The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

World Year of PHYSICS 2005

SMR.1670 -31

INTRODUCTION TO MICROFLUIDICS

8 - 26 August 2005

Chip-based GC

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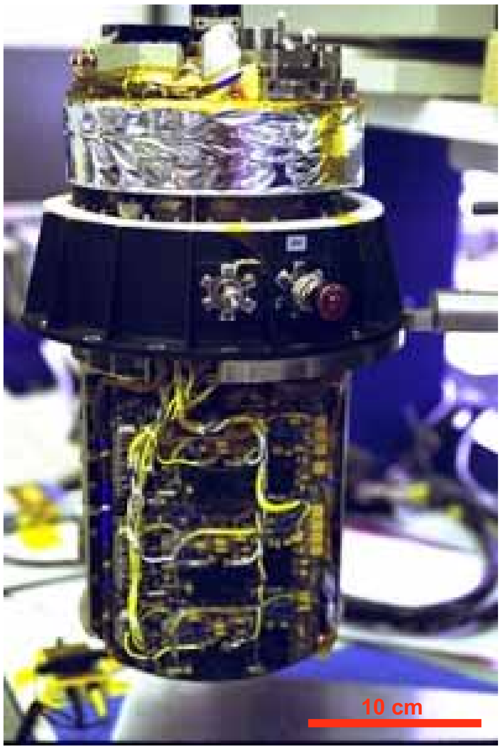
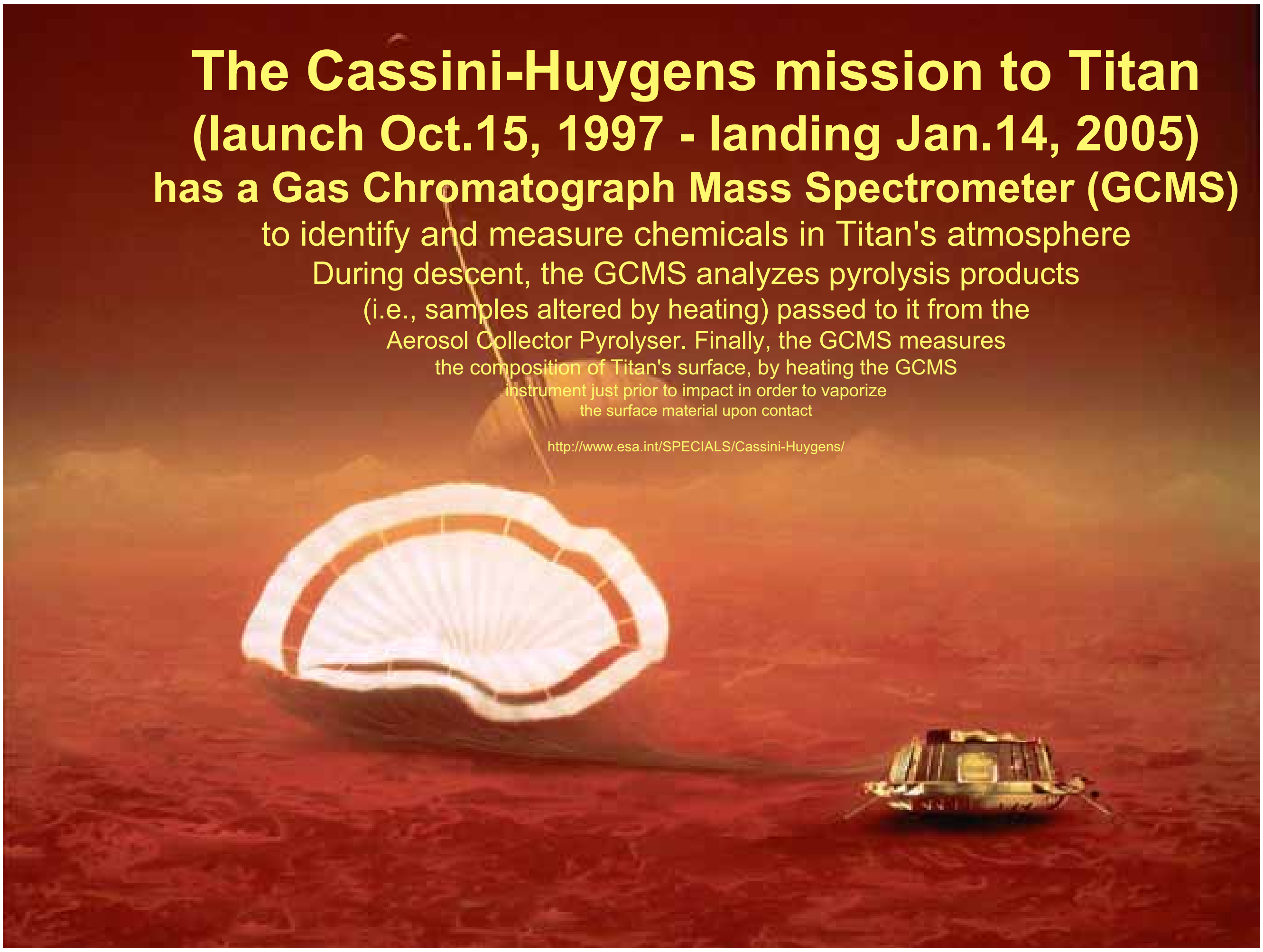
Chip-based GC

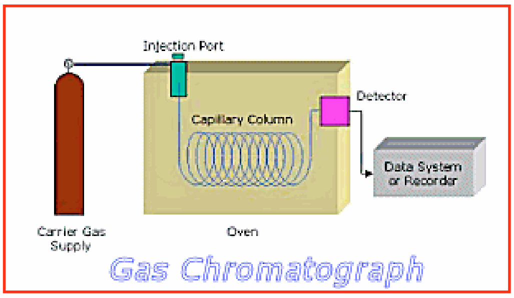
Han Gardeniers
MESA+ Institute for Nanotechnology
University of Twente

Summer School in Microfluidics
ICTP, Trieste, Italy

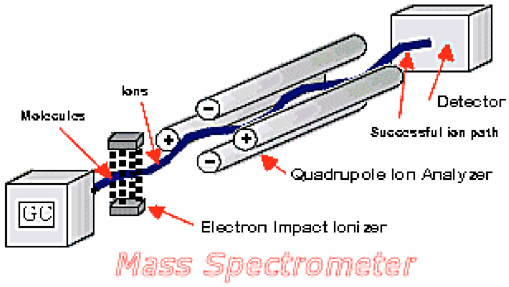




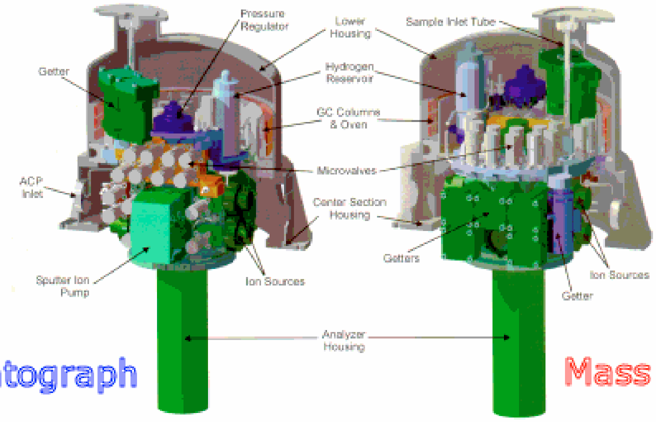
Cassini-Huygens GCMS



Divides Titan's atmosphere mixture into its separate components



Provies information about the compounds in Titan's atmosphere



Gas Chromatograph

Mass Spectrometer!

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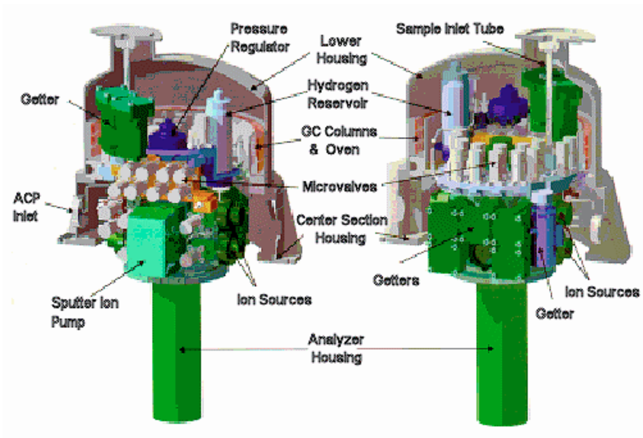
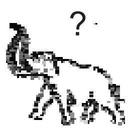
GCMS overview and some components

capillary separation column



The enrichment cell (right) is a separate instrument that uses the MS detector to analyze its samples. It is essentially a small container coated with carbon absorber on which organic components will collect. Whatever compounds do not stick to the enrichment cell pass into a rare gas cell



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source: http://huygensgcms.gsfc.nasa.gov/

Why small GC's?

Table 1. Classification of portable chromatographs

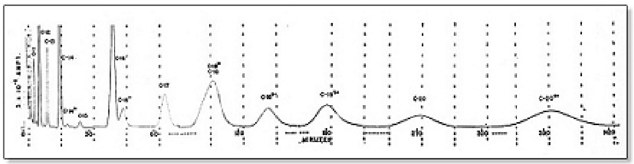
Type	Purpose	Advantages, capabilities
Compact	For mobile and stationary laboratories	Saving of costs, power, materials, and space with analytical characteristics similar to those of stationary chromatographs, weight 10–25 kg
Portable, transportable, field	For on-site analysis	Small weight, rapid analysis, gas and power self-supporting, weight 5–15 kg
Chip-based chromatographs (silicon micromachining technology), handheld, personal, pocket	For on-site analysis, handheld	For the fast resolution of relatively simple analytical problems, fully self-supporting, restricted analytical capabilities, weight 0.2–3 kg
Specially designed chromatographs, micro chromatographs	For space investigations	Automated analysis, small weight, resistant to impact and shaking

from: Yashin e.a. J.Anal.Chem. 56, 794–805 (2001) -mainly Russian developments

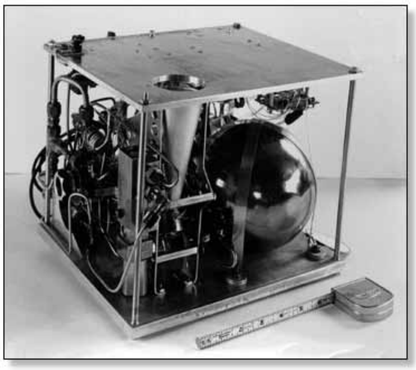
GC instrumentation

GC in the ol'days

Gas chromatograph of the late 1950's



Fatty acid gas chromatogram (1951)



Lunar Gas Chromatograph designed in 1962.

1941: Gas chromatography mentioned by Martin and Synge in paper on liquid chromatography (1)
1951: Martin and James publish first gas chromatograph (2)
1979: Dandeneau developes polymer-coated fused silica capillary (3)

1. A.J.P. Martin and R.L.M. Synge, Biochem. J. 35, 1358 (1941)
2. A.T. James and A.J.P. Martin, Biochem. J. 50, 679 (1952)
3. R.D. Dandeneau and E.H. Zerenner, High Res.Chrom.&Chrom.Commun. 2(6), 351–356 (1979)

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http://www.chromatography-online.org/GC/
http://www.quadrexcorp.com/new/history.htm

