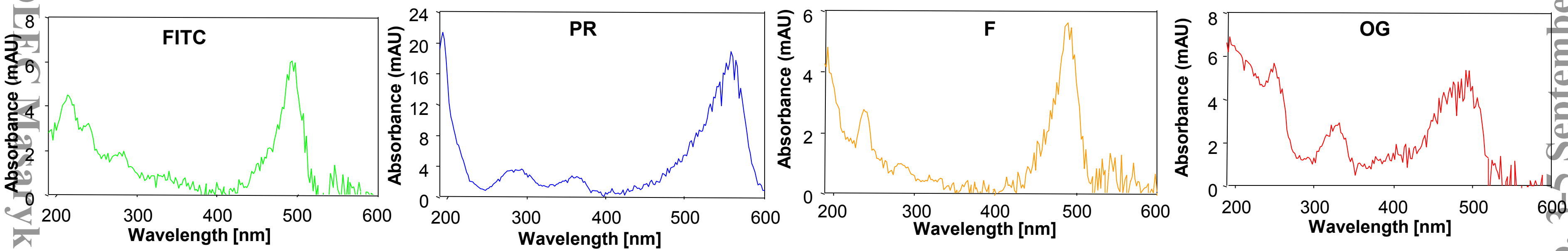
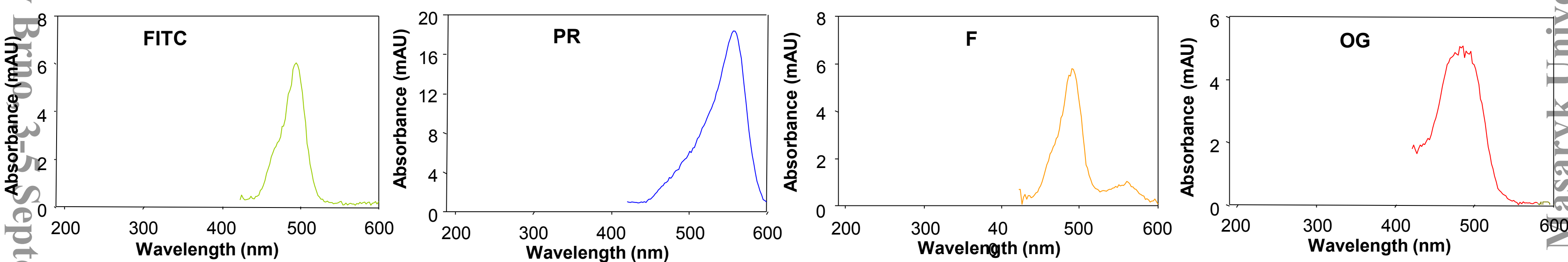
Photometric detection for CE

- Deuterium Lamp



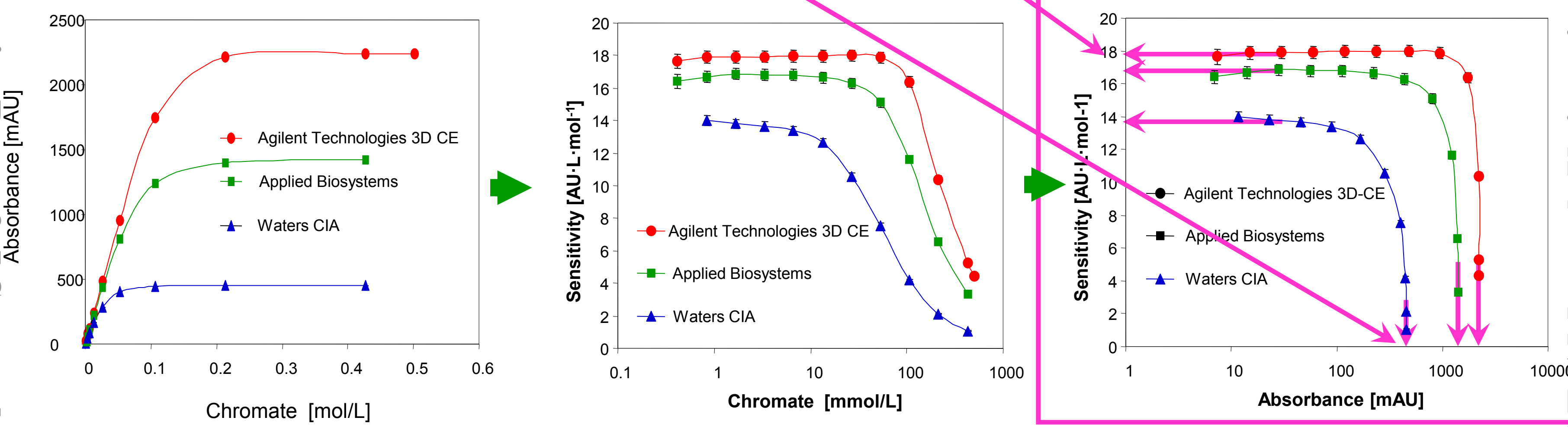
- LEDs



$ White LEDs can be used as a broad-spectrum light source for spectrophotometers in vis range

Photometry and photometric detection

- Quality of detection optical setup easily checked: Sensitivity vs. absorbance graph
  - Effective pathlength
  - Stray light %
    - Linearity evaluation



Johns C., Macka M., Haddad P.R., King M., Paull B., Practical Method for Evaluation of Linearity and Effective Pathlength of On-Capillary Photometric Detectors in Capillary Electrophoresis, *J. Chromatogr. A, 927(1-2)*, 237-241, 2001

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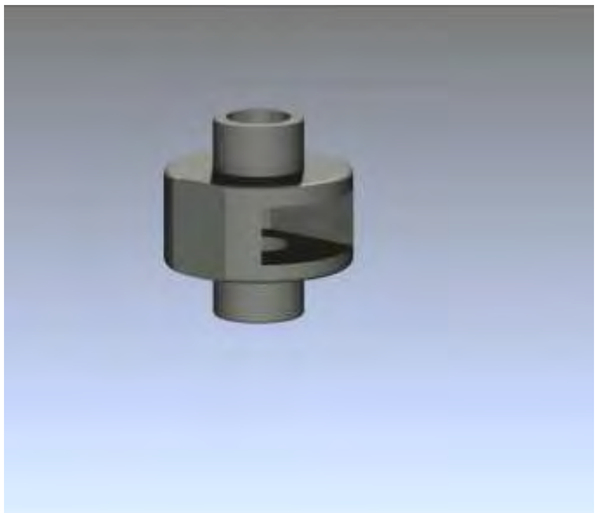
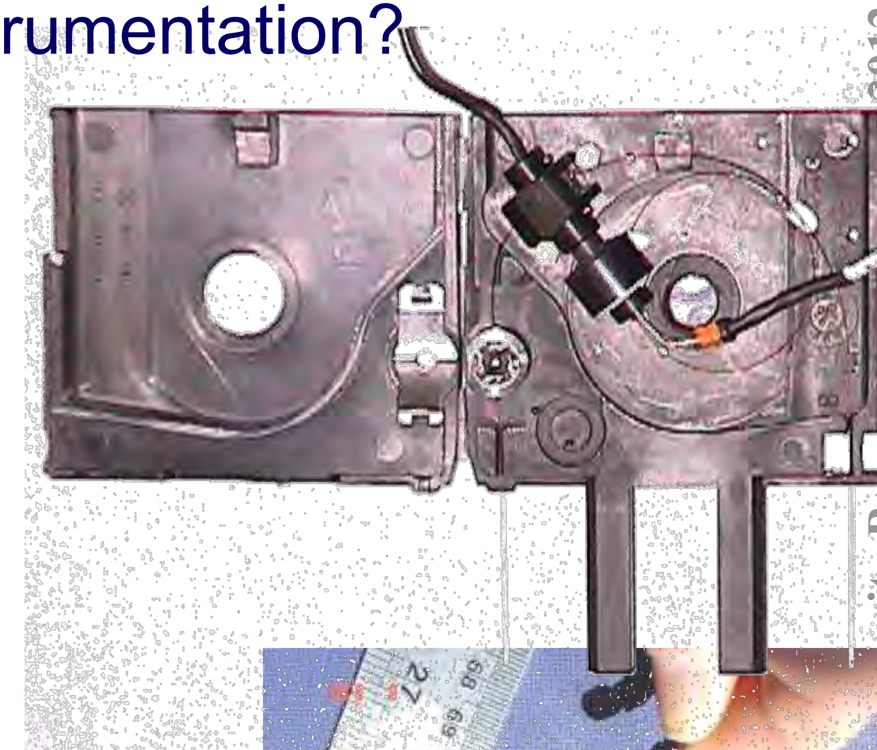
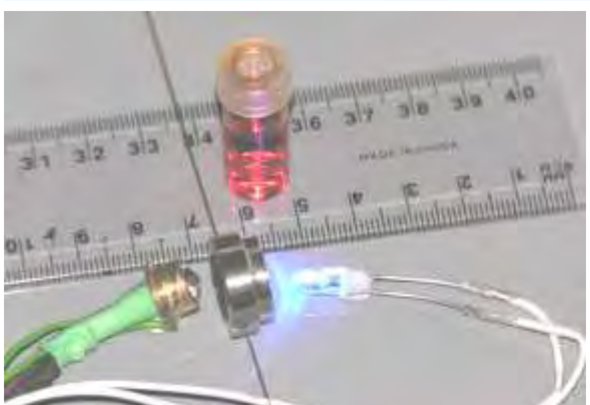
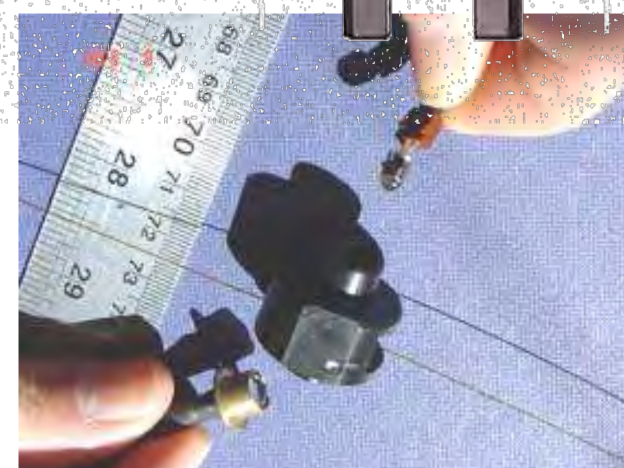
On-capillary detection with LEDs

- LEDs in commercial CE instrumentation?
  ANIMATED









Johns C., Macka M., Paul R. Haddad, Electrophoresis, 25(18-19), 3145-3152, **2004**.

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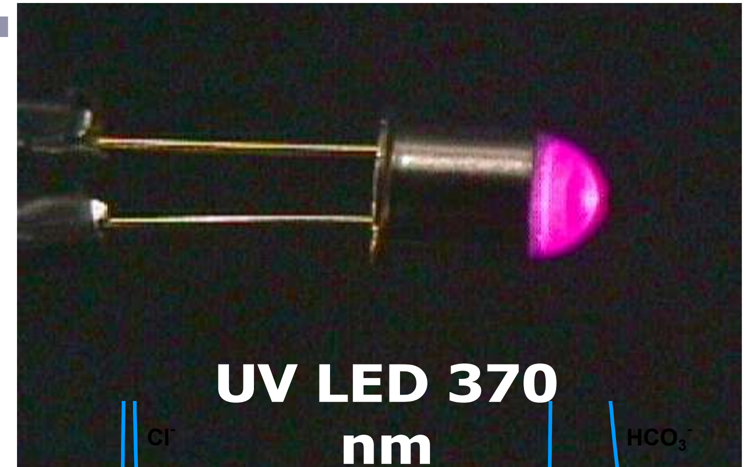
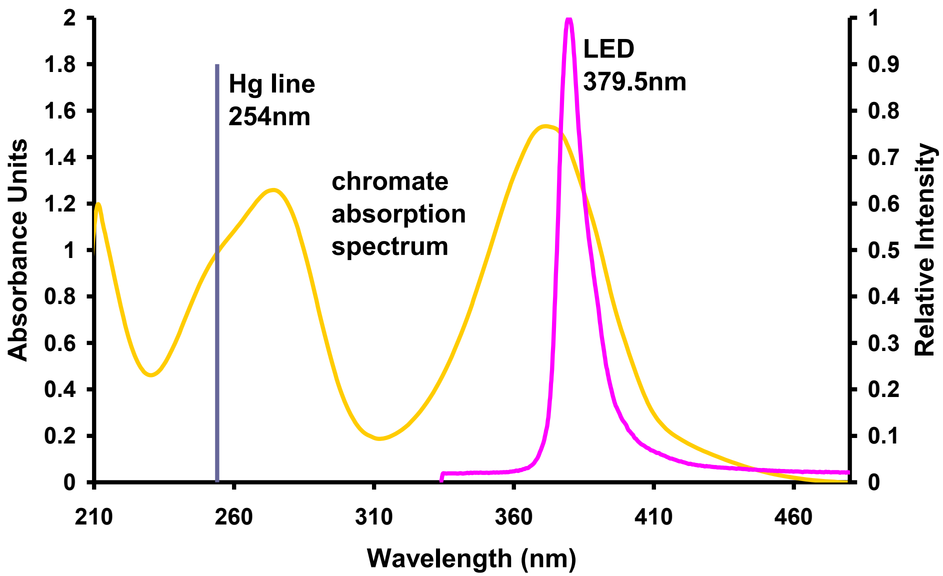
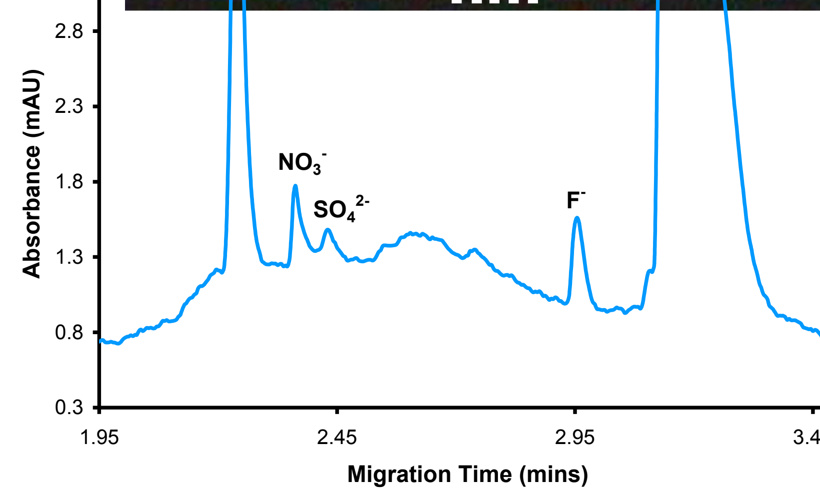
On-capillary detection with LEDs

- UV LED 370 nm
  - Buffered chromate electrolyte
  - LODs ~10x lower vs. Hg 254 nm



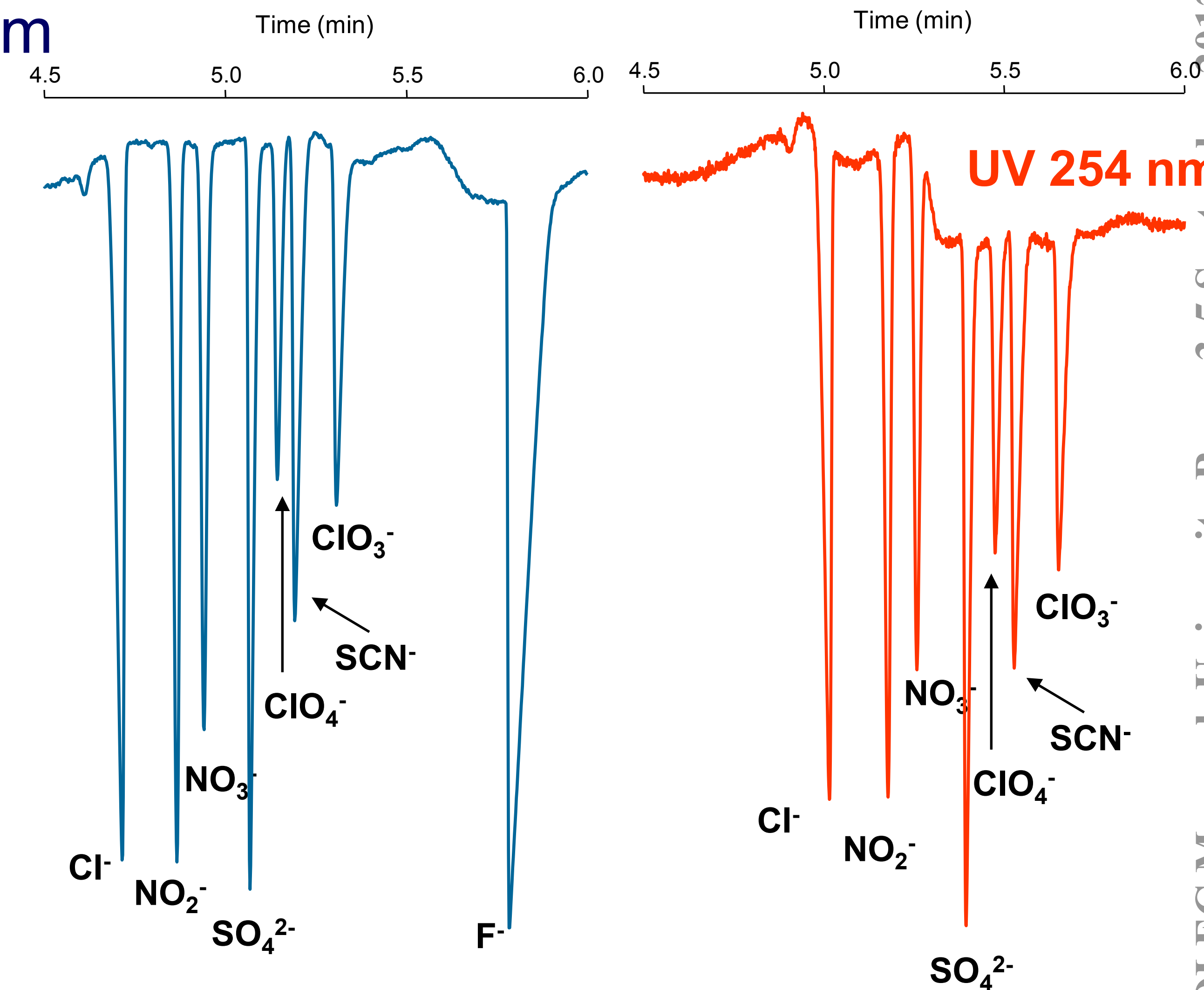




- ✓ King M., Macka M., Paull B., Haddad P. R., 27th International Symposium on High Performance Liquid Phase Separations & Related Techniques - HPLC-2003, Nice, France, 15-19 June **2003**, poster presentation No. 399.
- ✓ King M., Macka M., Paull B., Haddad P. R., Analyst, 127(12), 1564-1567, **2002**.

On-capillary detection with LEDs

- UV LED 370 nm
  - Chromate



LODs improve by ~10x with LED (0.2 – 0.5 ppm)

Conditions

Capillary: L_t = 90.0 L_{det} = 81.5 cm to detector, -30 kV. Electrolyte: 10 mM CrO_3, 20 mM K_2CrO_4, 40 mM TRIS, pH 8.1. Detection: indirect photometric (LED) @ 370 nm

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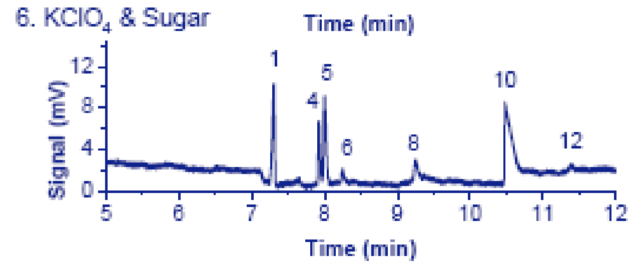
On-capillary detection with LEDs

- Post-blast identification of improvised explosive devices using a portable CE



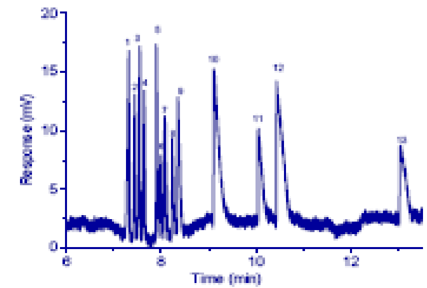


Fig. 6 : Separation of 13 Target Anions at 10 ppm
Peak identities: 1.chloride, 2. thiosulfate, 3. nitrite, 4.nitrate, 5. sulfate, 6. perchlorate, 7. thiocyanate, 8. chlorate, 9. cyanate, 10. fluoride, 11. phosphate, 12. carbonate and 13. benzoate

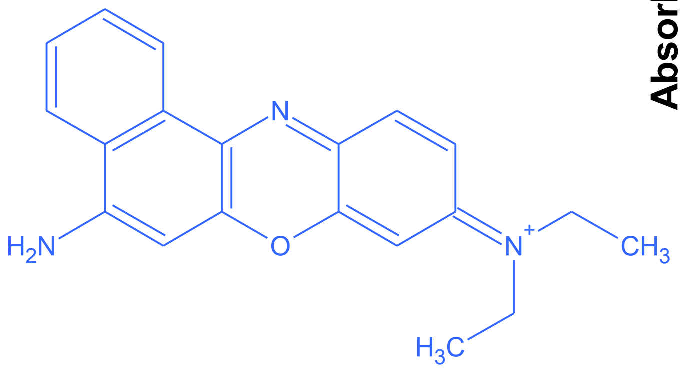
Conditions: fused silica capillary Ltot = 90 cm, Ldet = 80 cm from HV, internal diameter 50 μm.
Conditioning of capillary: 10 min flush with 1 M NaOH followed by 10 min flush with MilliQ water. Detector 379 nm LED source I = 40 mA with in-house extended UV photodiode detector.
2-min preflush at 20 psi (138 kPa) with 1% hexadimethrine bromide (HDMB for EOF reversal) followed by 4 min flush at 20 psi with 10 mM Na_2CrO_4 + 10 mM CrO_3 + 40mM tris(hyroxymethyl)aminomethane (TRIS)
Sample Injection 0.72 psi (5.0 kPa) x 60s

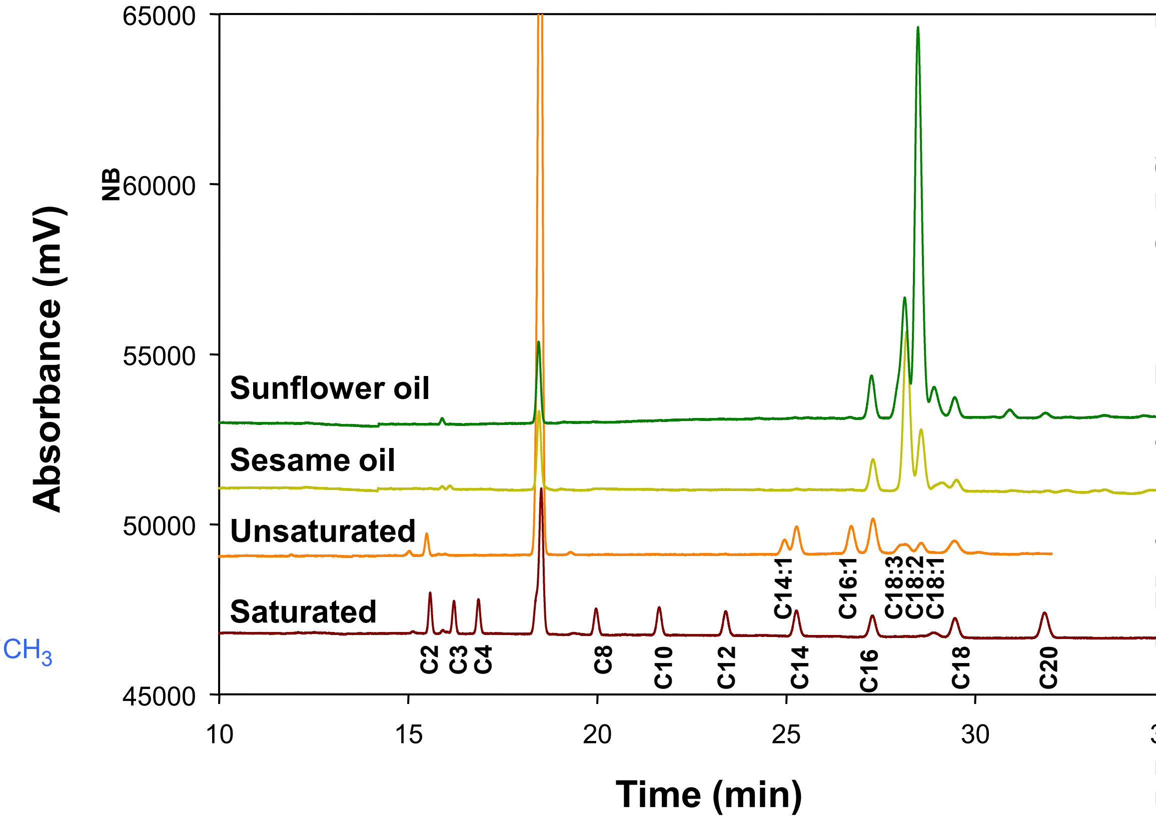
Evenhuis C.J., Guijt R.M., Kazarian A.A., Breadmore M.C., Hilder E.F. Macka M., Haddad P.R., ISC2006, Copenhagen, Dennmark, August 2006, poster presentation No. 71 – **1st Prize**

On-capillary detection with LEDs

- CE of Nile blue-derivatised carboxylic acids
  - Saturated and unsaturated fatty acids

Nile Blue A (NB)
ε ~ 76,000 L . mol^{-1} . cm^{-1}
ϕ ~ 0.27





Conditions
Capillary: L_t = 72.0 cm, L_{det} = 58.0 cm, voltage +25 kV
Electrolyte: 100 mM CH_3COONH_4, 1700 mM CH_3COOH in ACN
Detection: Photometric **(LED) @ 635 nm**
Sampling: 20 μM, hydrodynamic injection 5s @ 50 mbar
LOD ~5x10^{-7} mol/L (100x better then previously, 10x then indirect FLD, only inferior to LIF)

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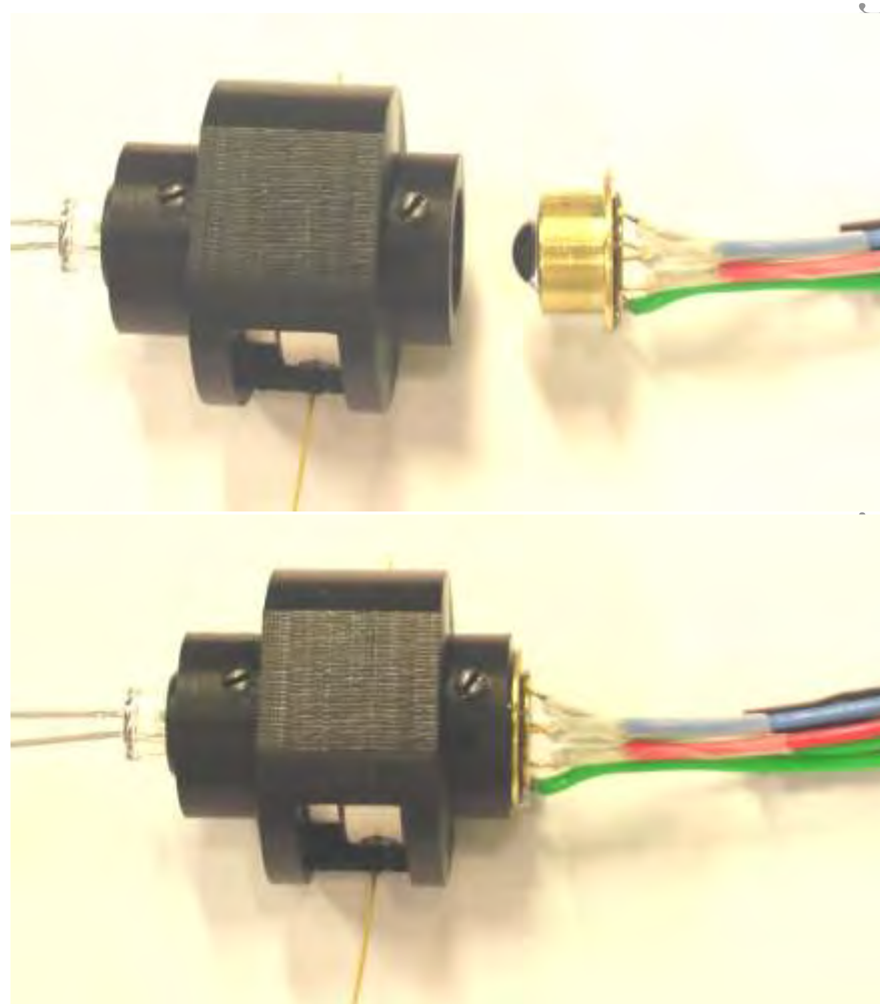
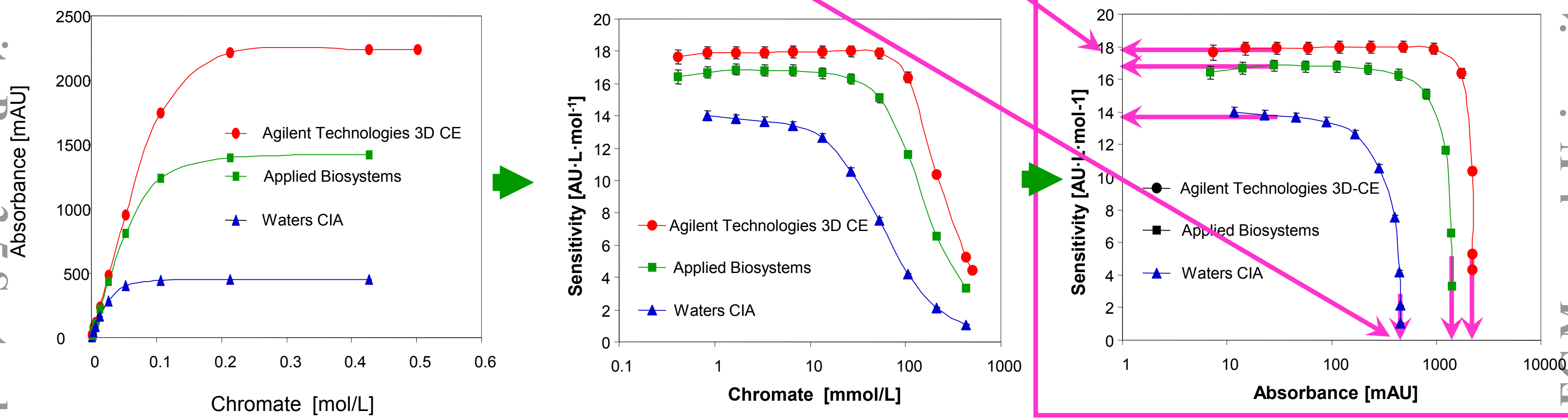
On-capillary detection with LEDs

- An ‘in-house assembled’ detector
  - No custom made electronics!
  - All parts but 1 can be purchased
  - Low cost (~$$10^2$)



On-capillary detection with LEDs

- Quality of detection optical setup easily checked: Sensitivity vs. absorbance graph
  - Effective pathlength
  - Stray light %
    - Linearity evaluation



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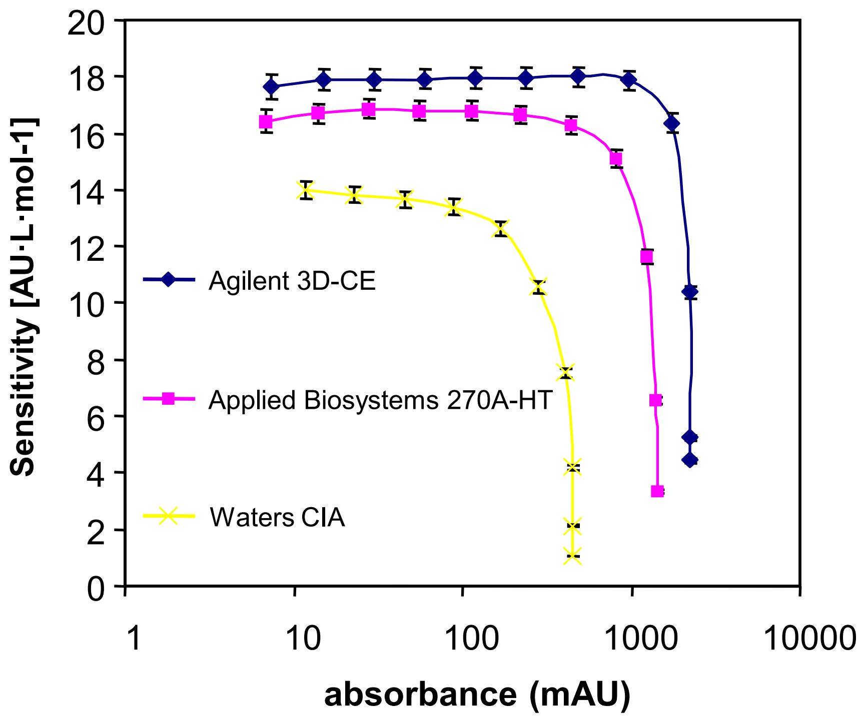
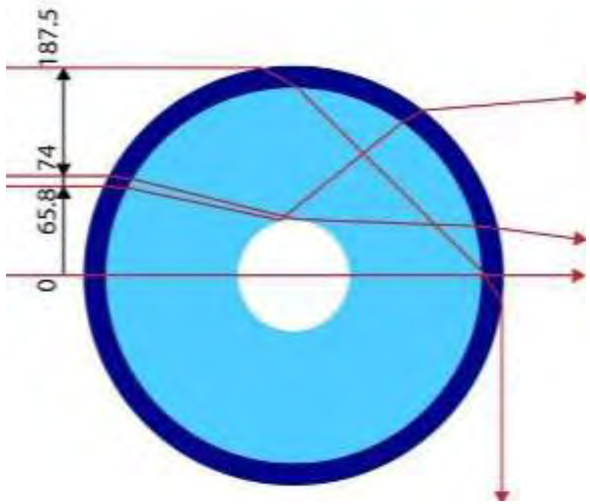
On-capillary detection with LEDs

- Quality of detection optical setup easily checked
  - Effective pathlength
  - Stray light %





Instrument	Detector linearity upper limit (AU)	Effective pathlength (mm)
Agilent ^{3D}CE	1.2	64.6
AB 270A-HT	0.75	60.5
Waters CIA	0.175	49.7

[Johns C, Macka M, Haddad PR, King M, Paull B, J. Chromatogr. A, 927(1-2), 237-241, 2001]

[Johns C., Macka M., Haddad P.R., LC-GC Europe, 16(5), 290, 292, 294-295, 2003]

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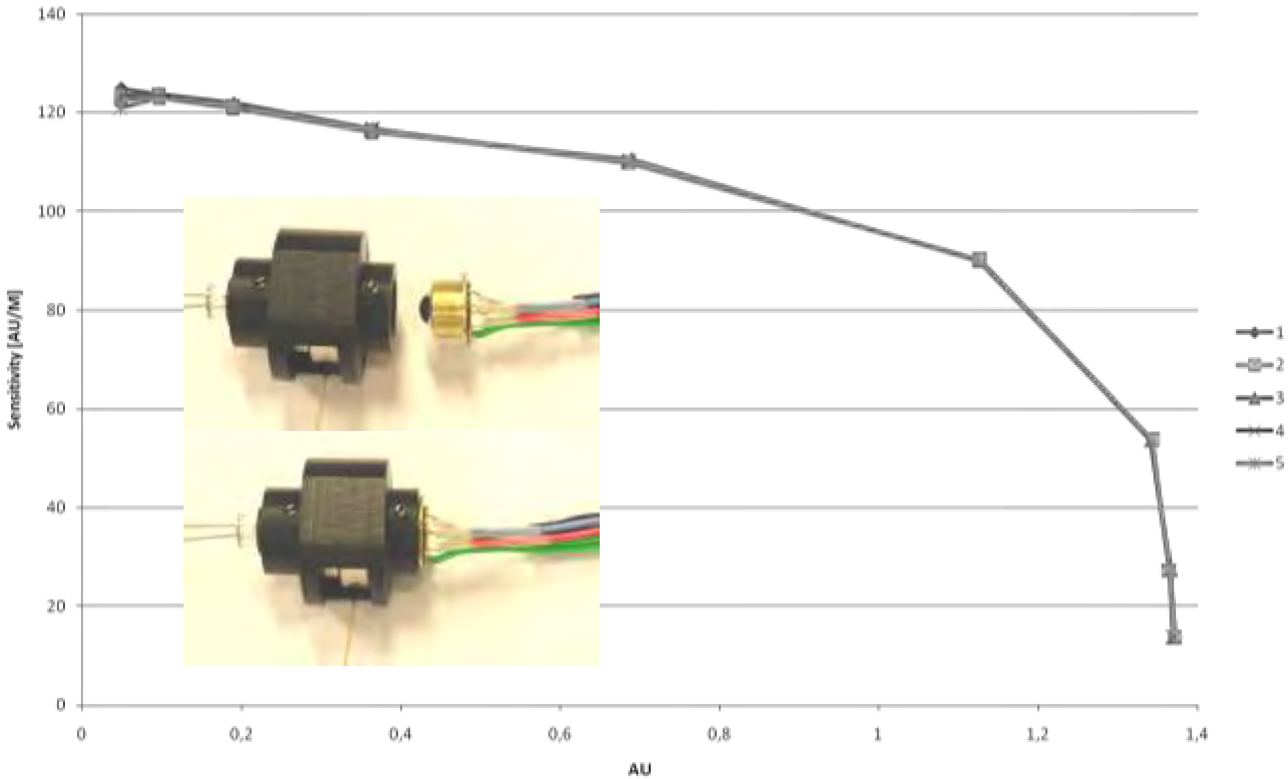
On-capillary detection with LEDs

- Quality of detection optical setup easily checked
  - In-house assembled from all commercial parts but 1
    - Effective pathlength: 74 µm (75 µm i.d.)
    - Stray light: 4.3 %



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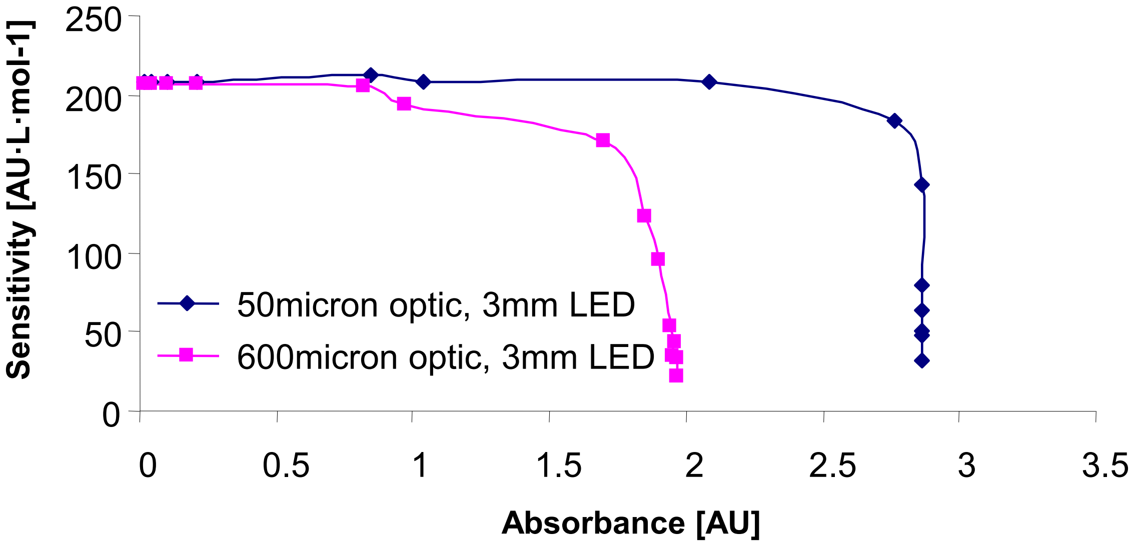
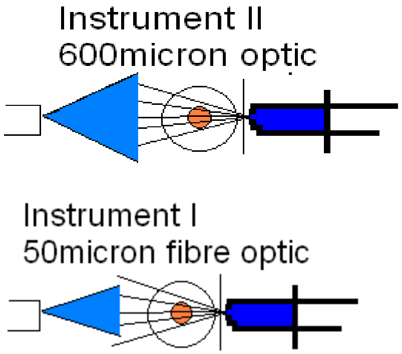
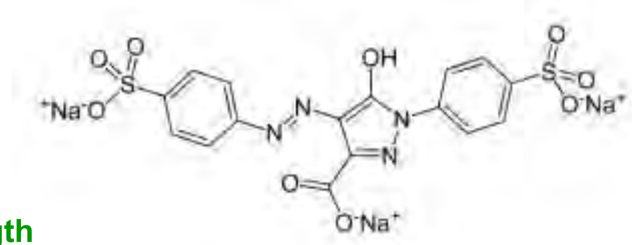
On-capillary detection with LEDs

- Quality of detection optical setup easily checked
  - In-house assembled: Fibre optics CCD + capillary holder from Beckman CE
    - Effective pathlength: 92 um (100 um i.d.)
    - Stray light: 0.13 – 1.0 %







Set-up	Stray Light	Effective Pathlength
50 micron optic, 3 mm LED	0.13%	92 µm (100 µm i.d.)
600 micron optic, 3 mm LED	1%	92 µm (100 µm i.d.)

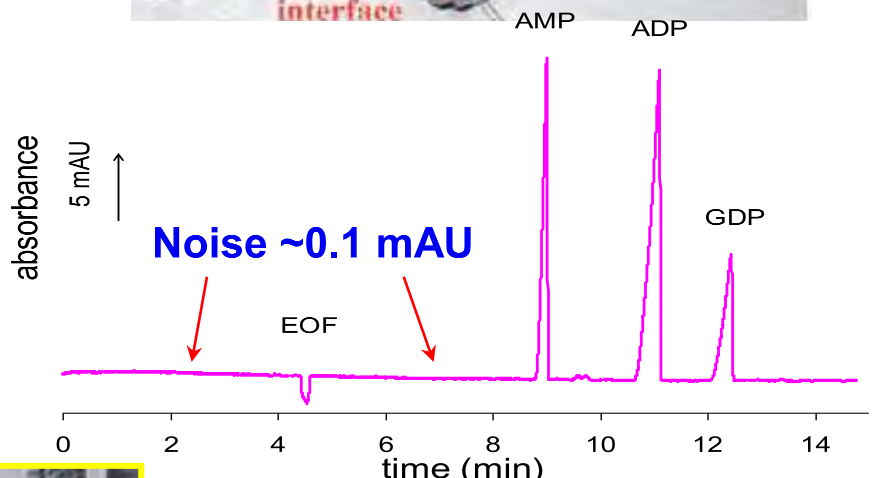
Photometric (single-detector)

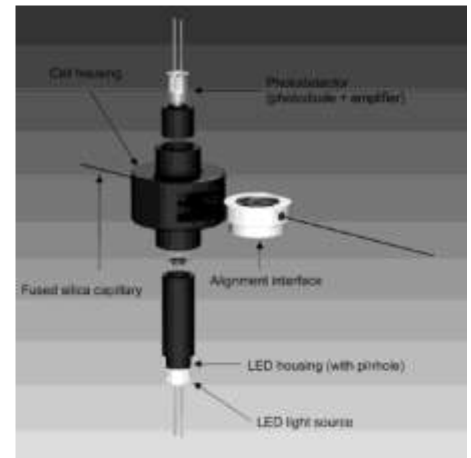
- Deep-UV-LEDs: 255 nm
  - Photometric detection

$200-300, ~20-300 μW

no optical components

light utilisation: ~0.1%





✓ Johns C. et al., Electrophoresis, 2004, 25, 3145–3152

✓ Lenka Krcmova, Anna Stjernlof, Sebastien Mehlen, Peter Hauser, Silvija Abele, Brett Paull, Mirek Macka, Analyst, 134, 2394 – 2396, 2009 (DOI:10.1039/ B916081G)

✓ Stefan Schmid, Mirek Macka, Peter Hauser, UV-absorbance detector for HPLC based on a light-emitting diode, Analyst, 133, 465-469, 2008 (DOI 10.1039/b715681b)

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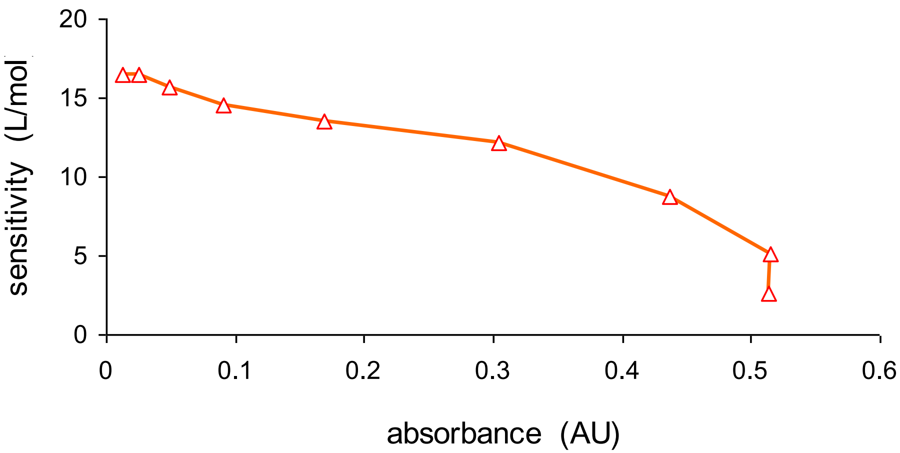
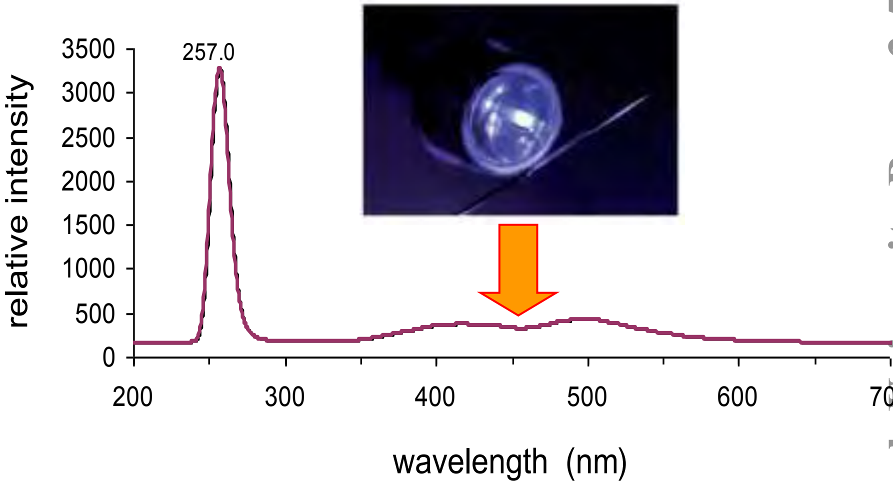
Photometric (single-detector)

- Deep-UV-LEDs: 255nm
  - Performance
    - Baseline noise N~0.1mAU
    - Poor linearity => stray light?





- **Need for better deep-UV-LEDs!**

✓ Lenka Krcmova, Anna Stjernlof, Sebastien Mehlen, Peter Hauser, Silvija Abele, Brett Paull, Mirek Macka, Analyst, 134, 2394 – 2396, 2009 (DOI:10.1039/ B916081G)

✓ Stefan Schmid, Mirek Macka, Peter Hauser, UV-absorbance detector for HPLC based on a light-emitting diode, Analyst, 133, 465-469, 2008 (DOI 10.1039/b715681b)

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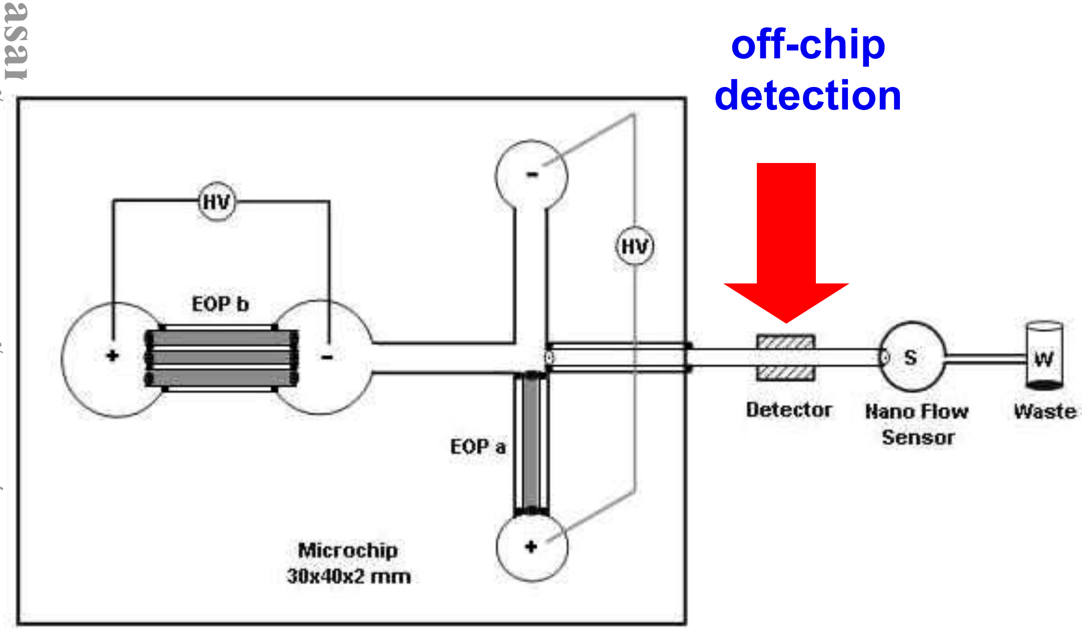
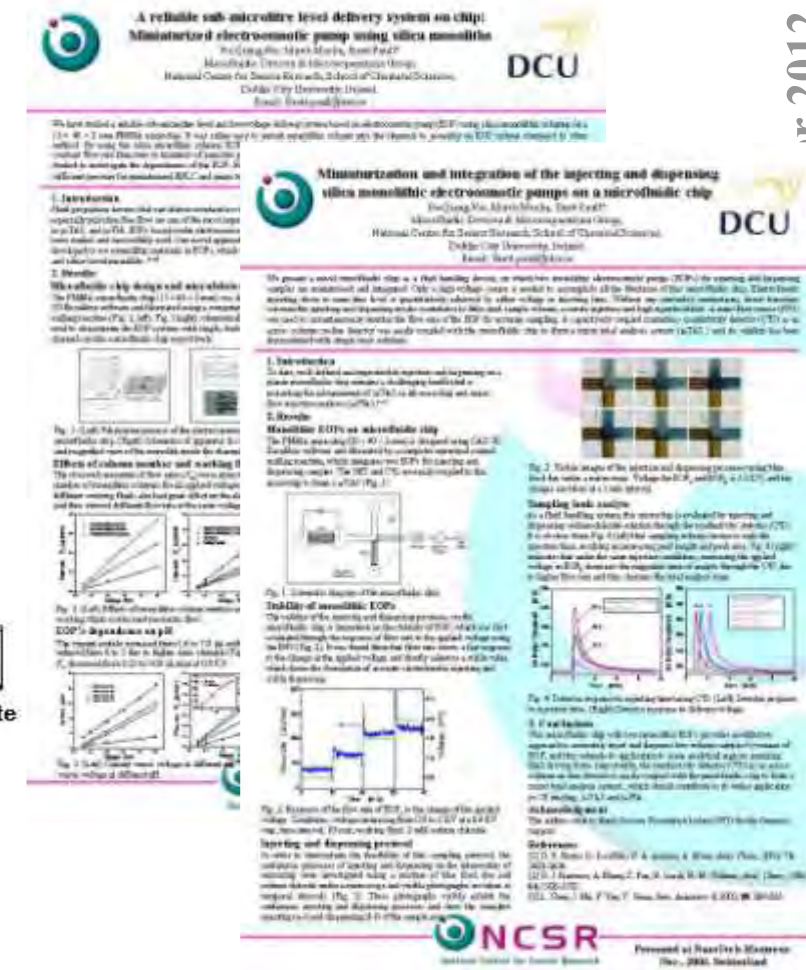
On-capillary detection with LEDs

- Off-chip detection in uTAS
  - Integration of 2 monolithic electroosmotic pumps





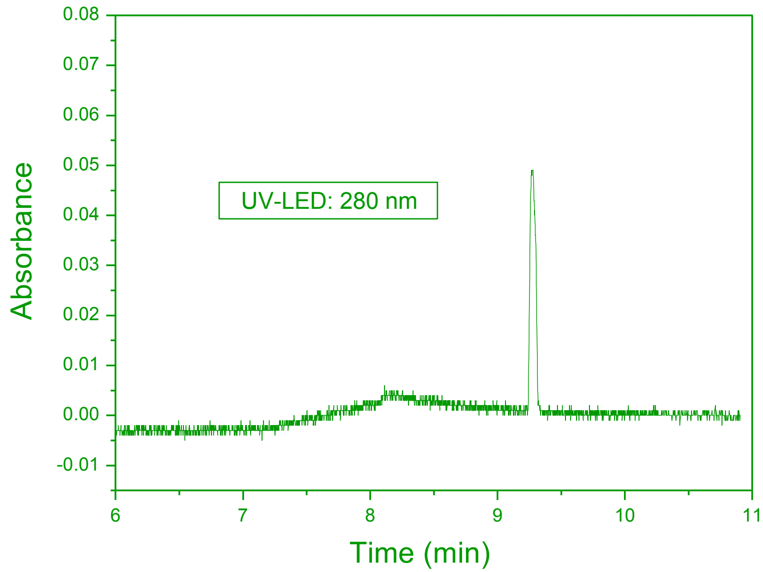
[Nie F.-Q., Macka M., Brett Paull, Miniaturized electroosmotic pump using silica monoliths, *Proc. NanoTech 2006*, Montreux, Switzerland, 13 - 16 November **2006**, poster presentation.]

