TEL AVIV UNIVERSITY אוניברסיטת תל-אביב

School of Chemistry
Raymond and Beverly Sackler Faculty of Exact Sciences

Figures for the course:

Advanced methods in analytical chemistry

Given in 2019-2020 by

Prof. Aviv Amirav

The students are requested to bring the figures for
EVERY MEETING

Figures for the course:

"Advanced methods in analytical chemistry"

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The following are figures for the course above, arranged in six main subjects:

1. Chromatography and GC – Figures 1-9 and 21-25.
2. Gas chromatography detectors – Figures 10-20.
3. Liquid chromatography – Figures 26-32.
4. Mass spectrometry including GC-MS and LC-MS Figs 33-50.
5. Atomic spectroscopy and elemental analysis – Figures 51-58.

The students are requested to bring the figures for
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The figures can also be viewed and downloaded from the course web site:

http://www.tau.ac.il/~instanal/Instrumental%20Analytical%20Chemistry.htm

Internet Links

http://www.shsu.edu/~chm_tgc/sounds/sound.html

Contains informative short animation clips describing a range of analytical instrumentation, including GC (in general, split splitless injection, detectors), HPLC 6-port injector, GC-MS and Atomic Absorption.
Some of the clips include audio narrations.

http://svmsl.chem.cmu.edu/vmsl/

The Virtual Mass Spectrometry Laboratory. Includes general information, tutorials (GC-MS), and case studies

http://www.ionsource.com/tutorial/chromatography/rphplc.htm#Introduction

http://shula-lc.co.il/

An informative and user-friendly site. HPLC, LC-MS and FTIR courses, including short clips.

http://www.separationsnow.com

Including news from the field of chromatography, several training tests and links.

http://www.lcms.com/

You can download this page from the website of the course (http://www.tau.ac.il/~instanal/Instrumental%20Analytical%20Chemistry.htm), and then just click on the links.

Please let us know at amirav@tau.ac.il on any other website that you find as useful and informative for it's inclusion in next year's links.

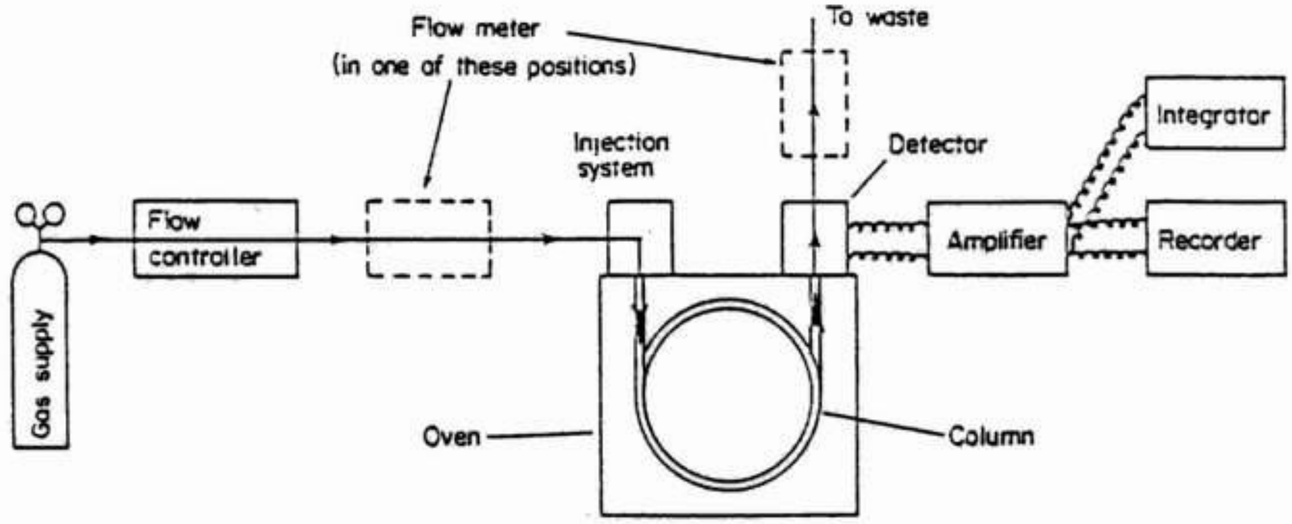


Fig. 1 *Block diagram of a gas chromatograph*

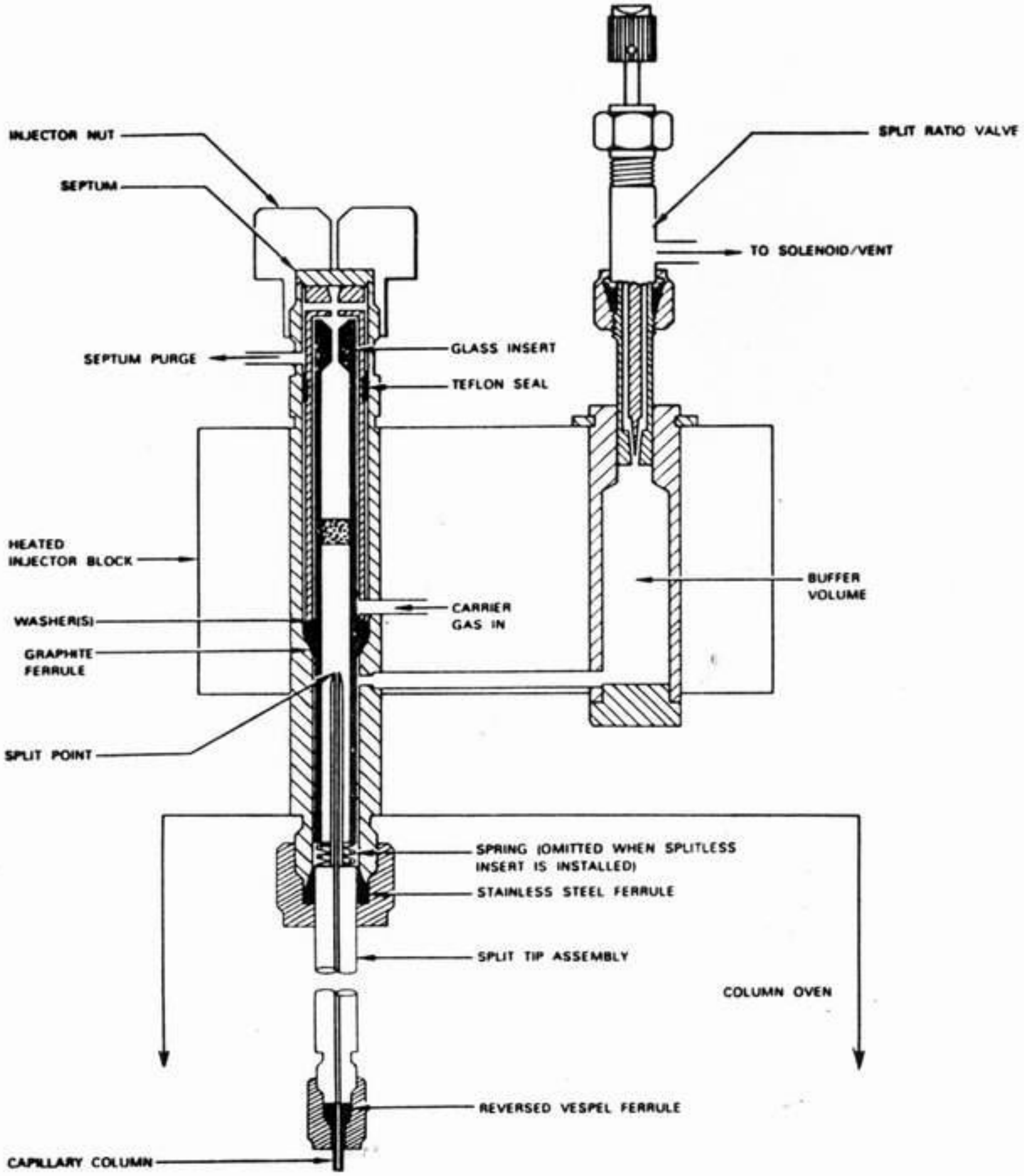


Fig. 2 Cross-sectional view of a split-splitless injection assembly. (Reproduced with permission from Varian Associates).

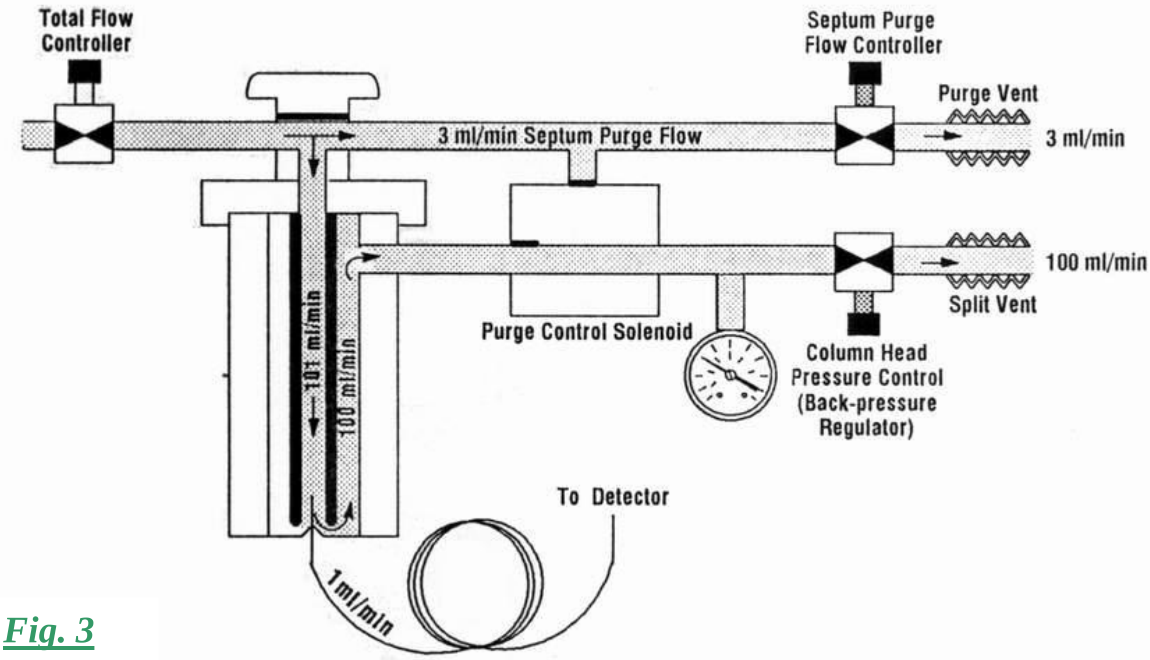


Fig. 3

Several liners used with split inlets.

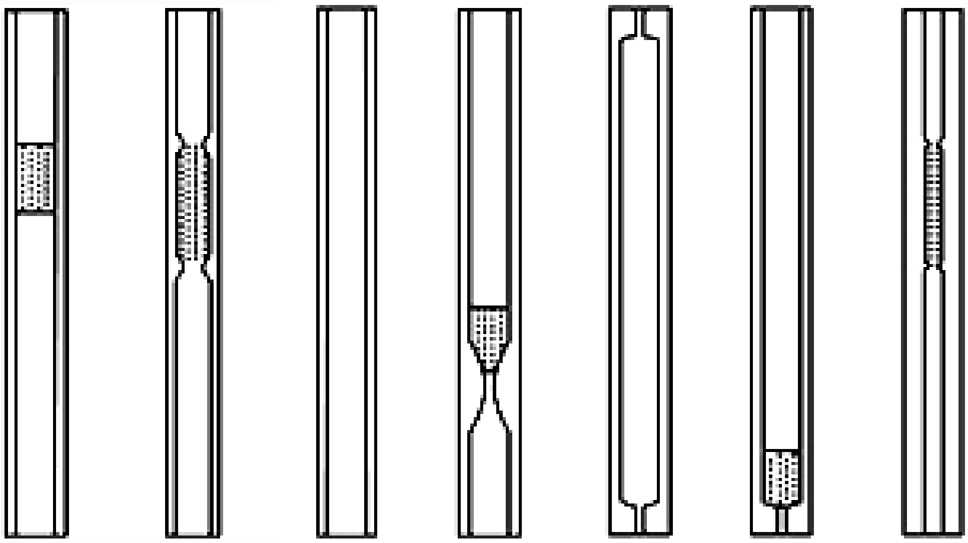


Fig. 4

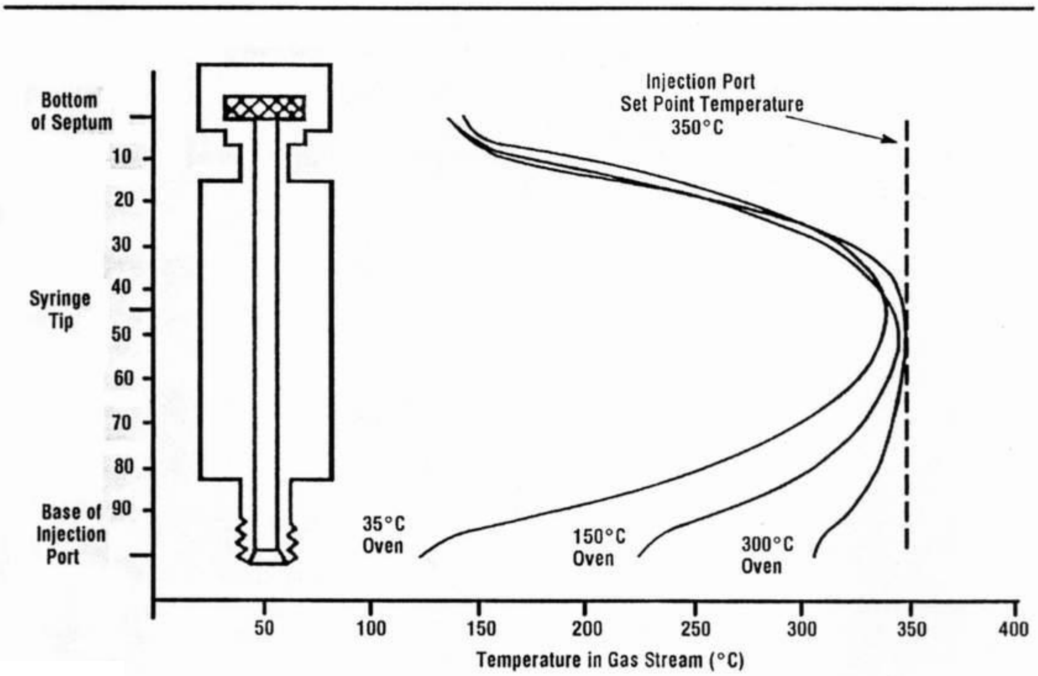


Fig. 5 **Thermal profiles of a typical inlet.**

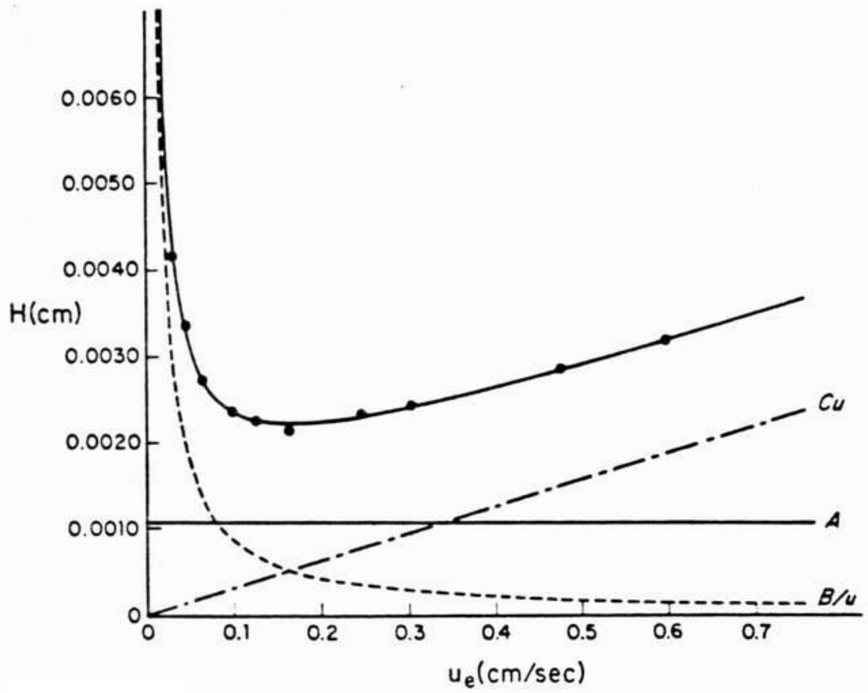


Fig. 6 Relationship between band broadening and mobile phase velocity (van Deemter equation). (Reproduced with permission from ref. 48. Copyright Elsevier Scientific Publishing Co.)