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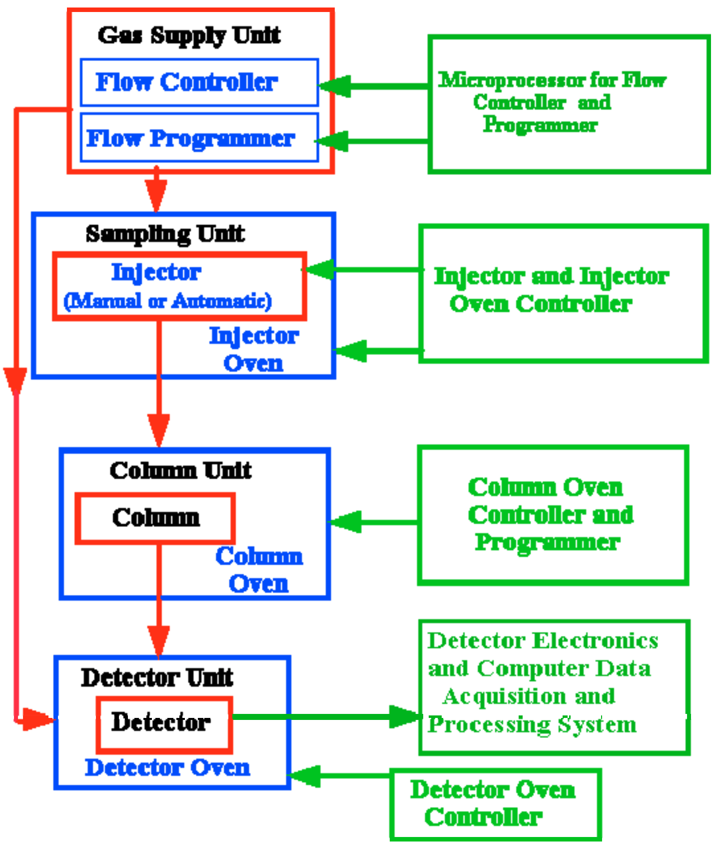
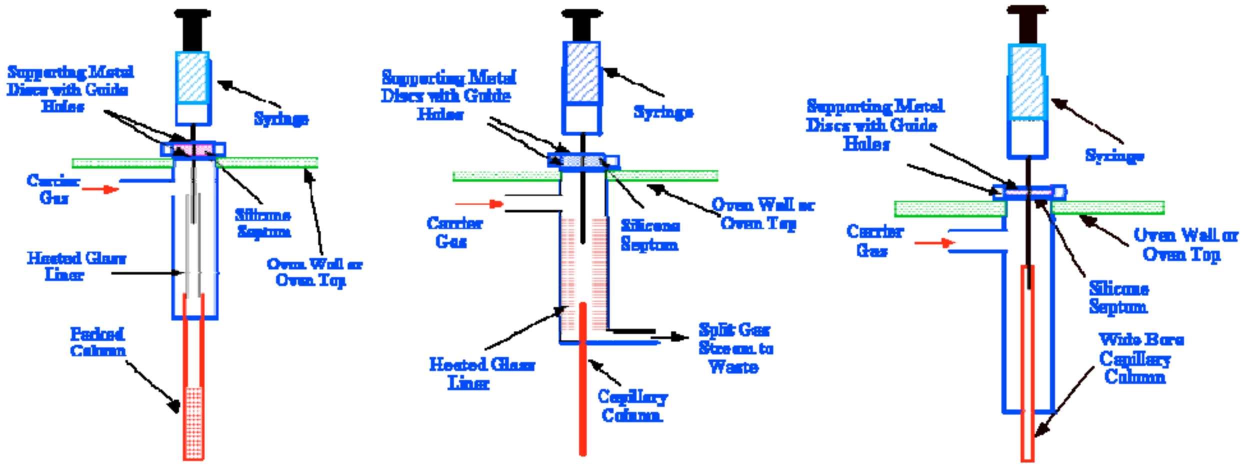
The modern GC

source: http://www.chromatography-online.org/GC/

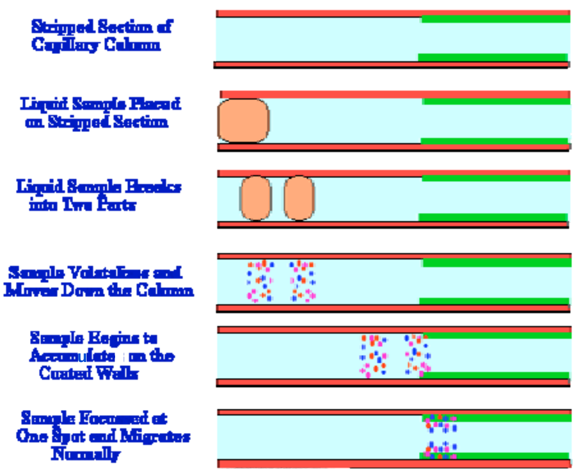


Modern injectors

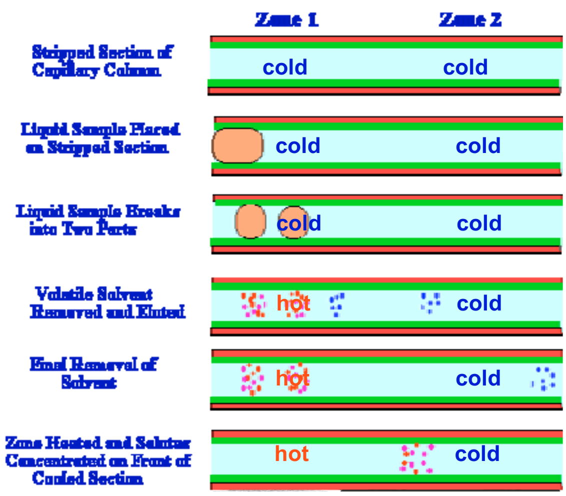


source: http://www.chromatography-online.org/GC/

Injection procedures to reduce plug width



Retention Gap Method of Sampling

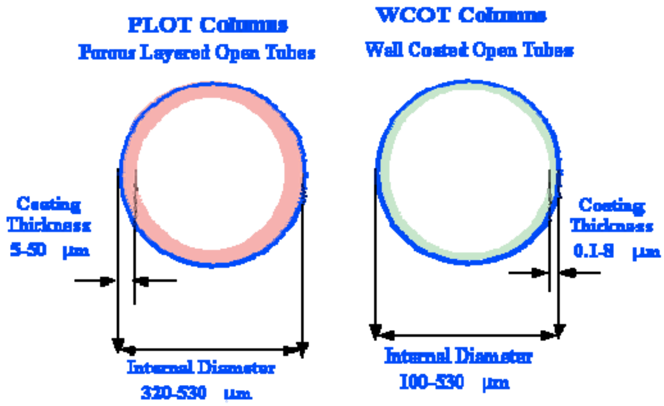


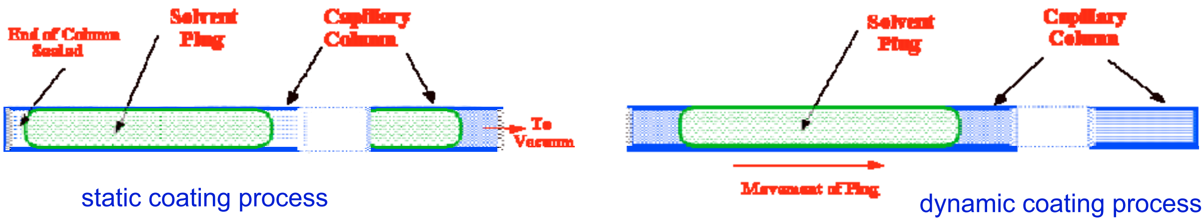
Solute Focusing Method sampling

The injector is designed such that there are two consecutive, independently heated and cooled zones located at the beginning of the column.

source: http://www.chromatography-online.org/GC/

Different stationary coatings and coating procedures





static coating process

dynamic coating process

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http://www.chromatography-online.org/GC/

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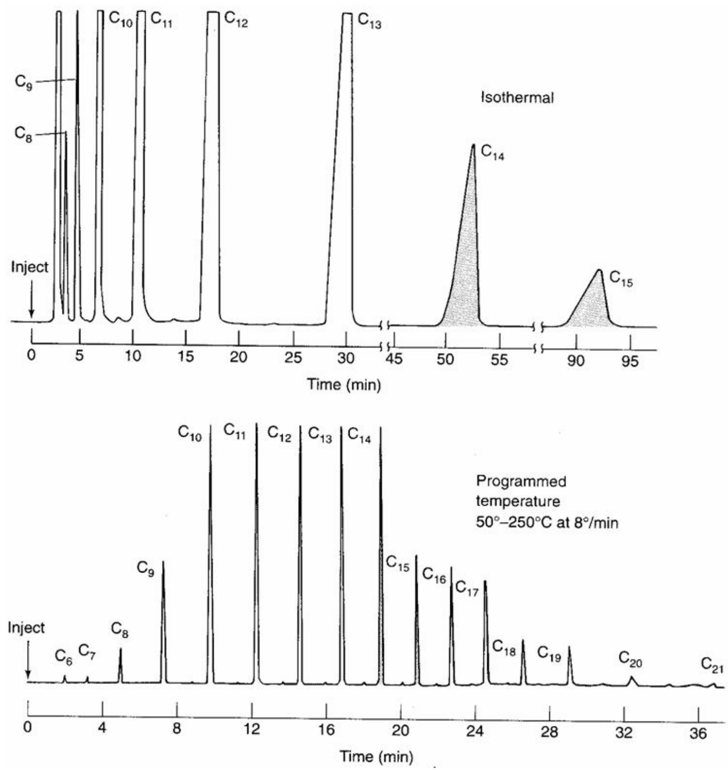
Temperature programming



Slowly ramping T throughout the separation provides a basis for the separation of sample components based on boiling point.

Comparison of of isothermal (top) and programmed temperature chromatography. Column: 1.6 mm ID and 6 m long, containing 3% Apiezon L (liquid phase) on 100/120 mesh VarAport 30 solid support. He flow rate 10 ml/min. Detector sensitivity in top graph is 16 times that of bottom.

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H.M. Mcnair and E.J. Boneli, Basic gas chromatography, Palo Alto, CA, Varian Istrument Div. 1968

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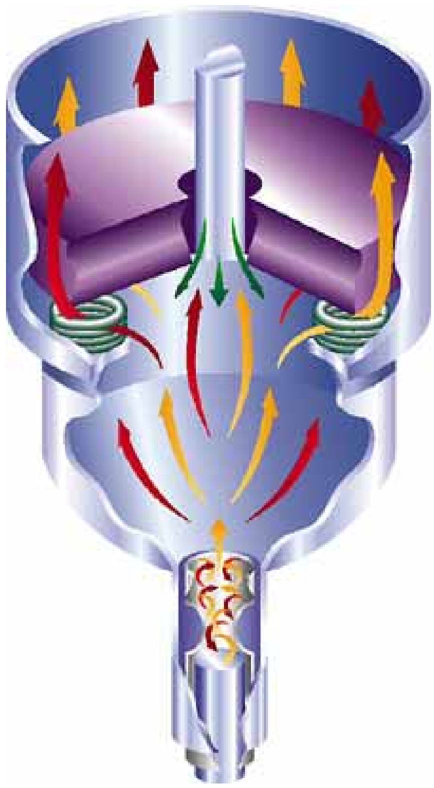
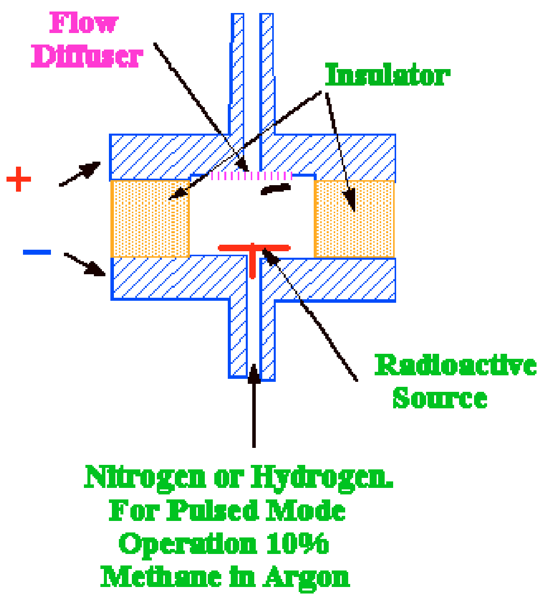
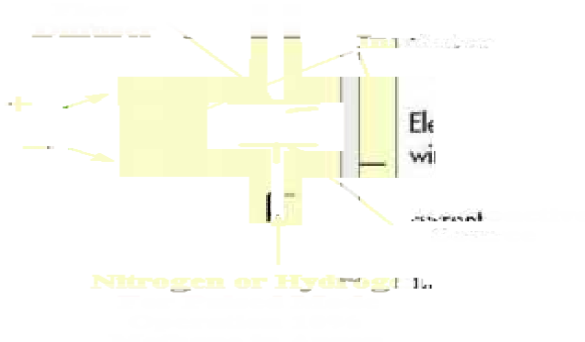
Gas Chromatography Detector Overview

