

Une histoire de la CG-SM pour l'analyse des produits naturels

Daniel Joulain

CECM, 9 octobre 2026



Cannes, 25 mai 1986

Medium interactif par numérisation d'information téléphonique (« Minitel », 1980 -2012)





Iphone18
2026

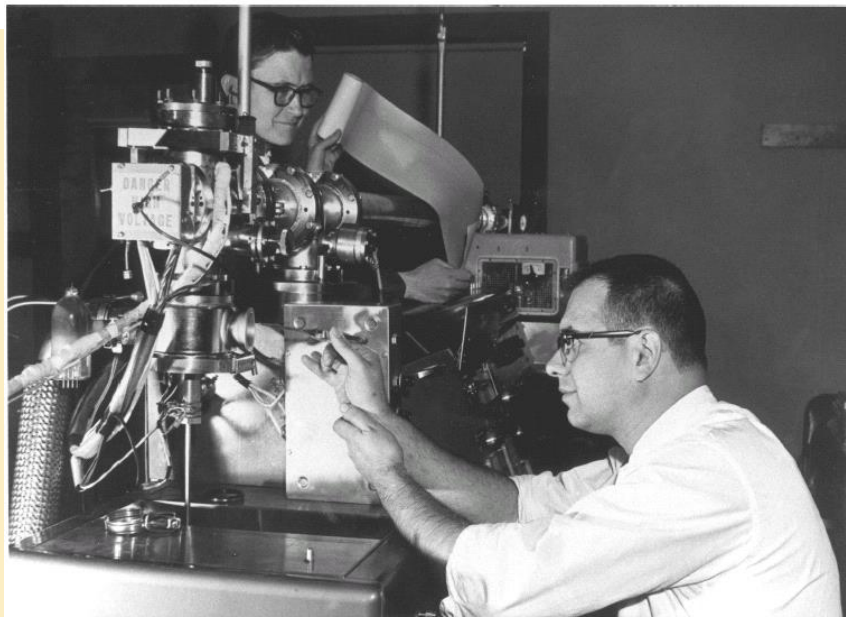
Early Gas Chromatography/Mass Spectrometry

Roland S. Gohlke* and Fred W. McLafferty

Spectroscopy Laboratory, The Dow Chemical Company, Midland, Michigan, USA

JASMS, 1993, 4, 367

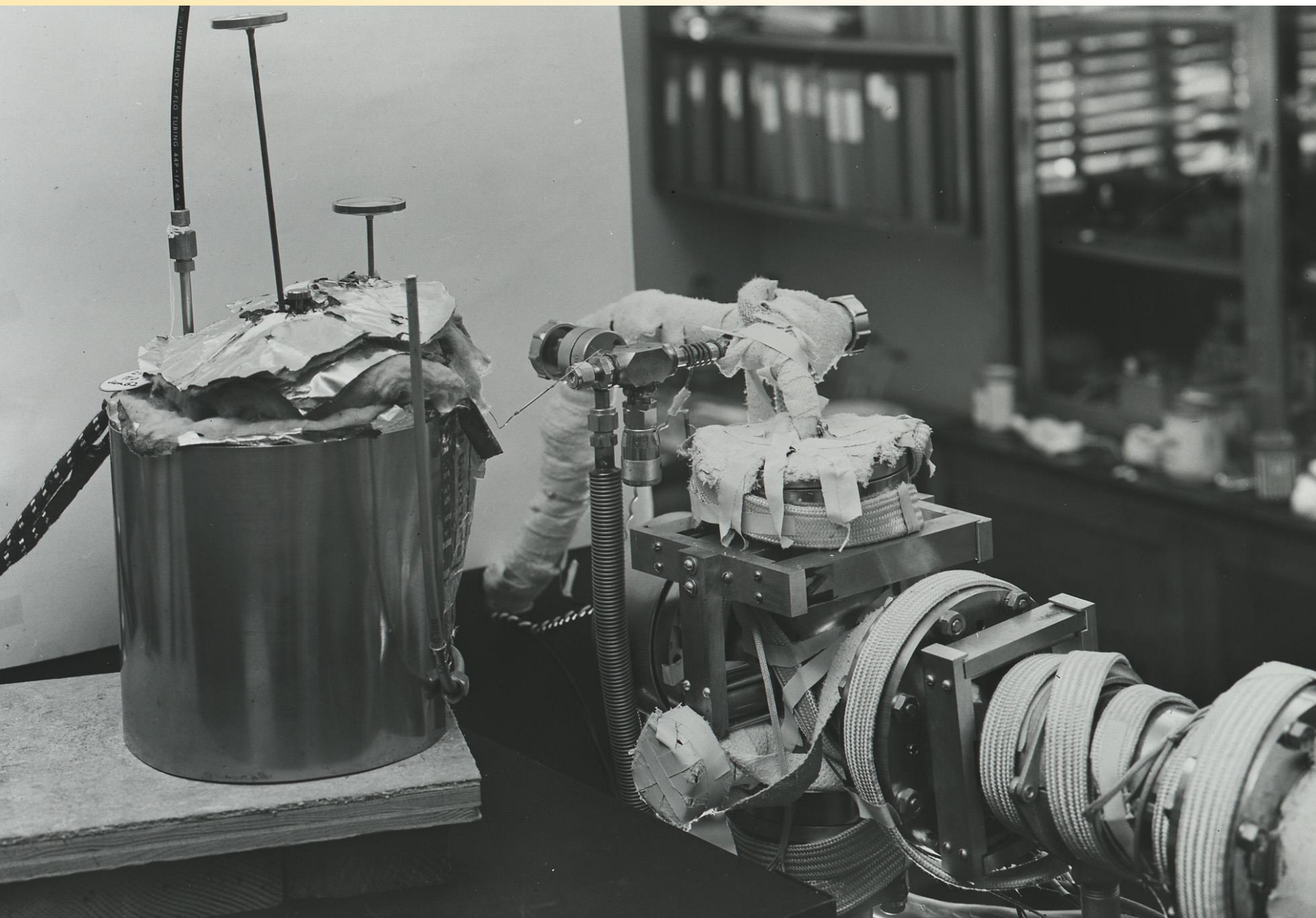
In December 1955 or thereabouts, the authors coupled a homemade gas chromatograph to a research time-of-flight mass spectrometer constructed by W. C. Wiley, I. H. McLaren, and D. B. Harrington. This unique gas chromatography/mass spectrometry (GC/MS) instrument generated mass spectra at a 10-kHz rate for display on an oscilloscope; eluted gas chromatographic components, such as methanol, acetone, benzene, toluene, and carbon tetrachloride, could be visually identified immediately from the oscilloscope display. Many years of further research and development in many laboratories worldwide were necessary, however, to make continuous on-line GC/MS the uniquely valuable analytical tool that it is today. (*J Am Soc Mass Spectrom* 1993, 4, 367-371)



Bendix Co. Model 10-101 GC-TOF-MS (ca 1960)

W. H. McFadden





**FAST-SCAN MASS SPECTROMETRY WITH CAPILLARY GAS-LIQUID
CHROMATOGRAPHY IN INVESTIGATION OF FRUIT
VOLATILES**

By W. H. McFADDEN and R. TERANISHI

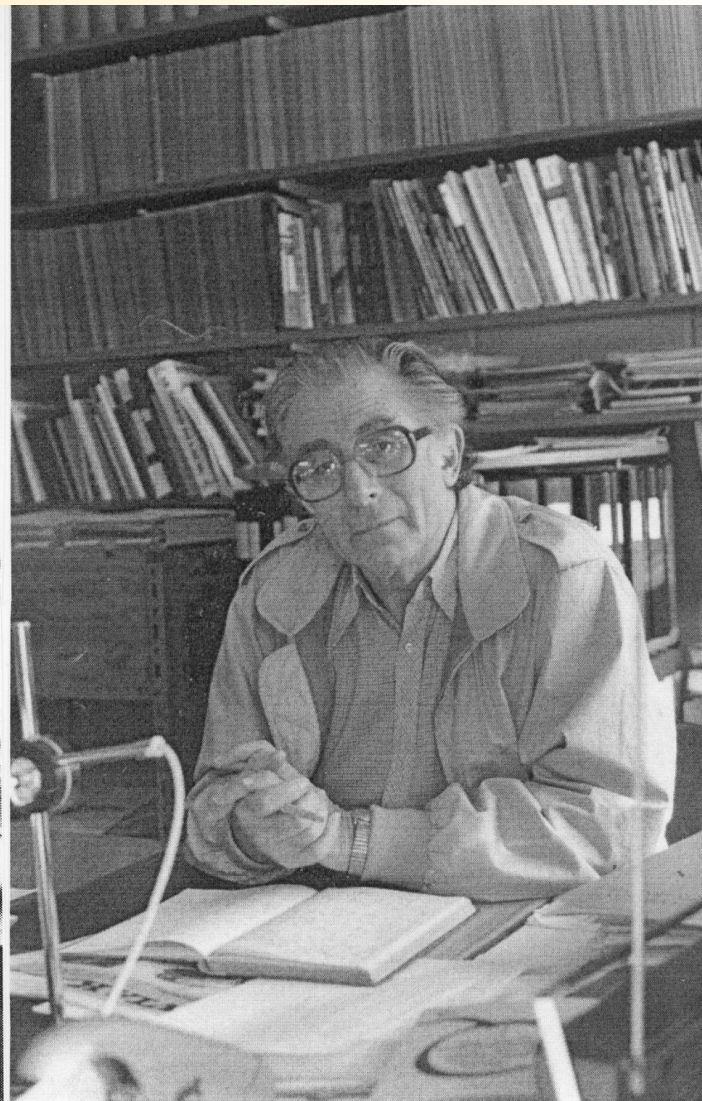
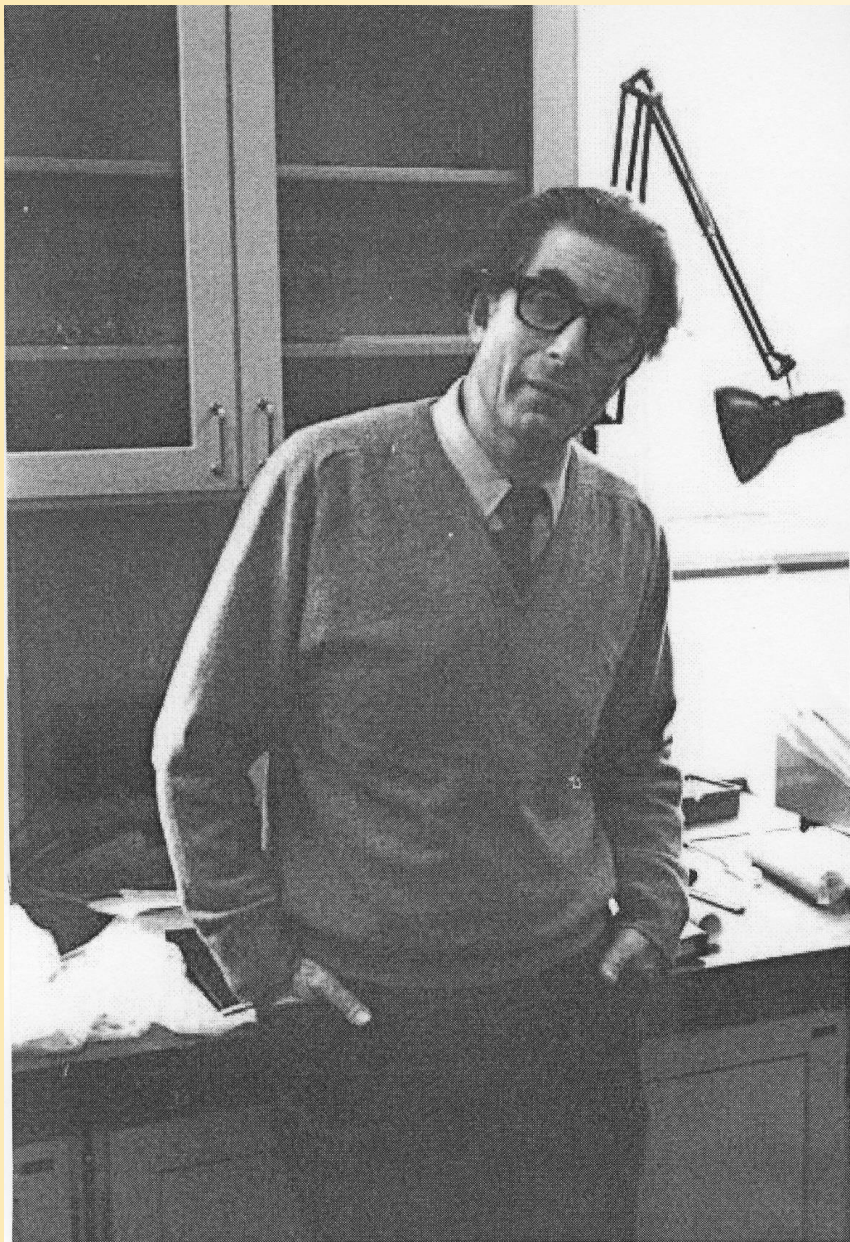
Western Utilization Research and Development Division, U.S. Department of Agriculture, Albany 10, California

CONSTITUENTS OF HOP OIL

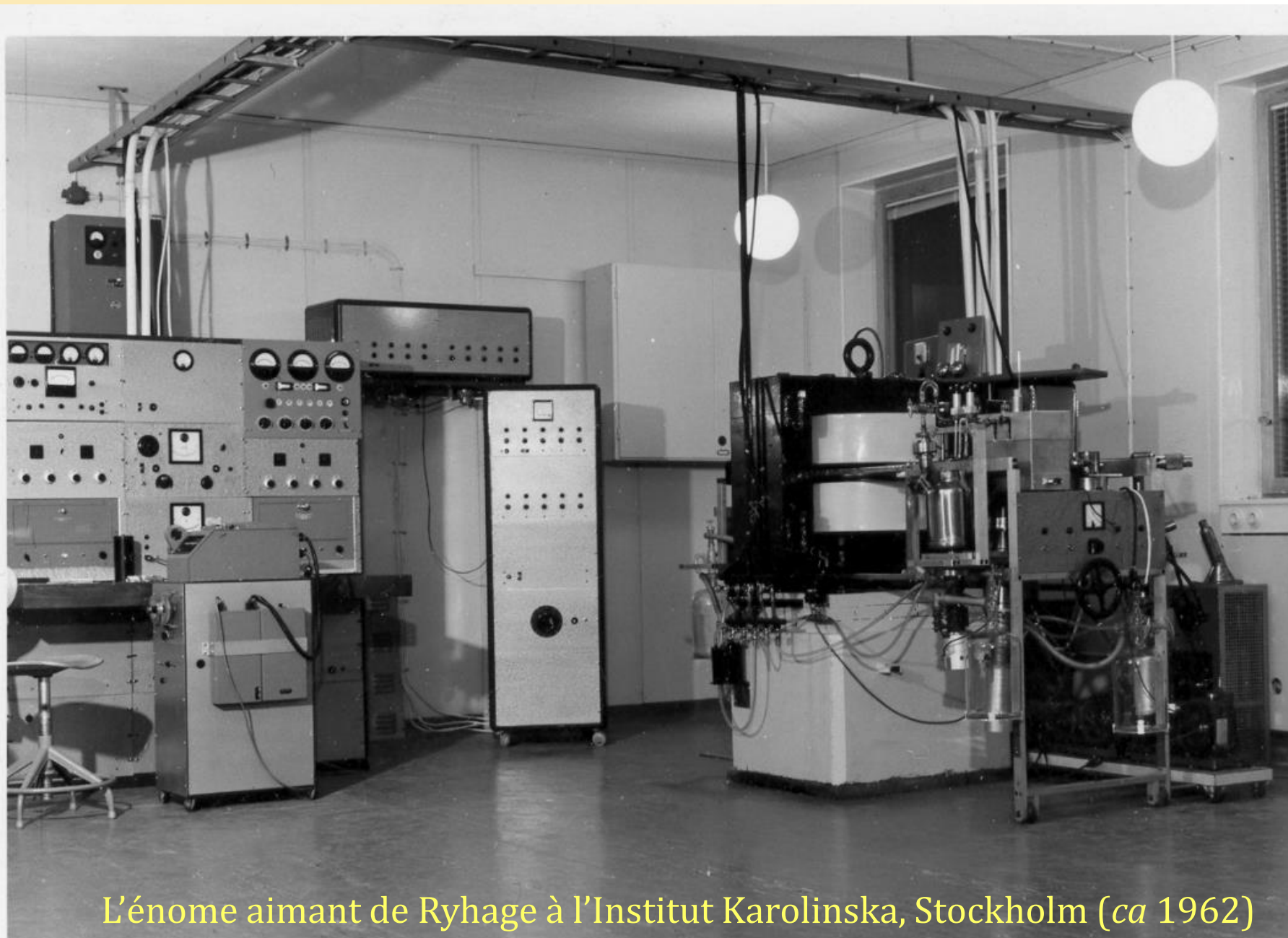
By DR. RON G. BUTTERY*, DR. W. H. McFADDEN, DR. R. TERANISHI, MARY P. KEALY*
and T. R. MON