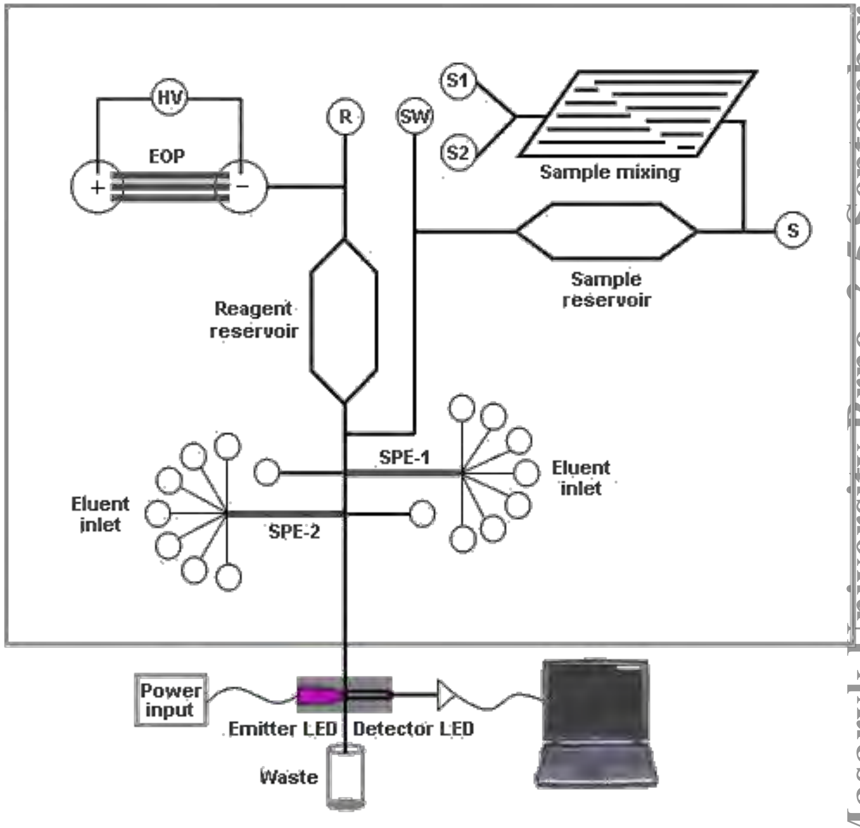
[Nie F.-Q., Macka M., Brett Paull, Miniaturization and integration of the injecting and dispensing silica monolithic electroosmotic pumps on a microfluidic chip, *Proc. NanoTech 2006*, Montreux, Switzerland, 13 - 16 November **2006**, poster presentation.]

[Nie F.-Q., Kent N., Macka Miroslav, Paull Brett, Robust Monolithic Silica Based On-Chip Electro-Osmotic Micro-Pump, Analyst, in press **2007**]

On-capillary detection with LEDs

- Peptide detection @ 280 nm



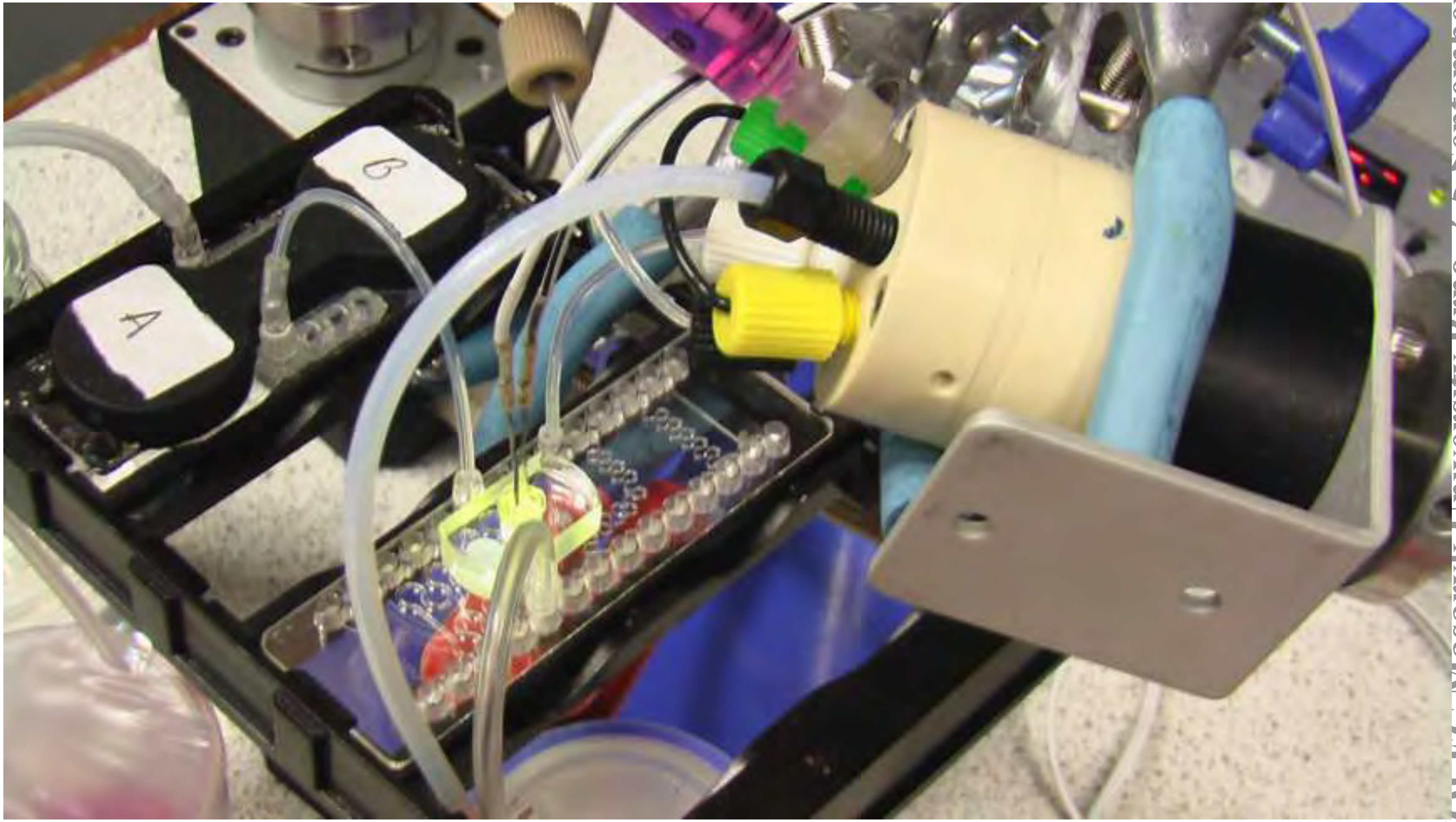


  - Detector: CCD
    - Dynamic range ~300:1

$ LED on-capillary off-chip detection very simple

On-chip photometric detection

- Commercial PMMA chip with snake mixers



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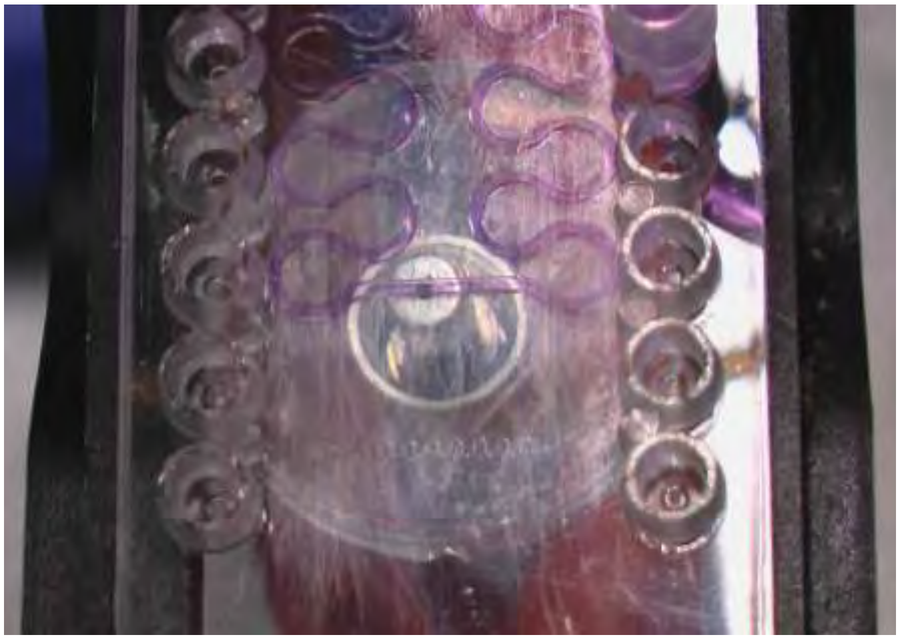
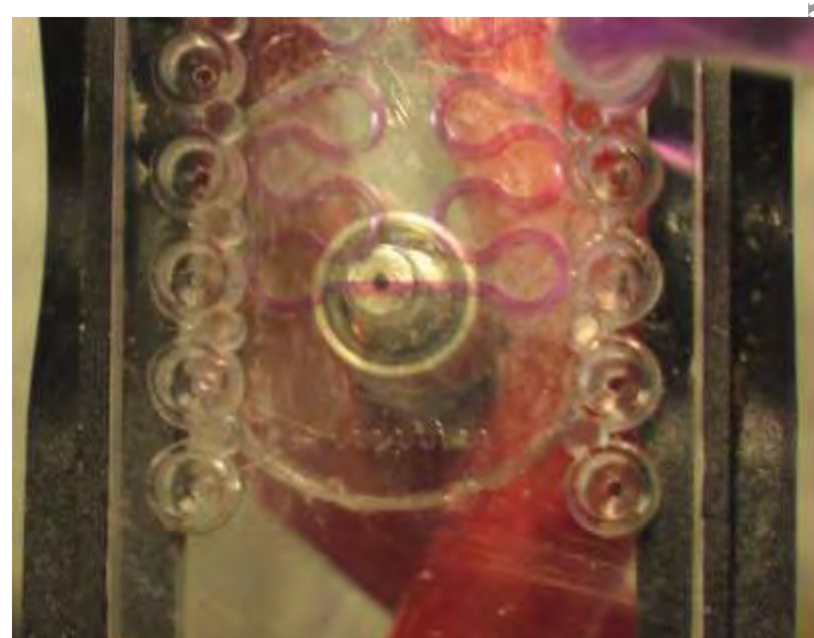
On-chip photometric detection

- Fibre - channel geometry



600 μm optic fibre
across the 640 μm wide channel

600 μm optical fibre
aside of 640 μm wide channel



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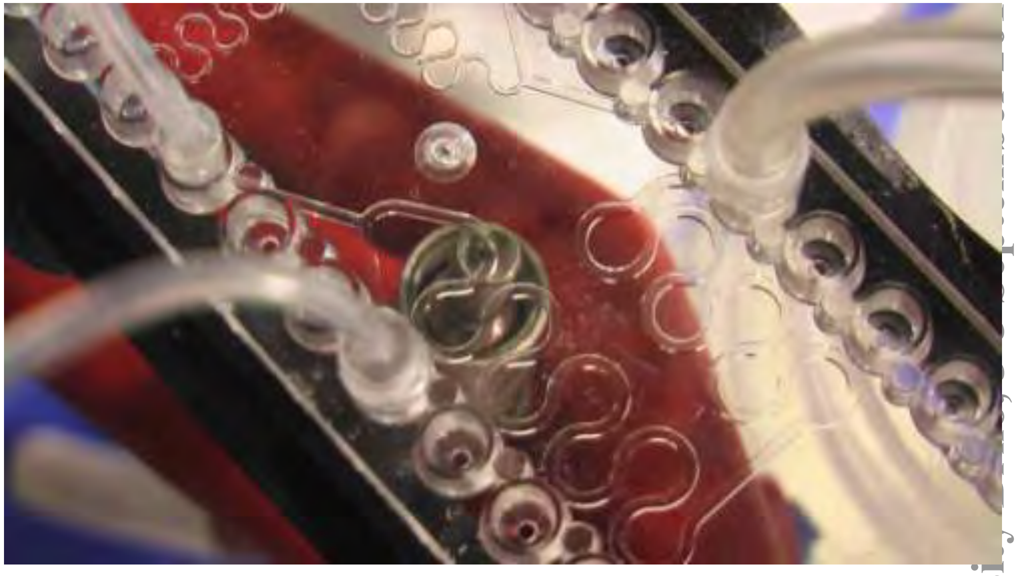
On-chip photometric detection

- Optimal channel – fibre geometry: smaller fibre

100 µm optic fibre in the centre of 640 µm channel

On-chip photometric detection

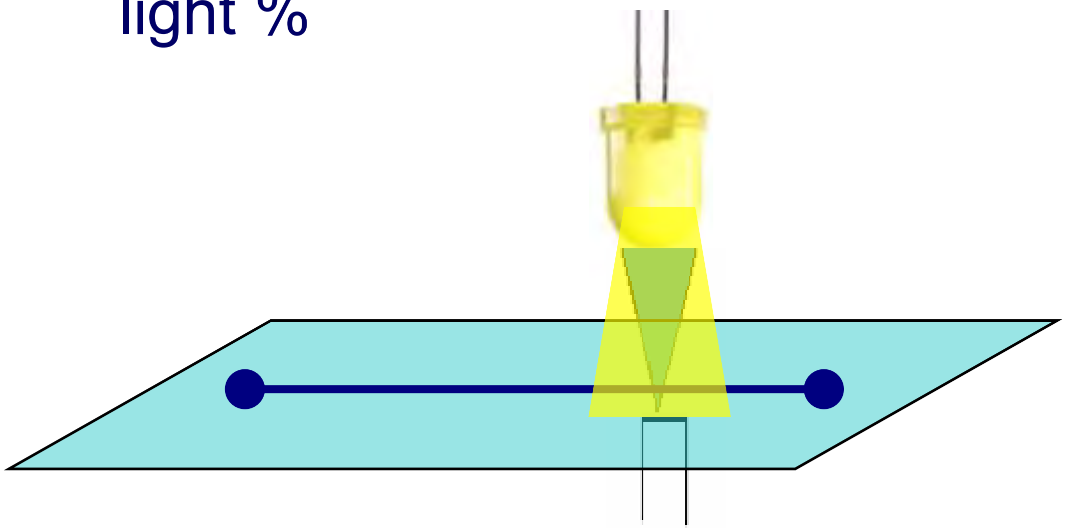
- LED – fibre geometry

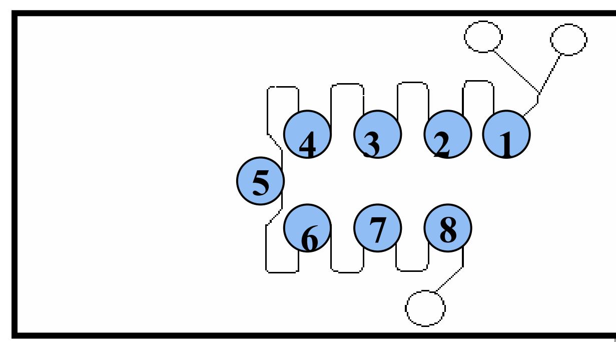


LED: 575 nm
Chip: snake mixer SMS0104
Optical fibre: 600 µm

On-chip photometric detection

- For applications requiring moderate sensitivity
  - FIA on a chip, reactions on a chip etc.
- A simple setup and optics
  - Optical fibre to collect the transmitted light
  - Simple to relocate the point of detection around the chip
  - Simple characterisation of effective pathlength and stray light %





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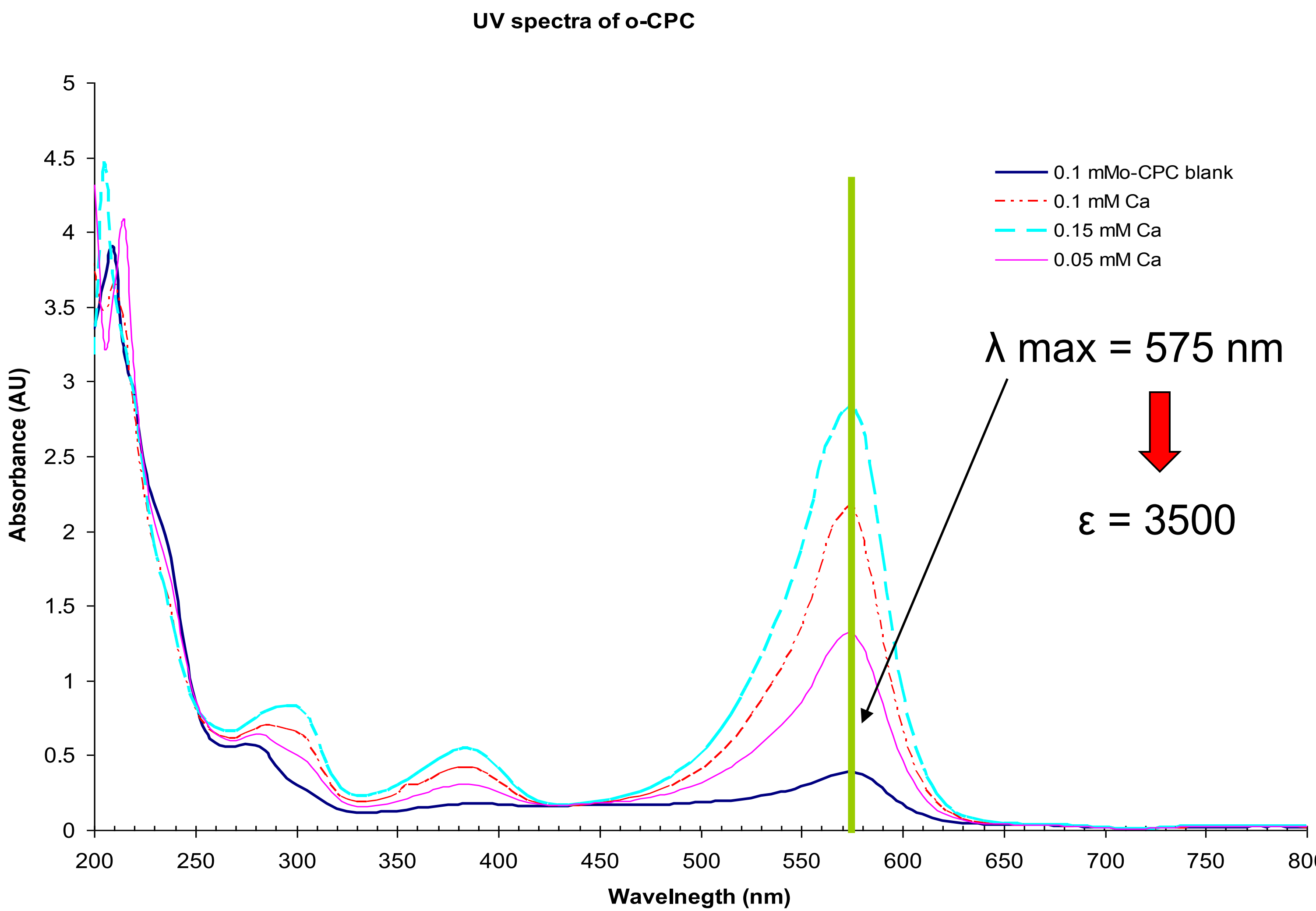
On-chip photometric detection

- Ca^{2+} + o-CPC



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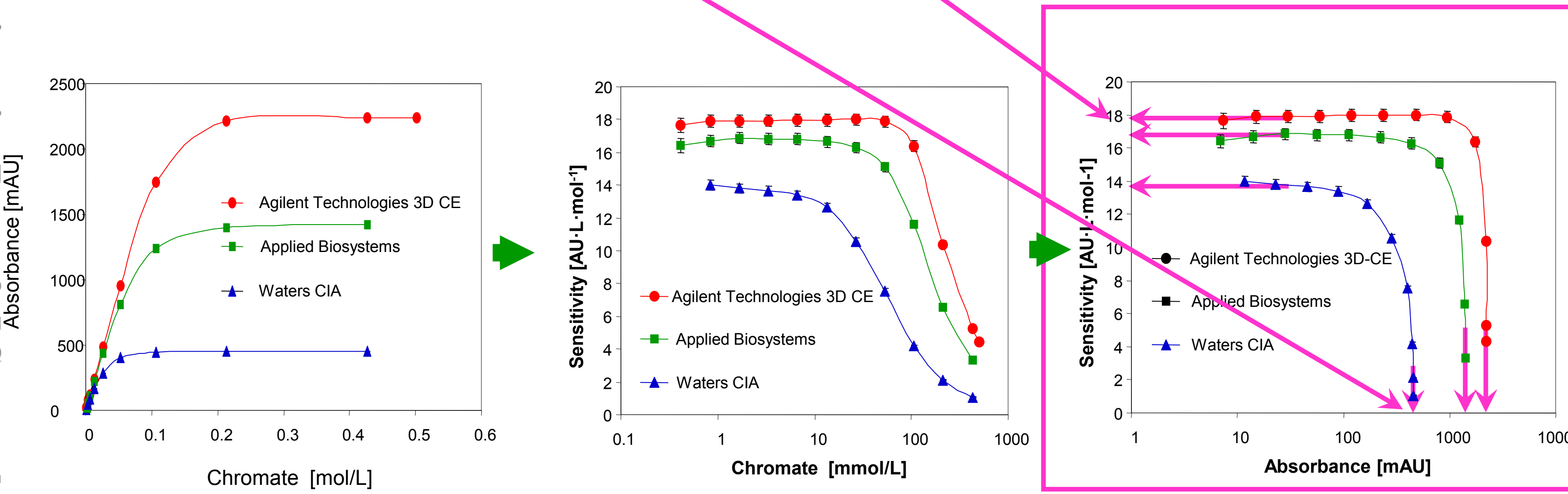
- Quality of detection optical setup easily checked: Sensitivity vs. absorbance graph
  - Effective pathlength
  - Stray light %
    - Linearity evaluation



Johns C., Macka M., Haddad P.R., King M., Paull B., Practical Method for Evaluation of Linearity and Effective Pathlength of On-Capillary Photometric Detectors in Capillary Electrophoresis, *J. Chromatogr. A, 927(1-2)*, 237-241, 2001

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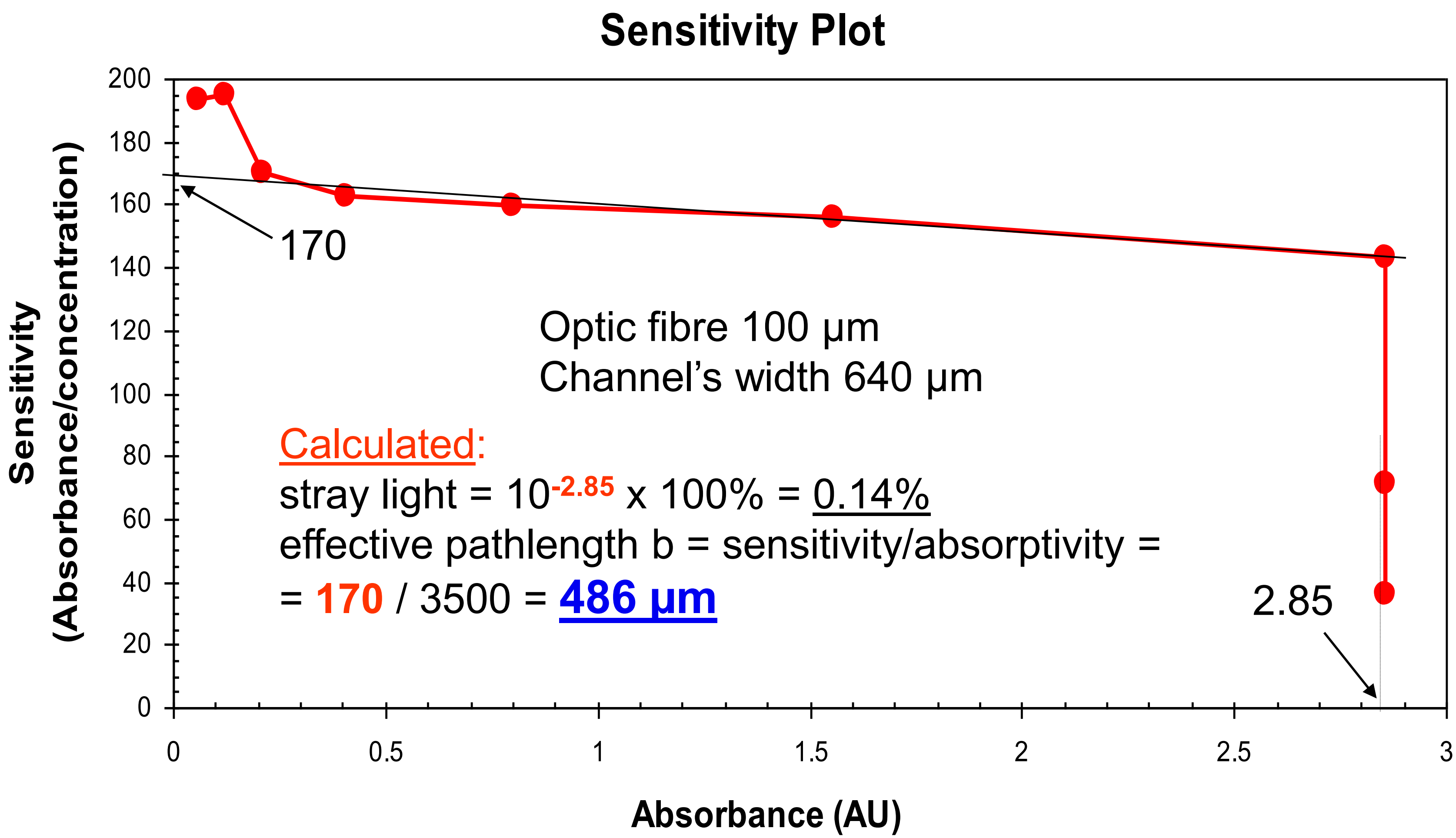
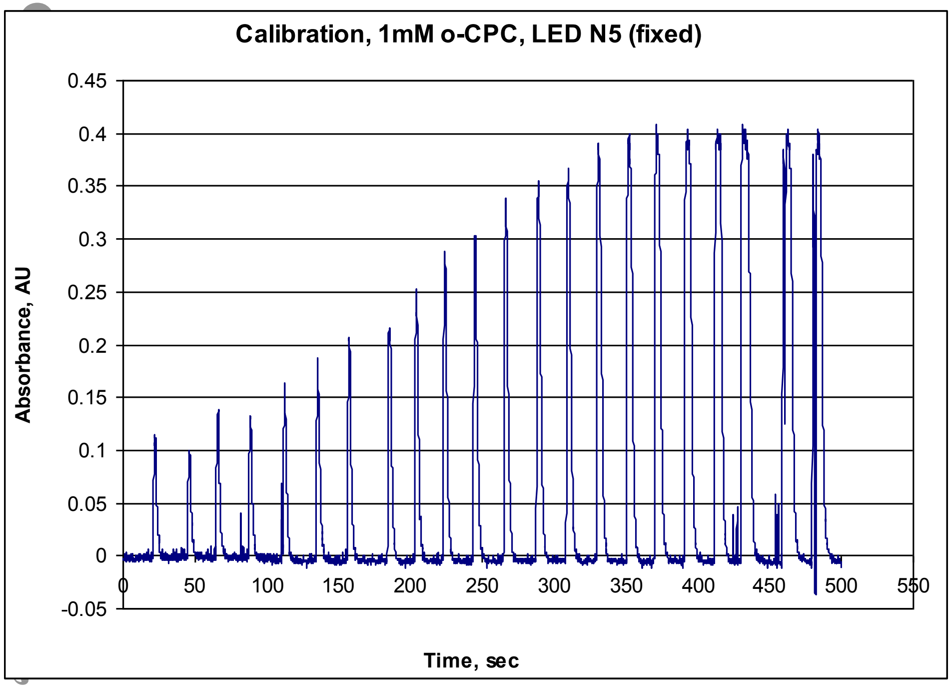
On-chip photometric detection

- Effective detection pathlength, stray light

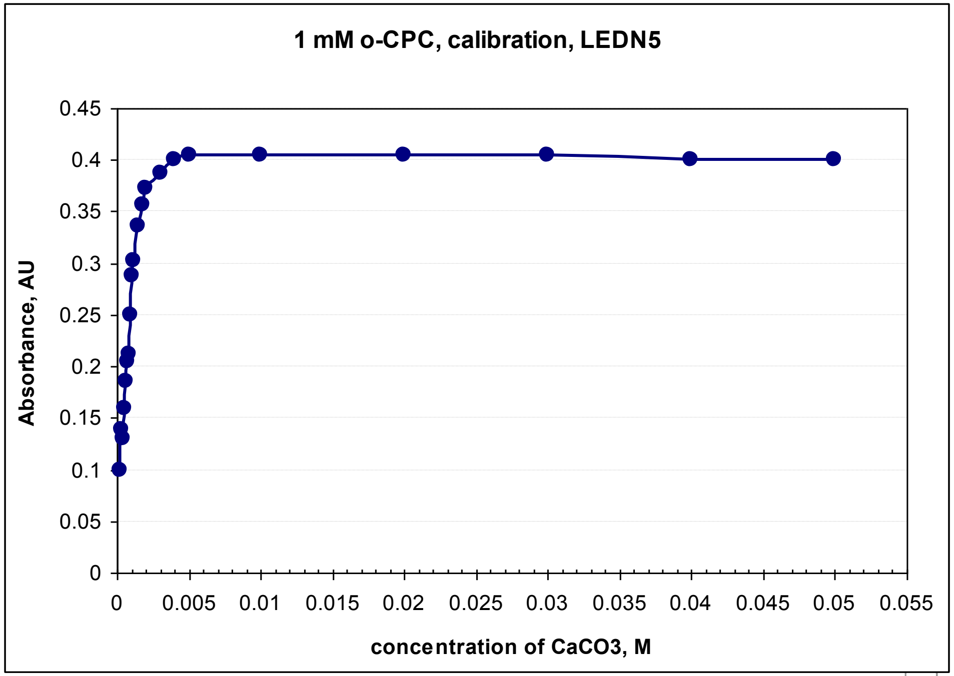


On-chip photometric detection

- Test analyte: Calcium - oPCP



Calibration graph:
1mM o-Cresolphthaleine Complexone
Ca^{2+} 0.1-50 mM
Position N5 - middle of the snake
600 µm optic fibre



$ LED on-chip detection relatively simple

LEDs in Chemistry: Outline

- LEDs properties in respect to their applications in chemistry
  - Practical considerations of usage of LEDs
- **Applications I**
  - **Optical methods in chemical analysis**
    - Photometry and photometric detection
    - **Fluorometry**
  - LEDs for sensors

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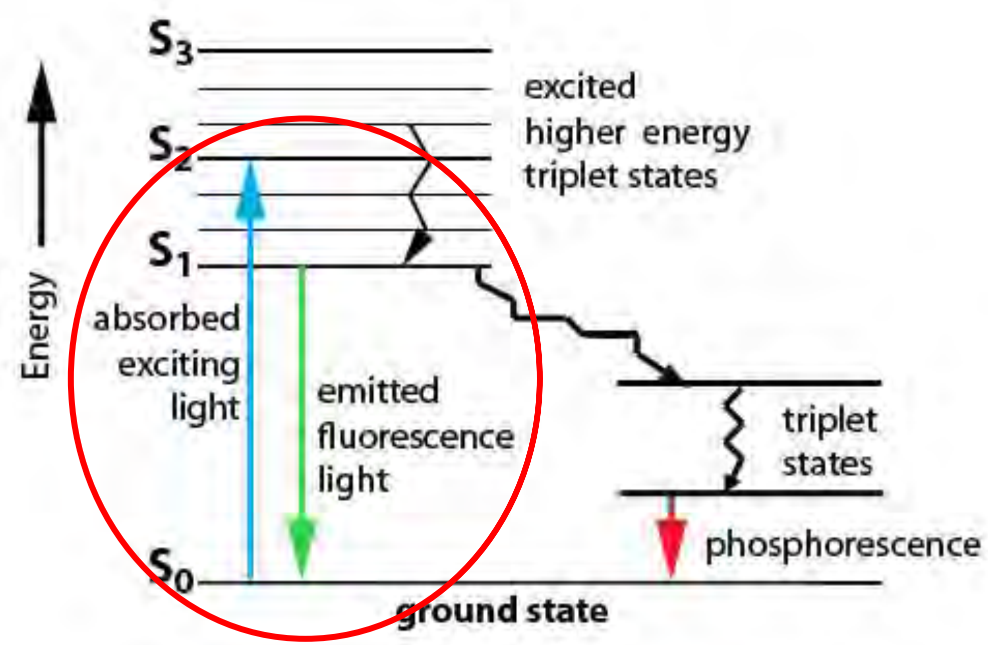
Fluorometry

- Radiative transitions
  - Jablonski diagram



web.uvic.ca

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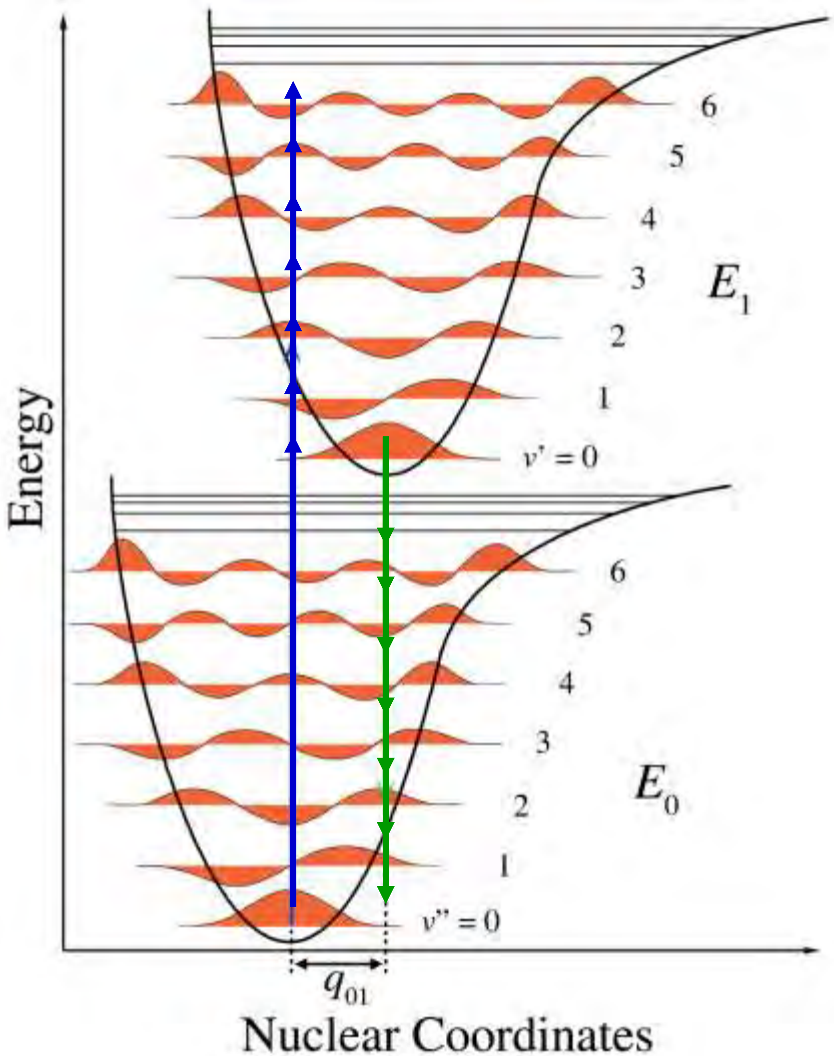
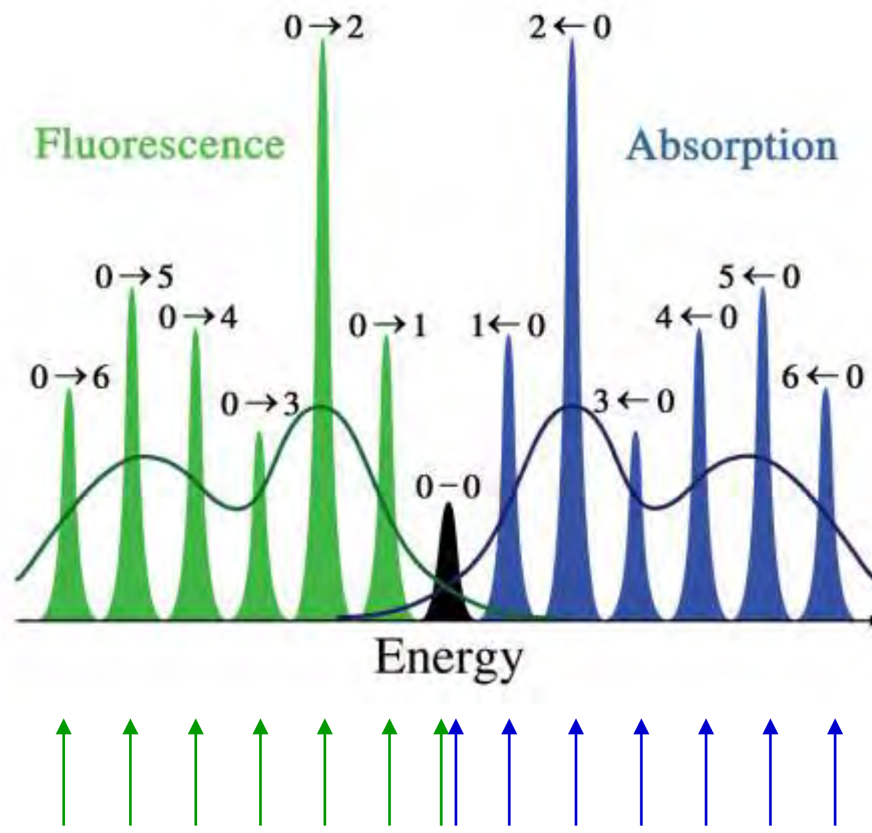
Fluorometry

- Franck-Condon principle

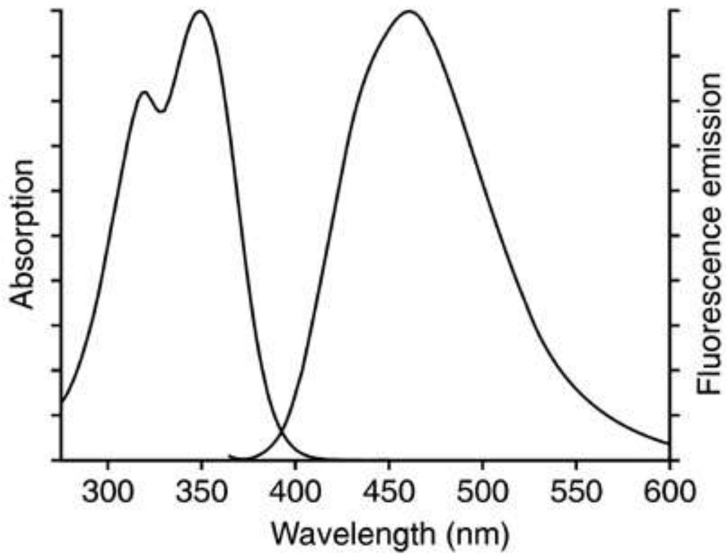




Fluorometry

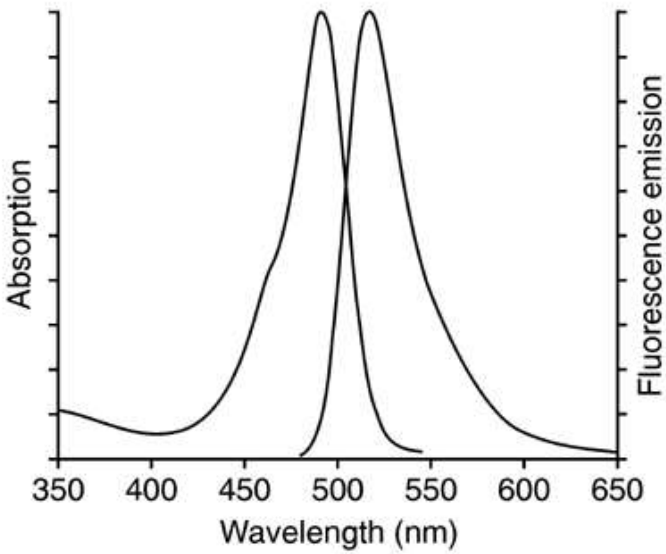
- Exemplary absorbance and emission spectra

Quinine sulphate 0.5 M/H_2SO_4



www.invitrogen.com

Fluorescein goat anti-mouse IgG antibody in pH 8.0 buffer



www.invitrogen.com

- **Experiment: Quinine**

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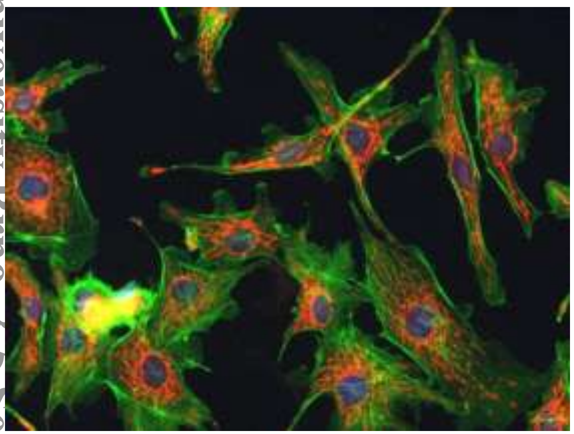
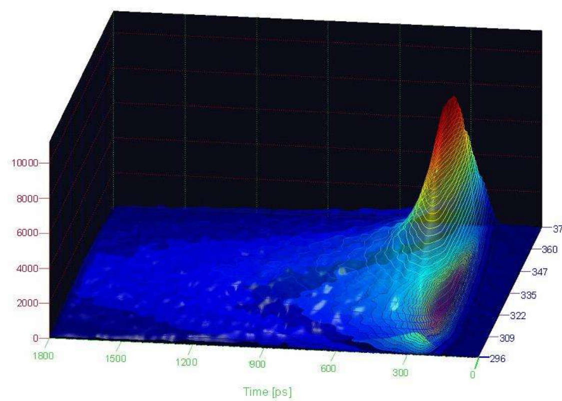
Fluorometry

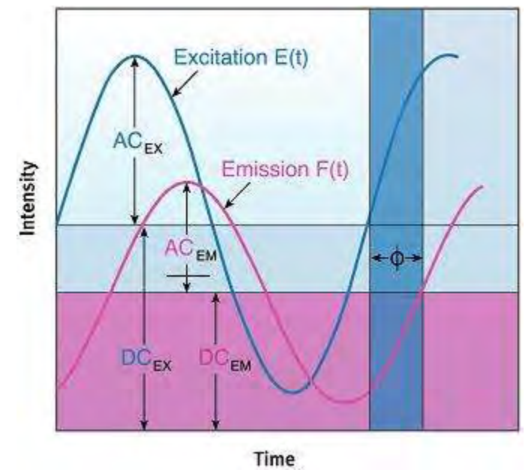
- Main areas of interests
  - Time-resolved techniques
  - Frequency-domain
    - Fluorescence microscopy



www.rp-photonics.com



www.nanobio.dk



www.iss.com

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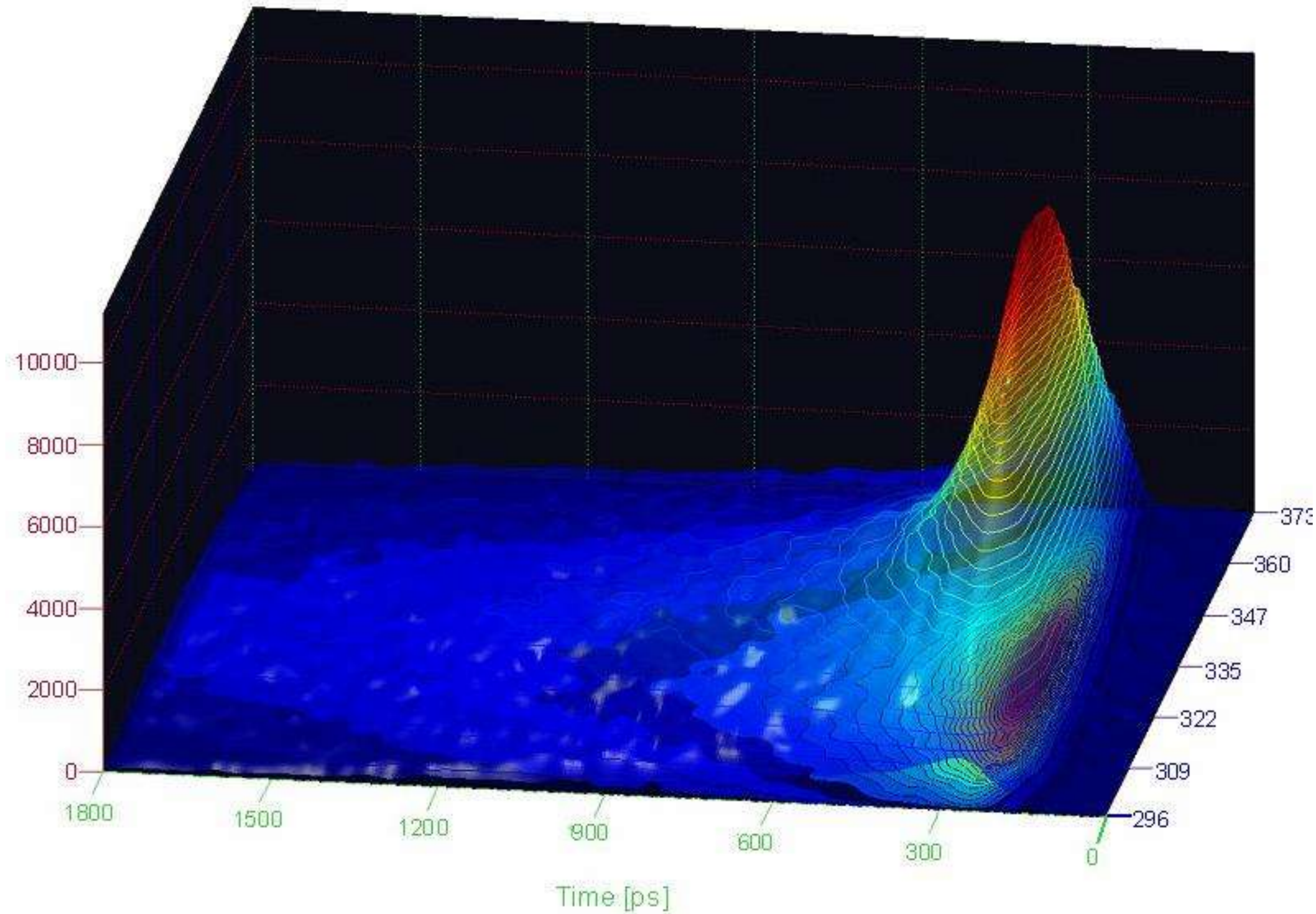
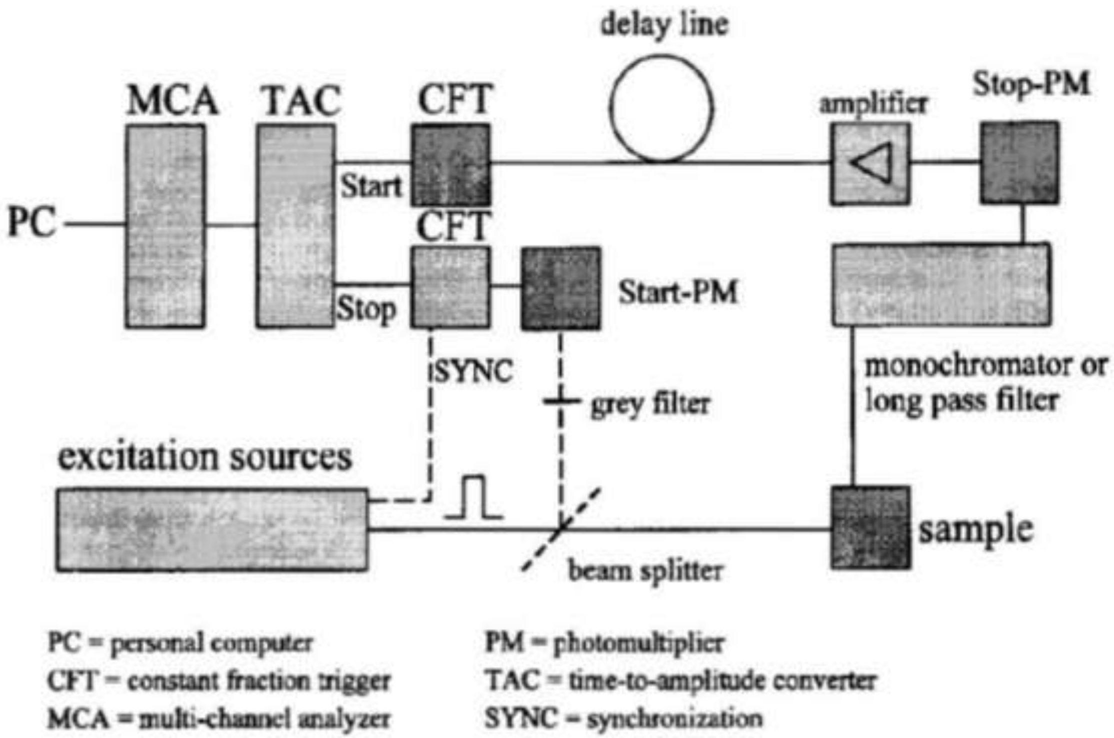
Time-resolved techniques



www.nanobio.dk

Time-resolved techniques

- LEDs for time-resolved techniques
  - Alternative to xenon flash lamps and nitrogen lasers
    - ~MHz scale modulation frequency → ns scale
    - LEDs are much cheaper than lasers