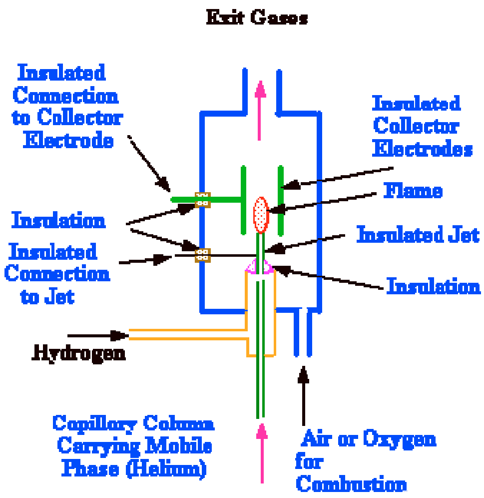


Electron capture

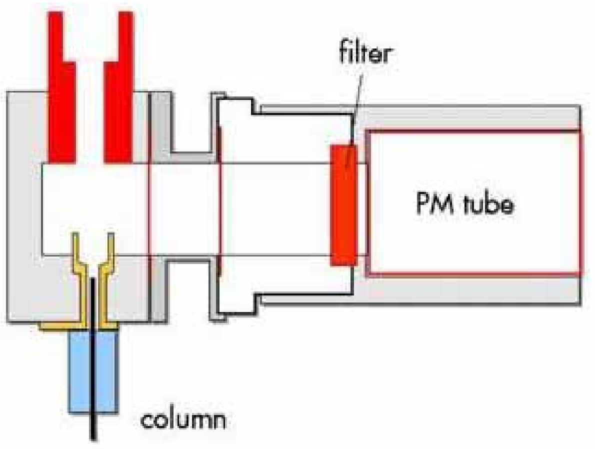




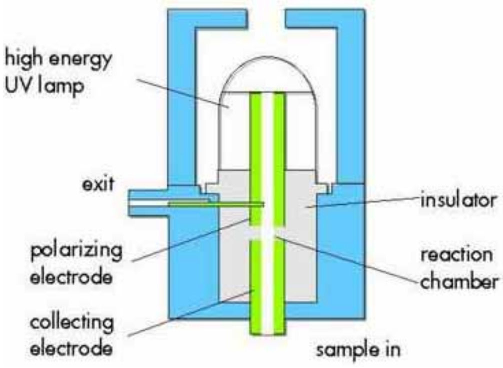
Flame detector overview



Flame ionisation

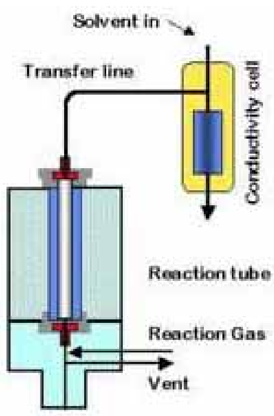


Flame photometric detector

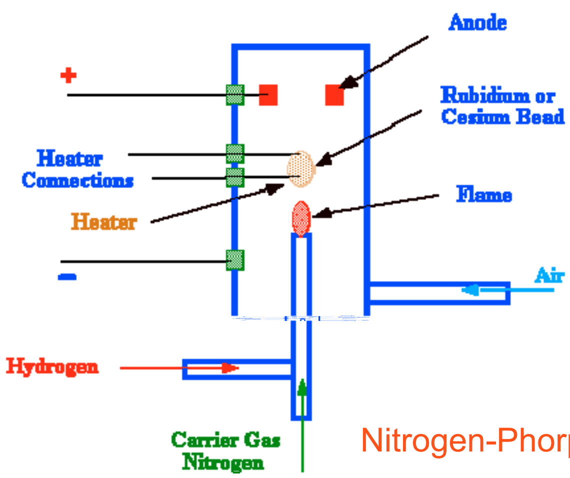


Photoionisation detector

Compounds are mixed with a reaction gas and passed through a high temperature reaction tube. Products mix with solvent and pass through electrolytic conductivity cell



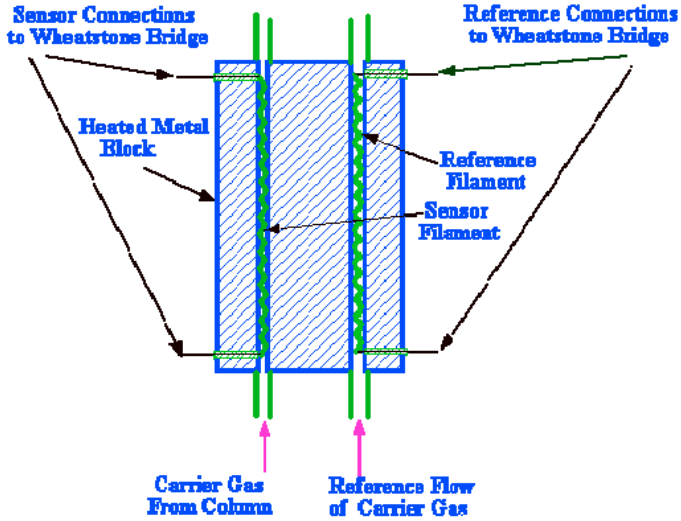
Electrolytic conductivity detector



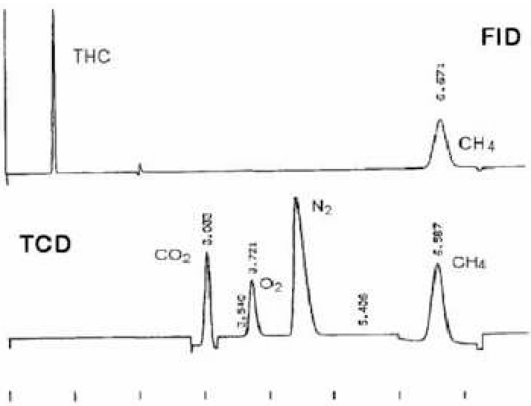
Alkali bead is heated by current passing through coil and emits electrons by thermionic emission, which are collected at the anode and thus produce an ion current. When solute containing N or P is eluted, combusted N and P materials adsorb on bead, which reduces work function and therewith electron emission

Nitrogen-Phorphorus Detector

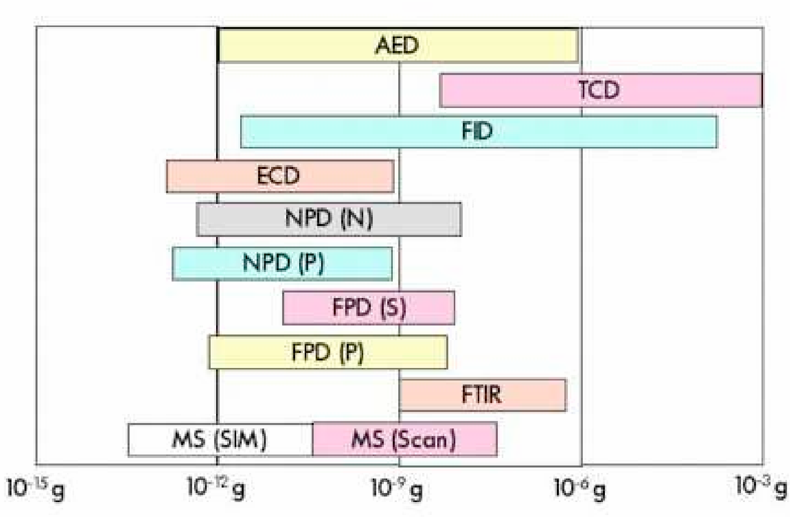
Thermal Conductivity Detector or "Katherometer"



Comparison FID and TCD

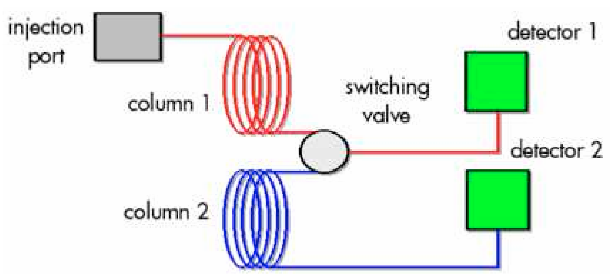


Sensitivity of different detection methods

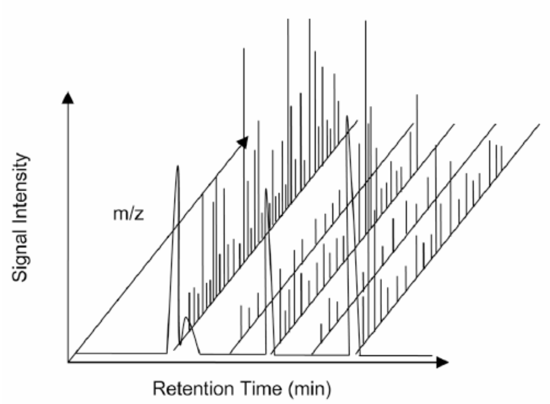


http://ull.chemistry.uakron.edu/chemsep/

Hyphenated GC

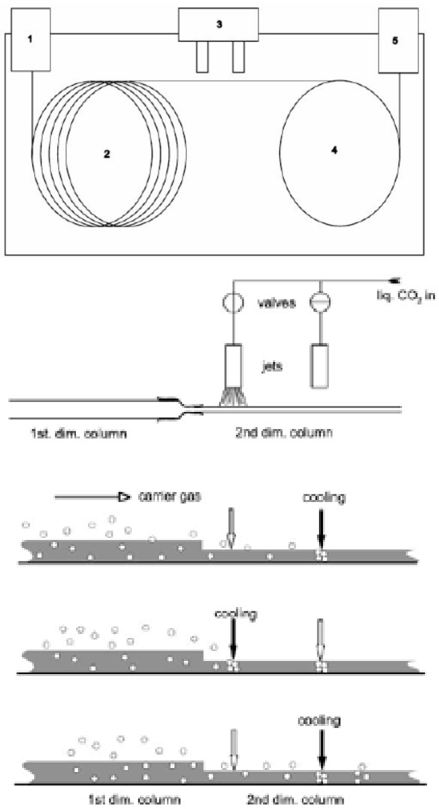


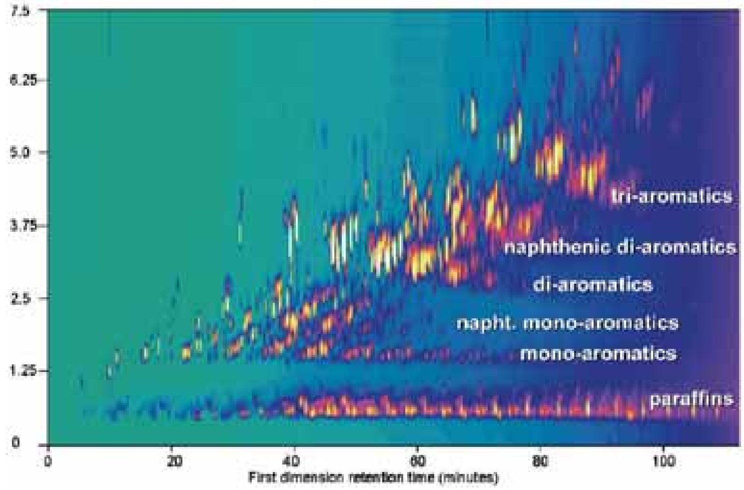
2-D GC relies on passing a portion of effluent to a second column using flow switching



GC-MS

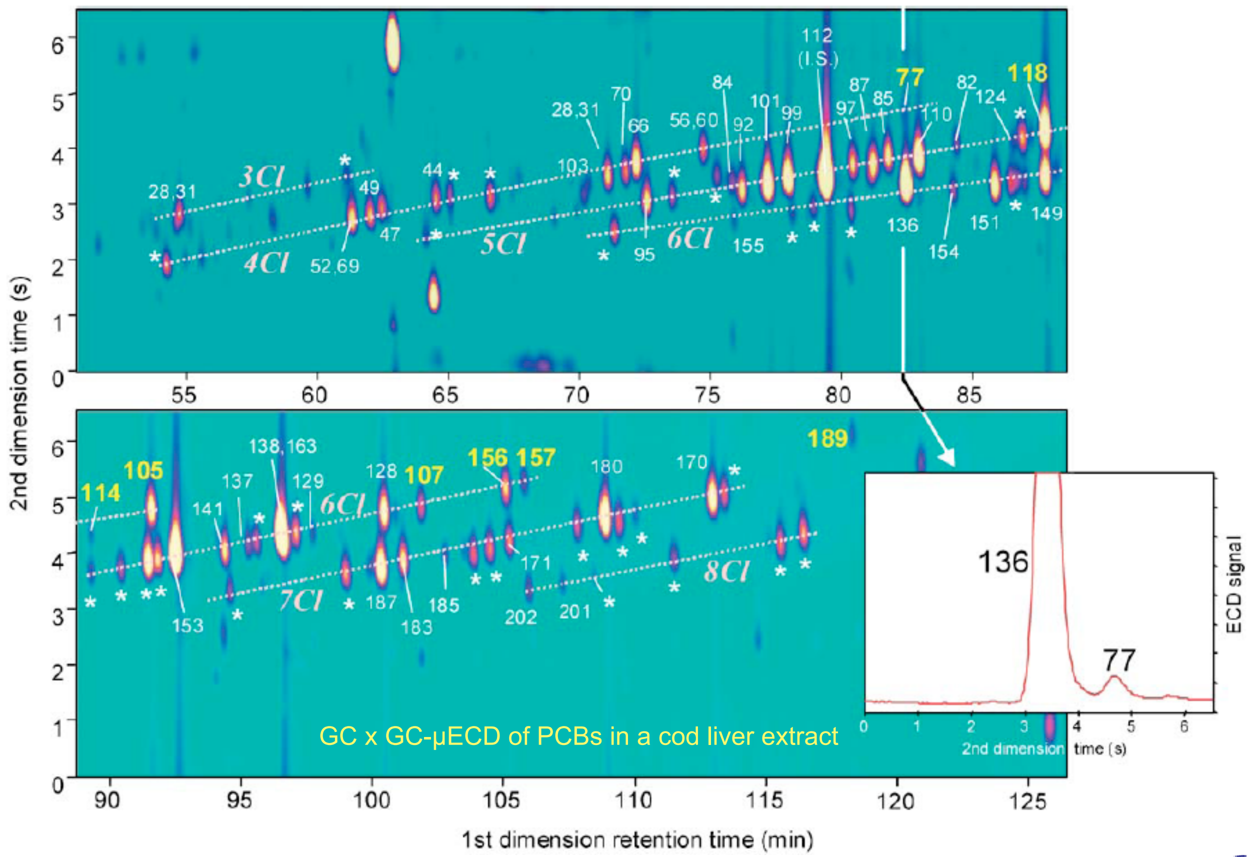
Comprehensive 2-D gas chromatography





GCxGC–FID of a light cycle oil
on DB-1xOV-1701 column combination.