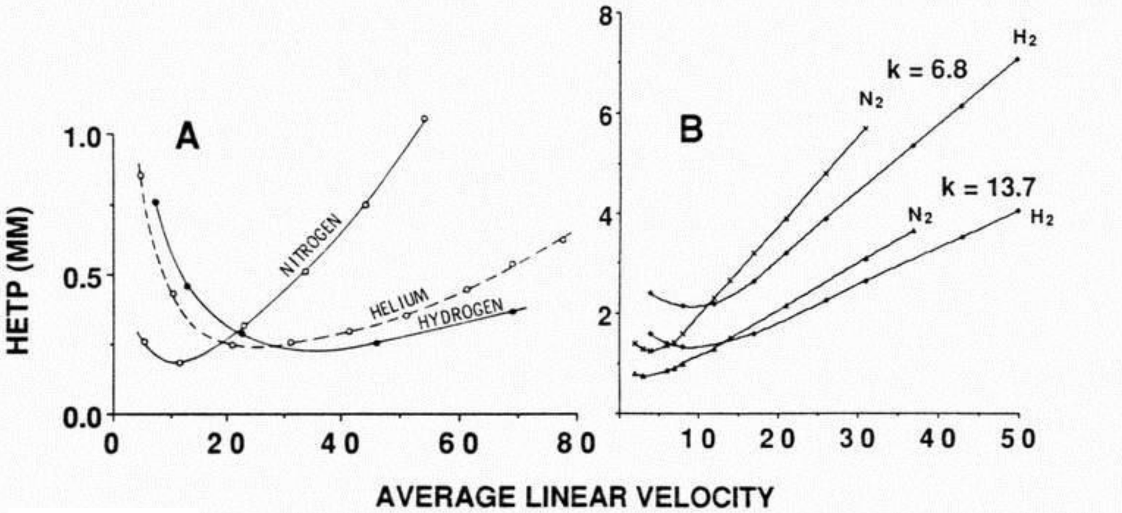


Fig. 7 Van Deemter curves indicating the influence of the choice of carrier gas on the separation performance of a thin-film open tubular column (A), and a thick-film open tubular column for two solutes with different capacity factor vales (B).

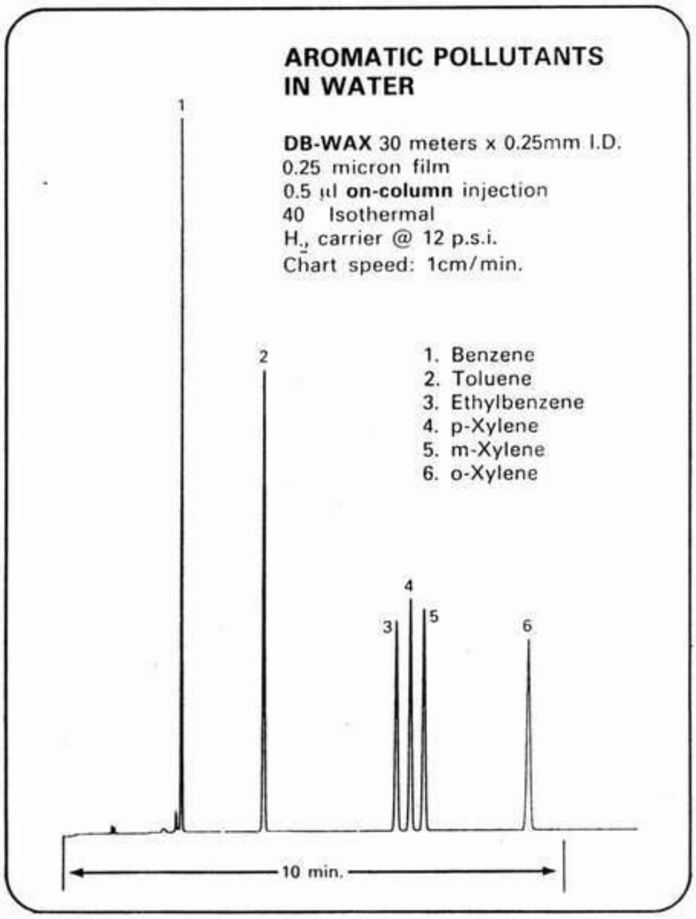


Fig. 8 Separation of xylene isomers on a polar column, DB-Wax. Courtesy of J & W Scientific.

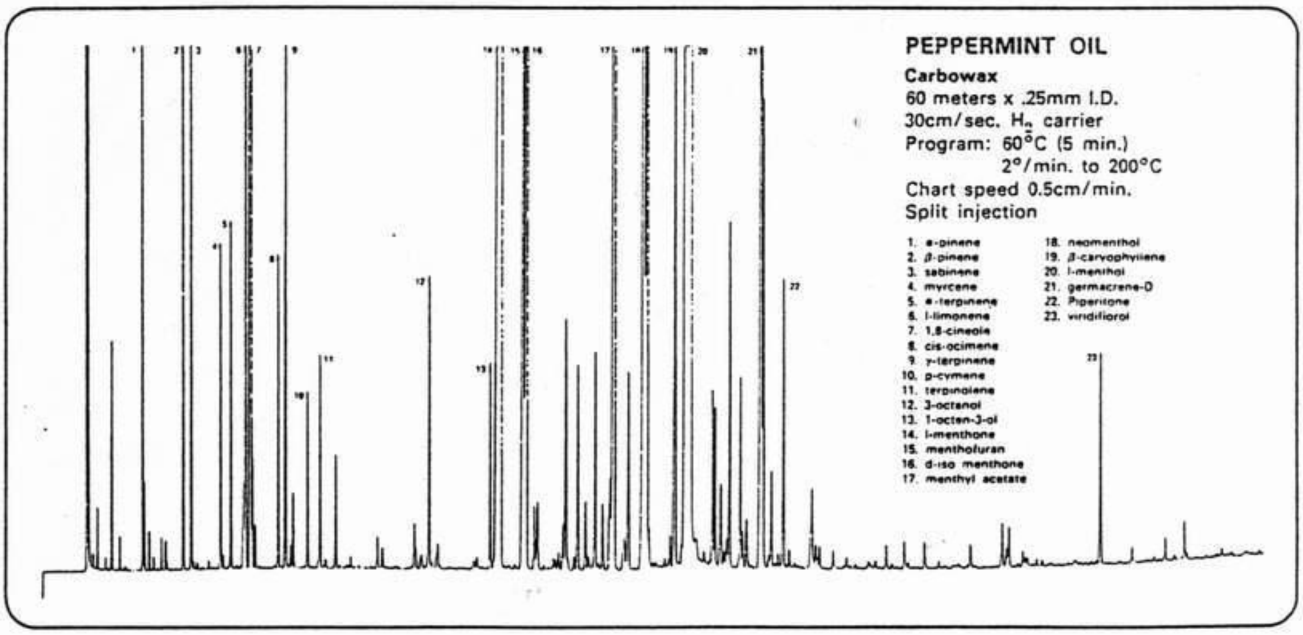


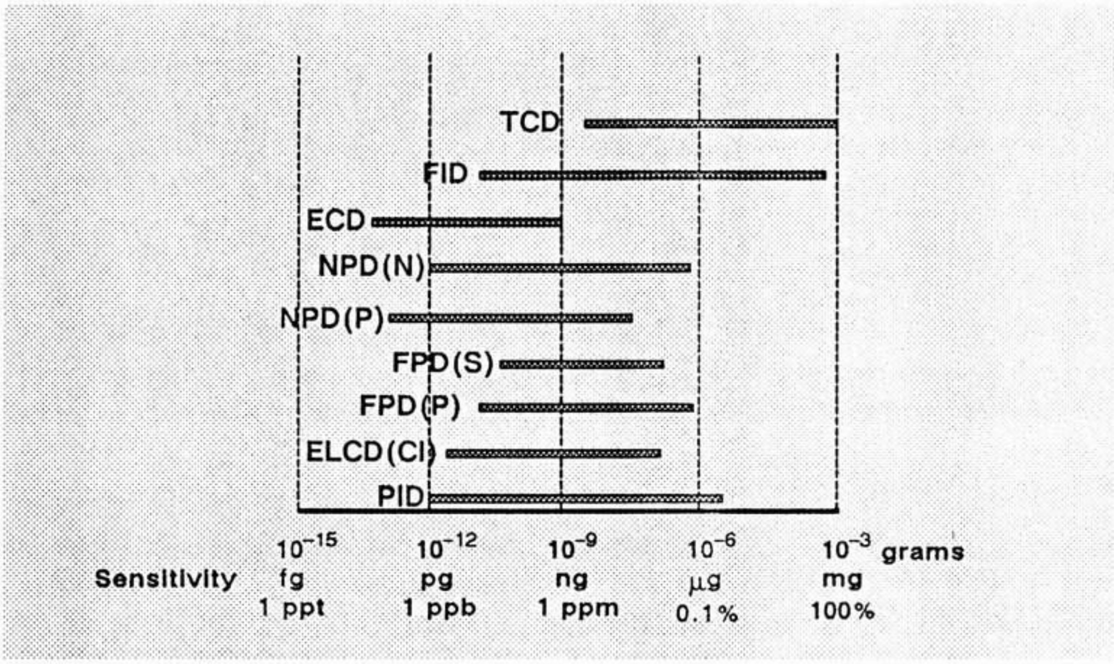
Fig. 9 Typical gas chromatographic separation showing the high efficiency of this method. Courtesy of J & W Scientific.

GC Detectors

General Characteristics of GC Detectors

Name	Type	Selective For:	Typical Min. Detectible Level (S/N = 2)	Linear Dynamic Range
FID	Selective	Materials that ionize in air/H2 flame	5 pg C/sec	10^7
TCD	Universal	Anything with thermal cond. different from carrier	400 pg/ml carrier	10^6
ECD	Selective	Gas-phase electrophores	0.1 pg Cl/sec (varies w/structure)	10^4
PID	Selective	Compounds ionized by UV	2 pg C/sec	10^7
Thermionic	Selective	N,P, heteroatoms	0.4 pg N/sec 0.2 pg P/sec	10^4
ELCD	Selective	Halogens, N,S	0.5 pg Cl/sec 2 pg S/sec 4 pg N/sec	10^6 10^4 10^4
FPD	Specific	P,S	20 pg S/sec 0.9 pg P/sec	10^3 10^4
FTIR	Universal	Molecular vibrations	1000 pg of strong absorber	10^3
MSD	Universal	Tunable for any species	10pg to 10 ng (depending on SIM vs. scan	10^6
AED	Universal	Tunable for any element	0.1 – 20 pg/sec (depending on element)	10^4

Fig. 10

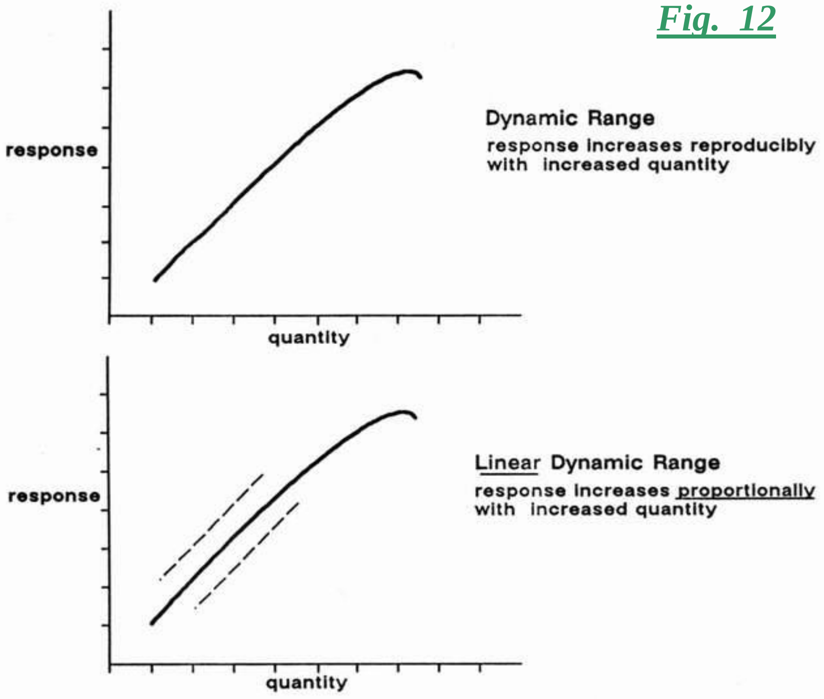


Comparison of various common GC detectors.

Fig. 11

Detectors for Gas Chromatography

Fig. 12



The response/quantity curve is another way to represent detector response; at the top is the full dynamic range curve, below is the linear portion. Note: the plot on the previous page (response factor/quantity) is less likely to be misinterpreted, since the linear portion will always be horizontal.

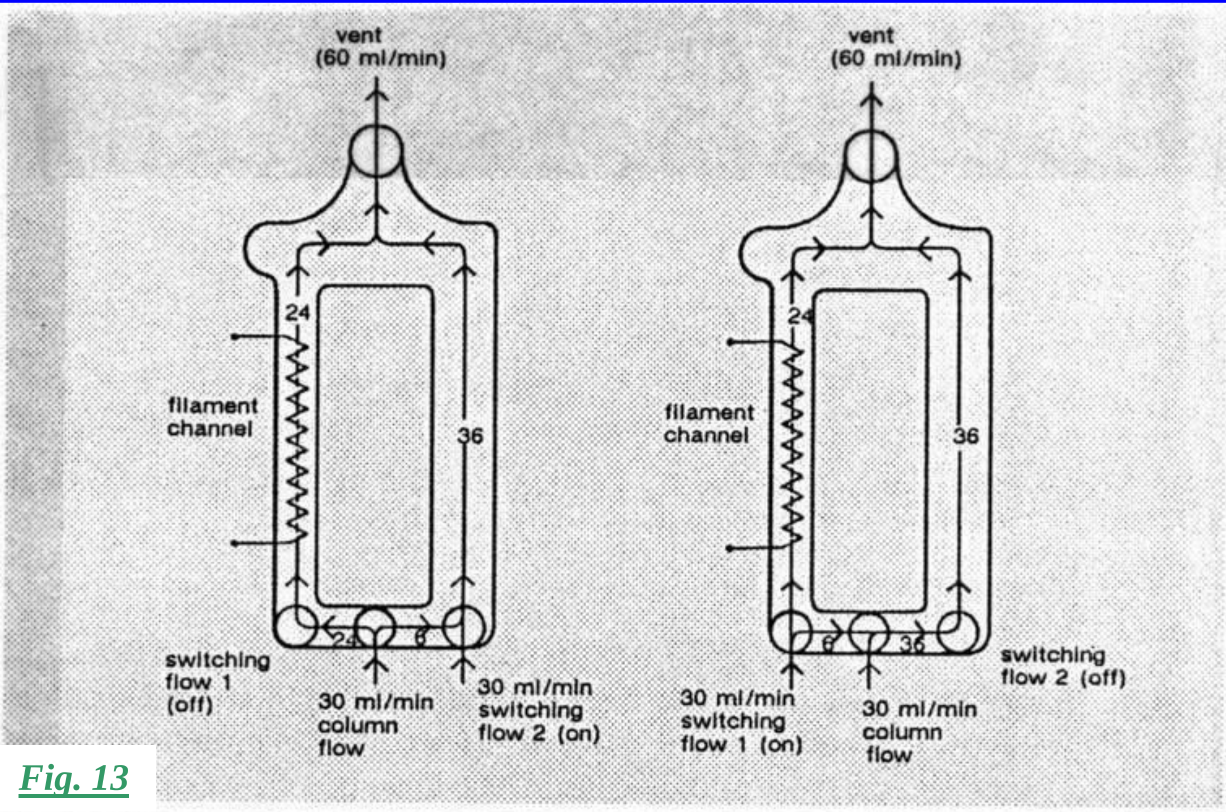


Fig. 13

Flow diagram of a commercially available TCD cell. In the left diagram, the switching flow causes the column effluent to pass through the filament channel. When the switching flow changes (right diagram), the column effluent will pass through the empty channel. During this time the filament channel fills with the switching gas, and reference measurements are made. Switching between the column effluent and reference gas occurs every 100 milliseconds.

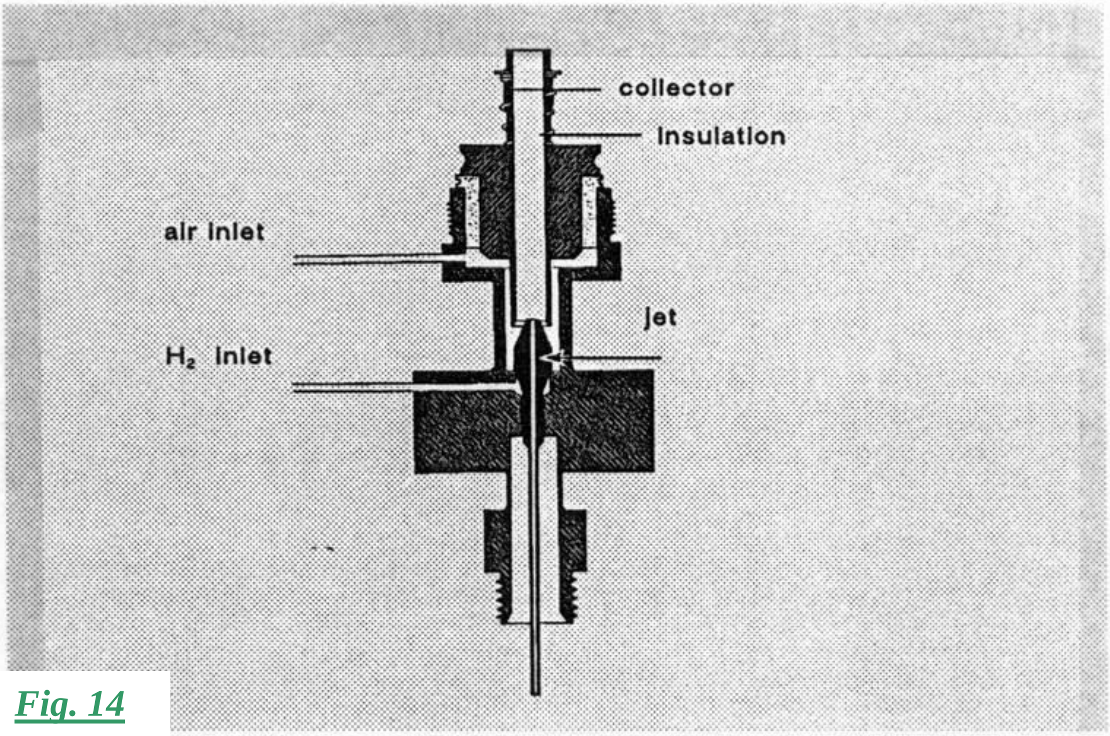


Fig. 14

Design of a commercially available flame ionization detector.