Landgraf, S. *Handbook of Luminescence Display Materials and Devices*; Nalwa, H. S., Rohwer, L. S.; American Scientific Publishers: 25650 North Lewis Way, Stevenson Ranch, CA, **2003**; Vol. 3

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Frequency-domain fluorescence

- Fast-pulsed modulation up to 300 MHz*
  - Wavelength barrier
    - 255 nm commercially available
    - 210 nm reported
  - Spectra overlaps – filters

*Szmacinski, H.; Chang, Q. *Applied Spectroscopy* **2000**, 54, 106-109

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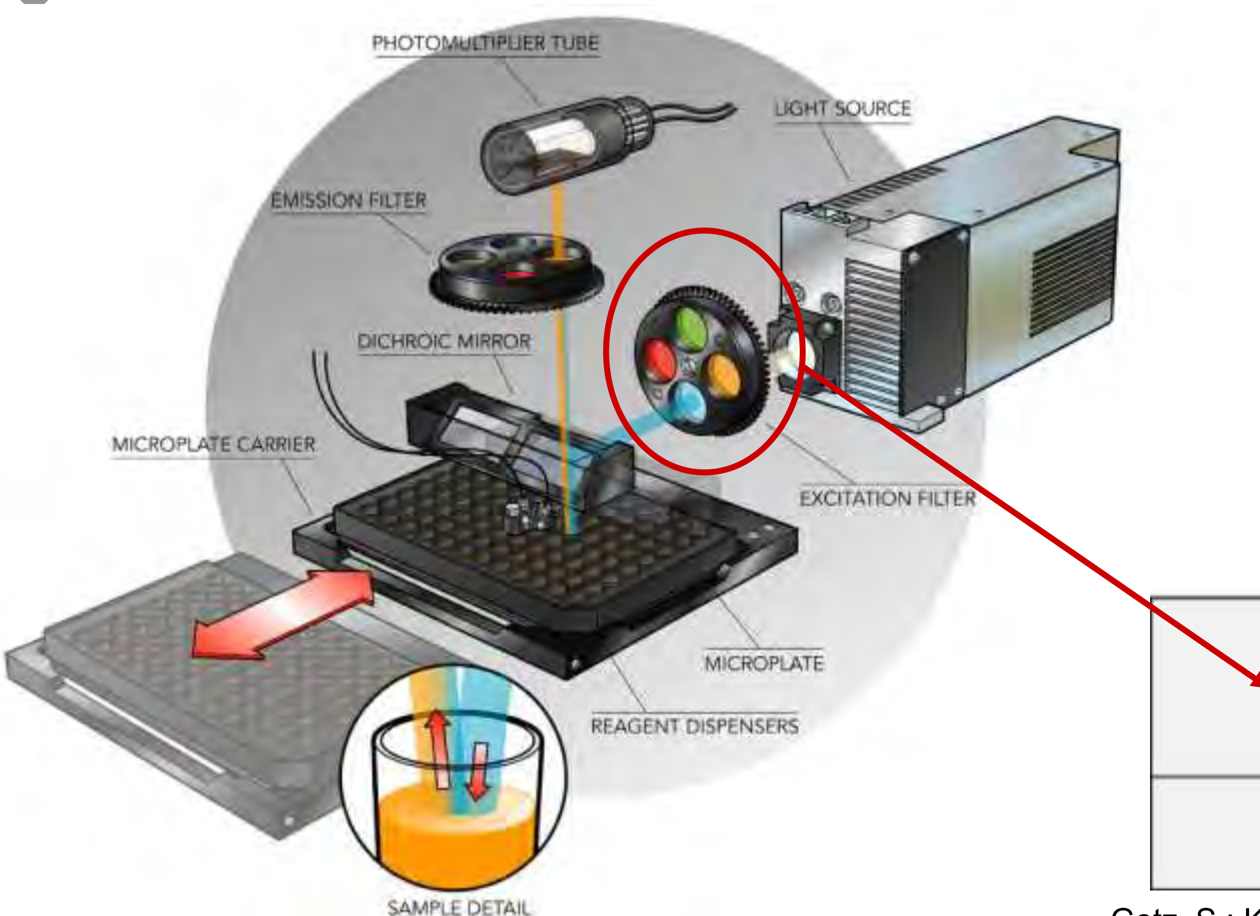
Frequency-domain fluorescence

- An example of fluorometry setup

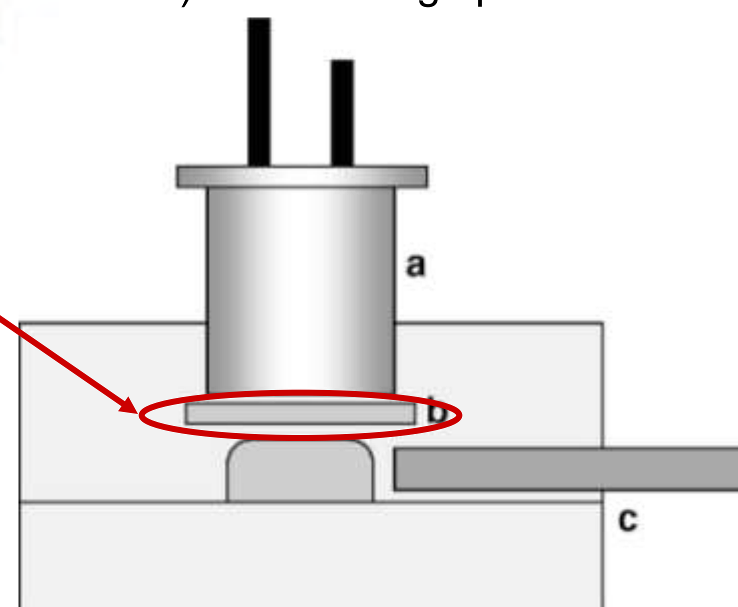


mktg.biotek.com

a) LED

b) Spectral filter

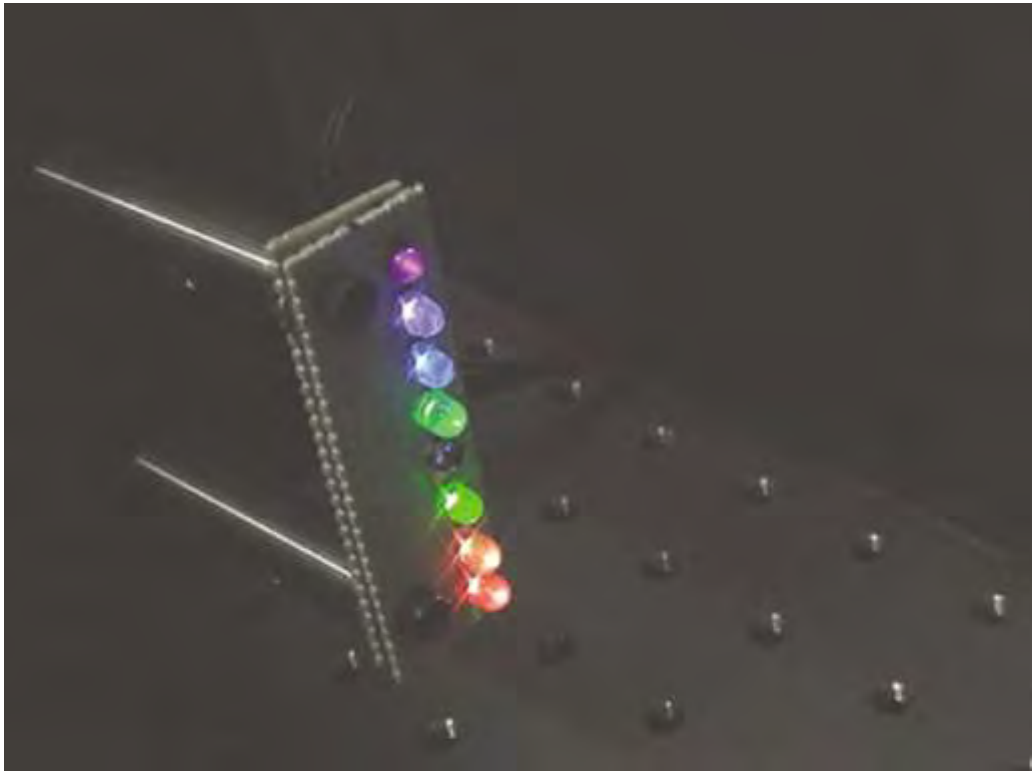
c) Collecting optical fibre



Gotz, S.; Karst, U. *Analytical and Bioanalytical Chemistry* **2007**, 387, 183-192

Excitation emission matrix

- Powerful method for complex mixture analysis
  - Instrumentation – expensive and bulky
  - LEDs – simple way to solve the problem*



*Hart, S. J.; JiJi, R. D. *Analyst* **2002**, 127, 1693-1699 (and picture)

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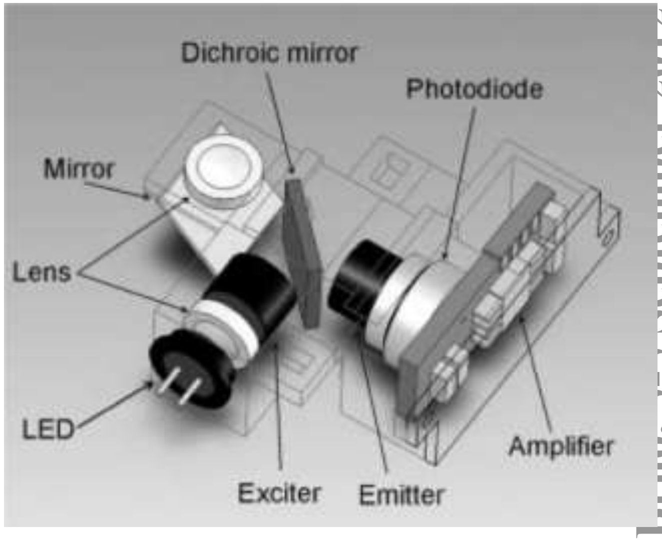
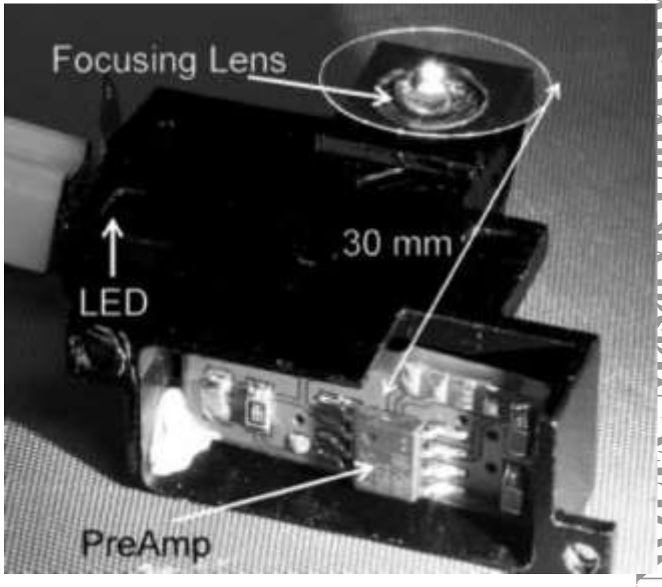
Compact fluorometric detection

- LED-based fluorometric detection system
  - Miniaturized
  - Cost-effective
  - Lab-on-chip application
  - Can be used for real-time PCR
  - Built-in lock-in amplifier for measurements under ambient light





Novak, L., et al. *Lab. Chip.* 2007, 1, 27-29

LED vs. Lasers

- Laser Induced Fluorescence (LIF)
  - $$$

Light source	Price
Ar^+ laser (488 nm, 50 mW) Edmund optics	€ 7315
LD (473 nm, 20 mW) Nichia	€ 2066
LED (470 nm, 1W) Luxeon	€ 4.99
HB-LED (470 nm)	€ 0.21

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LED-IF on-capillary detection

- LIF: lasers = $,$$$
  - ZetaLIF Picometrics

http://www.picometrics.com/html/somprod.htm

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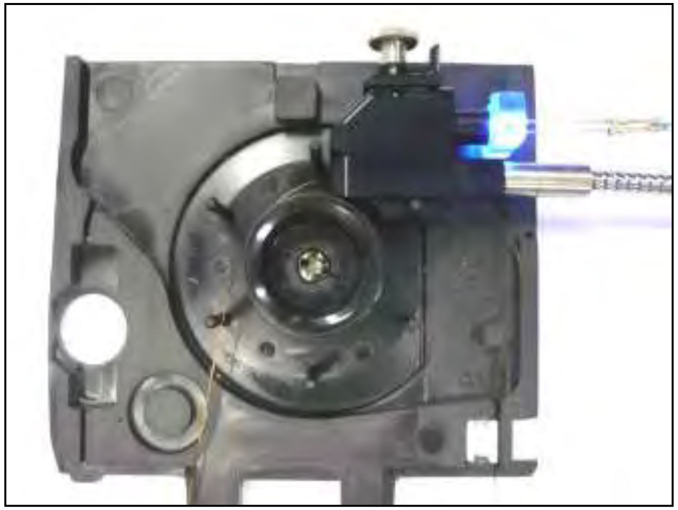
LED-IF on-capillary detection

- ZetaLIF Picometrics



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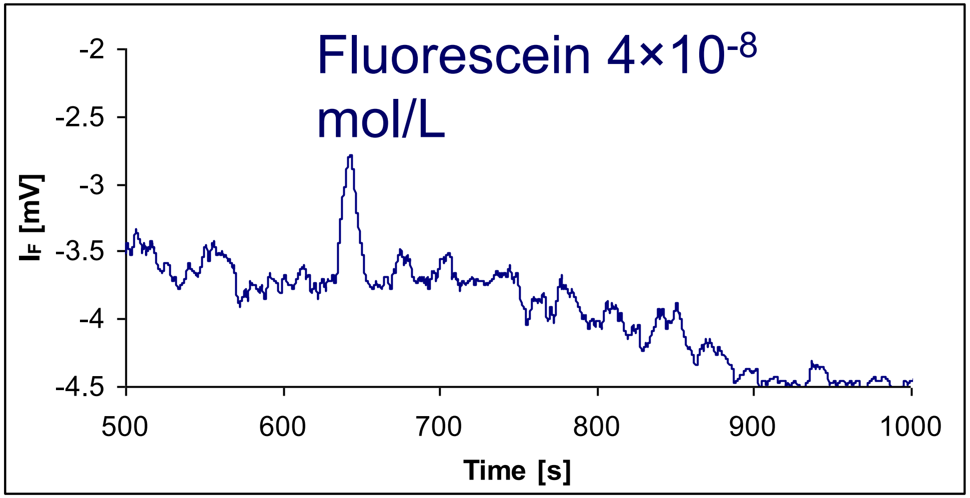
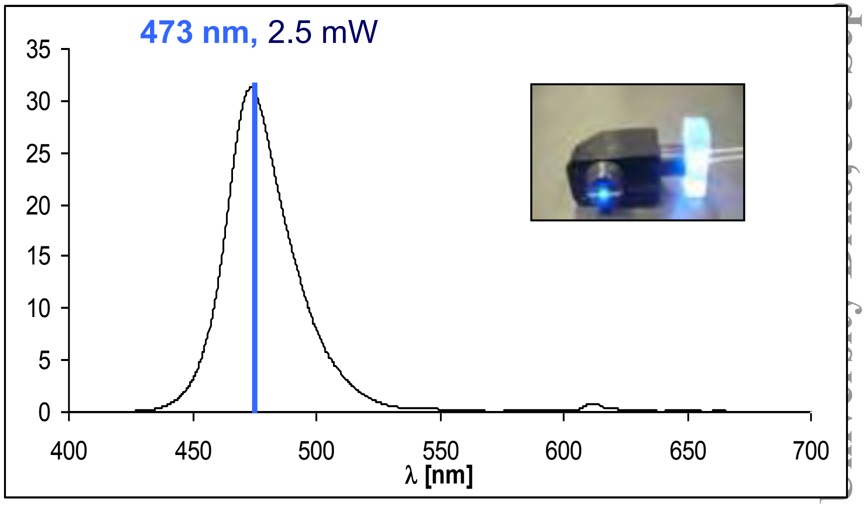
- ZetaLIF Picometrics
  - Blue (473 nm) LED: common ‘ultribright’ LED <€1

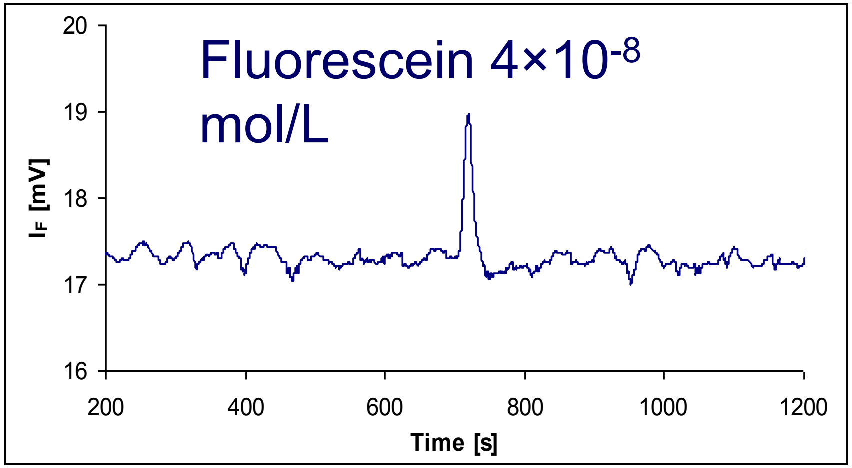


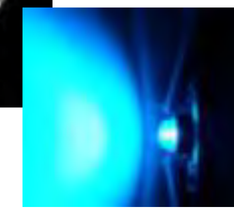


LOD = 1.3 × 10^{-8} M

LED-IF on-capillary detection

- ZetaLIF Picometrics



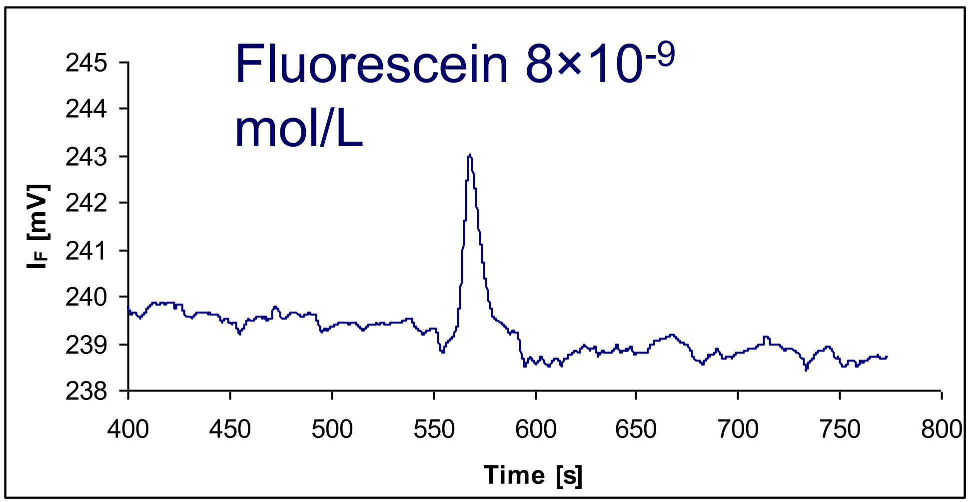


LUXEON 470 nm,

1W @ 350 mA, 4 V

12 lm, 110º

LOD = 4.6×10^{-9} M



LUXEON 470 nm,

3W @ 700 mA, 3.7 V

30 lm, 140º

~50 mW → ~1 mW

LOD = 5.5×10^{-10} M

$ High-power blue LEDs can be used for LED-IF

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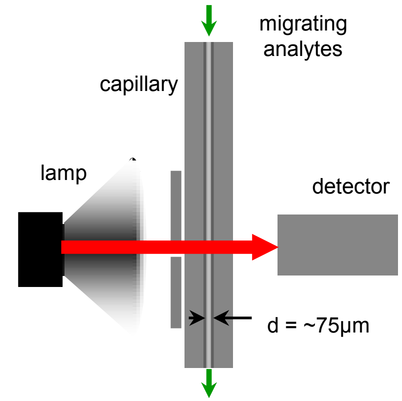
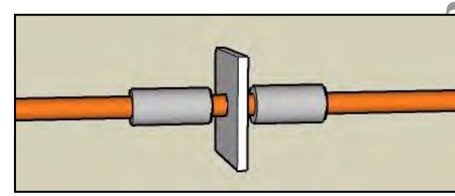
3-in-1 on-capillary detector

- **3 on-capillary detection techniques to combine:**
  - Photometric detection (PD)
    - Universal in deep-UV
  - Fluorometric detection (FD)
    - Selective & sensitive
  - Contactless conductivity detection (C^4D)
    - Universal





- All (PD, FD, C^4D)
  - Well established but have NOT been combined all

3-in-1 detector
1 point-of-detection (1-PD)

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2-in-1 detectors

- Photodetection
  +
  C^{4}D

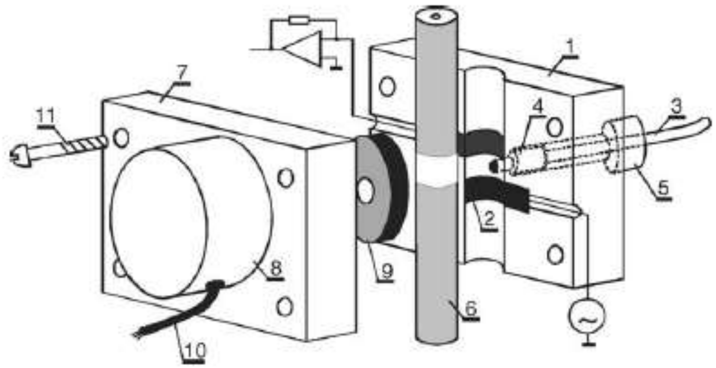

Table 1
Principal parameters of the photometric (test solution, salicylic acid in 0.02M TRIS, 210 nm) and conductometric (test solution, K^+ ion, sine wave voltage 10 Vp–p, 200 kHz) part of the dual detector

Parameter	UV detector	Contactless conductivity detector
Concentration range tested (µM)	50–10000	0.1–1000
Linear dynamic range (µM)	50–5000	10–1000
Slope (sensitivity)[a] (mAU.s.L.mol^{-1})	2.10×10^5 (4500)	1.05×10^5 (2800)
Absolute sensitivity (mAU.s.pg^{-1})	0.14	0.13
Intercept[a] (mAU s)	−0.13 (1.33)	3.6 (1.4)
Standard error (mAU s)	1.56	2.3
Correlation coefficient	0.999	0.999
LOD, µM (pg)[b]	20 (33)	0.1 (0.08)
HETP (µm)	2.51 ± 0.18	1.65 ± 0.11

Running electrolyte, 20 mM H_3BO_3 plus 10 mM LiOH (pH 9.2). The calibration plot parameters were determined from the linear part of the peak area dependences on the concentration. The HETP value was determined from six measurements with the solution of 10 µM salicylic acid or from five measurements on a solution of 10 µM K^+.

[a] Standard deviation is given in the parentheses.
[b] LOD expressed in terms of the absolute amount of analyte introduced into the capillary under the sampling conditions used.

- Novotny et al., *Anal. Chim. Acta*, 525, 17–21, **2004**

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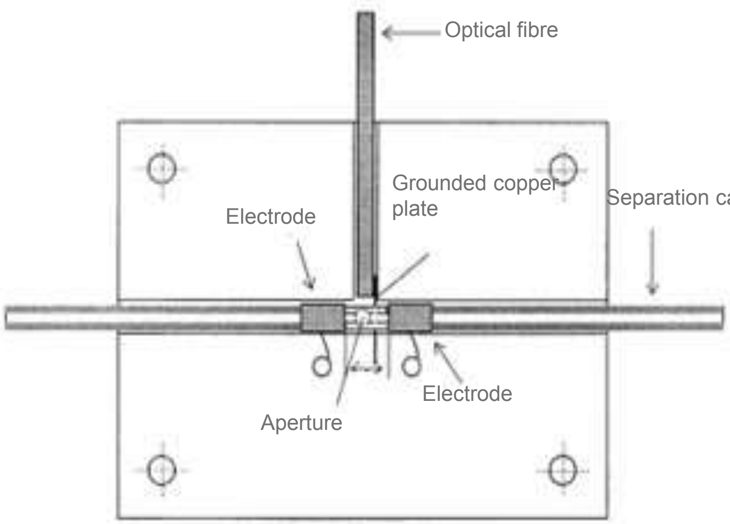
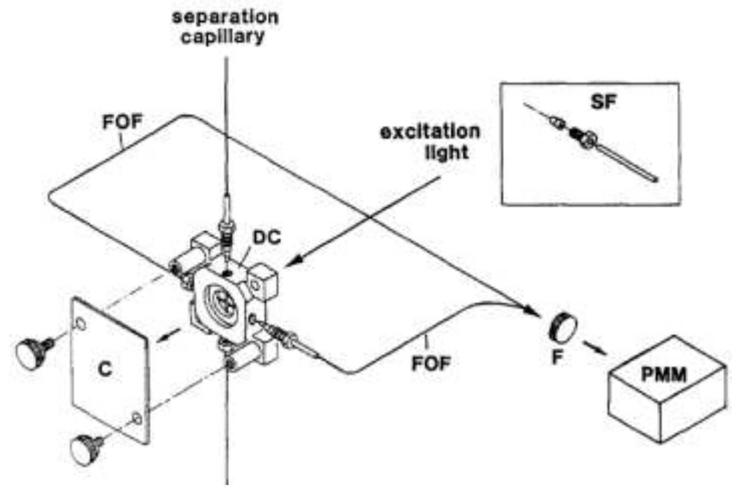
2-in-1 detectors

- **Fluorometric detection**
  +
  C⁴D



- Tan et al., *Anal. Sci.*, 21, 583-585, **2005**



- Caslavska et al., *J. Chromatogr. A*, 709, 147-156, **1995**

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3-in-1 on-capillary detector

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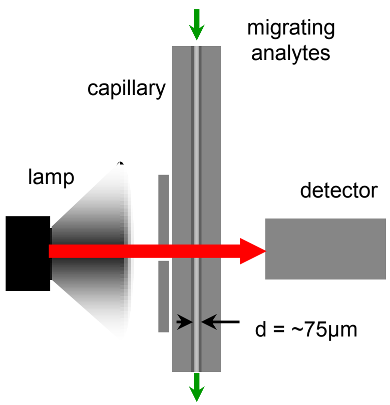

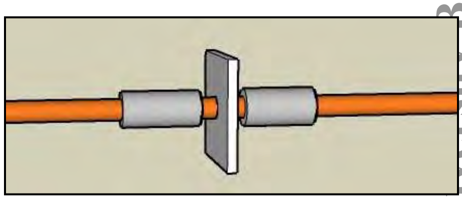

- All (PD, FD, C^4D)
  - Well established but have NOT been combined all

3-in-1 detector
1 point-of-detection (1-PD)

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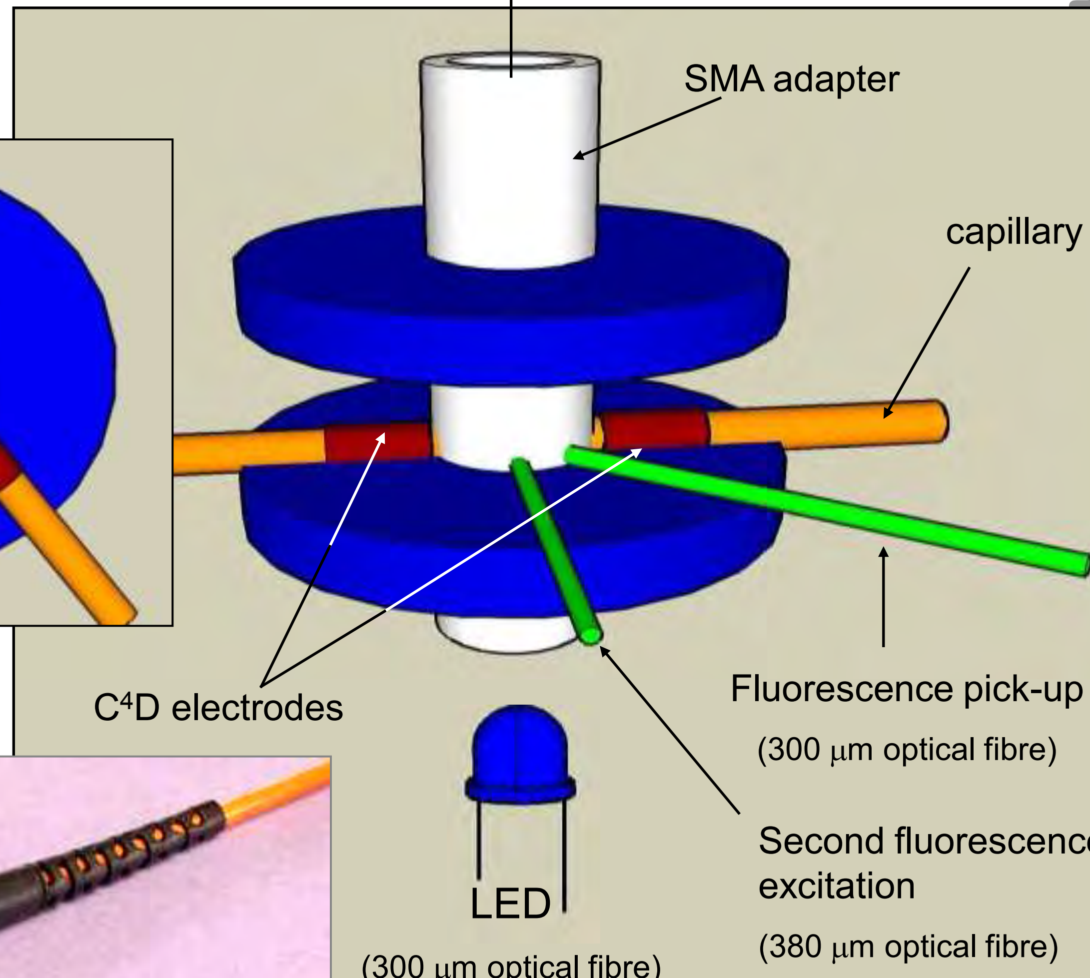
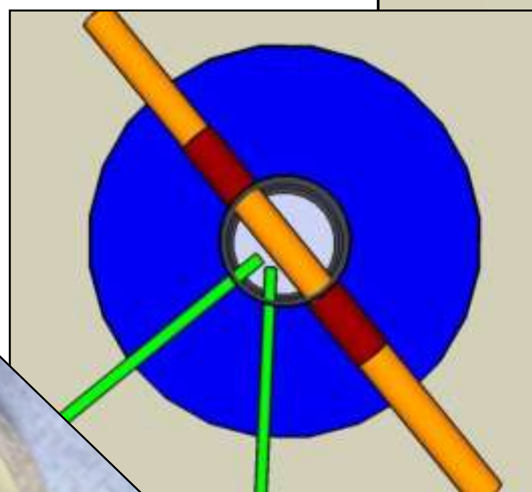
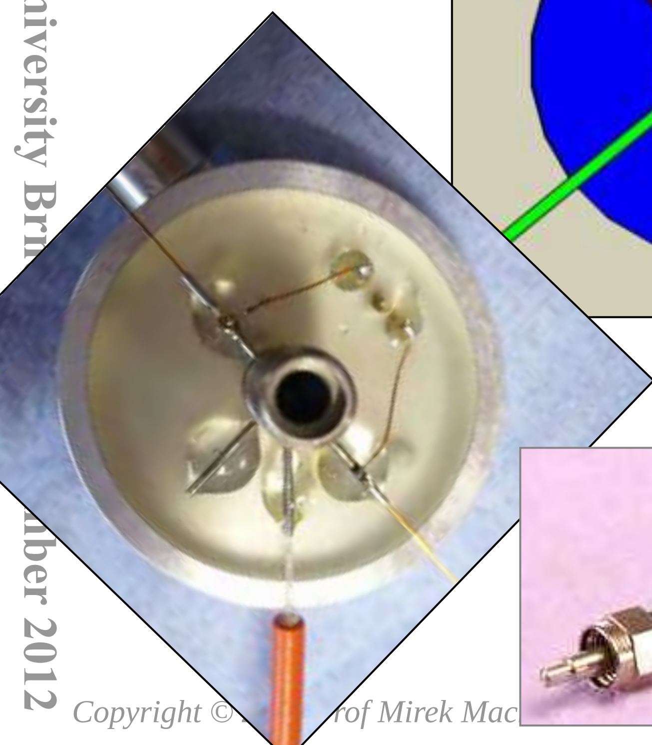
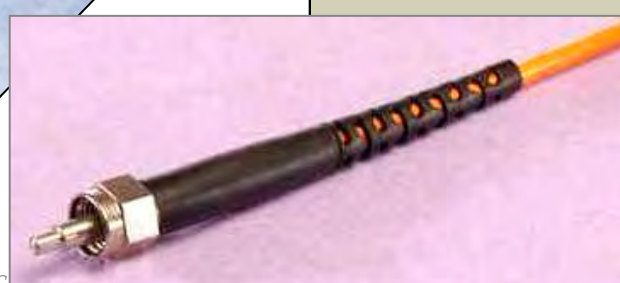
3-in-1 on-capillary detector

- Design & construction
- **1 point-of-detection (1-PD)**



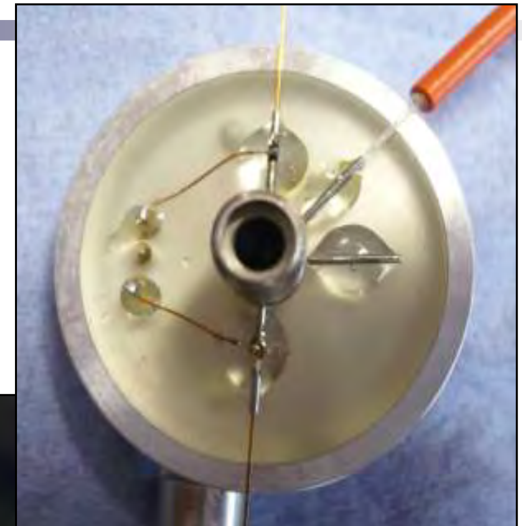


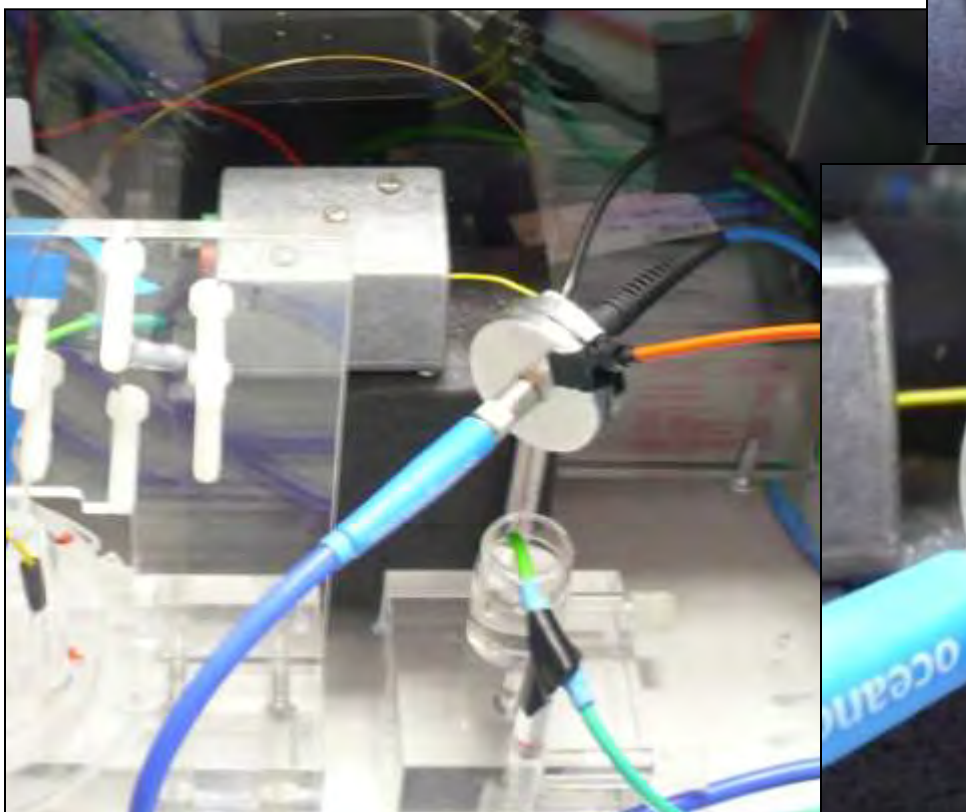




3-in-1 on-capillary detector

- Design & construction
- **1 point-of-detection (1-PD)**





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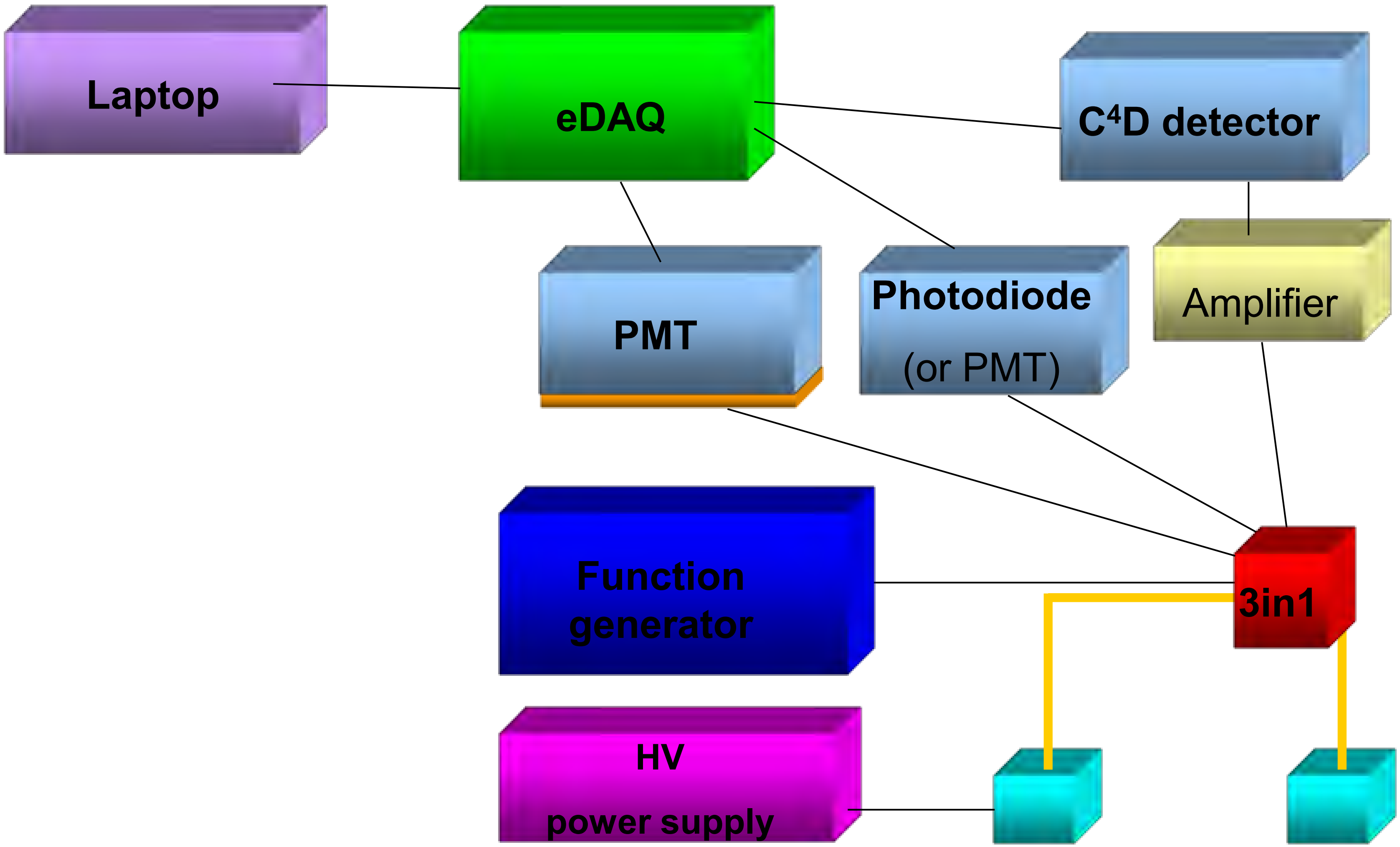
3-in-1 on-capillary detector

- Block scheme



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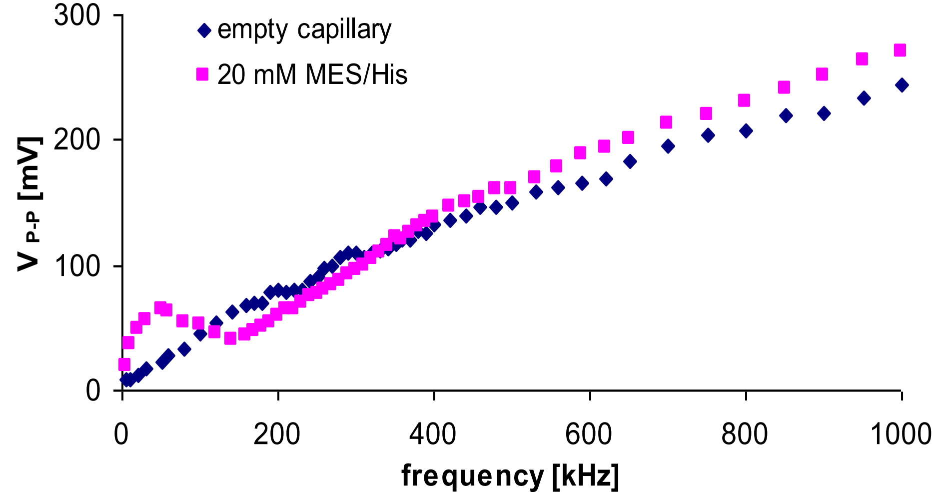
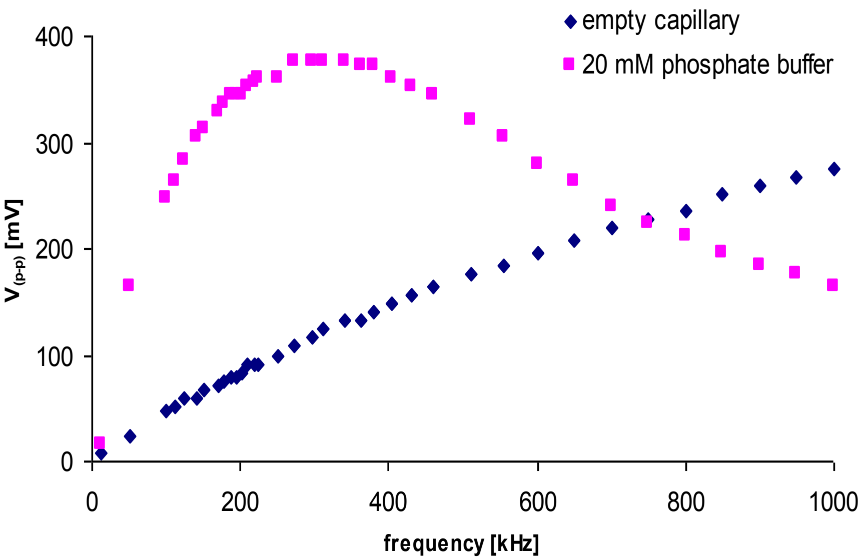
3-in-1 on-capillary detector

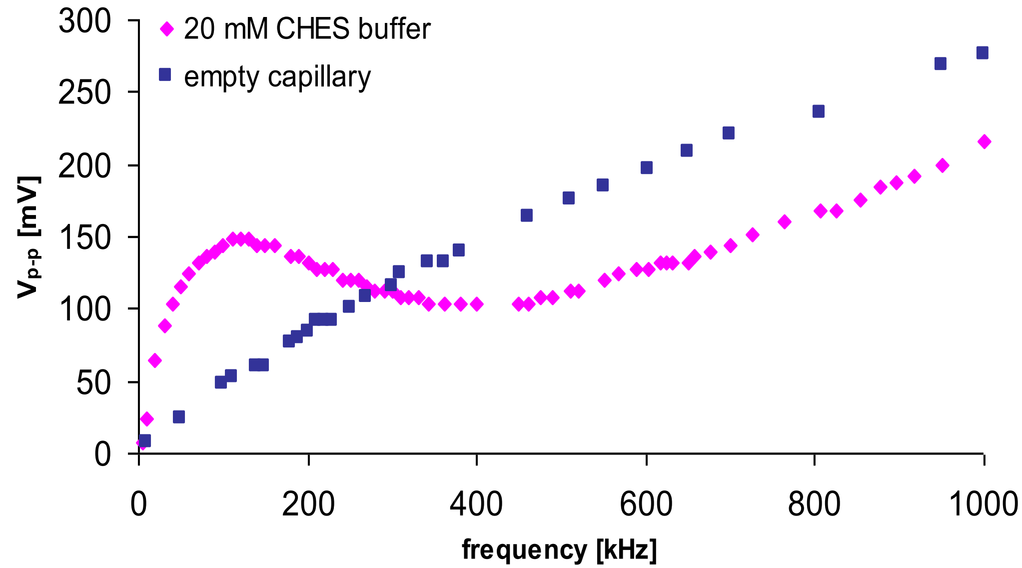
- C^4D
  - **Bode plots**

Low conductivity buffers:
MES/His (pH 6) , CHES (pH 9)

High conductivity buffers:
Phosphate (pH 11)