Beens e.a. Analyst 130, 123-127 (2005)



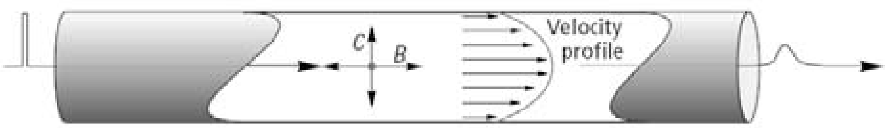
Beens e.a. Analyst 130, 123-127 (2005)

Gas Chromatograph Miniaturisation

GC basics: open-tubular column

Revisit the (classic) van Deemter equation (no A-term):

$$H = \frac{B}{u} + (c_m + c_s)u$$



with $B = 2D_m$ (~ axial diffusion)

$$C_m = \frac{4(1 + 9k + 25.5k^2)z_0^2}{105(1+k)^2 D_m} \quad \text{and} \quad C_s = \frac{2k^3 z_0^2}{3(1+k)^2 K^2 D_s}$$

C_s and C_m can be regarded as mass transfer resistances of the analyte in the stationary phase (e.g. a liquid film) and the mobile phase (the carrier gas), i.e. ~ radial diffusion

z_0: half column height
D_m , D_s: diffusivities in m and s phases, resp.

k: partition ratio (depends on z_0)
K: partition coefficient

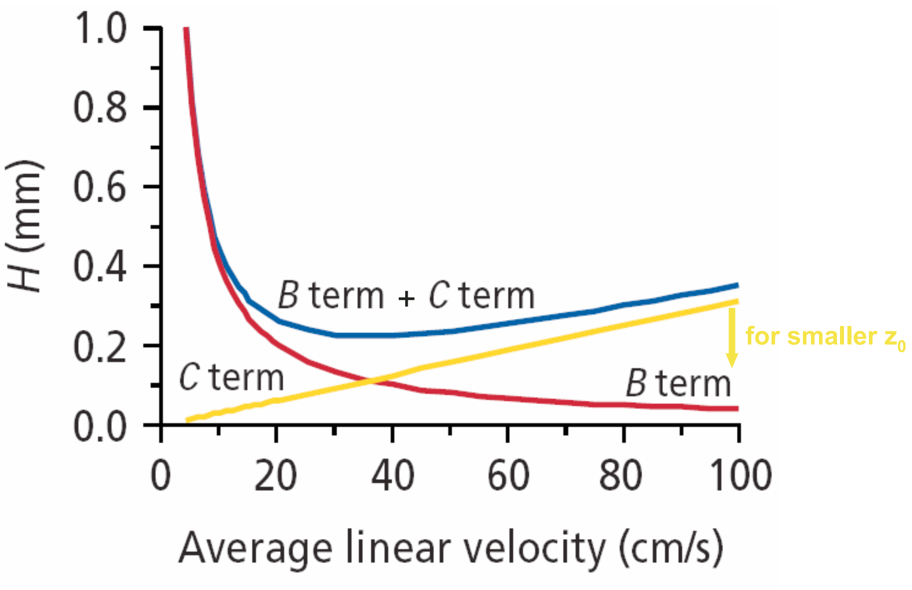
Golay, in "Gas Chromatography", 1958, ed. Desty, Butterworths, London, p.36

Miniaturized open-tubular GC

Generally, the C_s term dominates over C_m (thin film of stationary phase), and even more so in miniaturised columns.

In first order, a smaller column diameter leads to lower H (=better performance)

But smaller diameter also means: higher pressure drop!



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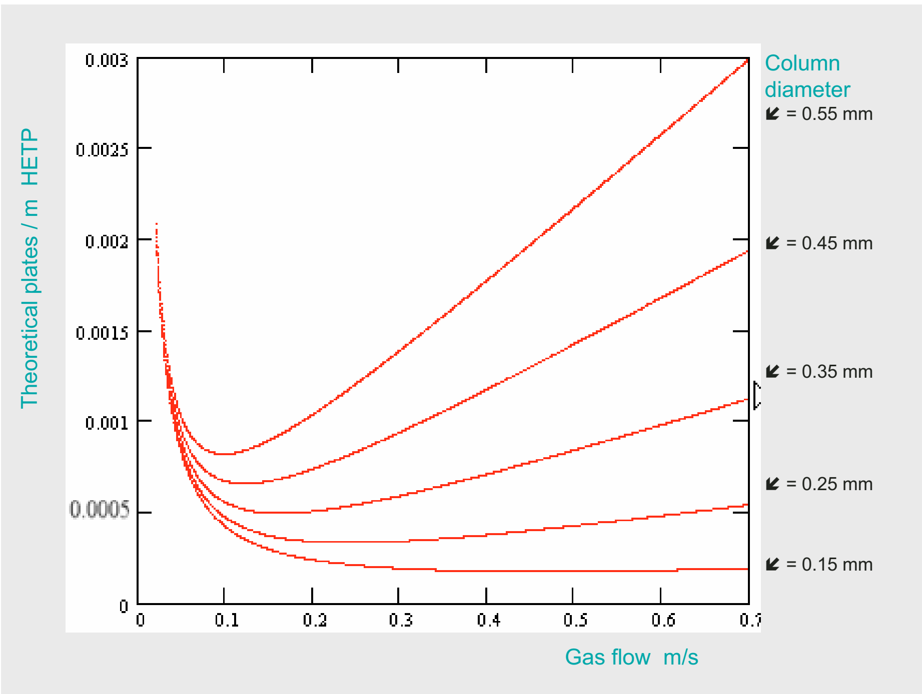
Advantage of narrow-bore columns



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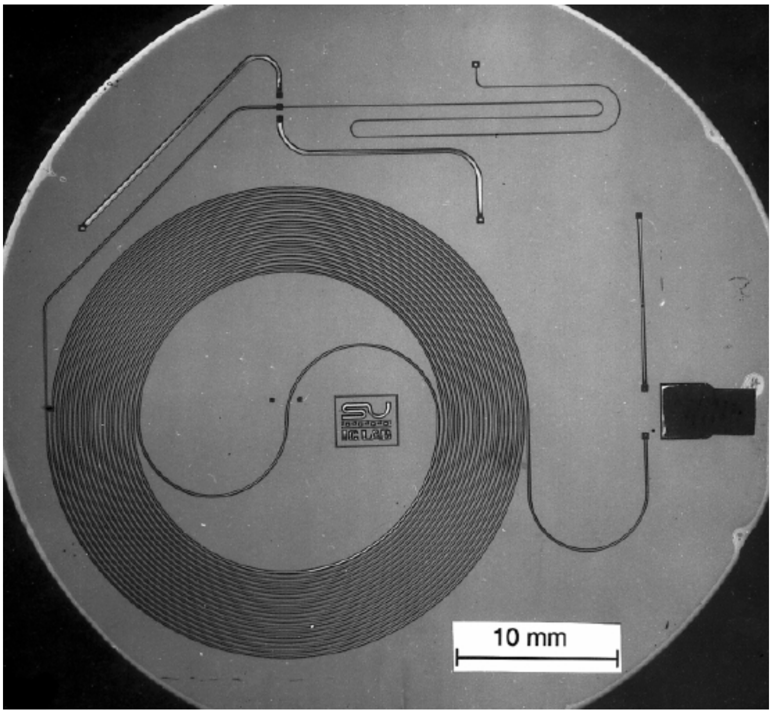
The first GC on a chip



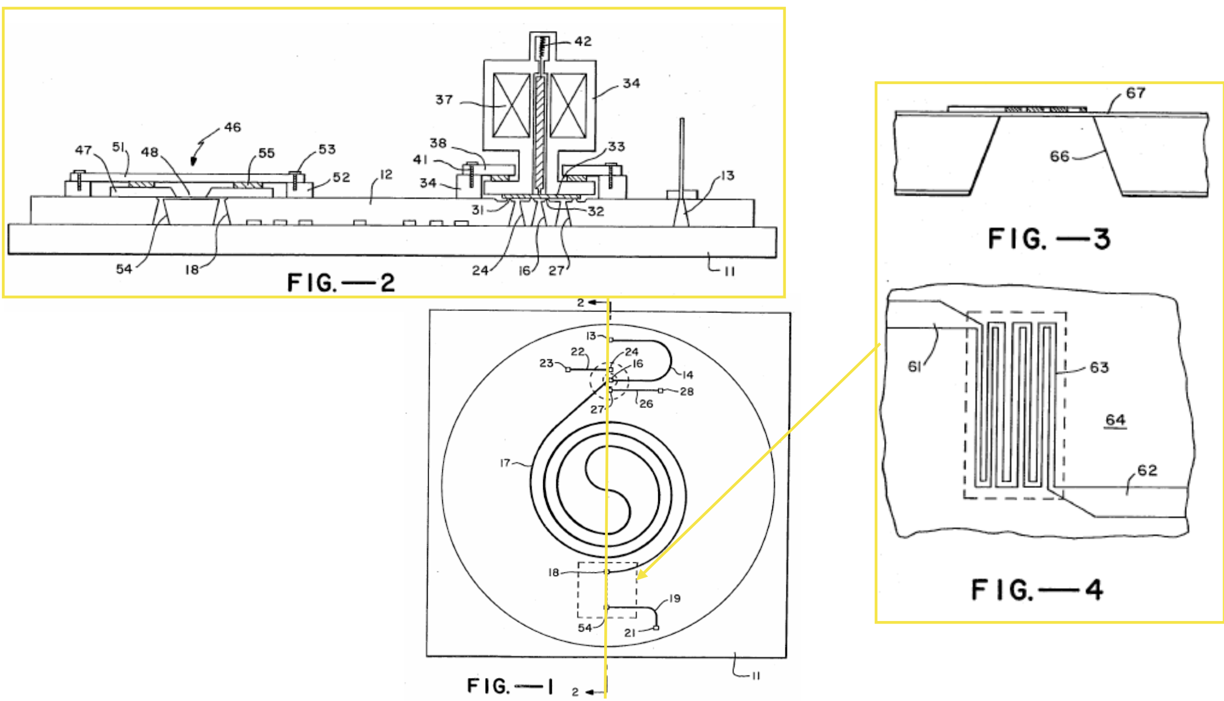
Separately fabricated TCD chip was mounted at outlet

Integrated micromachined membrane valves
1.5 m long column

Low performance due to non-uniform liquid stationary phase

Terry e.a. IEEE Tr. Electron. Dev. ED-26, 1880-1886 (1979)
PhD thesis Terry, 1975, Stanford University

Improved GC chip design



From US patent 4,471,647 "Gas chromatography systems and detector and method", issued Sep.18, 1984, by Jerman and Terry

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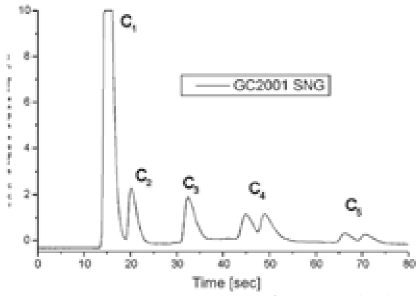
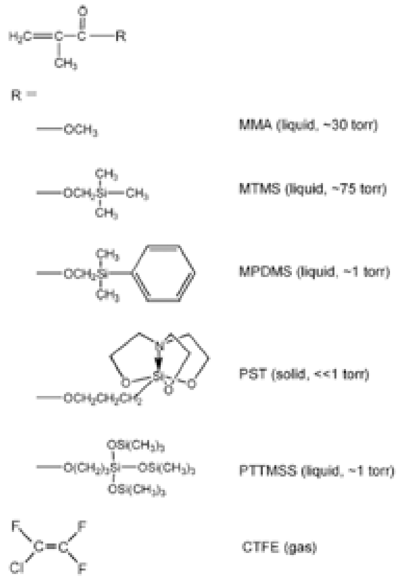
Alternative ways to coat in a chip

Plasma polymerised layer as stationary phase is applied in a reactive-ion etched trench in silicon before anodic bonding to Pyrex



Chromatogram of several alkanes



Photopolymerisation of these monomers was tried in open channels in silicon, glass and quartz

Hsieh e.a. Sens.Act.B 82, 287-296 (2002)

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http://www.tu-harburg.de/mst/english/forschung/gc.shtml

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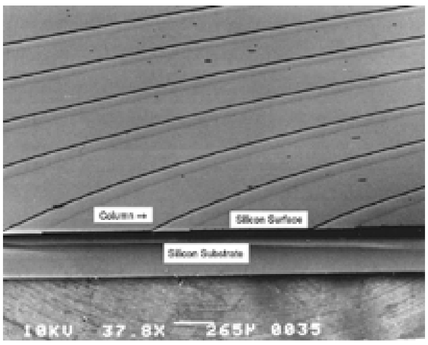
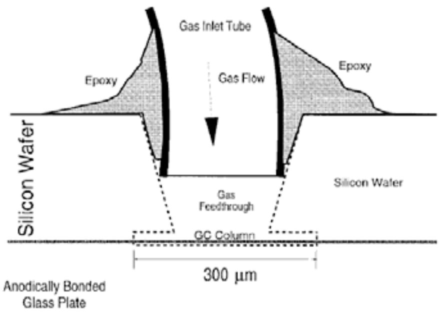
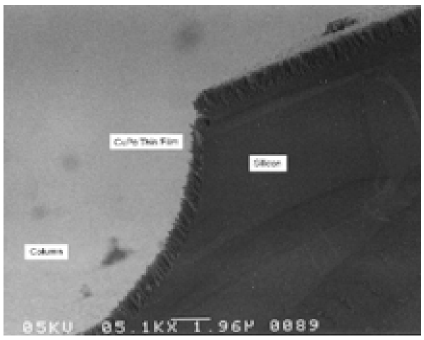
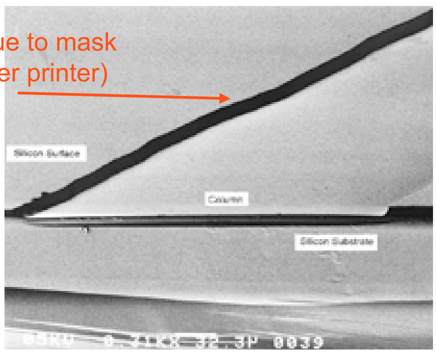
Silicon micromachined GC ...