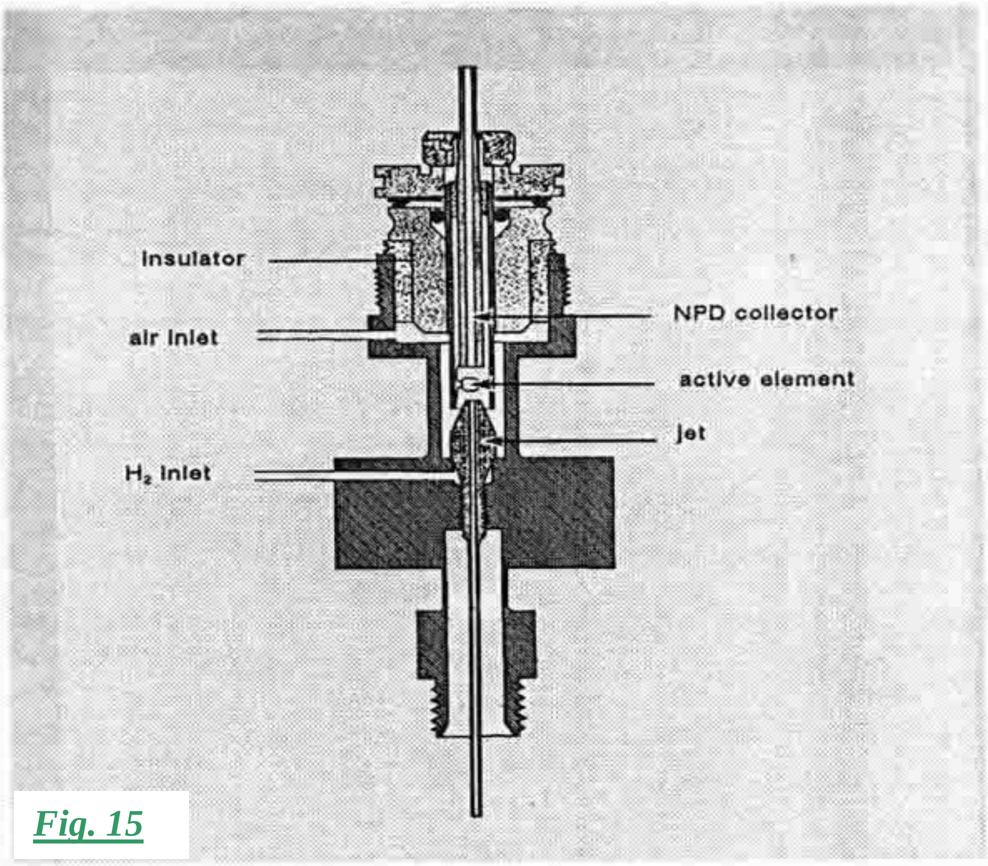


Fig. 15

Design of a commercially available nitrogen/phosphorus detector.

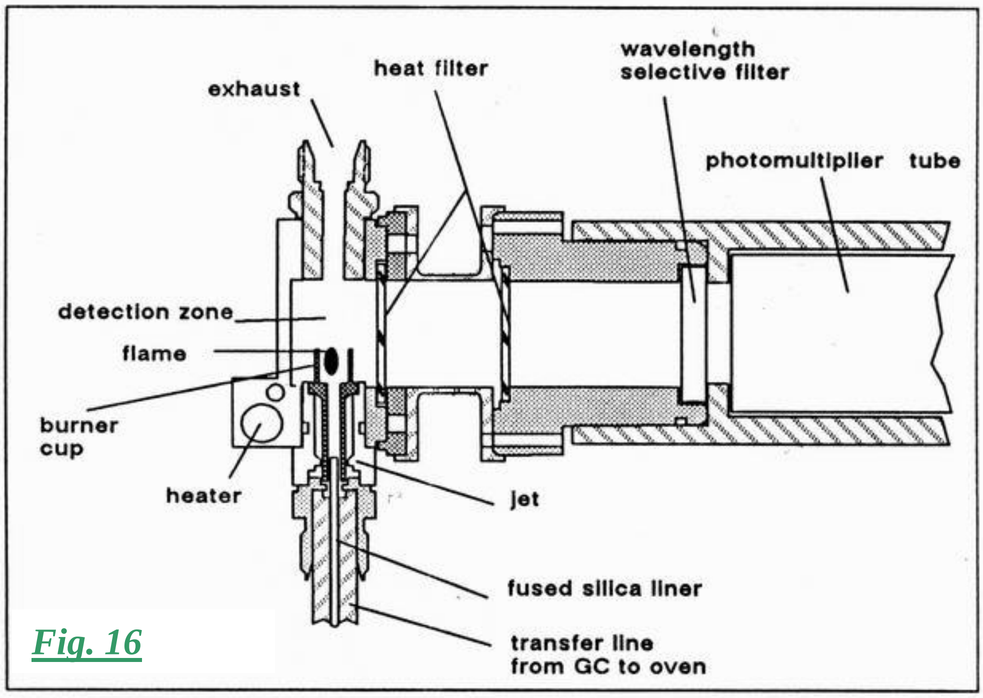


Fig. 16

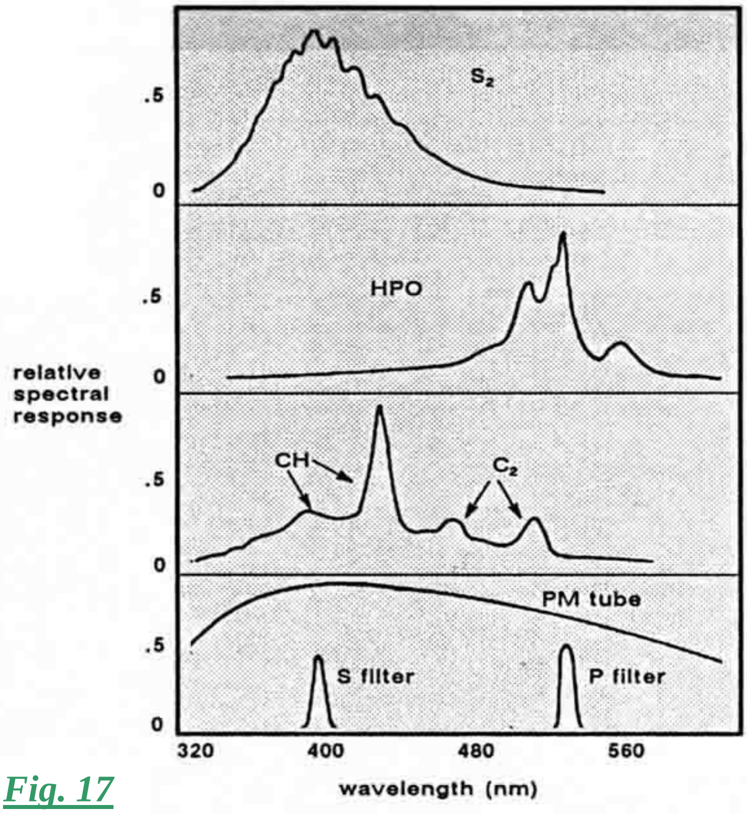


Fig. 17

Relative spectral response curves for sulfur, phosphorus and carbon. Note the effect of filters selective for sulfur and phosphorus.

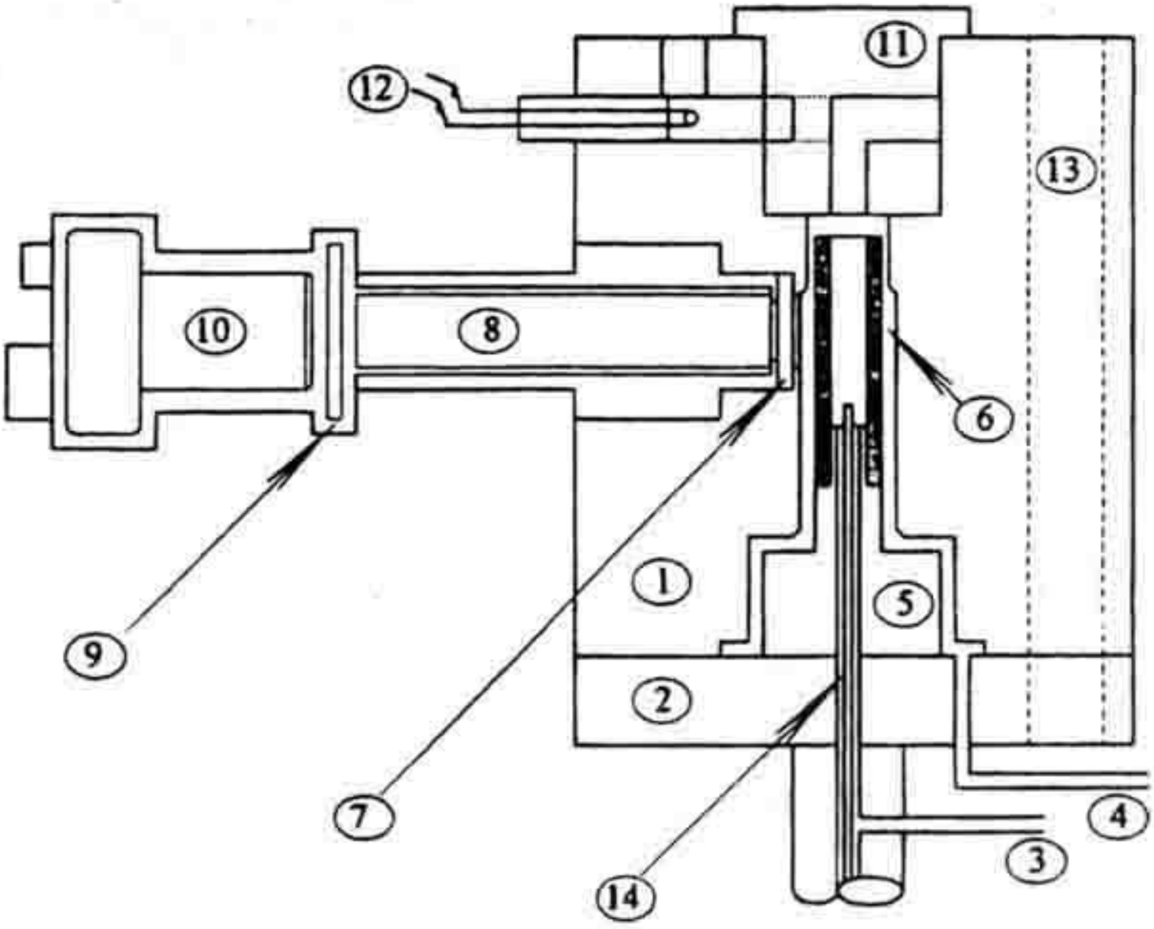


Fig. 18 Schematic diagram of the new PFPD design. (1) PFPD body; (2) GC-heated detector base; (3) central hydrogen-rich H_2/air mixture tube leading to the combustor; (4) outer bypass H_2/air mixture tube; (5) combustor holder (6) quartz combustor tube; (7) sapphire window; (8) light guide; (9) colored glass filter; (10) photomultiplier; (11) spiral igniter light shield; (12) heated wire igniter; (13) assembly guiding rod in a guiding hole; (14) column.

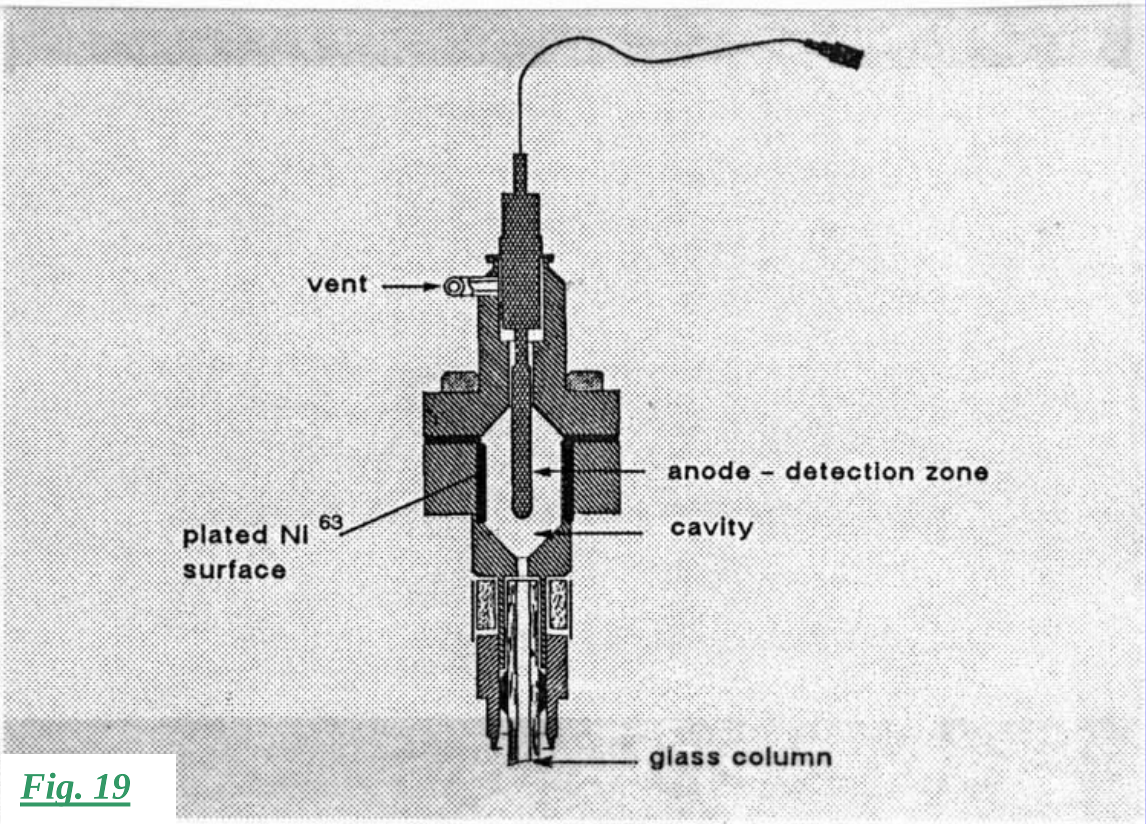


Fig. 19

Design of a commercially available electron capture detector.

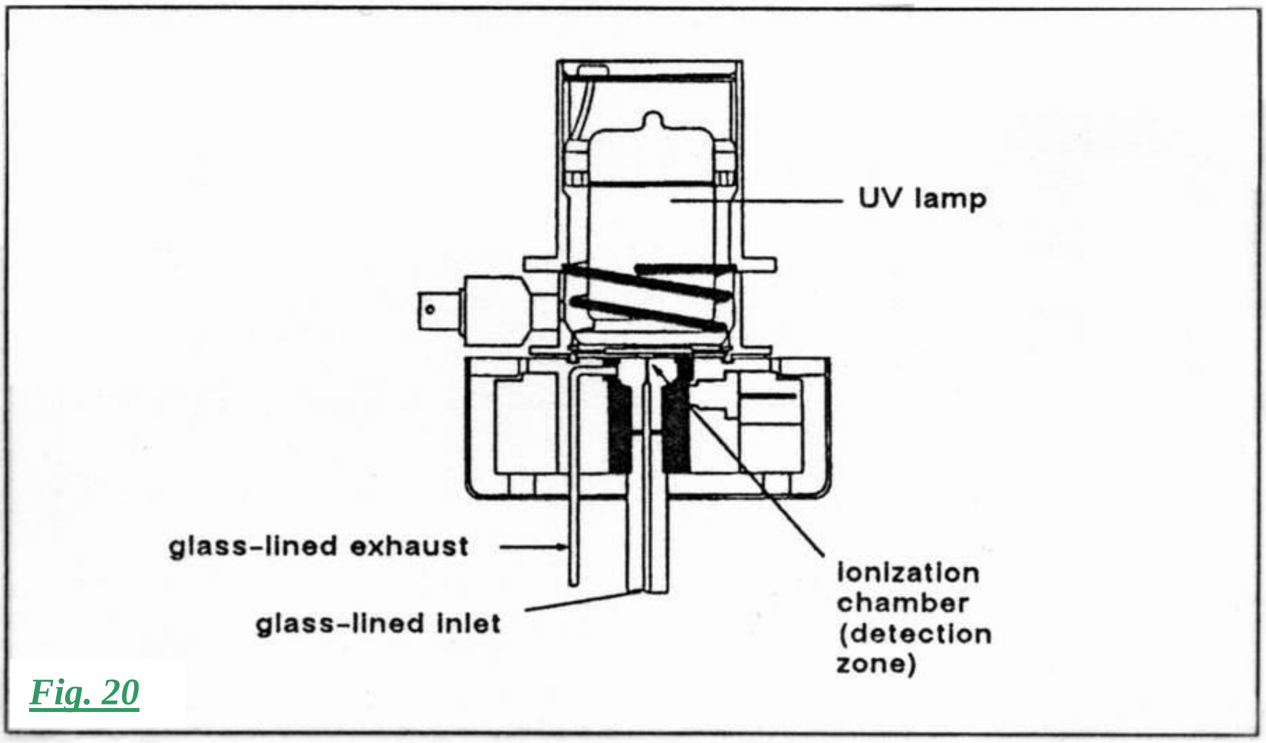


Fig. 20

Diagram of a commercially available photoionization detector.
Courtesy, HNU Systems, Inc.