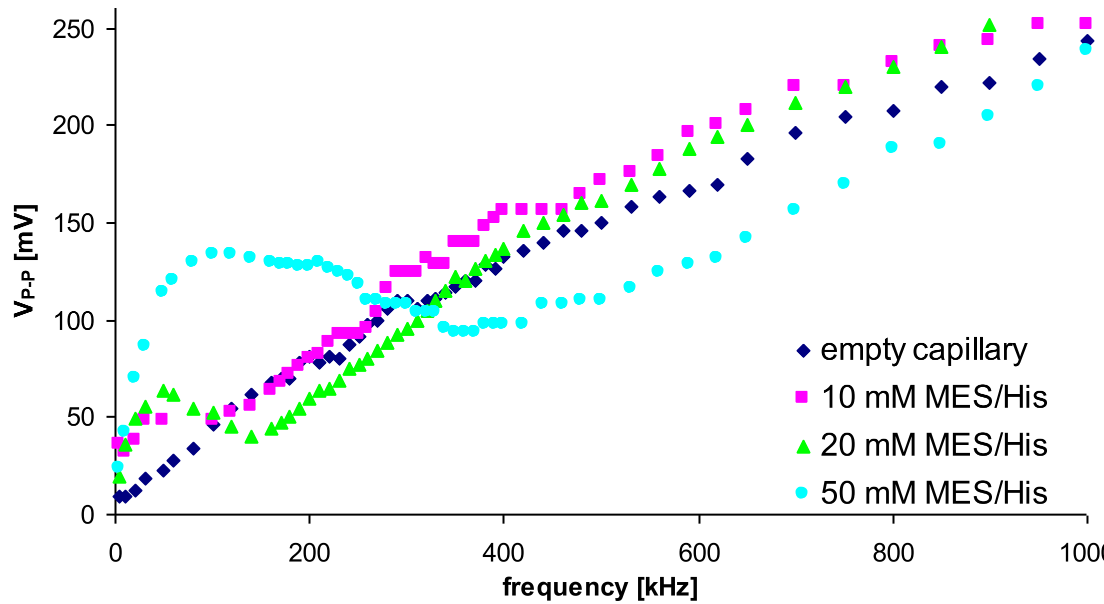


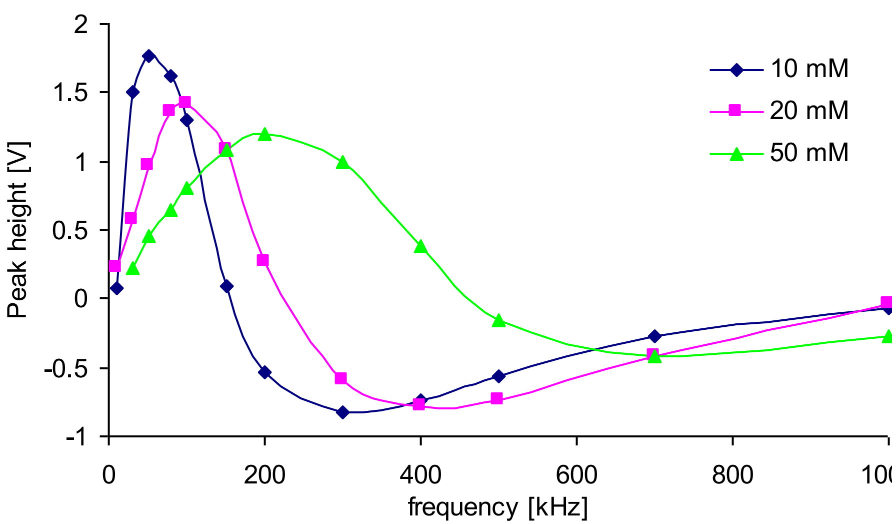


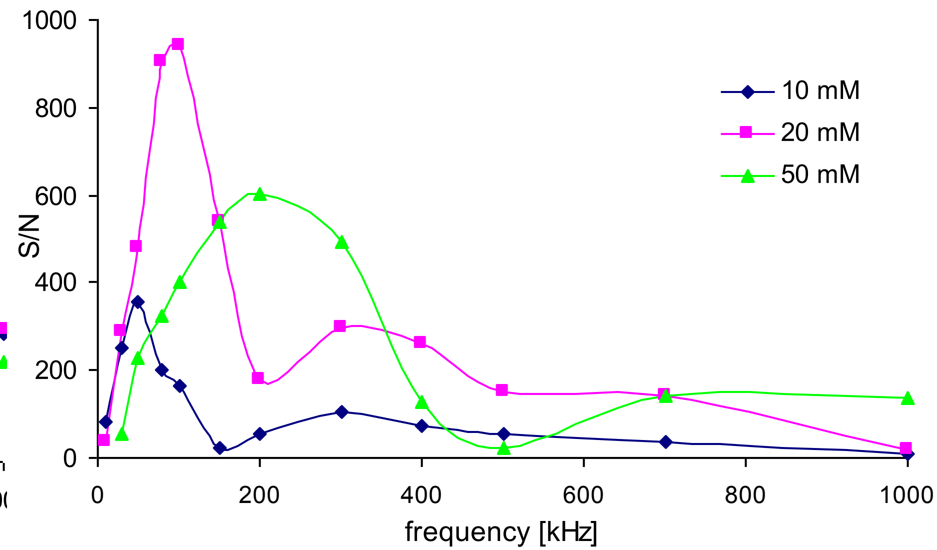


3-in-1 on-capillary detector

- C^{4}D
  - MES/His BGE
  - Sample: KCl 1 mM

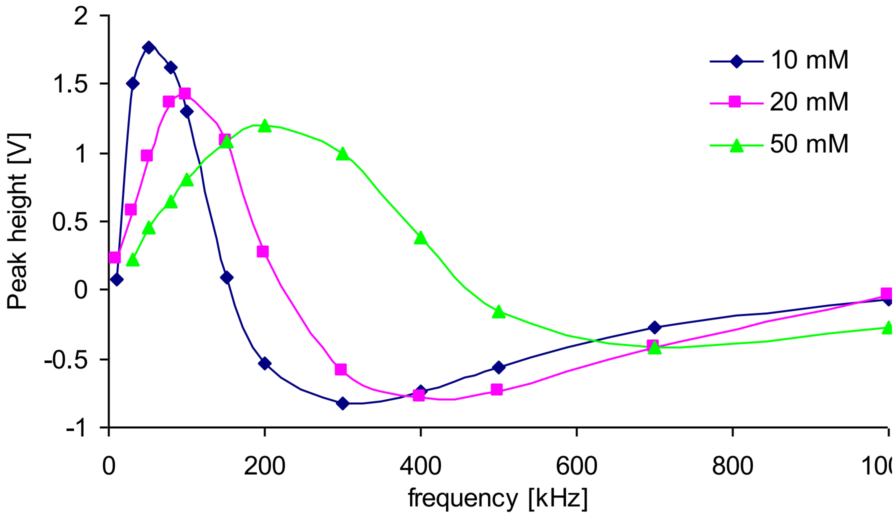


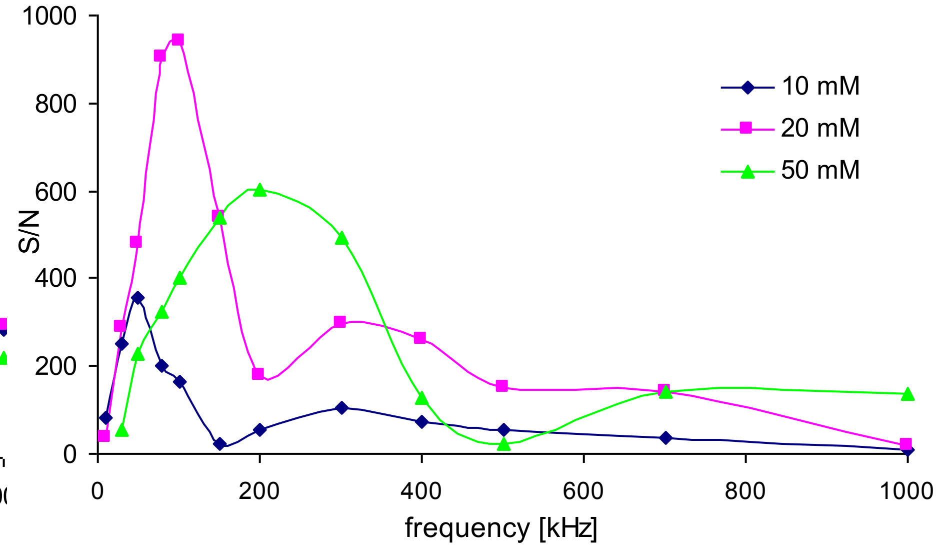




3-in-1 on-capillary detector

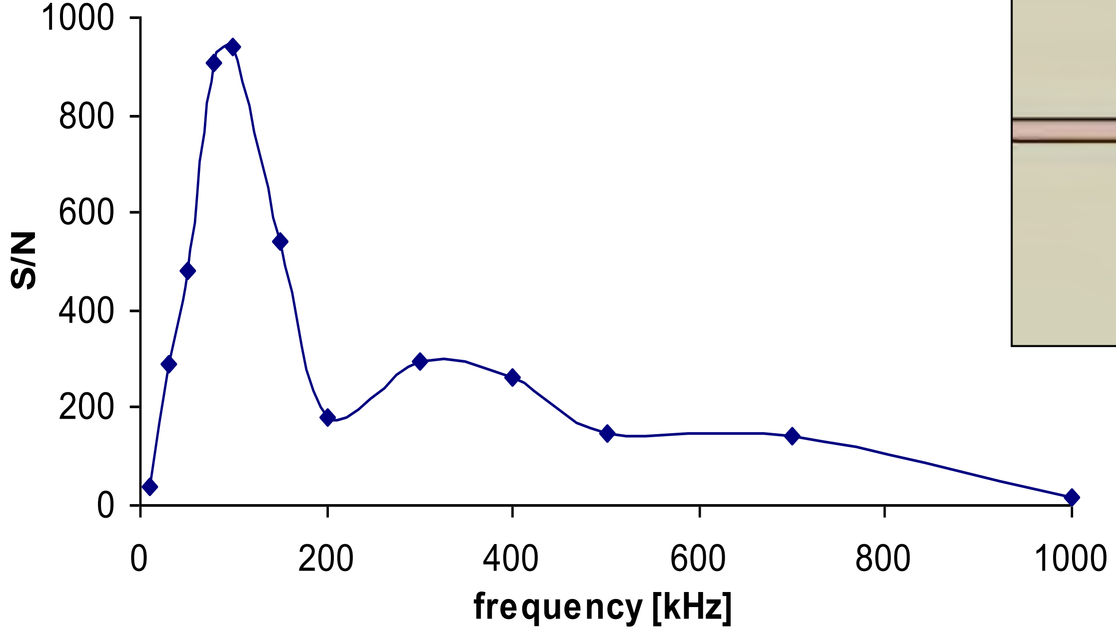
- C^4D
  - MES/His BGE
  - Sample: KCl 1 mM
  - 20 mM MES/His optimal

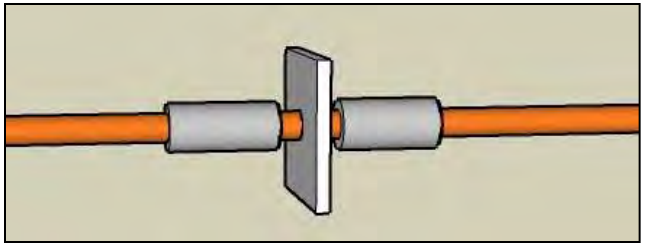


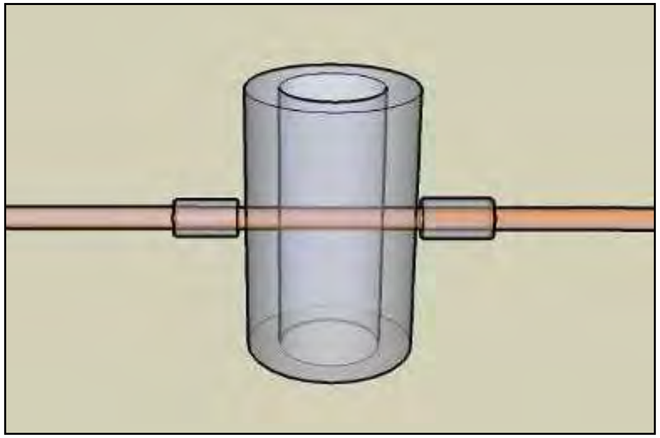


3-in-1 on-capillary detector

- C^4D
  - BGE: 20 mM MES/His, pH 6.1
  - Sample: KCl 1 mM







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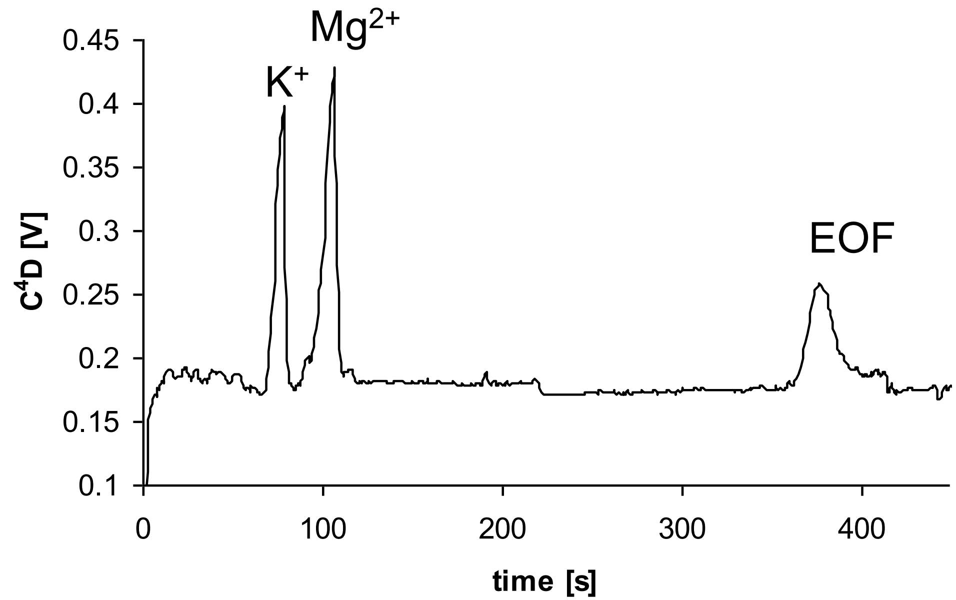
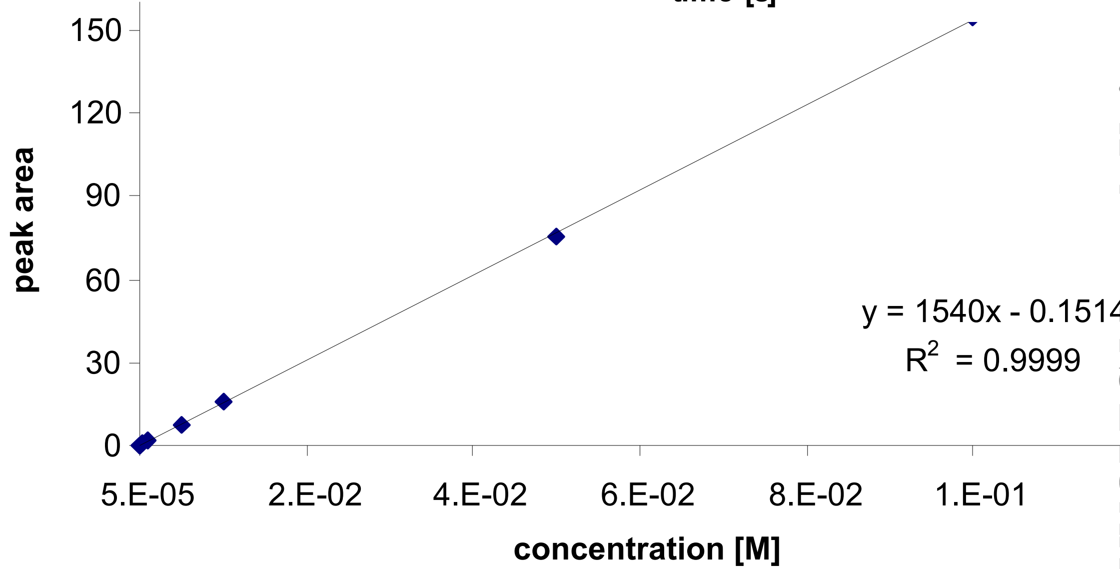
3-in-1 on-capillary detector

- C^4D
  - BGE: 20 mM MES/His, pH 6.1
  - E = 15 kV
  - Inj.: t = 10 s, ΔH = 10 cm
  - Cap.: 31.5/39 cm, 75 µm
  - f = 100 kHz
  - **LOD (Mg^{2+}) ~ 5.0 × 10^{-6} mol/L**





▪ C^4D – Literature LOD values

Electrode material	Shield	L (mm)	Gap (mm)	Freq. (kHz)	V_{pp} (V)	LOD	Linear range
Zemann							
Stainless steel (hypodermic needle)	No	20	2	40	10	6 µM for Cl^-, 9 µM for Na^+	1 µM – 25 mM for Na^+ and Cl^- resp.
Stainless steel (hypodermic needle)	Yes	20	1	40–100	10	0.4 µM for Cl^-, 0.2 µM for NH_4^+	2 µM – 25 mM for small cations and anions
Stainless steel (hypodermic needle)	Yes	5	1	100	10	0.14 µM for Cl^-	0.25 – 5 µM for Cl^-
Da Silva / Do Lago							
Copper wire	No	2	1	600	2	0.43 µM for Na^+	n.a.
Copper wire	No	2	1	550	2	0.5 µM for Na^+	0.5 µM – 2 mM for Na^+
Kubáň							
Hypodermic needle	Yes	20	1.1	290	20	0.5 µM for Na^+, 0.2 µM for Cl^-	2 µM – 2 mM for small anions and cations
Hypodermic needle	Yes	20	1.1	290	10	0.7 µM for Na^+, 0.4 µM for Cl^-	n.a.
Hypodermic needle	Yes	4	1	150	225	0.2 µM for Na^+, 0.2 µM for Cl^-	10 µM – 0.2 mM for Na^+
Jelínek							
Aluminum foil (semi-circular)	No	2	1	200	10	0.5 µM for K^+	5 µM – 1 mM for K^+
Copper wire	No	3	2	200	20	3.5 µM for K^+	0.1 – 5 mM for K^+
Vuorinen							
Copper wire	No	7	0.4	291	25	10 µM for Na^+, 32 µM for Li^+	50 – 220 µM for Na^+ 0.14 – 0.72 mM for Li^+

Guijt et al., *Electrophoresis* 2004, *25*, 4032–4057

	LOD (µM)
C^4D with miniaturized cell	
Potassium	1.5
Calcium	1.5
Magnesium	1.5
Lithium	2.5
High-voltage C^4D	
Potassium	0.15
Calcium	0.15
Magnesium	0.15
Lithium	0.35
TraceDec	
Potassium	0.075
Calcium	0.075
Magnesium	0.075
Lithium	0.2
Battery powered C^4D	
Potassium	0.25
Calcium	0.2
Magnesium	0.2
Lithium	0.5

Kubáň et al., *Electroanalysis 18*, 2006, No. 13-14, 1289 – 1296

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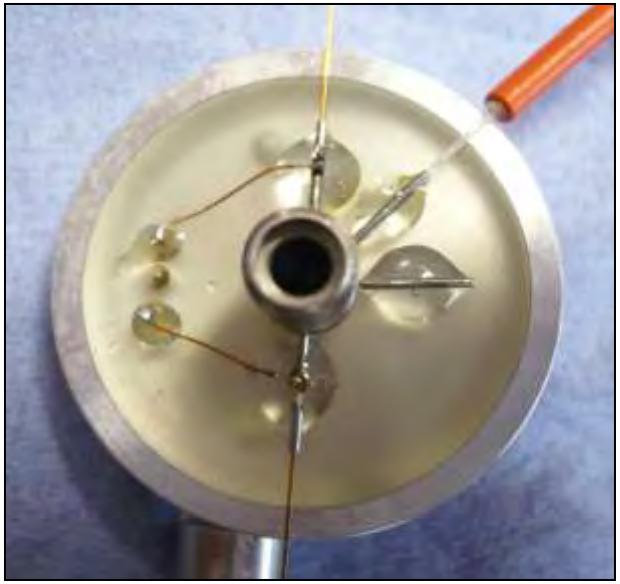
3-in-1 on-capillary detector

- Further developments

Amplifier integrated in the cell – lower LOD ?



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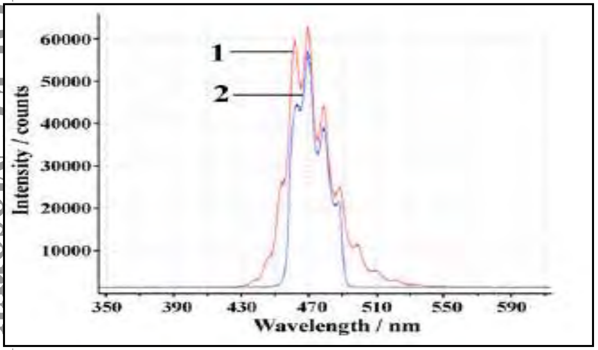
3-in-1 on-capillary detector

- FD – Literature LOD values

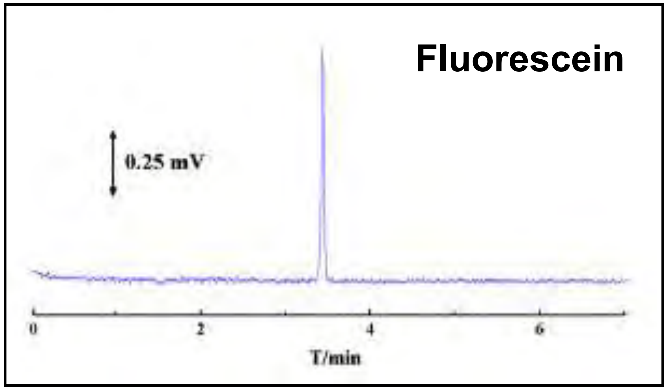


LED lamp

emission spectra

(1) without filter

(2) with filter



Injection: 10 cm, 10 s, Voltage: 20 kV

BGE: $Na_2B_4O_7$(20 mM)/AcN (15/4)

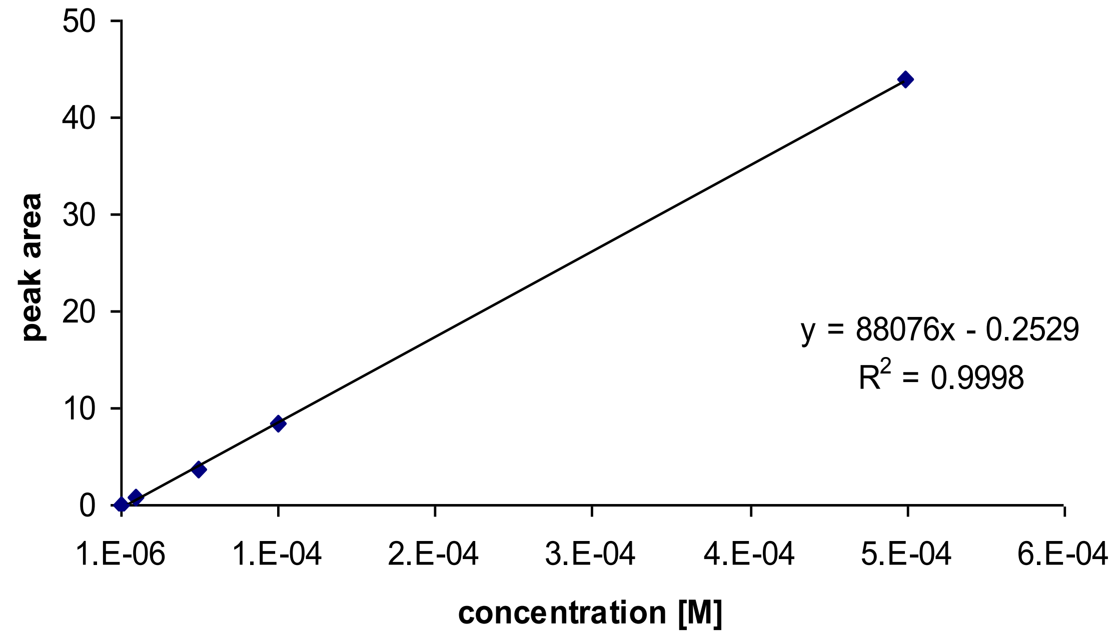
LOD = 1.5 10^{-9}M

Xu J., Xiong Y.,Chen S.,Guan Y., Talanta, 76, 369-372, **2008**.

Brand	LOD [M] Analyte	Light Source
Picomerics	**10^{-12} M** Rhodamine 123	488 nm Ar^+ laser @ 10 mW
Unimicrotech	**10^{-12} M** FITC	473 nm DPSS laser @ 10 mW

3-in-1 on-capillary detector

- FD
  - BGE: 20 mM phosphate, pH 11
  - Sample: Fluorescein
  - E: 15 kV
  - Inj.: t = 10 s, ΔH = 10 cm
  - Wavelength: 470 nm



- **LOD: 1 × 10^{-8} mol/L**
- Potential for improvement: Micropackaged fibre-micro-LED arrays ~10mW

Tyndall National Institute

3-in-1 on-capillary detector

- PD – Literature LOD values and expectations
- **Literature LODs**
  - **10^{-5} – 10^{-6} M**

    Review: **CE detector based on light-emitting diodes**

    Xiao et al., Electrophoresis, 2007,28, 233-242
- **Theoretical values**
- Baseline noise (BLN) ~ 8.5×10^{-5} AU
- 75 μm i.d. cap. → $l_{eff.}$ <75 μm → ~~50 μm
- $\varepsilon_{(tart)}$ = 21,600 cm.L.mol-1
- Theoretical $LOD_{(3 \times BLN)}$ = **1.8×10^{-6} AU**

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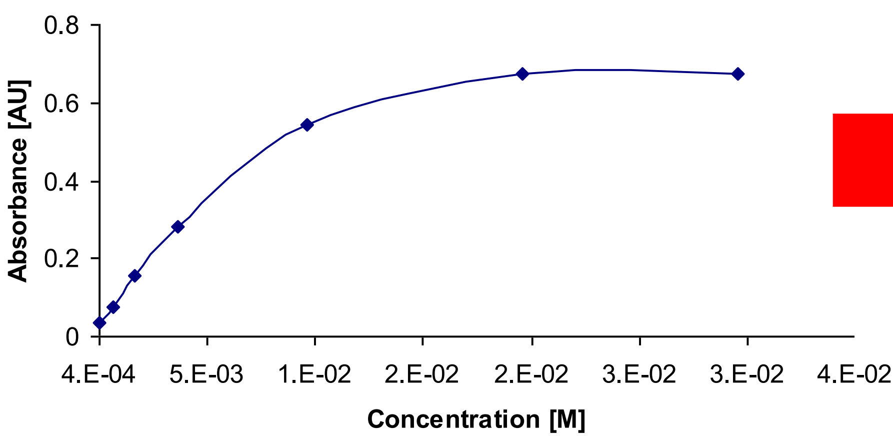
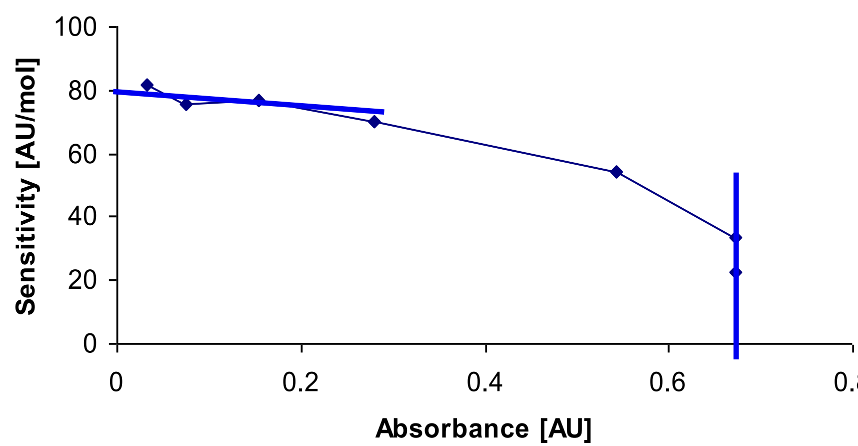
3-in-1 on-capillary detector

- PD
  - ε (tartrazine @ 426 nm) 21,600 $l.mol^{-1}.cm^{-1}$
  - Effective pathlength $\ell = s/\varepsilon$ **37.0 - 41.2 μm**
  - Stray light $\% SL = I/I_0 = 10^{-Amax}$ **11.5 – 21.2 %**
  - **5.5×10^{-6} mol/L**

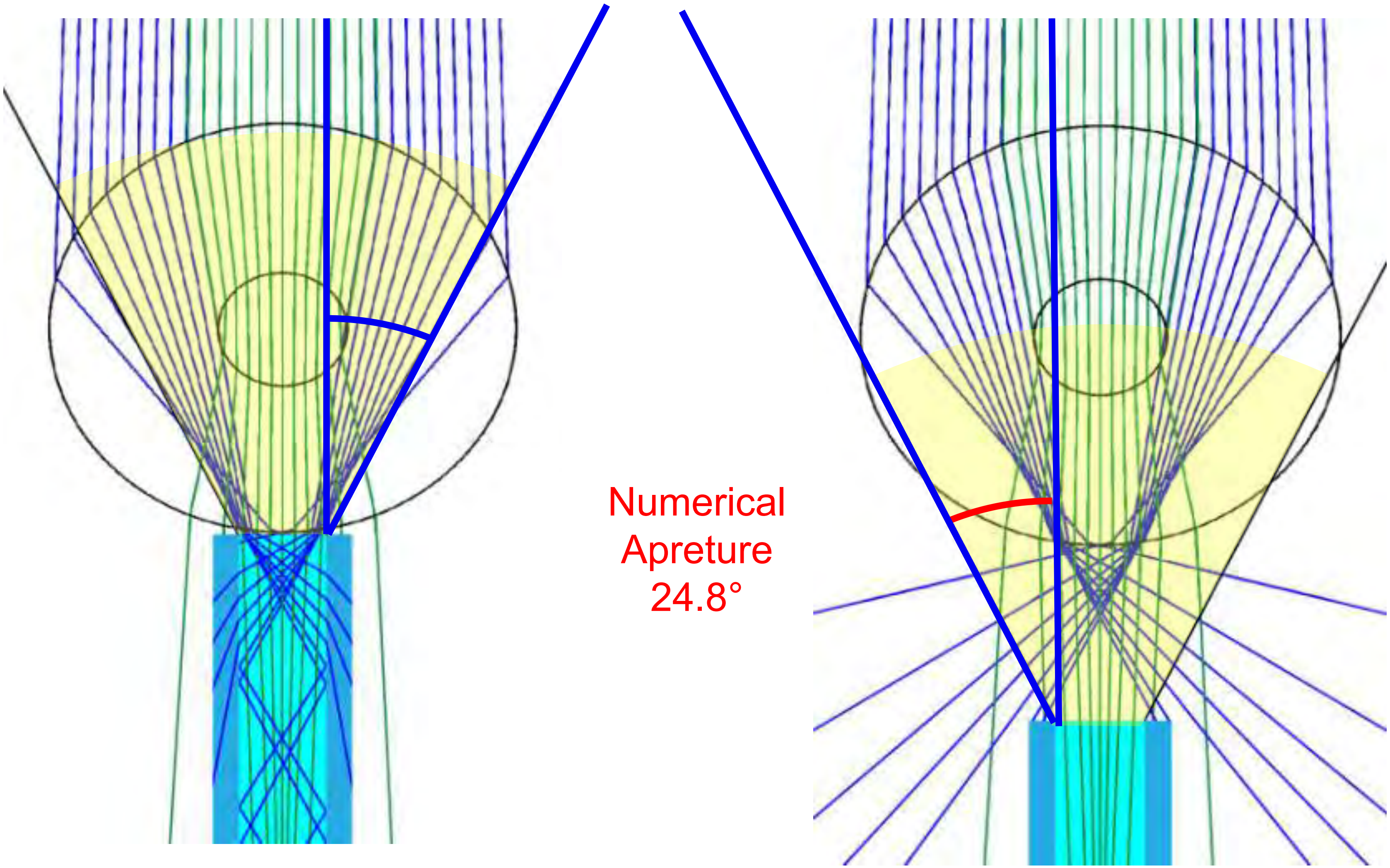
- Sample: Tartrazine
- Wavelength: 470 nm
- 20 mM CHES, pH 9





3-in-1 on-capillary detector

- Optics design



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3-in-1 on-capillary detector

- Literature LODs
  - PD 10^{-5} – 10^{-6} M
    - (Xiao et al., Electrophoresis, 2007,28, 233-242)
  - FD 10^{-8} – 10^{-9} M
    - (Xiao et al., Electrophoresis, 2007,28, 233-242)
  - C^4D 10^{-7} M
    - (Kuban et al, Electroanalysis, 2006, 13-14, 1289-1296)

Detection	Analyte	LOD [M]
PD	Tartrazine	5.5×10^{-6}
FD	Fluorescein	1.0×10^{-8}
C^4D	Mg^{2+} (MES/His pH 6)	5.0×10^{-6}

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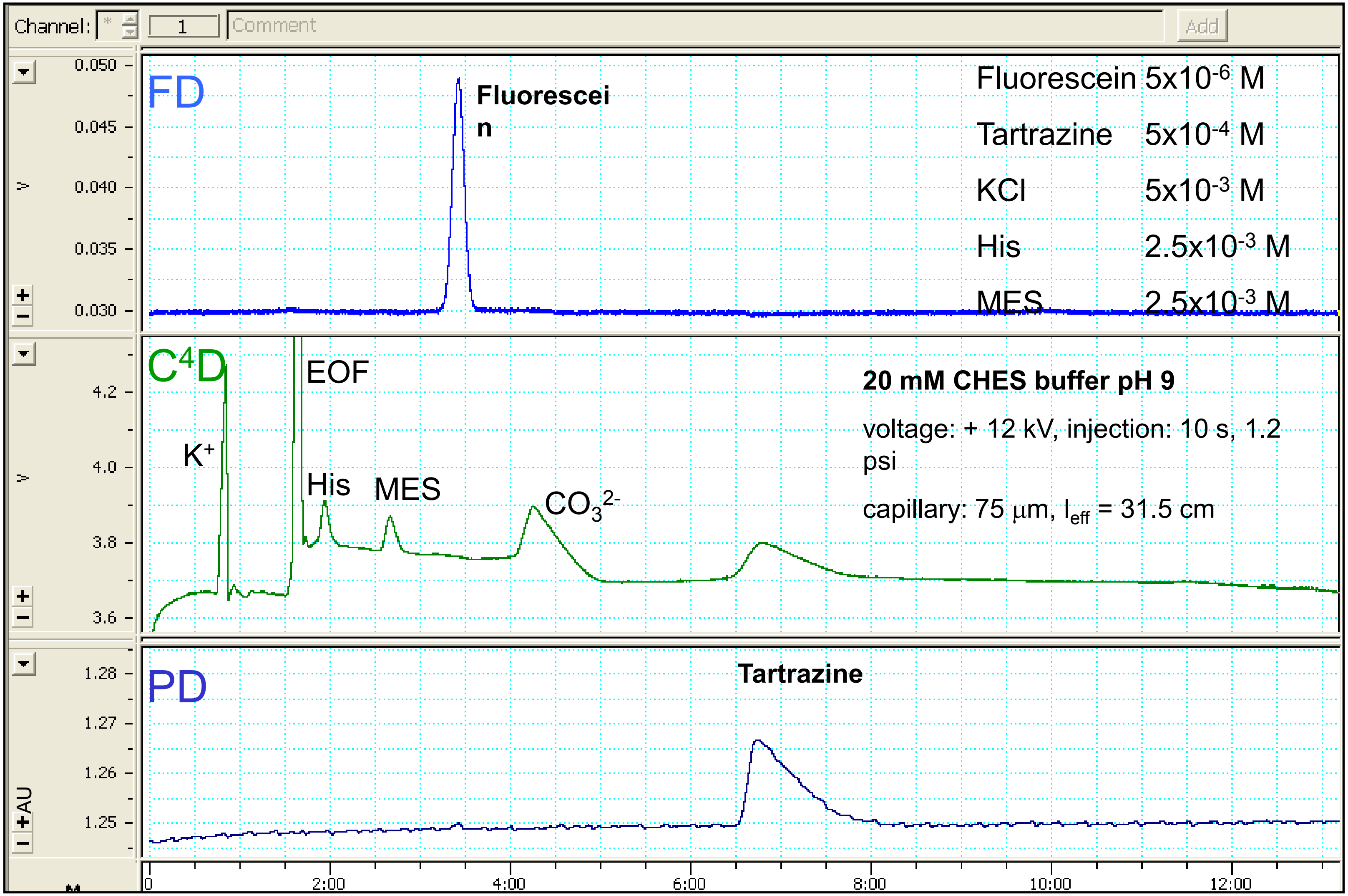
3-in-1 on-capillary detector

- Model separation



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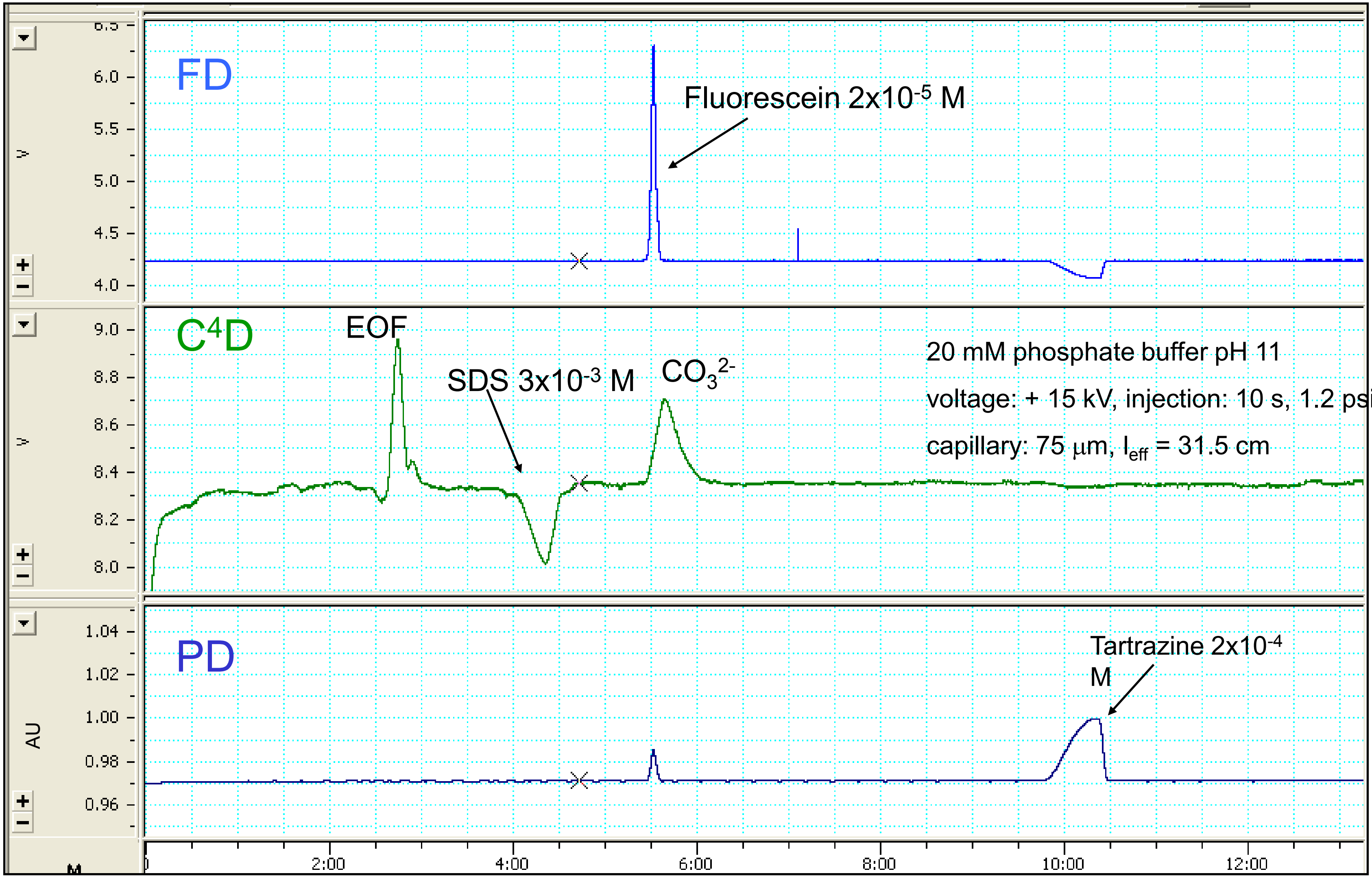
3-in-1 on-capillary detector

- Model separation



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3-in-1 on-capillary detector

- Model separations
  - 20 mM CHES buffer pH 9
  - voltage: + 15 kV,
  - injection: 10 s, 1.2 psi
  - capillary: 75 mm, leff = 31.5 cm
    - Fluorescein 2x10-5 M
    - Tartrazine 2x10-3 M
    - FITC 5x10-4 M
    - RhB 2x10-4 M
    - Trp 3.7x10-4 M
    - Tyr 7.5x10-4 M
    - Cys 9.4x10-4 M
    - NAC 5.6x10-4 M

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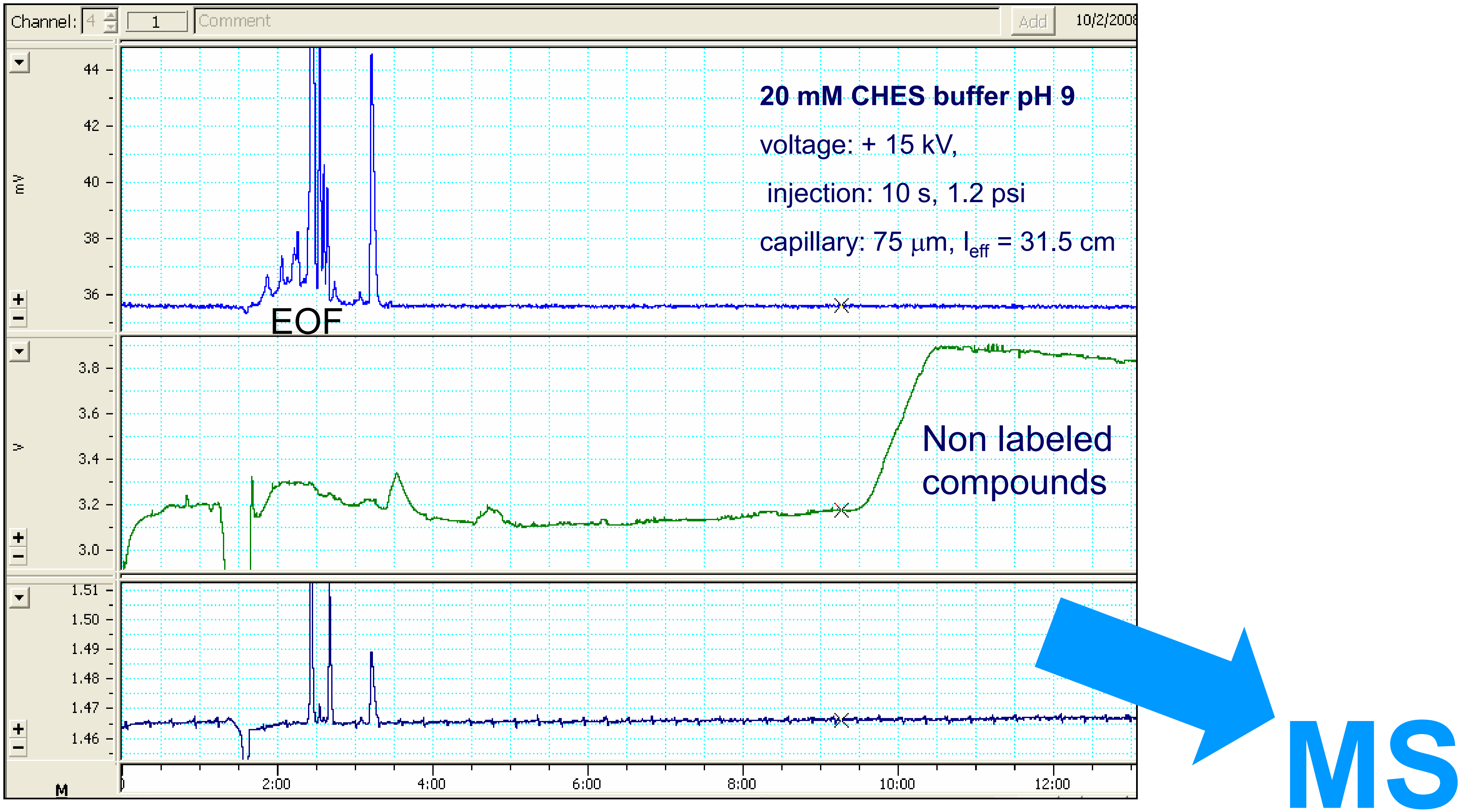
3-in-1 on-capillary detector

- FITC-BSA digest



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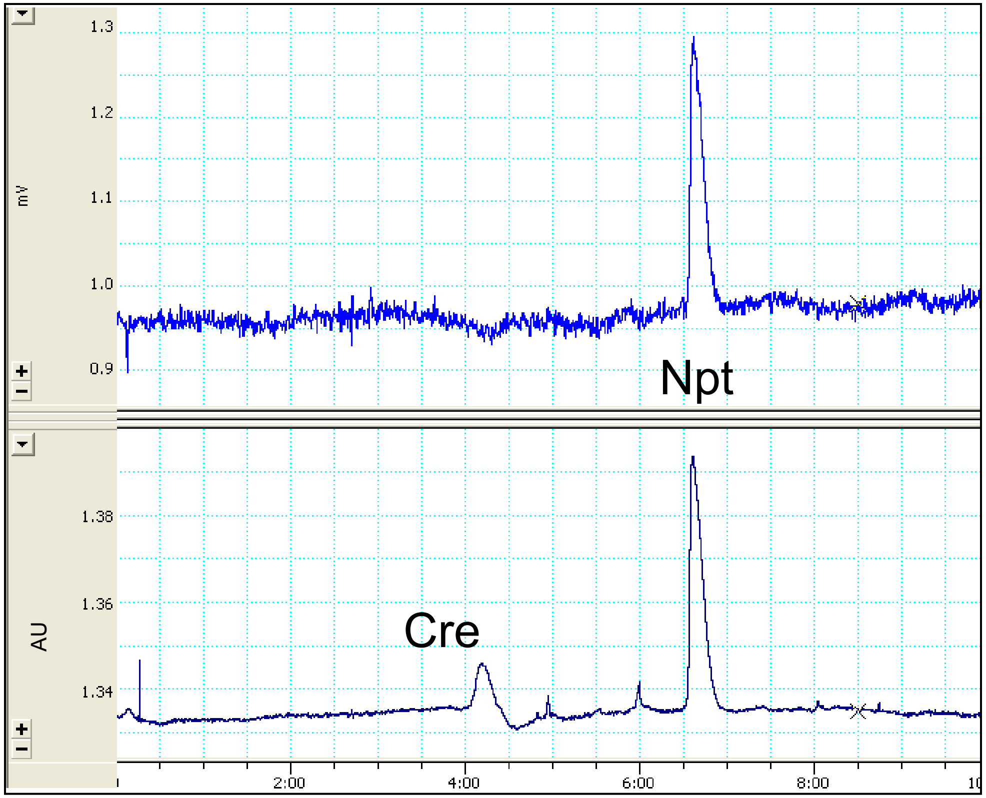
3-in-1 on-capillary detector

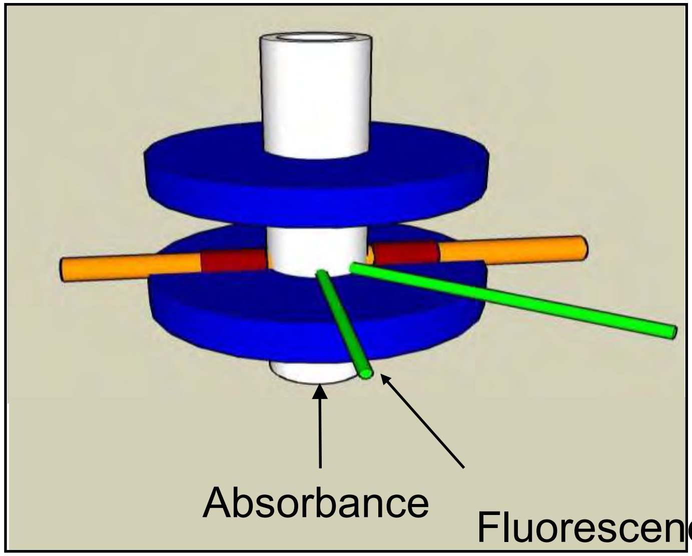
- Neopterin and creatinine



BGE: Tris-borate-SDS (each 100 mM) pH 8.75
Capillary: 75 µm i.d., l_{tot} = 39 cm, l_{eff} = 31.5 cm
Voltage: +7.5 kV
Injection: 10 s, 0.96 psi

LOD

Npt: 2.3×10^{-6} M
Cre: 1.0×10^{-4} M



255 nm excitation

350 nm

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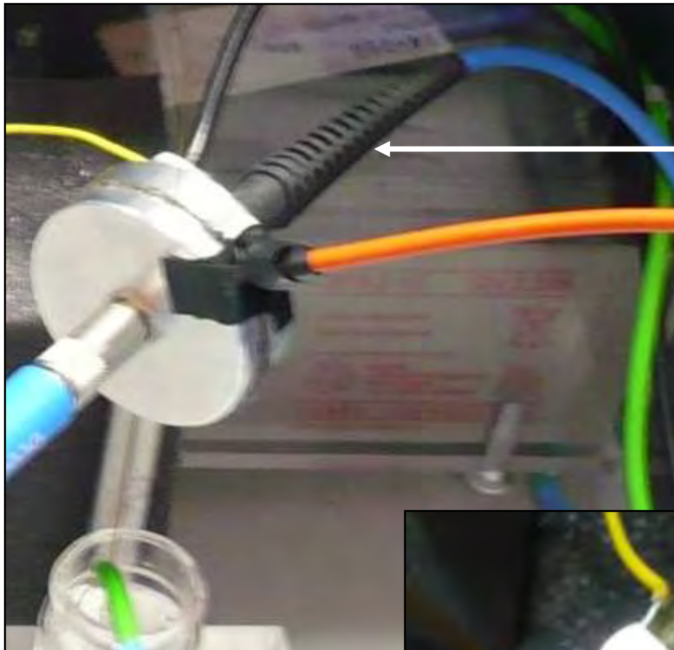
3-in-1 on-capillary detector

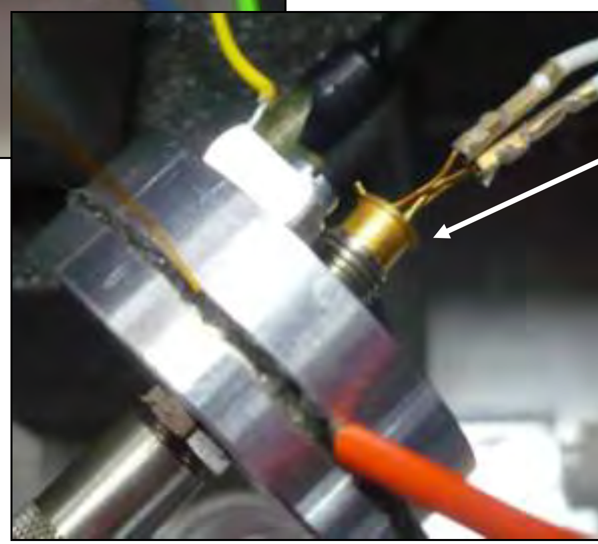
- Further developments



Optical fibre

Trp (FD) LOD = **4.8×10^{-5} M**

(PD) LOD = **5.7×10^{-5} M**



LED (255 nm)

Trp (FD) LOD = **1.6×10^{-5} M**

(PD) LOD = **8.4×10^{-5} M**

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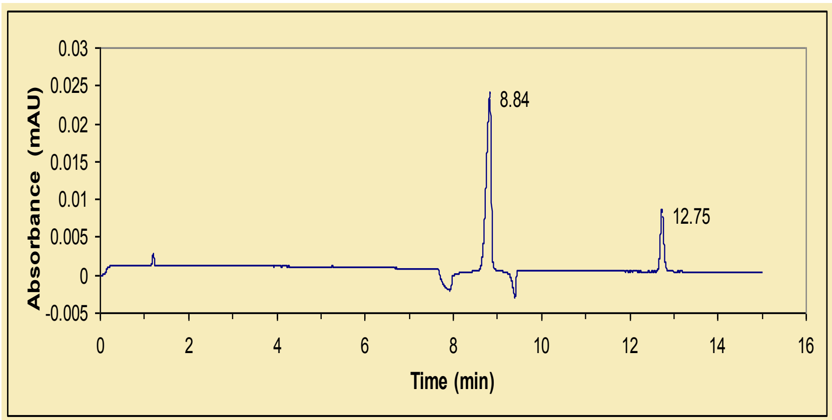
Applications: Neopterin (Npt) in urine

- Methods of determination
  - CE for simult. Npt & Cre

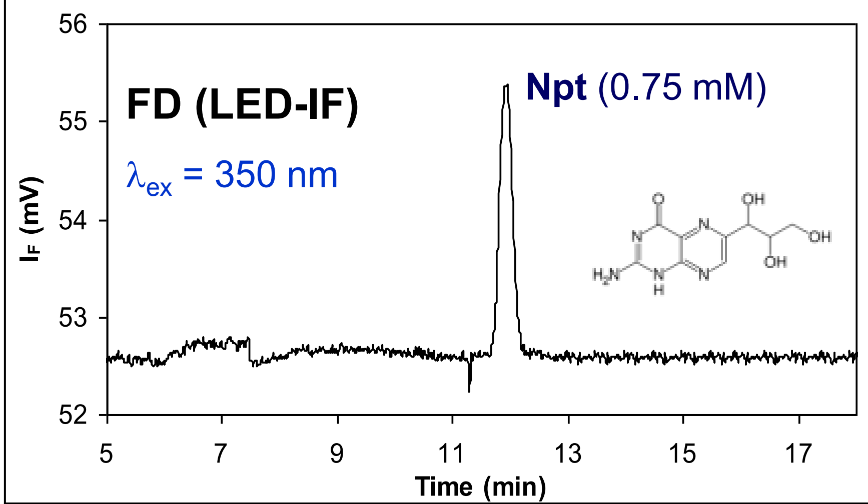


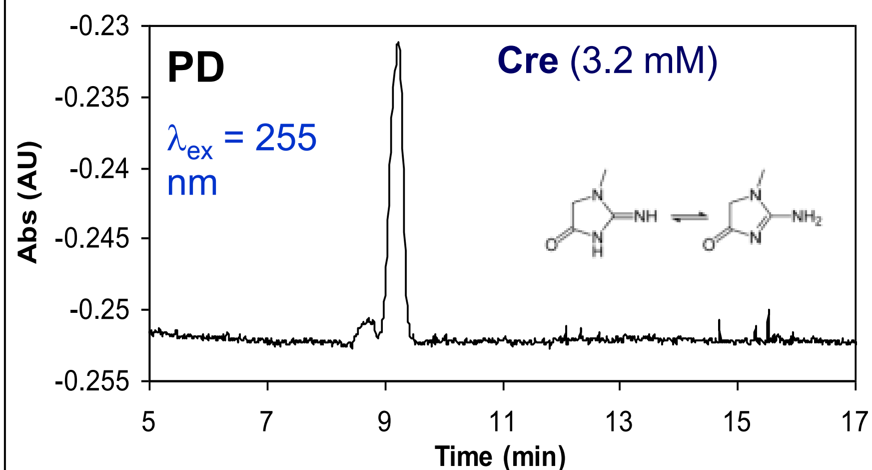
Npt (1,12mM) and Cre (0,53mM). Tris-borate-SDS BGE (each 100 mM) pH 8.75, FS capillary (75 µm i.d., 64.5 cm length, 55.0 cm effective length), +15 kV (40 µA).