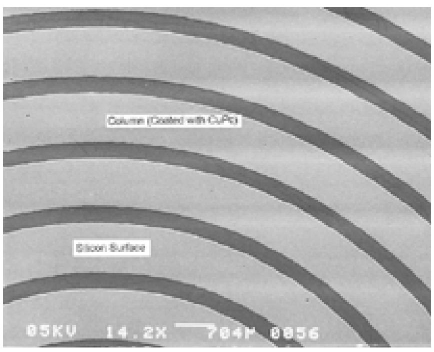






waviness due to mask
(600 dpi laser printer)





0.2 µm α-phase Cu-phtalocyanine coating was sublimed on Si and Pyrex surfaces before anodic bonding; column was 0.9 m long, 300 µm wide and 10 µm deep

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Kolesar e.a. IEEE Tr.Comp.Packaging Manufact.Technol.B 21, 324-328 (1998)

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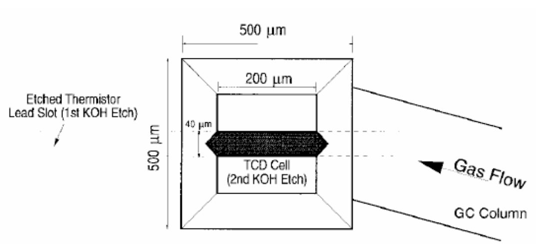
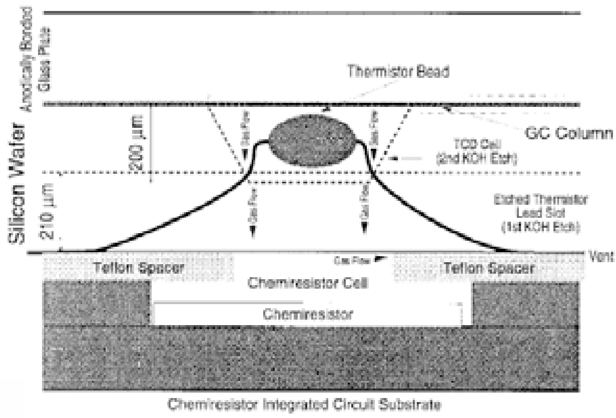
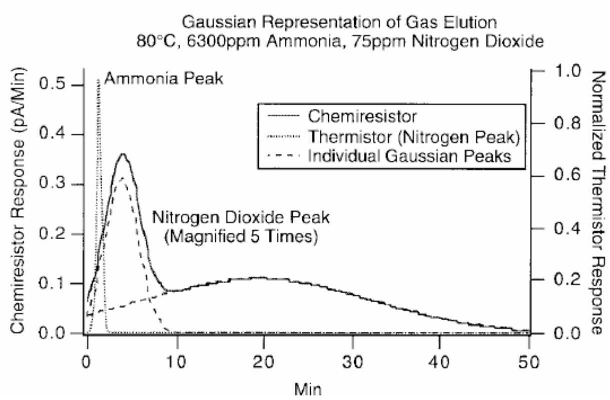
... with integrated detectors

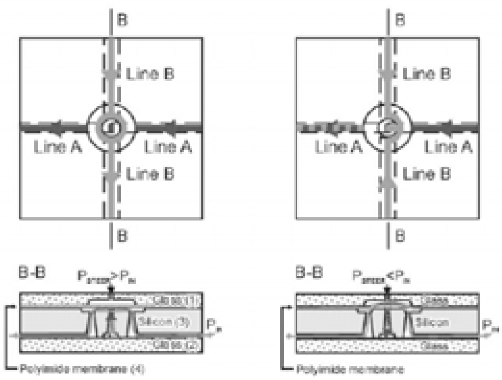




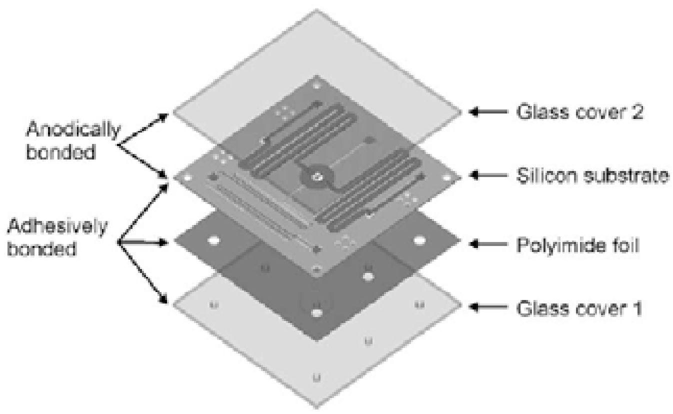


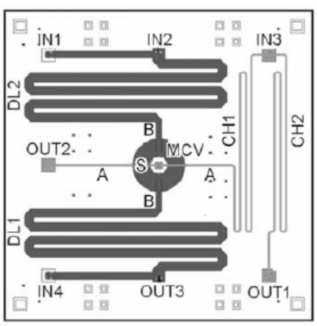
Kolesar e.a. IEEE Tr.Comp.Packaging Manufact.Technol.B 21, 324-328 (1998)

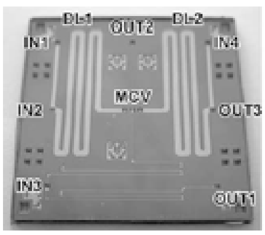
Si double-GC with integrated valves...

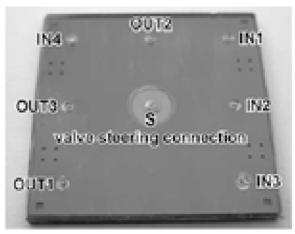


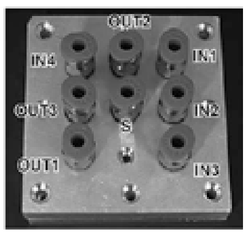
closed open





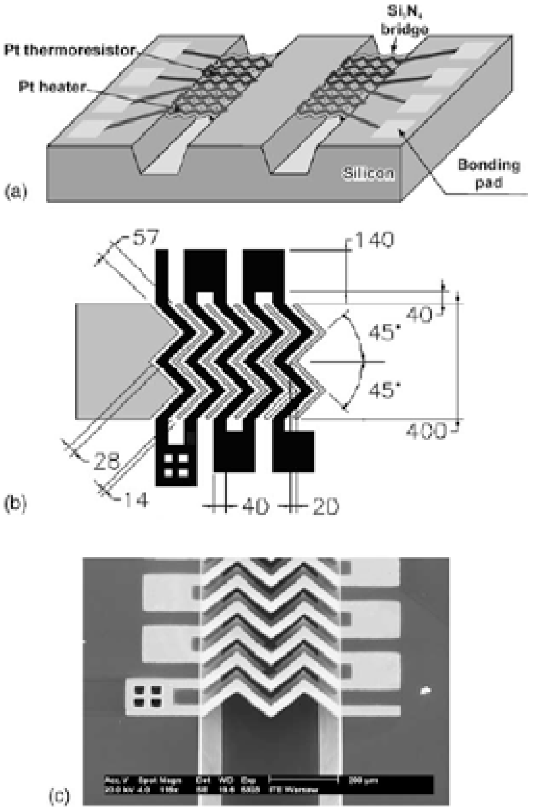


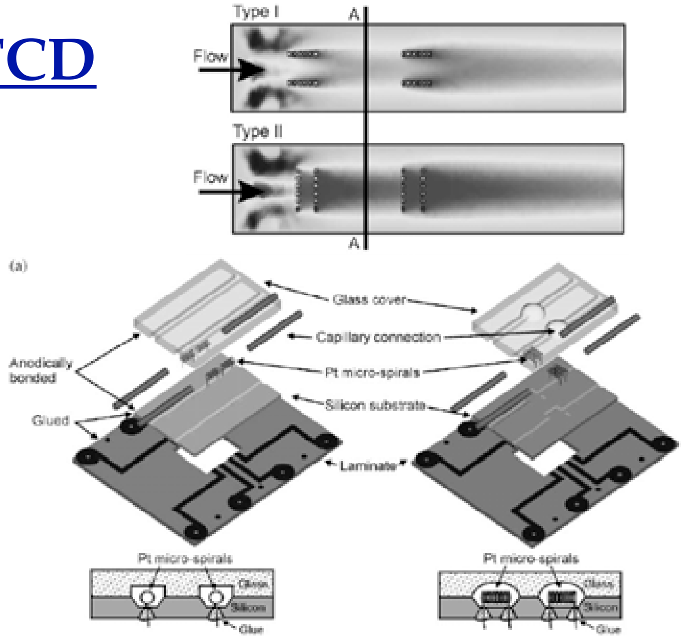


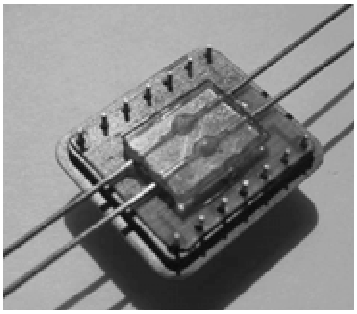


Dziuban e.a. Sens.Act.A 115, 318-330 (2004)

... and integrated TCD

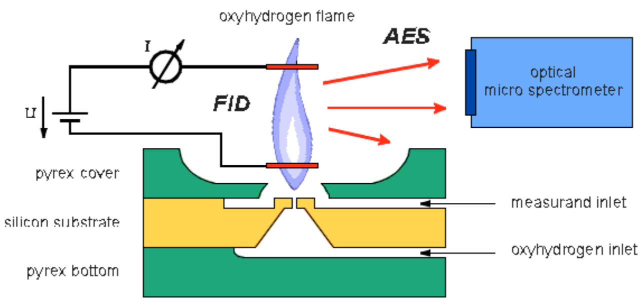


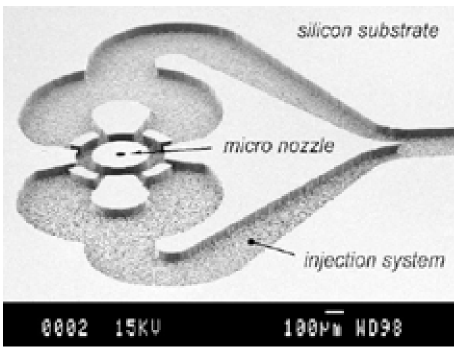


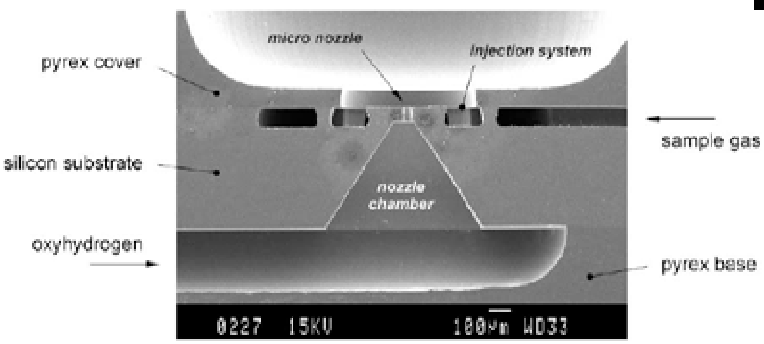


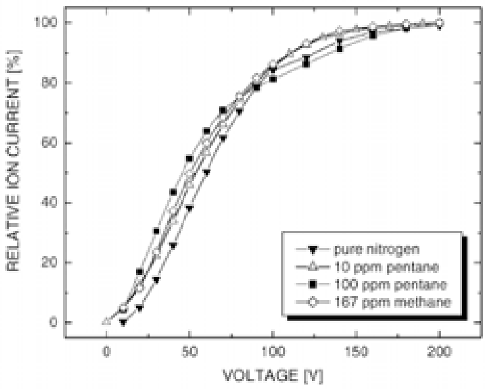
Dziuban e.a. Sens.Act.A 115, 318-330 (2004)