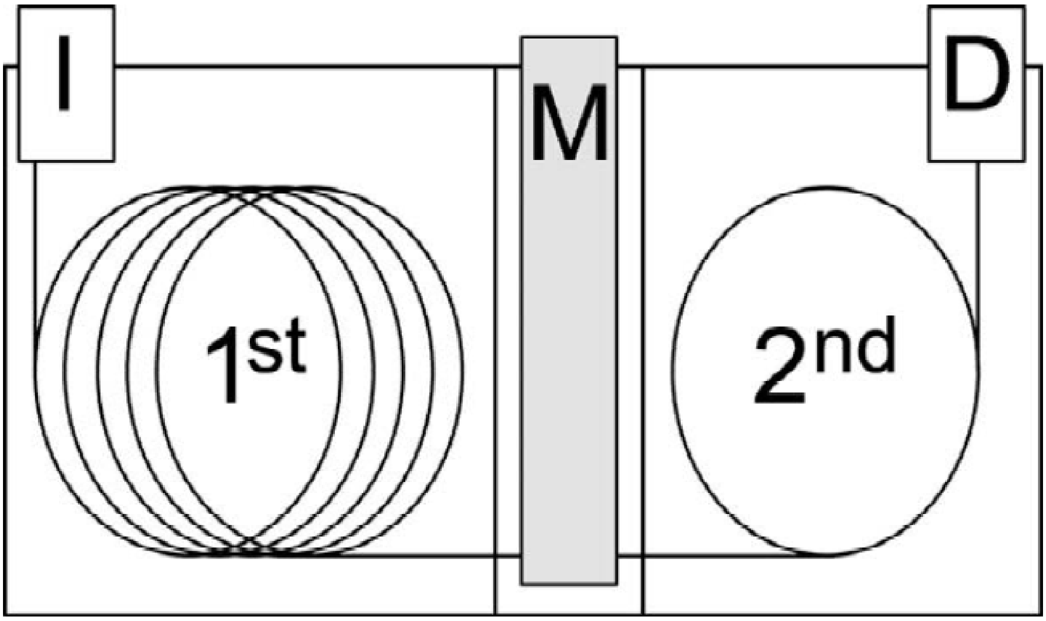


Fig. 21 Schematic of a GC×GC system. I, injector; M, modulator; D, detector; 1st, GC oven with first-dimension column; 2nd, (separate) GC oven with second-dimension column.

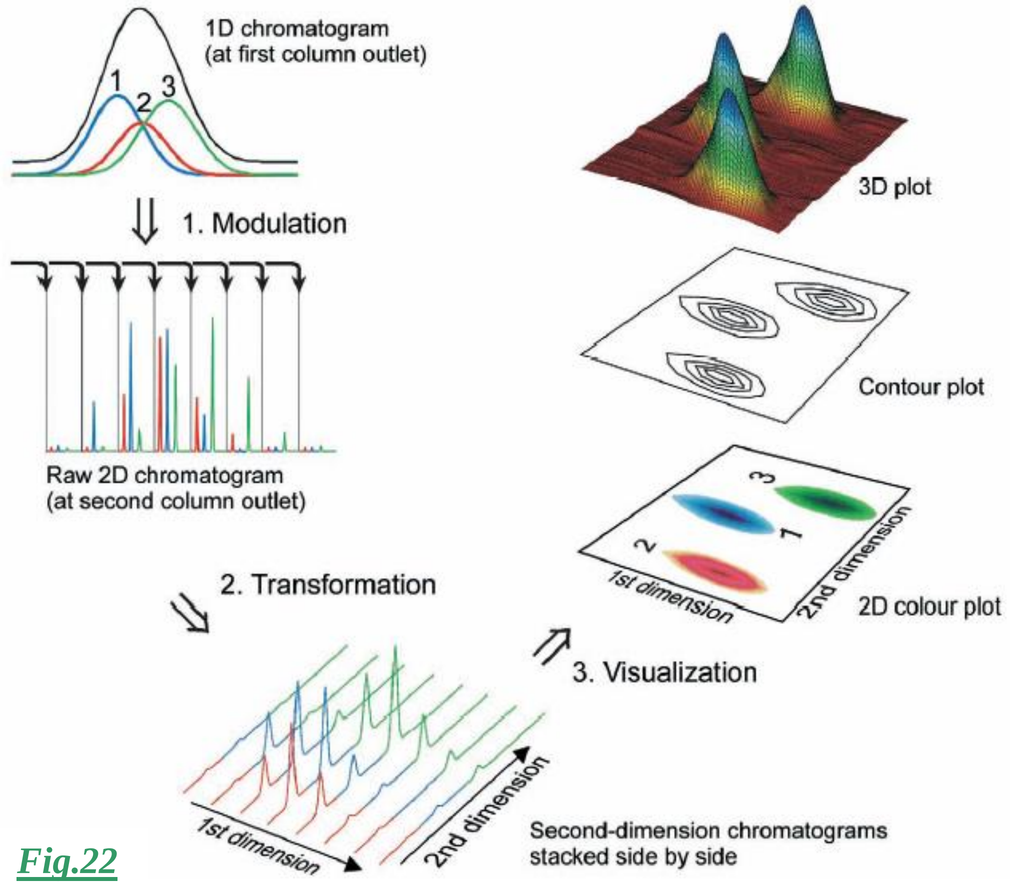


Fig.22

Generation and visualisation of a GC×GC chromatogram.

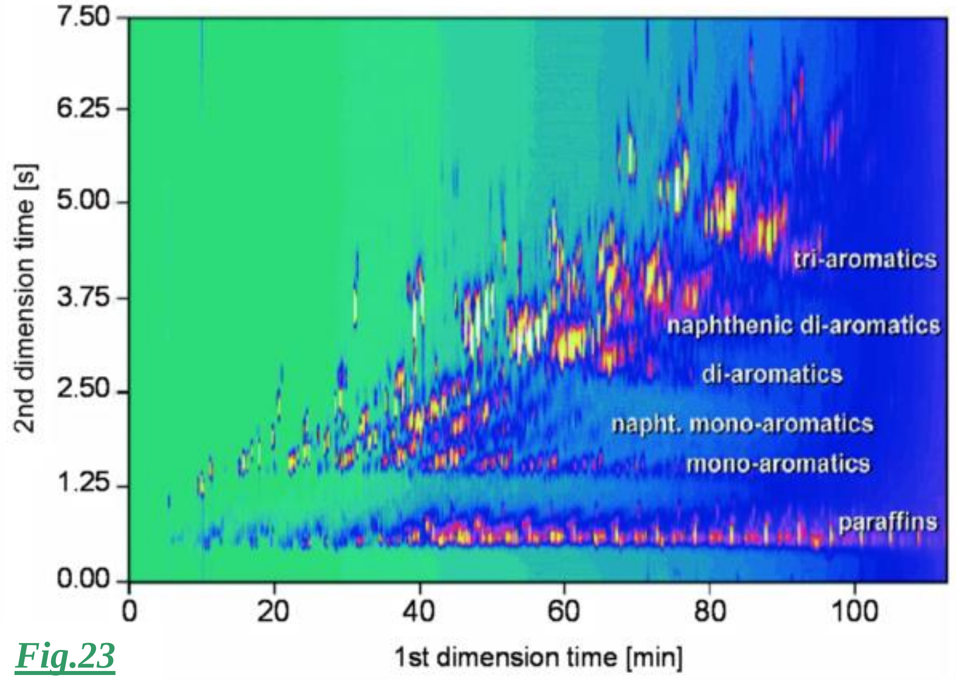


Fig.23

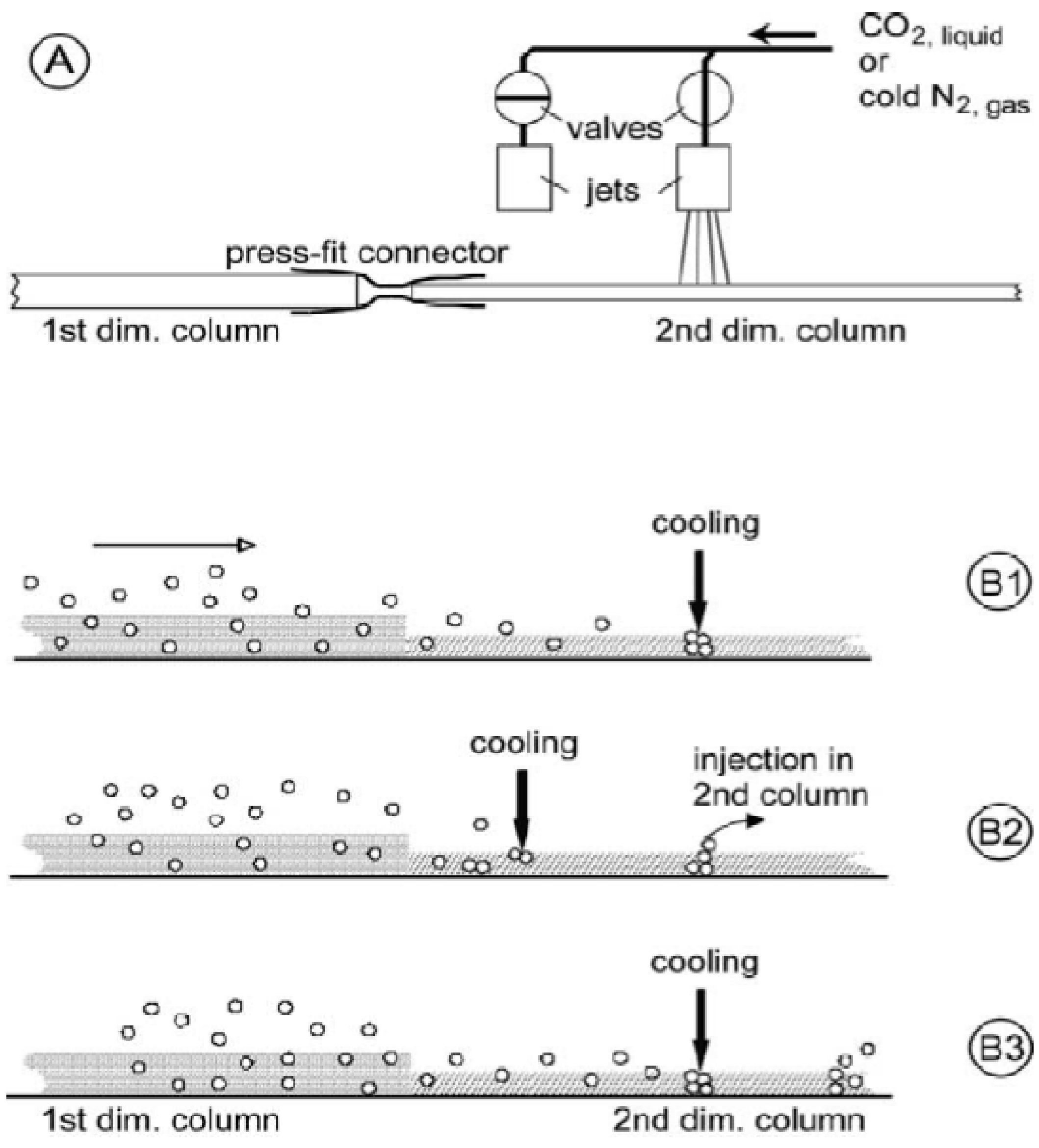
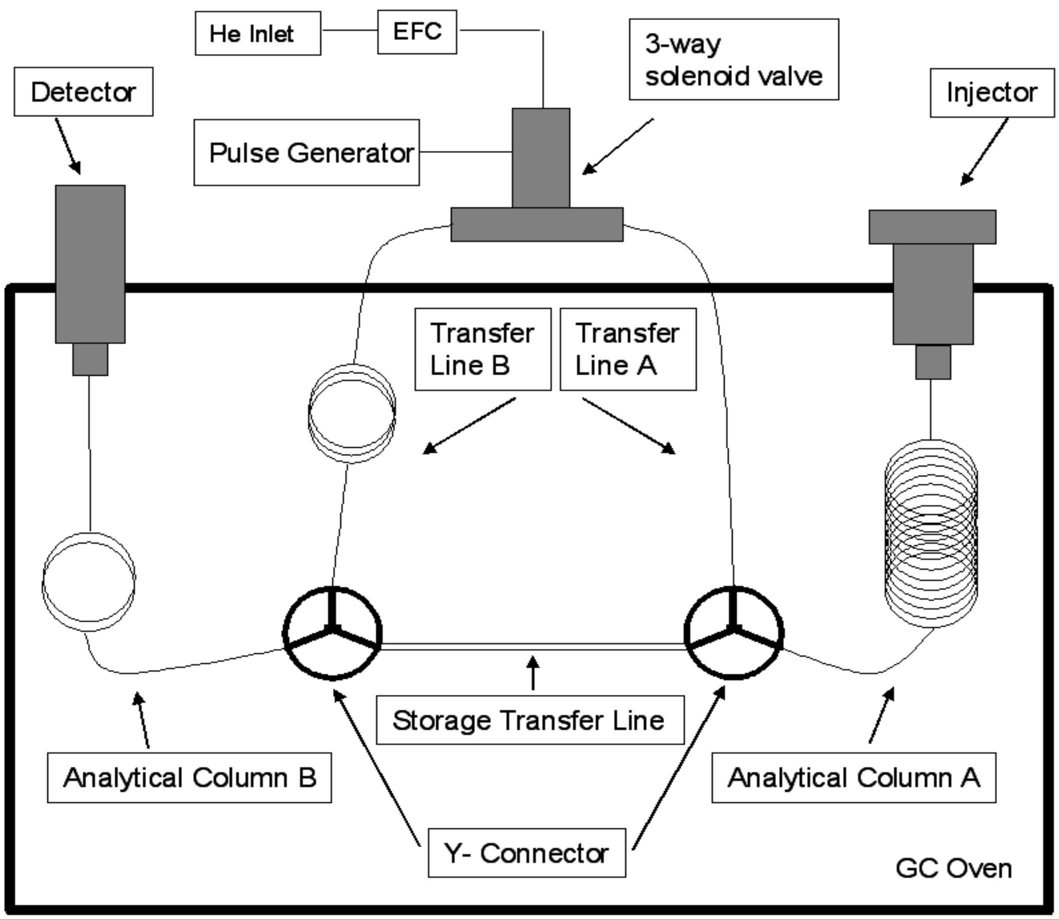


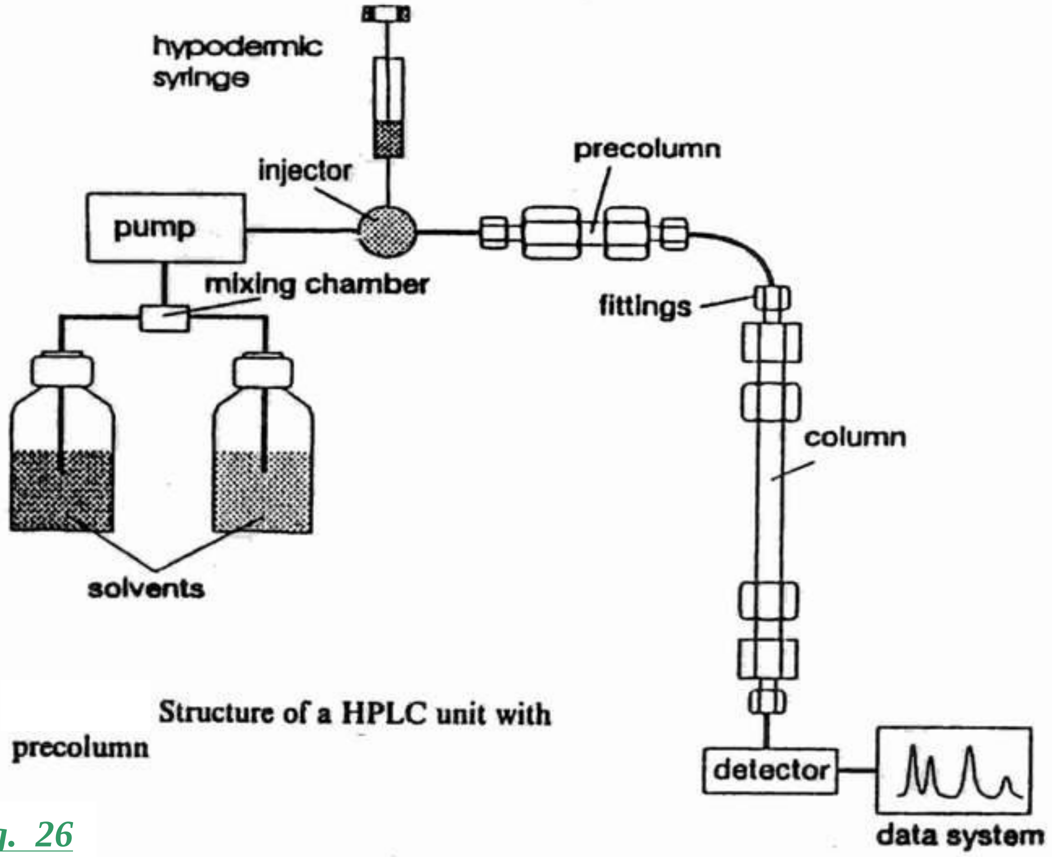
Fig. 24 (A) Schematic of a two-jet cryogenic modulator; (B1–3) principle of cryogenic modulation. (B1) The modulator (right-hand jet) retains part of a peak eluting from the first column. (B2) The right-hand jet is switched off, the cold spot heats up very quickly and the analytes are released and launched for separation in the second column. Meanwhile, the left-hand jet is switched on to prevent material eluting from the first column to interfere with the focused fraction. (B3) The right-hand jet is switched on again and the next modulation cycle is started.