- Lenka Krčmová, Hana Kalábová, Marketa Ryvolová, Tomasz Piasecki, Silvija Abele, Jan Preisler, Brett Paull, Peter Hauser, Petr Solich, Mirek Macka, A simple MECK method for the rapid determination of neopterin and creatinine in urine for clinical monitoring in anticancer therapy using UV-LED-photometric and fluorimetric detection, 32nd International Symposium on Capillary Chromatography, Riva del Garda, Italy, 27 May – 2 June **2008**.
- Krčmová L., Kalábová H., Kašparová M., Solichová D., Melichar B., Solich P., Liquid chromatography and capillary electrophoresis for the monitoring of neopterin in cancer patients, XXI Biochemicky sjezd, Ceske Budejovice, 14-17 September **2008**.

Applications: Neopterin (Npt) in urine

- Applications
  - Neopterin in urine
- MEKC
  - Tris-borate-SDS electrolyte (each 100 mM) pH 8.75
    Fused silica capillary (75 µm i.d., ltot = 39 cm, leff = 31.5 cm)
    Voltage: +7.5 kV
    Injection: 10 s, 0.96 psi
- **LODs**
  - Npt 2.3×10^{-6} M
  - Cre 1.0×10^{-4} M





$ '3-in-1' PD+FD+C^{4}D is an attractive combined detection

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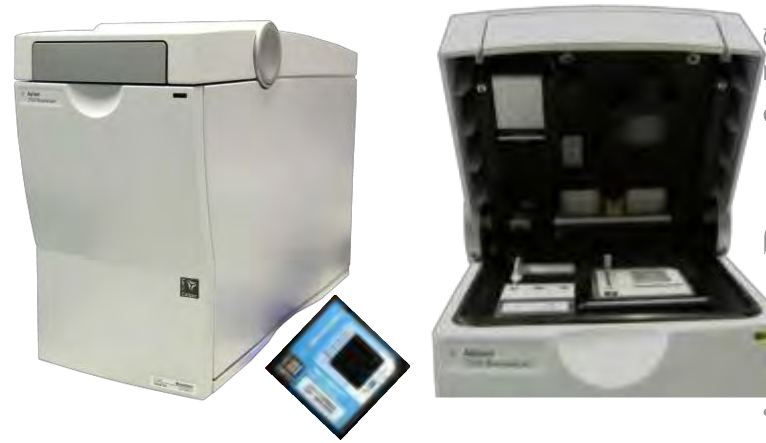
Commercial instrumentation

Petr Smejkal

- Philosophy
  - "Chip-in-a-lab" → Compact commercial platform



- Approach
  - Agilent Bioanalyzer platform
    - Chip-CE & LIF/LEDIF
    - ITP & Indirect Fluorescence Detection (IFD)
      - **Fluorescent counter-ion dye as non-focusing tracer**

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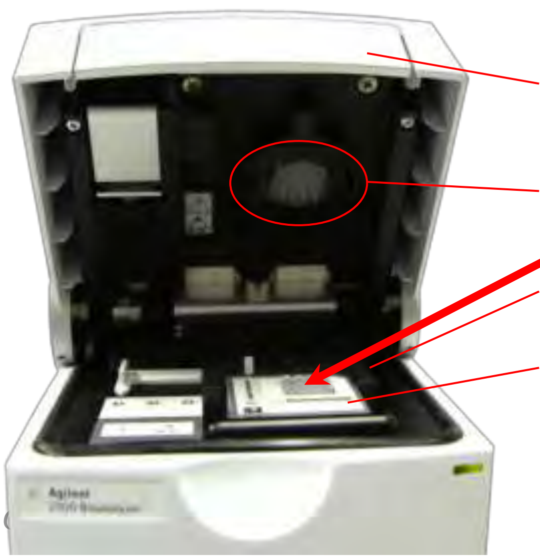
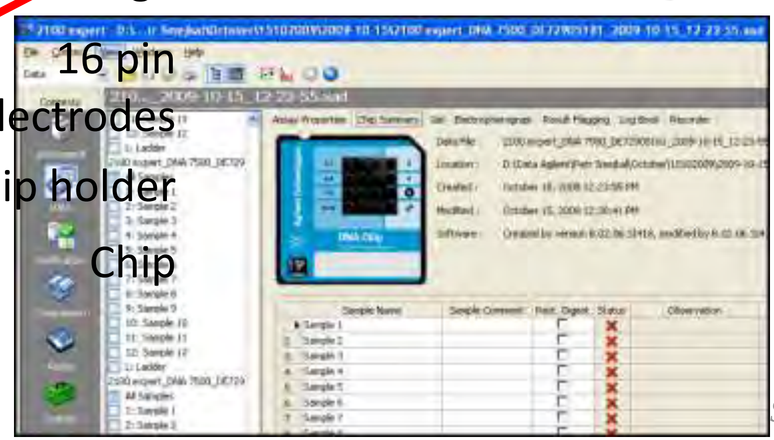
Chip-CE with LIF + LEDIF detection

Petr Smejkal

- **The approach taken & aims**
  - Commercial ready to use platform
    - Agilent Bioanalyzer 2010
    - Chip-CE platform
    - For DNA, RNA and protein analysis
  - Use in a 'research mode'
    - Access to Script Editor

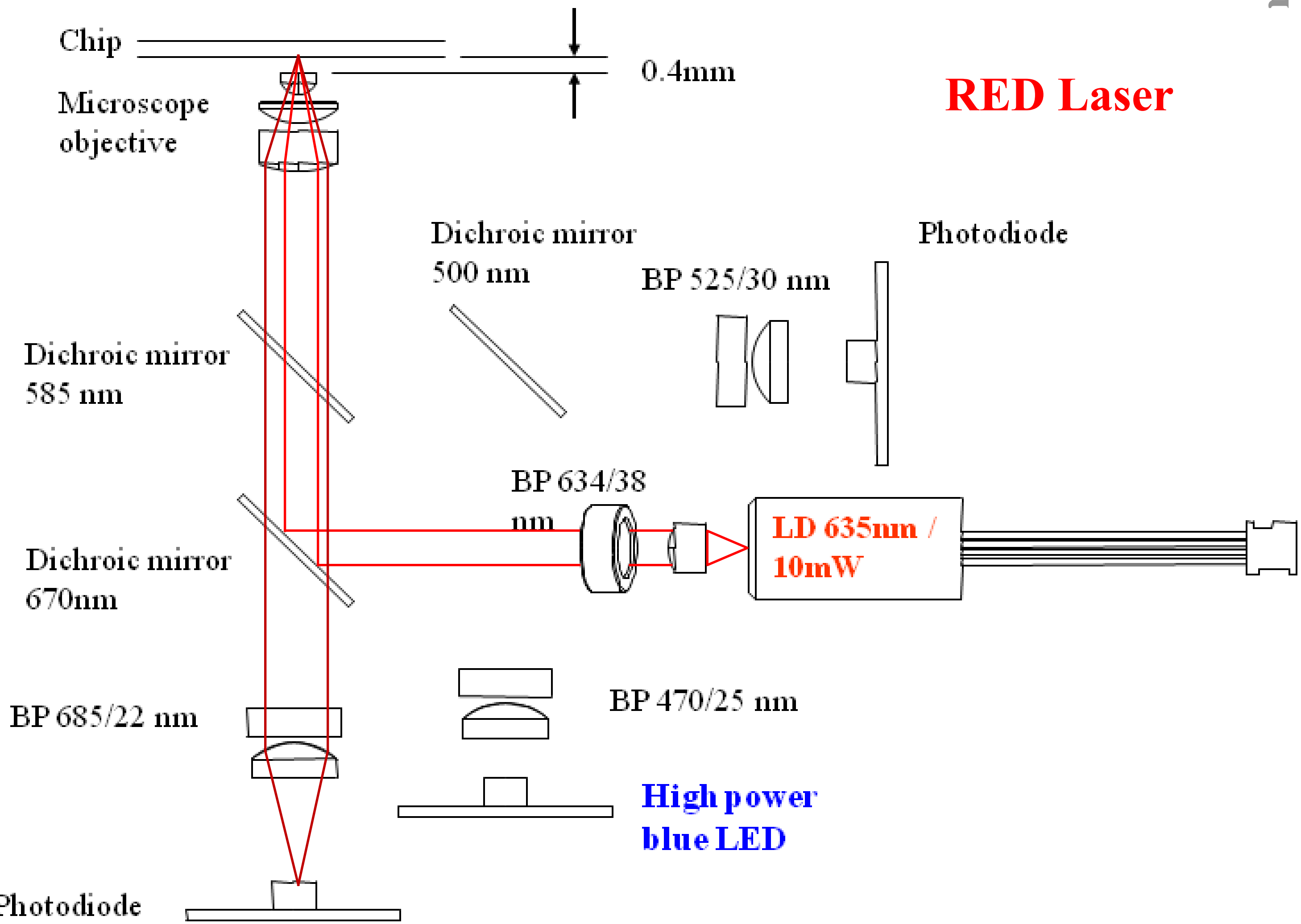




Agilent Bioanalyzer

➢ Red Laser

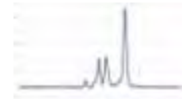
- Red LIF + blue LEDIF detection
  - **Red LIF**: LOD ~ 2 nM Nile Blue



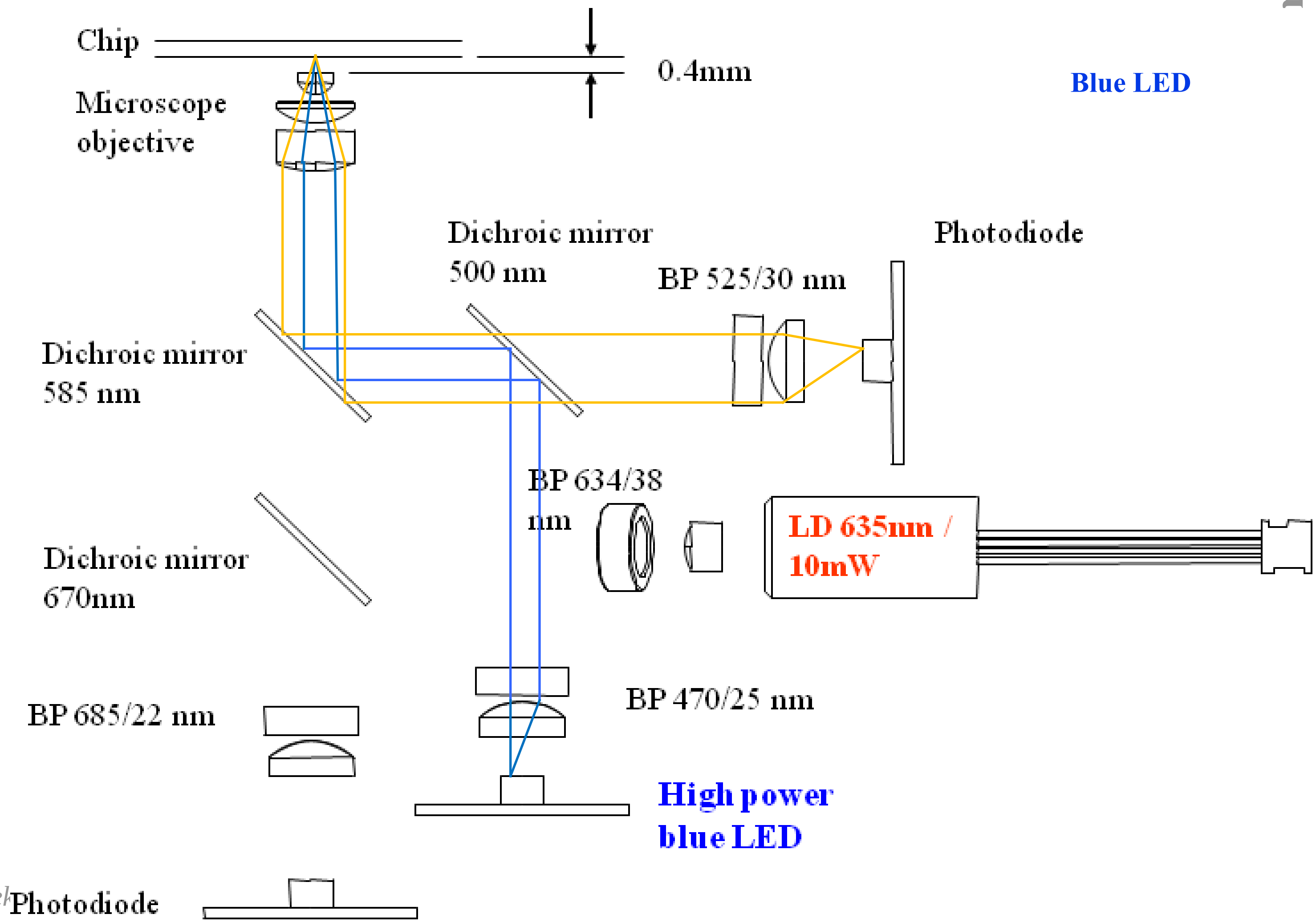
nber 2012

Agilent Bioanalyzer

- Red LIF + blue LEDIF detection
  - **Blue LEDIF**: LOD ~ 20 nM Fluorescein



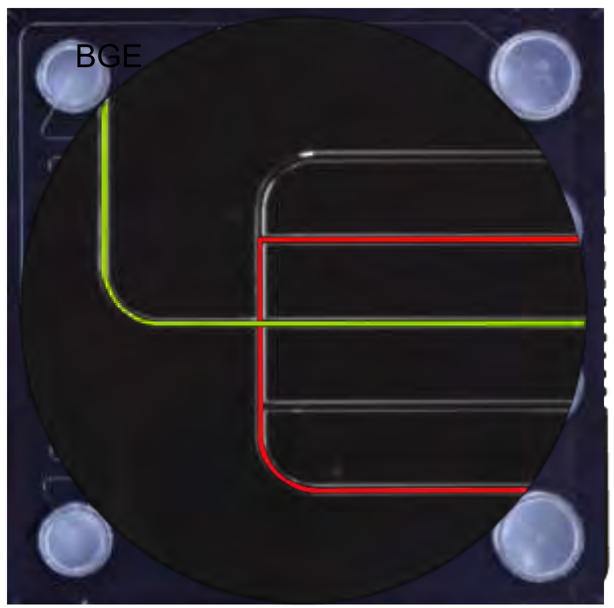
➤ Blue LED

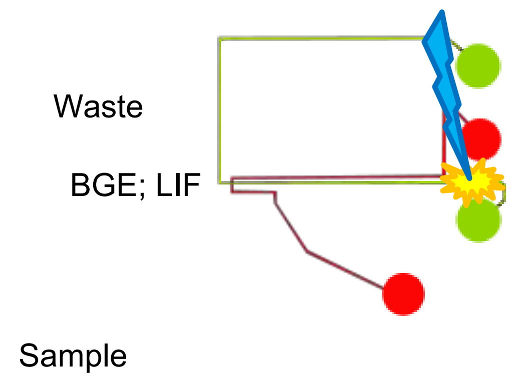


Agilent Bioanalyzer

- Injection & running CE
  - Plastic chip holder (black PMMA)
  - Sample introduction: usual CE cross

Channel dimensions	
Length ($l_{tot.}$)	= 39.9 mm
Length ($l_{ef.}$)	= 14.0 mm
Width	= 40.0 µm
Depth	= 15.0 µm





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LEDs in Chemistry: Outline

- LEDs properties in respect to their applications in chemistry
  - Practical considerations of usage of LEDs
- **Applications I**
  - Optical methods in chemical analysis
    - Photometry and photometric detection
    - Fluorometry
  - **LEDs for sensors**

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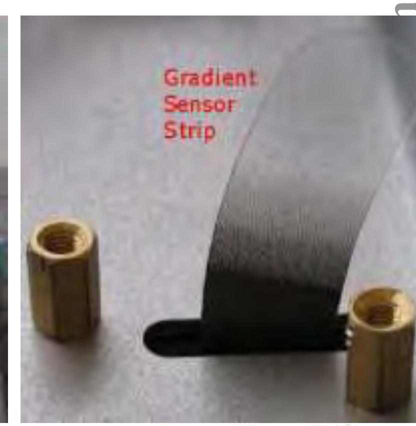
Sensors

- Sensor = a (quasi)continuous signal
  - In response to the measured physical property
- Sensing method?
  - For LEDs
    - Optical
    - Photometry
    - Fluorimetry
    - Turbidimetry
    - RI …etc…
- Used detectors
  - Photodiode
  - Photomultiplier
  - Another LED

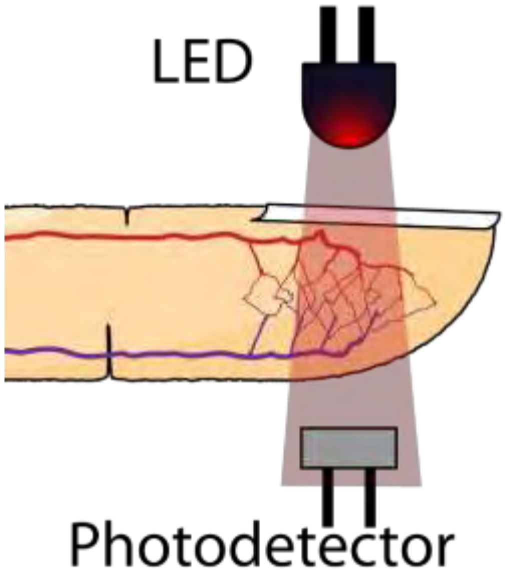


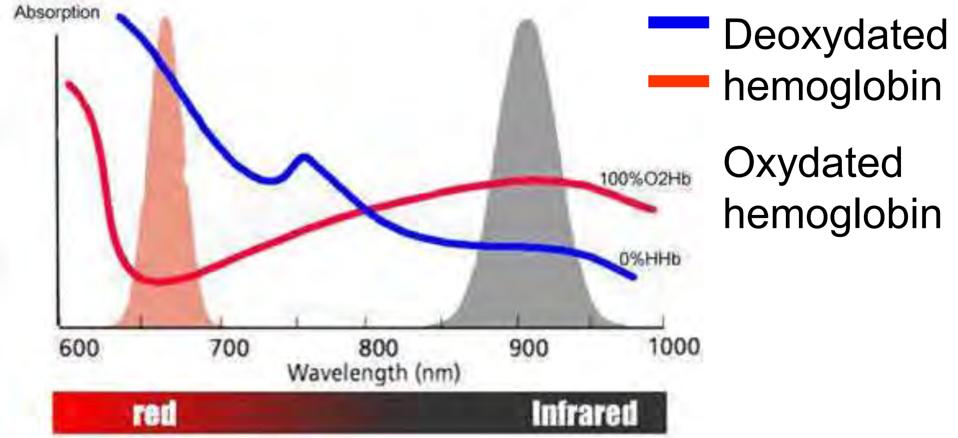
www.el34world.com

Wall proximity sensor based on IR LED and a phototransistor – Tamiya Inc.

Sensors

- Example – a big-$ application
  - Pulse oximetry – LED-based monitoring
    - Different absorbance for red and IR waves
      - Human body is transparent in sufficient degree for those wavelengths
    - Fast reliable method of non-invasive health monitoring





oximeter.holisticphysio.com

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Sensors

- LEDs are ideally suited for sensors
  - Small size → miniaturization
  - Low power consumption
  - Life expectancy
  - Reliability
  - Price

$ For sensors based on an optical method think LED!

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LEDs in Chemistry: Outline

- **Applications II**
  - **Illumination and visualisation**
    - **Emission patterns**
    - “White” LEDs
  - Light sources in photochemistry
- Workshop
  - Questions
  - Discussion forum
  - Exchange of experience
  - Discussion of specific intended usages
  - Experiments

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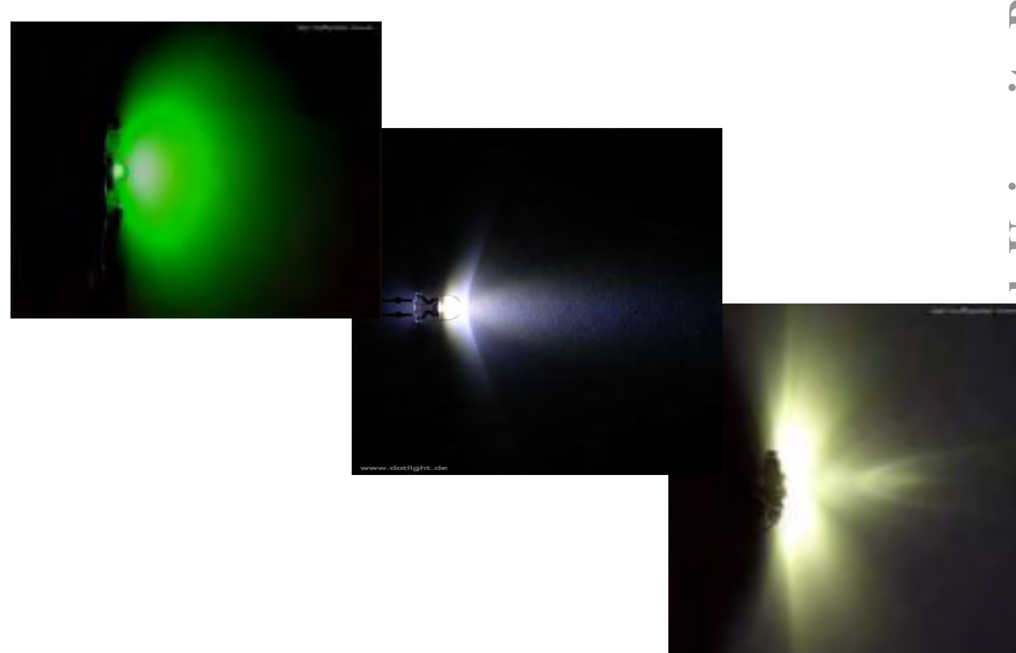
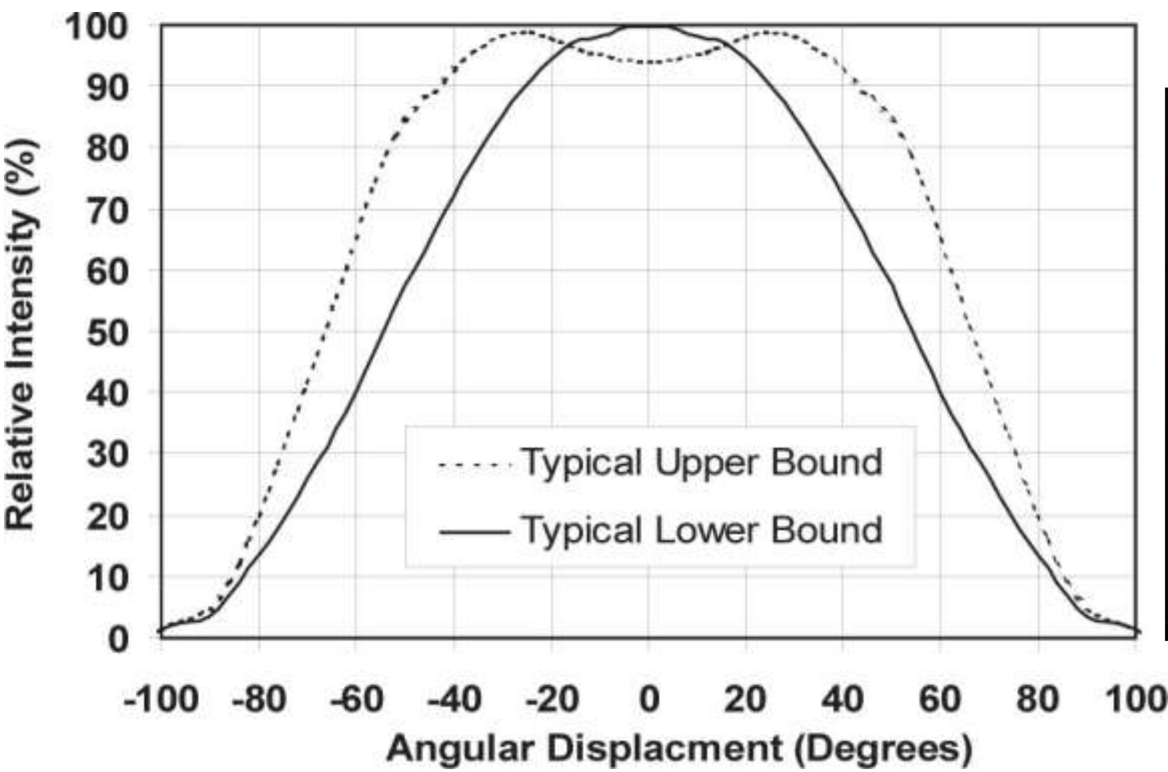
Emission patterns

- Emission pattern of LEDs
  - Light emitting diodes are not omni-directional light sources
  - There are three main types of emission pattern:
    - Lambertian
    - Side-emitting
    - “Batwing”

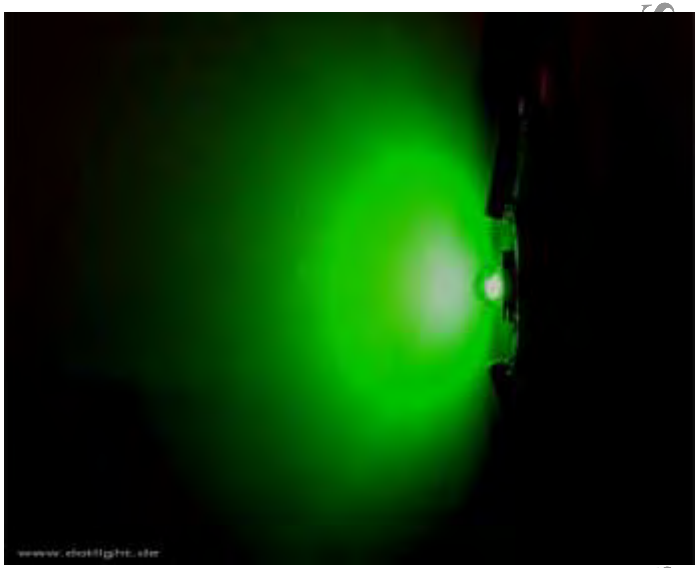


Emission patterns

- Lambertian pattern – in agreement with Lambert cosine law



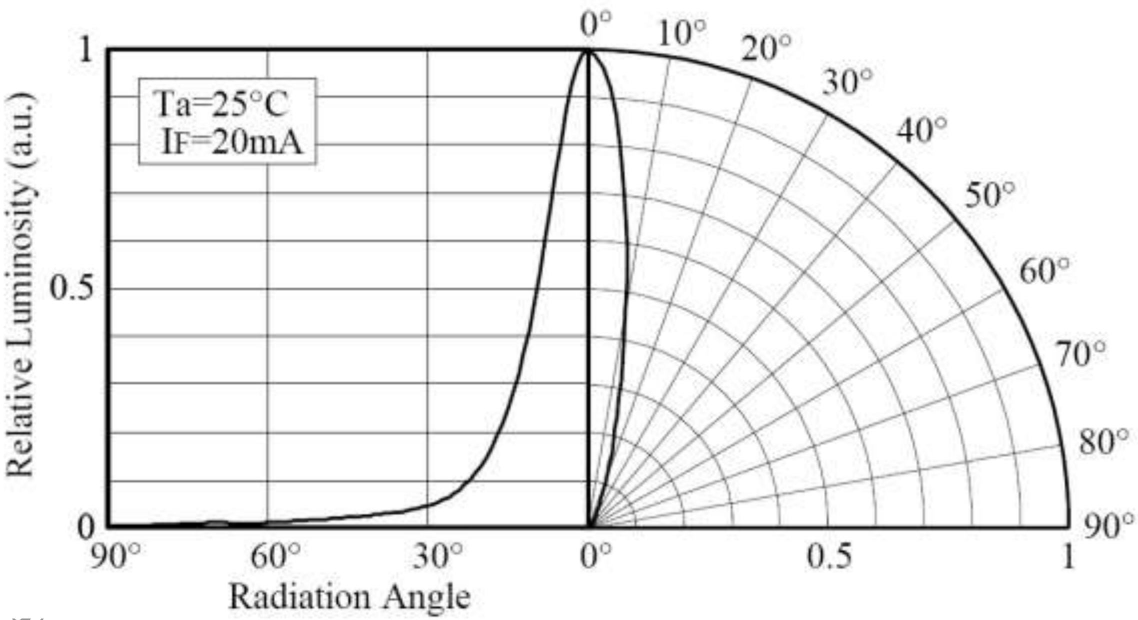
www.philipslumileds.com



www.dotlight.de

Emission patterns

- Application of external optics can narrow down emission pattern significantly



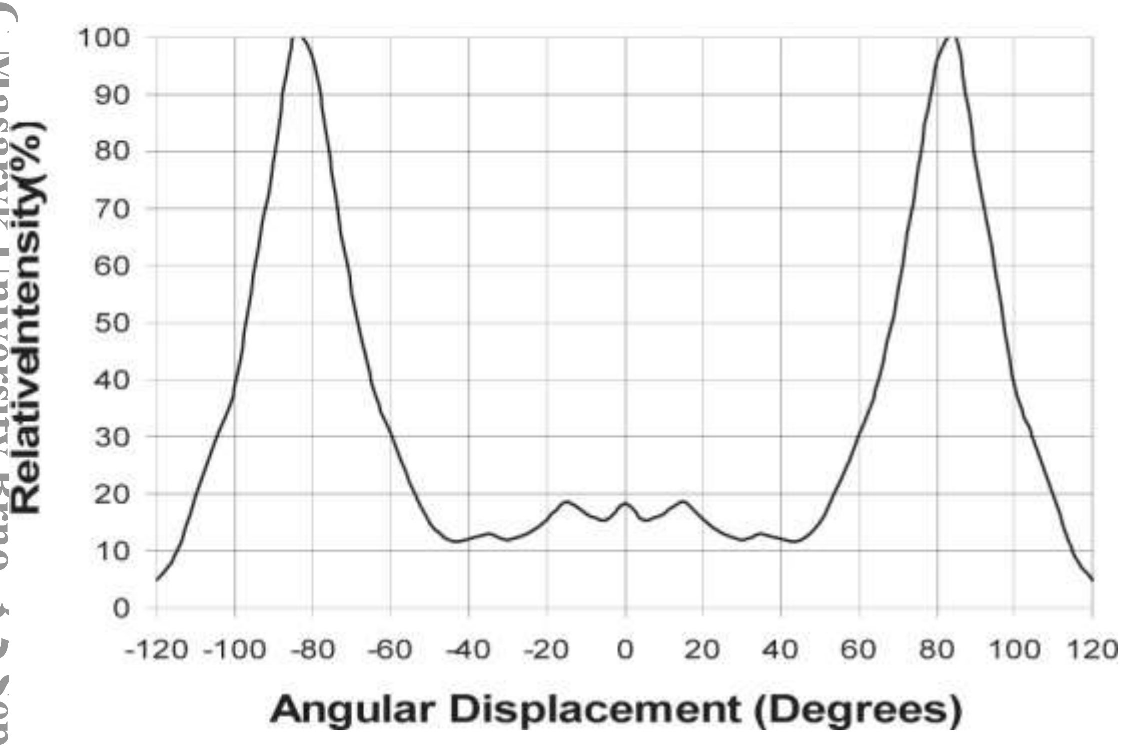
Nichia Corp.

www.dotlight.de

$ Know that LEDs can have very “pointy” spatial characteristic

Emission patterns

- Side-emitting pattern is second type of LED emission pattern



www.philipslumileds.com

www.dotlight.de

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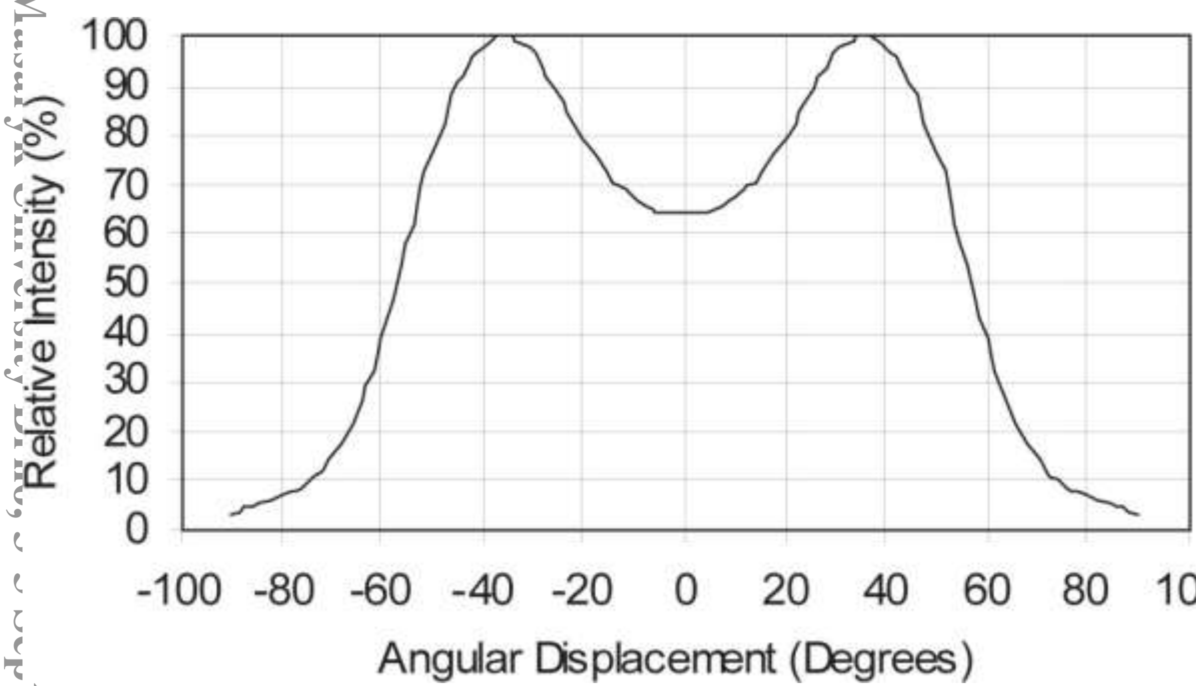
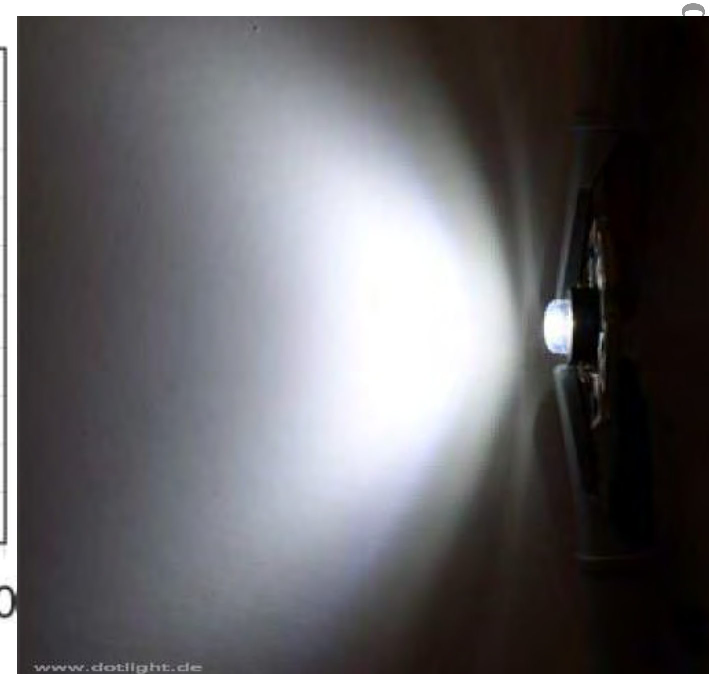
Emission patterns

- Batwing emission pattern is something in between Lambertian and side-emitting



www.philipslumileds.com



www.dotlight.de

$ Know that LEDs can also have broad emission pattern

LEDs in Chemistry: Outline

- Applications II
  - **Illumination and visualisation**
    - Emission patterns
    - **“White” LEDs**
  - Light sources in photochemistry
- Workshop
  - Questions
  - Discussion forum
  - Exchange of experience
  - Discussion of specific intended usages
  - Experiments

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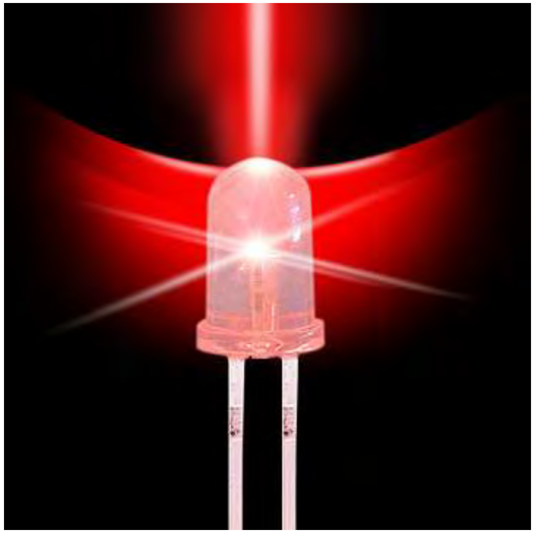
"White" LEDs

- Why "white" given in ""?
  - Broadband LEDs are not true white light sources
- Single LEDs are light sources of characteristic emission wavelength and narrow spectrum
  - Quasi-monochromatic



www.germes-online.com

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“White” LEDs

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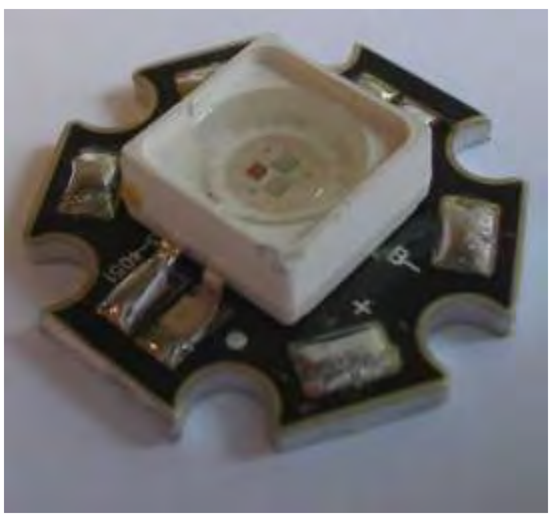
- Broadband solid state light sources
  - Two approaches:
    - Observed “broadband” – RGB-type LEDs
    - Broad emission spectra LEDs – blue + phosphorus type

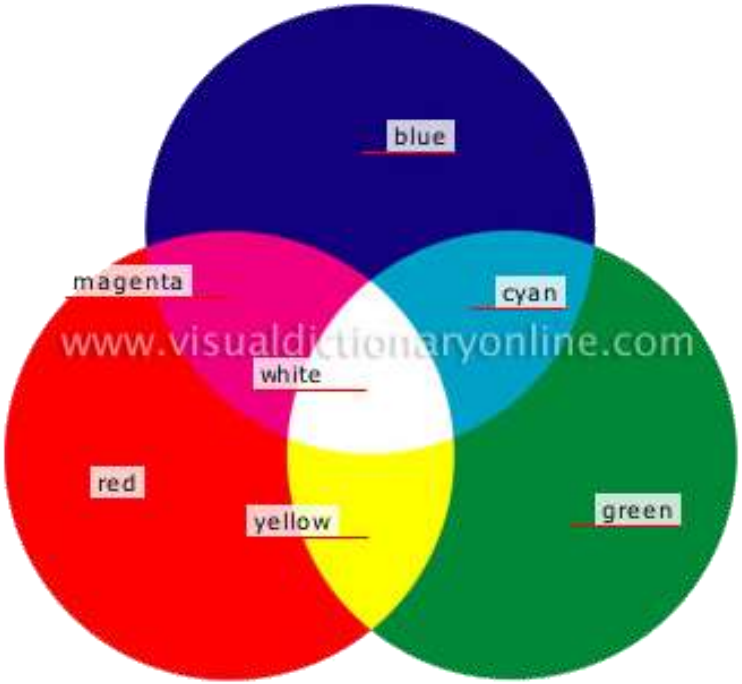


RGB LED

Blue + phosphorus

"White" LEDs

- Technology
  - RGB LED – 3 different emitting chips (red, green and blue) in one casing
  - Basing on additive colour synthesis



visual.merriam-webster.com

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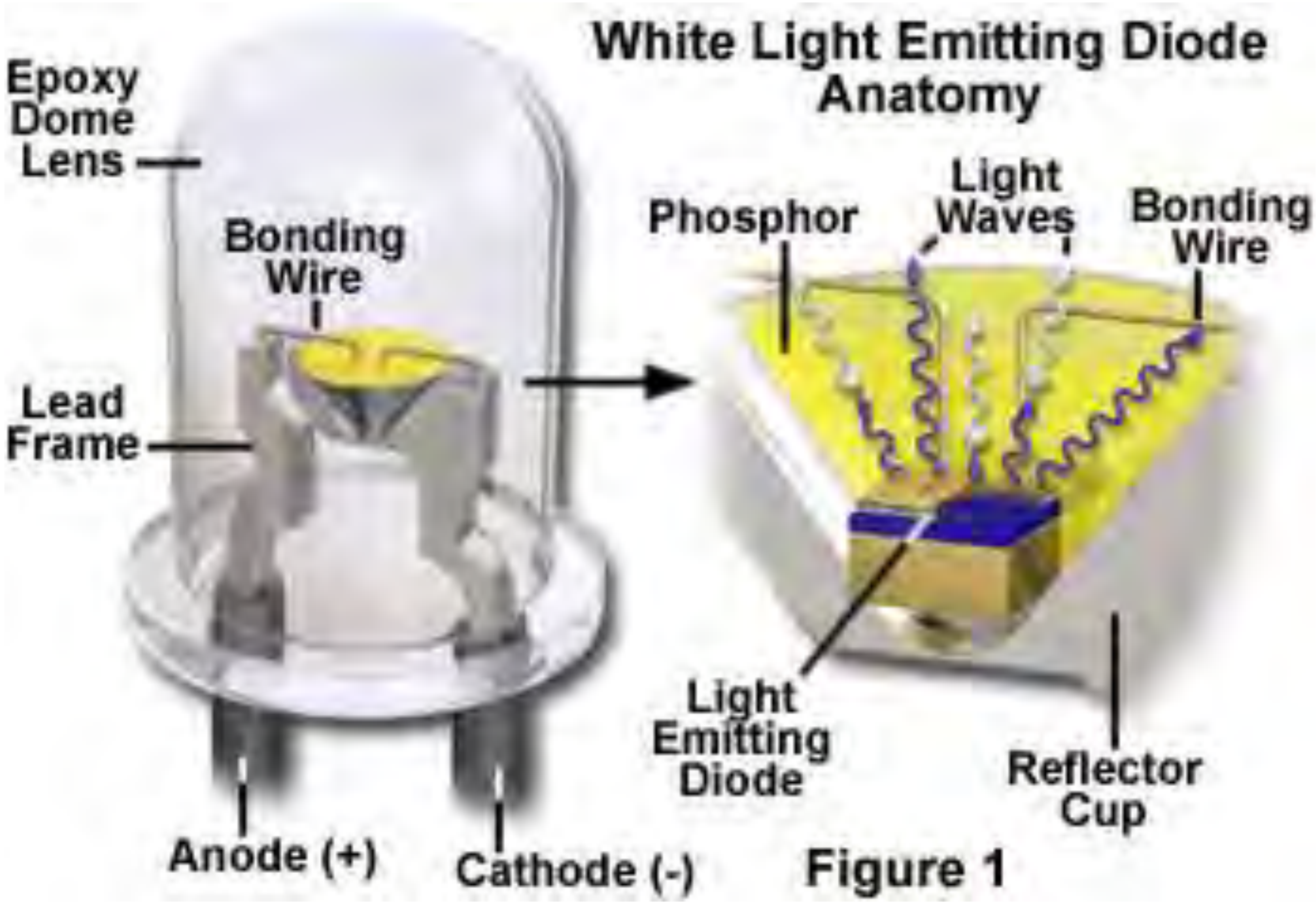
“White” LEDs

- Blue + phosphorus type



micro.magnet.fsu.edu

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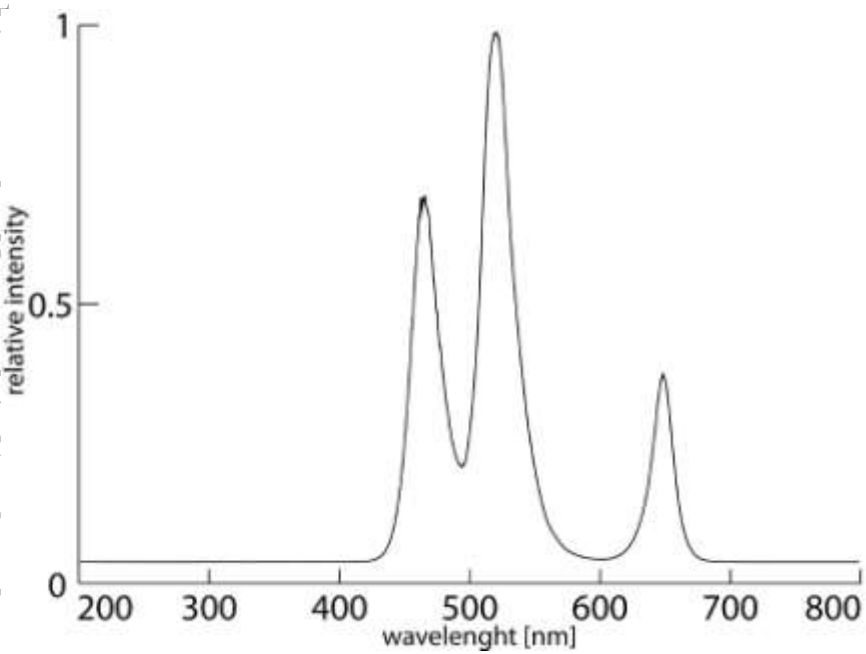
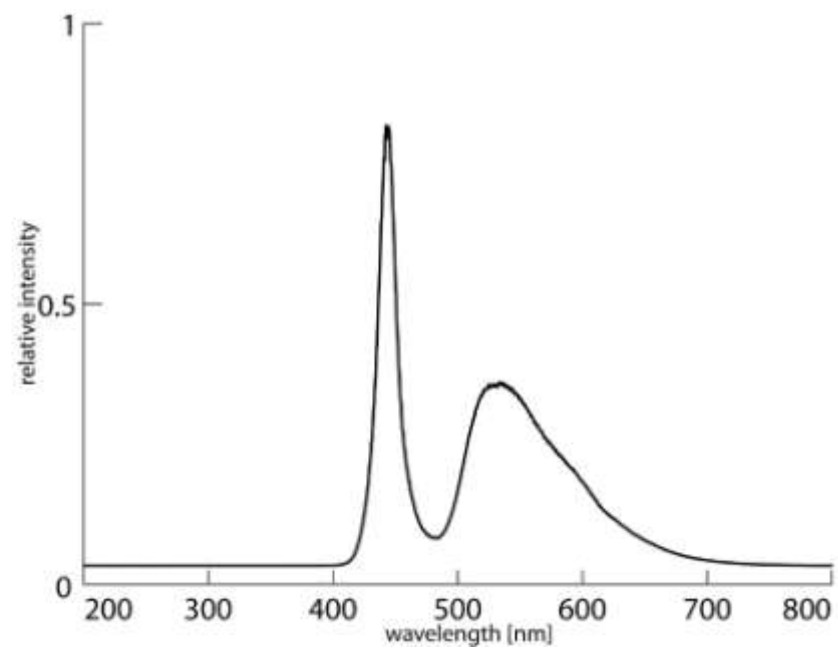
"White" LEDs

- Spectral composition
  - RGB type has three distinctive emission peaks
  - Blue + phosphorus has continuous spectrum



RGB type



Blue + phosphorus type

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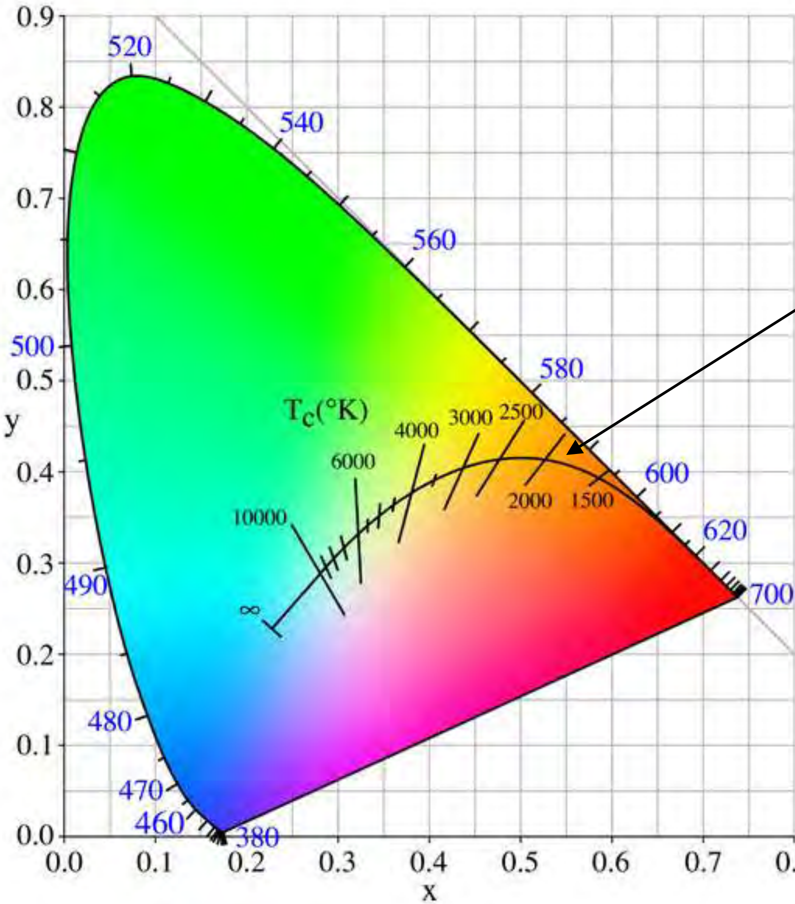
"White" LEDs

- White light is standardized by International Commission on Illumination (CIE)