Miniaturized flame ionization and AES detector for gas chromatography



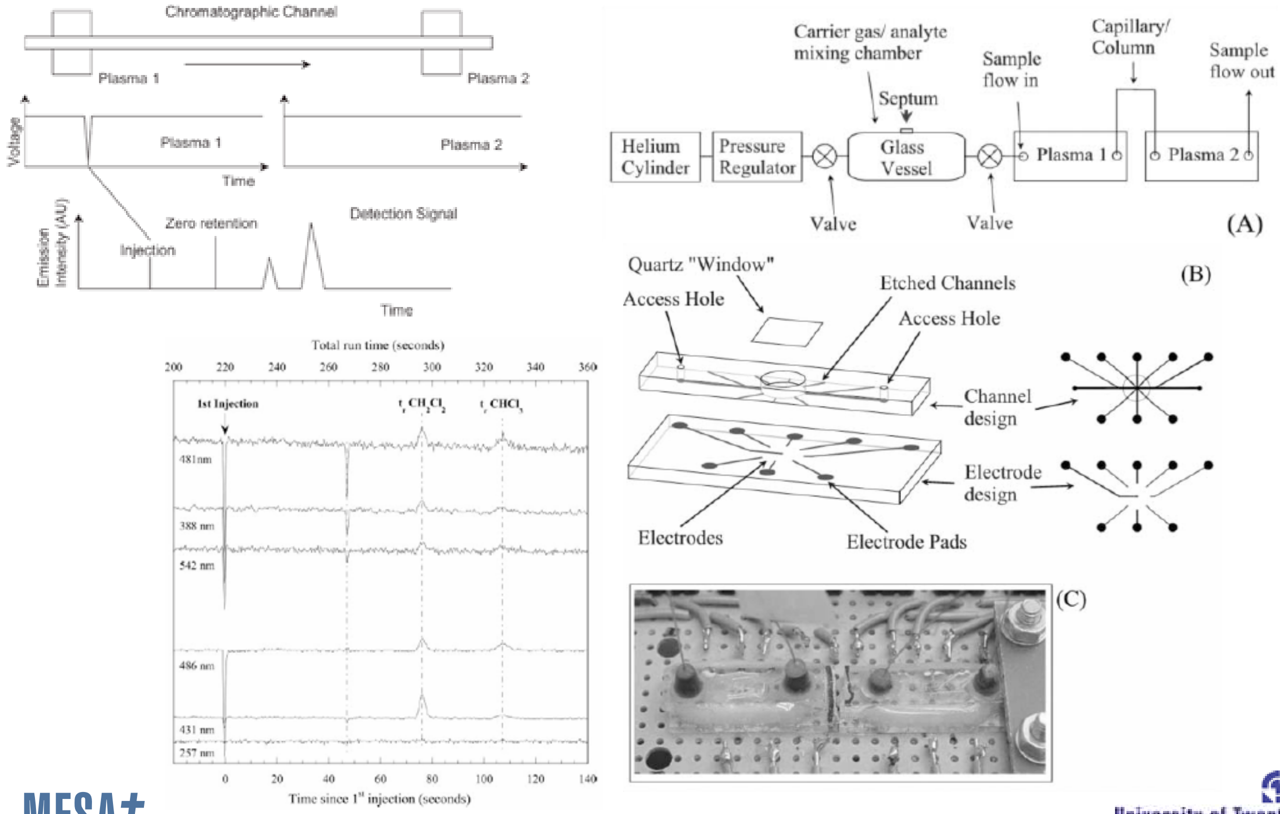






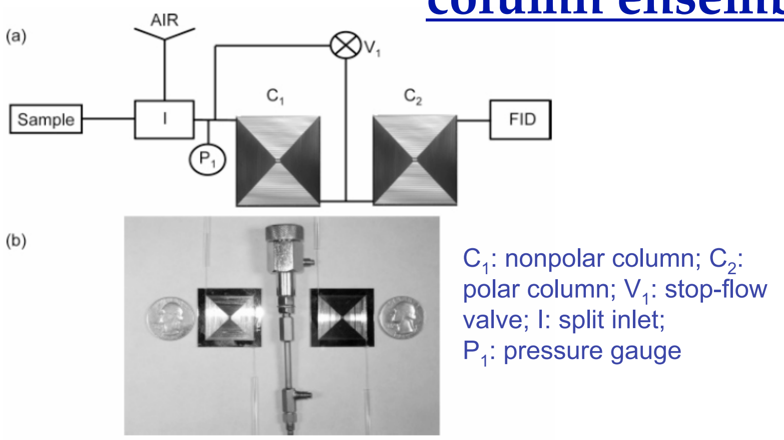
Zimmermann e.a. Sens.Act.B 63, 159-166 (2000) & 83, 285-289 (2002)

Double plasma GC injector and detector

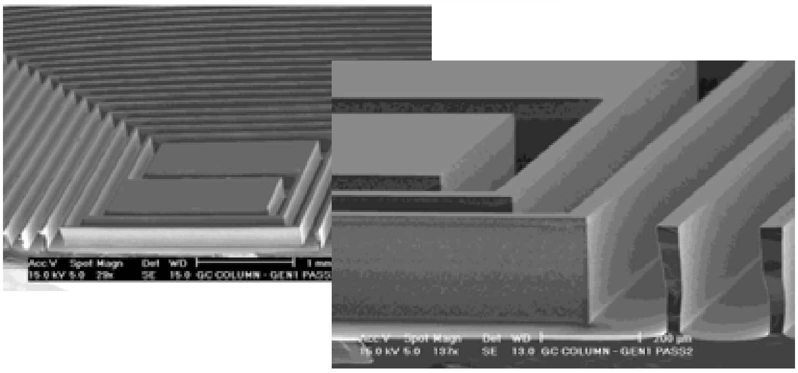


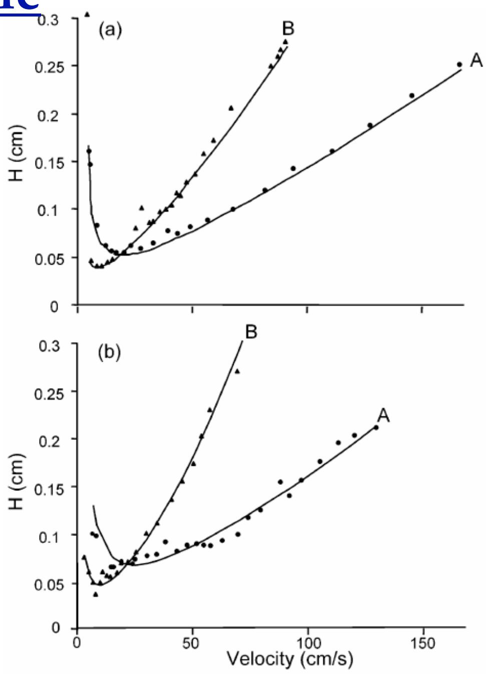
Naji e.a. Lab Chip 4, 431-437 (2004)

Stop-flow programmable selectivity with a dual-column ensemble



C_1: nonpolar column; C_2: polar column; V_1: stop-flow valve; I: split inlet; P_1: pressure gauge



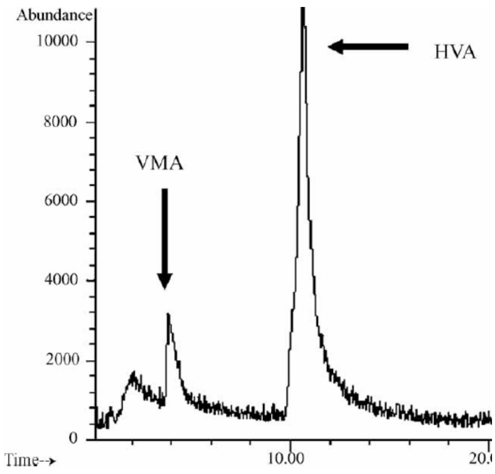


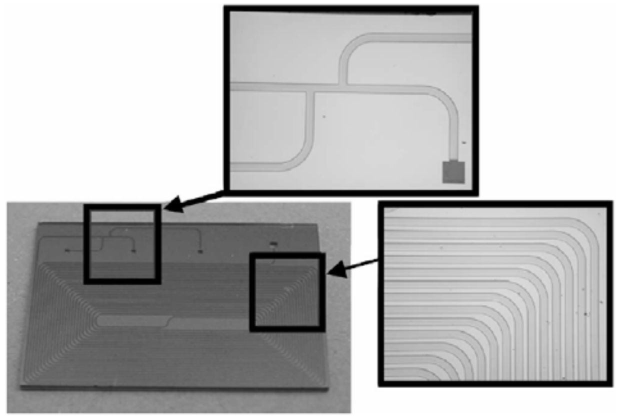
HETP for 3 m Si channels. (a) native Si; (b) oxidised Si; A: H_2, B: air carrier gas; nonpolar stationary phase

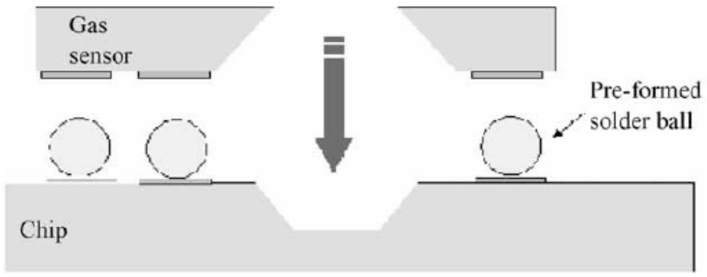
Lambertus e.a. Anal.Chem. 76, 2629-2637 (2004) & 77, 2078-2084 (2005)

Micromachined GC for clinical diagnostics

aim: monitor the homovanillic acid (HVA) and vanillylmandelic acid (VMA) ratios in mass population screening for neuroblastoma diagnosis and prognosis.

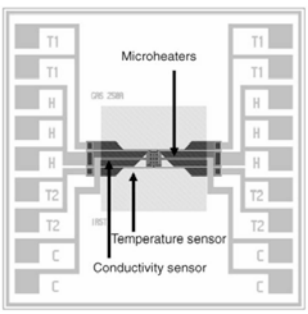


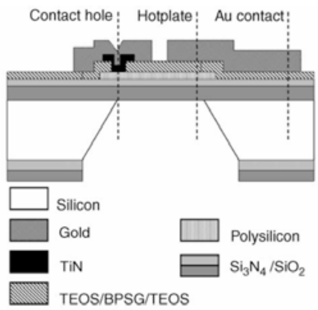




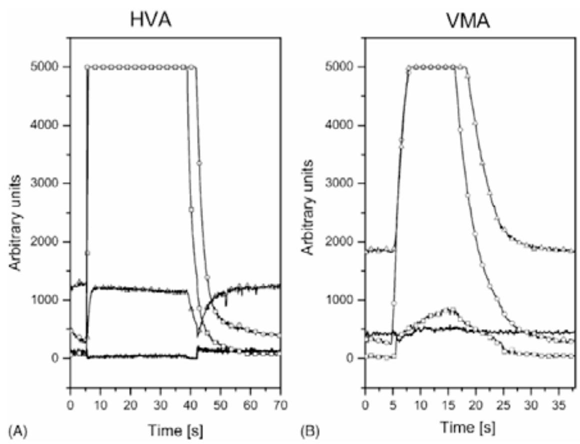
Lorenzelli e.a. Biosens.Bioel. 20, 1968-1976 (2005)

Gas sensor for micro-GC

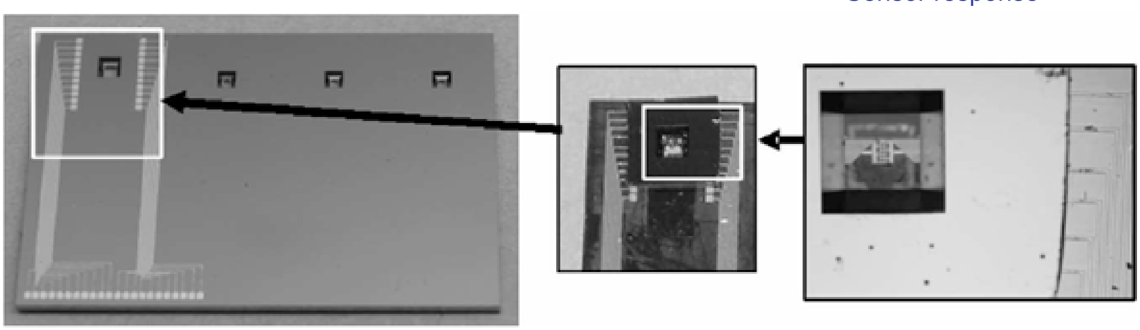




Suspended membrane with microheater, temperature sensor and interdigitated microelectrode covered by a SnO_2-based sensitive layer