Pulsed Flow Modulation for GCxGC

Two-Dimensional Comprehensive Gas Chromatography

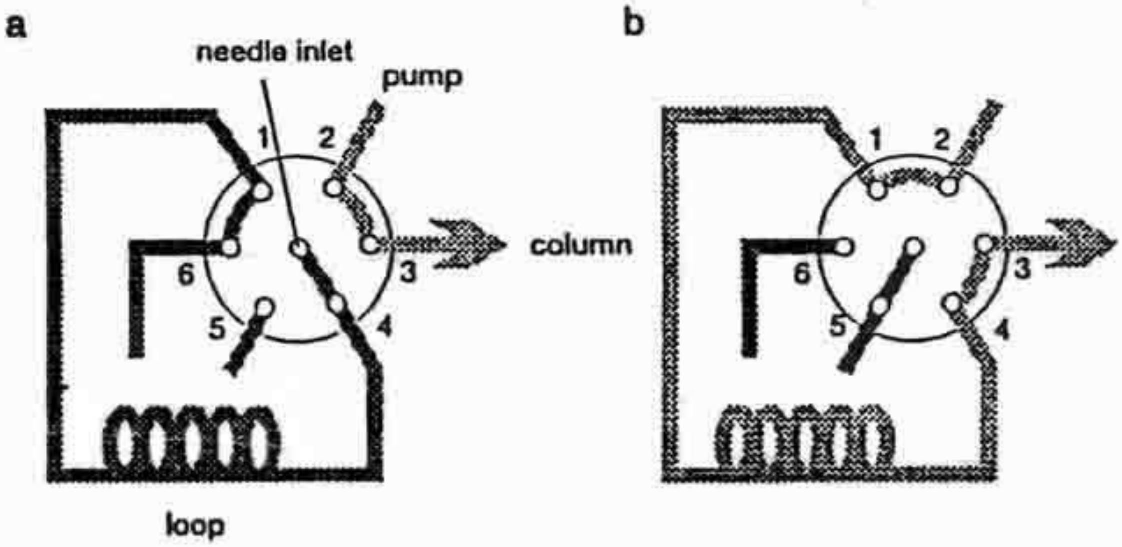
Fig. 25





Structure of a HPLC unit with precolumn

Fig. 26



Injection valve for HPLC.
(a) Filling the sample loop; (b) Injection

Fig. 27

Roger Blain

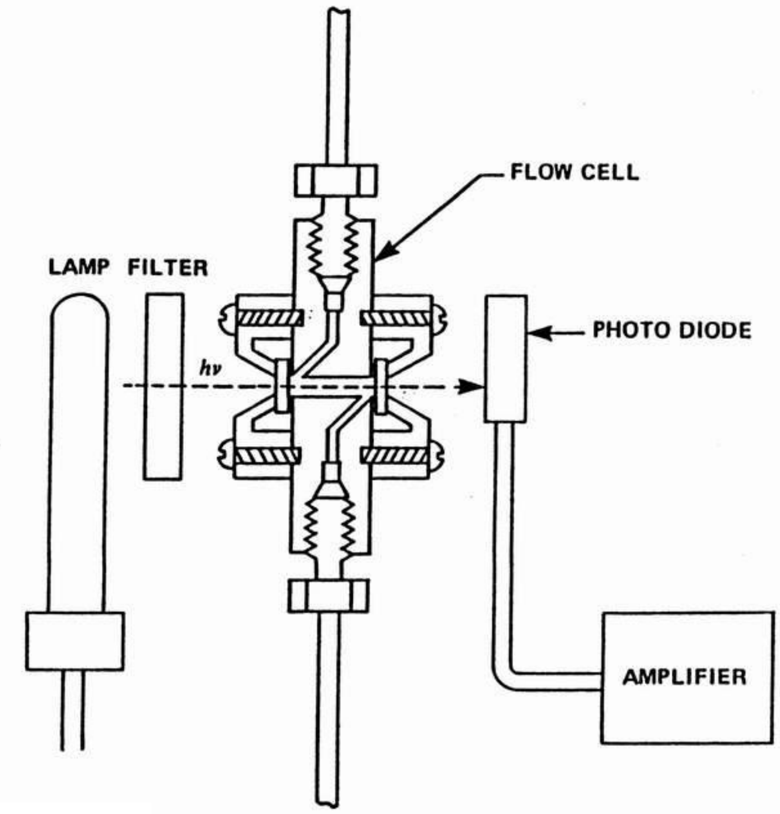


Fig. 28 IG. 3-1 Schematic of a typical absorbance detector.

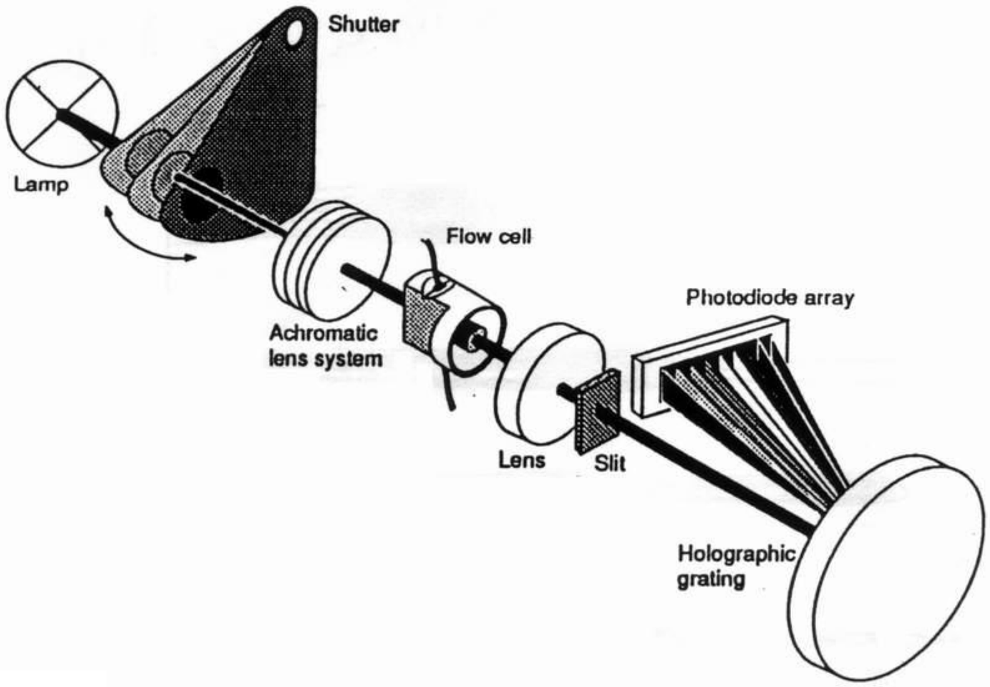


Fig. 29 A single beam diode array detector employing reverse optics. In reverse optics, the flow cell is located before the dispersion grating so that "white" light passes through the sample and is then broken down into its spectral components. Note that the spectrum produced by the grating is focused directly on the diode array. Reproduced with permission of Hewlett-Packard Company.

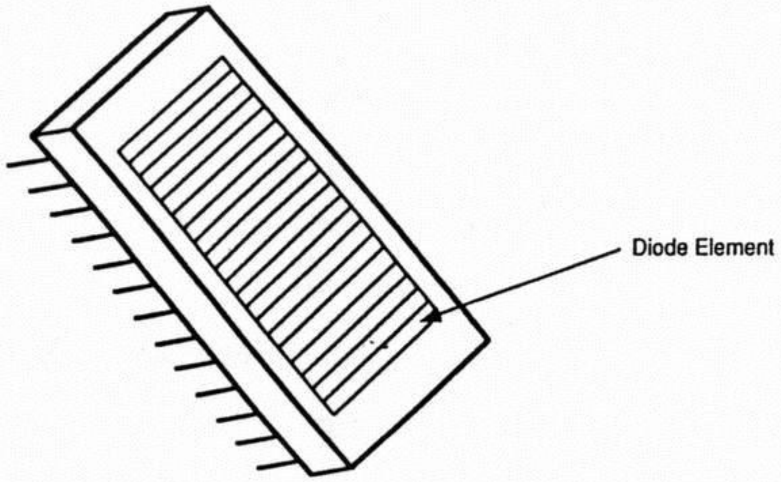


Fig. 30 A typical photodiode array. An array can possess from 35 to 512 photosensitive elements; each element responds to a specific portion of the spectrum based on its position relative to the grating.

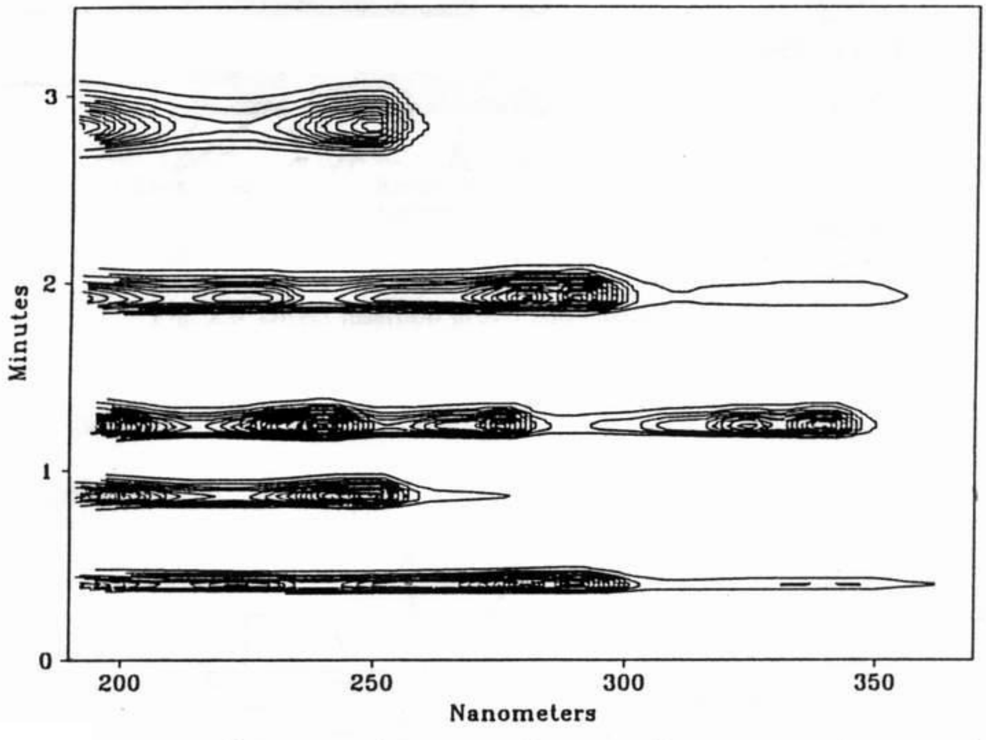


Fig. 31 A contour plot is a top-down view of a spectrochromatogram. The contour lines represent absorbance levels (colors can be used instead of lines). This plot is easier to use than a 3-D plot when trying to view all the spectral data simultaneously, especially when looking for hidden peaks or during survey work for method development.

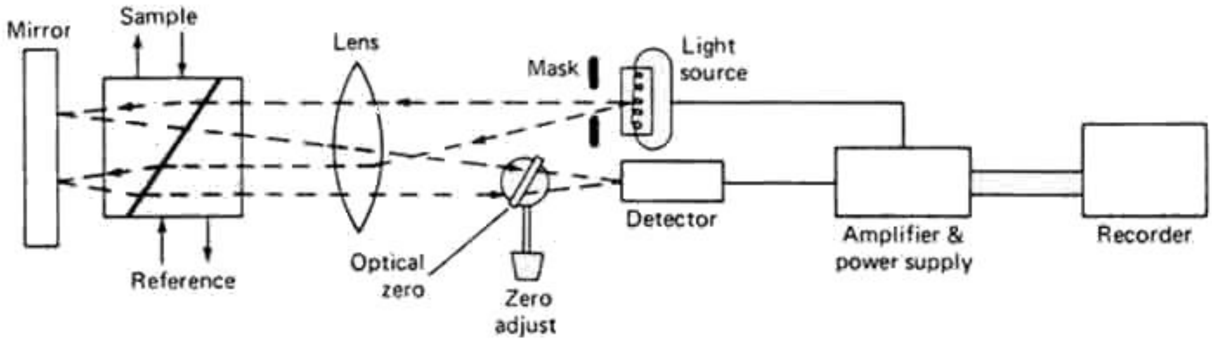


Fig. 32 Schematic diagram of a differential refractive-index detector. (Courtesy of Waters Associates, Inc., Milford, MA 01757.)