Chromacity graph - wikipedia.org

Colour of black body radiating at different temperature

wikipedia.org

Tungsten
2856K

Sun
4870K direct sunlight

Sun
6504K daylight
6770K overcast

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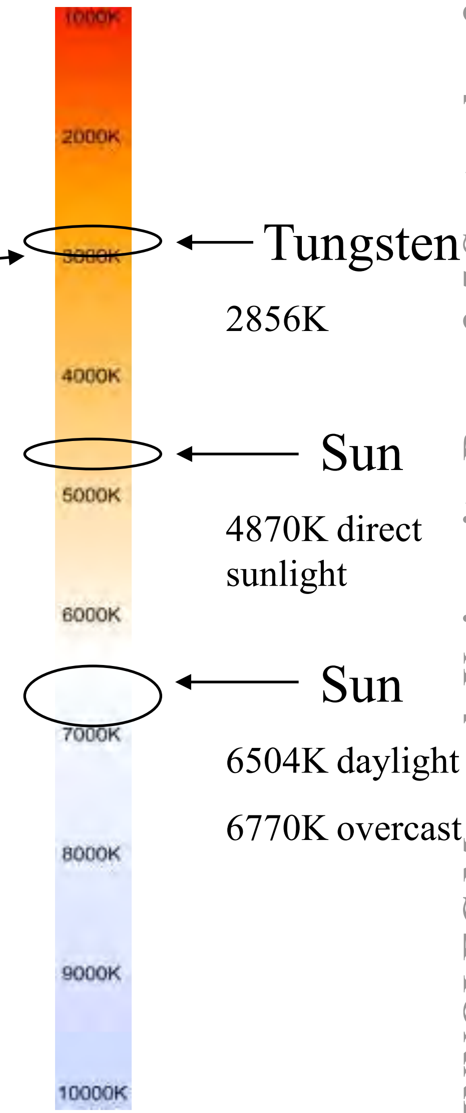
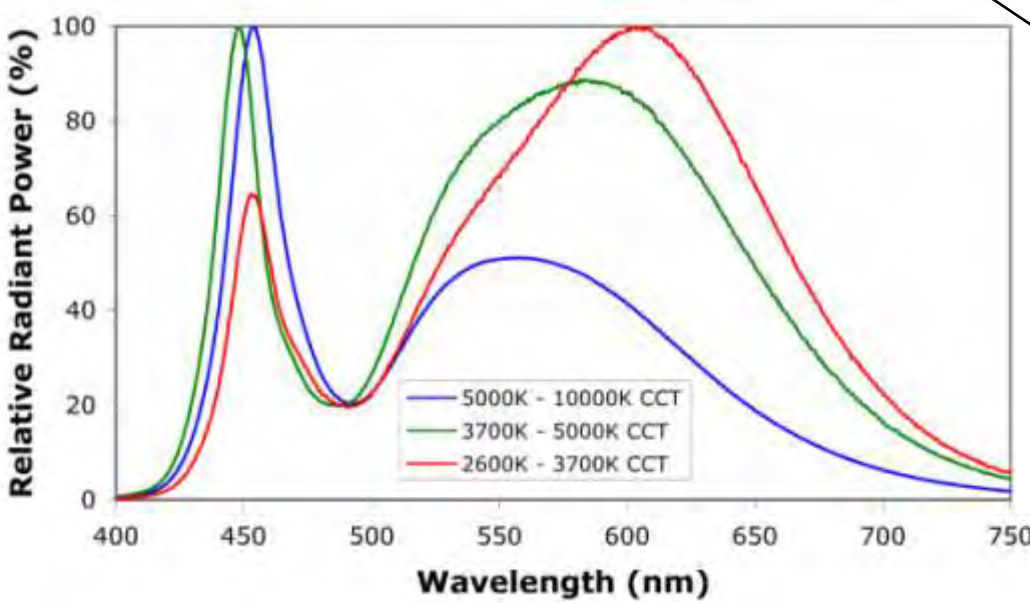
"White" LEDs

- RGB LEDs generally are not labelled with temperature of "white" emission
- Blue + phosphorous are often called:
  - "Warm white" (2600-3700K)
  - "Neutral white" (3700-5000K)
  - "Cold white" (5000-10000K)





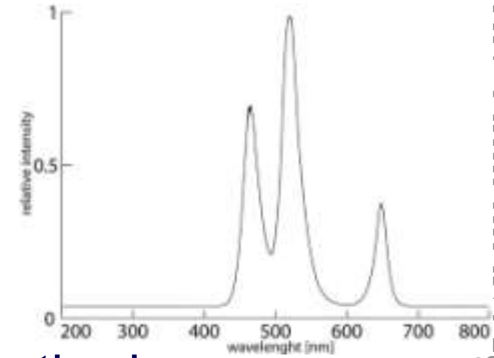
“White” LEDs

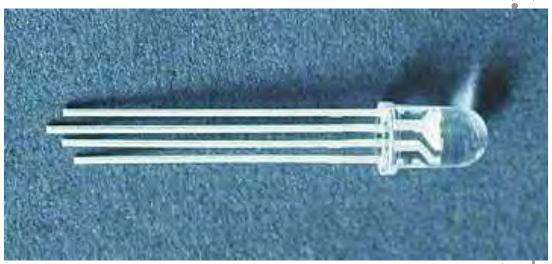
- Different white LEDs with varying light temperature
  - Gold white
  - Warm white
  - White
  - Cold white

- “Whiteness” of LED light depends on spectral compostion

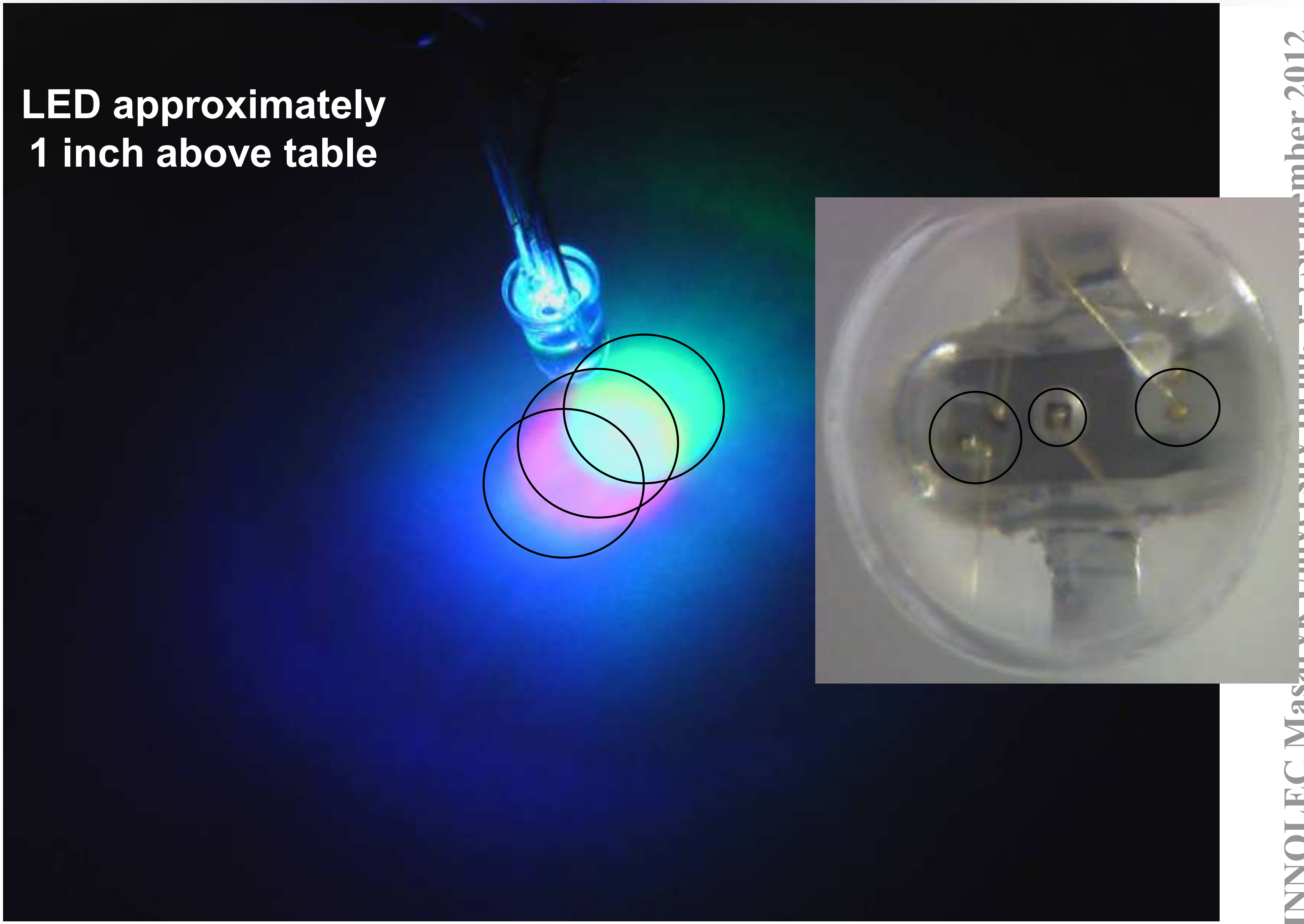
"White" LEDs

- Practical considerations of "white" LEDs
  - RGB-type
    - 3 peak emission spectra
    - 4-6-legged
      - 3 cathodes + 1 anode or 3 anodes and 1 cathode
      - 3+3 cathodes + anodes
    - Specialised power supply unit required
    - Inhomogeneous emission pattern
      - Coupling to optical fibre – 'light mixing'
    - Advantage:
    - Each colour can be turned on and off separately
    - 'Tuning' of white colour





“White” LEDs



"White" LEDs

- Blue + phosphorus type
  - From electrical point of view – regular LEDs
  - Technology has been tremendously upgraded – today it is the brightest LED type available
  - Has to be precisely chosen depending on application
  - System calibrated for one LED not necessarily will work properly with other (effect of colour temperature on colour rendering)
  - Homogenous colour distribution in entire emission pattern – light has same spectrum everywhere

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LEDs in Chemistry: Outline

- Applications II
  - **Illumination and visualisation**
    - Emission patterns
    - “White” LEDs
  - Light sources in photochemistry
- Workshop
  - Questions
  - Discussion forum
  - Exchange of experience
  - Discussion of specific intended usages
  - Experiments

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Illumination and visualisation

- Light sources for scientific applications
  - Microscopy
    - Over 300 years of development
    - Tungsten bulbs
    - Mercury lamp
    - Xenon arc lamps

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Microscopy

- LED illuminated microscopes are not popular
  - Separate LED panels can be bought
  - www.professionalmicroscopes.com
    universal LED ring - $157

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Microscopy

- Leica DM IL LED – first inverted routine microscope with LED illumination
  - High stability
  - Constant colour temperature
  - No heat build-up
  - Low power consumption
  - Estimated lifetime for LEDs – 50,000 hours

www.leica-microsystems.com

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Microscopy

- Digital imaging/microscopy
  - Inverted epifluorescence video microscope ~$5,000
    - Microfluidics, microbiology, forensics, engineering etc. etc.
    - Size of a top-loading balance
    - Motorized traverse and focus
    - Synchronously pulsed illuminator with LEDs

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Microscopy

- Miniature portable digital microscopes
  - Powered via USB interface
    - LEDs as light sources
  - Light, portable, easy to use
  - Cost ~$100

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Microscopy

- USB Microscopes
  - Dino-Lite http://www.bigc.com/

  - Cheap (~$50) Chinese

- http://www.dinodirect.com/microscopes-optical-magnification-repairing-jewelry-currency-GBP.html

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LED-Fluorescence imaging

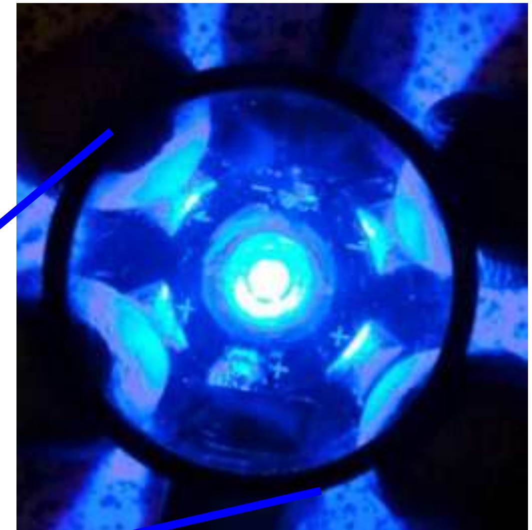
- From ***single-point*** to an ***array of points***:
- From ***detection*** to ***imaging***
- **Potential for portable/in-field analysis?**
- Fluorescent microscopes:
  - Big, expensive, requiring a lot of power
    - Far from being portable
  - <500$ portable alternative?

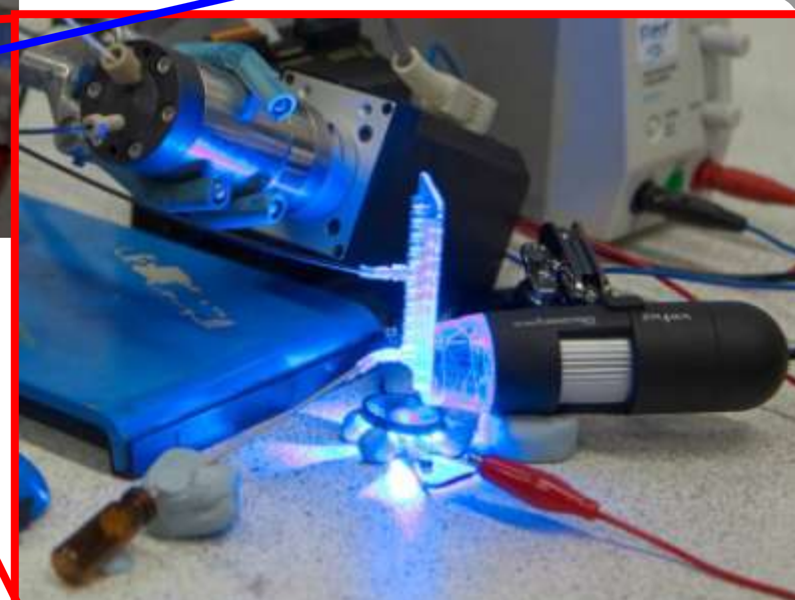
Tomasz Piasecki

?
≈

LED-Fluorescence imaging

- Example 1: COC chip
- High power blue LED 130 lm, ~$10
- USB microscope $100





- IF filters ~$400
  - Low pass = excitation
  - High pass = emission

LED-Fluorescence imaging

- Commercial COC chip
  - Fluorescein LOD < 10^{-7} mol/L
    - Excitation filter
      - ‘narrow’ (€42)
      - ‘optimal’ (€266)
    - Emission filter
      - (€142.50)

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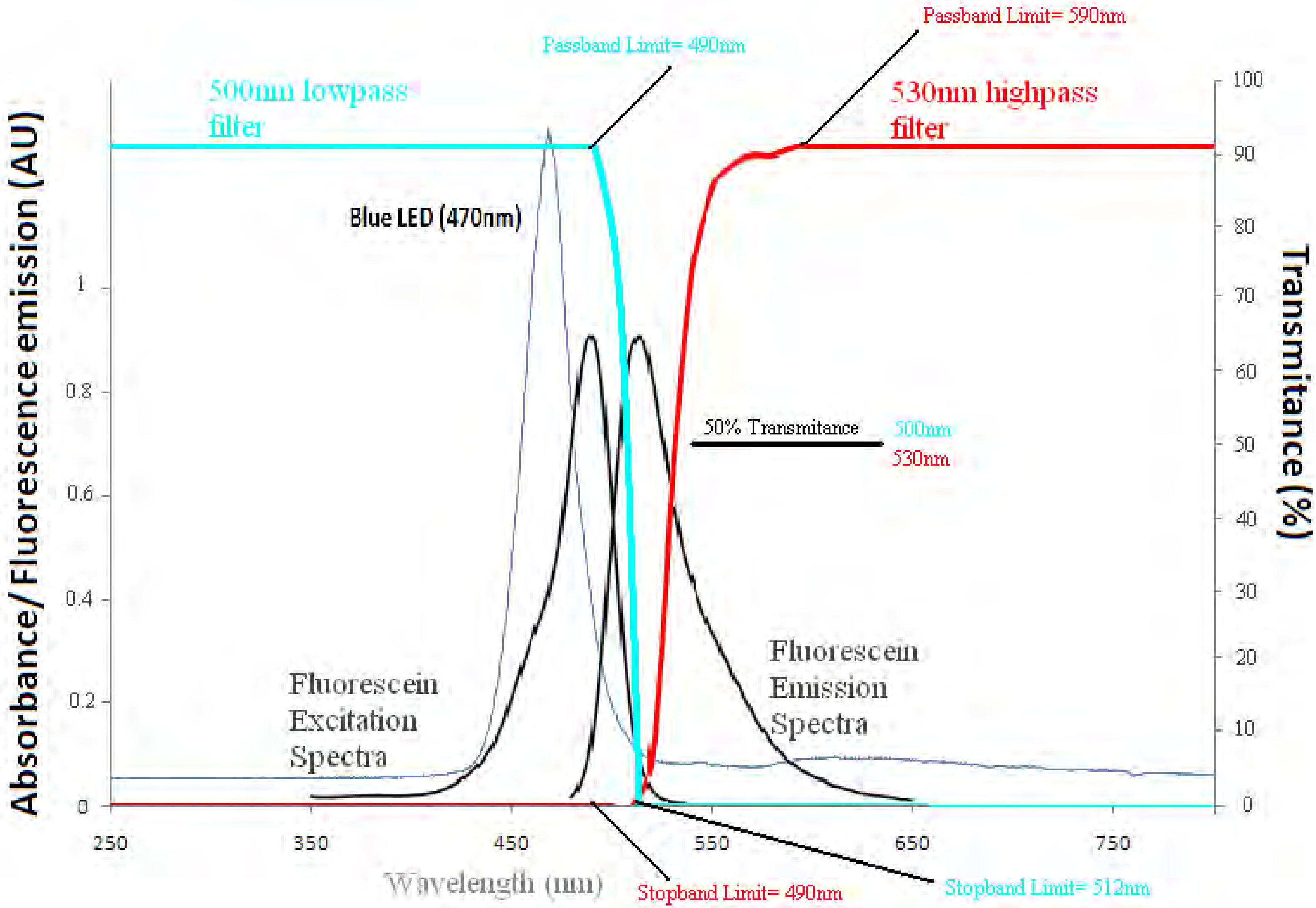
Fluorescence imaging

- Spectral design is crucial for sensitivity!



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Fluorescence imaging

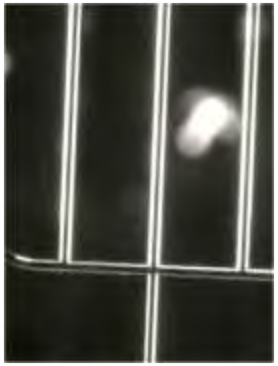
Portable USB microscope

(Digiscope: magnification= 200x, 1.2MP)

Agilent DNA chip channels, Magnification= 197x, LOD (Flu) = 5×10^{-3} mM, size of one pixel= 1.3 μm

Small benchtop microscope

(Labsmith SVM340: objective= 4x, 0.31MP)



Agilent DNA chip channels, Magnification= 175x, LOD (Flu) = 2×10^{-3} mM, size of one pixel= 6.8 μm

Large benchtop microscope

(Nikon eclipse ti-u: objective= 4x, 4.9MP)

Agilent DNA chip channels, Magnification= 247x, LOD (Flu) = 7×10^{-4} mM with gain= 16x and exposure= 300mS , size of one pixel= 0.42 μm

Fluorescence imaging

- Conditions
  - Agilent DNA chips: channel width= ??µm
  - 1st Row: Empty (air), white light illumination
  - 2nd Row: 0.092mM fluorescein in 20mM borate and DMSO pH~9

Digimicro:

Light: Blue LED 470nm, 350mA, ca. ~ 70deg
Emission filter: OG530 stopband limit=490nm, passband limit=590nm
Excitation Filter: Transmission wavelength= 250nm – 490nm, Rejection Wavelength= 512nm-715nm, Cut off wavelength= 500nm

Labsmith:

Light: Blue LED's labsmith
Emission filter: OG530 stopband limit=490nm, passband limit=590nm
Excitation Filter: None

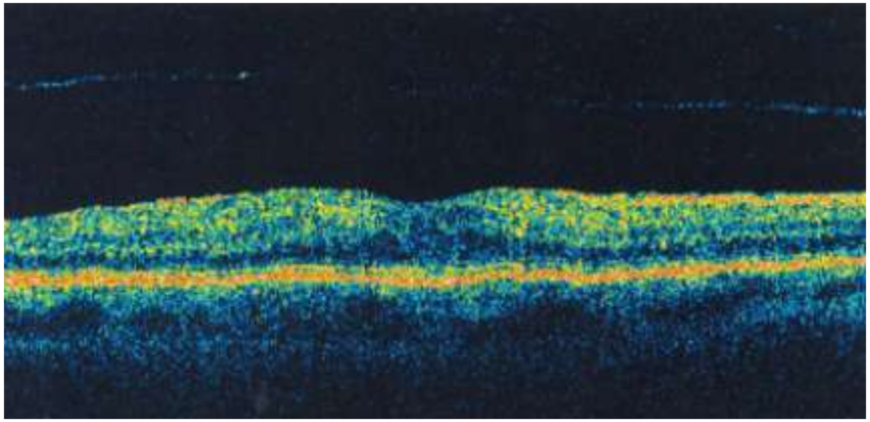
NIKON:

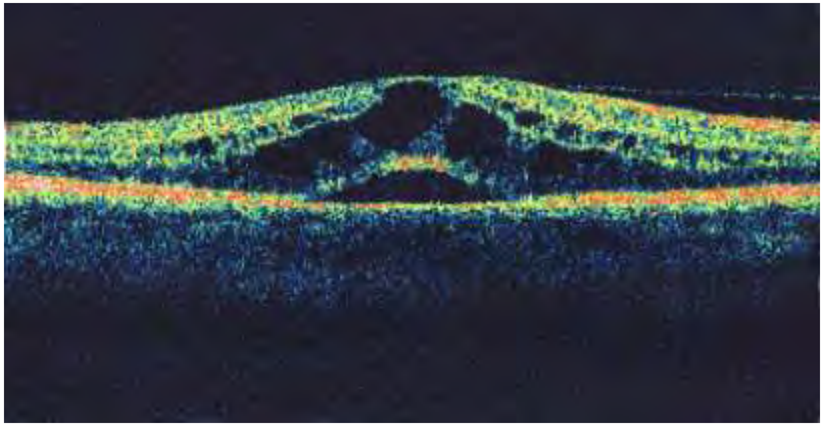
Light: Deuterium Lamp

Excitation Filter: 450nm-490nm

Optical coherence tomography

- Relatively new imaging techniques dating back to 1990
- Build on high brightness LEDs
  - Excellent for imaging of biological samples like tissues
  - Penetration depth ~1-2 mm
  - Non-invasive





Example of detecting abnormal fluid in the back of the eye

www.eyetumour.com

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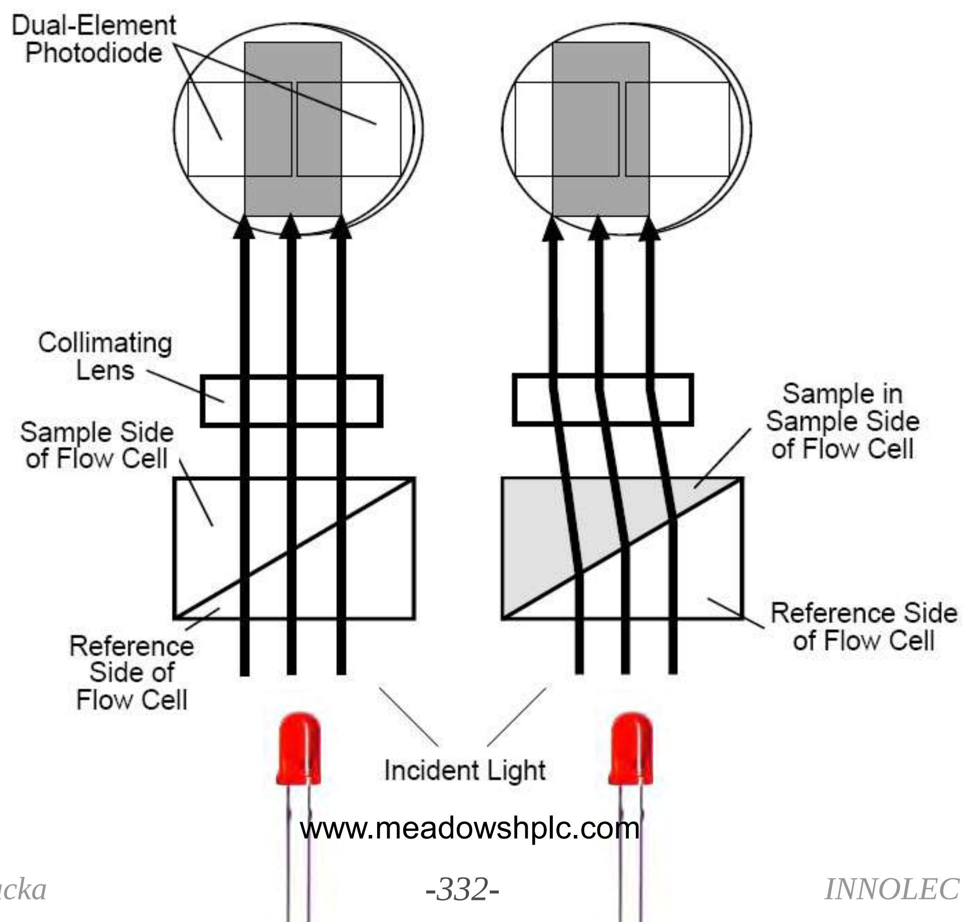
Refractometry

- Measurements based on different refractive indices
- LEDs are also used in refractometers, especially in category of differential refractometers



www.meadowshplc.com

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LEDs in Chemistry: Outline

- Applications II
  - Illumination and visualisation
  - Light sources in photochemistry
- Workshop
  - Questions
  - Discussion forum
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LEDs in Chemistry: Outline

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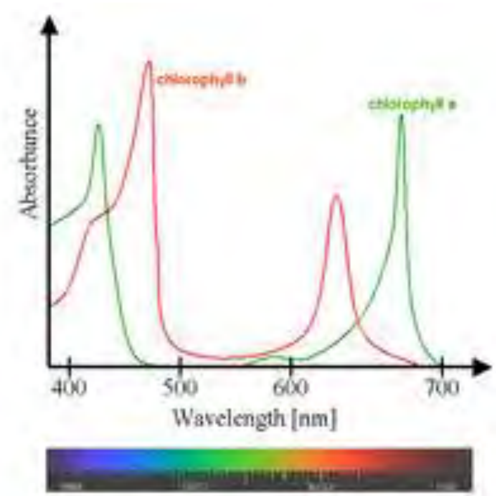
Plant science and horticulture

- Applications: photosynthesis – plant growth

- Spectrum needed:
  - Chlorophyl spectrum
    - http://en.wikipedia.org/wiki/Chlorophyl
  - Red + blue



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Plant science and horticulture

- Applications: photosynthesis – plant growth

  - Vertical Farms, Silicon Chip, March 1012, pp.16-23 siliconchip.com.au

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Photochemistry

- Dental LED Light Curing Units
  - Cold light sources
  - Low power consumption
  - Miniaturization
  - Long life
  - Reliable
  - Desired wavelength

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LEDs for photochemistry

- Classical light sources
  - UV Lamps / UV Tubes

BondWand® UV Curing Light
Output power
25 mW / cm^2 at 365 nm 640$

http://www.edmundoptics.com

UV/Visible Light Exposure Chamber
Output power
26 mW / cm^2 at 365nm 995$

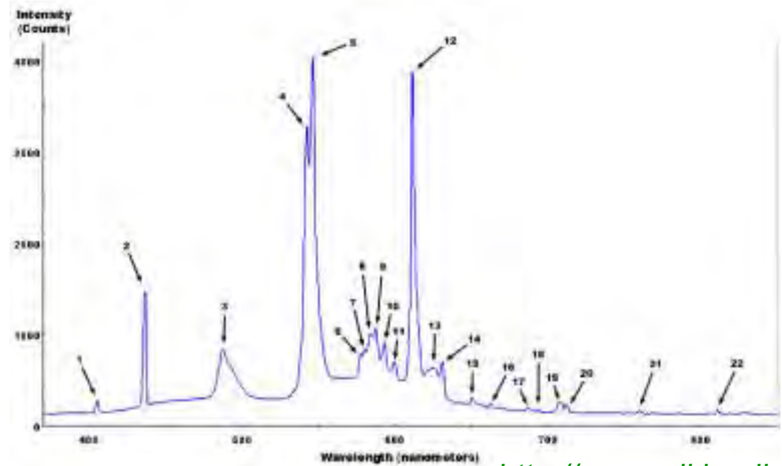
http://www.edmundoptics.com

UV Reactor RPR-100

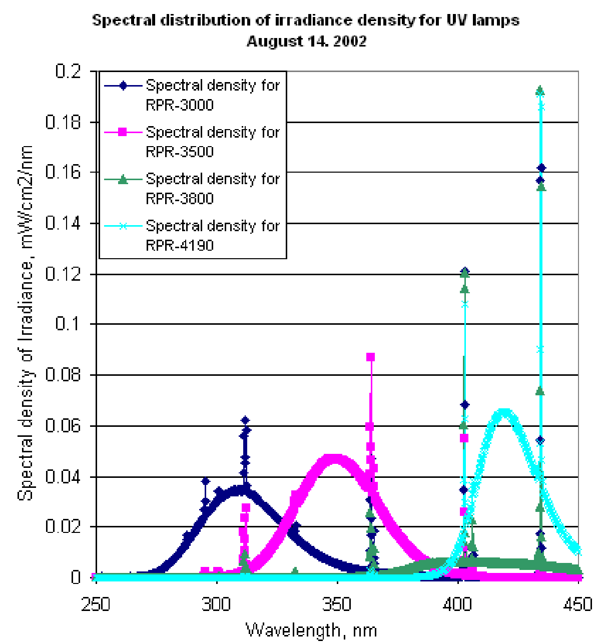
7 interchangeable light sources available
Output power
16-21 mW / cm^2 at 254 nm
0.27-0.35 mW/ cm^2 at 365 nm

http://www.rayonet.org/reactor.htm

Fluorescent lighting spectrum peaks



http://www.wikipedia.org



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LEDs for photochemistry

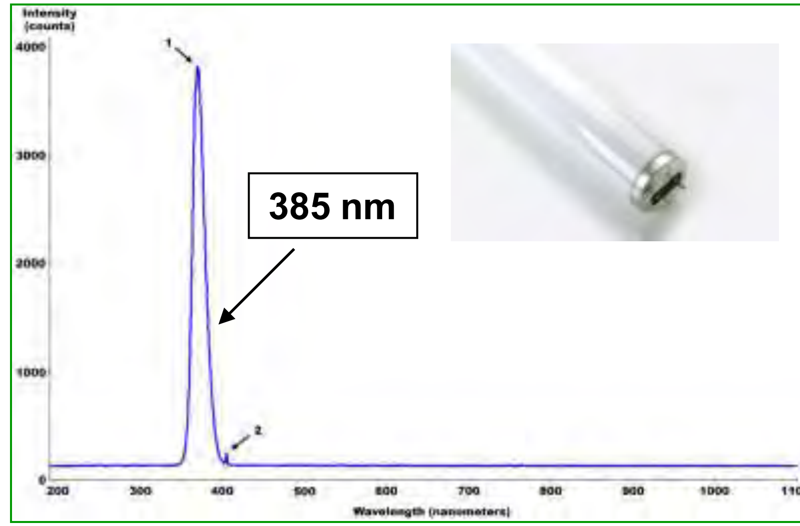
- Classical light sources
  - Fluorescent blacklight lamps

Spectrolinker XL-1500

6 15-watt 254 nm UV tubes
Typical Intensity
5.5-6.5 mW/cm^2 550$

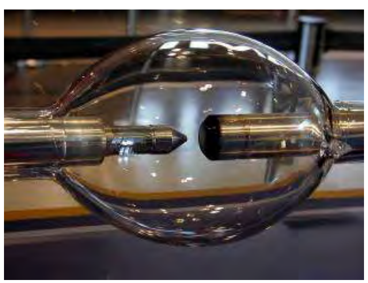
http://www.spectroline.com

Fluorescent Black-Light spectrum



http://www.wikipedia.org

  - HgXe short arc lamps



http://www.wikipedia.org

Disadvantages of classical UV sources

- **Complex spectra**
- **IR radiation**
  - **Heating (undesirable for photopolymerisations)**
- **Non collimated light**
- **Bulky**
- **Expensive (10^2-10^3$)**

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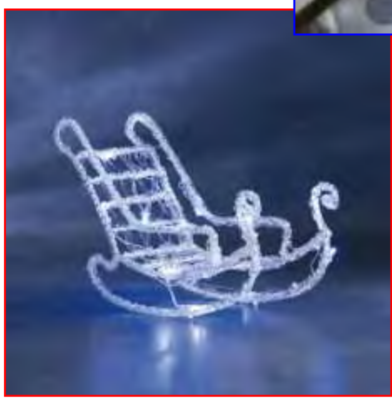
LEDs for photochemistry

- LED arrays ☺



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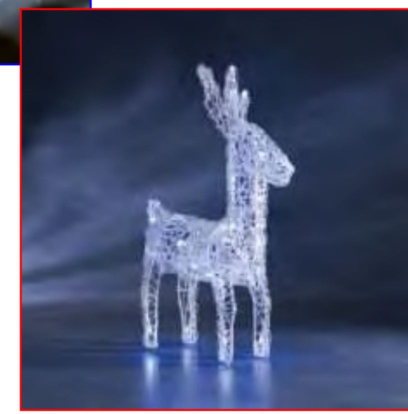

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www.lumitronix.de

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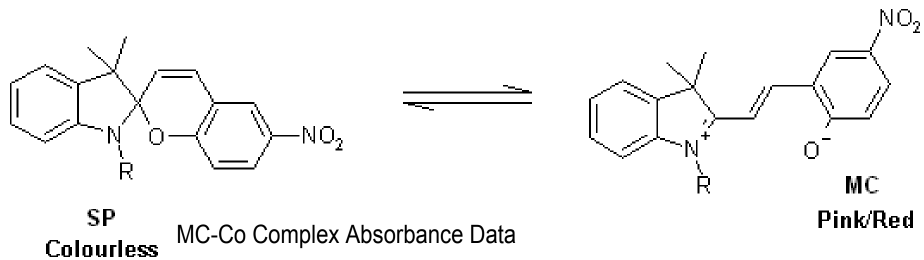
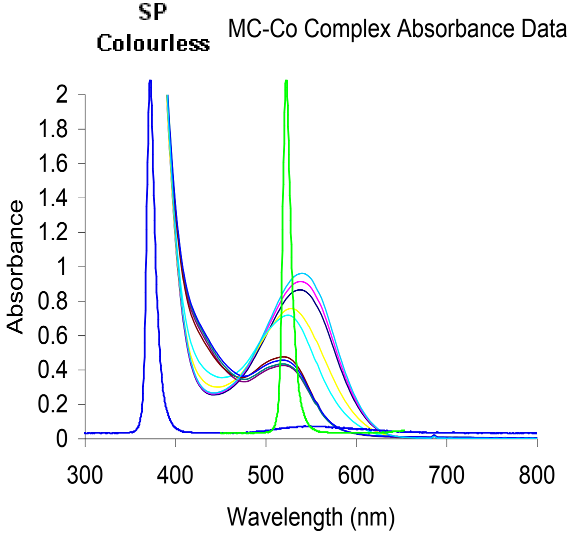
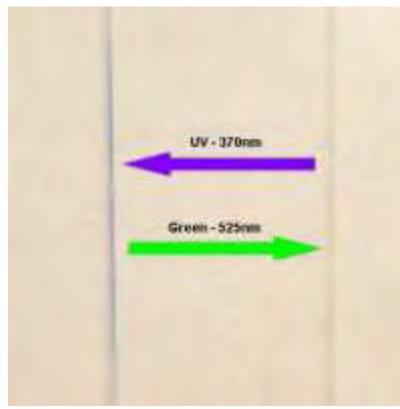
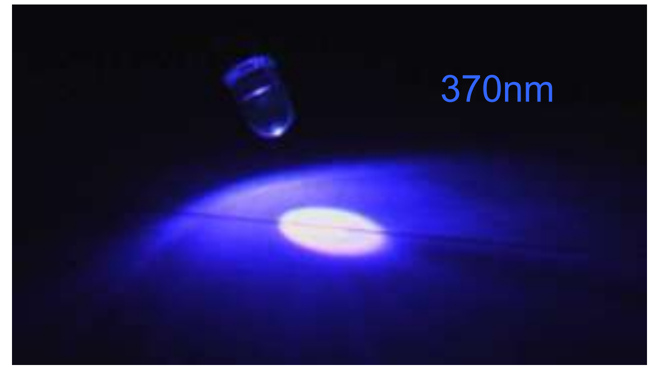
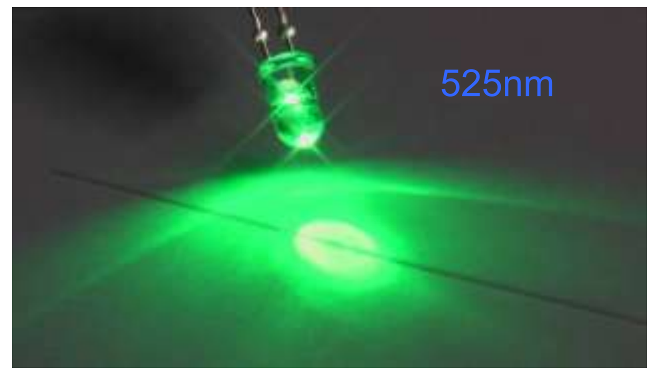
- LEDs in the photoswitching of photochromic molecules











Walsh Z., Connolly D., Abele S., Alhashimi N., Scarmagnani S., Paull B., Diamond D., Macka M., "Elution with light: Photochromic monolithic stationary phase with light switchable retention", Proc. 31st International Symposium on High Performance Liquid Phase Separations and Related Techniques – HPLC 2007, Gent, Belgium, 17 - 21 June 2007, poster presentation P01.19.

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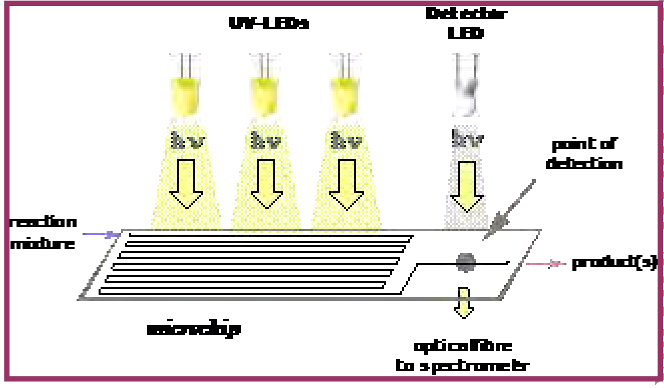
Micro-Photochemistry

- Micro-Photochemistry
  - Thin layers/films allow extensive penetration of light
  - Short residence times avoid decompositions
  - Automation and scale-up option
  - Reduction of waste and materials
  - Implementation of LEDs
  - Option of online monitoring (UV, IR)



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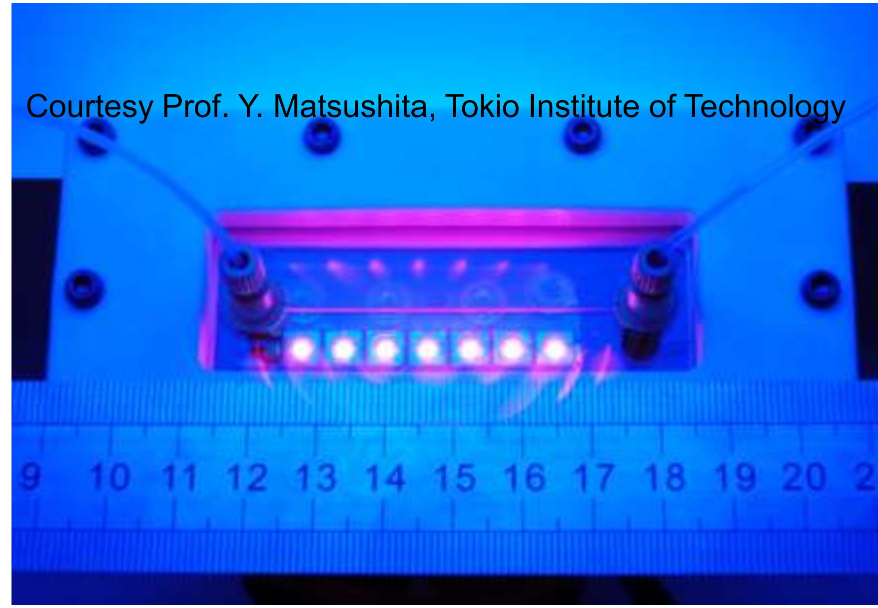
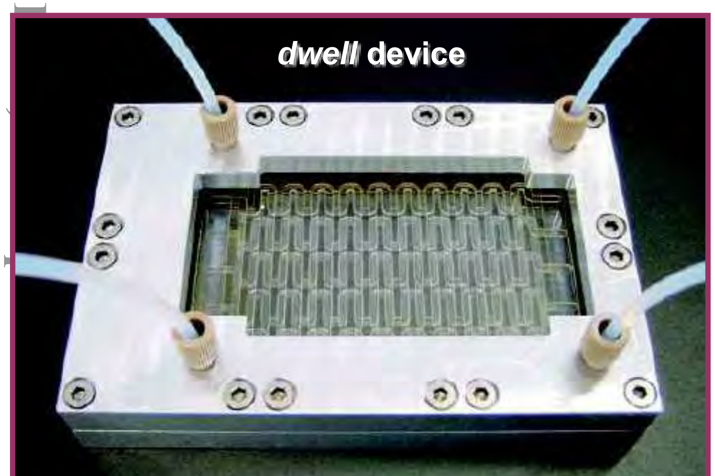
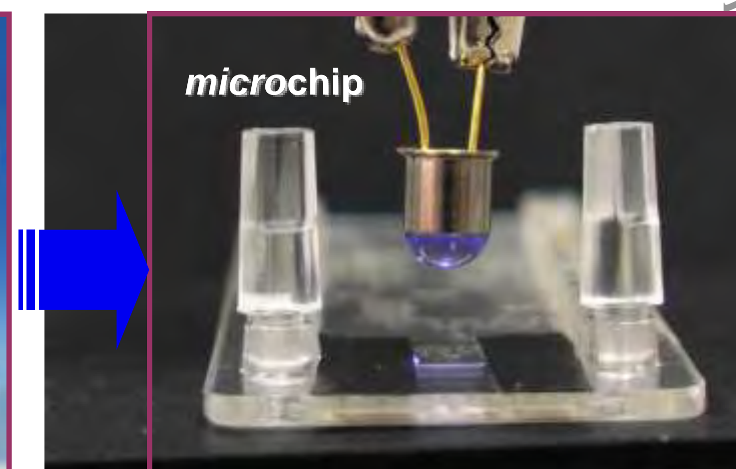
Micro-Photochemistry

- Reactors
  - Miniaturisation
  - Lab-on-chip microfluidic devices

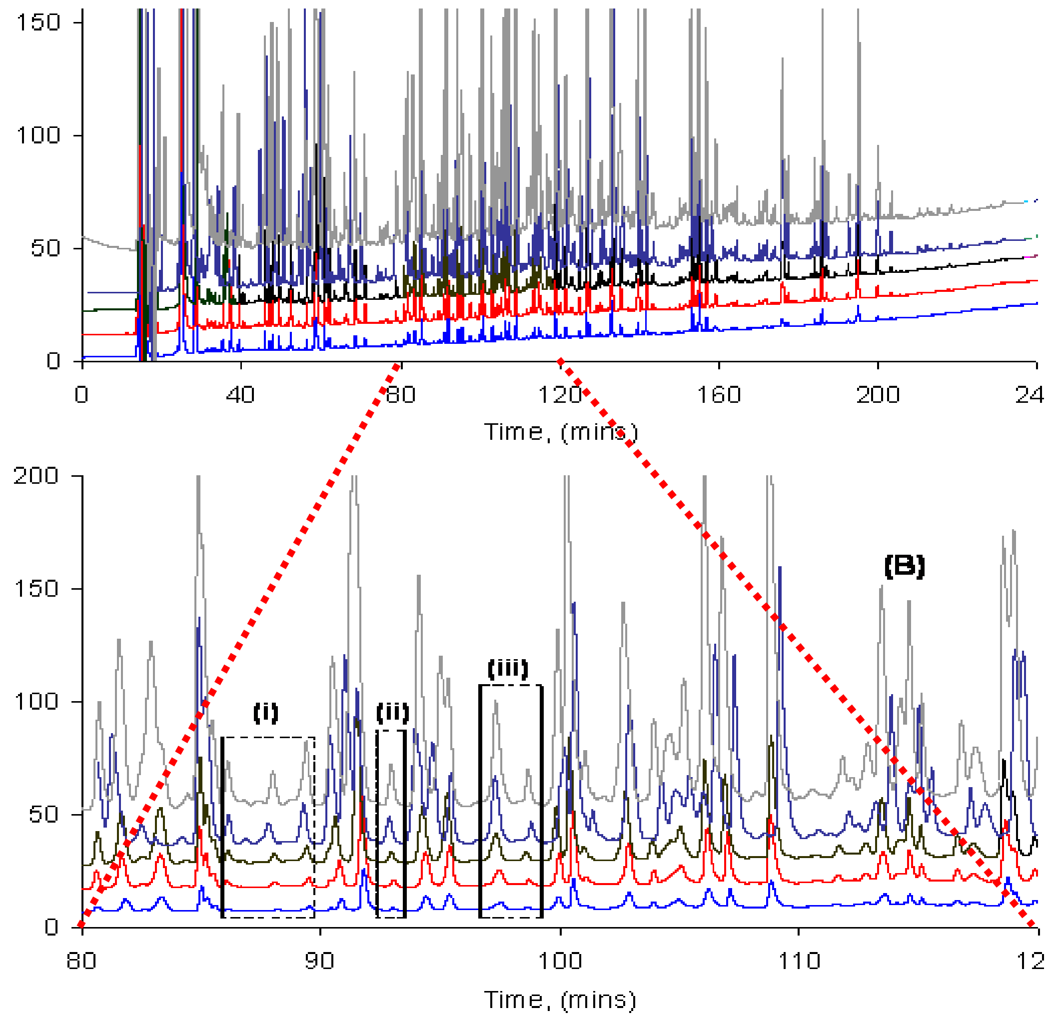






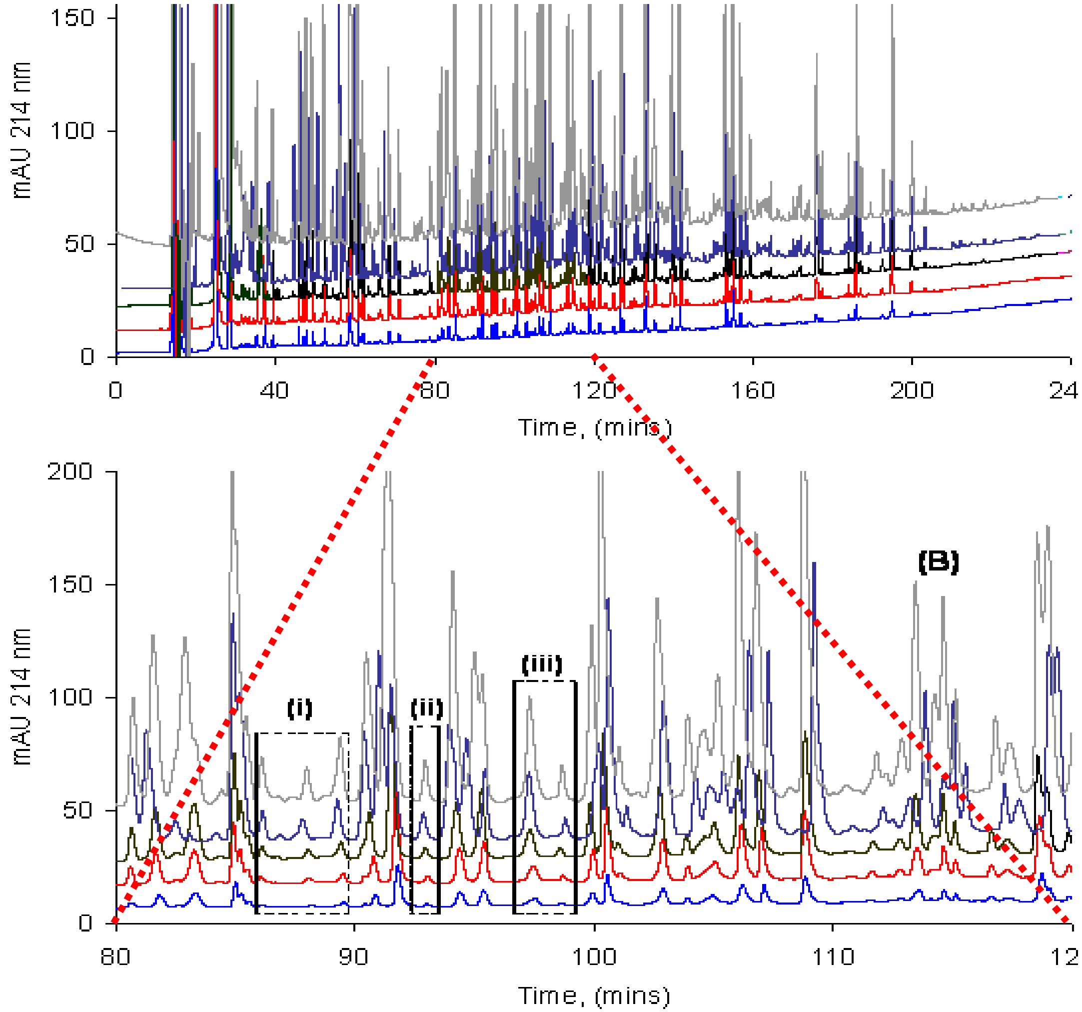
Monoliths: What for?

- What separation method is this?



Monoliths: What for?

- This might convince you:
  - 10 x 10 cm = 1m monolithic column
  - Peak capacity of 1180 in 290 min
  - Standard HPLC (not UHPLC!)



- Bones J., Duffy C., Macka M., Paull B., *Analyst*, 133(2), 180-183, **2008**

- Bones J., Duffy C., Macka M., Paull B., Pushing the boundaries in LC – high efficiency separations using meter long coupled monolithic silica columns in LC-ESI-MS, Proc. 31st International Symposium on High Performance Liquid Phase Separations and Related Techniques – HPLC 2007, Gent, Belgium, 17 - 21 June **2007**, poster presentation P03.23. **Chosen by a jury among the top 15 out of totally close to 900 posters**.