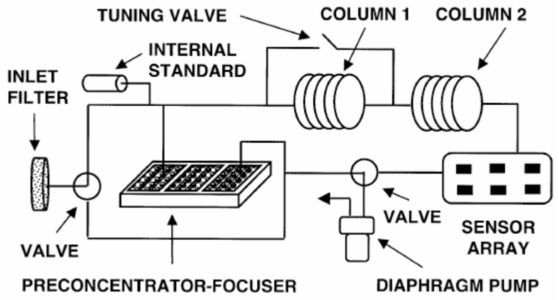


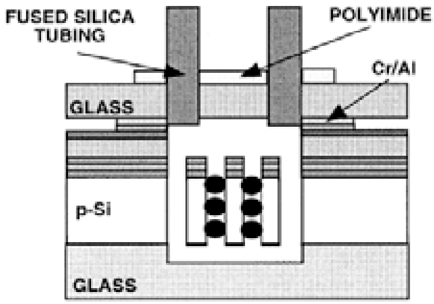
Sensor response

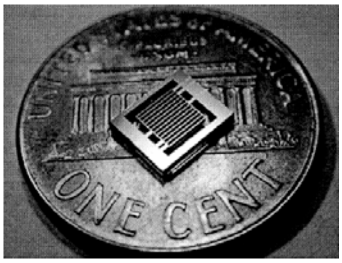


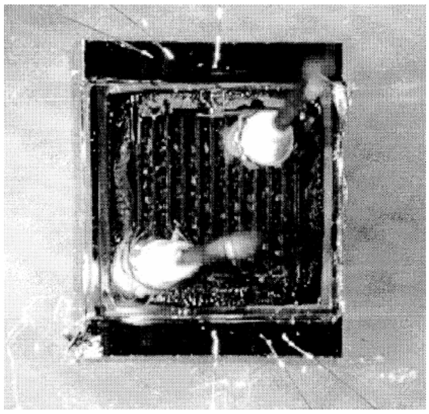
Lorenzelli e.a. Biosens.Bioel. 20, 1968-1976 (2005)

Preconcentrator-focuser for GC









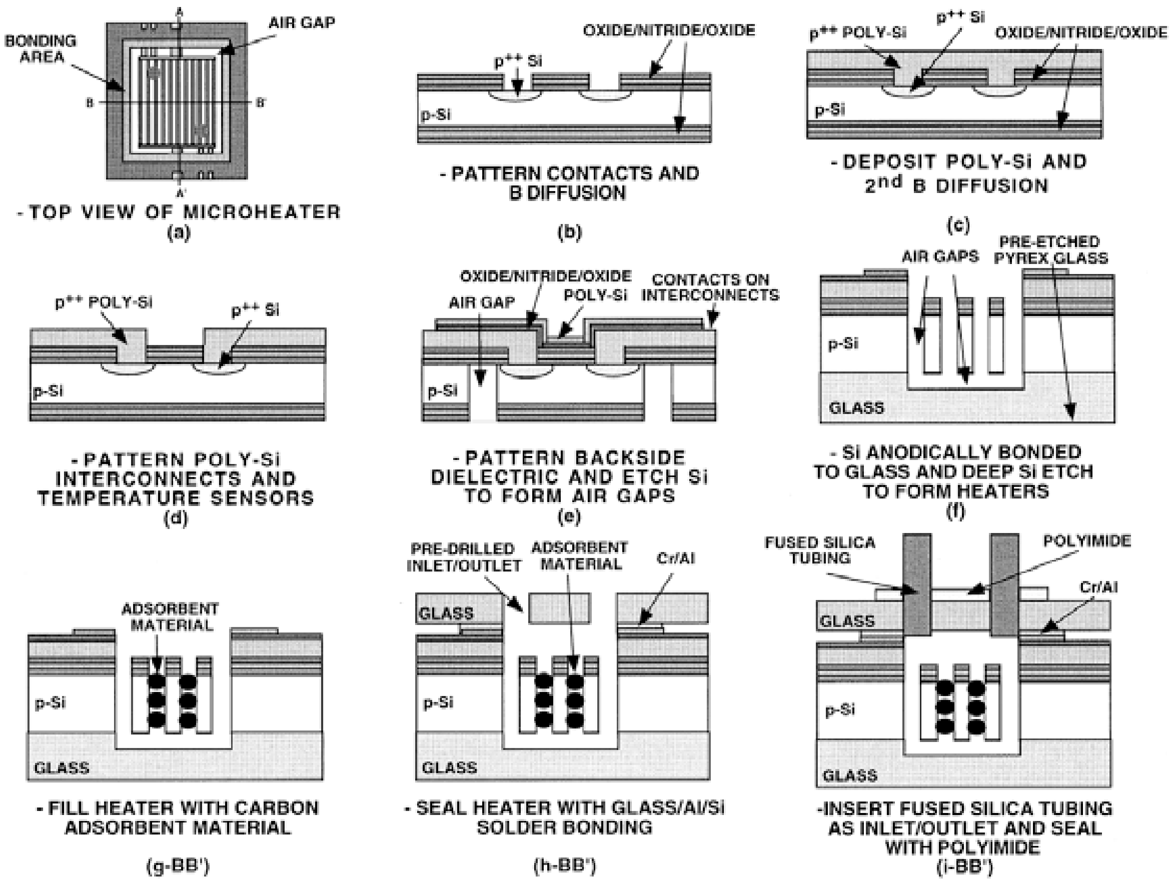
Microheater with Carbopack X adsorbent granules loaded between the heating elements

Preconcentration factors as high as 5600 and desorbed peak widths as narrow as 0.8 s are achieved from 0.25-L samples of benzene at modest heating rates.

MESA+

Tian e.a. J.MEMS 12, 264-272 (2003)

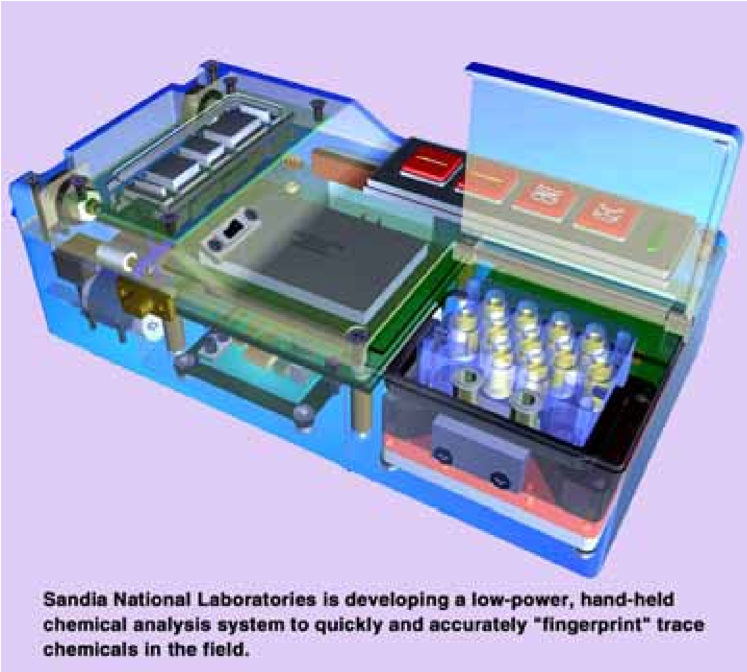
University of Twente
The Netherlands



MESA+

University of Twente
The Netherlands

µChemLab™ project at Sandia

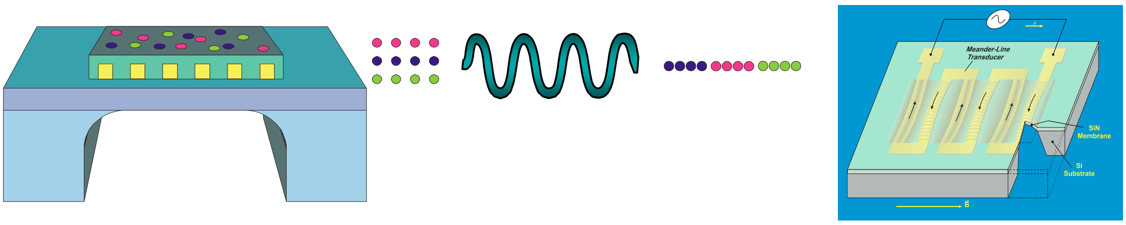


MESA+

For an overview see: D.Lindner, Lab Chip 1, 15N-19N (2001)

University of Twente
The Netherlands

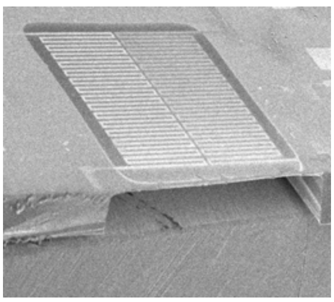
Concept of GC-based mChemLabTM

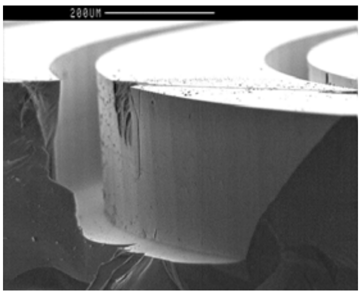


Preconcentrator accumulates species of interest

GasChromatograph separates species in time

Acoustic Sensors provide sensitive detection



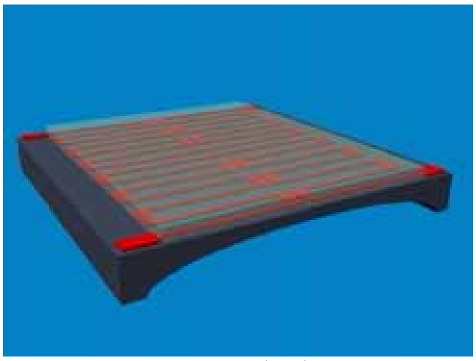


MESA+

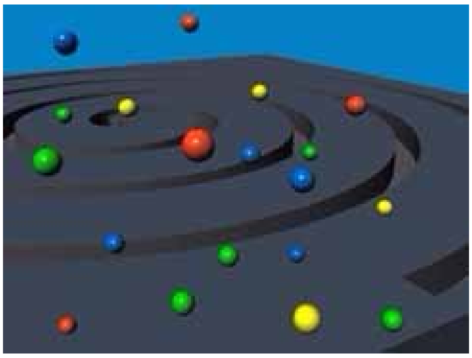
Courtesy of W. David Williams

Sandia National Laboratories

University of Twente
The Netherlands

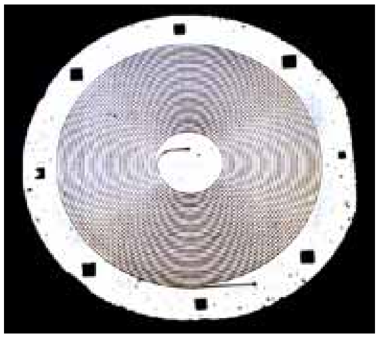


☞ preconcentrator

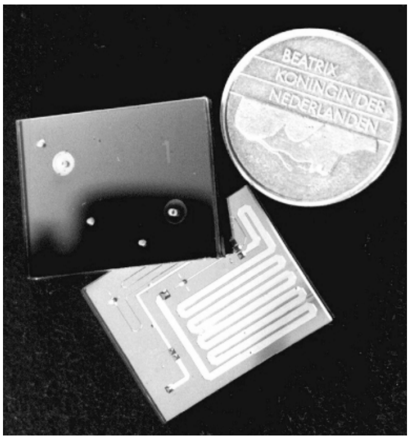


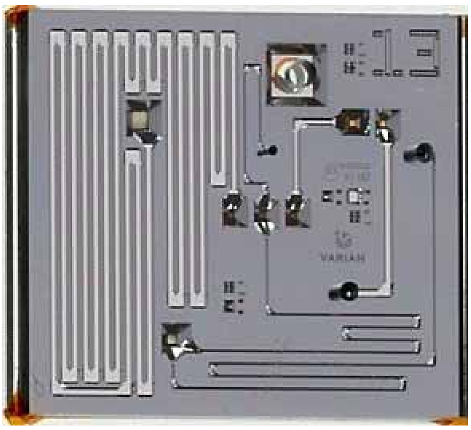
gas chromatograph

acoustic mass detector



Silicon micromachined injectors

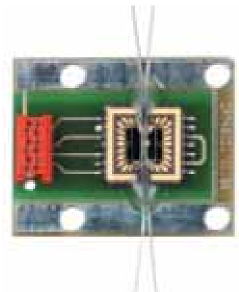




left: older format; right: format used in Varian CP-4900 micro-GC
injector info: www.xensor.nl/txtfiles/ projects/xi-proj/injec.htm