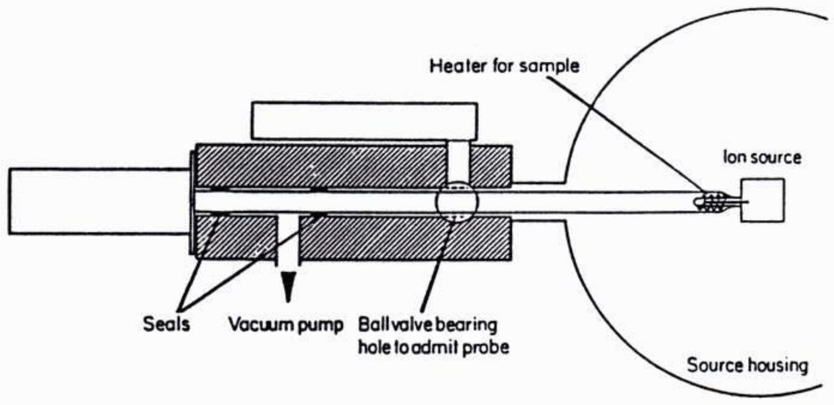


Fig. 33 Direct insertion probe and vacuum lock

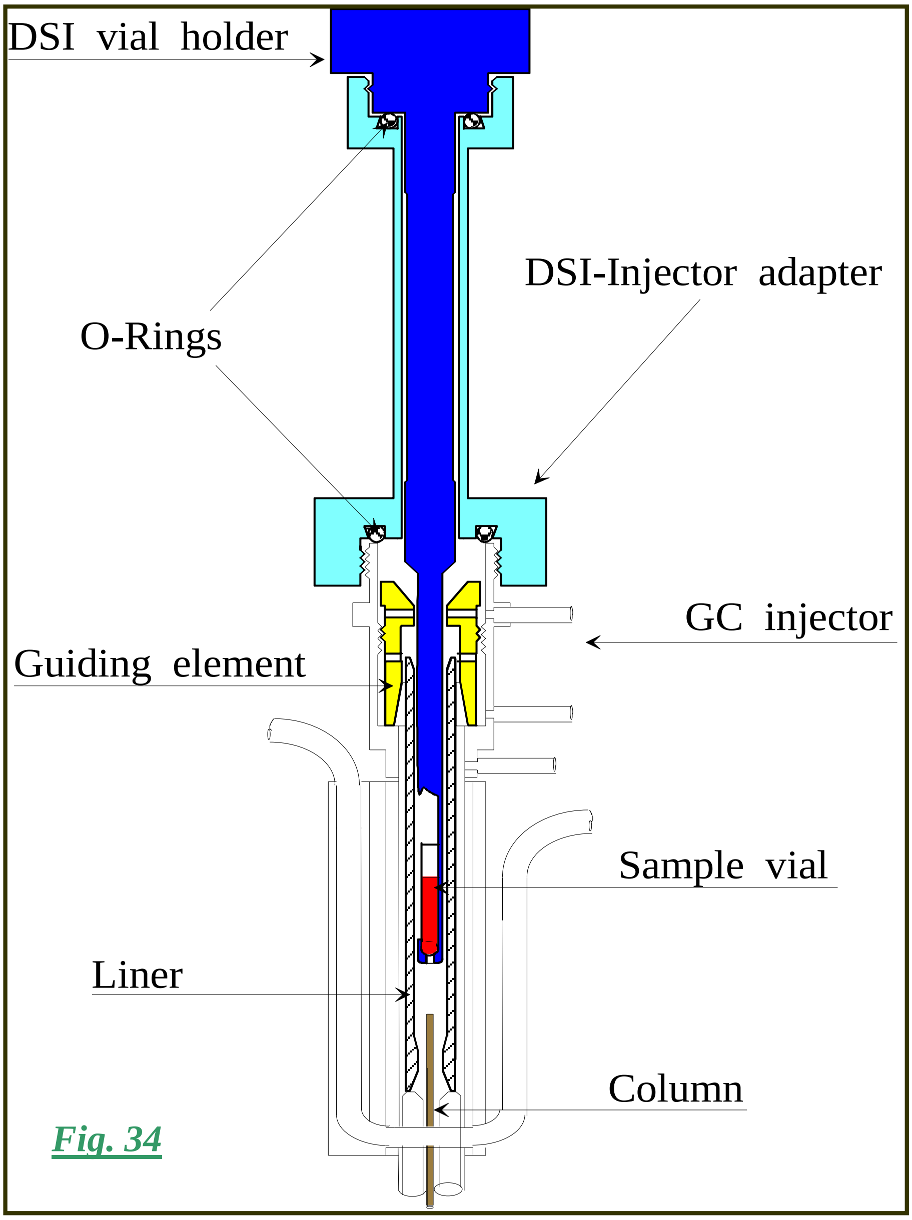


Fig. 34

ChromatoProbe sample introduction device

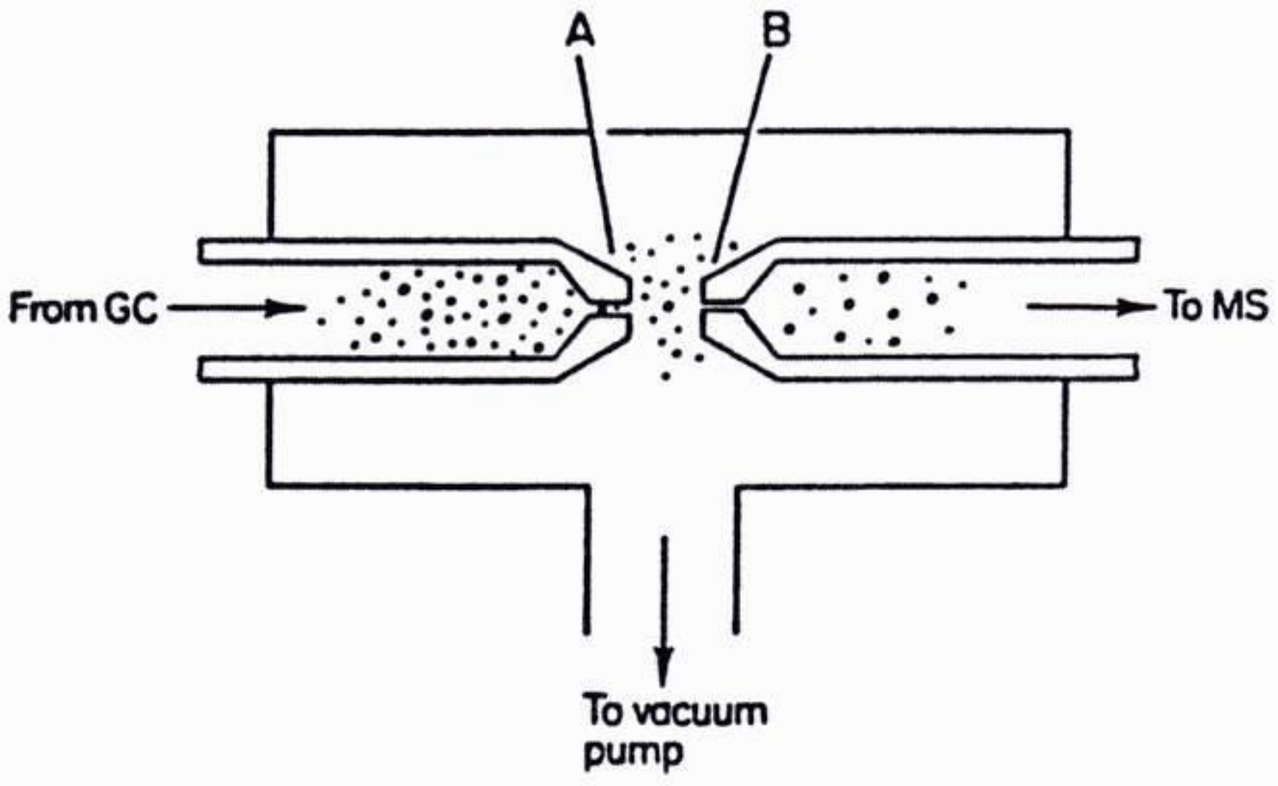
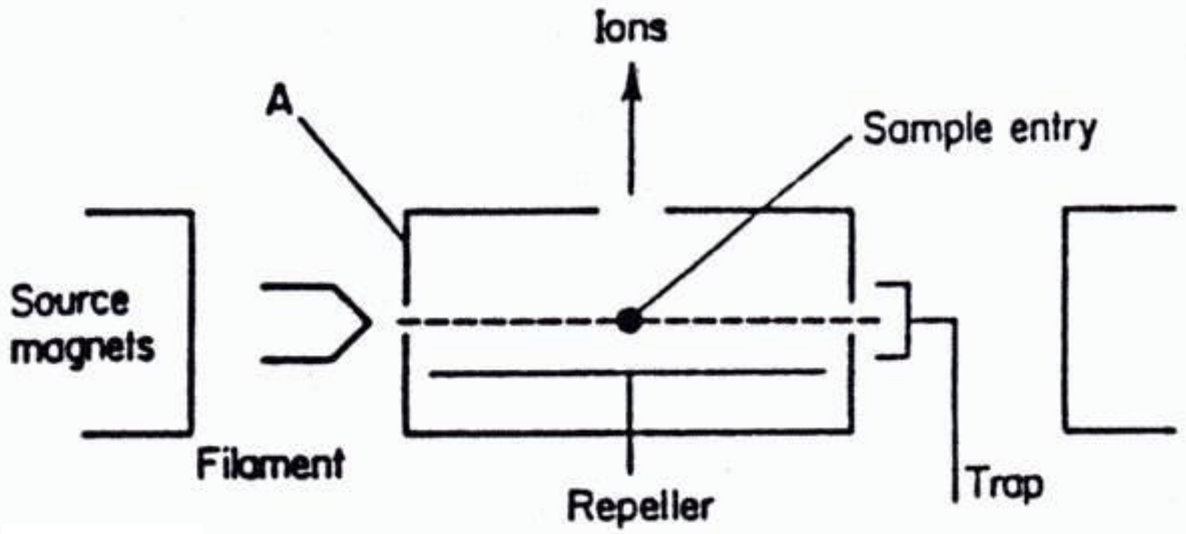


Fig. 35 Schematic diagram of a jet separator



Schematic diagram of electron impact ion source

Fig. 36

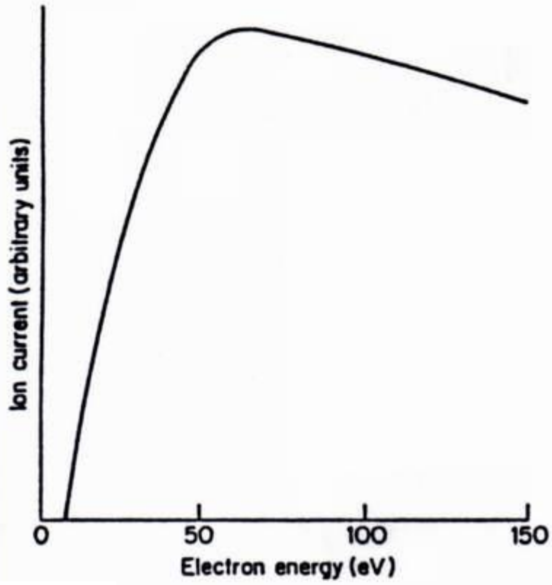
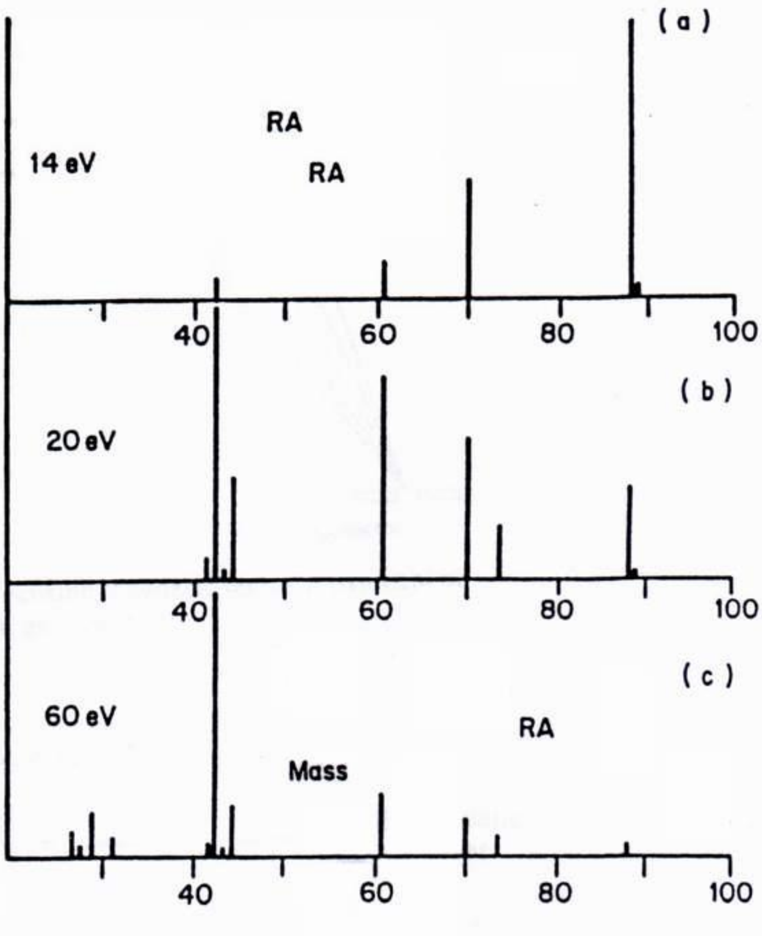


Fig.37 Plot of ion current versus electron energy



Mass spectrum of ethyl acetate as a function of electron energy: (a) 14eV : (b) 20eV : (c) 60eV

Fig. 38

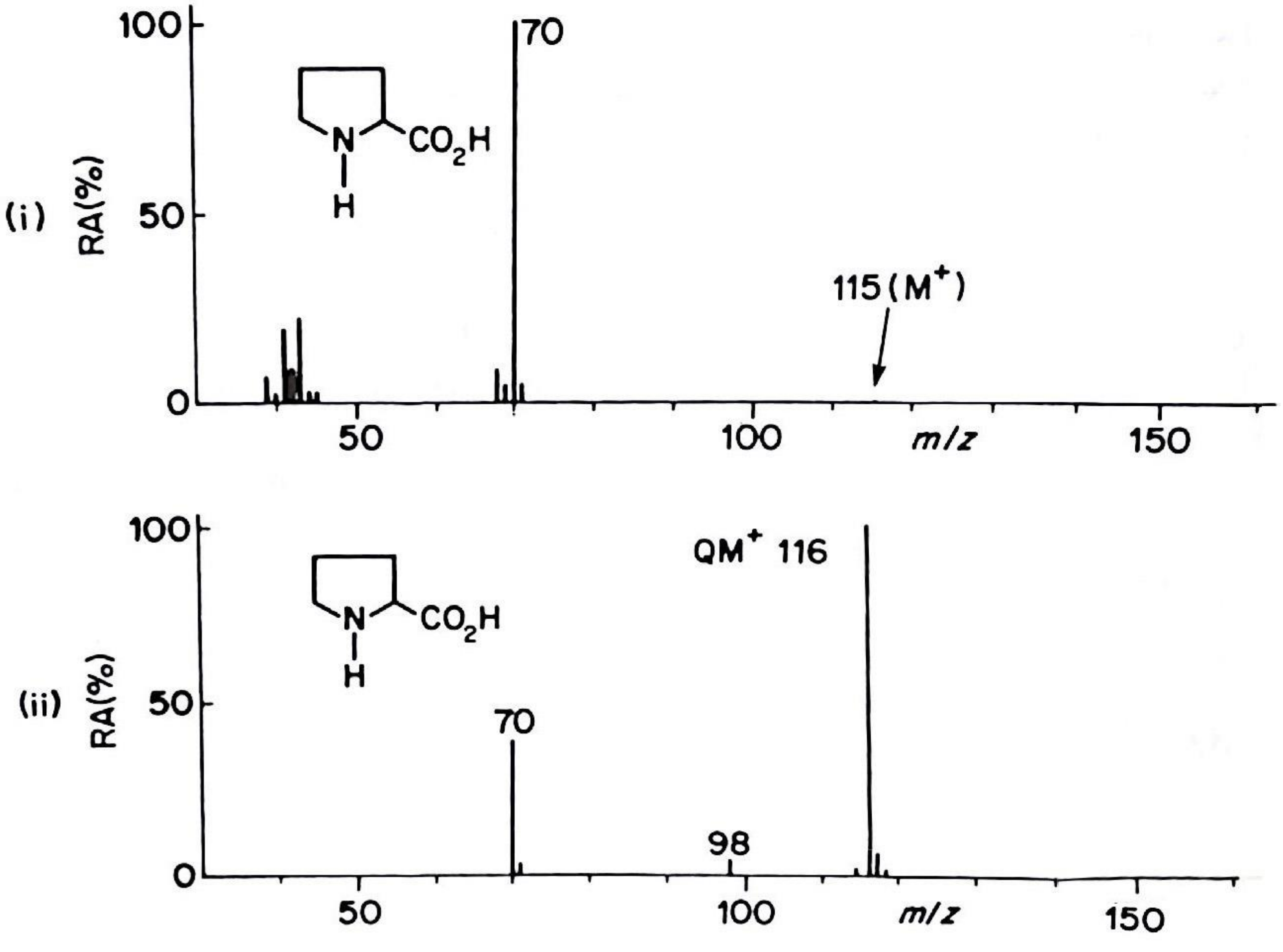


Fig. 39 *Mass spectrum of proline (i) by electron impact, (ii) by chemical ionisation*

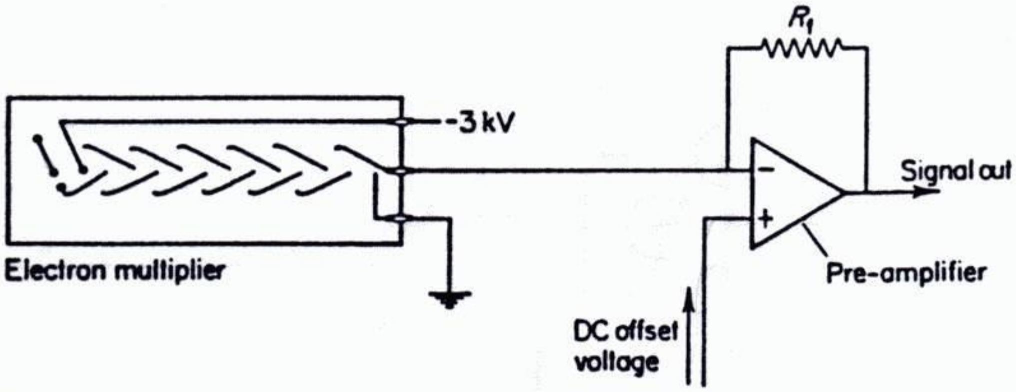


Fig. 40 **Schematic diagram of electron multiplier (resistive network omitted) and pre-amplifier**

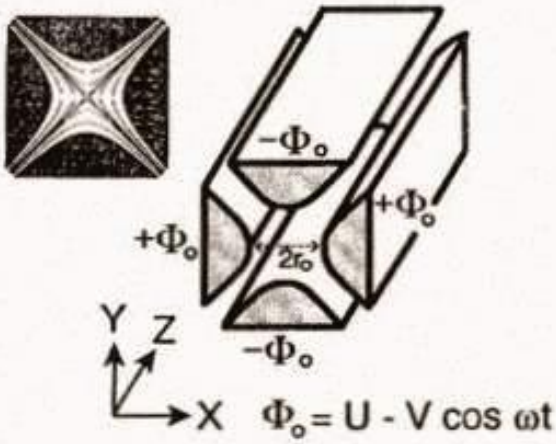


Fig. 41 : Quadrupole with hyperbolic rods and applied potentials. The equipotential lines are represented above, on the left[2].