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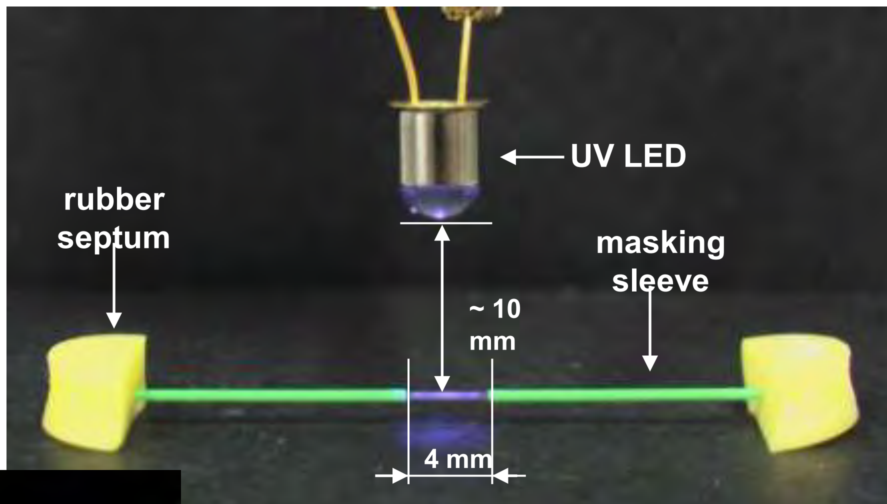
Monoliths: Synthesis with UV LEDs

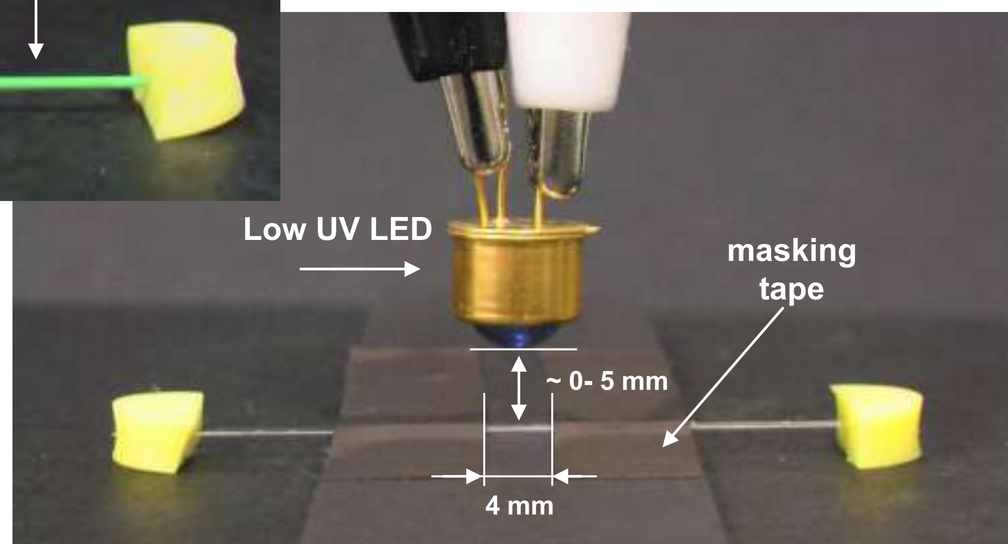
- UV-LED Photopolymerisations of monoliths
  - Transparent fused silica capillaries (100 µm i.d.)



High power UVLED365-10
365 nm
1.4 mW at 20 mA
Glass hemispherical lens
14$
http://www.roithner-laser.com

Optical micrograph of monolith in the channel of a microfluidic chip

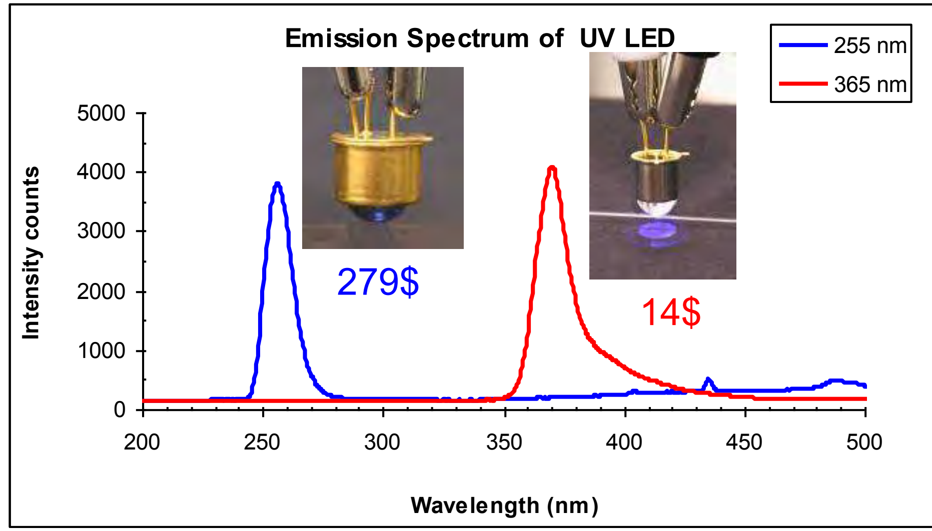
UVTOP255-HL-TO39
255 nm **+/- 5 nm**
0.5 mW 20 mA
Hemispherical lens (collimated light)
279$
http://www.s-et.com



Monoliths: Synthesis with UV LEDs

- LED Photopolymerisations
- UV LEDs

http://www.s-et.com
http://www.roithner-laser.com



- Advantages
  - **Emit cold light (no radiative heating)**
  - Compatible with miniaturisation
  - Long life time (10^5 h ~ 11 years)
  - Low costs (for well established LEDs)

http://www.wikipedia.org

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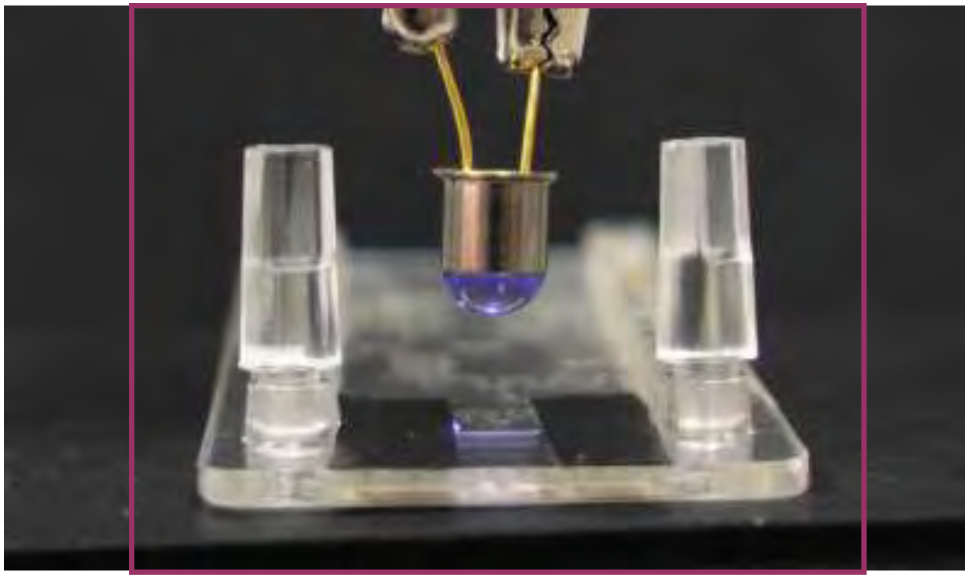
Monoliths: Synthesis with UV LEDs

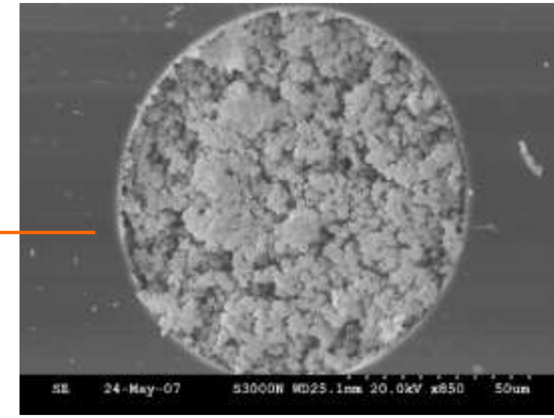
- Microfluidic chips – easily made in situ where needed
  - http://www.rsc.org/publishing/journals/AN/article.asp?doi=b802693a

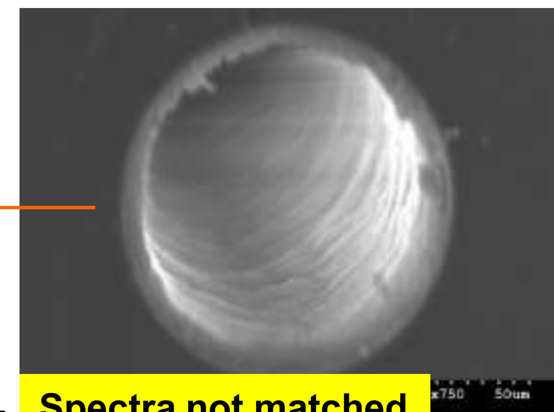


- Abele S., Nie F.-Q., Foret F., Paull B., Macka M., *Analyst*, 132, 864 - 866, **2008** (published on-line 18 Apr 2008, DOI:10.1039/B802693A)

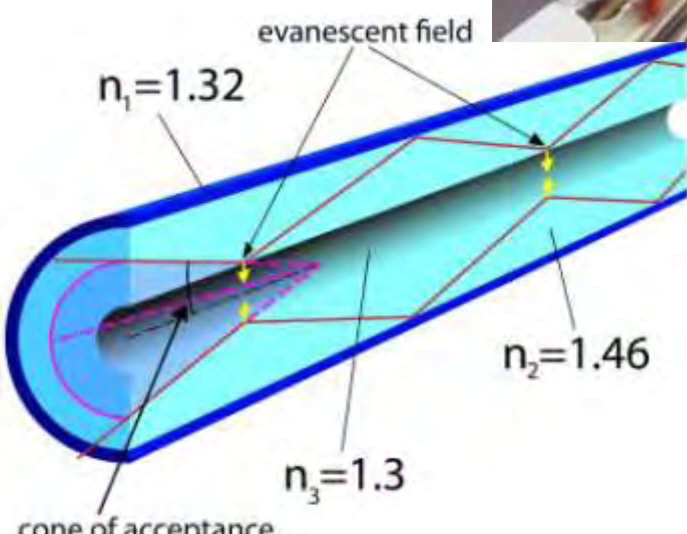
Evanescent wave photoinitiation

- Evanescent wave photoinitiation (EWP)
- EWP in transparent PTFE-coated fused silica capillaries





Spectra not matched



Conditions

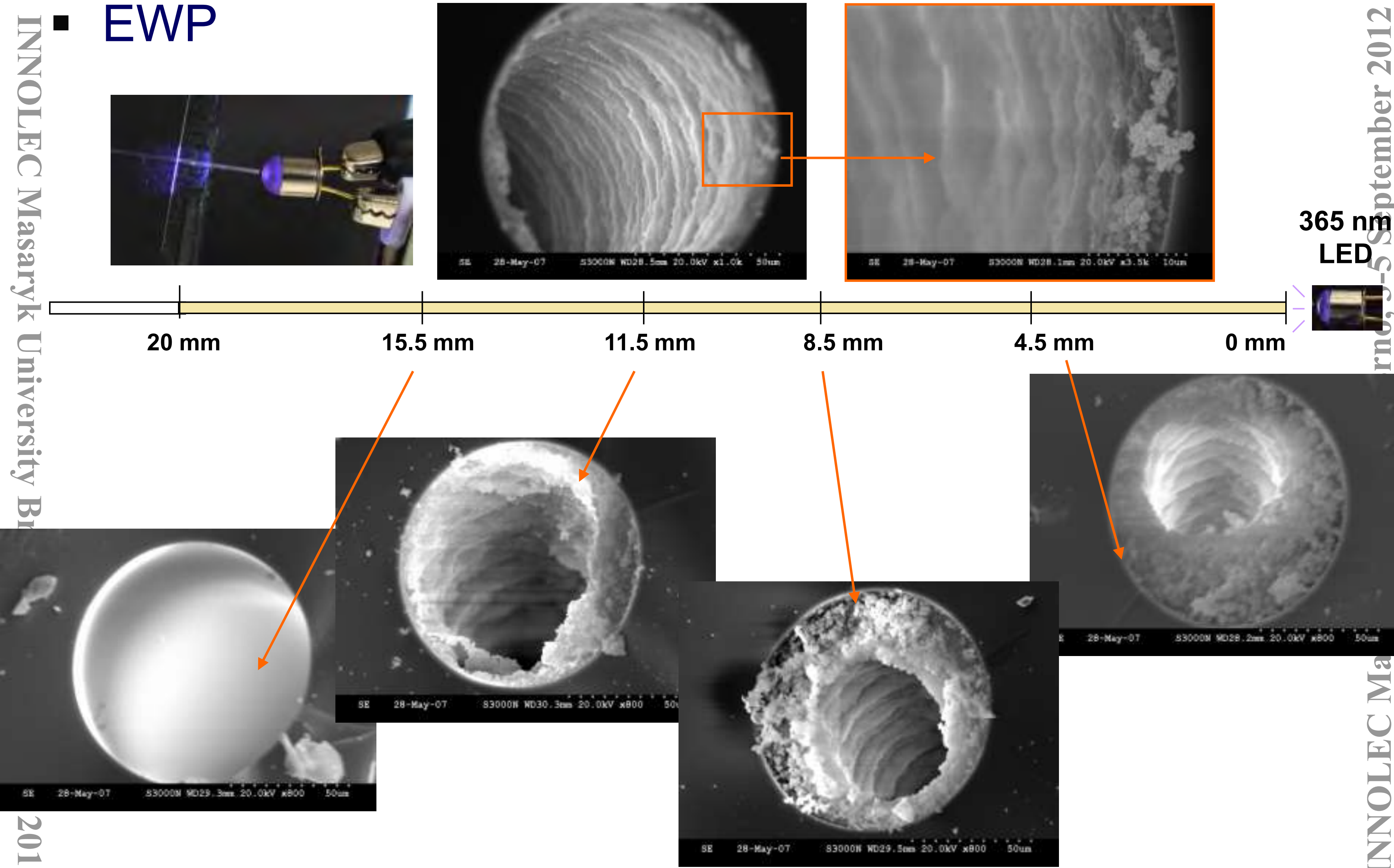
- initiator - **DAP**
- LED - **365 nm**
- polymerisation time 15 min

Results

5 cm of capillary filled with polymer, but top end is whiter, bottom end – paler (polymer only around the wall proved by SEM)

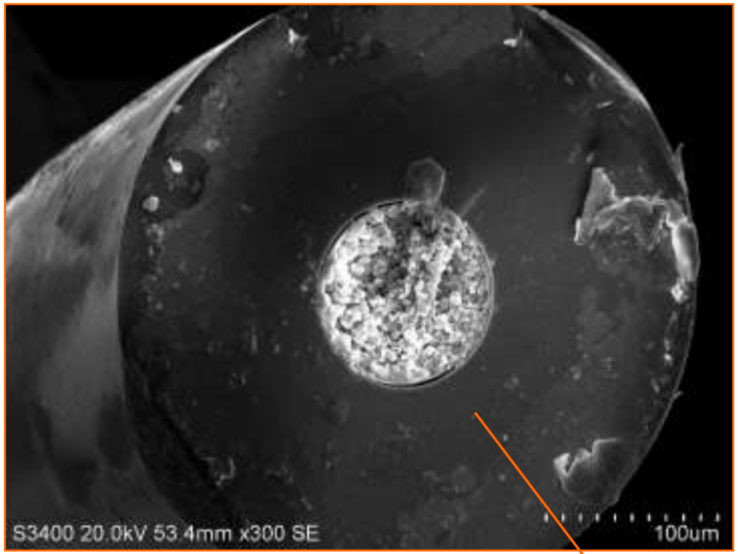
Evanescent wave photoinitiation

- EWP



Evanescent wave photoinitiation

- EWP in transparent PTFE-coated fused silica capillaries



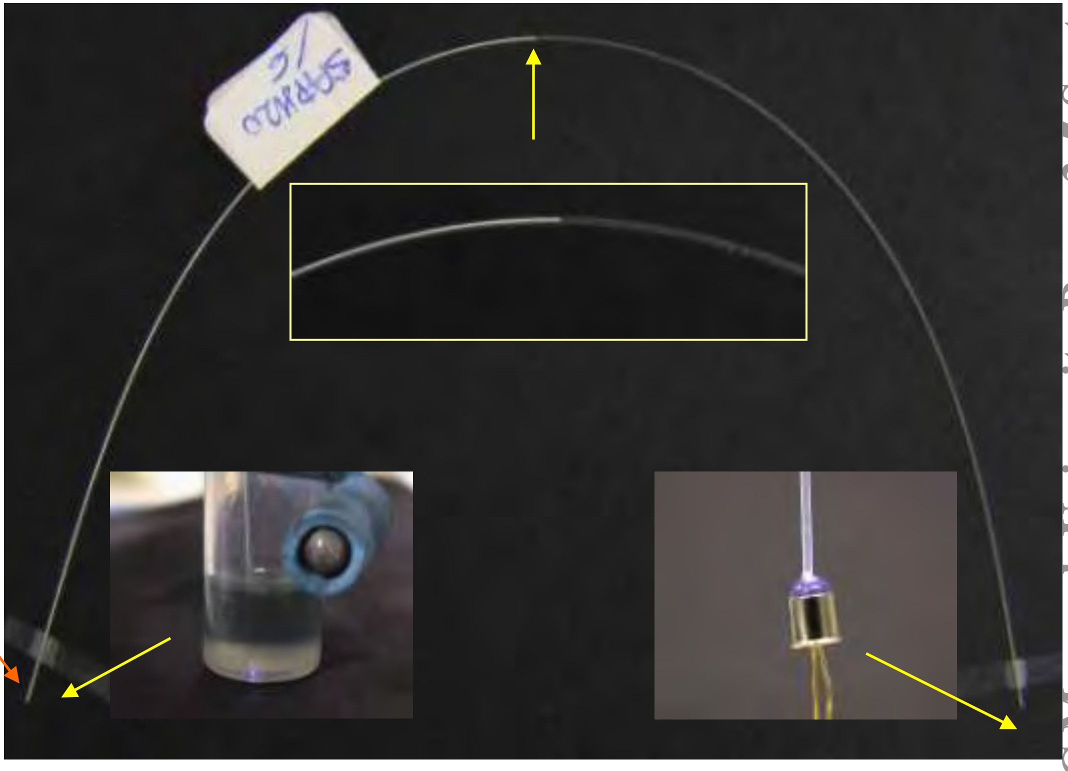
- SEM sample 6 mm from solution end
- No good attachment of monolith to the capillary walls as capillary not silanised

Polymerisation conditions

385 nm LED, 20 mA, 65 h

24 cm non silanised capillary

Experimental setup



Result

12.2 cm of monolith formed

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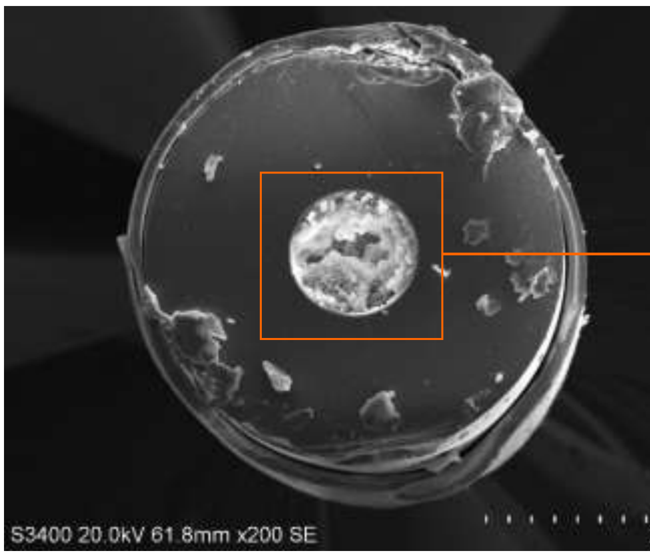
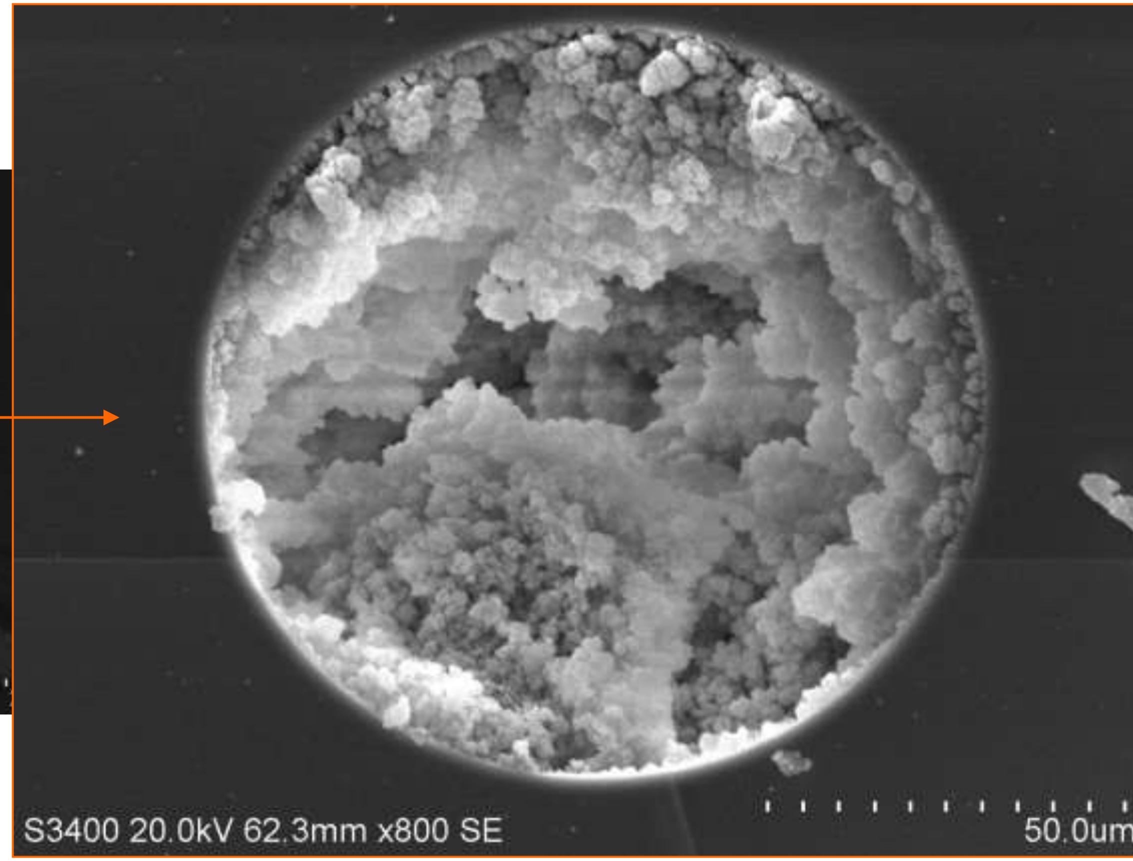
Evanescent wave photoinitiation

- EWP in transparent PTFE-coated fused silica capillaries



SEM sample 10 mm from solution end



<u>Polymerisation conditions</u>

365 nm LED, 30 mA, 5 h

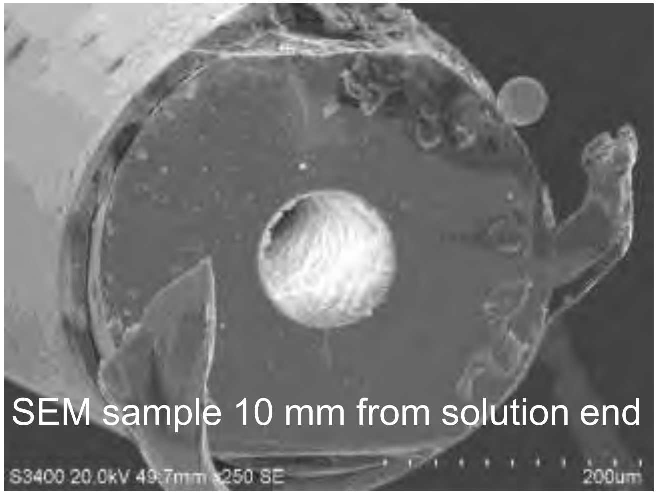
9.2 cm silanised capillary

<u>Result</u>

8 cm monolith formed

Evanescent wave photoinitiation

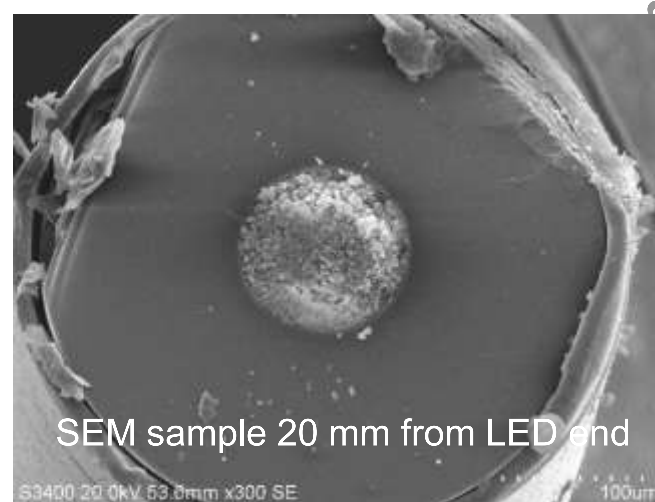
- EWP in fused silica capillaries



SEM sample 10 mm from solution end

385 nm LED, 40 mA, 4.5 h
27 cm silanised capillary

2.7 cm monolith formed



SEM sample 20 mm from LED end

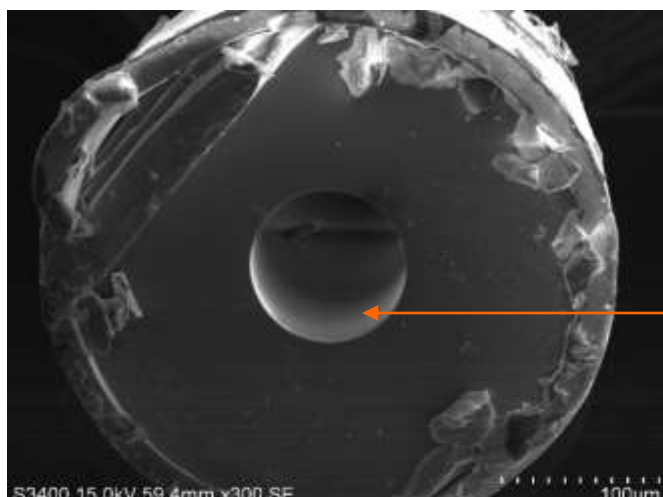
365 nm LED, 30 mA, 5 h
9.2 cm silanised capillary

monolith formed in all length

- PI-coated

Polyimide coated FS capillary
385 nm LED, 40 mA, 23 h

monolith not formed



EWP not observed in Polyimide coated FS capillaries

Monolith not formed

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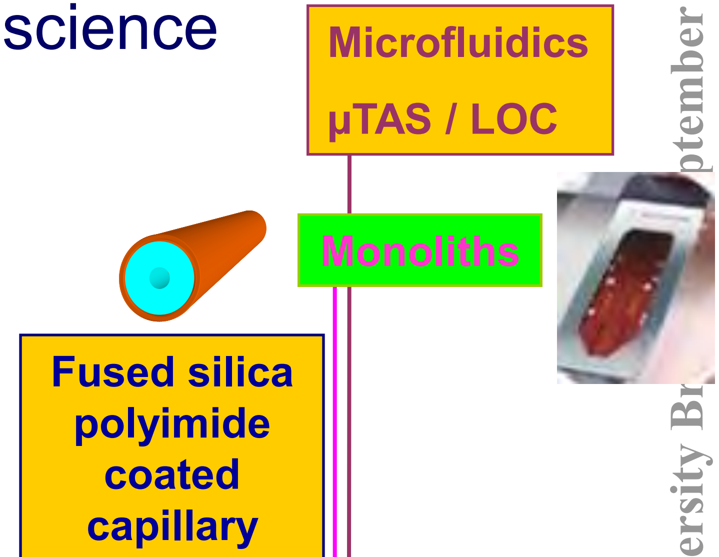
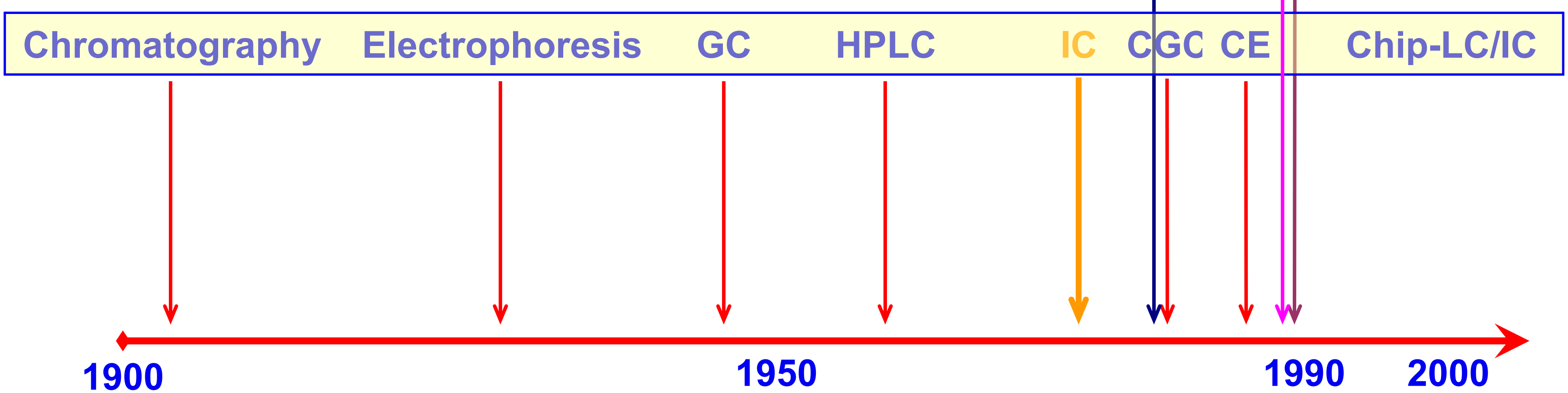
Red-LED photoinitiation in polyimide..

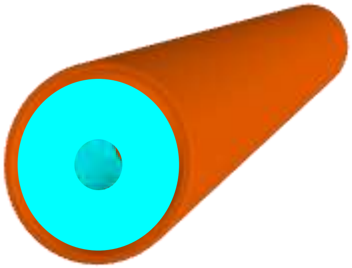
- Why to bother with polyimide (PI)?
  - Major achievements in separation science
    - Concepts
    - Technologies
  - Fused silica polyimide (PI) coated capillary: a major technology breakthrough
    - Dandeneau, R. D., Zerenner, E. H., *HRC&CC*, 2, 351-356, **1979**

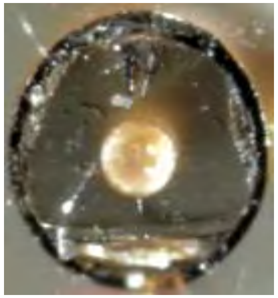




Why capillaries?

- Fused silica polyimide coated capillary
  - PI-coated FS is a well-established technology
    - Introduced for capillary GC in 1979
      - Dandeneau, R. D., Zerenner, E. H., HRC&CC 2(6), (1979) 351-356
  - Column format for GC, CE and (most of) nano-LC
  - Extremely strong & durable
  - FS transparent from UV to NIR





http://www.polymicro.com

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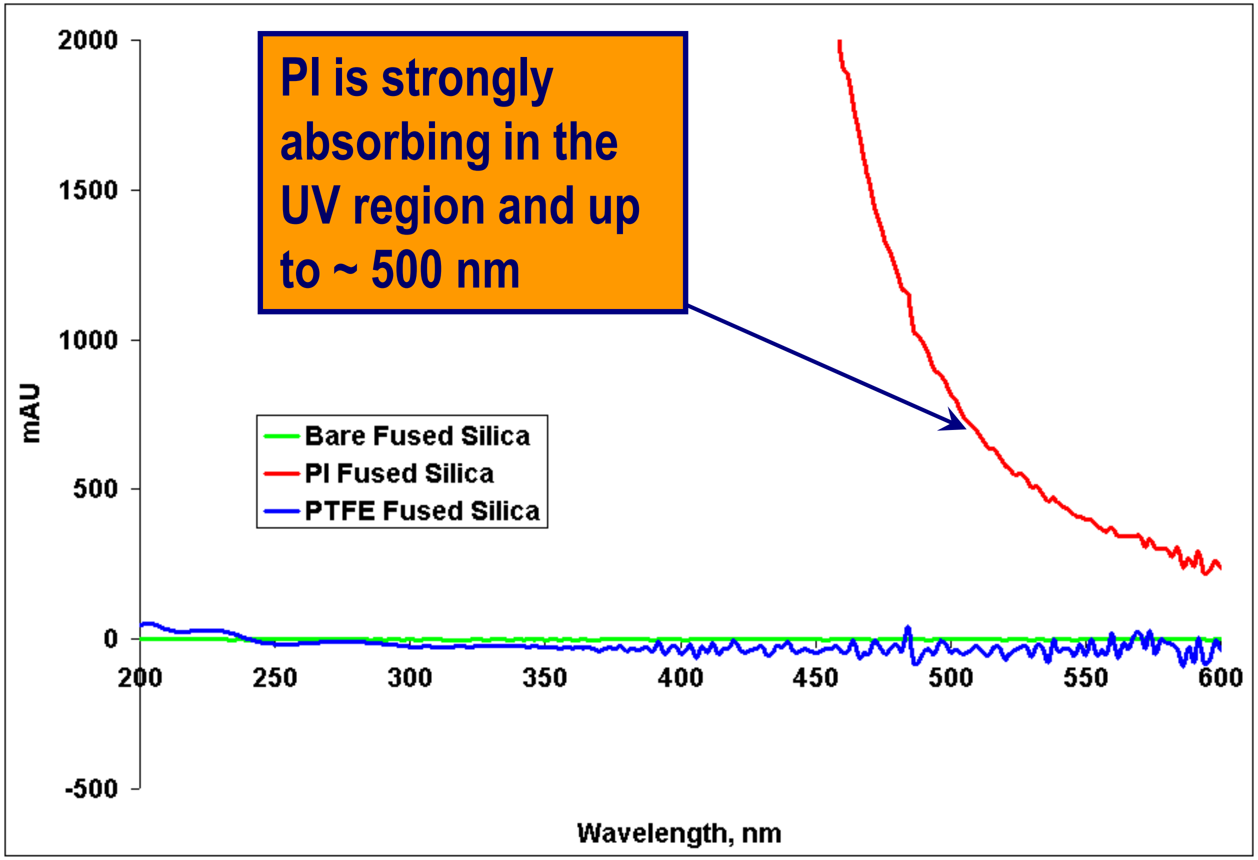
Red-LED photoinitiation in polyimide..

- Photoinitiated polymerisation in PI?



Zarah Walsh, Silvija Abele, Brian Lawless, Dominik Heger, Petr Klán, Michael C. Breadmore, Brett Paull, Mirek Macka, Photo-initiated Polymerisation of Monolithic Stationary Phases Using Visible Region LEDs, *Chem. Commun., (48)*, 6504 – 6506, **2008**, DOI: 10.1039/B816958F (published on-line 7 Nov 2008)

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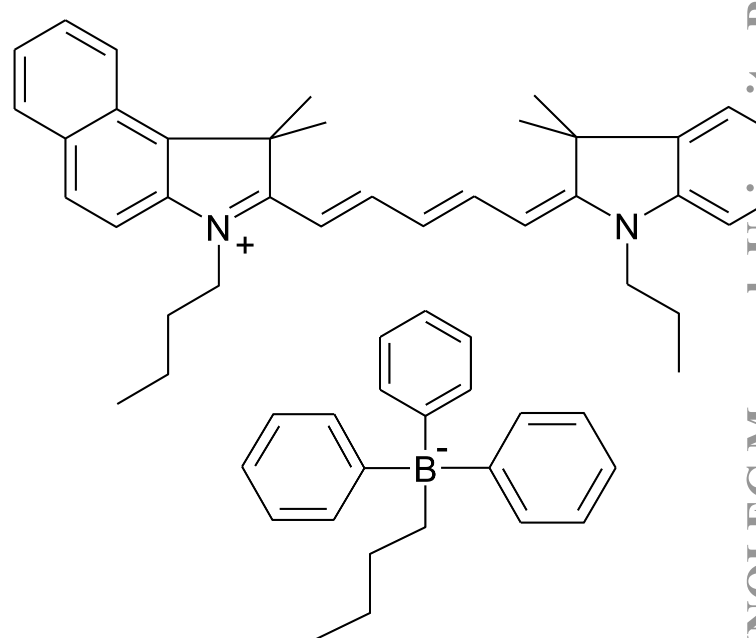
Red-LED photoinitiation in polyimide..

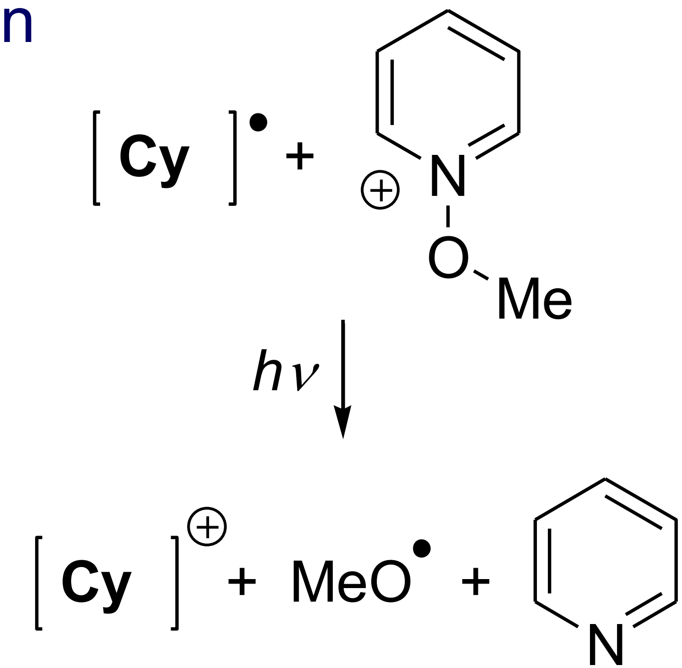
- So how can it be done??
  - Use an initiator absorbing in the vis-region > 550 nm
  - Cyanine dye absorbing light at 660 nm:
    - 3-butyl-2-[1,3-dihydro-3,3-dimethyl-1-propyl-2H-indolylidene)-penta-1,3-dienyl]-1,1-dimethyl-1H-benzo[e]indolium butyl triphenyl borate (HNB 660)
  - Use a matching light source @ 660 nm
    - 660 nm ultrabright LED
    - **LEDs are ‘cold’ light sources**



Zarah Walsh, Silvija Abele, Brian Lawless, Dominik Heger, Petr Klán, Michael C. Breadmore, Brett Paull, Mirek Macka, Photo-initiated Polymerisation of Monolithic Stationary Phases Using Visible Region LEDs, *Chem. Commun., (48)*, 6504 – 6506, **2008**, DOI: 10.1039/B816958F (published on-line 7 Nov 2008)

Red-LED photoinitiation in polyimide..

- Adding a second radical species
  - Cyanine-borate + Alkoxyphenylpyridinium salt
  - As reported by Kabatc et al, generation of two radical species significantly increases rate of polymerisation
  - Polymerisation time 30-40 min



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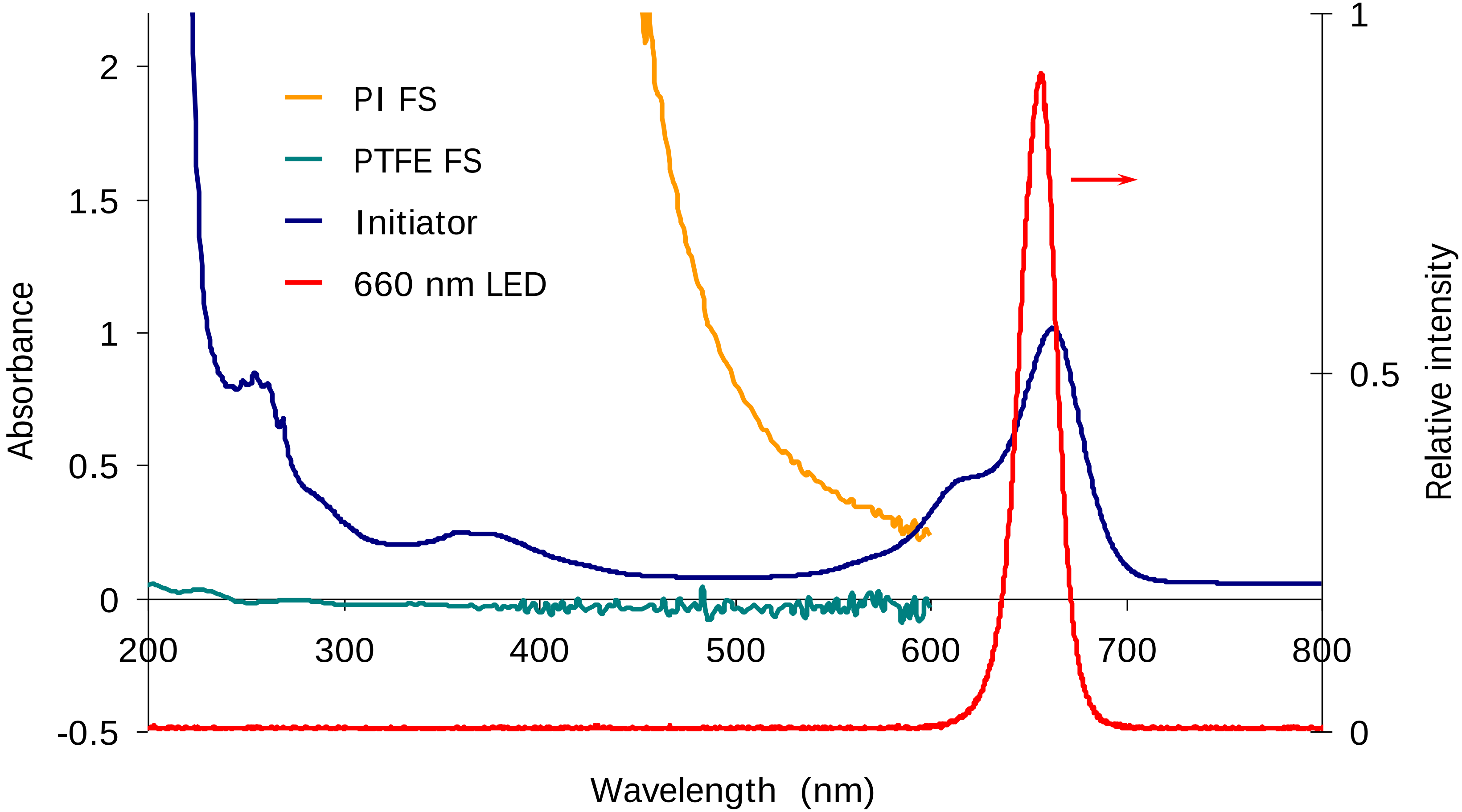
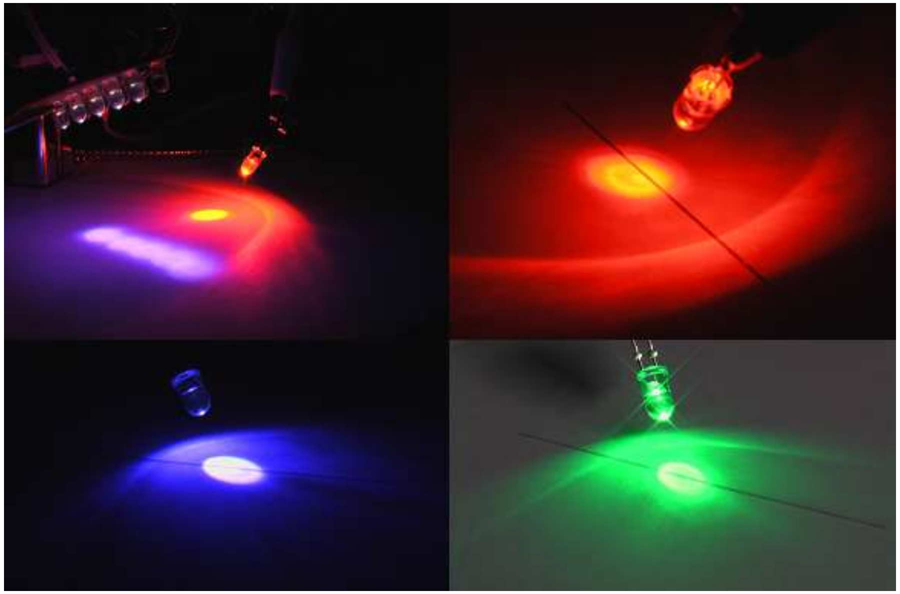
Red-LED photoinitiation in polyimide..

- Spectra of initiator and light source:
  - Red LED (660 nm)



Red-LED photoinitiation in polyimide..

- LED as the light source
  - LEDs are used instead of conventional high-power light sources to aid the decomposition of the initiators to free radicals
  - LEDs are used as they are
    - Quasi-monochromatic
    - Cheap
    - Robust
    - Long life
    - **'Cold' light sources**



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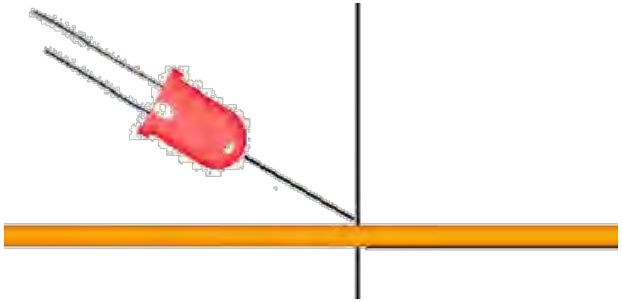
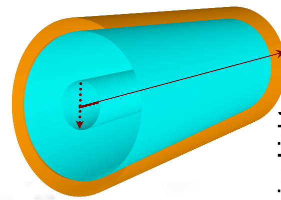
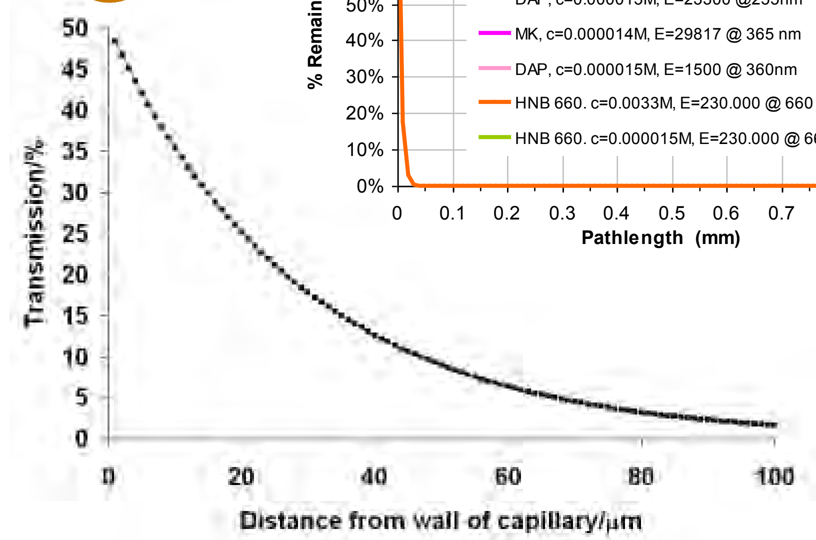
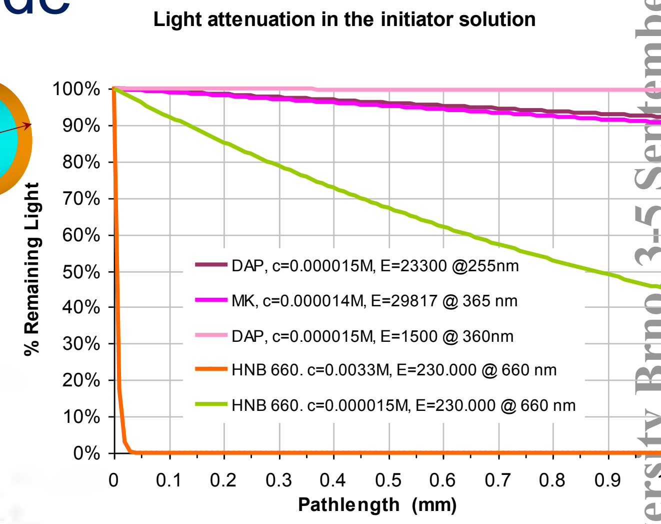
Red-LED photoinitiation in polyimide..

- Light transmission and homogeneity
  - More polymer formed on the LED side
  - Light attenuation
  - Irradiation under an angle





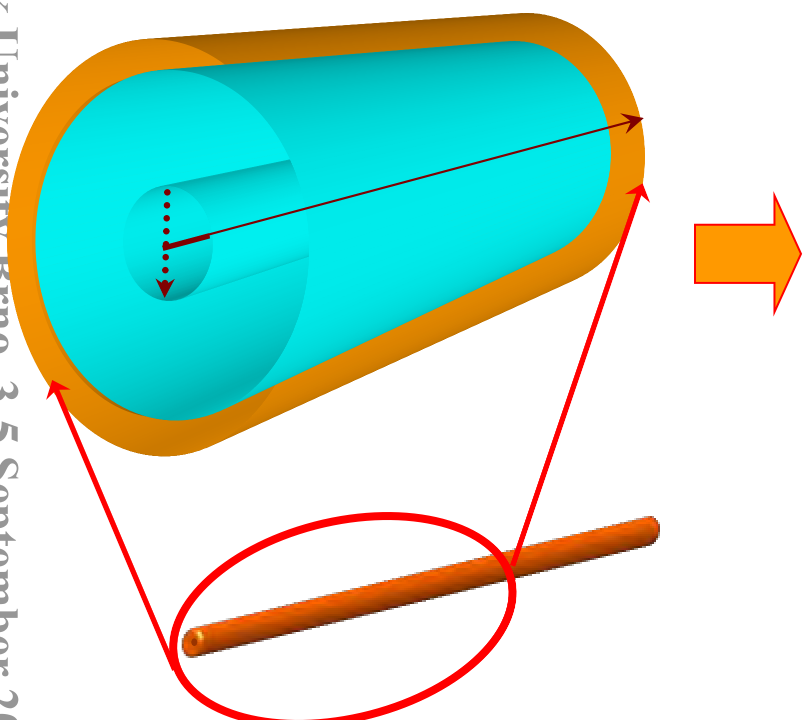


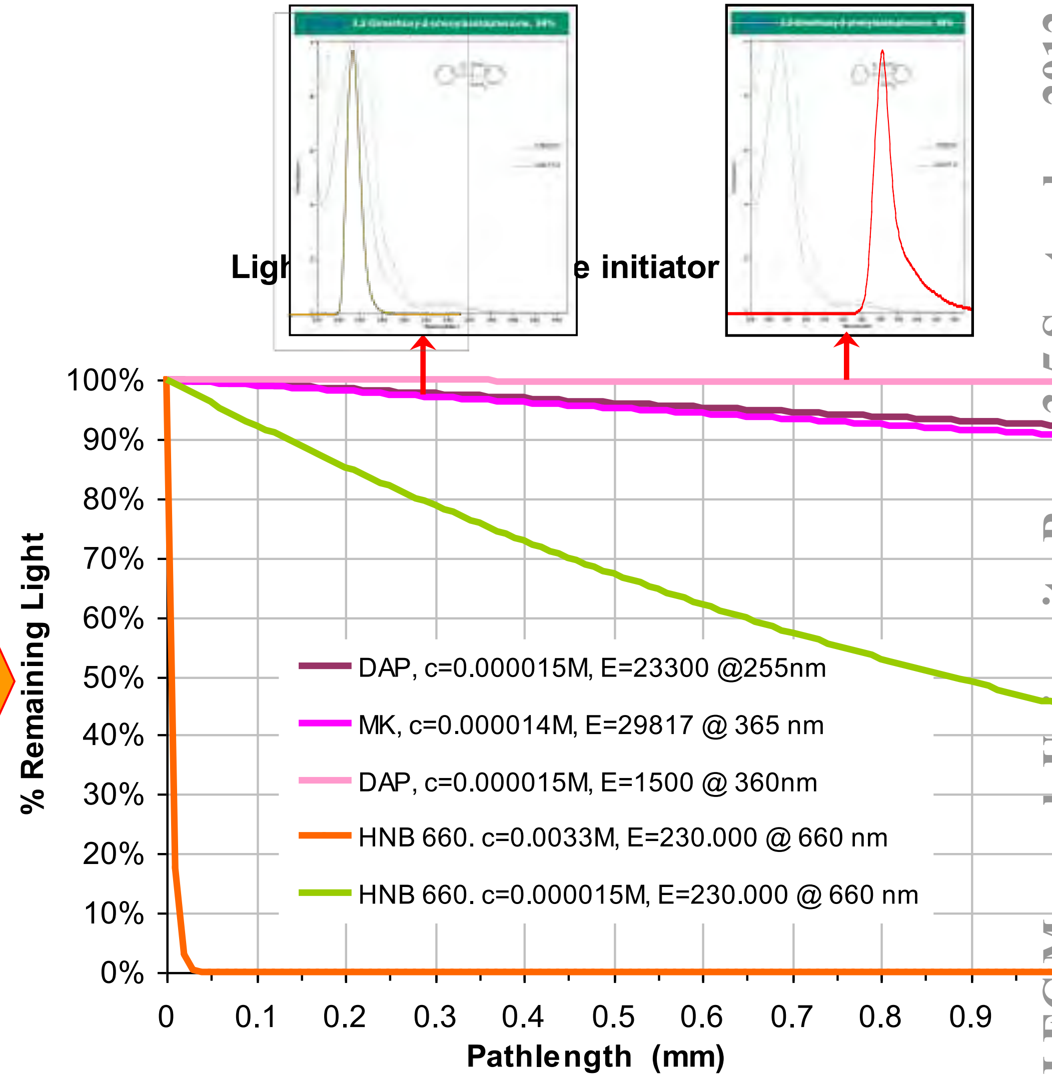


  - Rotating the capillary during polymerisation → a more homogeneous monolith

Red-LED photoinitiation in polyimide..