Western Utilization Research and Development Division, Albany 10, California

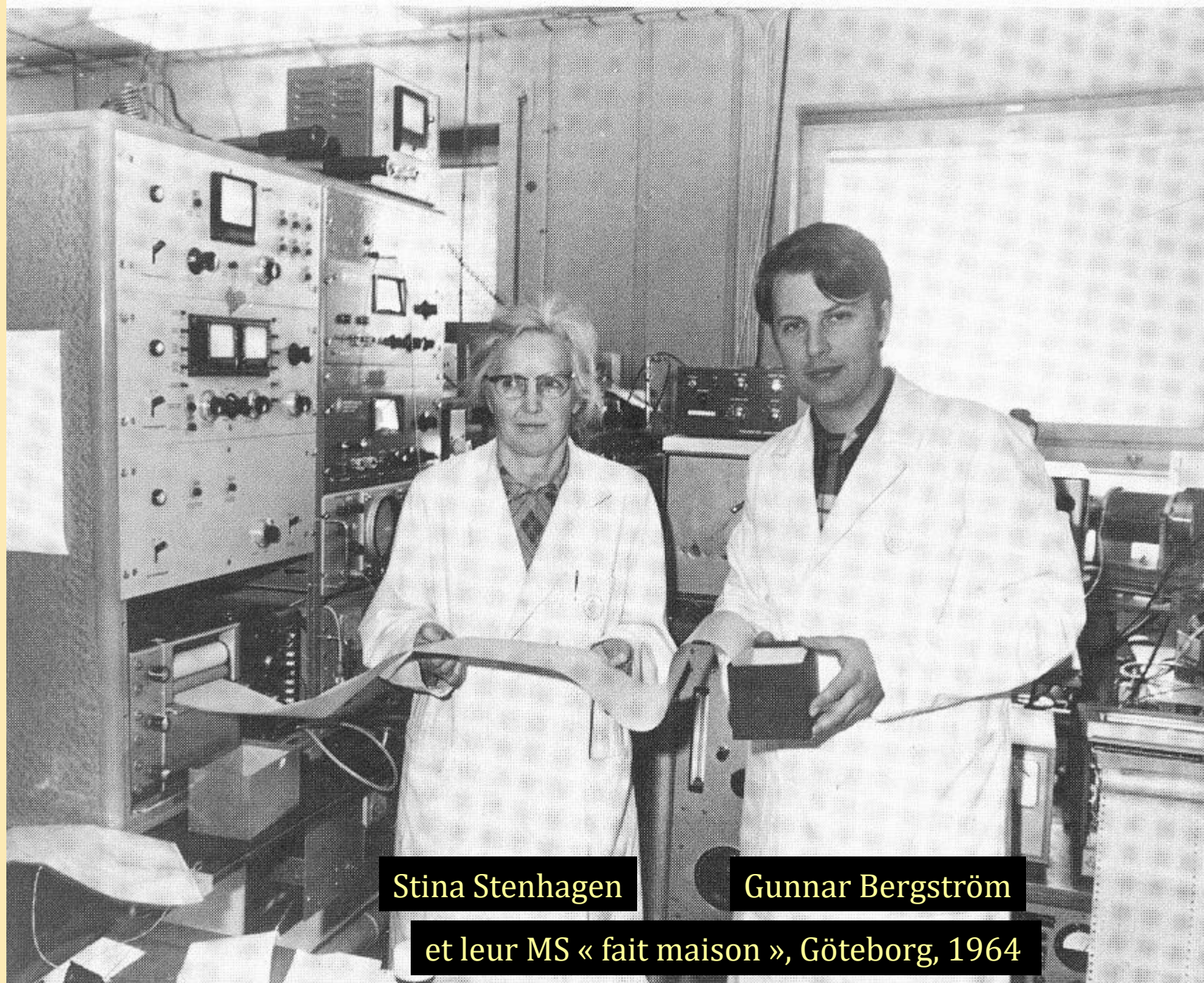
L'école suédoise



Ragnar Ryhage



L'énorme aimant de Ryhage à l'Institut Karolinska, Stockholm (ca 1962)



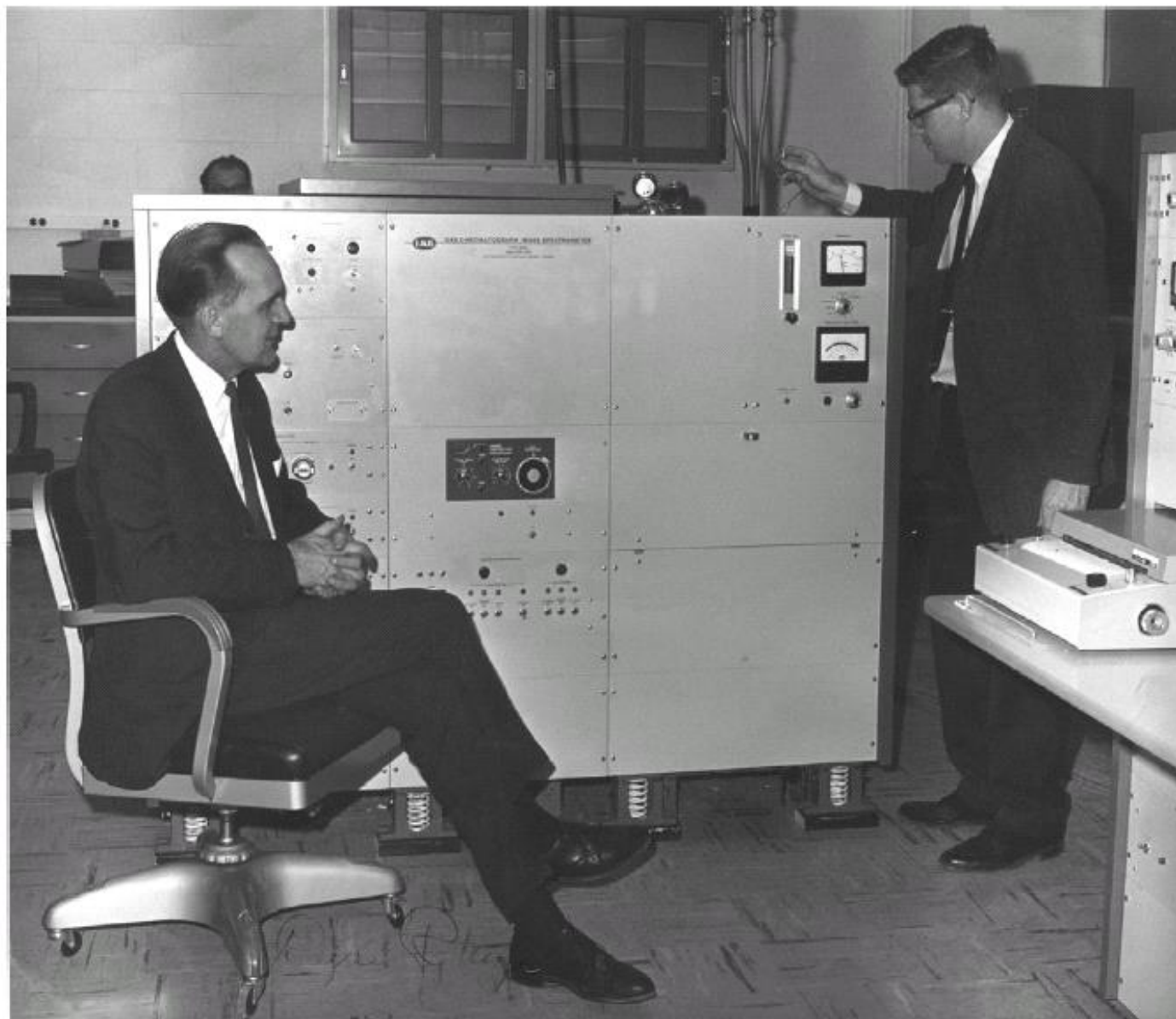
Stina Stenhagen

Gunnar Bergström

et leur MS « fait maison », Göteborg, 1964



Ryhage &
Sweeley
avec le
LKB-9000
vers 1965



Use of a Mass Spectrometer as a Detector and Analyzer for Effluents Emerging from High Temperature Gas Liquid Chromatography Columns

RAGNAR RYHAGE

Laboratory for Mass Spectrometry, Karolinska Institutet, Stockholm, Sweden

« Molecular jet separator »

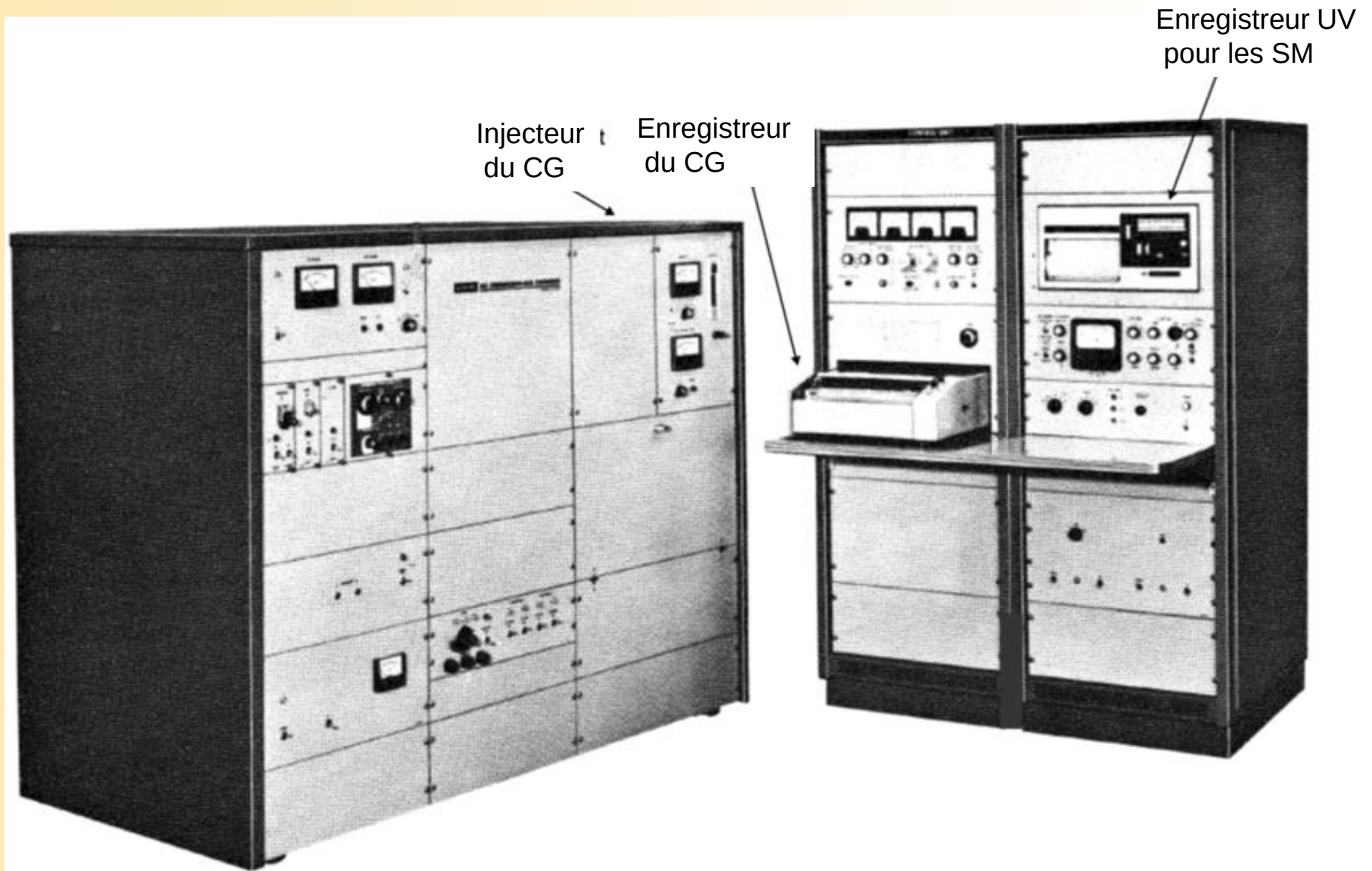
VOL. 36, NO. 4, APRIL 1964 • 759

J. T. Watson, K. Biemann, *Anal. Chem.* 1965

« Molecular effusion separator »

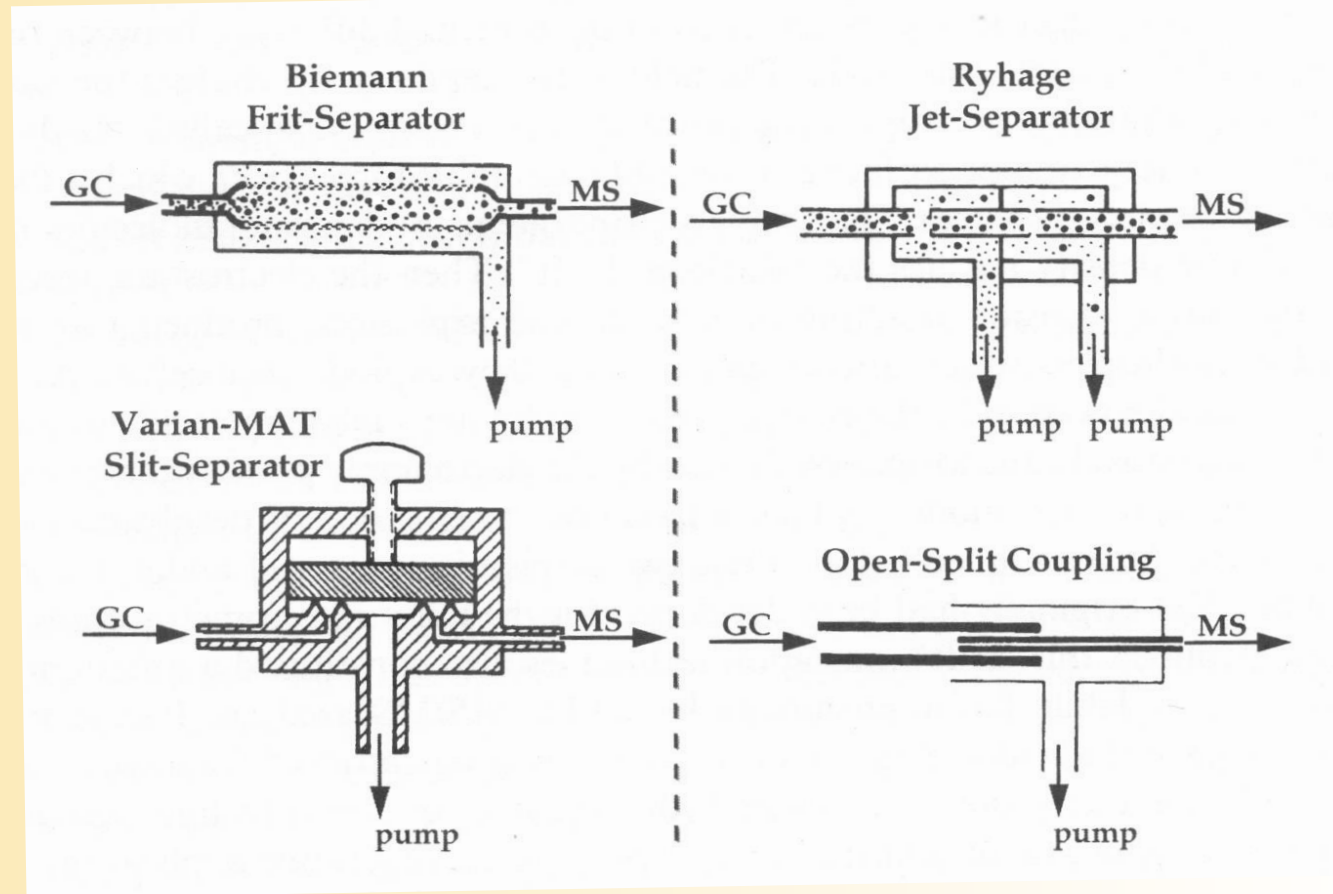
P. M. Llewelly, D. P. Littlejohn, Pittsburgh conference, 1966

« solution diffusion separator »



LKB 9000

Interfaces du couplage CG-SM

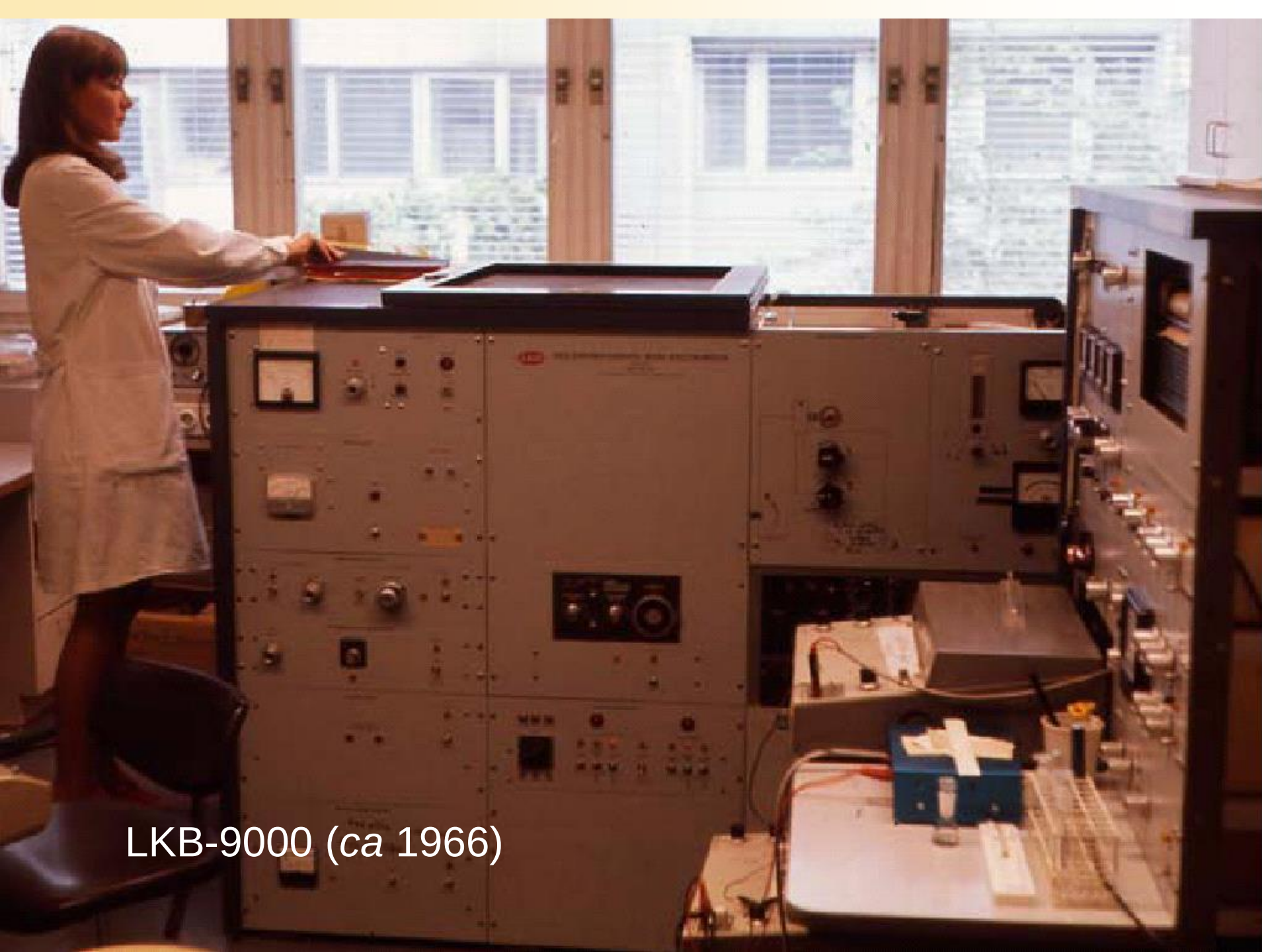


Ryhage et son groupe de l'Institut Karolinska à Stockholm ont été parmi les premiers à appliquer la nouvelle technique CG-SM à des études biochimiques très diverses.

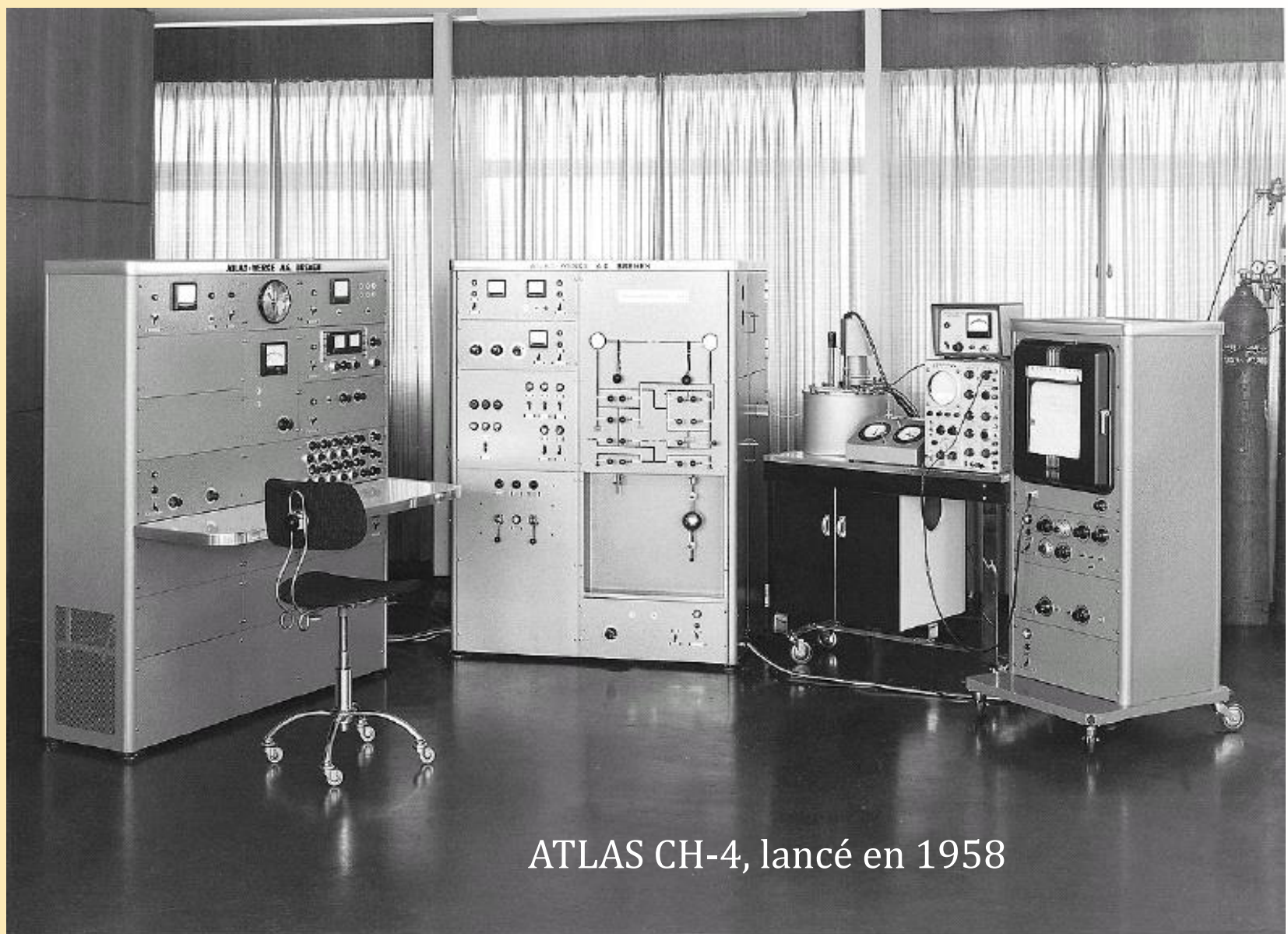
Le groupe a joué un rôle-clé pour la création de l'Instrument LKB 9000.

Le LKB 9000 a été lancé en 1965 et présenté comme le premier CG-SM **commercial** sur le marché. Il revendiquait alors l'unique solution au problème frustrant de la connexion de deux instruments opérant à deux pressions extrêmes et opposées, au moyen d'une interface appelée «molecular jet separator »

La spectrométrie de masse a connu un essor fantastique dans les sciences biologiques avec le lancement du LKB 9000. La société bénéficia d'une forte renommée dans la communauté scientifique, ce qui lui permit d'introduire la puissance analytique de la spectrométrie de masse dans des laboratoires qui n'auraient jamais considéré auparavant l'acquisition d'un tel instrument conçu pour l'industrie pétrochimique.



LKB-9000 (ca 1966)

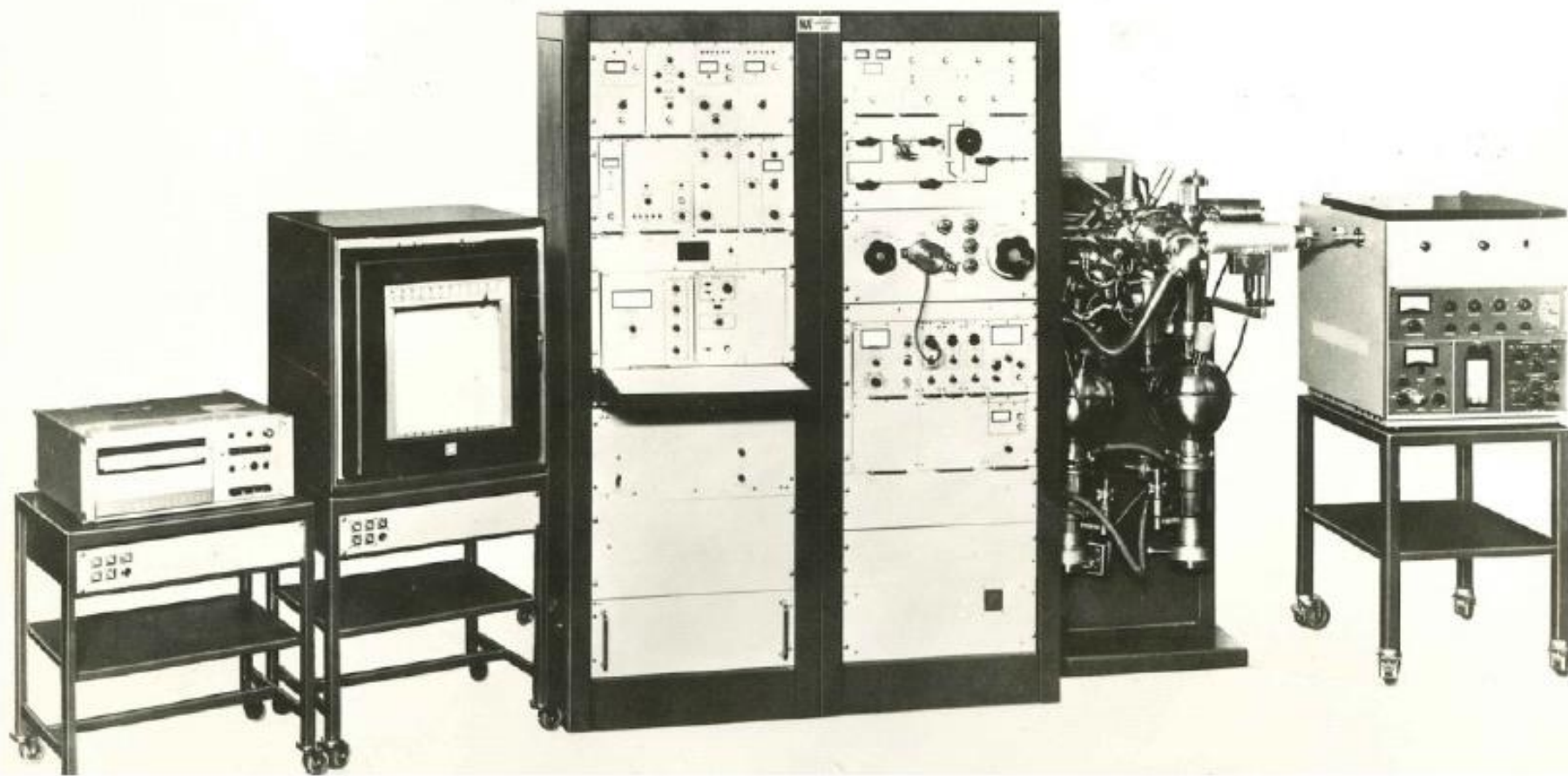


ATLAS CH-4, lancé en 1958

400 unités installées
arôme de café, parfums,
fumées de cigarettes...

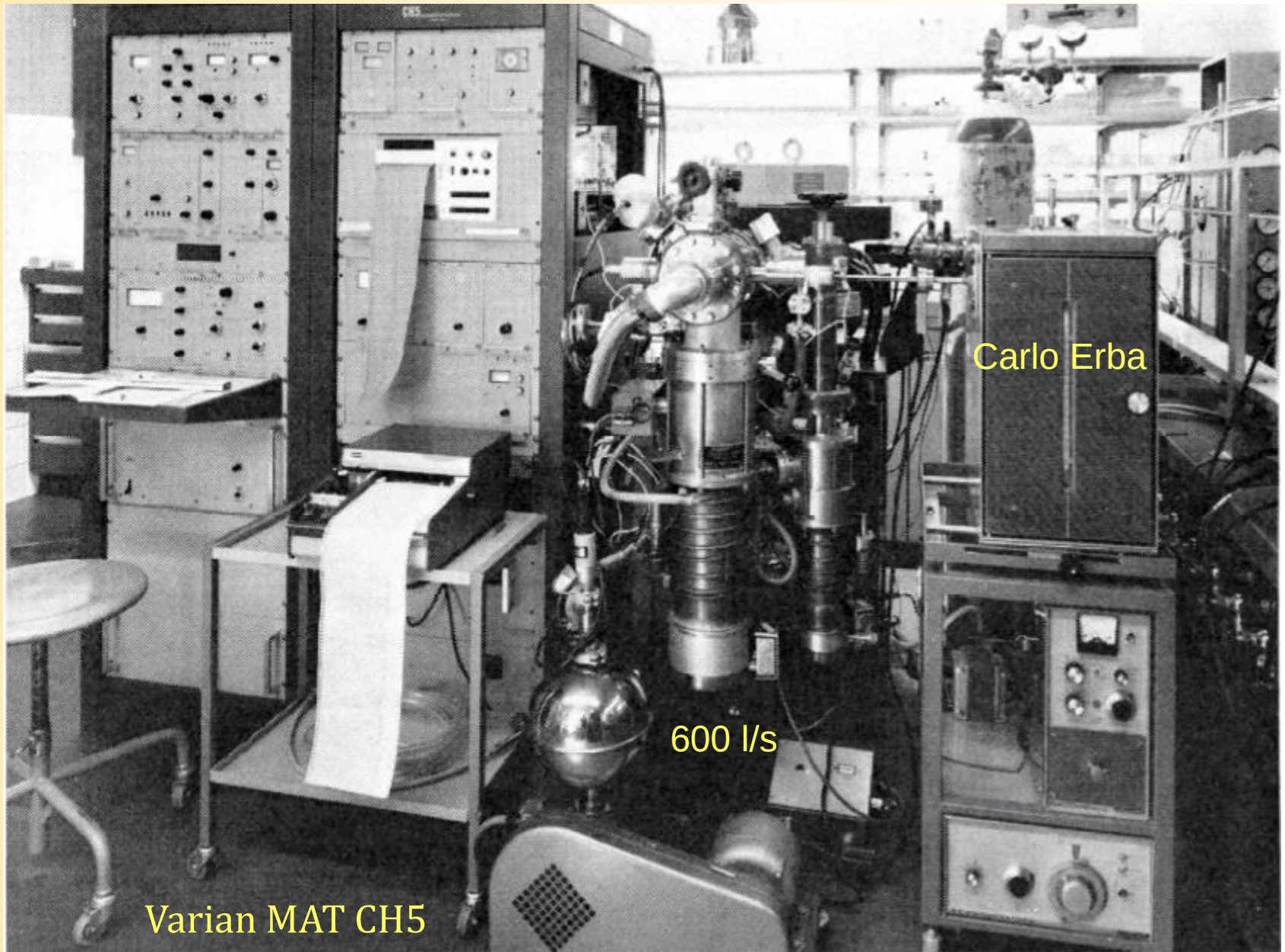
GC-CH4 présenté à ACHEMA
comme « curiosité »
... sans intérêt!!!

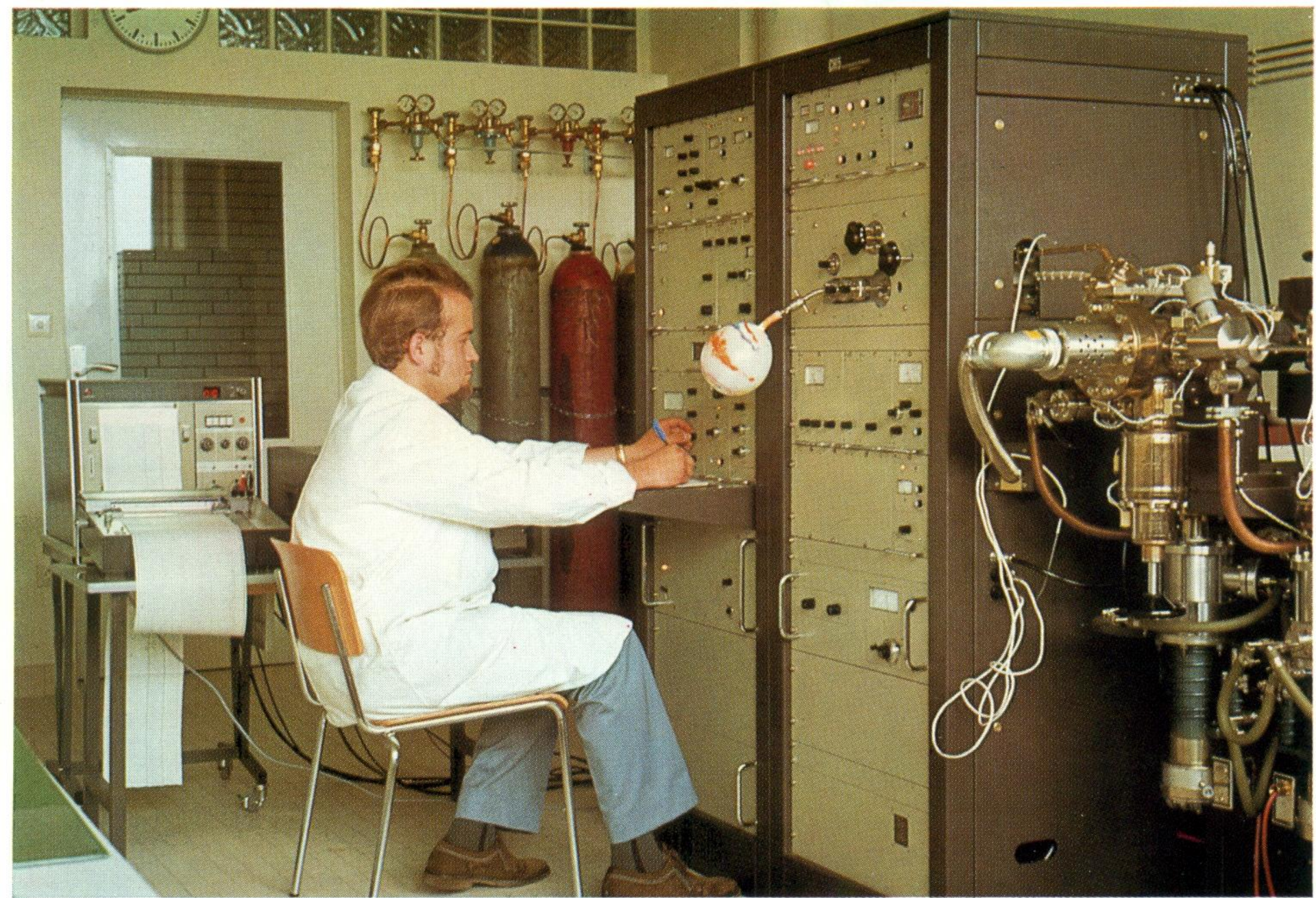
MAT CH5 High Resolution « routine MS » (1967)



Resolution > 10 000

K. Grob and G. Grob, *ca.* 1970





Dragoco

Communication présentée au 5th International Congress of essential Oils
San Paolo, Brazil (1971)

The Flower Oils of Lily of the Valley and Lilac

Heinz Mack, Manfred Kopsel and Wolfgang Pilz
Haarmann & Reimer GmbH

Gas chromatograph : Aerograph 1740

Colonne : 50 m capillary , polar

Mass spectrometer : **Varian CH-5**

Carrier gas separator : Biemann/Watson

La connection japonaise avec Perkin-Elmer



Hitachi RMU-6M

Commercialisé en Europe par Perkin Elmer (1965-1970)

Publicité de Perkin Elmer
dans *Analytical Chemistry* (décembre 1964)

HITACHI RMU-6D mass spectrometer

« ...with gas chromatography accessory »

« ...allows spectral analysis of trace components separated by capillary G.L.C. »

« ...it is priced at about **\$40,000** installed, depending on accessories »

質 量 分 析

報 文

Vol. 19. No. 3, September 1971

Shitsuryo Bunseki

電子計算機による GC/MS の自動分析
(I) GC/MS のオンラインデータ処理

Data Processing System by Computer for GC/MS.

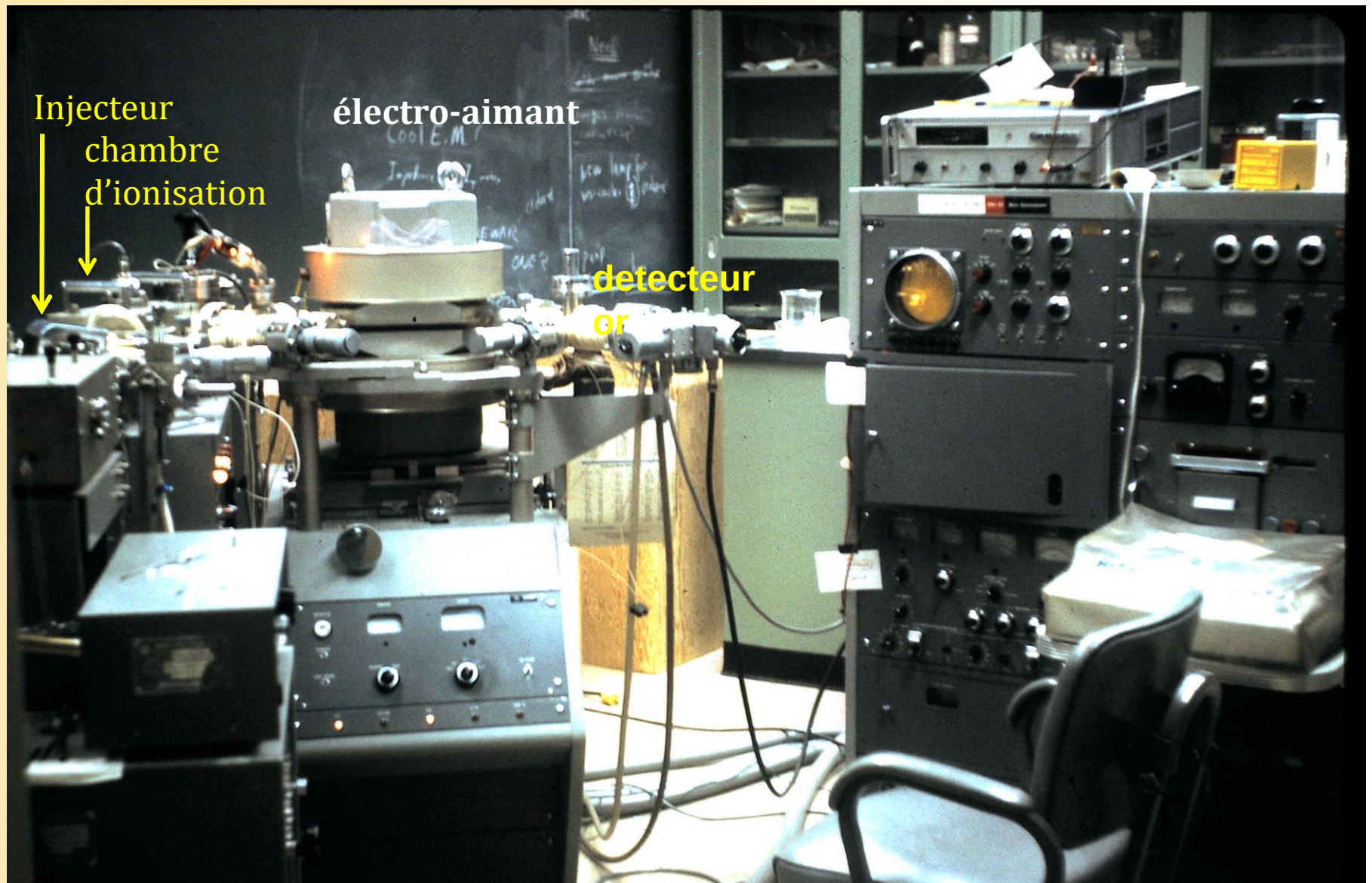
(I) On-line Data Reduction System for GC/MS

能 代 誠*・後 藤 正 二 郎*・赤 塚 米 三*・山 岸 良 司*・富 樫 典 也**

MAKOTO NOSHIRO, SHOJIRO GOTO, YONEZO AKATSUKA, RYOJI YAMAGISHI AND NORIYA TOGASHI

(1971年8月8日受理)

Hitachi RMU-6 à secteur magnétique vers 1968





Hitachi RMU-6M
GC-MS
Neuchâtel, 1970

Spectral Atlas of Terpenes and the Related Compounds

[GC-MS with Hitachi RMU]

Compiled by
Japan Perfumery and Flavouring Association

Edited by
Yasuhide Yukawa Professor of Osaka University
Shô Itô Professor of Tohoku University



Hirokawa Publishing Company, Inc.

Tokyo

1973

Analysis of Essential Oils by Gas Chromatography and Mass Spectrometry

[GC-MS with Hitachi RMU-6E]

Yoshiro Masada
Professor of Pharmaceutical Chemistry
Kyoto College of Pharmacy, Kyoto, Japan

A HALSTED PRESS BOOK

John Wiley & Sons, Inc.

New York-London-Sydney-Toronto

1976

WALTER JENNINGS
TAKAYUKI SHIBAMOTO

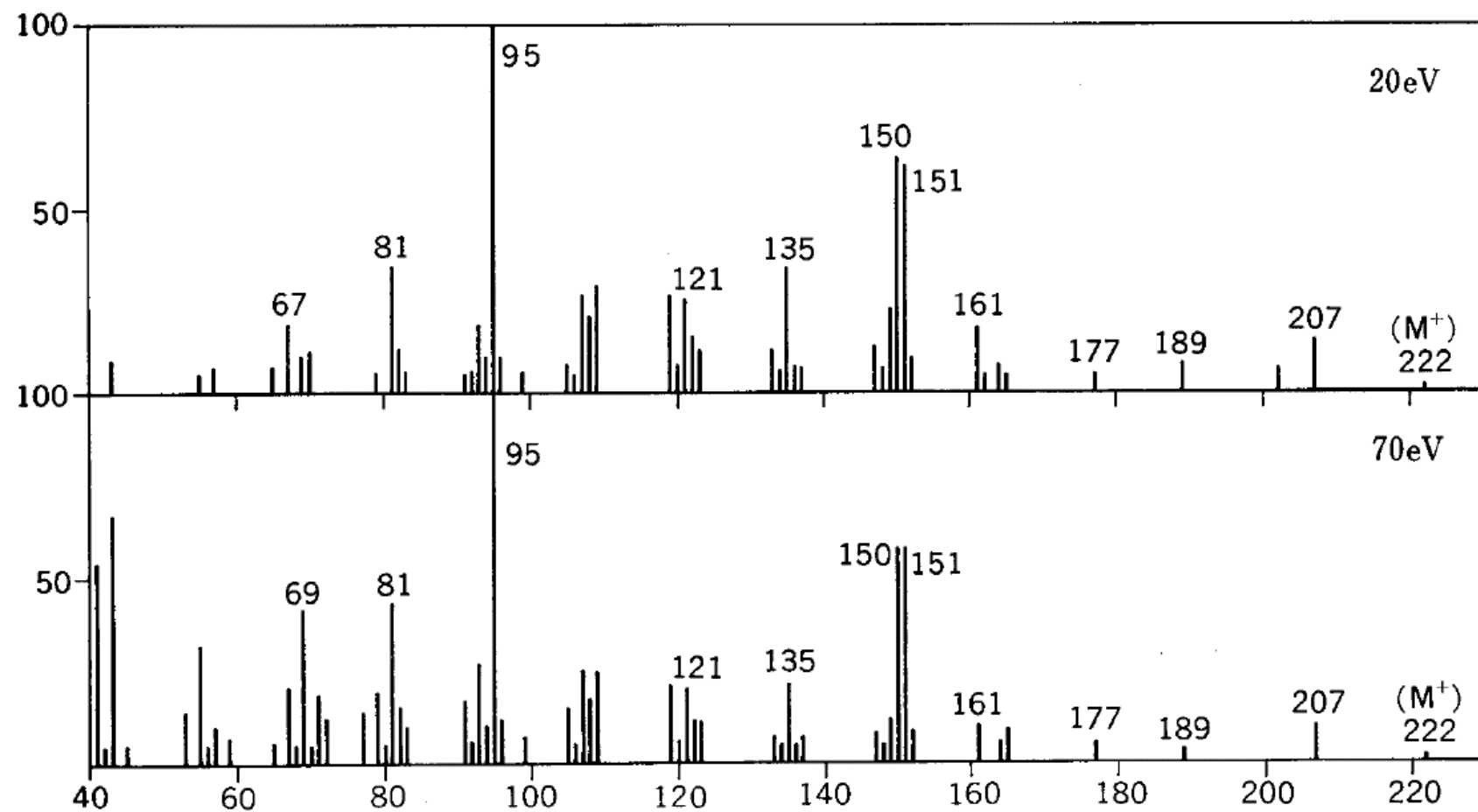
**Qualitative
Analysis
of Flavor
and Fragrance
Volatiles
by Glass
Capillary
Gas
Chromatography**

Academic Press

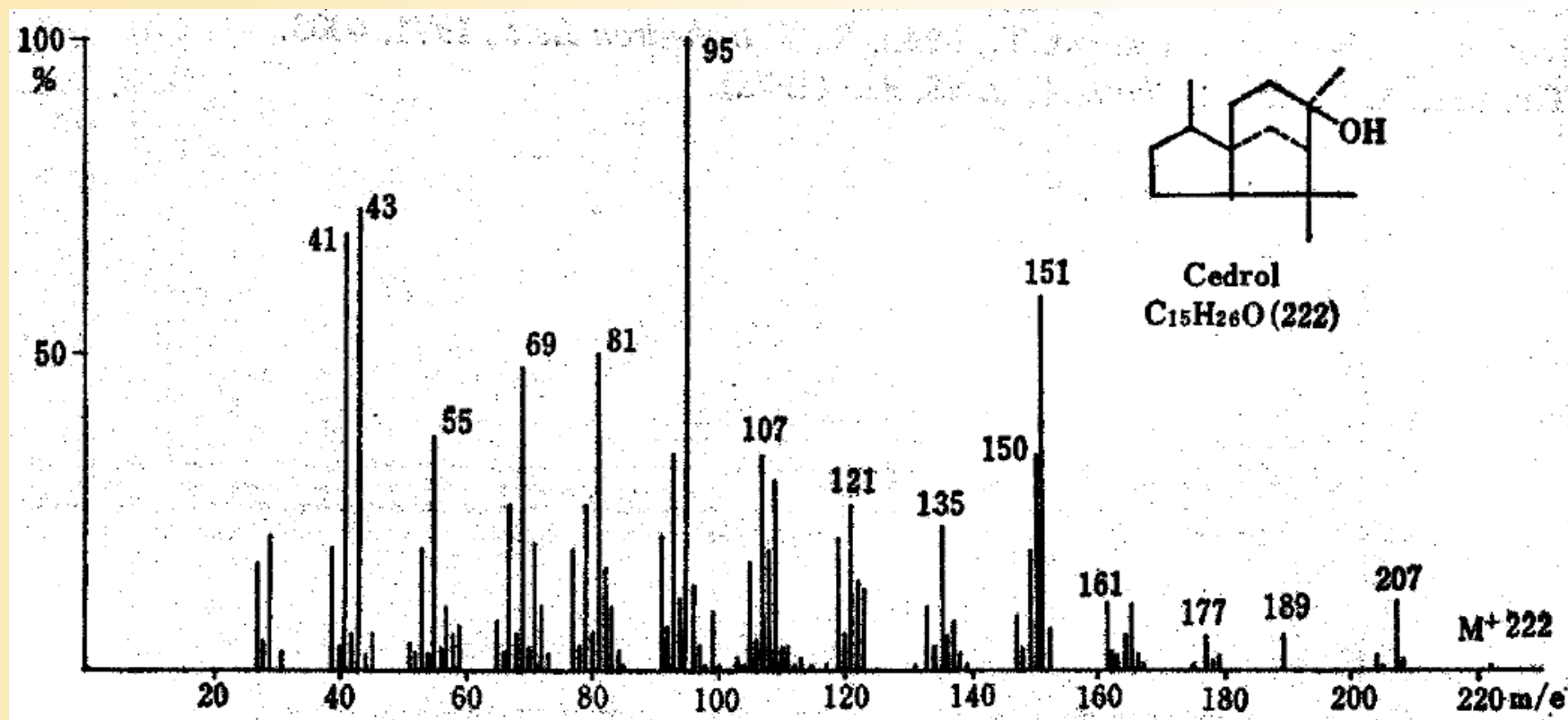
A Subsidiary of Harcourt Brace Jovanovich, Publishers

1980
Hitachi RMU-6M

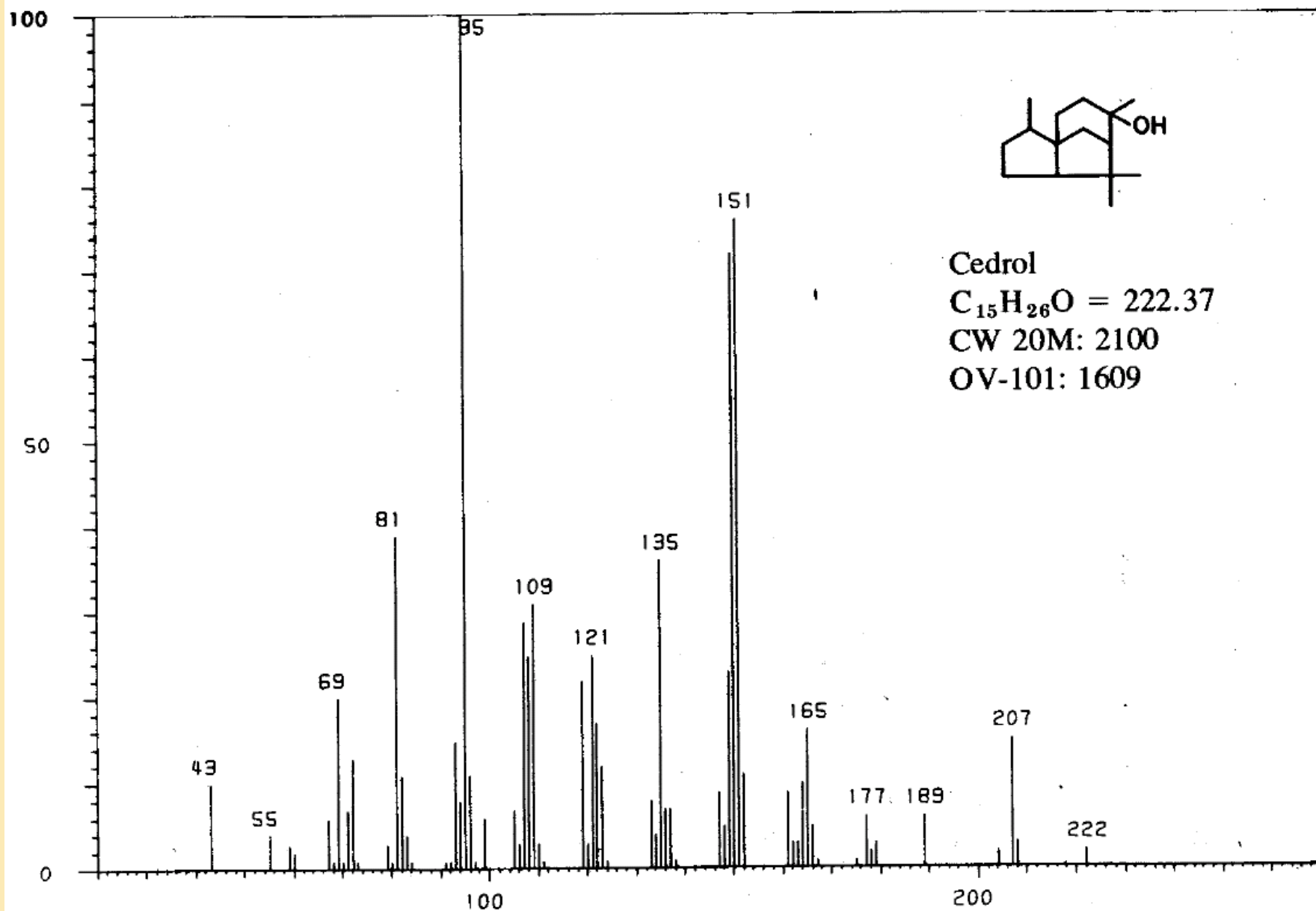
Yukawa (1973)



Masada (1976)

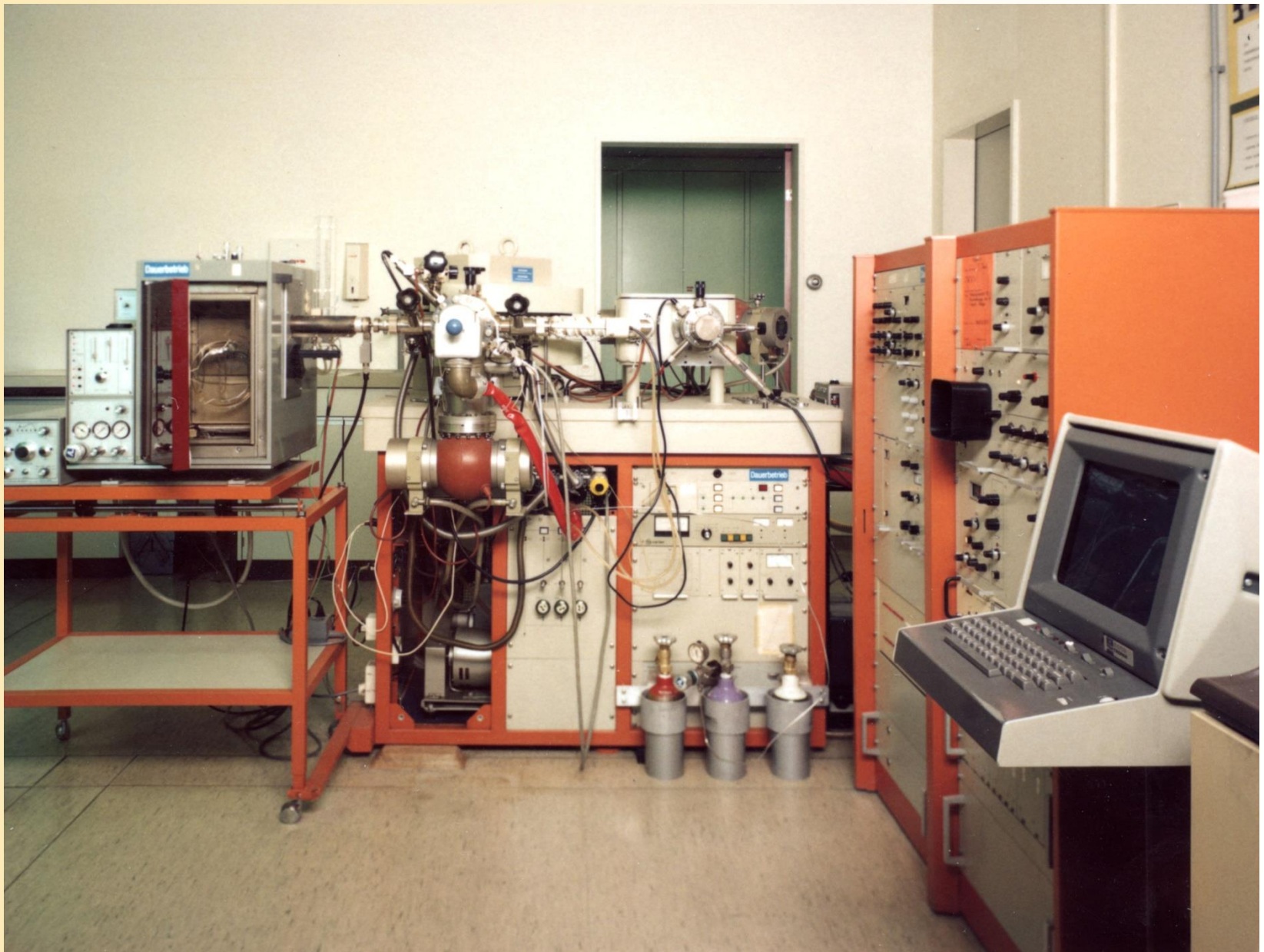


Jennings-Shibamoto (1980)