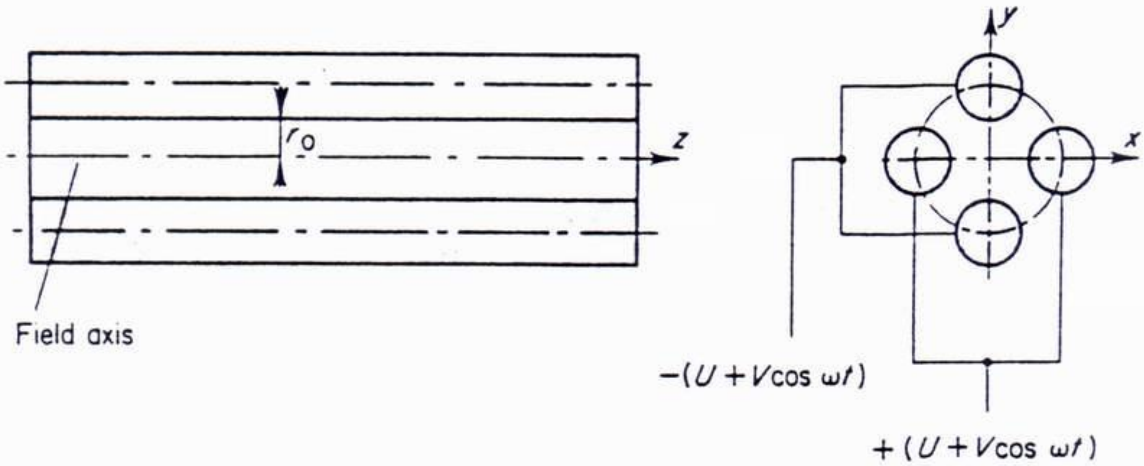


Fig. 42 Schematic diagram of a quadrupole analyser

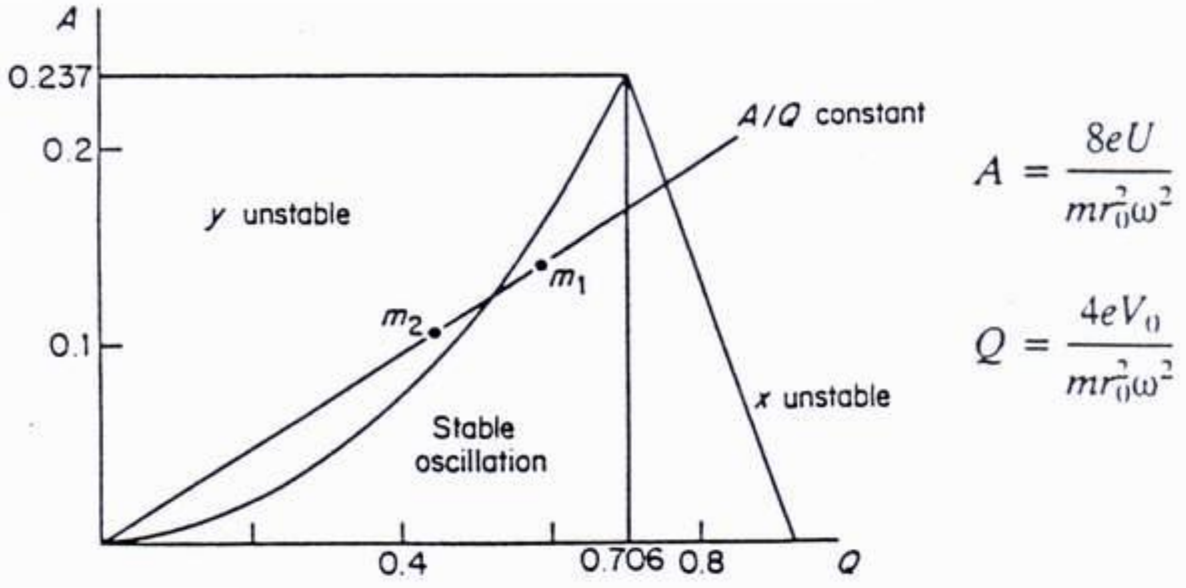


Fig. 43 Stability diagram for a quadrupole analyser

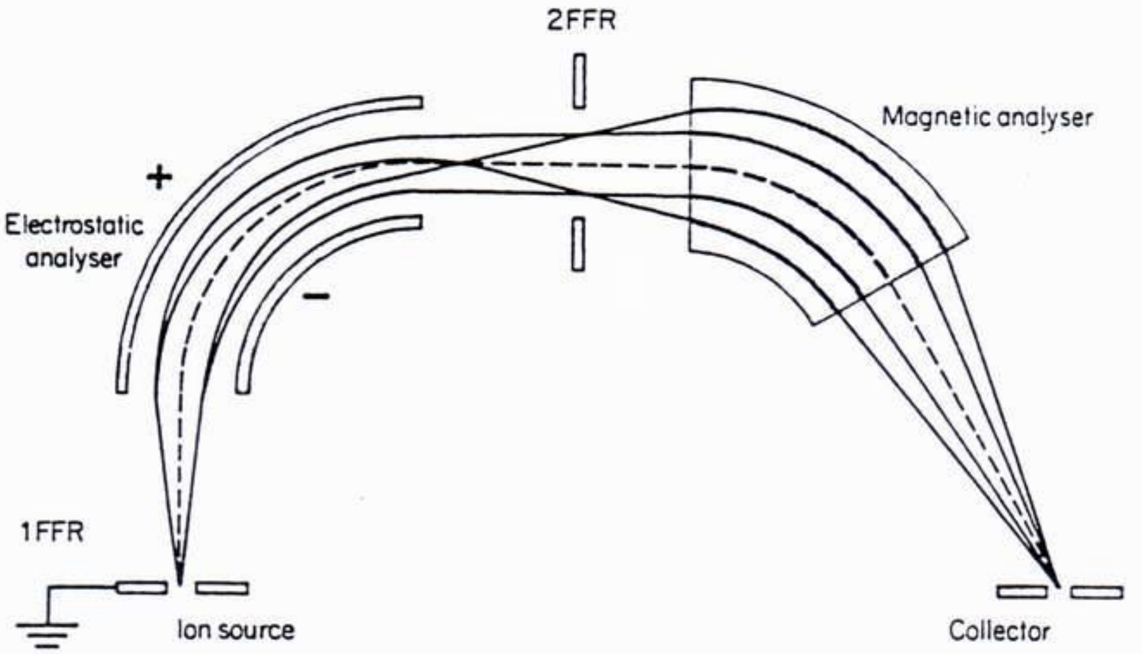
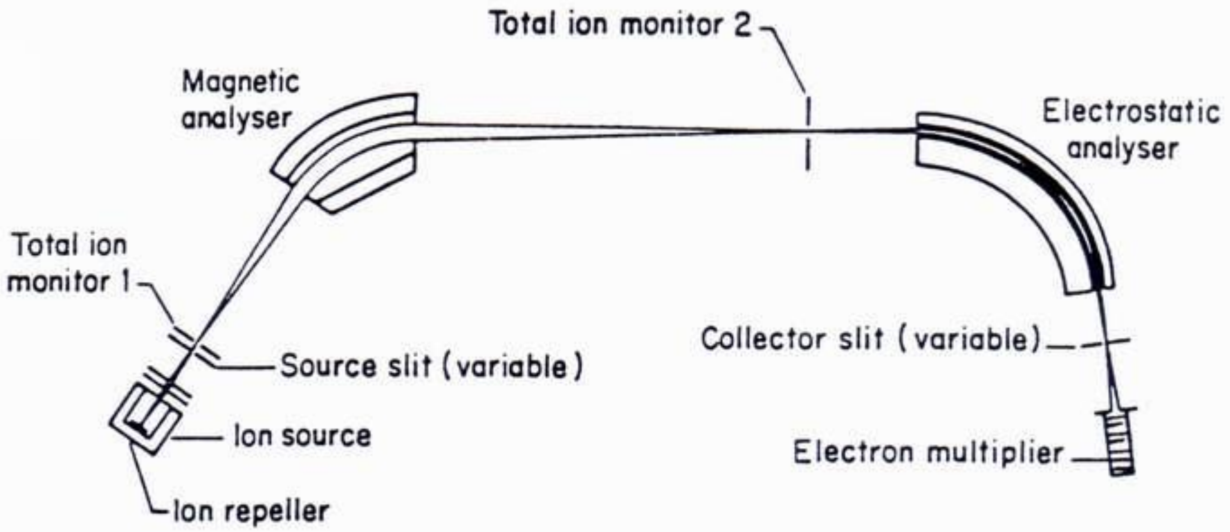


Fig. 44 Schematic diagram of double-focusing magnetic sector instrument of Nier-Johnson geometry



Schematic diagram of double-focusing magnetic sector instrument of reversed geometry. (Reproduced with permission from *Mass Spectrometry, Principles and Applications* (ref. 24))

Fig. 45

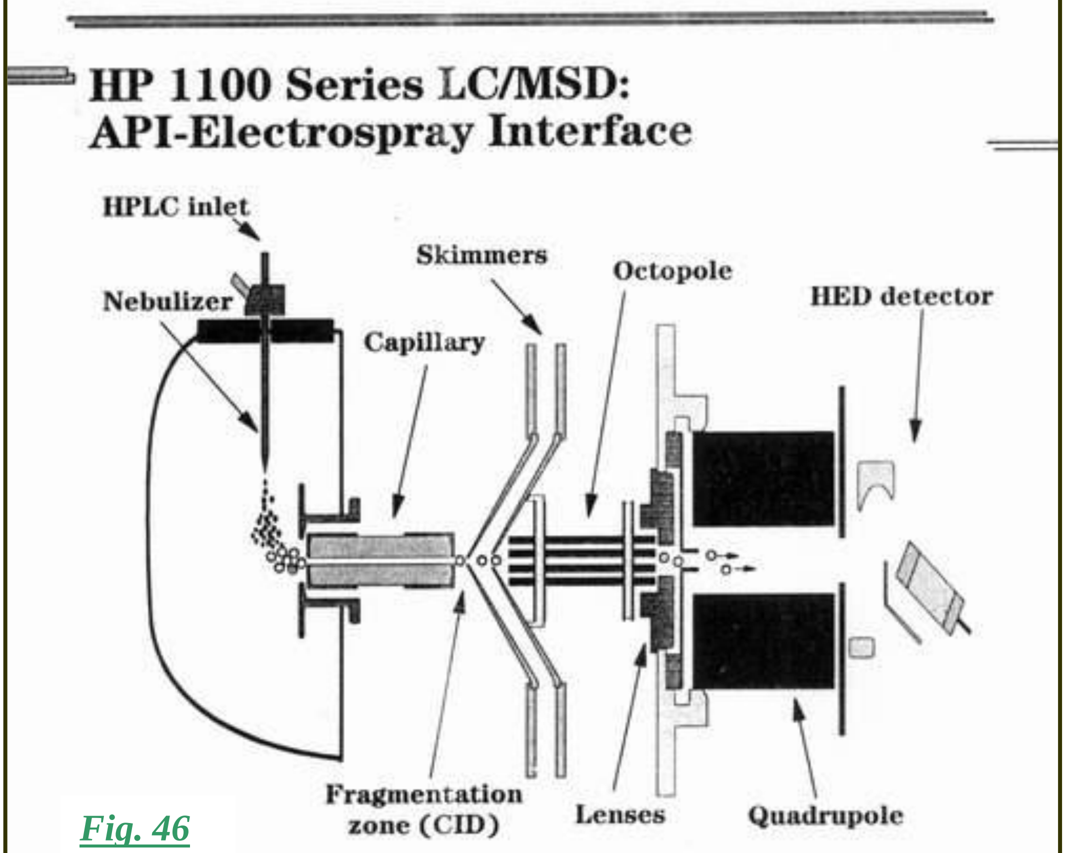


Fig. 46

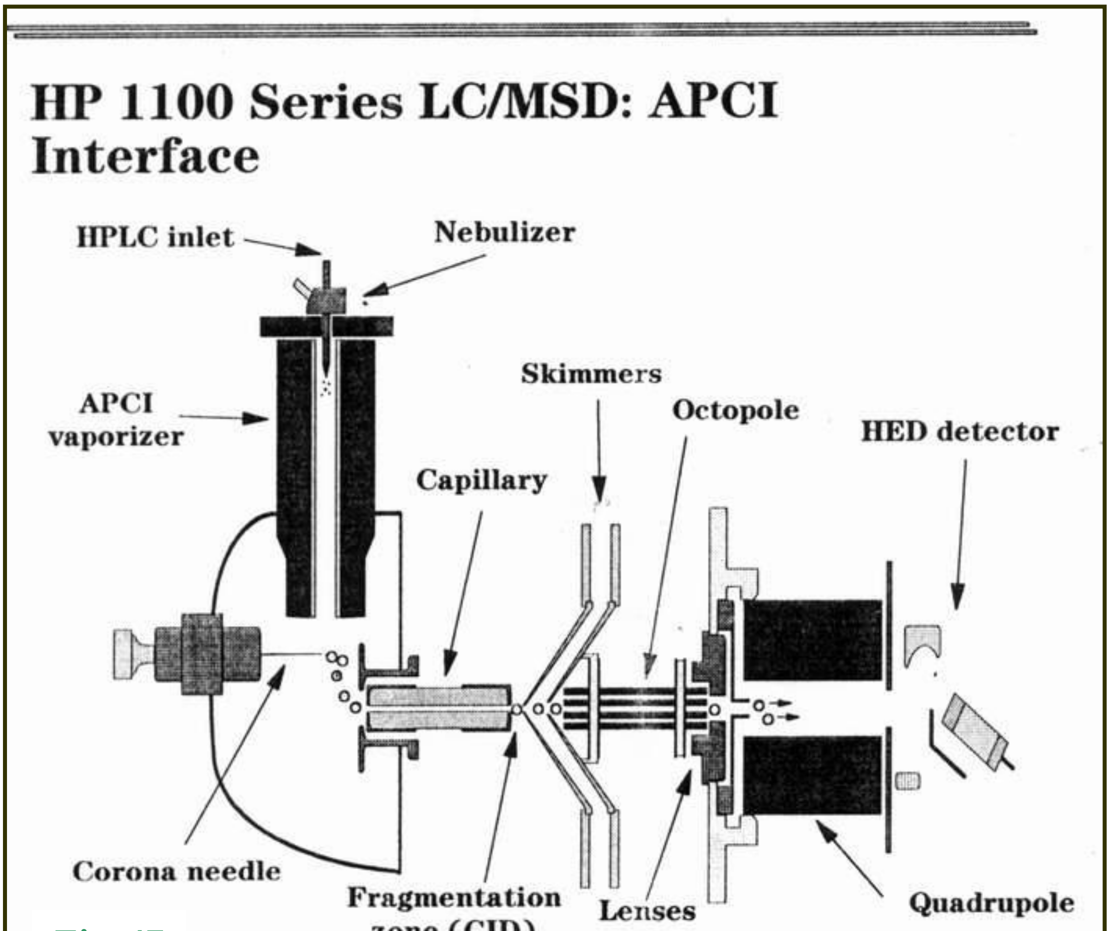

HP 1100 Series LC/MSD: APCI Interface
HPLC inlet
Nebulizer
APCI vaporizer
Skimmers
Octopole
HED detector
Capillary
Corona needle
Fragmentation zone (CID)
Lenses
Quadrupole

Fig. 47

HP's New, Unique API-Electrospray Ion Source Design

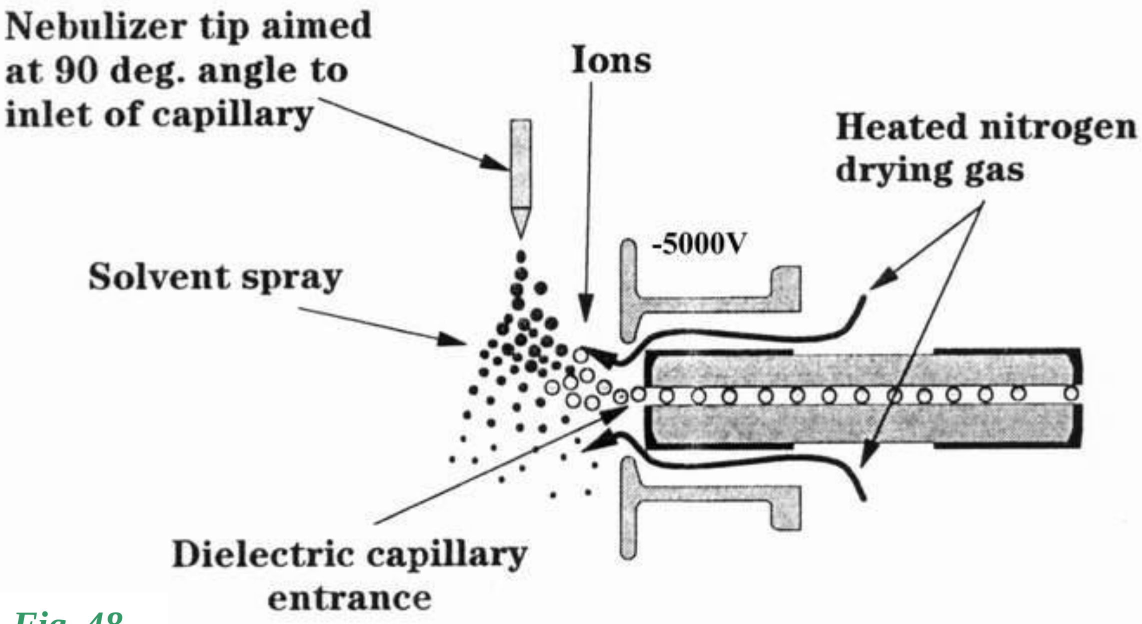


Fig. 48

Synthetic DNA 20-mer After Desalting

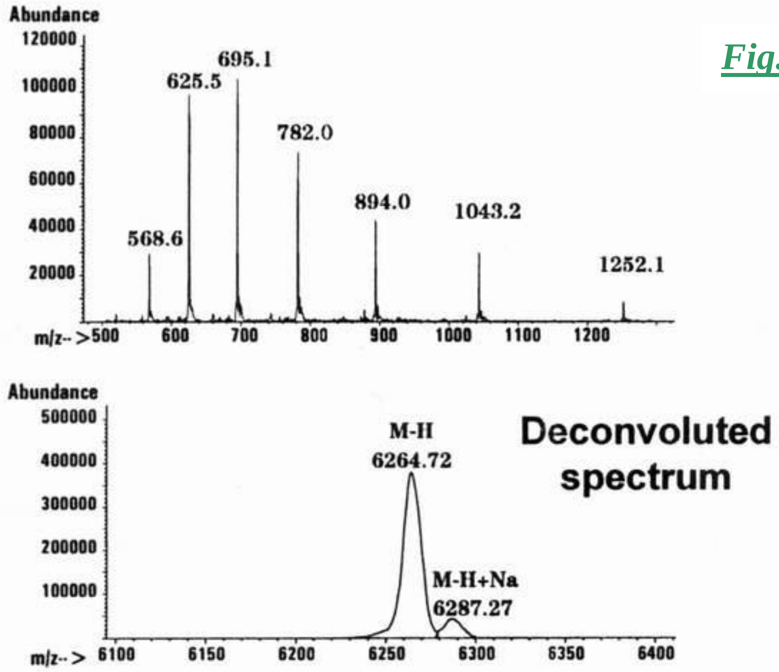


Fig. 49

Relative Applicability of LC/MS Techniques

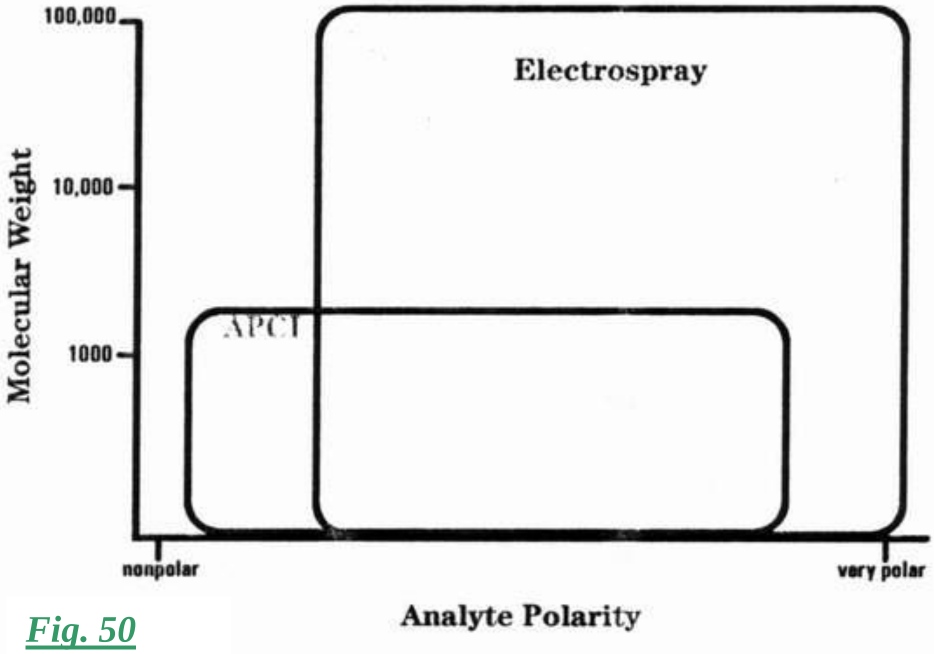


Fig. 50

Atomic Spectroscopy

Table 9-2
Flame Temperatures

Fig. 51

Fuel	Oxidant	Temperatures, °C
Natural gas	Air	1700–1900
Natural gas	Oxygen	2700–2800
Hydrogen	Air	2000–2100
Hydrogen	Oxygen	2550–2700
Acetylene	Air	2100–2400
Acetylene	Oxygen	3050–3150
Acetylene	Nitrous oxide	2600–2800