- Photochemistry
- Light attenuation
  - Due to absorption by initiator





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Red-LED photoinitiation in polyimide..

- Light transmission and homogeneity
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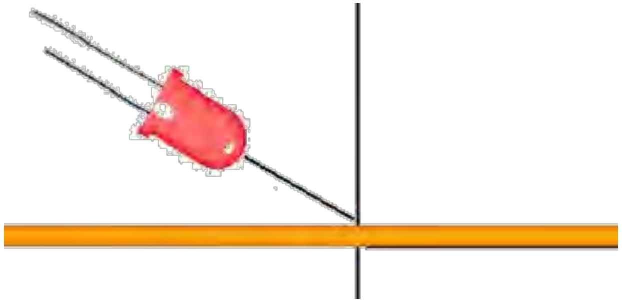

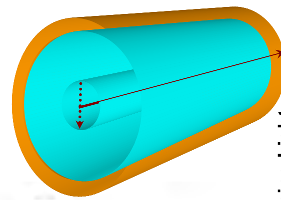

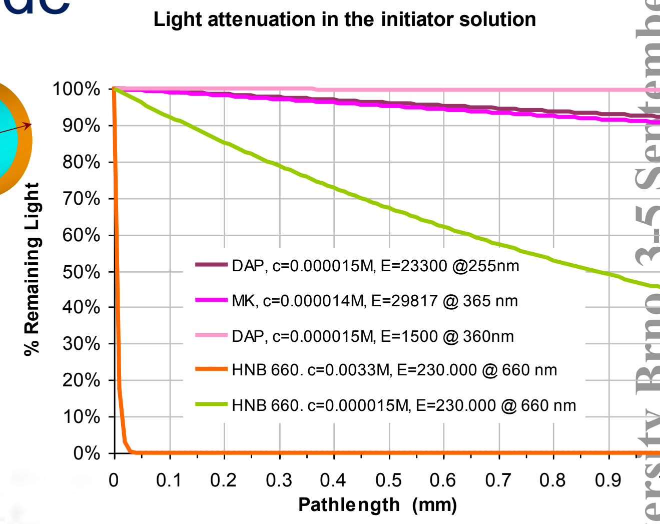

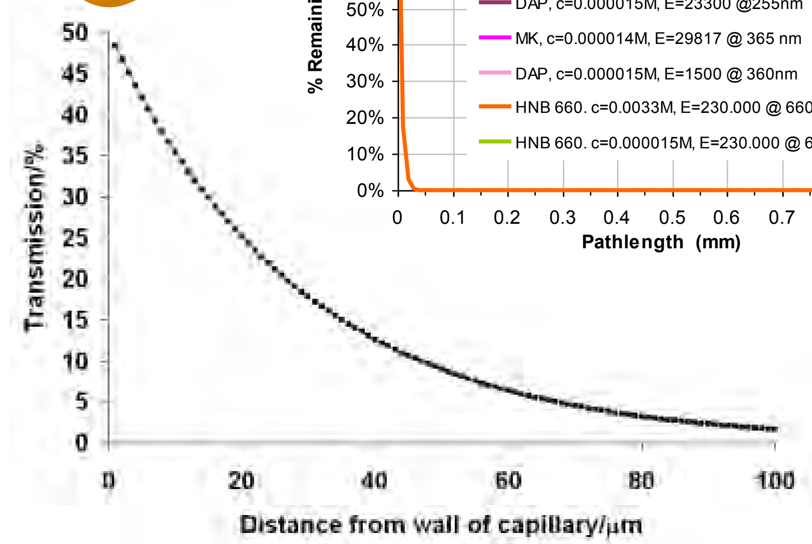

  - Rotating the capillary during polymerisation → a more homogeneous monolith

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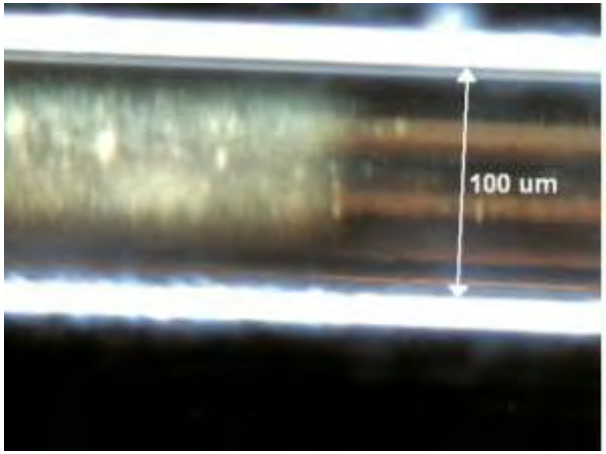
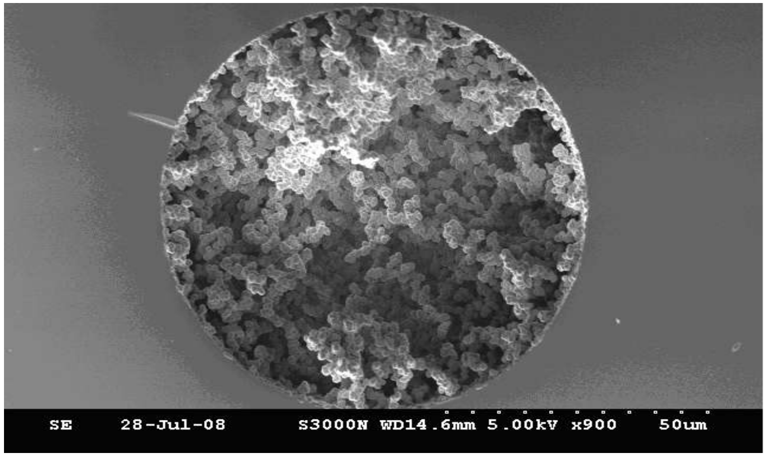
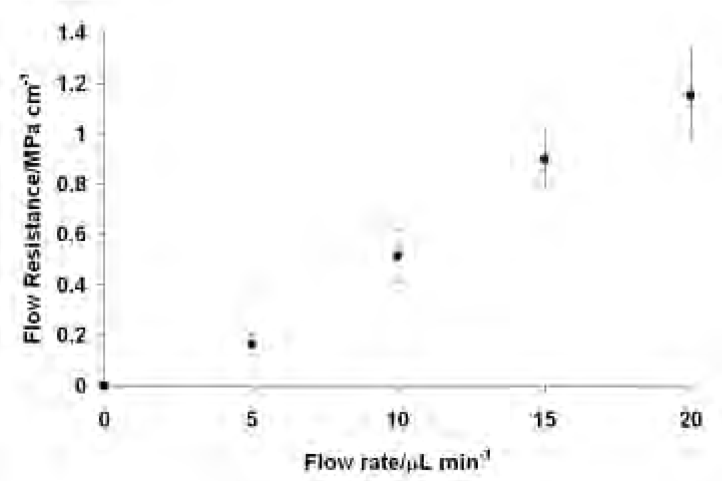
Red-LED photoinitiation in polyimide..

- Characterisation of the monolith





- The images show
  - Fills the capillary well
  - Is attached to the walls
  - Does not have diffuse ends
- The backpressure plot
  - A high permeability



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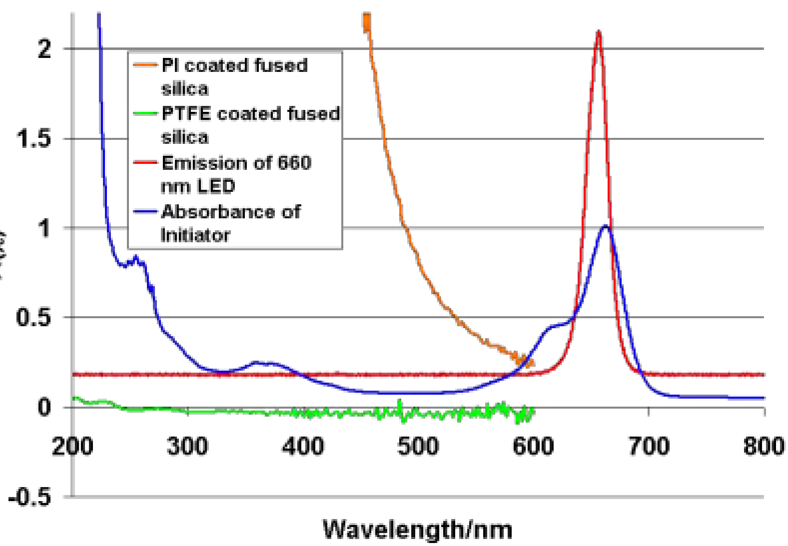
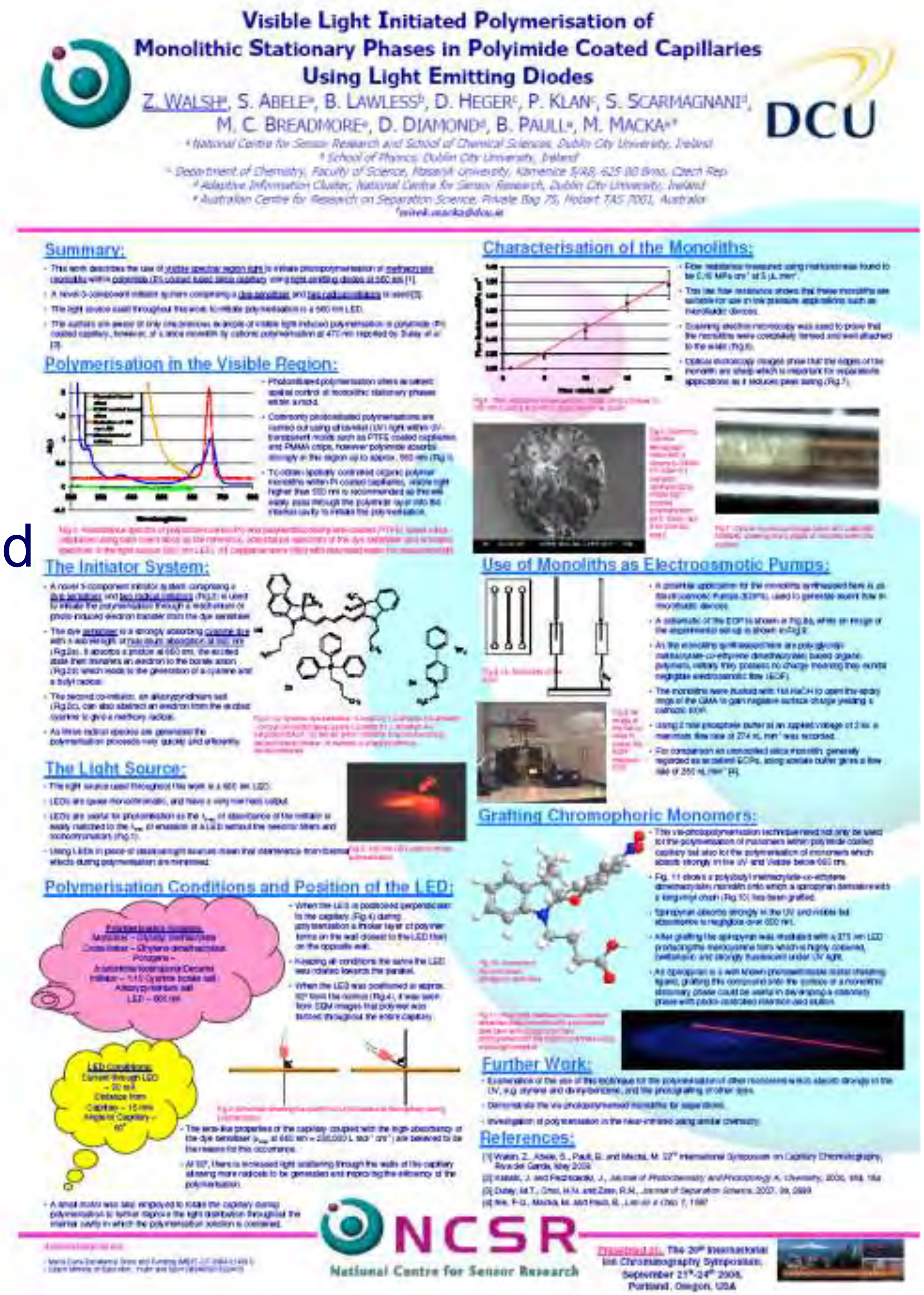
Vis-polymerisation

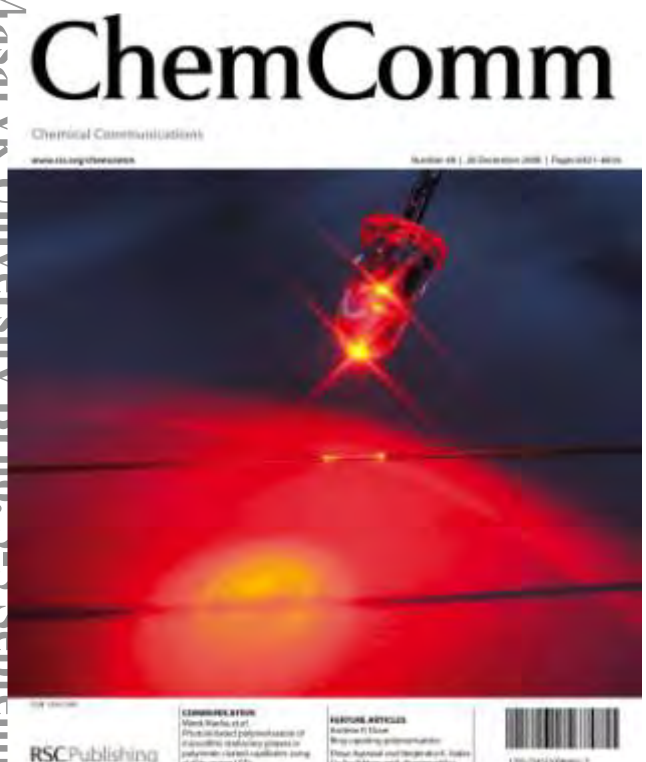
- Polyimide transparent above ~550 nm
  - UV photolymerisations not possible
  - Blue sensitizer dye for red LED photopolymerised monoliths in PI-FS





Red-LED photoinitiation in polyimide..

- "Photoinitiated polymerisation of monolithic stationary phases in polyimide coated capillaries using visible region LEDs"




Chemical Communications RSC Publishing

Photoinitiated polymerisation of monolithic stationary phases in polyimide coated capillaries using visible region LEDs

Zarah Walsh[a], Silvija Abele[a], Brian Lawless[a], Dominik Heger[c], Petr Klán[c], Michael C. Breadmore[d], Brett Paull[a] and Mirek Macka*[d]
[a]National Centre for Sensor Research and School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland.
[b]School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland
[c]Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5/A8, 625 00 Brno, Czech Republic
[d]Australian Centre for Research on Separation Science, Private Bag 75, Hobart TAS 7001, Australia

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First published on the web 7th November 2008

The spatially controlled synthesis of poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolithic stationary phases in polyimide coated fused silica capillaries by visible light induced radical polymerisation using a three-component initiator and a 660 nm light emitting diode (LED) as a light source is presented here.

Since the synthesis of the first organic monolith was reported by Svec and Fréchet in 1992, monolithic stationary phases have been recognised as one of most innovative developments since the conception of chromatography by Tswet in the early 1900s. Initiation by heat and ultraviolet (UV) radiation are the most common methods of inducing polymerisation, while other methods such as initiation by microwaves, γ-radiation and electron beam have been reported more recently. Photoinitiation is of particular interest as it is an excellent method of achieving sharp plugs of monolith in a specific location within a mold in a short amount of time.

Zarah Walsh, Silvija Abele, Brian Lawless, Dominik Heger, Petr Klán, Michael C. Breadmore, Brett Paull, Mirek Macka, Photo-initiated Polymerisation of Monolithic Stationary Phases Using Visible Region LEDs, *Chem. Commun., (48)*, 6504 – 6506, **2008**, DOI: 10.1039/B816958F (published on-line 7 Nov 2008)

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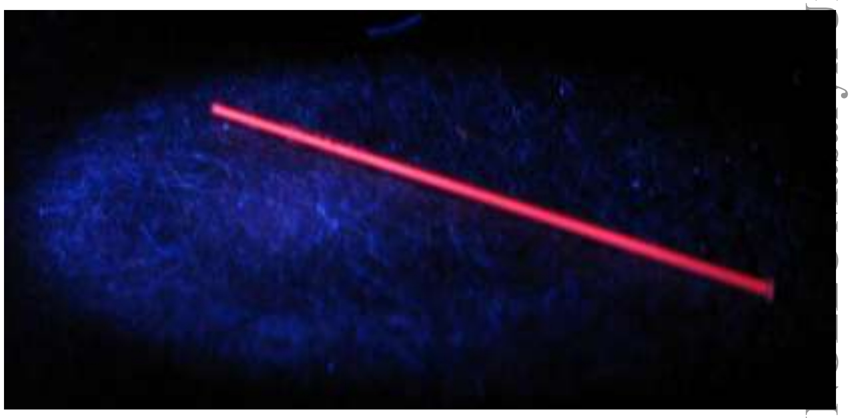
Red-LED photoinitiation in polyimide..

- Where do we go from here?
  - Applications of the visible light initiation method
    - Polyimide (coated) capillaries and chips
      - Monoliths as chromatographic/SPE columns
      - Monoliths as electroosmotic pumps
    - For highly absorbing monomers (e.g. UV absorbing)
    - To graft highly absorbing chromophoric monomers
      - Example

Monomeric spiropyran grafted onto the channels of a poly(butyl methacrylate-co-ethylene dimethacrylate) monolith



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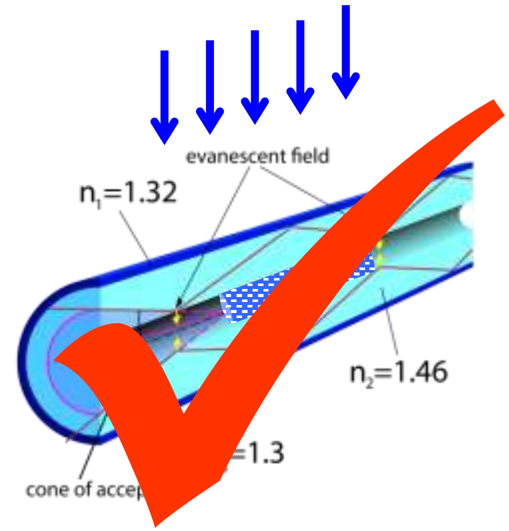
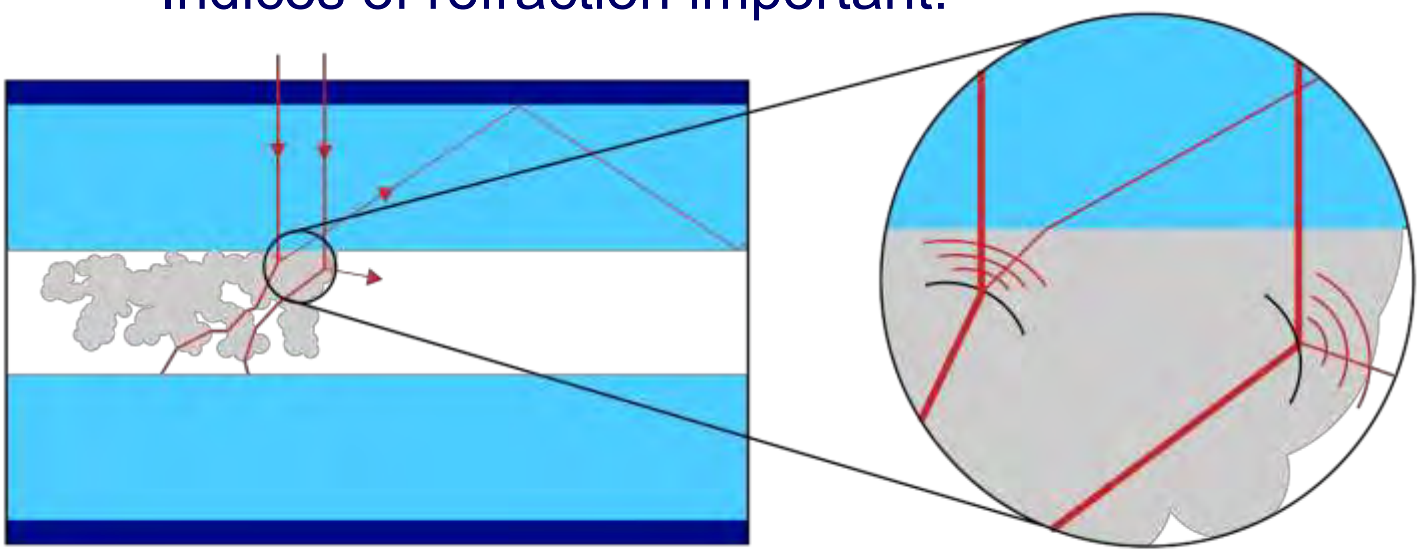
Red-LED photoinitiation in polyimide..

- Another reason why is PI good:
- Light waveguiding in PTFE coated FS
  - Monolith produces scattered light
  - This light can enter the fused silica capillary under an angle allowing waveguiding
    - Indices of refraction important!





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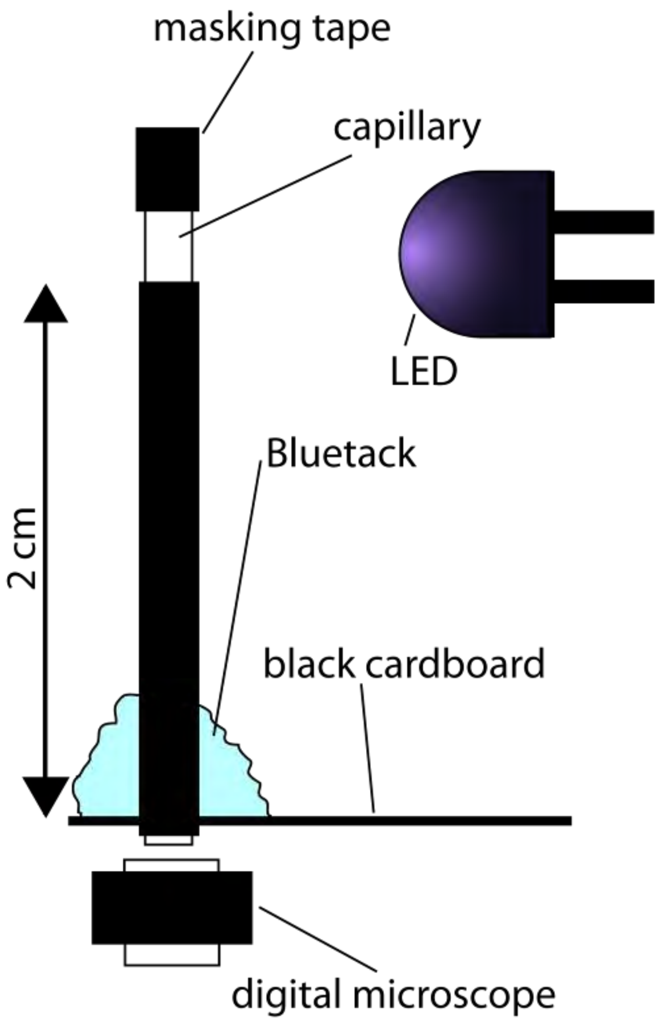
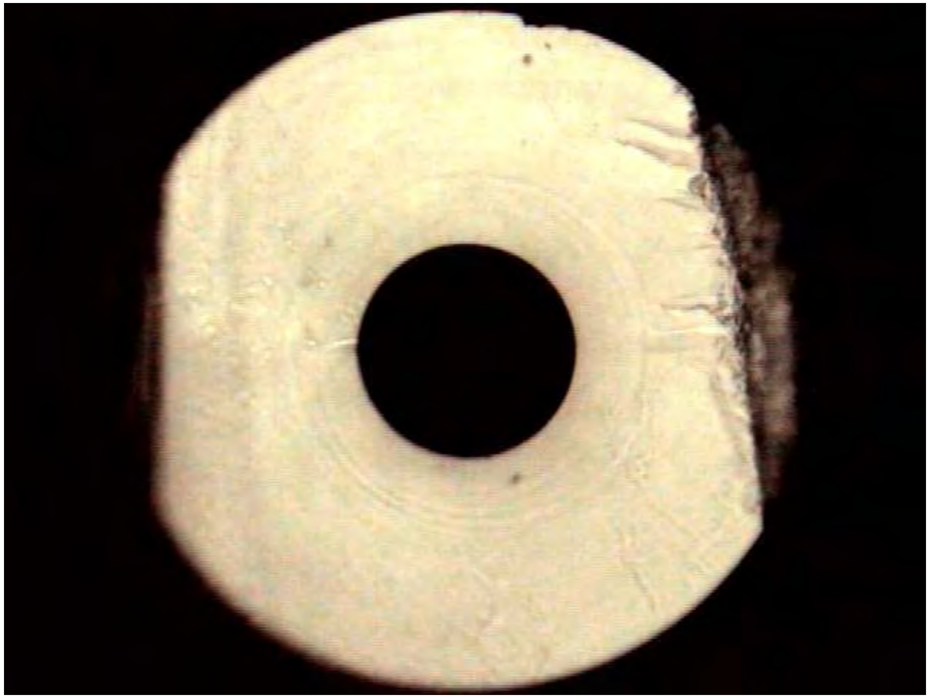
Geometrical optics

- Monolith causes waveguiding through fused silica





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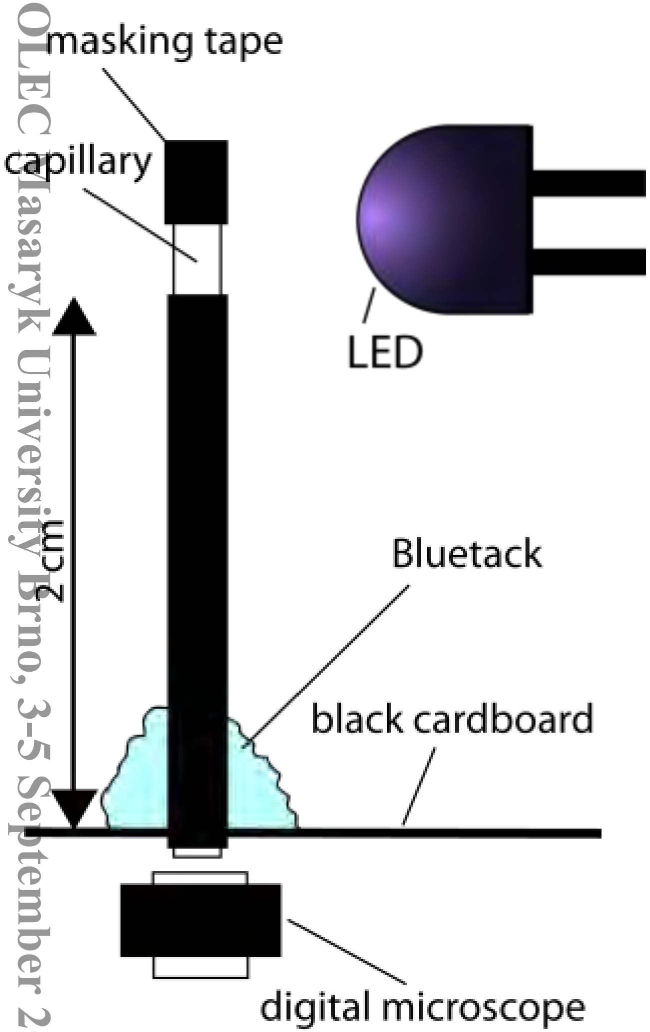
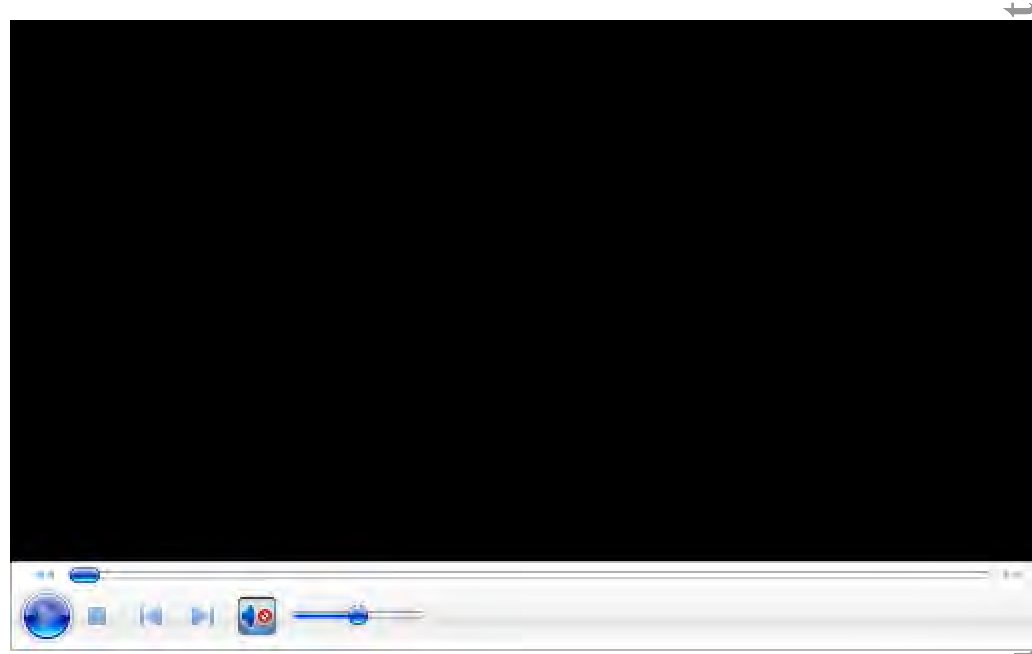
Geometrical optics

- Monolith causes waveguiding through fused silica

ANIMATED





Geometrical optics considerations

- Monolith causes waveguiding through fused silica

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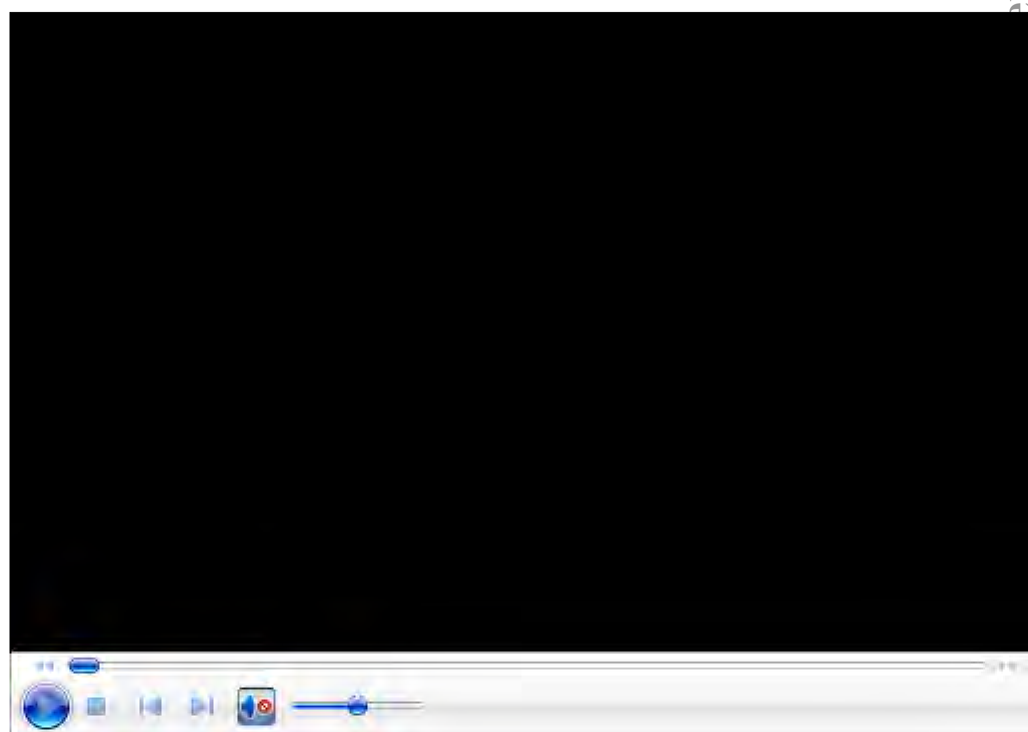
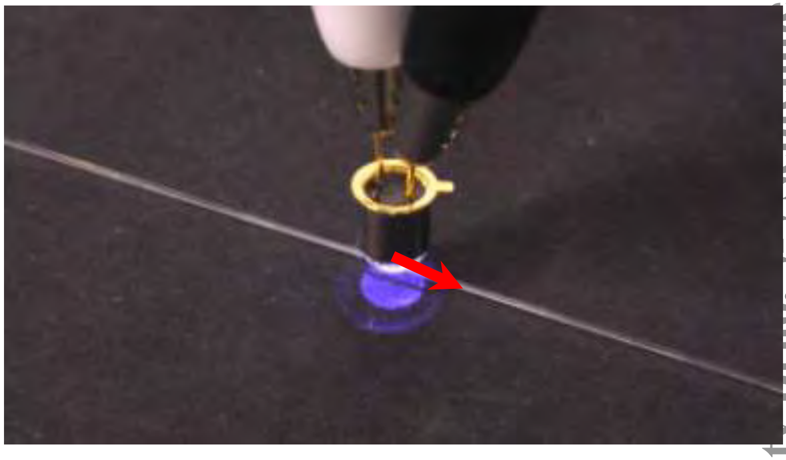
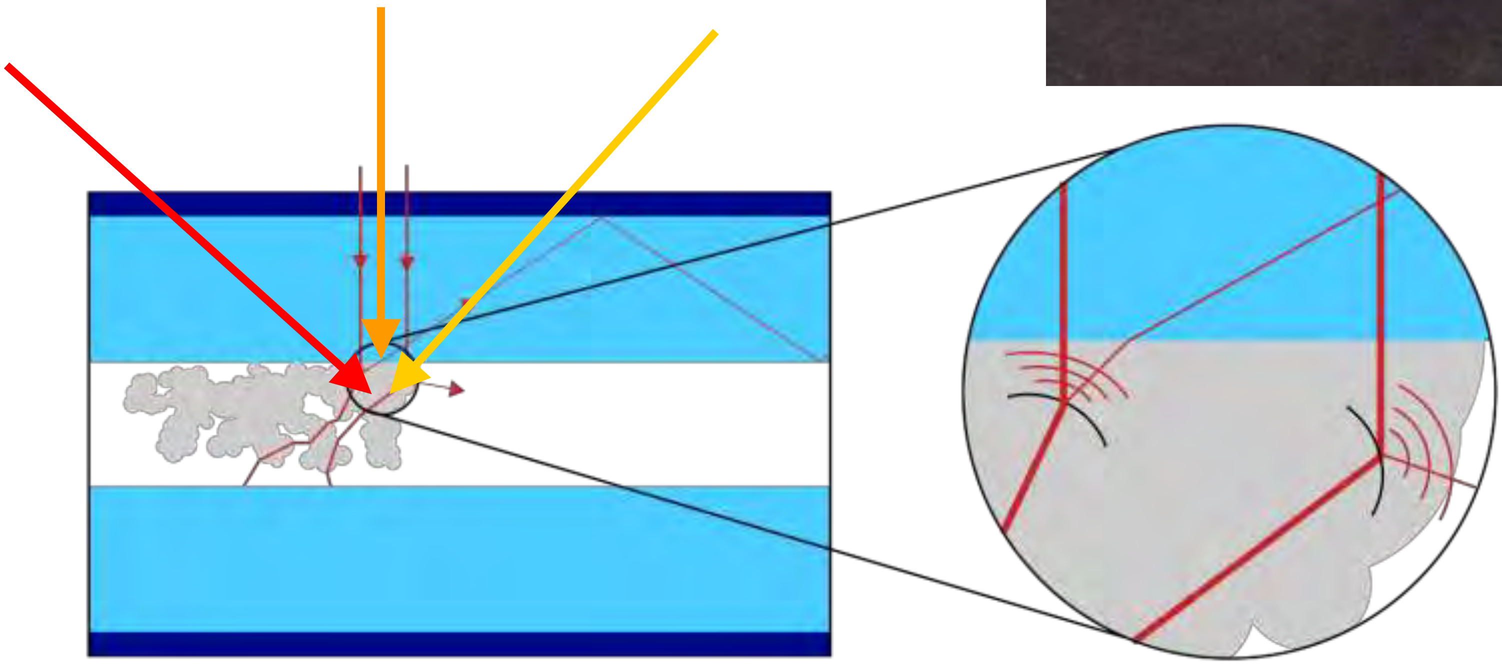


Red-LED photoinitiation in polyimide..

- Light scattering & waveguiding
  - Incident light angle





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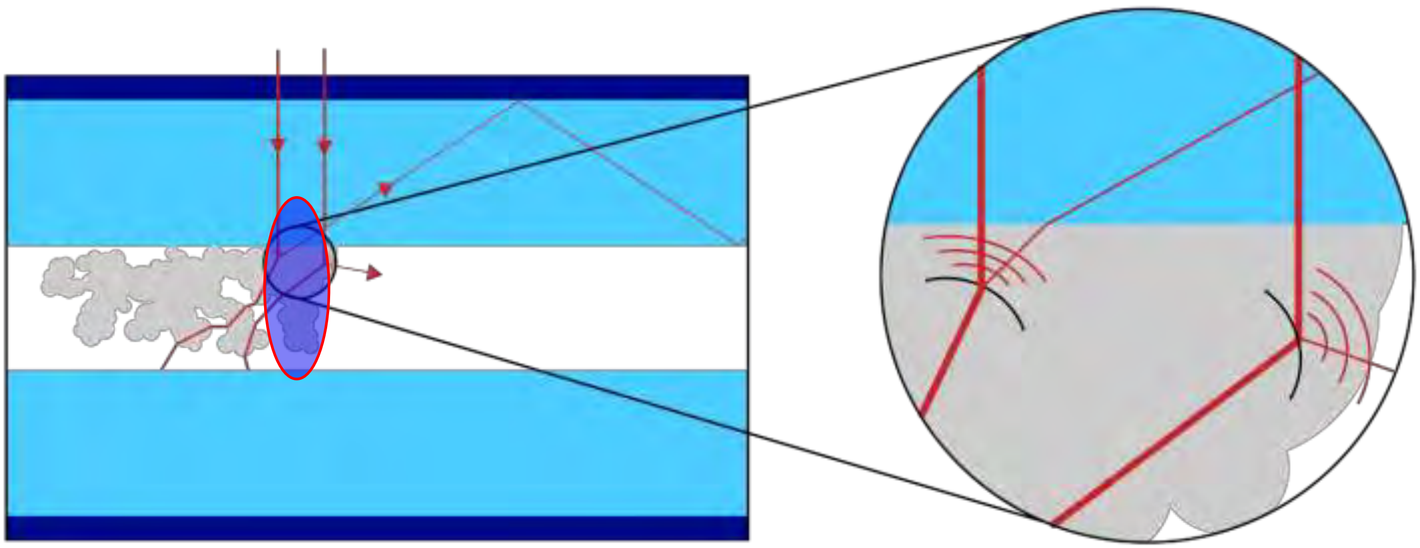

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Further readings

- Books
  - "Light Emitting Diodes, Second Edition" – E. F. Schubert , Cambridge University Press 2006
    - Physics, engineering and development of LEDs
  - "Introduction to Solid-state Lighting" – A. Zukauskas, M. Shur, R. Gaska, Wiley 2002
    - White LEDs, colour rendering, lighting
- Book chapter
  - S. Landgraf, Application of Laser Diodes and Ultrabright Light Emitting Diodes for Static and Time-Resolved Optical Methods in Physical Chemistry, in *Handbook of Luminescence Display Materials and Devices*, H.S. Nalwa and L.S. Rohwer (Eds.), Vol. 3, American Scientific Publishers 2003
    - **An excellent book chapter on TRF applications**

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Further readings

- Reviews
  - Dasgupta, P. K., et al. Analytica Chimica Acta 2003, 500, 337-364
    - **Excellent review on analytical applications**
  - Dupuis, R. D.; Krames, M. R. Journal of Lightwave Technology 2008, 26, 1154-1171
    - A well written history, development, and applications of LEDs
  - Tsao, J. Y. 2005 Conference on Lasers & Electro-Optics (CLEO), Vols 1-3 2005, 143-143
    - Great summary why LEDs are the light source of tomorrow
  - O'Toole, M.; Diamond, D. *Sensors* **2008**, *8*, 2453-2479
    - Comprehensive summary of absorbance based LED sensors

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Further readings

- Reviews (cont.)
  - Phillips, J. M., et al. *Laser & Photonics Reviews* **2007**, *1*, 307-333
    - Review on challenges of high efficiency light sources
  - Gotz, S.; Karst, U. *Analytical and Bioanalytical Chemistry* **2007**, 387, 183-192
    - General review on developments for microchip separations
  - Zysk, A. M., et al. *Journal of Biomedical Optics* **2007**
    - A review of clinical development of optical coherence tomography

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References

- Own publications on LEDs
  - We are scientists = thank you for citing us! ☺

- Review articles
  - Macka M., Johns C., Doble P., Haddad P.R., Indirect detection in capillary electrophoresis: I. Principles, an invited article for *LC-GC*, *19(1)*, 38-47, 2001
  - Macka M., Johns C., Doble P., Haddad P.R., Indirect detection in capillary electrophoresis: II. Practical Rules, an invited article for *LC-GC*, *19(2)*, 178-188, 2001
    - Sensitivity graphs illustrated on examples of 3 commercial CE instruments
  - Johns C., Macka M., Haddad P.R., Enhancement of Detection Sensitivity for Indirect Photometric Detection of Anions and Cations in Capillary Electrophoresis, a review, *Electrophoresis*, *24(12-13)*, 2150-2167, 2003, DOI:10.1002/elps.200305446

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- Original journal articles

  - Macka M., Andersson P., Haddad P.R., Linearity evaluation in absorbance detection: The use of light emitting diodes for on-capillary detection in capillary electrophoresis, *Electrophoresis*, *17(12)*, 1898-1905, 1996
    - **Linearity evaluation showing polychromacity of LEDs was not a concern**
  - Macka M., Paull B., Andersson P., Haddad P.R., Determination of barium and strontium by capillary zone electrophoresis using an electrolyte containing sulfonazo III, *J. Chromatogr. A*, *767(1-2)*, 303-310, 1997
  - Macka M., Paull B., Bogan D., Haddad P.R., The role of ligand purity upon separations of alkaline earth metals as complexes with arsenazo I by capillary electrophoresis, *J. Chromatogr. A*, *793(1)*, 177-185, 1998
  - Macka M., Nesterenko P., Andersson P., Haddad P.R., Separation of uranium(IV) and lanthanides by capillary electrophoresis using on-capillary complexation with arsenazo III, *J. Chromatogr. A*, *803(1-2)*, 279-290, 1998
  - Doble P., Macka M., Haddad P.R., Use of dyes as indirect detection probes for the high sensitivity determination of anions by CE, *J. Chromatogr. A*, *804(1-2)*, 327-336, 1998
  - Macka M., Nesterenko P., Haddad P.R., Investigation of solute-wall interactions in separation of lanthanides and uranyl by capillary electrophoresis using on-capillary complexation with arsenazo III, *J. Microcolumn Separations*, *11(1)*, 1-9, 1999

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      - *Chosen for promotion in the RSC supplement Chemical Technology; Featured on the cover of the issue . volume 133, pp. 864 – 866, 2008*
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      - *Featured on the cover of the issue.*

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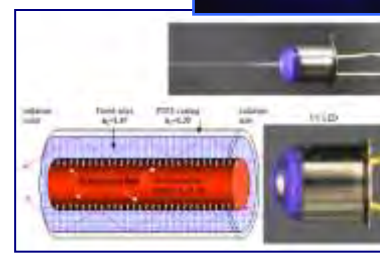
SSLSs – 'non-detection': our research

LEDs as light sources for photopolymerisations

- ✓ **UV: 255 nm:** Silvija Abele, Fu-Qiang Nie, František Foret, Brett Paull, Mirek Macka, UV-LED photopolymerised monoliths, Analyst, 133, 864 - 866, 2008, DOI:10.1039/B802693A
- ✓ **Vis: 660 nm**: Zarah Walsh, Silvija Abele, Brian Lawless, Dominik Heger, Petr Klán, Michael C. Breadmore, Brett Paull, Mirek Macka, Photo-initiated Polymerisation of Monolithic Stationary Phases Using Visible Region LEDs, Chem. Commun., (48), 6504 – 6506, 2008, DOI:10.1039/B816958F
- ✓ **Vis: 470 nm**: Zarah Walsh, Pavel A. Levkin, Brett Paull, Frantisek Svec and Mirek Macka, Visible light initiated polymerisation of styrenic monolithic stationary phases using 470 nm light emitting diodes, J.Sep.Sci., 33(1), 61-66, 2010 DOI:10.1002/jssc.200900624
- ✓ **UV: 365 nm**: Silvija Abele, Smejkal Petr, Yavorska Oksana, Frantisek Foret, Mirek Macka, Evanescent wave photoinitiated polymerization of open-tubular capillary monolithic columns , Analyst, in print 2010, DOI:10.1039/b920789a



➢ **OTC columns by transversal illumination – 'LED light oven'**

SSLSs – 'non-detection': our research

- LEDs as light sources for photopolymerisations
- Modelling/simulating ***light penetration***

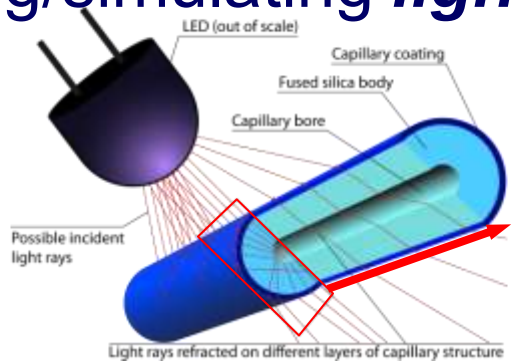


Fig. 4: Scheme of light ray paths propagating through the capillary from single light source placed above capillary; light source not in scale

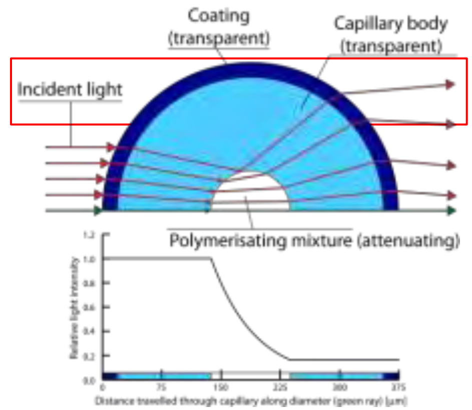


Fig. 8: Graph of relative light intensity along green light ray with (above) scheme of light paths positions inside capillary


Tomasz Piasecki

  - Counter-intuitive patterns

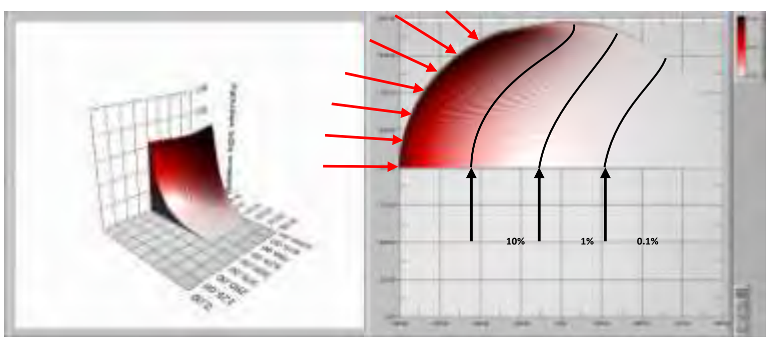


Fig. 10: Light intensity distribution in averagely absorbing medium (ε·c = 30,000) incident light marked with red arrows

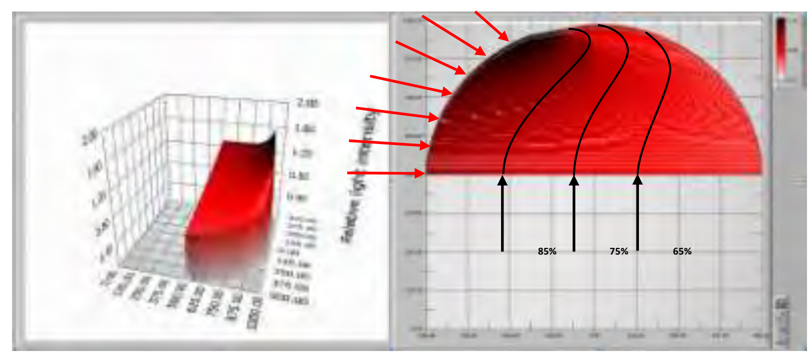


Fig. 11: Light intensity distribution in lowly absorbing medium (ε·c = 600) incident light marked with red arrows

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SSLSs: Future?

- Have become ***successful in many areas***
- Strengths very convincing: ***miniaturisation compatible***
  - Robustness, size, lifetime, $$$, ‘cool’ light, energy consumption, pulsed operation etc.
- Weaknesses still to overcome
  - Spectral coverage
    - Lack of deep-UV SSLSs (<250nm)
  - Low energy conversion in UV (WPE<1%), high heating and low luminosity <350nm
- **Further: SLEDs, IR: QCLs, UV-SSLSs**
- Low-costs: **Socio-economic benefits! ☺**
- The future: **BRIGHT!!! ☺**

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...

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...

LEDs in Chemistry: Outline

-

Thank you!

- Workshop
  - Questions
  - Discussion forum
  - Exchange of experience
  - Discussion of specific intended usages
  - ‘Experiments’

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LEDs are cool

RESERVE

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