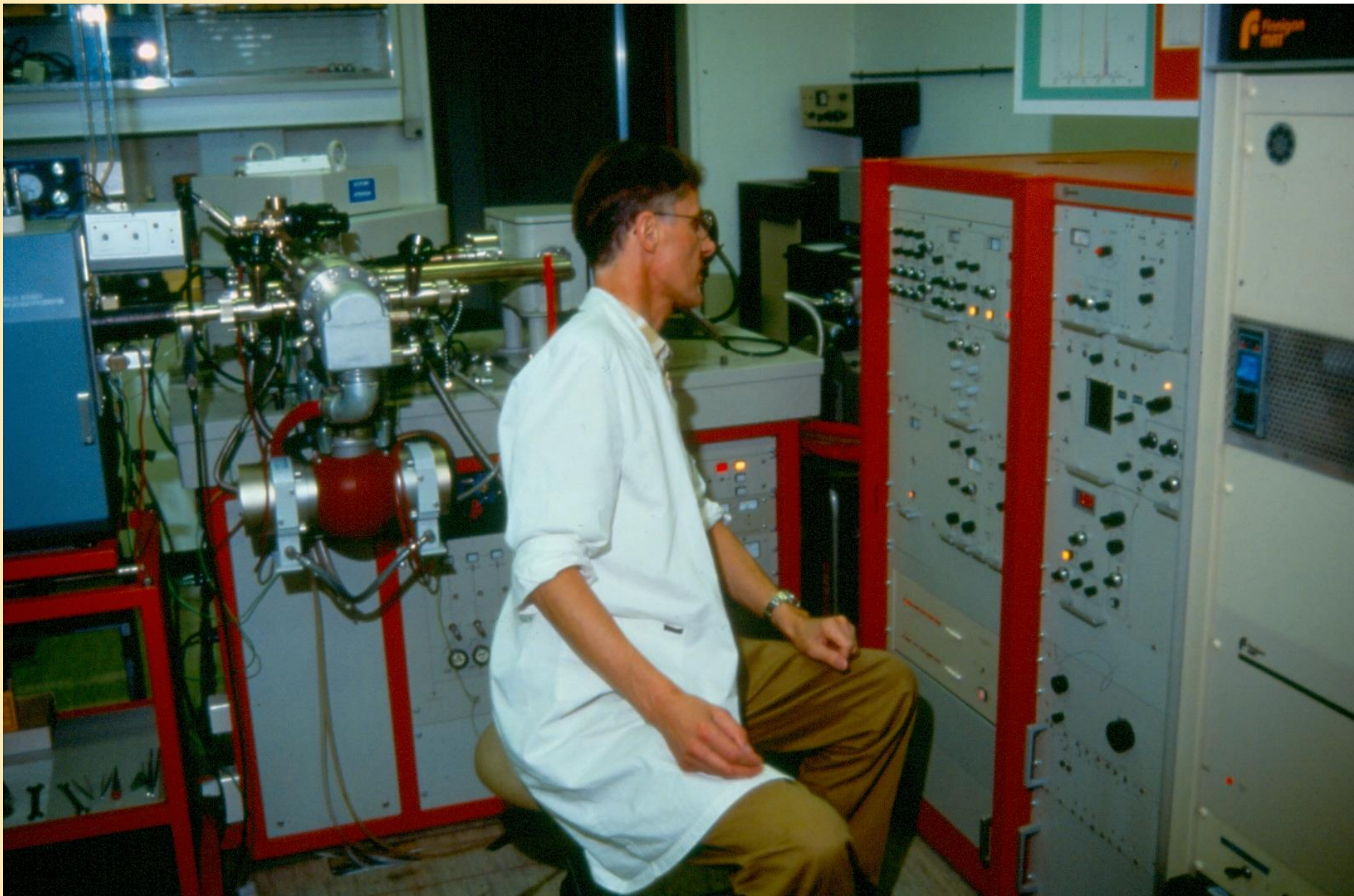


La technologie européenne

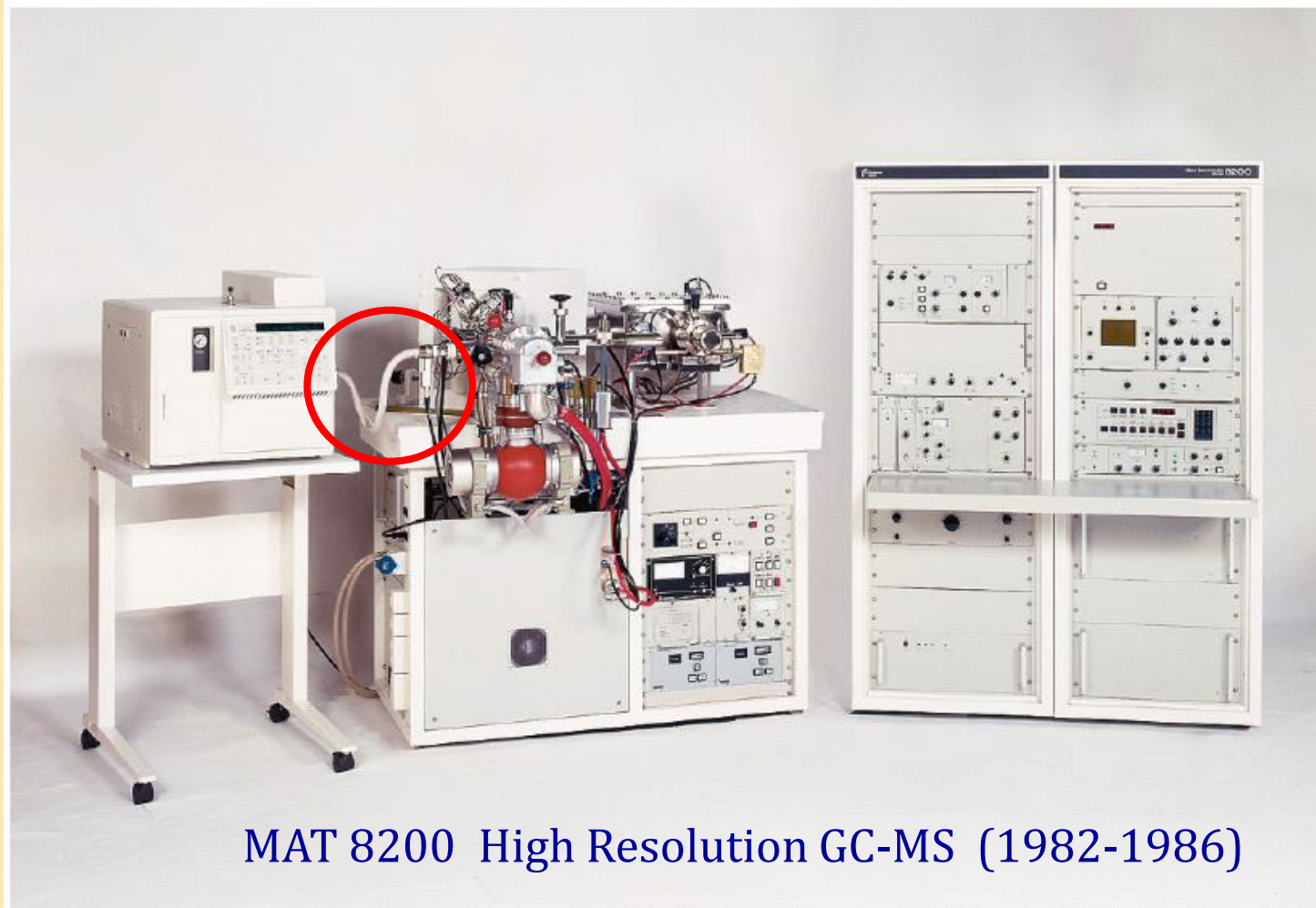
- **Mass und Analysen-Technik** (MAT, Bremen)
- **Vacuum Generators** (VG, Manchester)
- **Kratos Analytical Instruments** (Manchester)



MAT 212



Joachim Schmidt en opération sur le MAT 212
(Givaudan, Dübendorf, vers 1985)



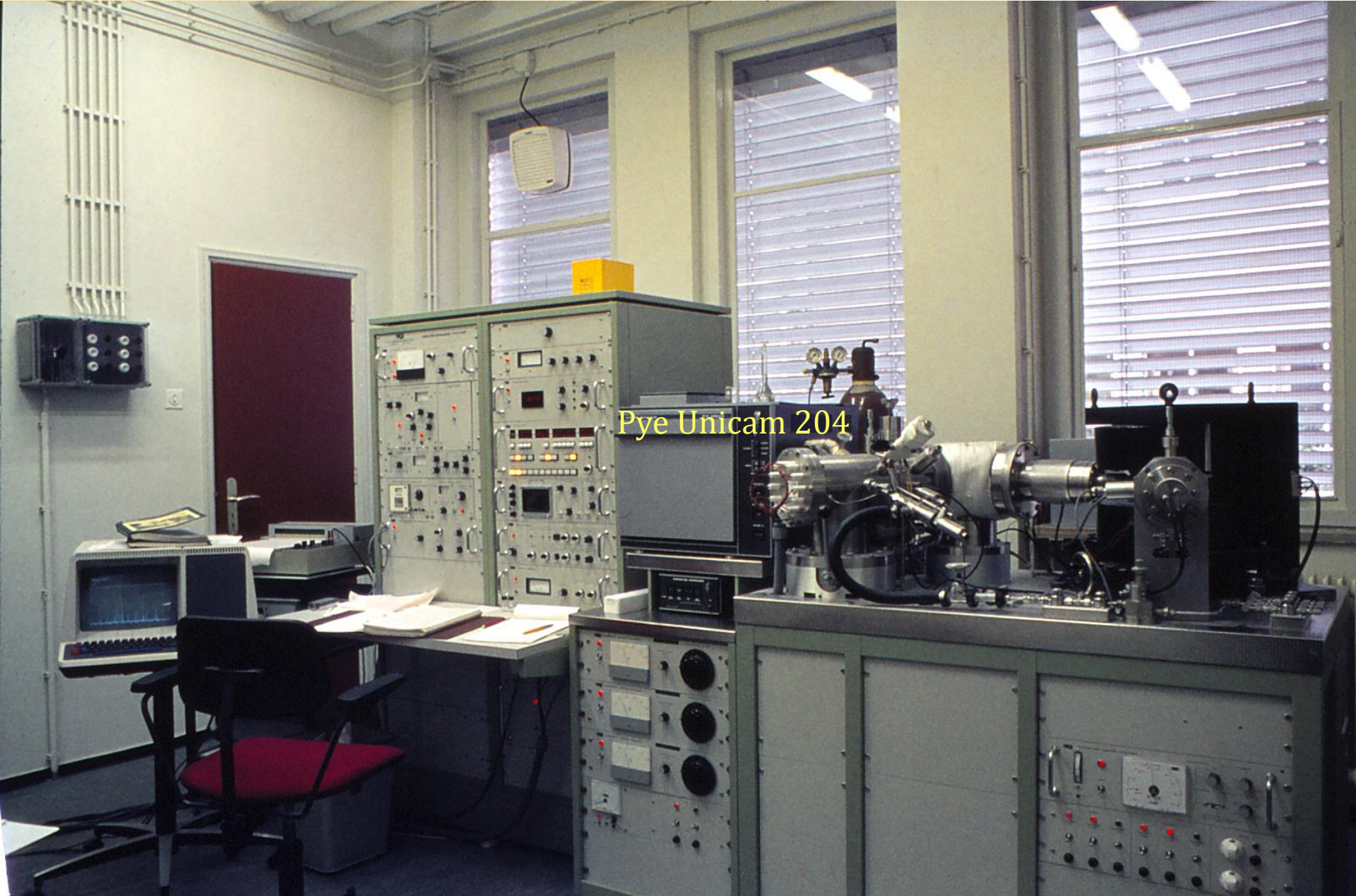
MAT 8200 High Resolution GC-MS (1982-1986)

**Routine
GC-HRMS**

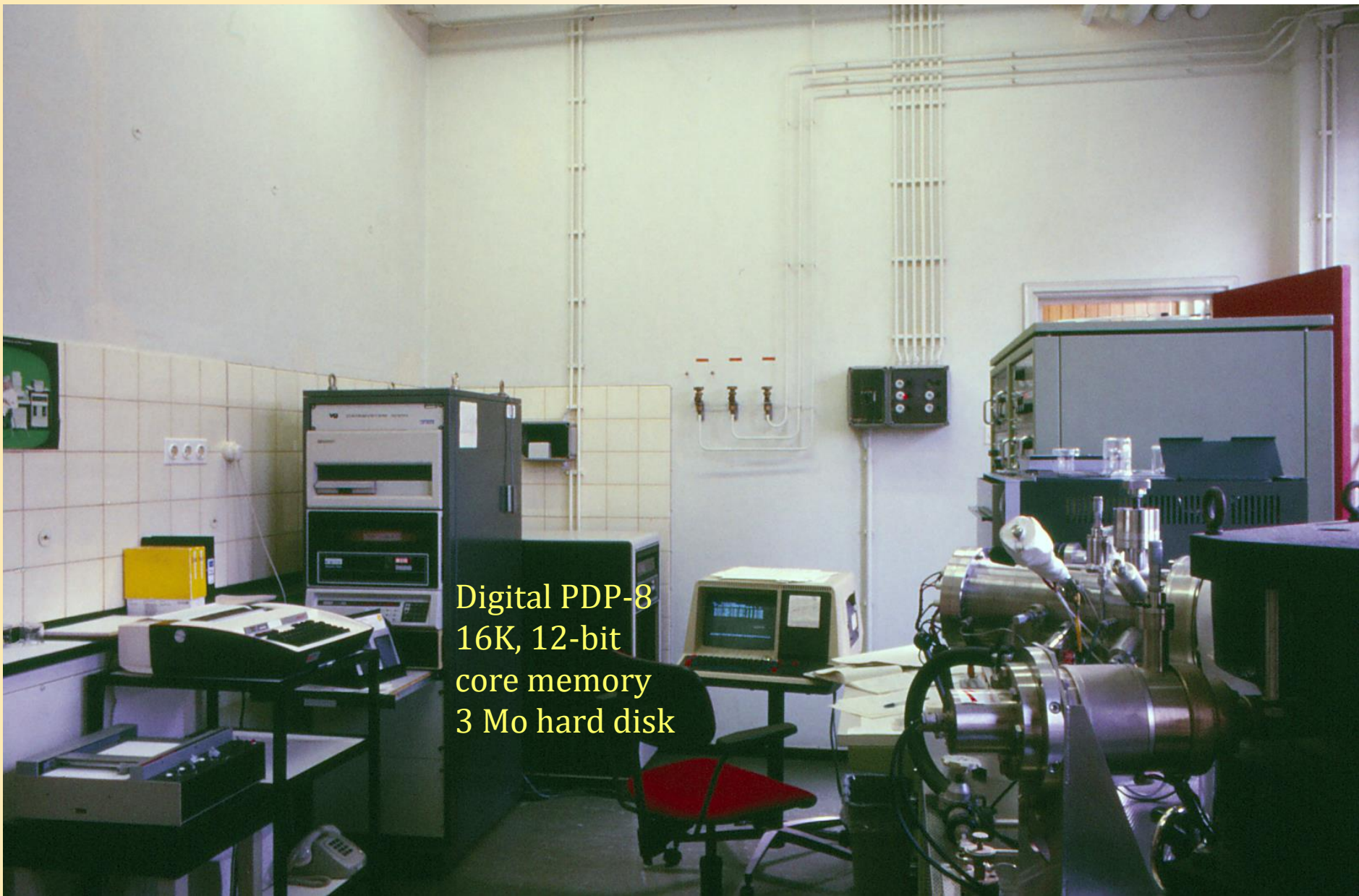
**First Dioxin
measurements!**

But:

Flexible GC
transfer line
with poor
performance

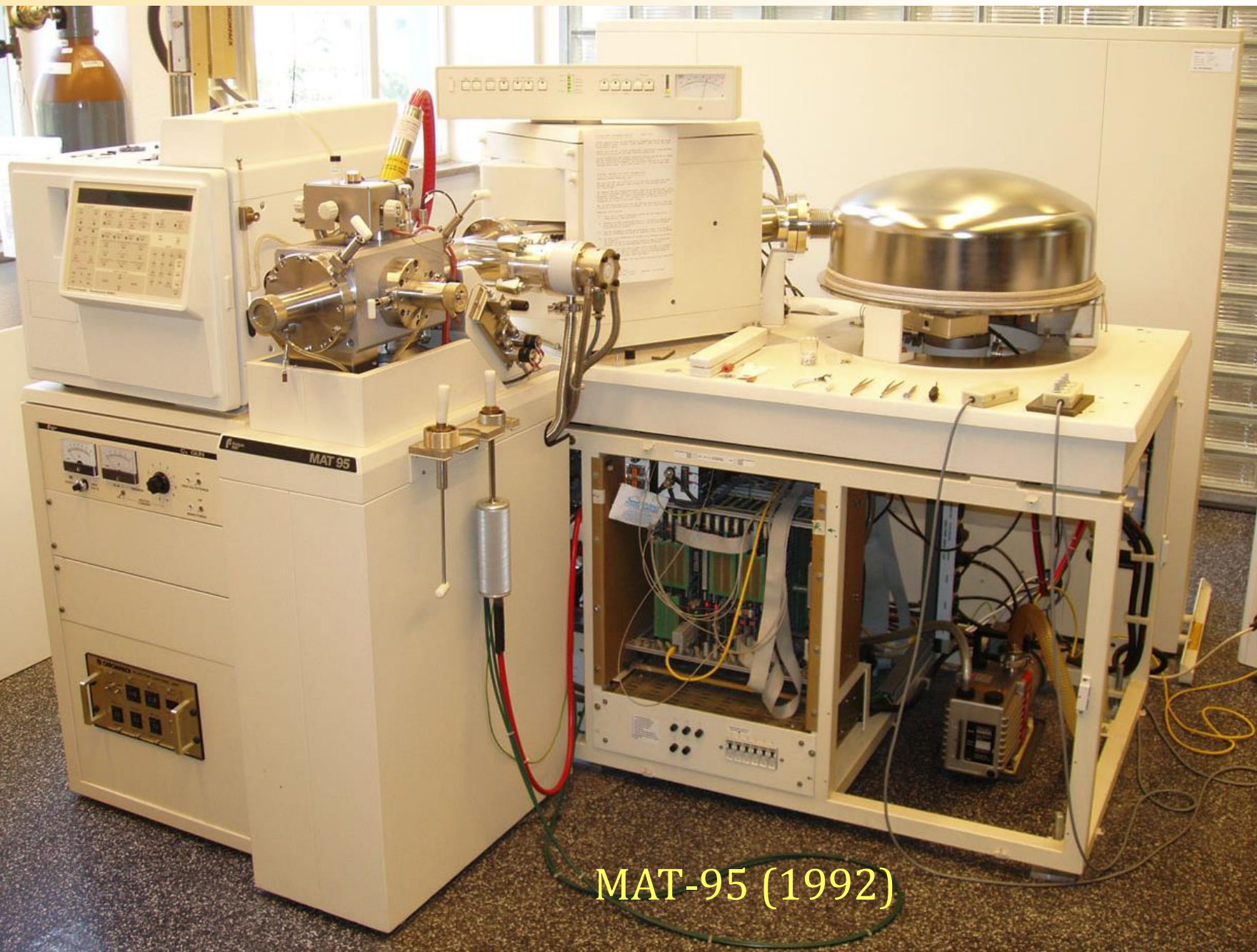


VG Micromass 70-70F
(Wageningen, 1979)



Digital PDP-8
16K, 12-bit
core memory
3 Mo hard disk

VG Micromass 70-70F
(Wageningen, 1979)



MAT-95 (1992)

LKB lance le premier
GC-MS « intégré »
(LK-9000)

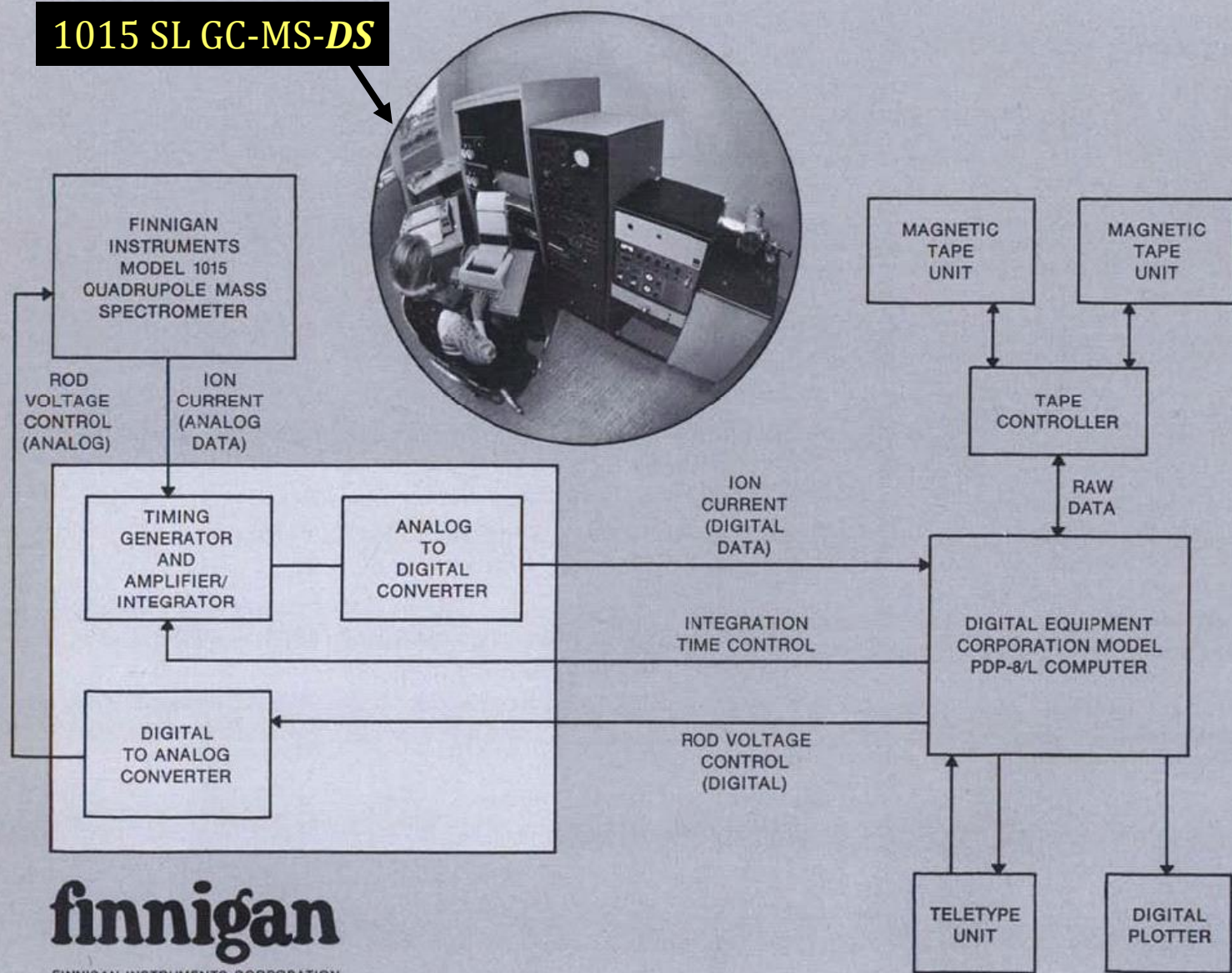
Discussions entre
Carl Djerassi avec Syntex
et **Robert Finnigan**

1966

William Hewlett
rencontre **Finnigan** et
commande un QUAD 300

ACS Meeting, New York City, Sept. 1969

1015 SL GC-MS-DS



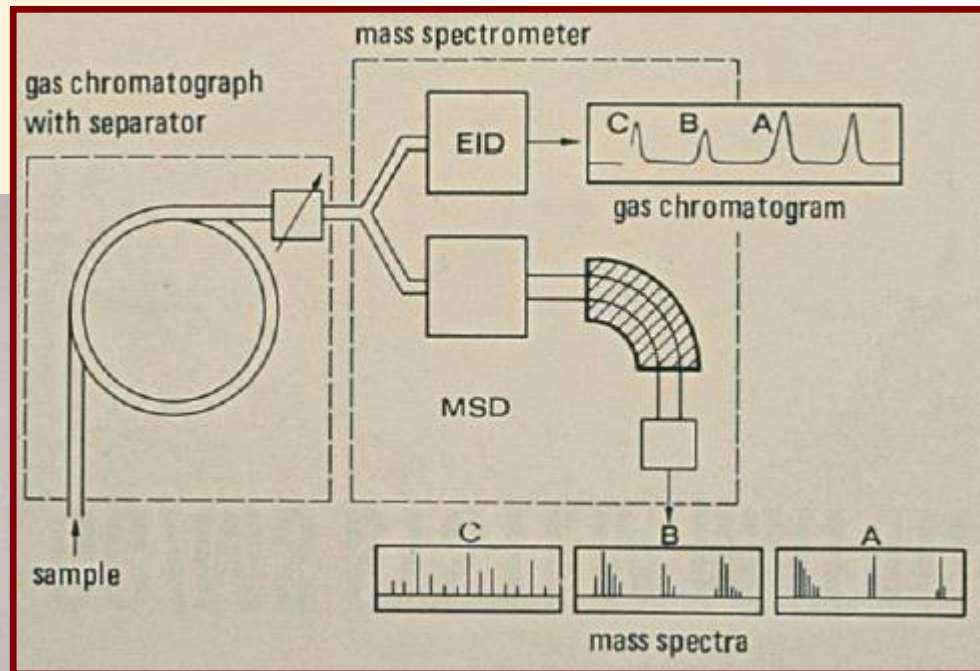
finnigan

FINNIGAN INSTRUMENTS CORPORATION

2631 Hanover Street, Palo Alto, California 94304



Finnigan Model 1015,
le premier Quad-GC/MS avec data system intégré



Single focussing
Resolution 1000

MAT 111 « Gnome » (1971)

« premier GC-MS de routine »

...Bill [William R.] Hewlett personally, saw GC and GC-MS as one business, you know, one product area. He recognized early on that mass spec was just another form of detector for gas chromatograph, and that the two were one and the same business. I would just say it was amazing, you know, how early he recognized that and saw the need for mass spec as an important detector for the gas chromatograph. On the other hand, we saw GC as one of the many sample introduction systems (inlets) for the mass spectrometer.

I think that at the time Hewlett was more correct than us.



Robert Finnigan
(en 1975)



William R. Hewlett

Fin 1966, Finnigan vend à HP
un Quad 300, juste après l'achat
par HP de F&M...

Le garage de
Bill Hewlett et
Dave Packard
à Palo Alto vers 1939





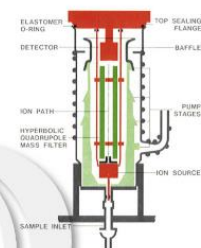
HP 5930 A « GC-MS-DS with oscilloscope »
(1973)

HP 5992 Gas Chromatograph/Mass Spectrometer/Data System

Wayne Duncan,
Agilent Technologies

Agilent/Hewlett Packard has had a rich history in the area of mass spectrometry. The company started to design quadrupole mass filters for GC/MS applications in the early 1970's. The 5930A was the first Hewlett Packard mass spectrometer introduced in 1971 for use as a general-purpose laboratory instrument.

A truly revolutionary approach in the industry was taken by Hewlett Packard with the introduction of the first "bench-top" GC/MS, the Model 5992A. It was introduced in 1976 in Florence, Italy and was radical in design. The concept developed by Ned Kuypers was refined in several generations to become the standard of the industry. Not only was it a bench-top instrument, but it also placed the quadrupole mass filter inside the diffusion pump.



HP 5992B/920B Diffusion Pump and Analyzer Assembly
Cross Section.



Design Considerations

The gas chromatograph was integrated with the mass spectrometer from the inception of the design. Up until this time, existing chromatographs had been retrofitted to existing mass spectrometers. Designing the two instruments into one package provided an opportunity to eliminate many of the problems associated with interfacing them. The mass analyzer, high vacuum system and electronics card cage were mounted above the GC oven so that the ion source was immediately above the GC oven. As capillary GC columns had not yet come into use, packed columns with their higher flow rates required a molecular separator and MS isolation valve which were conveniently positioned between the top of the GC oven and the ion source to minimize the length of the GC/MS transfer line. The hyperbolic quadrupole mass filter was eight inches in length and delivered ions to a continuous dynode electron multiplier. The entire source, mass filter and detector assembly was mounted on a single upper flange which used atmospheric pressure to seal the vacuum system.

The hardware design unique. The mass analyzer was surrounded by and built into the center of a newly designed diffusion pump. This approach offered several advantages including:

- lower cost due to compactness and fewer parts
- faster evacuation of minimum volume vacuum envelope
- the entire source, analyzer, and detector assembly operated in a controlled temperature gradient environment provided by the surrounding diffusion pump boiler and heated vapor zones
- only one high vacuum flange were no bolts or metal gaskets, thus minimizing leaks
- pump down and venting automatic minimizing operator involvement

The entire structure featured simple electrical connections and a minimum of mechanical parts.

HP5992 Specifications

HP 5700A Gas Chromatograph

- Microprocessor control of injection port and oven programming
- Column Oven: -50°C to 350° (Upper limit 280° with membrane separator installed.)
- Oven Temperature Programmer: 0.125 to 16°/minute in 0.125°C steps
- GC/MS Interface: Membrane separator supplied, Jet separator available as an option.

Mass Spectrometer

- Mass Range: 10 to 800 amu
- Resolution: Unit resolution throughout mass range
- Sensitivity: One ng methyl stearate injected on column will yield a spectrum with a signal-to-noise ratio 10:1 or better at the molecular ion (298.3) when scanned at 190 amu per second.
- Scan Rate: 620, 330, 190, and 100 amu per second from high to low mass
- Ion Source: Dual rhenium filaments at 70eV ionizing energy with patented Turner-Kruger lense to focus ions into the mass filter
- Detector: Continuous dynode electron multiplier
- Mass Filter: Hyperbolic quadrupole rods 203mm long
- Signal Amplifier: Field Effect Transistor (FET) logarithmic preamplifier with 5 decades dynamic range
- Vacuum System: Four-stage water-cooled diffusion pump with 150 liters/second pumping speed for helium. Direct drive mechanical pump at 50 liters/minute.

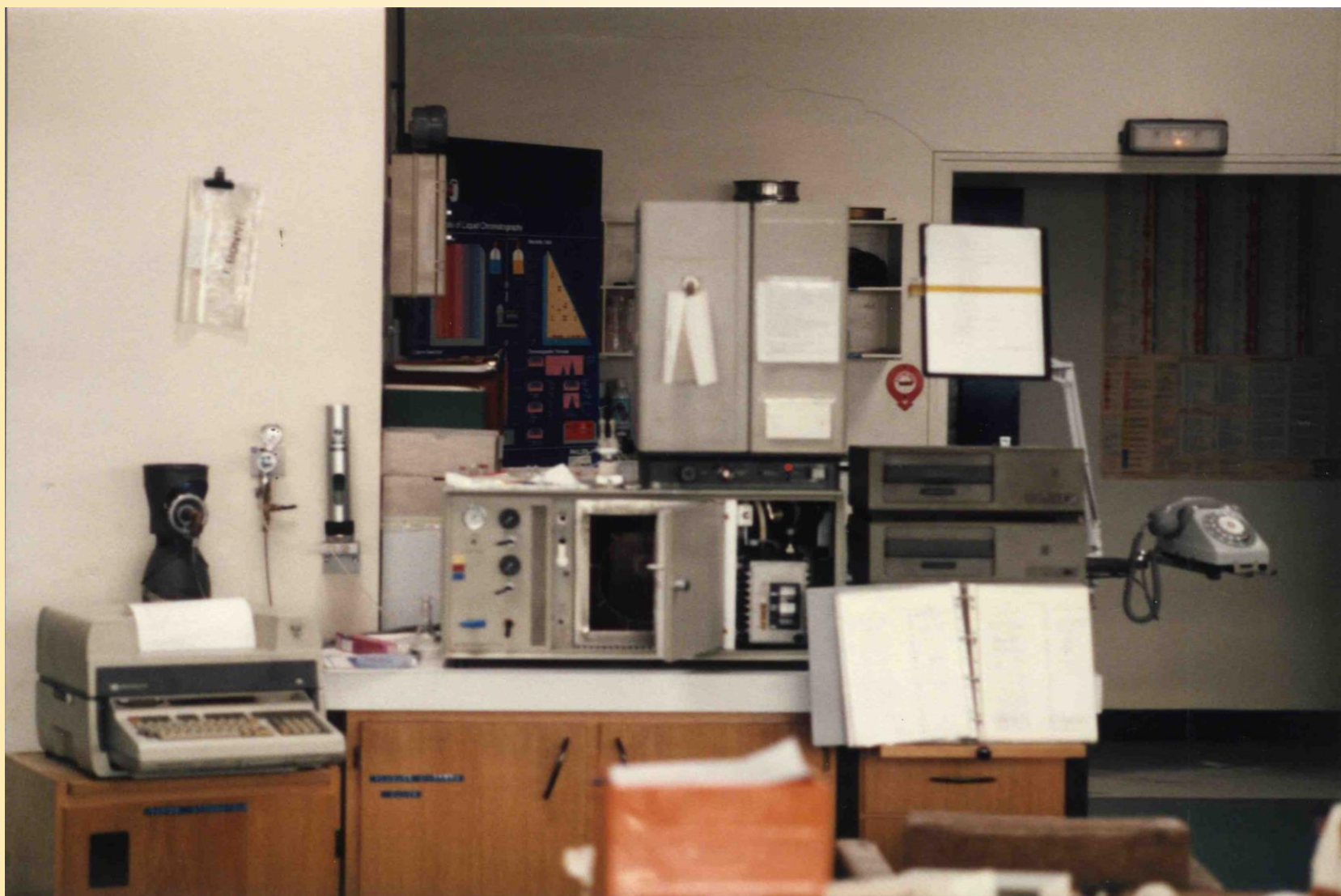
Data System

The HP 5992A was an integrated microprocessor controlled GC/MS instrument. The control terminal consisted of the HP 9825A Calculator with 16K of 16 bit words of memory and the HP 9866B Thermal Line Printer. A tape cartridge held the master system software and programs were supplied in either binary format or in secured Hewlett Packard Programming Language (HPL), the programming language of the HP 9825A Calculator. The 5992A was also the first GC/MS to be supplied with AUTOTUNE capability. Scientific Instruments Division (SID)-HPL was the language used for AUTOTUNE and operating the GC/MS for chemical analysis. AUTOTUNE adjusted the ion source elements, amu gain, and amu offset to achieve specified performance based on perfluorotributylamine ions at 69, 219 and 502. A communications interface option was offered permitting users to communicate with various computer timeshare networks. This allowed users to link the system through a phone line to help identify unknown spectra by searching libraries available from commercial timeshare services.

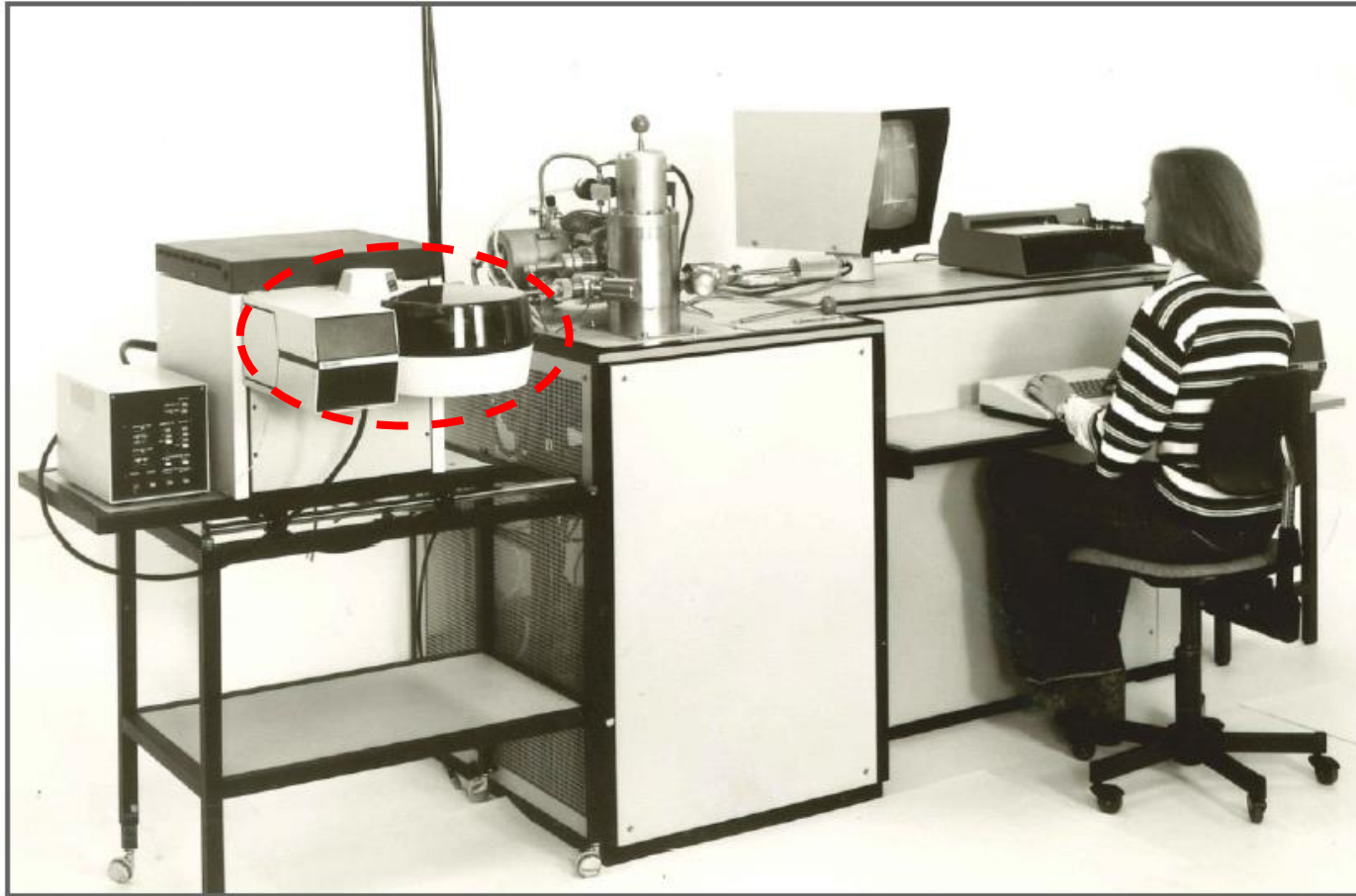
While critics predicted some technical problems with the design, the 5992 set the expectations of the market and was destined to be a big success. This was corroborated by the very broad-based acceptance of the HP 5992A which reached an installed base of many hundreds of instruments spanning many markets.



HP5992A (Martini)



MAT 44 : premier CG-SM à quadripole hyperbolique (1977)



Resolution

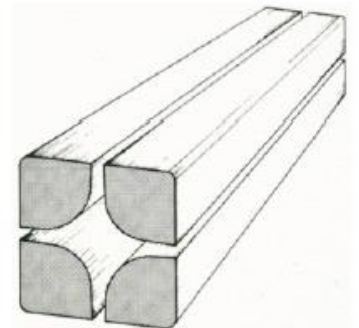
> 4 000 (10% val.)
@ 1166/1167 Da

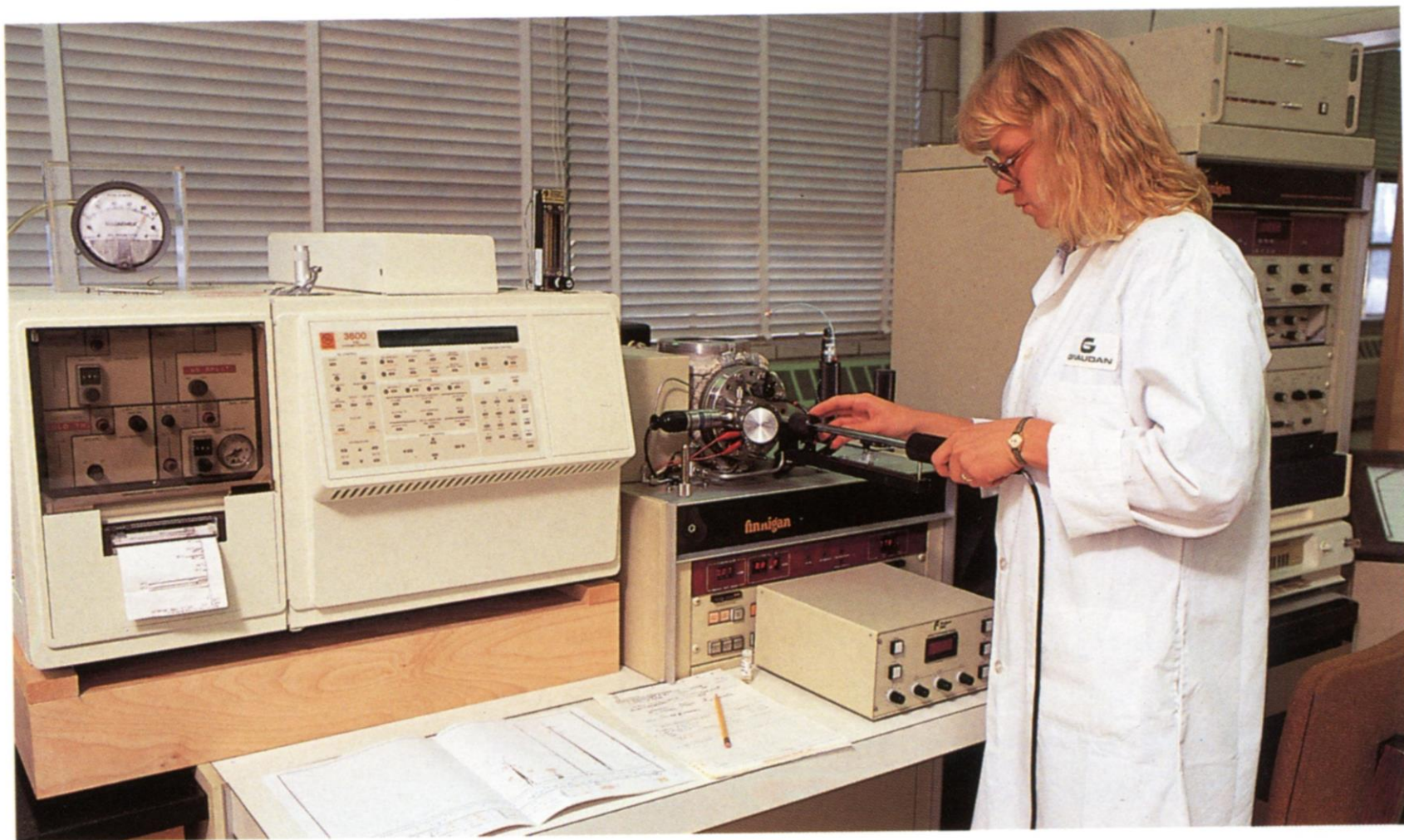
Sensitivity

1 ng Me-Stearate
S/N 20:1
(CI 1 ng BZP 50:1)

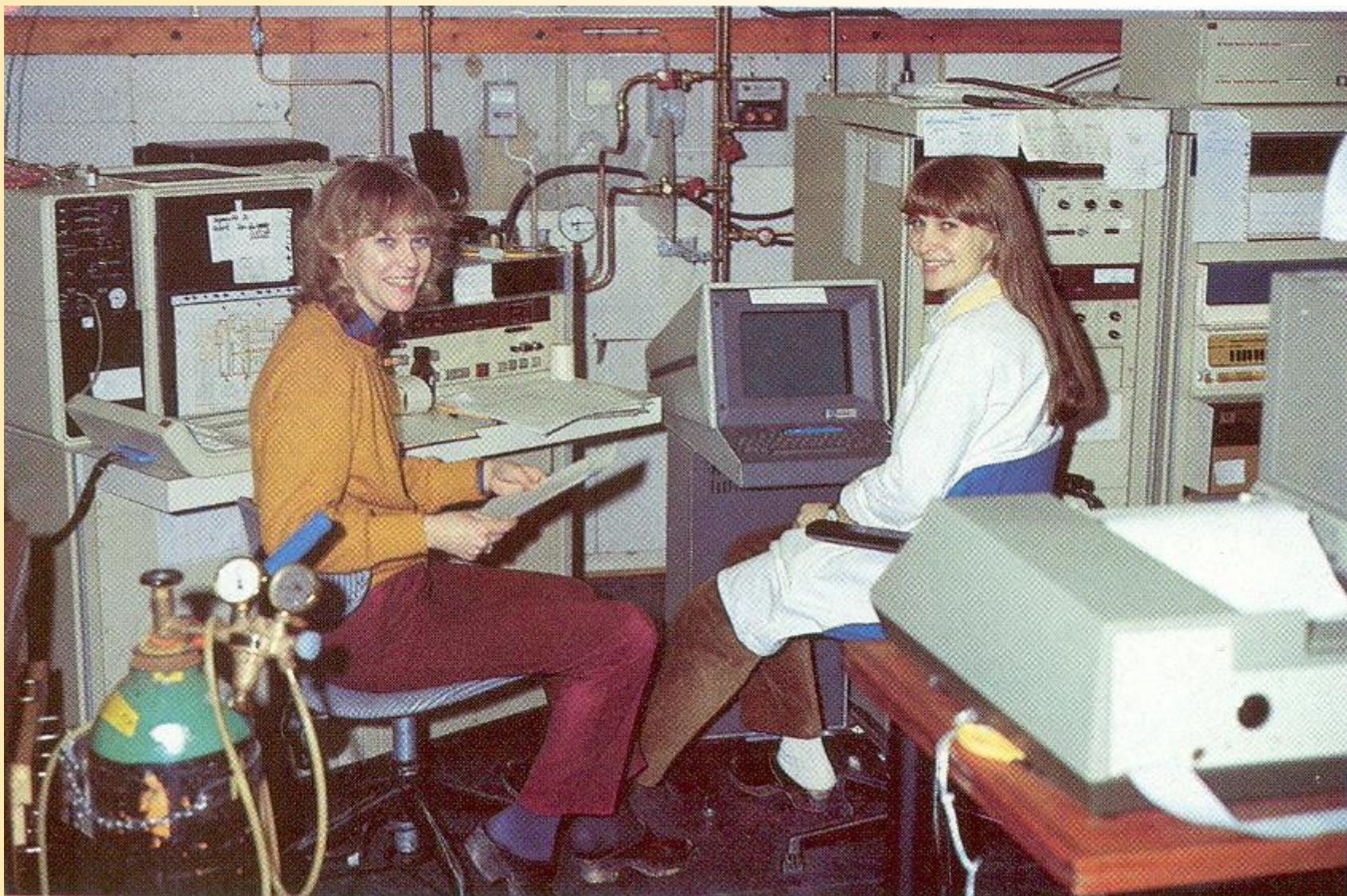
Data System

SS 200
64 k memory
4.7 Mb Dual Floppy
Disk storage

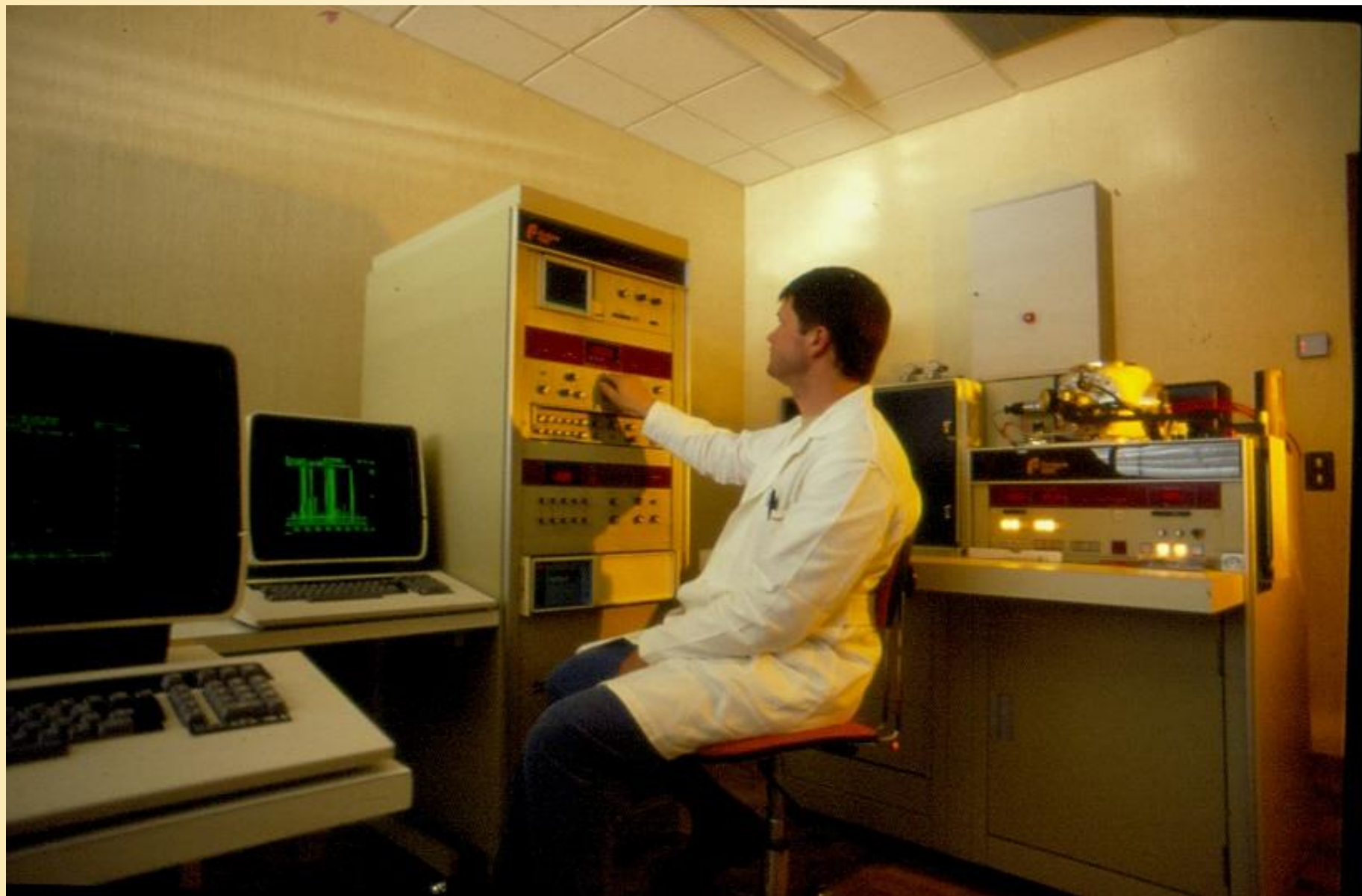




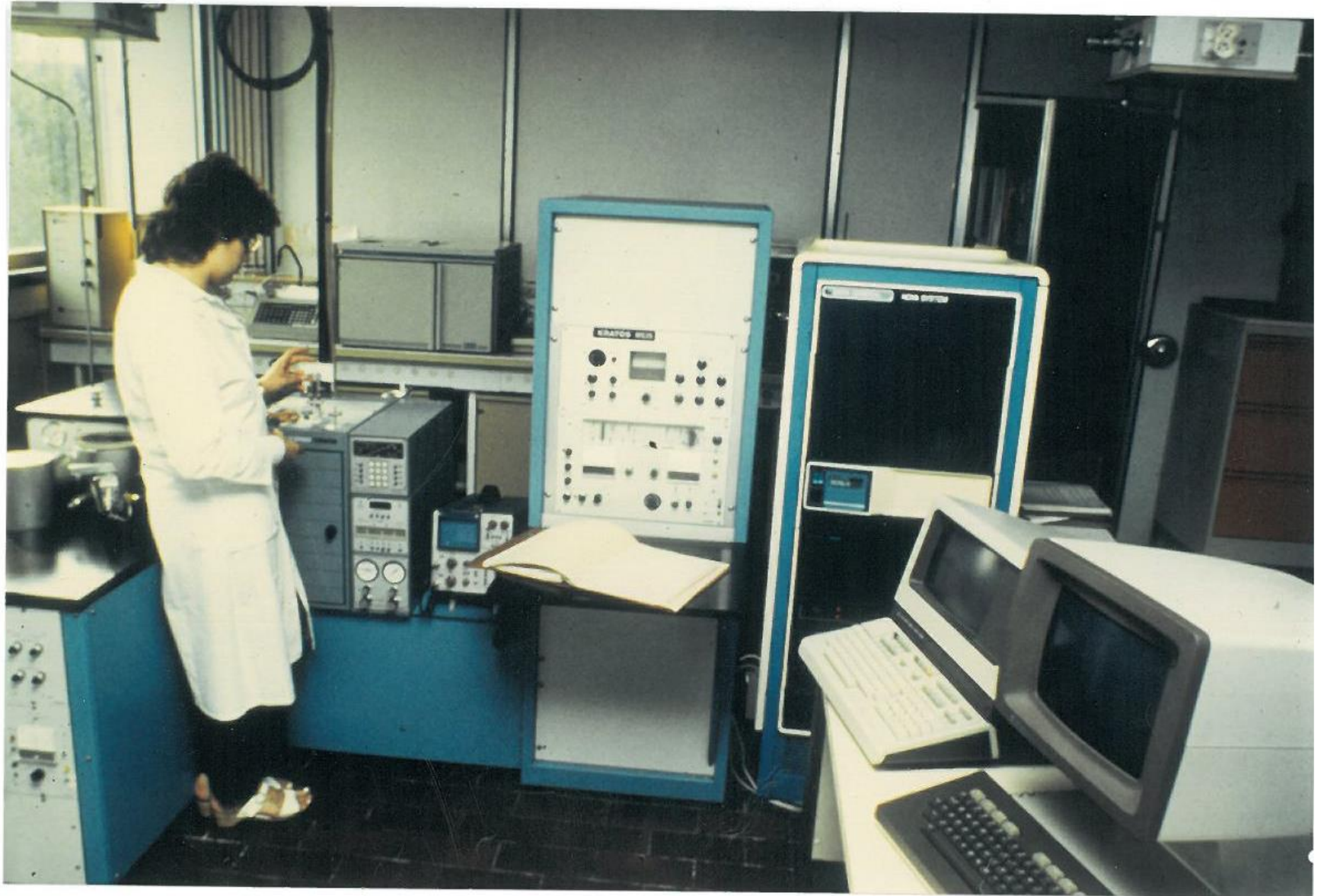
Finnigan 4500
Givaudan (Clifton, NJ)



PhD students in Göteborg



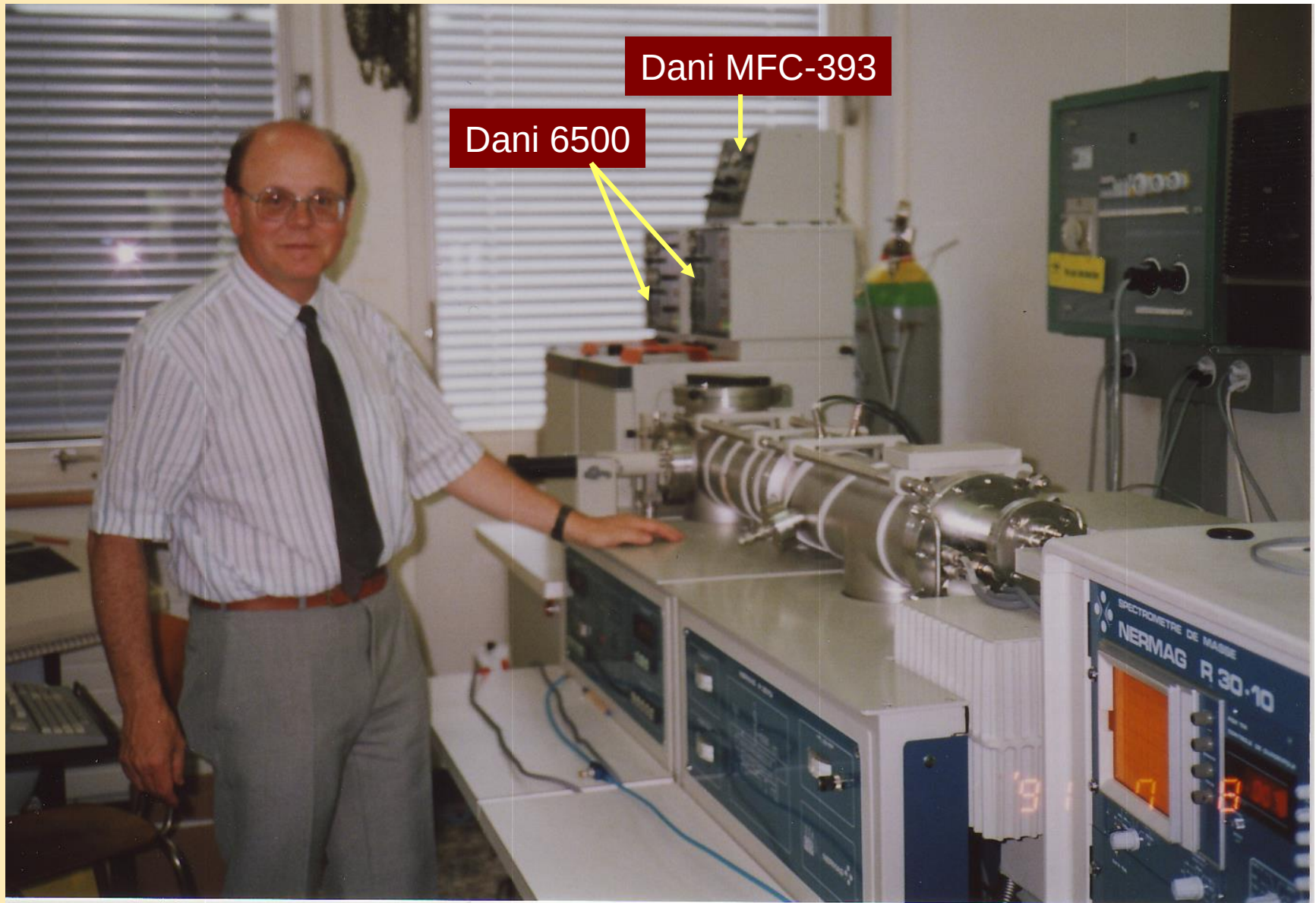
Kratos MS25 (Pernod-Ricard)





Ribermag/Nermag R10-10

Le premier CG x CG -TSQMS/MS Nermag 30-10 (Tabacchi *et coll.* Neuchâtel, 1987)



Journal of High Resolution Chromatography
(*J. Sep. Sci.*, 1988)

The Use of Multidimensional Capillary Chromatography in Conjunction with a Triple Quadropole Mass-Spectrometer in the Analysis of Complex Mixtures (GC – GC – MS – MS)

S. G. Claude and R. Tabacchi*

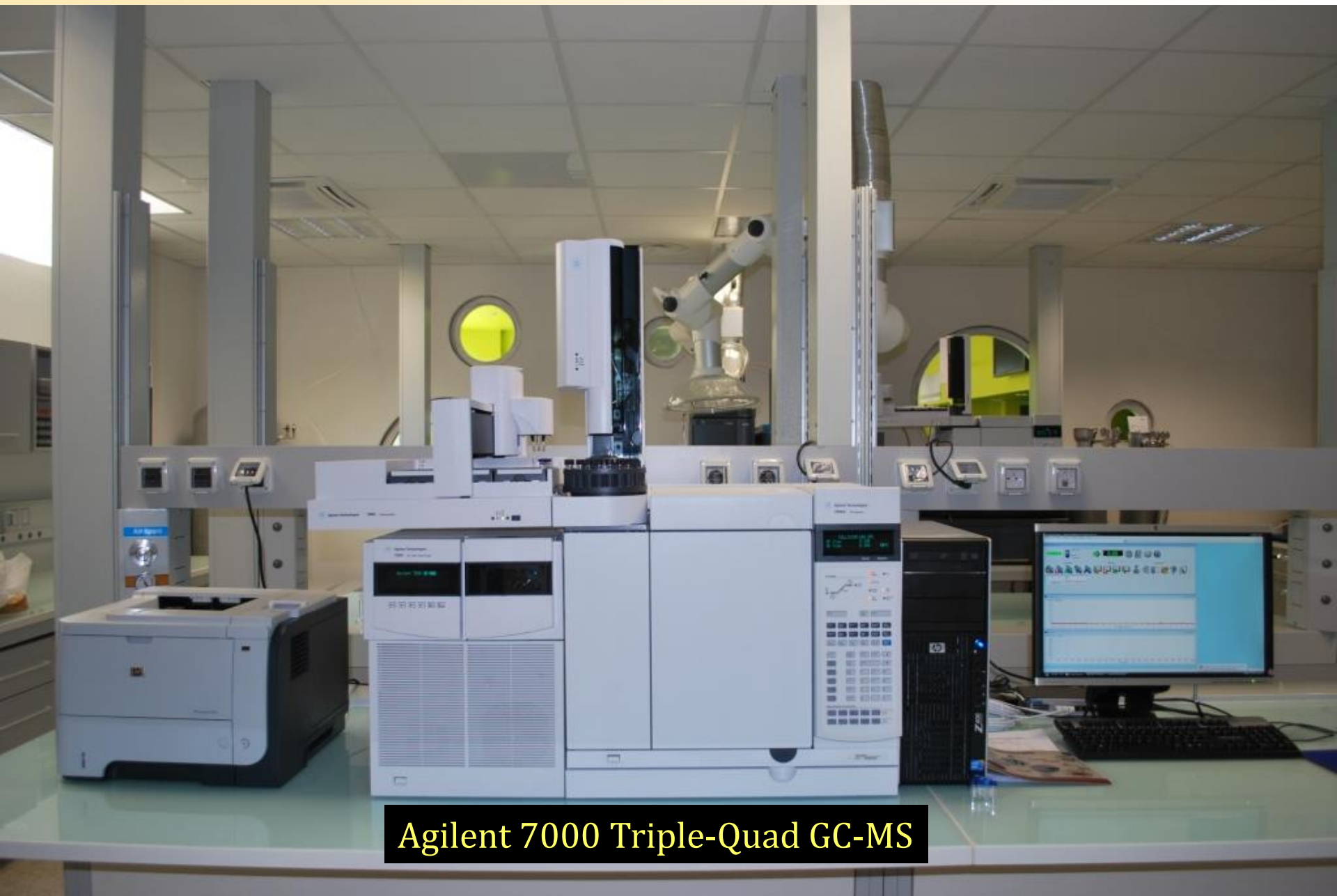
Institut de chimie de l'Université de Neuchâtel, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

Key Words:

Multidimensional capillary GC
GC-GC interface
GC-tandem mass spectrometry

*Presented at the
Eighth International Symposium
on Capillary Chromatography*

Huile essentielle de *Buddleia salvifolia* d'Afrique du Sud



Agilent 7000 Triple-Quad GC-MS

- 1957 **Marcel Golay**
capillary columns (« WCOT »)
Perkin-Elmer
- 1979 **Ray Dandeneau and Ern Zerenner**
fused silica capillary columns
Hewlett-Packard

Le tsunami HP/Agilent

Dans les années 1980, HP a tiré parti de ses innovations technologiques en matière de colonnes de chromatographie en phase gazeuse (GC) sur capillaire et de systèmes de paillasse pour révolutionner le marché de la GC-MS en lançant le **5970 MSD** : un système compact doté d'un réglage automatique, d'une conception à quadripôle hyperbolique d'une grande fiabilité... et d'un prix « abordable ». Peu après, HP a développé un système de traitement des données de SM basé sur le système d'exploitation multitâche HP RTE, capable de piloter plusieurs instruments pour plusieurs opérateurs. Cette innovation a joué un rôle clé dans le succès de HP sur deux marchés alors en pleine expansion des analyses environnementales et du dépistage de drogues, deux marchés ***régis par la réglementation américaine, qui imposait le recours à la CG-SM.***

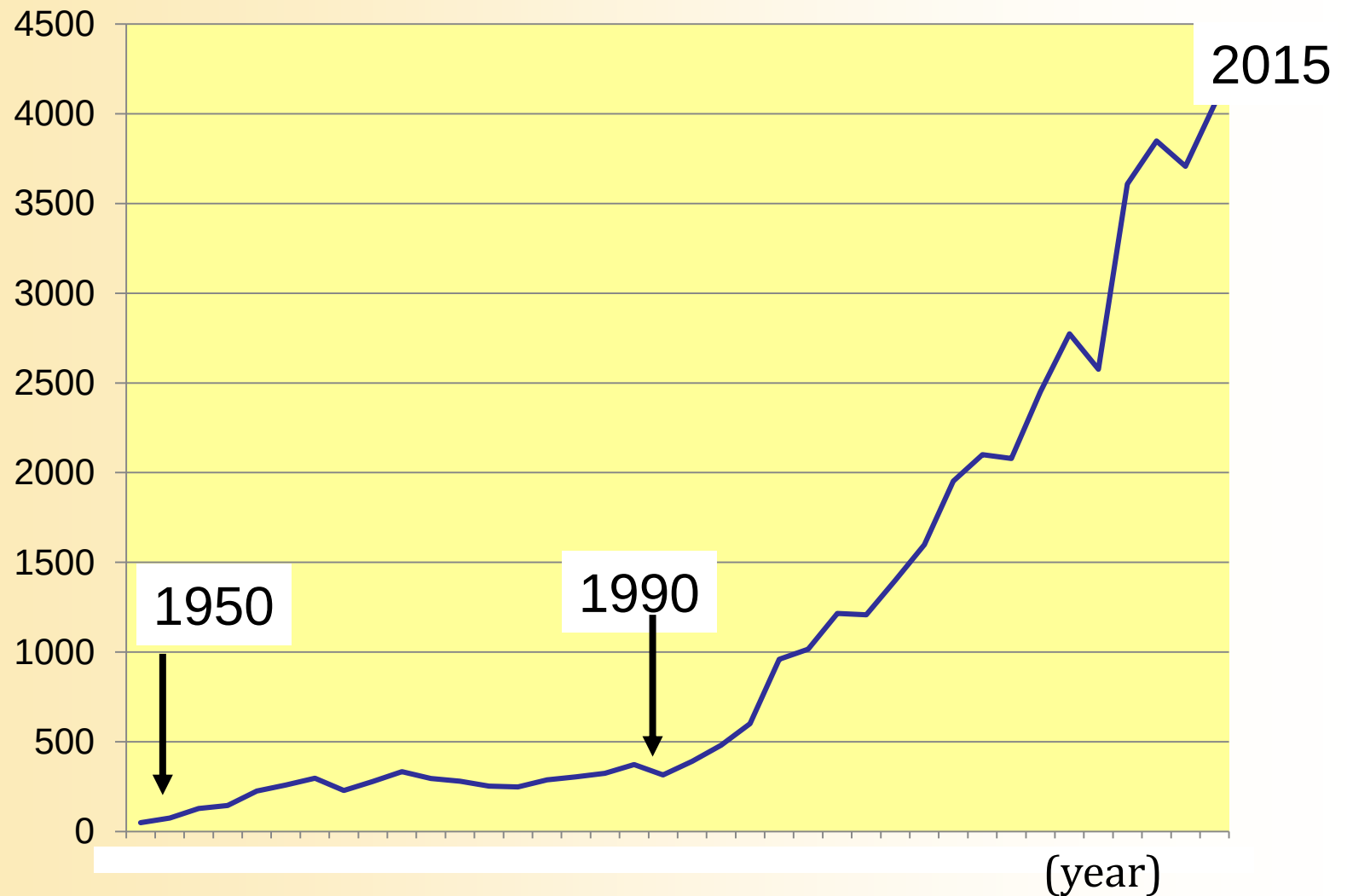
En 1988, HP a lancé son système GC-MS de paillasse de nouvelle génération : le **5971A MSD**. Optimisé pour fonctionner avec le chromatographe en phase gazeuse 5890, il offrait des performances révolutionnaires en spectrométrie de masse grâce à la toute première conception de quadripôle monolithique en quartz. Les instruments précédents étaient dotés d'analyseurs quadripolaires constitués de barres distinctes, alors que cette nouvelle conception reposait sur un quadripôle monolithique insensible au désalignement. Ce système a été développé pour améliorer les rendements de fabrication et garantir une qualité élevée, deux impératifs pour soutenir les volumes de production importants atteints par HP à l'époque.

Et le gagnant fut...

HP 5971A Mass Selective Detector (1990-91)



Nombre d'articles sur « huiles essentielles » publiés par année





Agilent 5975 series
10,000 unités vendues à la fin de 2008

The Power of Mass Spectrometry in a Routine GC Detector... Finnigan MAT Makes It a Reality



(1984)

à vendre \$150 sur ebay

Interference-Free Quantitation

With characteristic masses you can quantitate the analyte of interest even when complete separation is not achieved on the column. Errors due to coeluting peaks are eliminated. Sample throughput is increased as cleanup requirements are reduced. And, you can use isotopically-labelled analogs as quantitative standards, an option not available with conventional GC detectors.

Varian 1200 Triple Quad GC/MS anciennement Kodiak 1200 (Bear Instruments)



Awarded a Silver Medal at Pittcon'1999

GC-IRMS

1978

1984

1988

VG Isochrom



Es-MDGC-C-IRMS/qMS

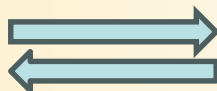


MS

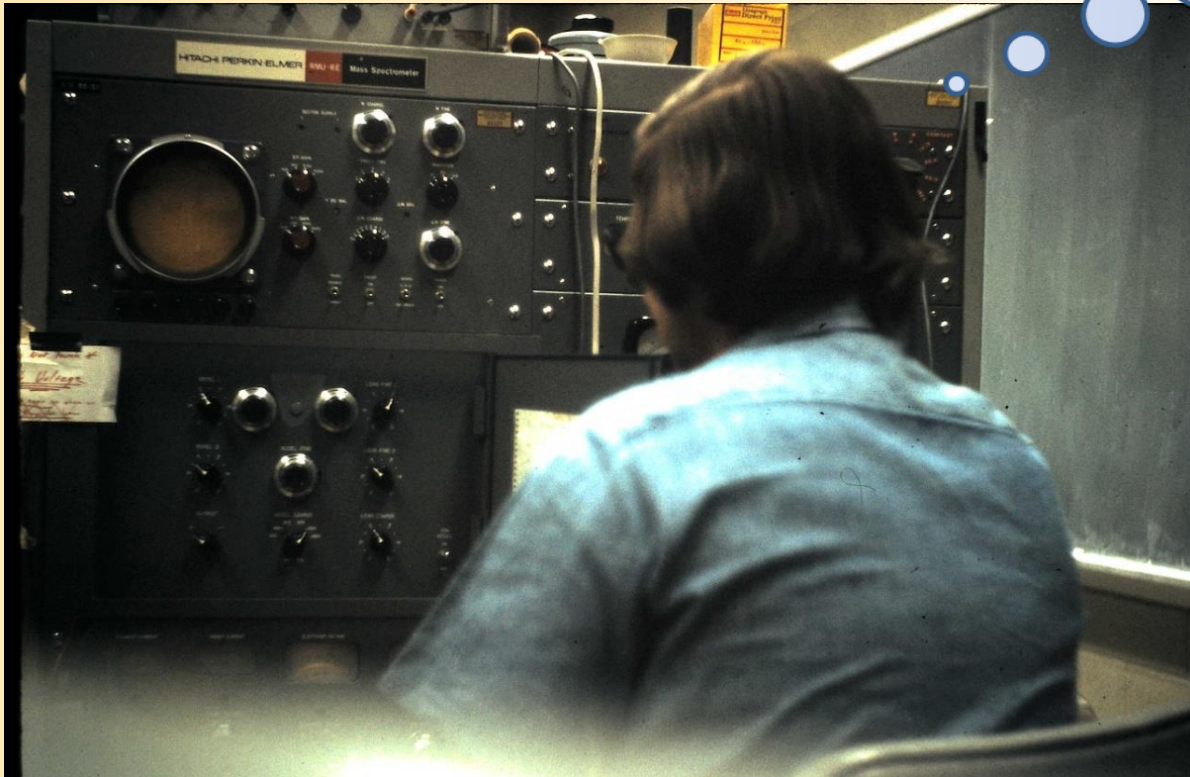
**1 D GC
(Shimadzu)**

2 D GC

**IRMS
(visION)**



Un jour,
ce sera le
“bon vieux
temps”



« Hitachi-Perkin Elmer RMU Mass Spectrometer »

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