Right: micromachined GC-column (replacable)
Left: 200 nl detection volume TCD

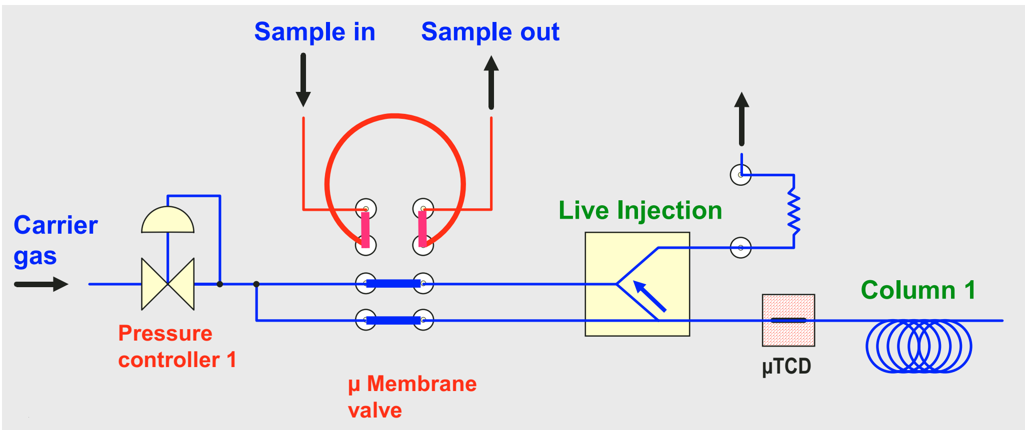
From Varian micro-GC brochure



A new definition of process gas chromatography

Slide courtesy of Arno Steckenborn, Siemens, Germany

Injection step 1: fill loop

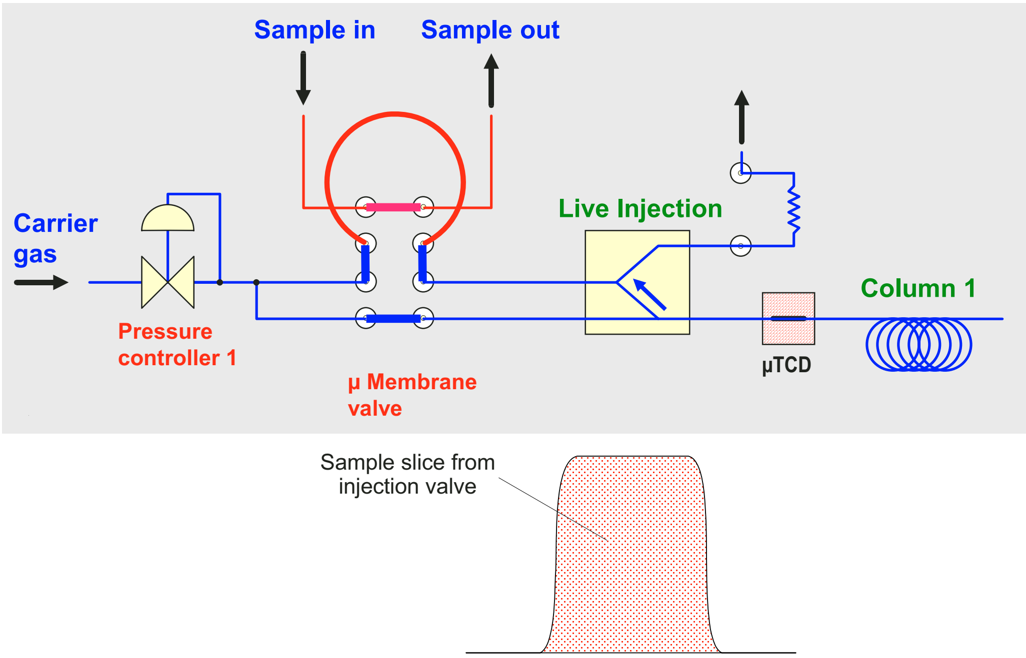


Advantages:

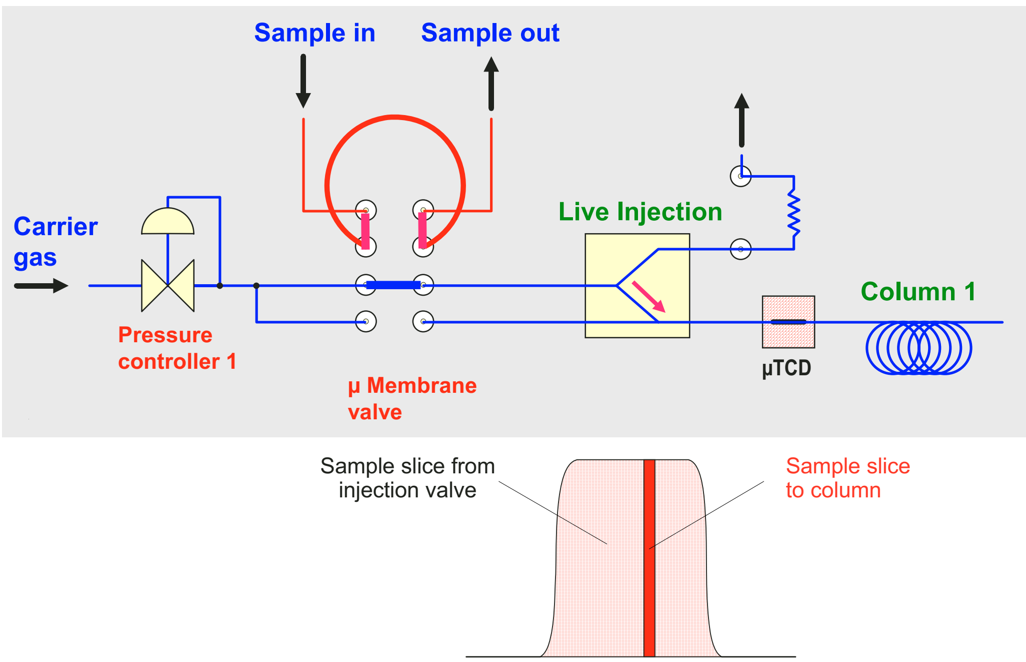
- Narrow start peak width
- Sample equilibrated to carrier gas pressure level (sample pressure independent)
- Injection volume adjustable by time
- Injection quality does no longer depend on valve quality
- Tolerance against quality and even leakage of the sample valve

Slide courtesy of Arno Steckenborn, Siemens, Germany

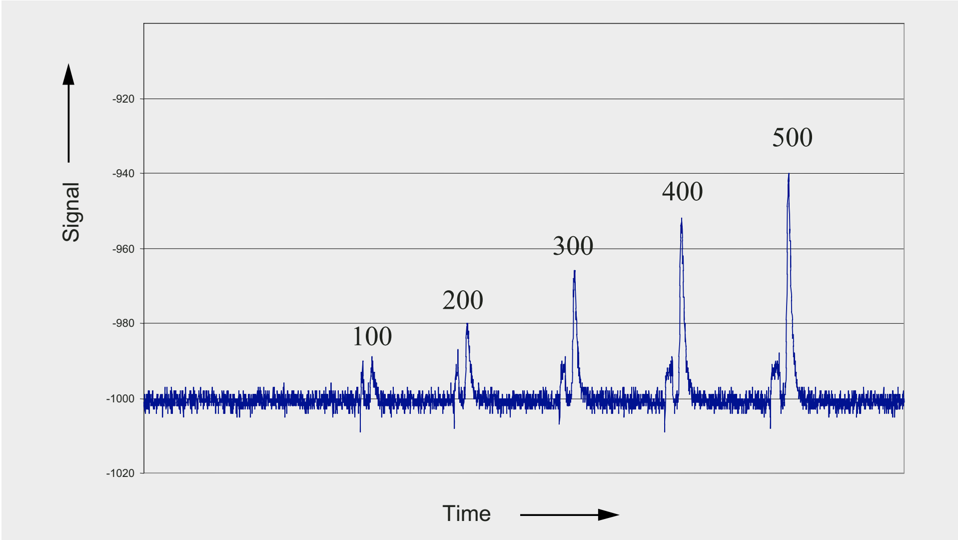
Injection step 2: flow to injector

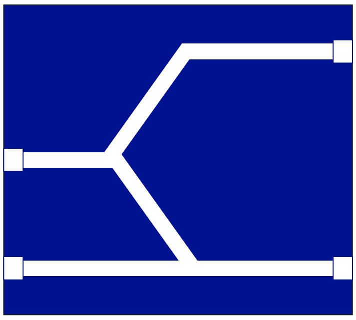


Injection step 3: split of slice



Detector response of injection quantity introduced with various injection times (in 0.01 s).

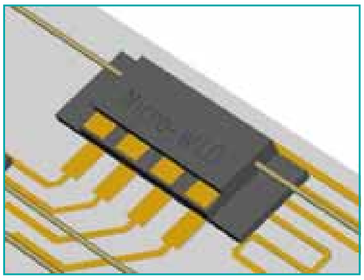


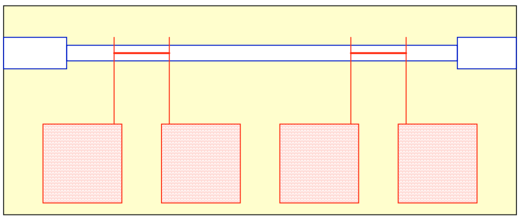


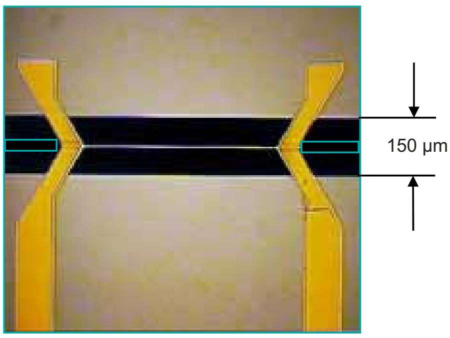
Micromachined splitter

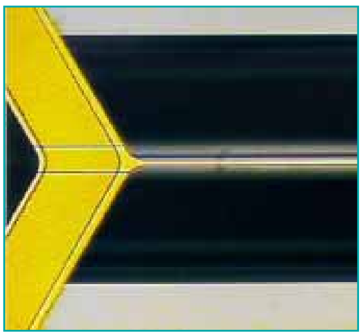
Slide courtesy of Arno Steckenborn, Siemens, Germany

Micro TCD



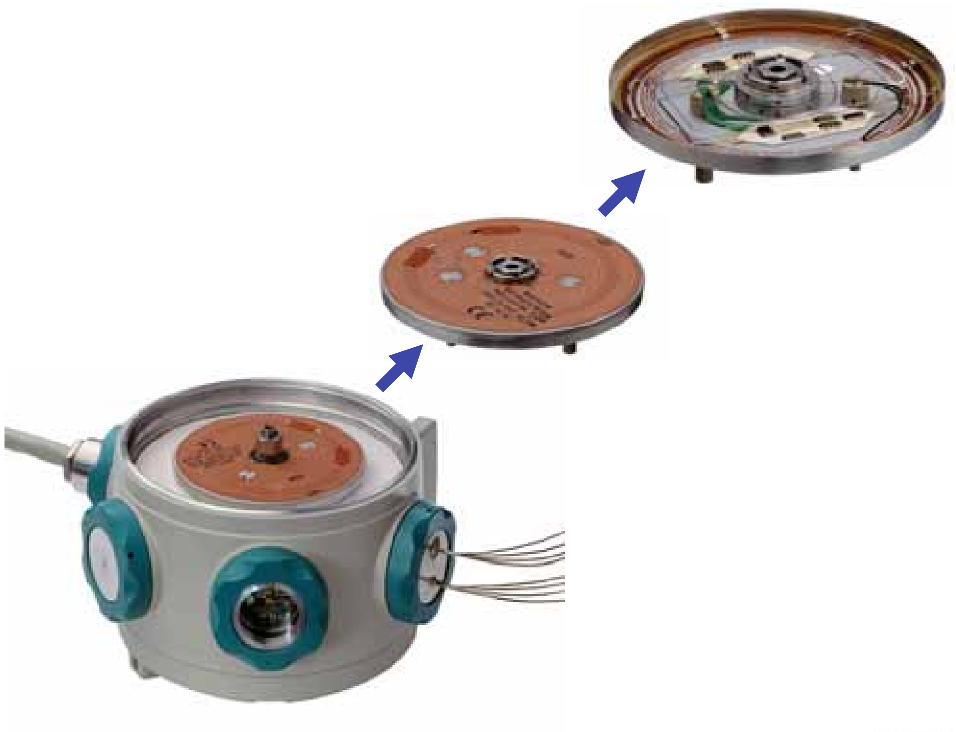






Slide courtesy of Arno Steckenborn, Siemens, Germany

Analyzer Module



Slide courtesy of Arno Steckenborn, Siemens, Germany