Table 9-1
Classification of Optical, Atomic Spectral Methods

Fig. 52

Atomization Method	Typical Atomization Temperature, °C	Phenomenological Basis of Method	Common Name and Abbreviation for Method
Flame	1700–3150	Absorption	Atomic absorption spectroscopy, AAS
		Emission	Atomic emission spectroscopy, AES
		Fluorescence	Atomic fluorescence spectroscopy, AFS
Electrothermal	1200–3000	Absorption	Electrothermal atomic absorption spectroscopy
		Fluorescence	Electrothermal atomic fluorescence spectroscopy
Inductively coupled argon plasma	6000–8000	Emission	Inductively coupled plasma spectroscopy, ICP
		Fluorescence	Inductively coupled plasma fluorescence spectroscopy
Direct current argon plasma	6000–10000	Emission	DC argon plasma spectroscopy, DCP
Electric arc	4000–5000	Emission	Arc-source emission spectroscopy
Electric spark	40000 (?)	Emission	Spark-source emission spectroscopy

Table 9-4
Sensitivity (ng/mL)[a] for Selected Elements[b]

Fig. 53

Element	AAS,[c] Flame	AAS,[d] Electrothermal	AES,[c] Flame	AES,[c] ICP	AFS,[c] Flame
Al	30	0.005	5	2	5
As	100	0.02	0.0005	40	100
Ca	1	0.02	0.1	0.02	0.001
Cd	1	0.0001	800	2	0.01
Cr	3	0.01	4	0.3	4
Cu	2	0.002	10	0.1	1
Fe	5	0.005	30	0.3	8
Hg	500	0.1	0.0004	1	20
Mg	0.1	0.00002	5	0.05	1
Mn	2	0.0002	5	0.06	2
Mo	30	0.005	100	0.2	60
Na	2	0.0002	0.1	0.2	—
Ni	5	0.02	20	0.4	3
Pb	10	0.002	100	2	10
Sn	20	0.1	300	30	50
V	20	0.1	10	0.2	70
Zn	2	0.00005	0.0005	2	0.02

[a] Nanogram/milliliter = 10^{-3} μg/mL = 10^{-3} ppm.

[b] AAS = atomic absorption spectroscopy; AES = atomic emission spectroscopy; AFS = atomic fluorescence spectroscopy; ICP = inductively coupled plasma.

[c] Reprinted with permission from V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, **1974**, *46*, 1111A. Copyright 1974 American Chemical Society.

[d] From C. W. Fuller, *Electrothermal Atomization for Atomic Absorption Spectroscopy*, pp. 65–83, The Chemical Society: London, 1977. With permission. The Royal Society of Chemistry, Burlington House: London.

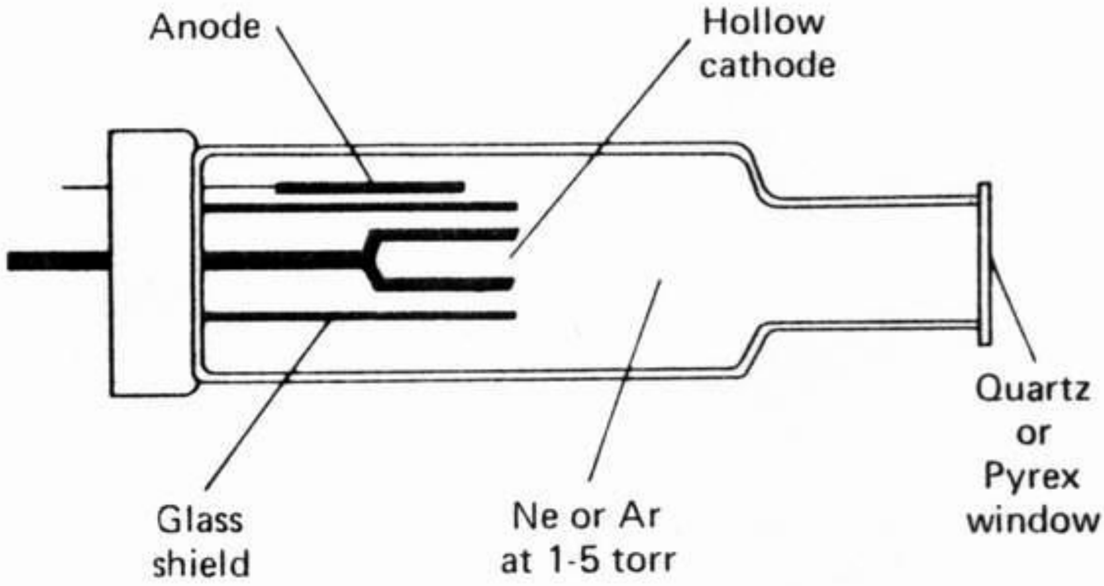


Fig. 54 Schematic cross section of a hollow cathode lamp.

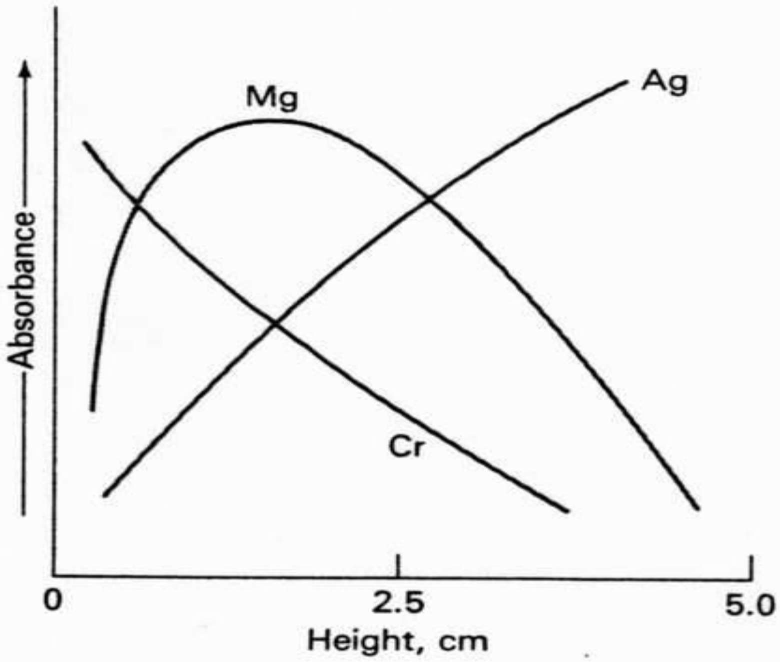


Fig. 55 Flame absorbance profile for three elements.

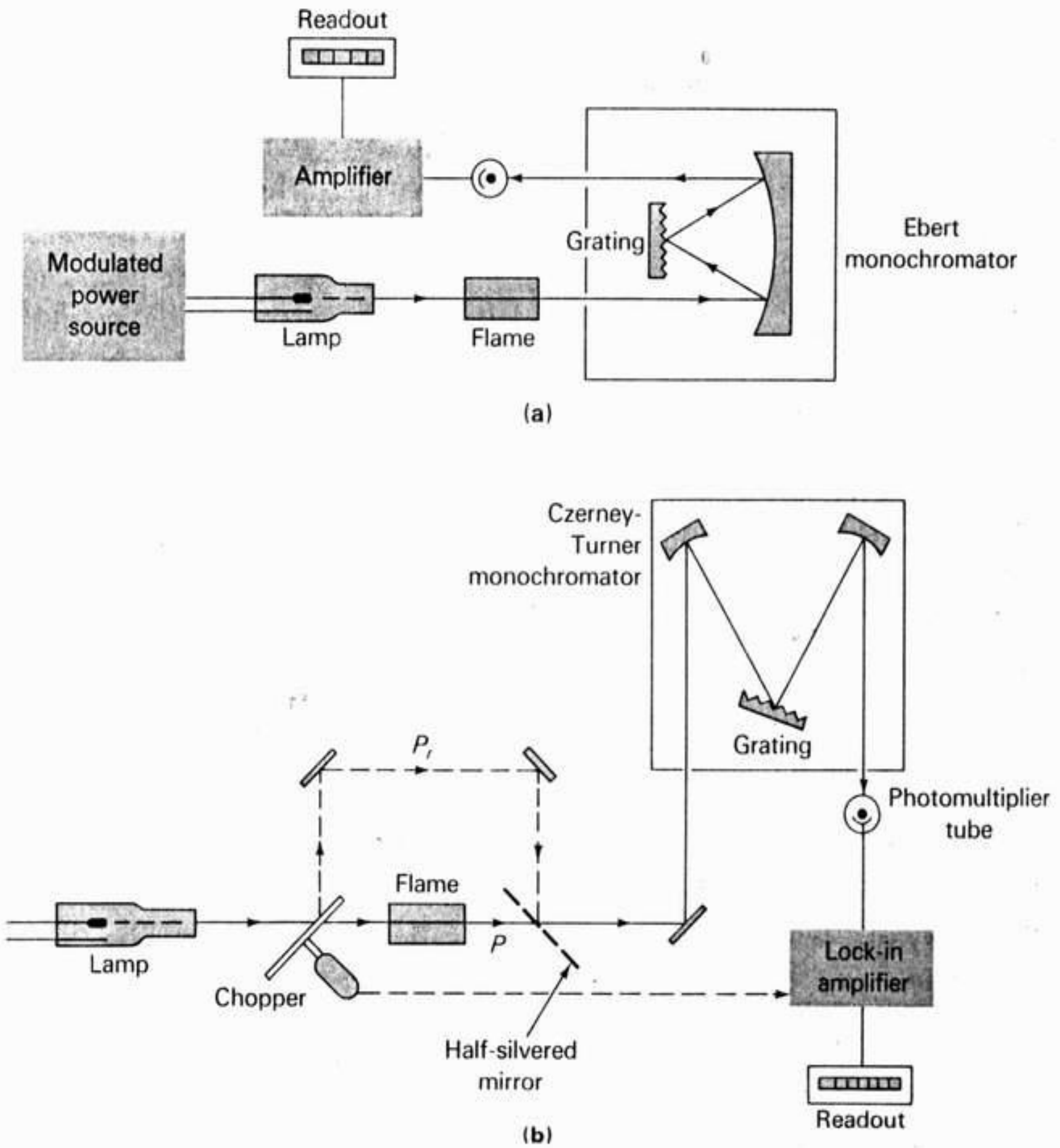


Fig. 56 Typical flame spectrophotometers: (**a**) single-beam design; (**b**) double-beam design.

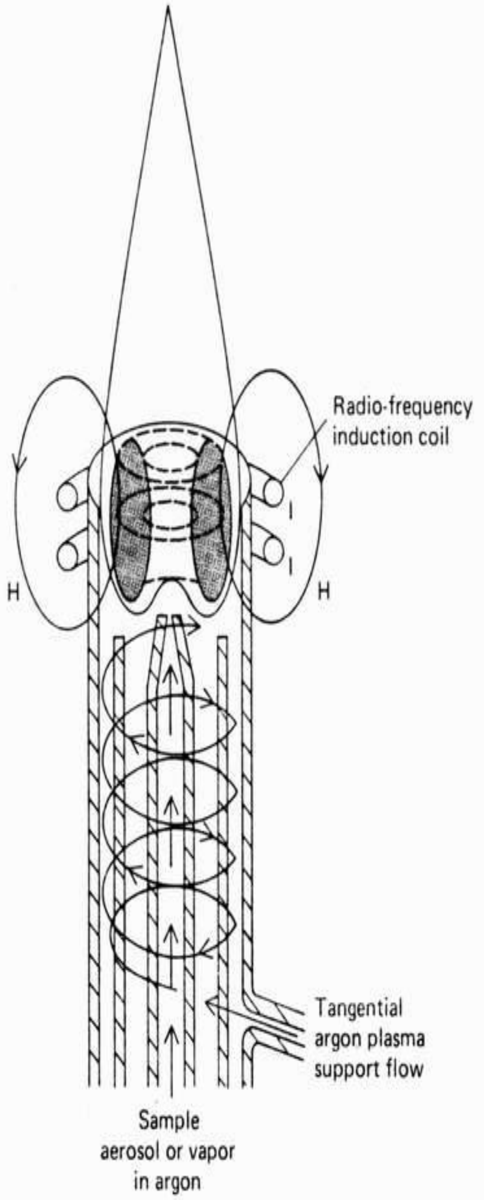


Fig. 57 A typical inductively coupled plasma source. (From: V. A. Fassel, *Science*, **1978,** *202*, 185. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

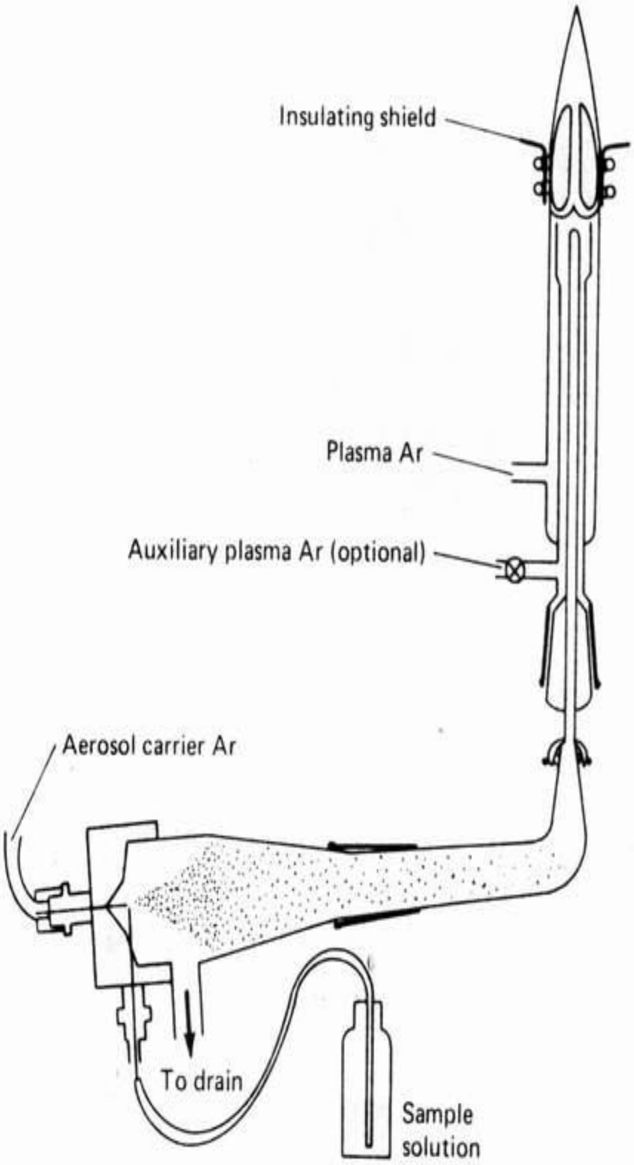


Fig. 58 A typical nebulizer for sample injection into a plasma source. (From: V. A. Fassel, *Science*, **1978,** *202*, 186. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

Notes: