Exerts of the History of Mass Spectrometry
The Dutch MS Family Album

Ir. M.C. ten Noever de Brauw

On the occasion of the 35th anniversary of the Dutch Society for Mass Spectrometry (NVMS)

Ladies and gentleman,

It is of course a great honor to be the last speaker of our jubilee conference. When the organizing committee asked me last November if I would be willing to present a paper on the history of our NVMS society I thought why not. I thought that this occasion would be a good moment to look back on the historical development of mass spectrometry on our planet and in Holland. After a while I started to regret my commitment because I underestimated the amount of work involved in the preparation of such a paper. In retrospect, it has been quite nice to see the accomplishments of the last 100 years and the big technological revolution of the last 50 years.

It is very difficult and time consuming to collect all the necessary information and documentation for such a history review, and I am far from ready. I am very much aware that the information is not complete and I apologize for the fact that not all contributors to Dutch mass spectrometry are mentioned in this paper. I had to restrict myself to the information I was able to collect with great help from the colleagues in the NVMS for which I am very grateful.

In the end I was confronted with a luxury problem. I obtained too many slides and had to discard many of them in order to stay within the time allotted to this lecture. My story will not be a scientific one as you have heard enough of science during the last few days. Before I start browsing through our Dutch MS family album I want to show some sheets of the real pioneers in mass spectrometry.

The pioneers of mass spectrometry.

It all started with JJ Thompson. It is perhaps difficult to realize that, at this time, for a generation grown up with modern Electronics, computers and Lasers that scientists in the days of Thompson and Aston still had problems to understand that there were really particles smaller then atoms.

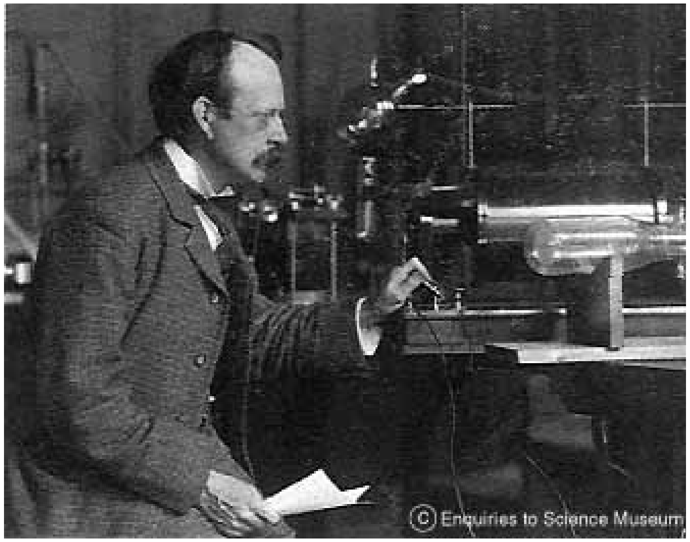
Thomson was able to measure with his cathode-ray tube the ratio of the electric charge carried by cathode rays to their mass. Prove the existence of an electron

A quote from JJ Thomson :

“At first there were very few who believed in the existence of these bodies smaller than atoms. I was even told long afterwards by a distinguished physicist who had been present at my [1897] lecture at the Royal institution that he thought I had been pulling their legs”

J.J. Thomson (1936), Recollections and reflections. G. Bell and Sons. London p 341.

J.J. Thomson (1856-1940)



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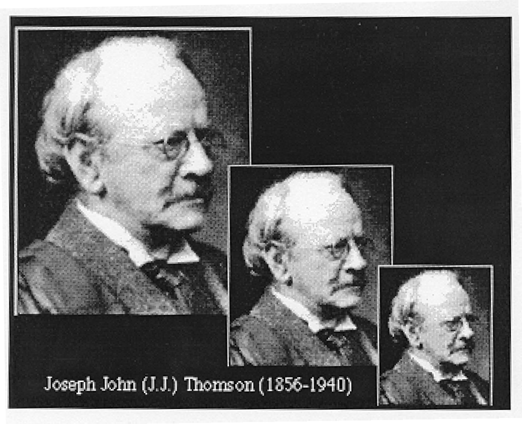
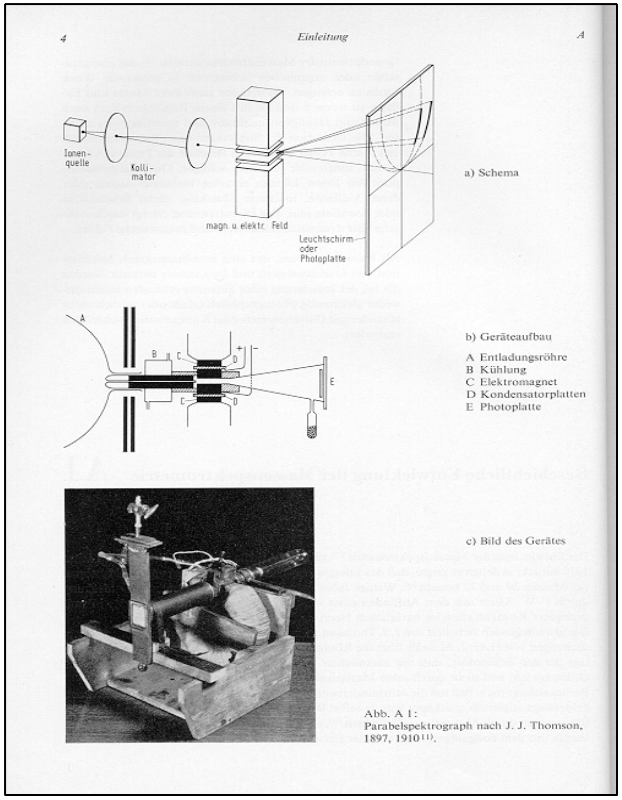


F.W. Aston (1877-1945)



4 *Einleitung* A

a) Schema

b) Geräteaufbau

A Entladungsröhre
B Kühlung
C Elektromagnet
D Kondensatorplatten
E Photoplatte

c) Bild des Gerätes

Abb. A 1:
Parabelspektrograph nach J. J. Thomson, 1897, 1910[11].

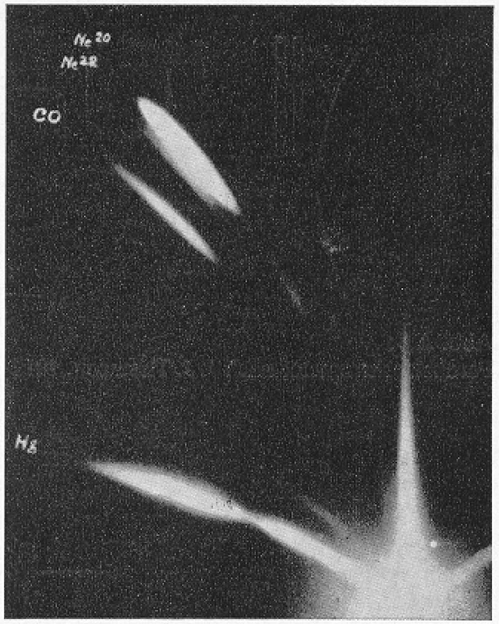
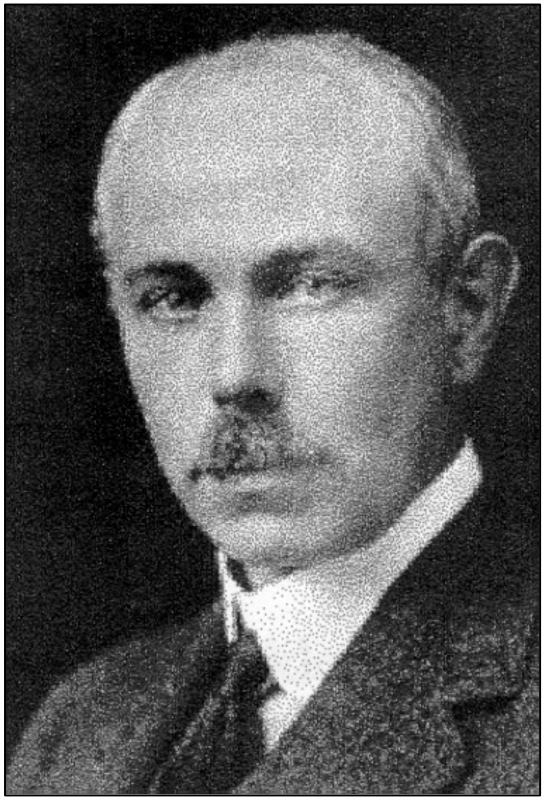
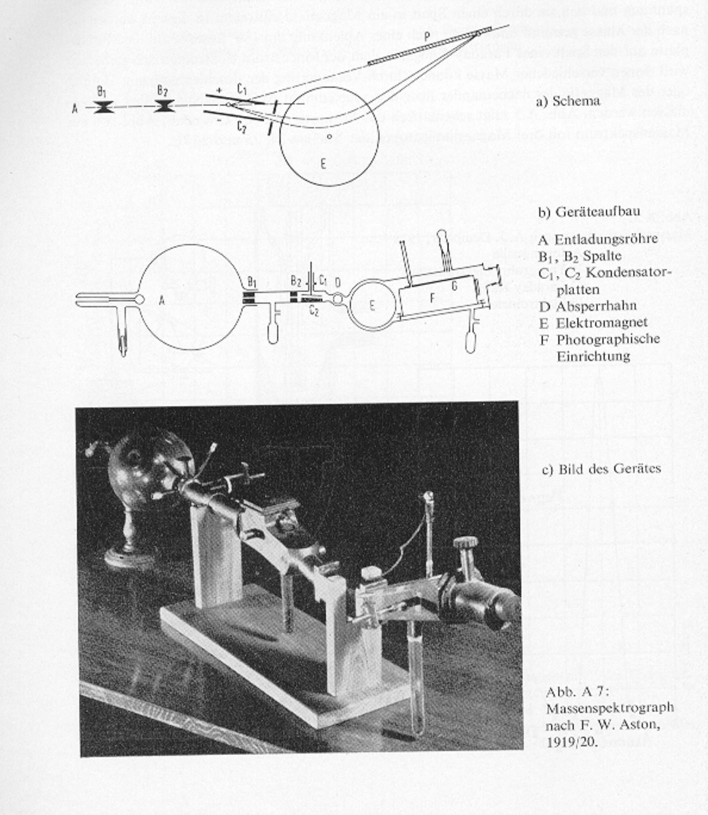


Abb. A 2:
Neon-Isotope der Massen 20 und 22, Aufnahme mit dem Parabelspektrograph nach J. J. Thomson, 1910.



The figures above show the schematic of the first Mass Spectrometer, that was able to measure the mass to charge ratio of Neon gas ions and their isotopes. The ion beam was deflected by a parallel electric and magnetic field and detected on a fluorescent screen showing a parabolic image of the Neon ion 20 and 22 isotope ion.

Two other famous pioneers are Aston and Dempster. Here a picture of F.W. Aston taken from the Internet



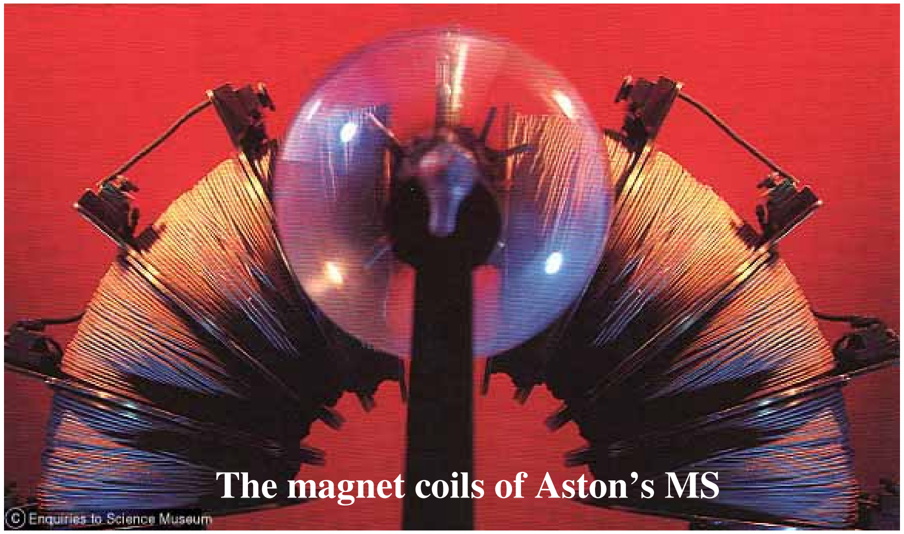
a) Schema

b) Geräteaufbau

A Entladungsröhre
B_1, B_2 Spalte
C_1, C_2 Kondensatorplatten
D Absperrhahn
E Elektromagnet
F Photographische Einrichtung

c) Bild des Gerätes

Abb. A 7: Massenspektrograph nach F. W. Aston, 1919/20.



The magnet coils of Aston’s MS

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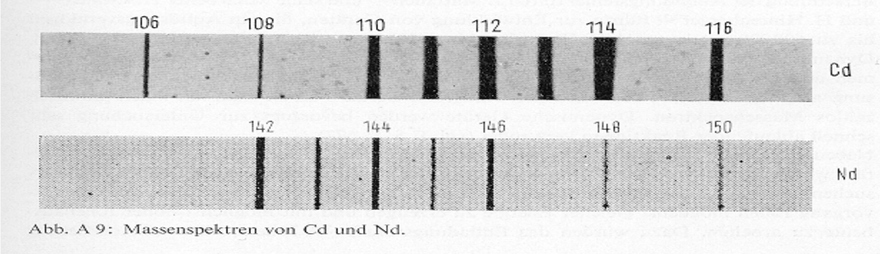


Abb. A 9: Massenspektren von Cd und Nd.

Aston was working in Thomson’s laboratory improving and constructing a more powerful Mass Spectrometer. The principle of this instrument is shown here. He applied separate electric and magnetic fields to focus the ion beam on a photographic plate.

This instrument built in 1919/20 improved mass resolution and mass range and can be regarded as the predecessor of the later Mattauch Herzog geometry mass spectrometer with photo plate detection. Here we see the ion traces of Cadmium Cd and Neodynium Nd with their isotopes. As we can see from these pictures Aston also designed the first desk top mass Spectrometers.

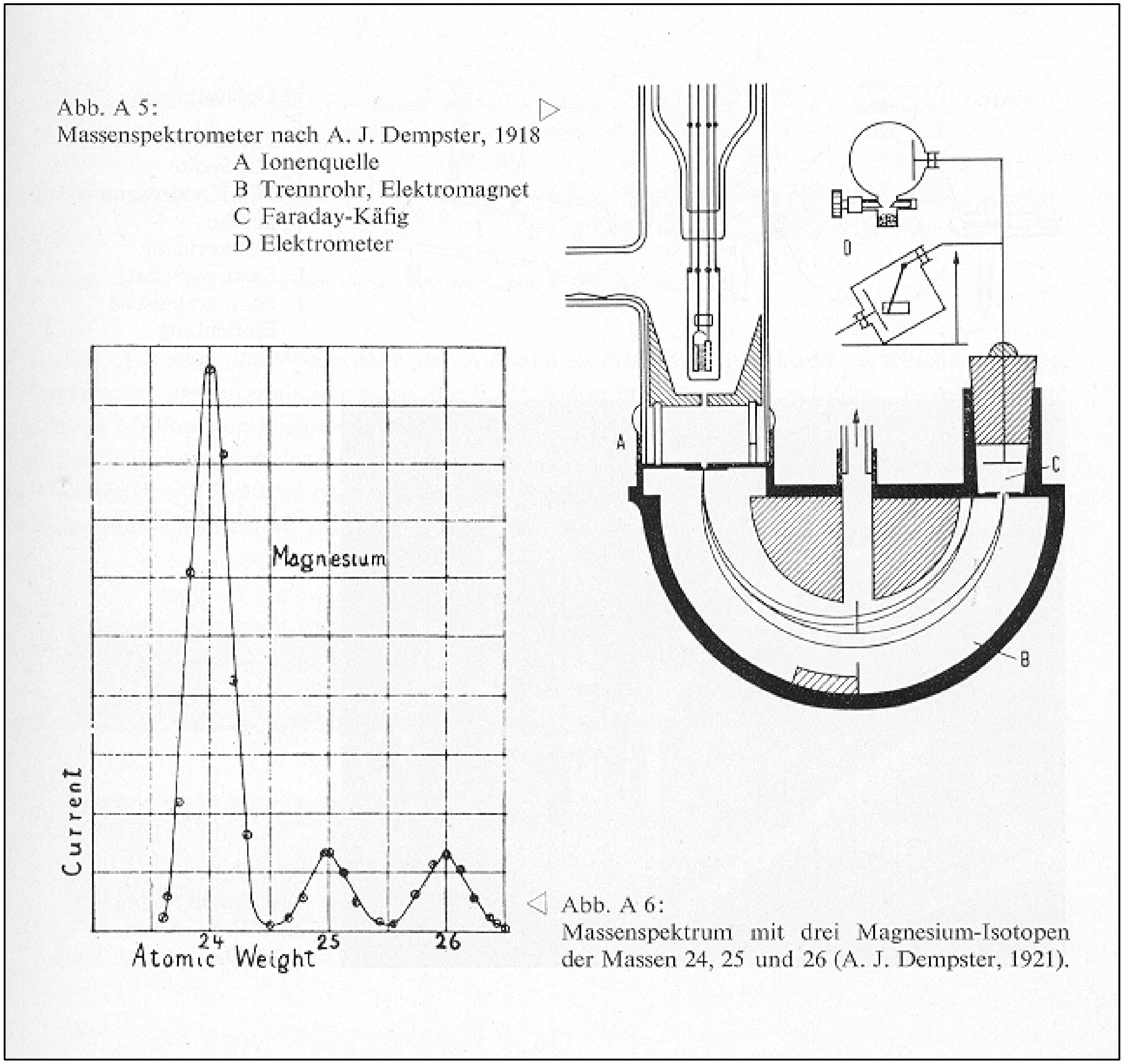
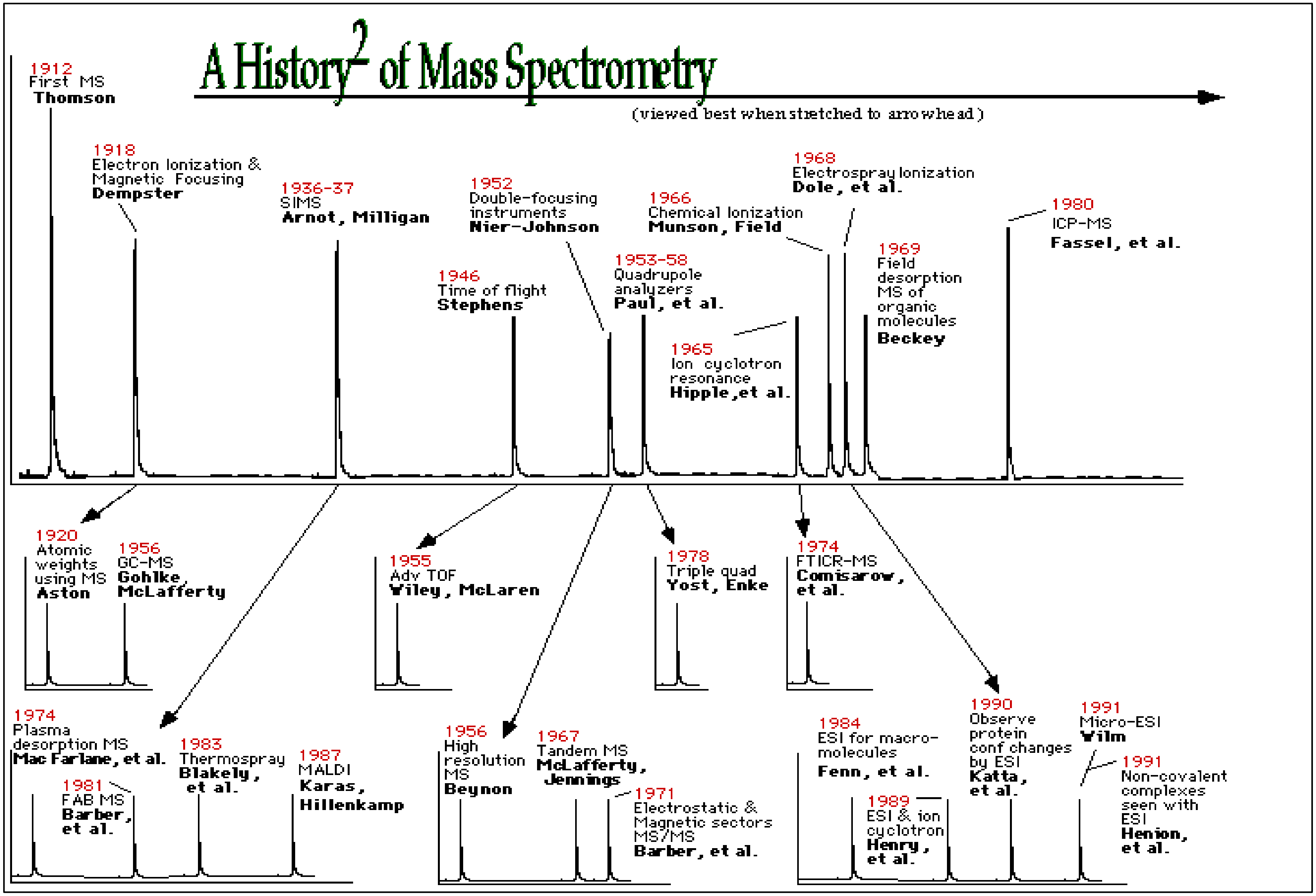


Abb. A 5:
Massenspektrometer nach A. J. Dempster, 1918
A Ionenquelle
B Trennrohr, Elektromagnet
C Faraday-Käfig
D Elektrometer

Abb. A 6:
Massenspektrum mit drei Magnesium-Isotopen der Massen 24, 25 und 26 (A. J. Dempster, 1921).

A.J. Demster (1921) built another type of instrument Here a schematic of Demster's geometry using a 180 degree magnetic field, separating the ion beams of different mass to charge ratio, and detecting them on a Faraday collector. Using an electron impact source the spectrum of Magnesium was recorded.

This geometry can be regarded as predecessor of the Nier Jonsen Geometry



This figure was also taken from the Internet and is a nice way to portrait the evolution of mass spectrometry (unknown source).

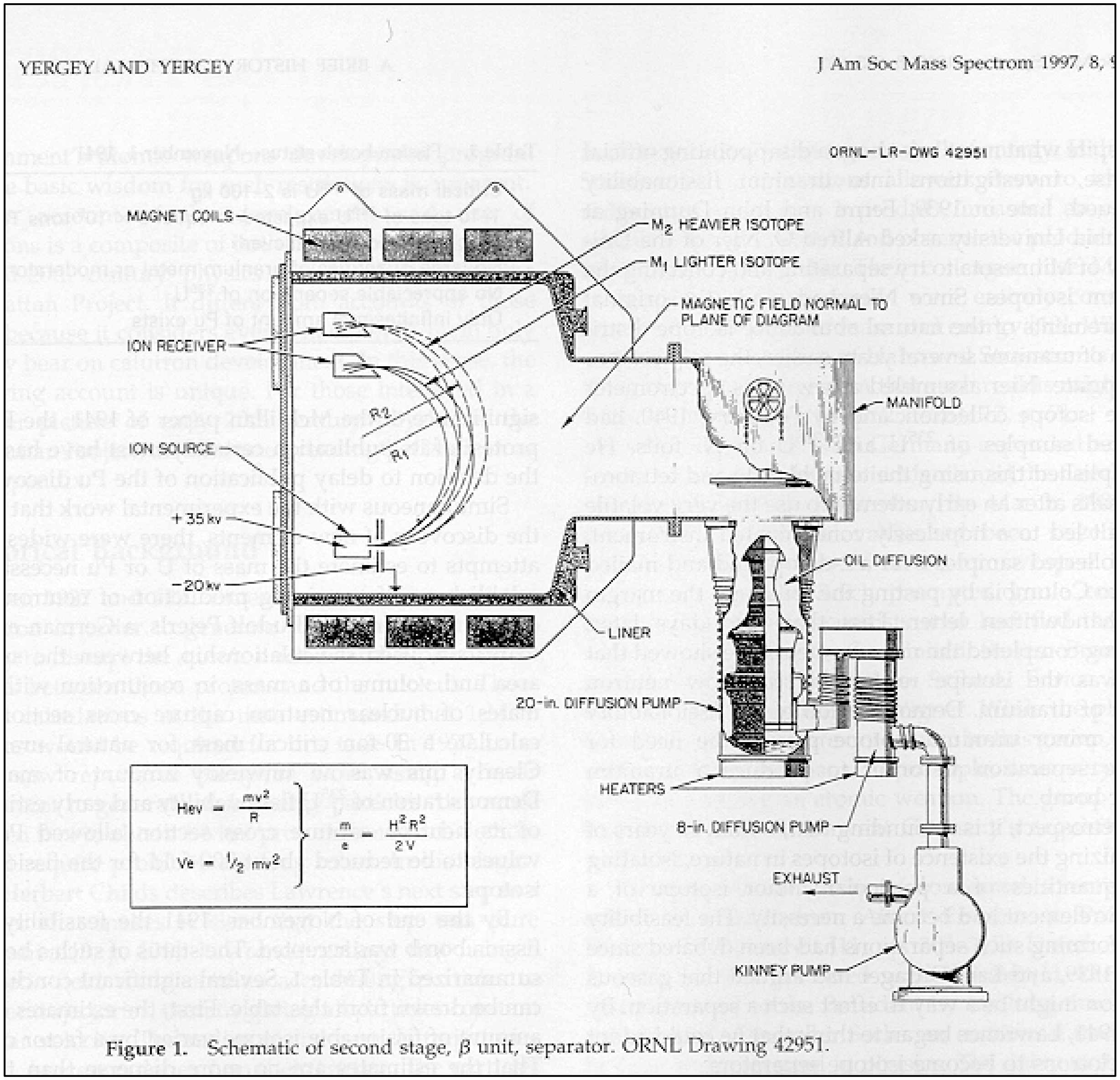
The Pioneers (cont'd)

The pioneers important to the applications of mass spectrometry in "Analytical organic Chemistry" are well known. Men like John Beynon, Fred MacLafferty, Klaus Biemann, Graham Cooks and many many other great scientists have been (and are) involved in a long list of developments in mass spectrometry. They developed new analyzers (Quads, Ion Trap, ICR, MS/MS, TOF etc.), new ionization methods (EI, FD, CI, DCI, FAB, LD, MALDI, TSP, API, ESI, ICP etc.) and the so called " hyphenated techniques" combining mass spectrometry with chromatographic separation techniques (GC/MS, LC/MS, CZE etc.).

The Manhattan project

Looking through the literature I came across an application which is not very well known, at least to the younger generation of mass spectrometrists. I thought it would be nice to show it here even if it is a little bit out of scope for this presentation. It does present a major part of the history of mass spectrometry and has a direct link to the history of Dutch MS.

In the beginning mass spectrometry was the domain of the physicists who used it mainly for atomic weight measurements, isotope ratio measurements, nuclear physics and also in some kind of preparative mass spectrometry (Isotope separators). Mass spectrometry was a tool with which uranium isotopes U235/U238 could be separated to produce the atomic bomb. I want to show you some elements of this bizarre application. The construction of the Calutrons for the Manhattan project (the development of the A-bomb) is nicely described in the article "Preparative scale Mass Spectrometry" by A.L & A.K. Yergey in the Journal of the American Society for Mass Spectrometry (1997) vol. 8 p943-953. I really recommend you to reed this article. .


YERGEY AND YERGEY

J Am Soc Mass Spectrom 1997, 8, 9

Figure 1. Schematic of second stage, β unit, separator. ORNL Drawing 42951.

This picture shows the schematic and principle of these huge magnetic isotope separation machines built in Oakridge National Laboratory's.

Ernst Lawrence, inventor of the Cyclotron had the idea of modifying a cyclotron into an isotope separator. Here one sees the two ion beams of U235 and U238, the ion sources and the collectors. There were two types of these instruments The Alpha and Beta separators but I will not go into details of the two.

The 96 so called tanks (analyzer tubes) are assembled in a racetrack configuration shown in the picture below. 864 of these units have been built, so the project was gigantic.

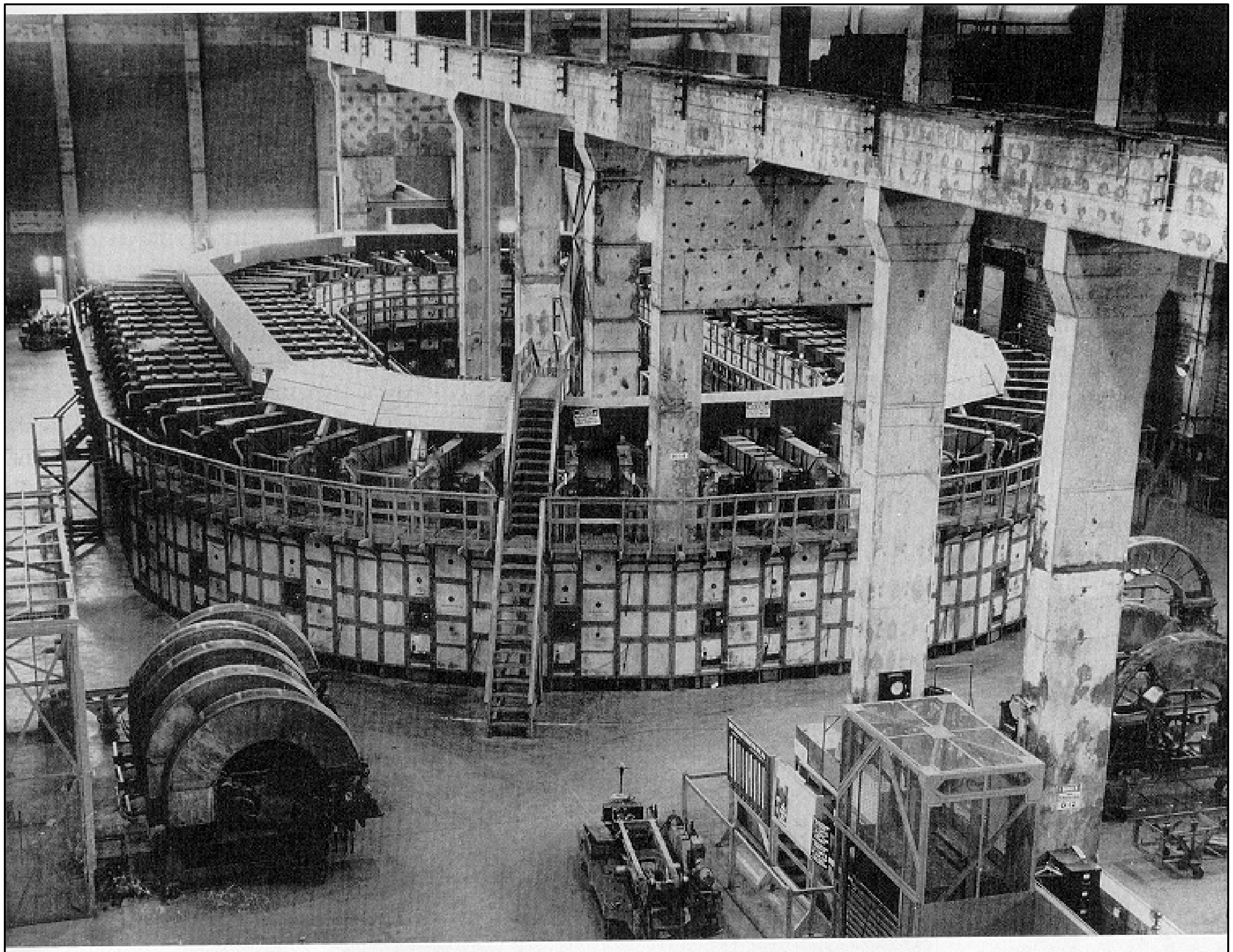


Figure 2. Photograph showing α unit "race track" assembly of calutrons. Photo source: ORD-PRO-2031.

The racetrack dimensions are immense

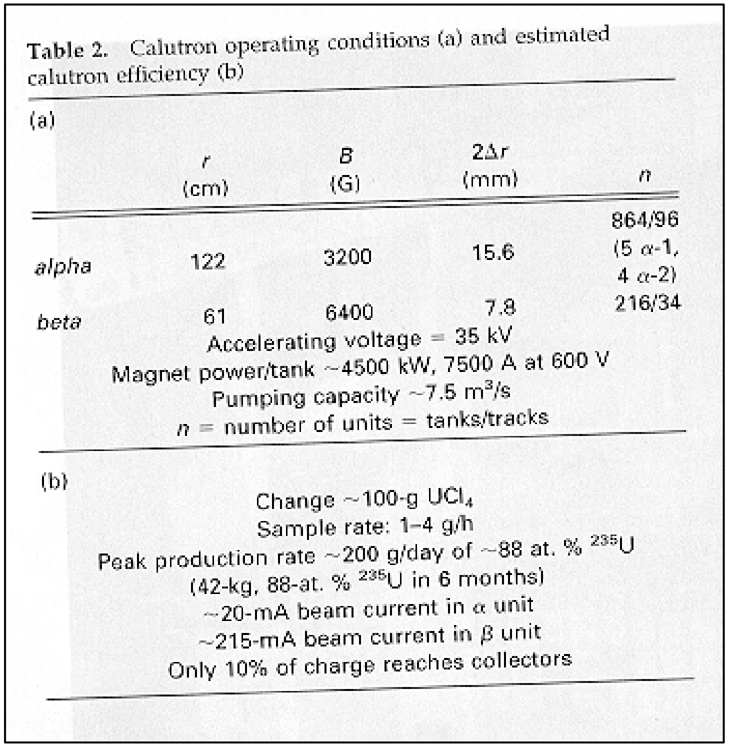


Table 2. Calutron operating conditions (a) and estimated calutron efficiency (b)

(a)

	r (cm)	B (G)	$2\Delta r$ (mm)	n
alpha	122	3200	15.6	864/96 (5 α-1, 4 α-2)
beta	61	6400	7.8	216/34

Accelerating voltage = 35 kV
Magnet power/tank ~4500 kW, 7500 A at 600 V
Pumping capacity ~7.5 m^3/s
n = number of units = tanks/tracks

(b)

Change ~100-g UCl_4
Sample rate: 1–4 g/h
Peak production rate ~200 g/day of ~88 at. % ^{235}U
(42-kg, 88-at. % ^{235}U in 6 months)
~20-mA beam current in α unit
~215-mA beam current in β unit
Only 10% of charge reaches collectors

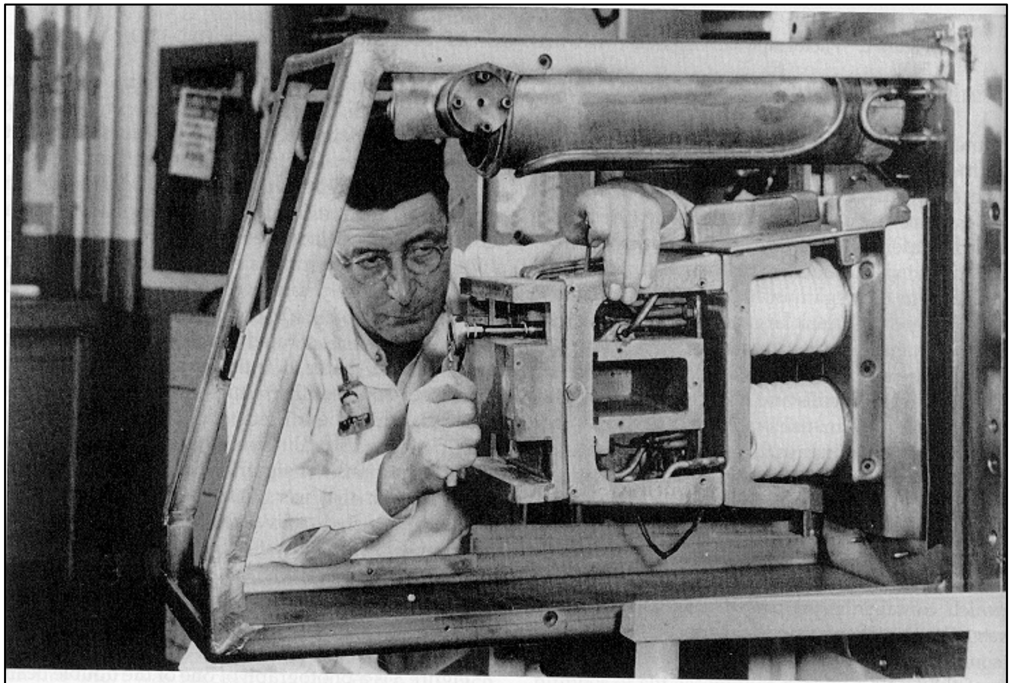


Figure 3. α one calutron source showing charge box heater and two sets of filament heater ceramic standoffs. ORNL Photo 24574.

The figures here show one of the many ion sources operating at 35 kV accelerating voltage. The sample was UCl_4 a salt that was heated cq. evaporated in the source at a rate of 1-4 gram/hr. The total loading of one ion source was 100 grams of UCL_4. 5100 Kg of natural Uranium was used to produce 42 kg 80% enriched U235 in 18 months. The Data Sheet on the right lists some of the operating conditions of the Calutron. Ion beams of 20 mA in the alpha system and 215 mA in beta system were collected in a collector assembly on graphite plates. The U235 was recovered in a special procedure (burning and washing) from these collector plates

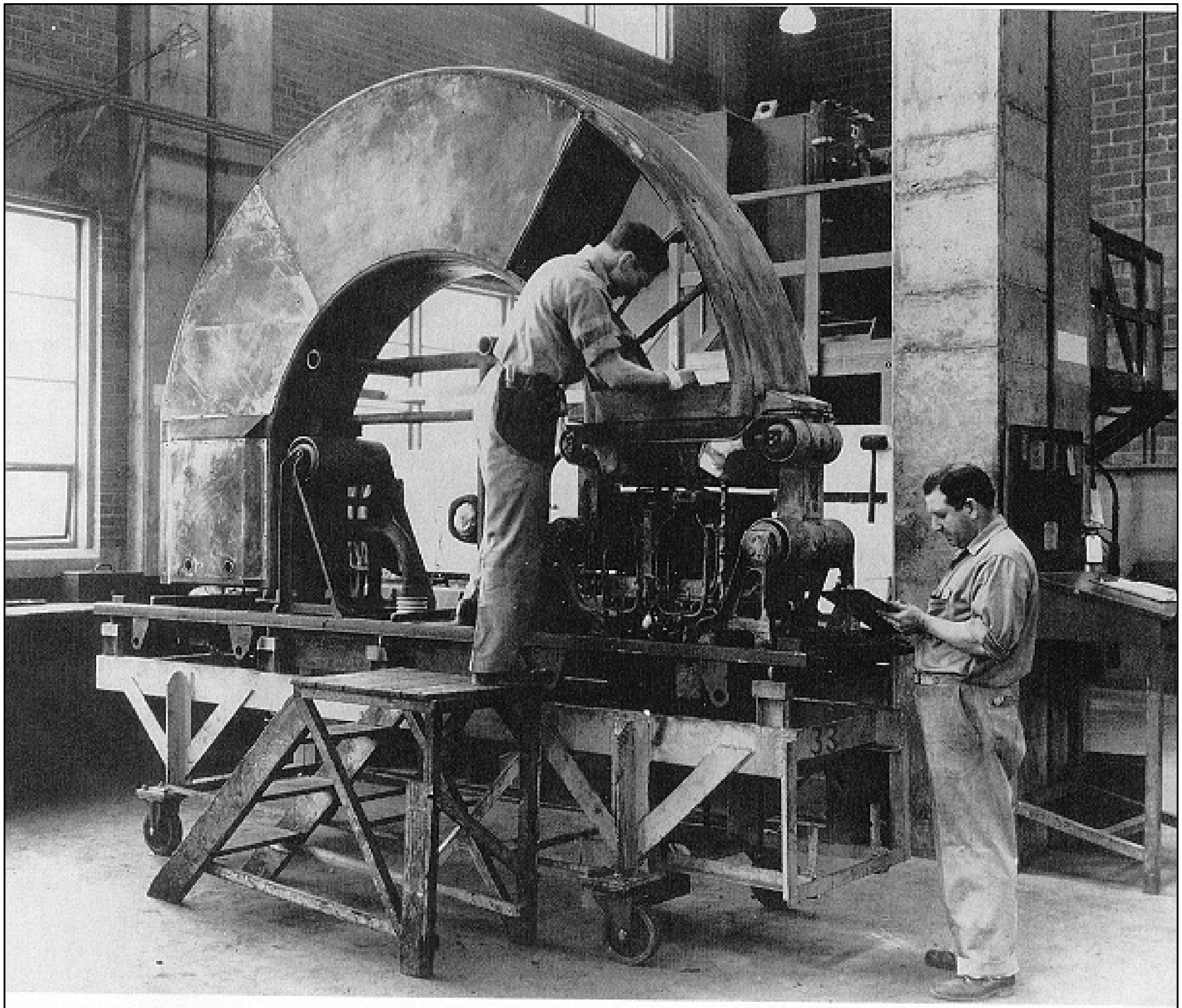


Figure 5. Tank liner during cleaning process. Photo source: Y-12 154.

The cleaning of the tank analyzer tube was a rough job. The Uranium salts needed to be scraped out and health hazards were not given too much attention at this time!!!!!.

The isotope separation project was a gigantic project involving thousands of scientists, very big power plants, huge material costs etc. It was one of the most secret projects and only a few persons knew what was really going on!!!!!

Some other anecdotes: To produce the magnet coils, huge amounts of copper wire were needed. However, in war time this was not available so the Oak Ridge physicists wanted to use silver instead of copper! Silver was not easy to come by either so the idea came up to contact the US Treasury department and approach them with the question, if it would be possible to borrow some silver for this important war time project.

Figure 7. Calutron silver coils before return to U.S. Treasury. Photo source: Y-12 126949.

The Treasury official asked how much they needed? The answer was 15000 tons. Although the official answered irritated *“Sir, we measure our Silver in Troy ounces and not in tons”* they got permission to loan the 300 million Troy ounces needed for their project. It was almost the whole silver stock of the US Treasury. The figure here show the coils prior to being melted down for return to the Treasury department. Note the huge dimensions. These were not table top mass spectrometers.

Figure 6. Y-12 shift change on August 11, 1945. Photo source: PRO 936.

For the operation of the Calutrons high school educated women were preferred over physicists because they could be relied to keep their eyes on the beam currents indicators and make only minimal adjustments to the operating voltages. Physicists, on the other hand had the bad reputation, always trying to improve the performance, fooling around with all the available buttons and parameters. This picture shows us a shift change of these brave women.

The Calutrons were used after the war for the production of stable isotopes for medical cancer research. This was seen as a beautiful transformation of this war time project to a peaceful application.

From Ron Heeren I received a picture showing the opening of the laboratory for Mass Spectography (the later FOM Inst.) taken on 6 Nov 1953 on the Hoogte Kadijk in Amsterdam where we see Dr Jaap Kistemaker, handing over 10 milligram. of enriched Uranium 235 to Prof. J. M. W. Milatz observed by Prof. J. Clay. In the background we can see a magnetic isotope separator in a much smaller configuration as we have just seen. Jaap Kistemaker was not only involved in the development of isotope separation with magnetic sector instruments, but also in the development of the ultracentrifuge (a new method to enrich Uranium 235) now used in a well-known plant; UCN in Almelo. He also became the first director of the FOM institute.

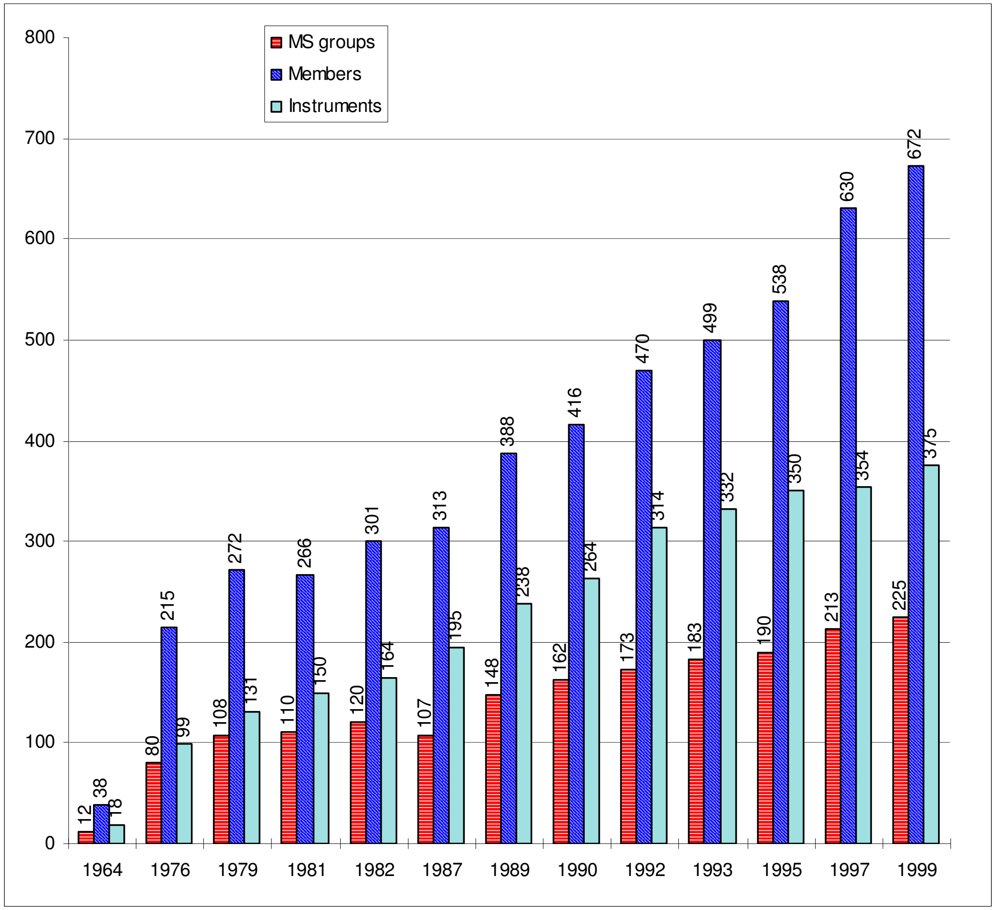
I will now continue with the history of mass spectrometry as it took place in Holland and Belgium (in an early stage we already had scientists from Belgium as members of our society)

From the beginning The Dutch Soc. for Mass spectrometry had the character of some kind of a nice pioneer family, which was founded on the 26th Feb. 1964 by Piet van der Haak and Henk Hofman at the laboratory for organic chemistry of the university of Amsterdam. The MSDG was born out of the Infrared discussion group under auspicious of the Royal Dutch Chemical Society KNCV.

We started with 38 members (out of 12 working groups) from the universities of Amsterdam ,Utrecht, Leiden, TU Eindhoven and semi-government R&D labs like FOM and TNO. Industrial R&D Labs like DSM, Shell, Phillips and Polak Frutel works as well as the UCN (Ultra centrifuge Uranium enrichment factory) also participated. At that time approximately 18 Instruments were operational in different disciplines (Physics, Geology and Chemistry). These Mass spectrometers were still huge and expensive instruments.

The main fields of applications were: Structure elucidation of organic chemical compounds, Process control, residual gas analysis, Isotope ratio measurements, and identification of unknown organic compounds in chemical matrices (Strawberry aroma or unknown compounds in the environment etc.) and not to be overlooked fundamental research. Ion chemistry was researched in an effort to understand the fragmentation patterns of chemical compounds in the ion source of the Mass Spectrometer.

Growth of the Dutch Society for MS (1954-1999)



In this presentation I will show you the development of the instrumentation used in the last 40 years, including the aging of some of their operators (some of them are even still operational). This MS story is illustrated with many pictures collected from our old honorable members! The goal of our society was and is; bringing the Dutch MS people together to exchange all kinds of information about the problems they encounter working in different fields with different instrumentation. For that purpose we held a symposium twice a year, elaborating on topics of interest to our community. These included ion chemistry, GC and LC/MS, hyphenated methods, ionization methods, Computer applications (Chemometry/Library search.) Quantitative MS, news from the vendors and many other interesting topics.

Our MS society flourished and has now, Jan 1999, about 672 Members in 225 work groups with 375 instruments. Fred MacLafferty calculated once that the Netherlands had the highest density of Mass Spectrometers per square km. In 1971 the memberships list was only 3 sheets of A4 long. The next sheet shows the honorable chairmen serving the NVMS until now. As we can see, they are all of the male sex. The successor of Andries might be female in the future.

Chairmen of the MSDG / NVMS 1964-1999


Piet van der Haak


Peter Korver


Bert Schram


Nico Nibbering


Henk van't Klooster


Johannes de Ridder


Rowald Neeter

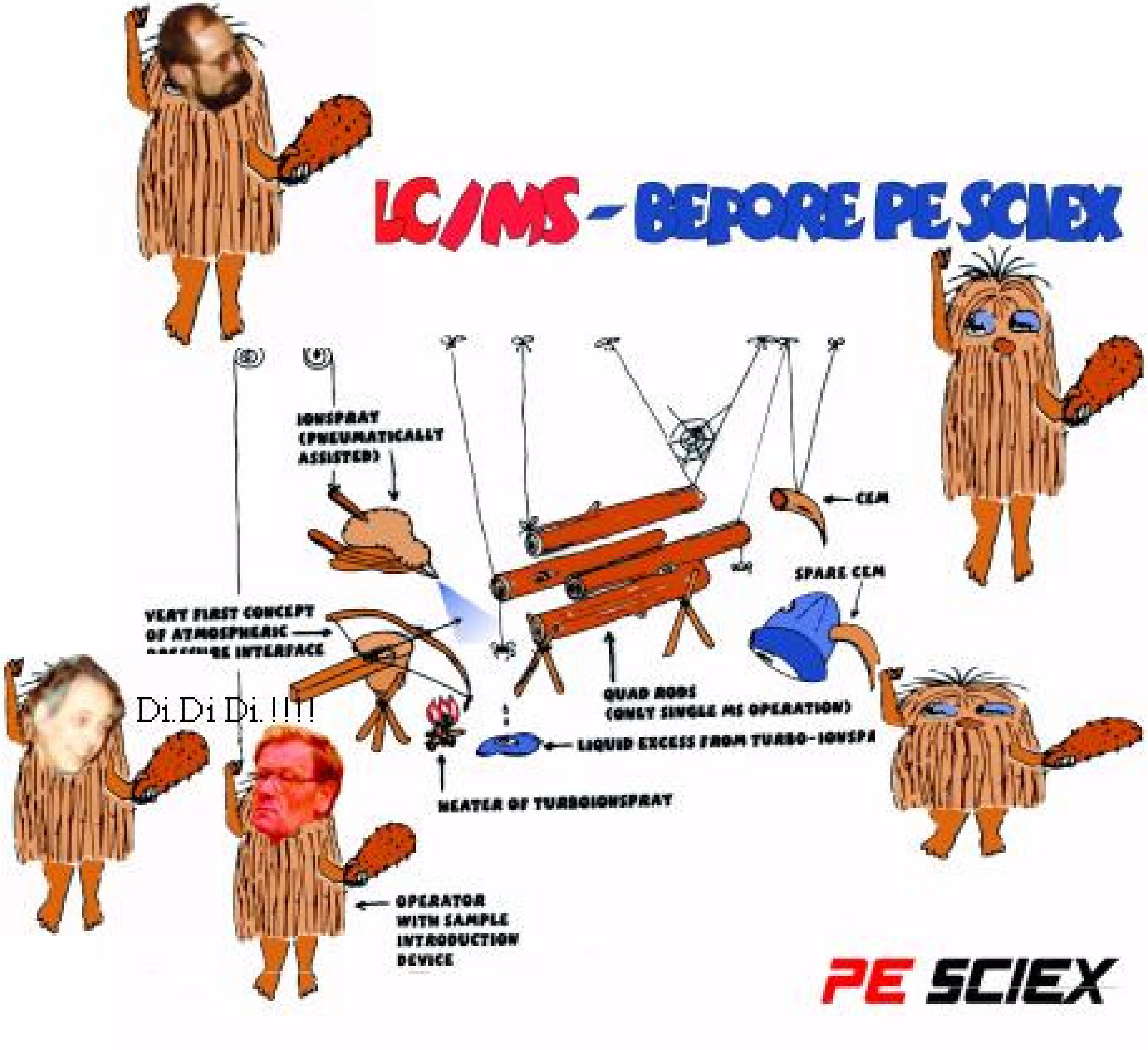

Piet Leclercq


Mike ten Noever de Brauw


Andries Bruins

1964 MSDG	P.van der Haak	University of Amsterdam
1971	P. Korver	Duphar
1972	B. L. Schram	Unilever
1974	N. M. M. Nibbering	University of Amsterdam
1976	H. van't Klooster	University of Utrecht
1977	J. de Ridder	Organon
1979	R. Neeter	NIZO
1981	P. Leclercq	TU Eindhoven
1983	M. C. t. N. de Brauw	TNO Nutrition Zeist
1992 NVMS.	M. C. t. N. de Brauw	TNO Nutrition Zeist
1997	A. P. Bruins	State university of Groningen

Prehistoric mass spectrometry in the Netherlands

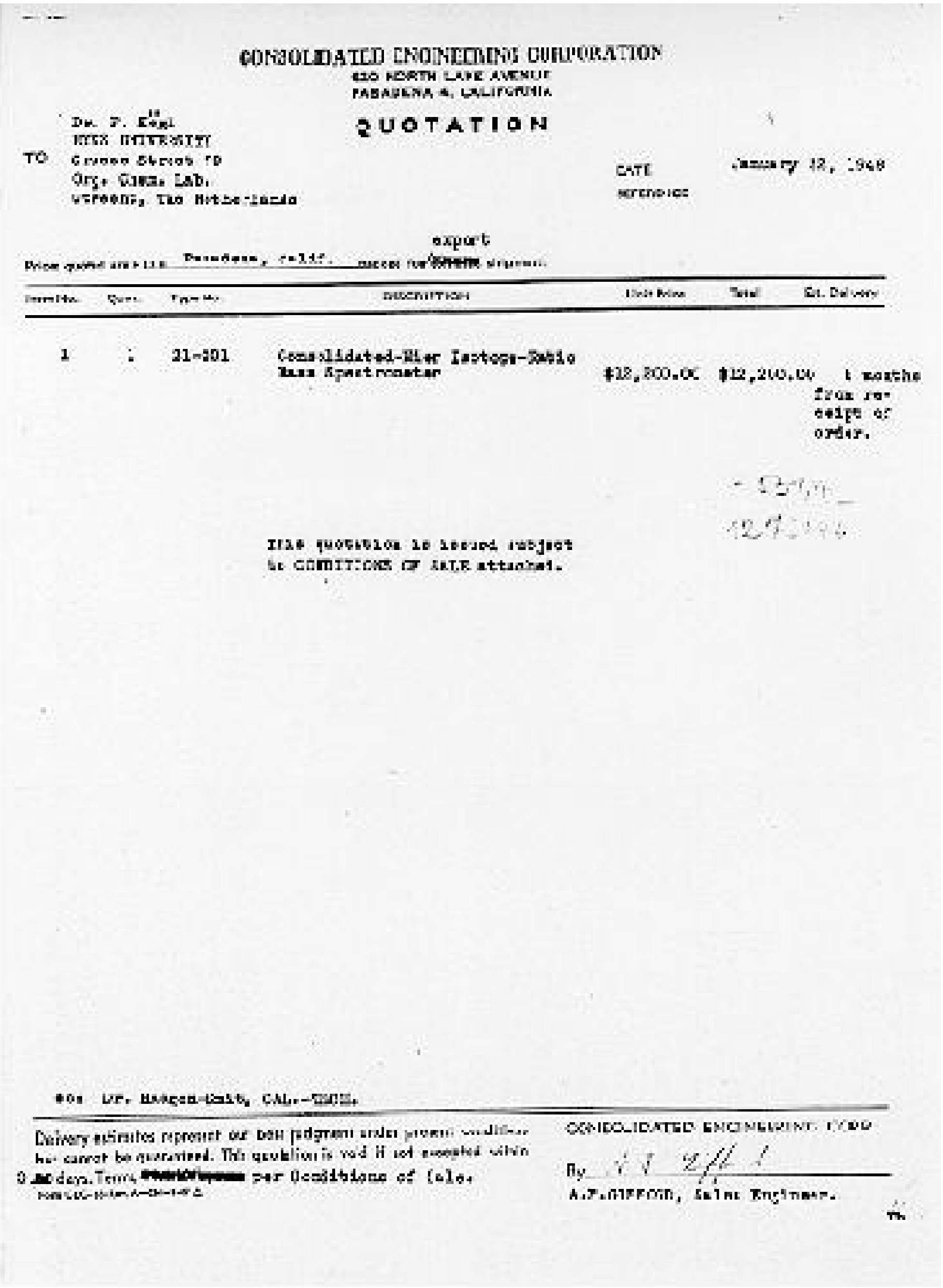


Information about Prehistoric Mass Spectrometry in the Netherlands as obtained by regression therapy

A long time ago, there were certain Tribes in our country trying to perform Mass Spectrometry in their own peculiar way!!

In old incarnations some of us were already in contact with the field and as we know from an English football coach one always has to bear the consequences of ones deeds in previous lives. The English football coach was fired for making similar remarks, so I will drop this subject and evaluate only the last 50 years of mass spectrometry in the Netherlands.

The first mass spectrometers in Holland were home made and if I am well informed there was already an instrument around 1935 at Prof. Zeeman’s lab at the Univ. of Amsterdam.



CONSOLIDATED ENGINEERING CORPORATION
620 NORTH LAKE AVENUE
PASADENA 4, CALIFORNIA

QUOTATION

TO
Dr. F. Kögl
RIJKS UNIVERSITEIT
Croese Straat 79
Org. Chem. Lab.
Utrecht, The Netherlands

DATE January 12, 1949
REFERENCE

Prices quoted are F.O.B. Pasadena, Calif. packed for export [redacted] shipment.

Item No.	Quan.	Type No.	DESCRIPTION	Unit Price	Total	Est. Delivery
1	1	21-201	Consolidated-Nier Isotope-Ratio Mass Spectrometer	$12,200.00	$12,200.00	6 months from receipt of order.

- 980.–
11220.–

This quotation is issued subject to CONDITIONS OF SALE attached.

cc: Dr. Haagen-Smit, CAL.-TECH.

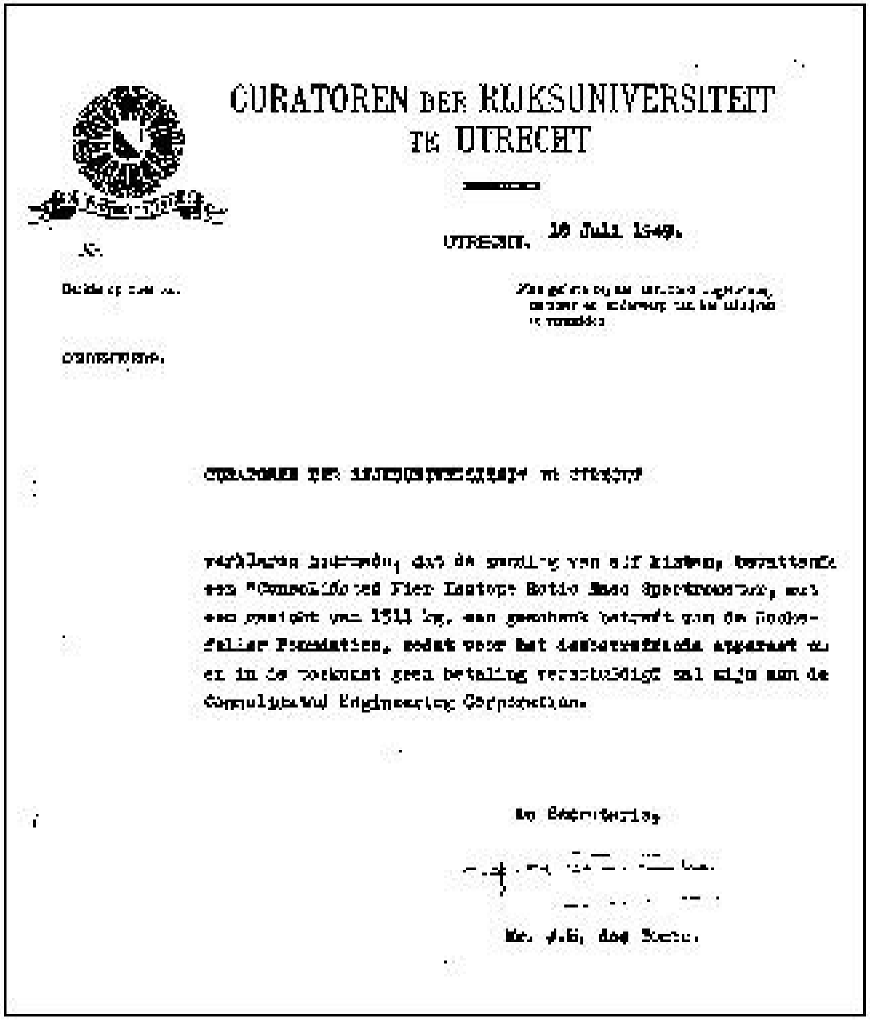
Delivery estimates represent our best judgment under present conditions but cannot be guaranteed. This quotation is void if not accepted within 30 days. Terms [redacted] per Conditions of Sale.

CONSOLIDATED ENGINEERING CORP.
By
A.F. GIFFORD, Sales Engineer.

The Dutch MS family album.

From Kees Versluis (State University of Utrecht) I collected some interesting historic material about the purchase of one of the first commercial Mass Spectrometers in the Netherlands, a CEC 21 - 201. Here, the quotation of this instrument dated 18 July 1949 and priced $11220,= is shown.

This was a lot of money at the time, but the Univ. of Utrecht was very lucky having a letter somewhere, stating that it was a present from the Rockefeller foundation.



CURATOREN DER RIJKSUNIVERSITEIT
TE UTRECHT

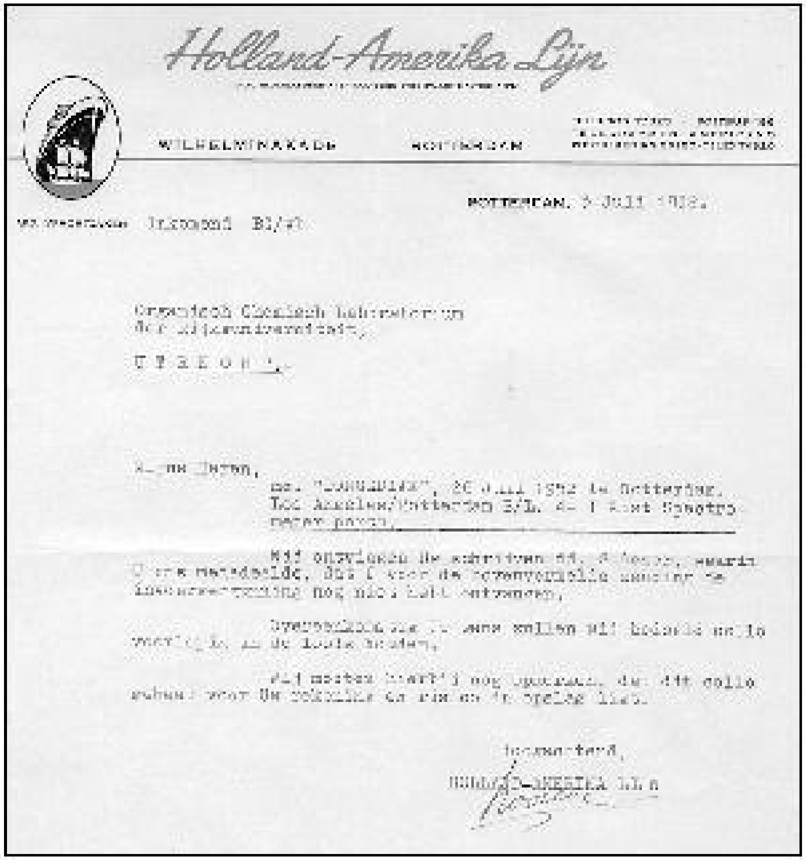
UTRECHT, 18 Juli 1949.

CURATOREN DER RIJKSUNIVERSITEIT TE UTRECHT

verklaren hierbij, dat de zending van elf kisten, bevattende een "Consolidated Vier Isotope Ratio Mass Spectrometer", met een gewicht van 1511 kg, een geschenk betreft van de Rockefeller Foundation, zodat voor het desbetreffende apparaat nu en in de toekomst geen betaling verschuldigd zal zijn aan de Consolidated Engineering Corporation.

De Secretaris,

Mr. [illegible] den Boer.



Holland-Amerika Lijn

WILHELMINAKADE ROTTERDAM

ROTTERDAM, [illegible] Juli 1952.

Inkomend B1/[illegible]

Organisch Chemisch Laboratorium
der Rijksuniversiteit,

UTRECHT.

Mijne Heren,

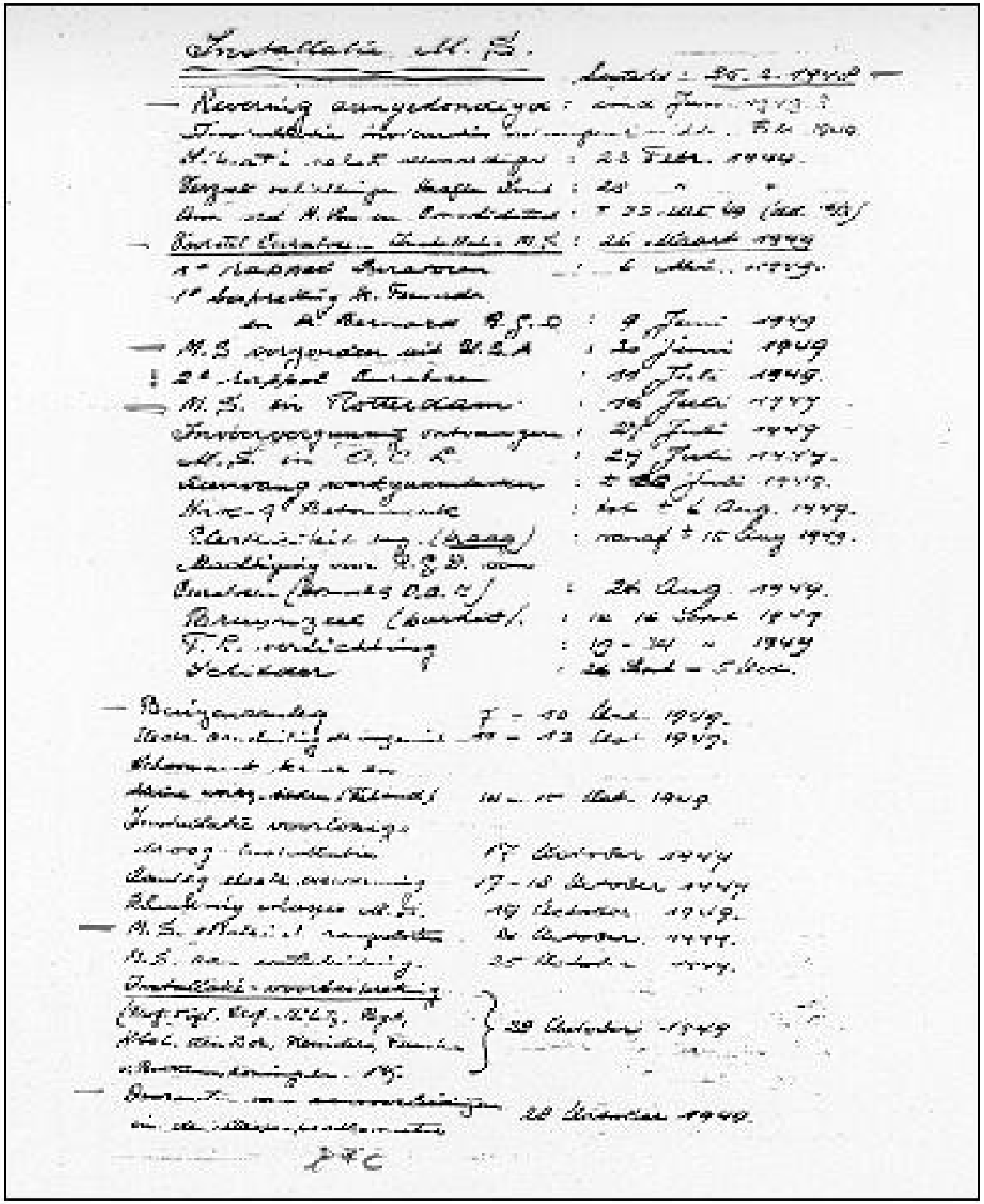
ms. "[illegible]", 20 Juli 1952 te Rotterdam.
[illegible] Amerika/Rotterdam B/L [illegible] 1 kist Spectro meter parts.

Wij ontvingen Uw schrijven dd. [illegible], waarin U ons mededelde, dat U voor de bovenvermelde zending de [illegible] nog niet hebt ontvangen,

Overeenkomstig Uw wens zullen wij bedoeld colli voorlopig in de loods houden,

Wij moeten hierbij nog opmerken, dat dit collo enkel voor Uw rekening en risico in opslag ligt.

Hoogachtend,
HOLLAND-AMERIKA LIJN



The university planned everything very carefully as we can see from the handwritten memo shown here. Order, shipment, arrival Rotterdam etc.; everything was meticulously planned.

Managers very often state that mass spectrometrists are not cost conscious and certainly not at universities. Well, I can prove that this is not the case. In Utrecht they calculated already in 1950 for a mass spectrometer, which they got free of charge, the price of instrument hours, almost unbelievable for a university. The next sheet gives us the calculation, giving a cost-price of Hfl. 1140 per month taking all kinds of costs into account Today this would amount to approximately Hfl. 28000,=. A student room in 1950, rented in Delft cost about Hfl. 20,= p/month and 100 gr. beefsteak cost 50 cents.

Kostenberekening M.S.

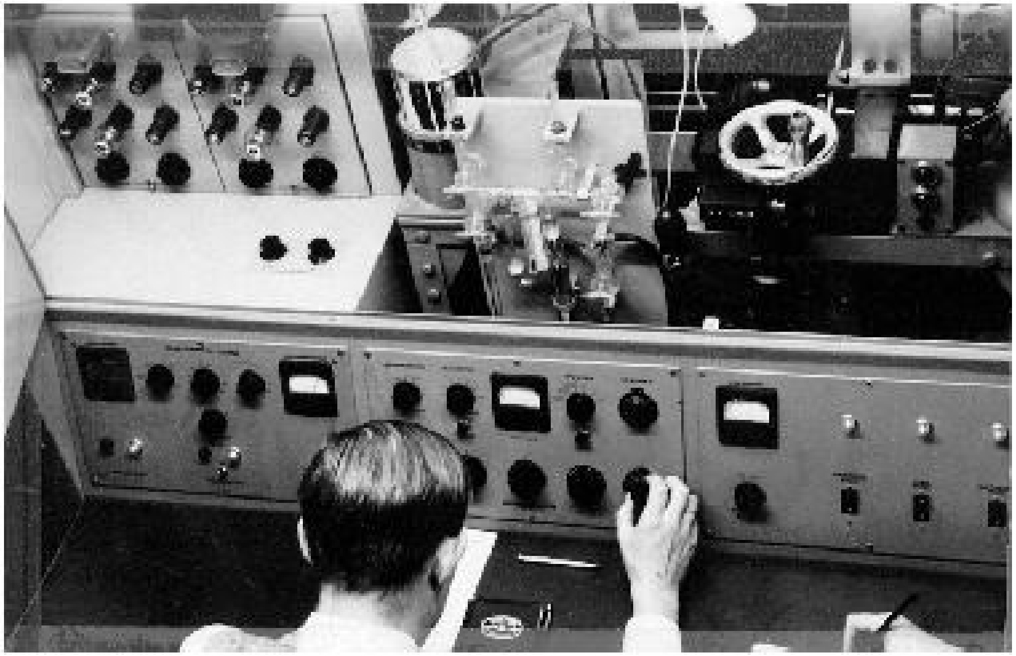
Apparaat uit U.S.A	$ 12.200.-	
Vracht	" 531.46	
à fl. 3.80	$ 12.731.46	fl. 48.380.=
[illegible] en - belanding		6600.-
[illegible] + [illegible] kosten		7030.75
Trafo 240.-, [illegible] 175.-, 2 [illegible] 60.- 4 [illegible] [illegible]		709.-
[illegible] (3) 145.-, [illegible] (3) 75.-, [illegible] 12.50, [illegible] 55.-		454.50
[illegible] 262.50, [illegible] [illegible], [illegible] 208.-, [illegible] 70 - [illegible] 42.-		705.50
[illegible] 200.- [illegible] 500.-, [illegible] 10.-, [illegible] [illegible] 150.-		960.=
[illegible] 250.-, [illegible] 475.-		725.=
		fl. 65.424.75

Afschrijving + rente per jaar	fl. 7000.-
Electriciteit kracht + licht	" 900.-
Waterverbruik	" 300.-
Vast [illegible]	" 1800.-
Klein [illegible] (Stoffen + enz.)	" 1650.-
[illegible]	" 2000.-
	fl. 13.650.=

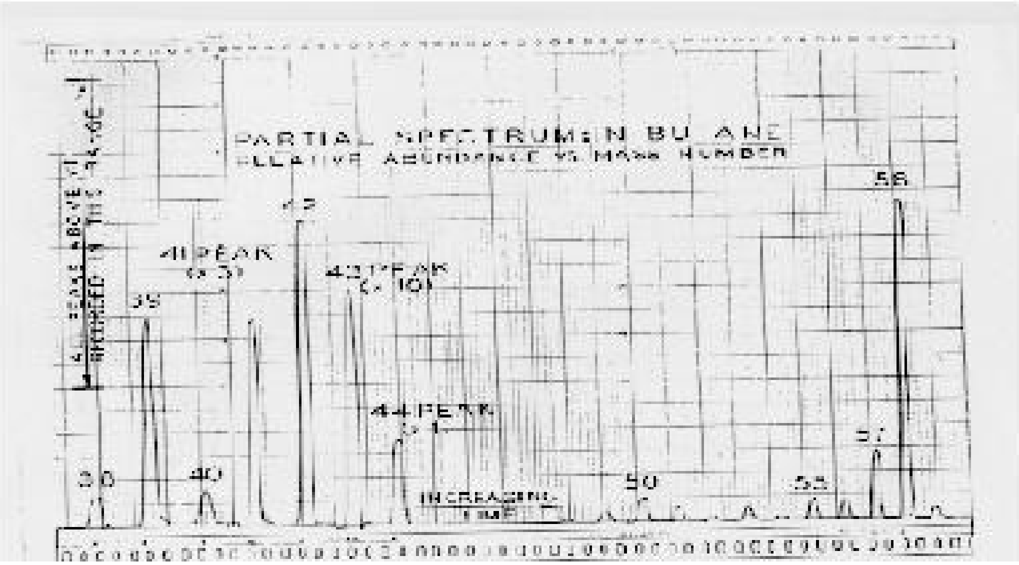
Globaal per maand fl. 1140.=

Beta-analyse
([illegible])
in Nov 1957
berekend
fl. 40.= 16/10/57
([illegible])

20/10/57

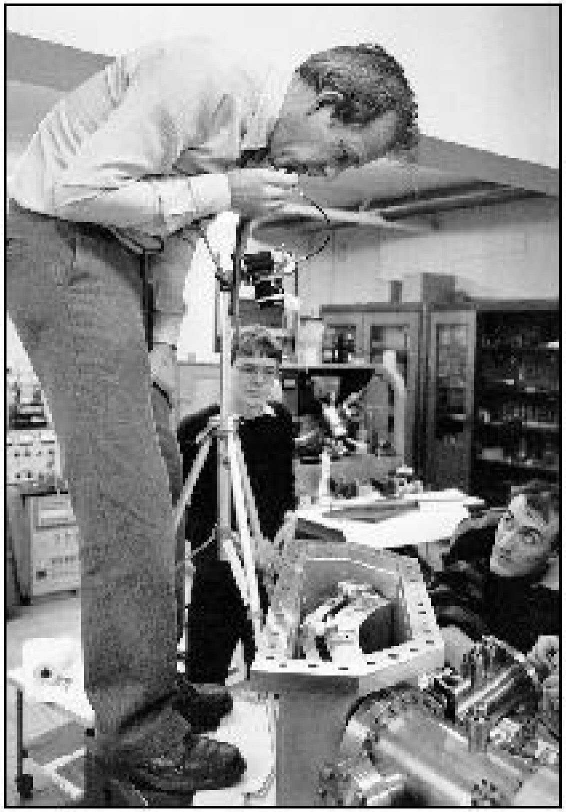


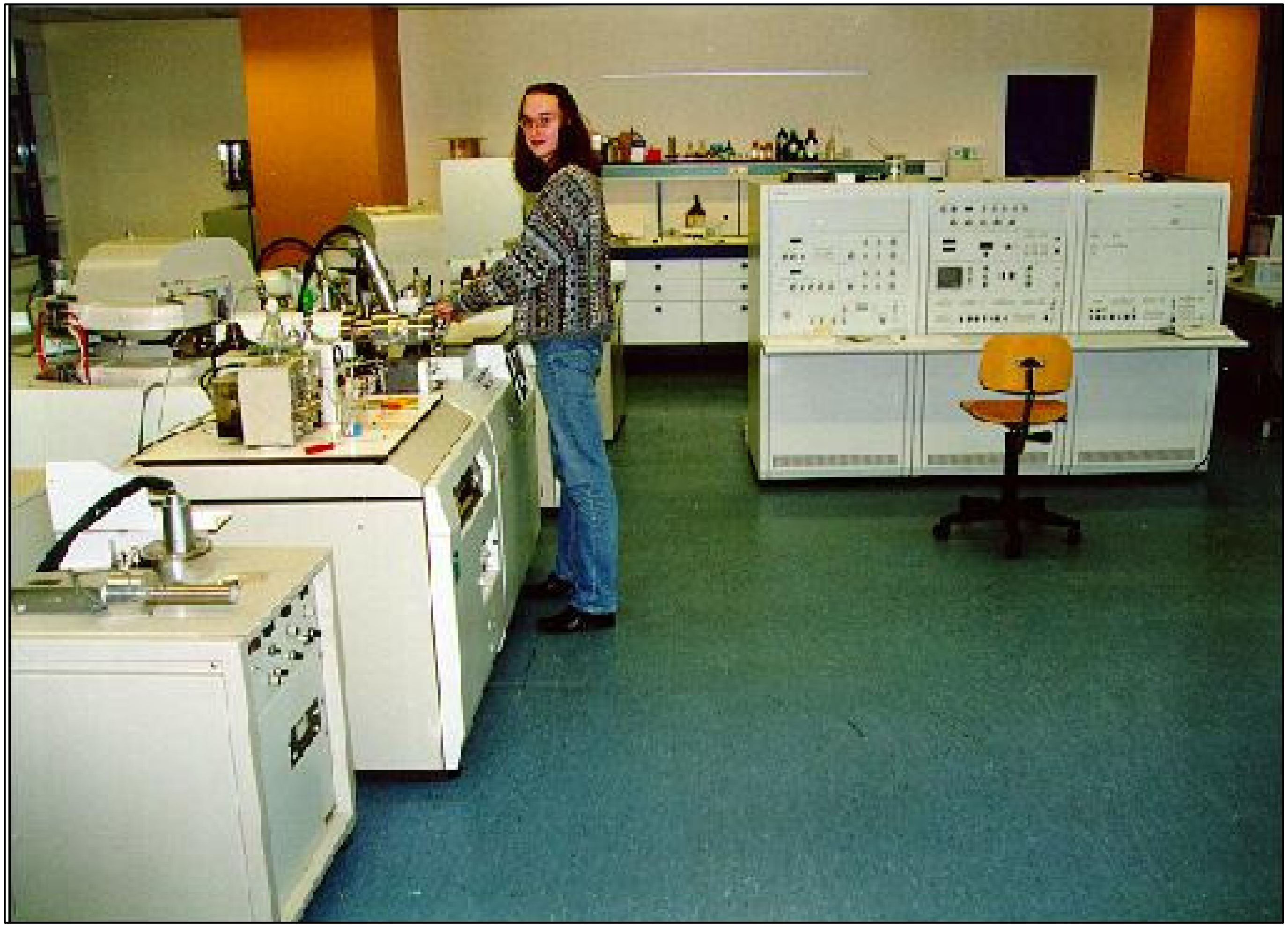
Here we can see the CEC instrument with its fragile glass inlet systems and Wik Heerma behind the wheels and buttons. It was a good instrument and remained operational until the 70s.



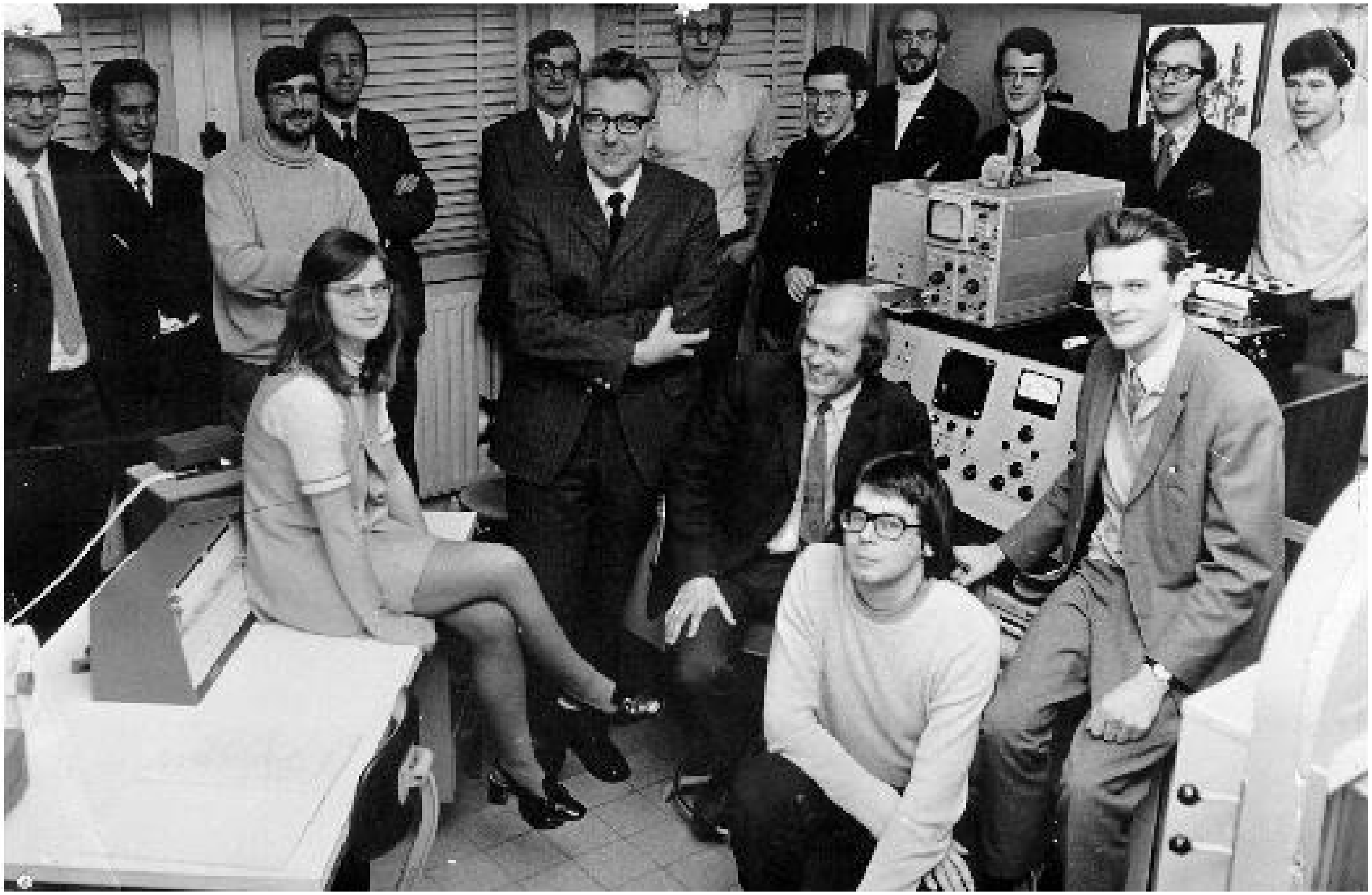
CEC spectrum of N-butane

Later the RU got more modern instruments like ZAB, JEOL 4 sector, Q TOF and many others. Below we see the arrival of the ZAB and Wik Heerma documenting every part very carefully.



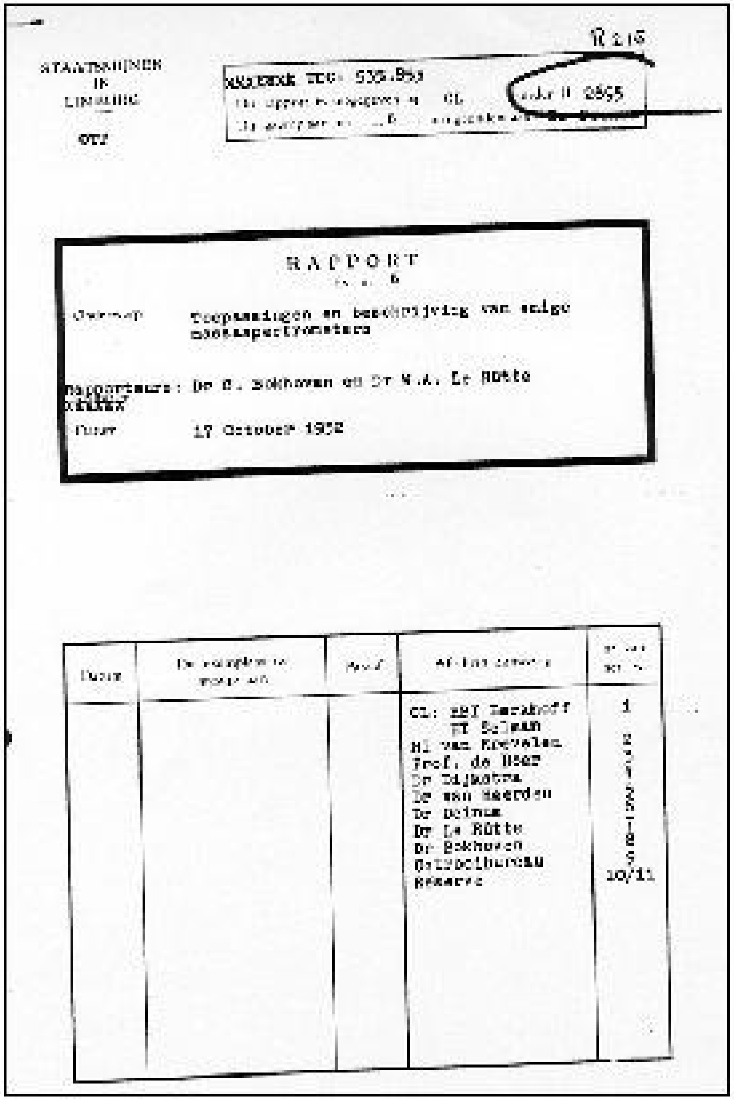


The Jeol SX102/SX102 4-sector MS at Utrecht



The group of Geo Dijkstra c.s. (Gerrit van de Werke, Henk van't Klooster, Jan Vink etc.) sitting on the console of the MS9 and the paper tape reader of their Ferranti computer system

From Chris de Koster from the state mines DSM I received an old report concerning the evaluation of some mass spectrometers. It was dated 17 Oct. 1952 written by Dr. C. Bokhoven and Dr. W.A. Rutte. They wanted to explore the Mass Spectrometers available on the market at that time and the possible applications of MS in the Central research laboratory. They visited 4 labs haying some experience with the technique and concluded that Mass Spectrometry could be of great benefit for the lab. Here, parts of these documents are shown.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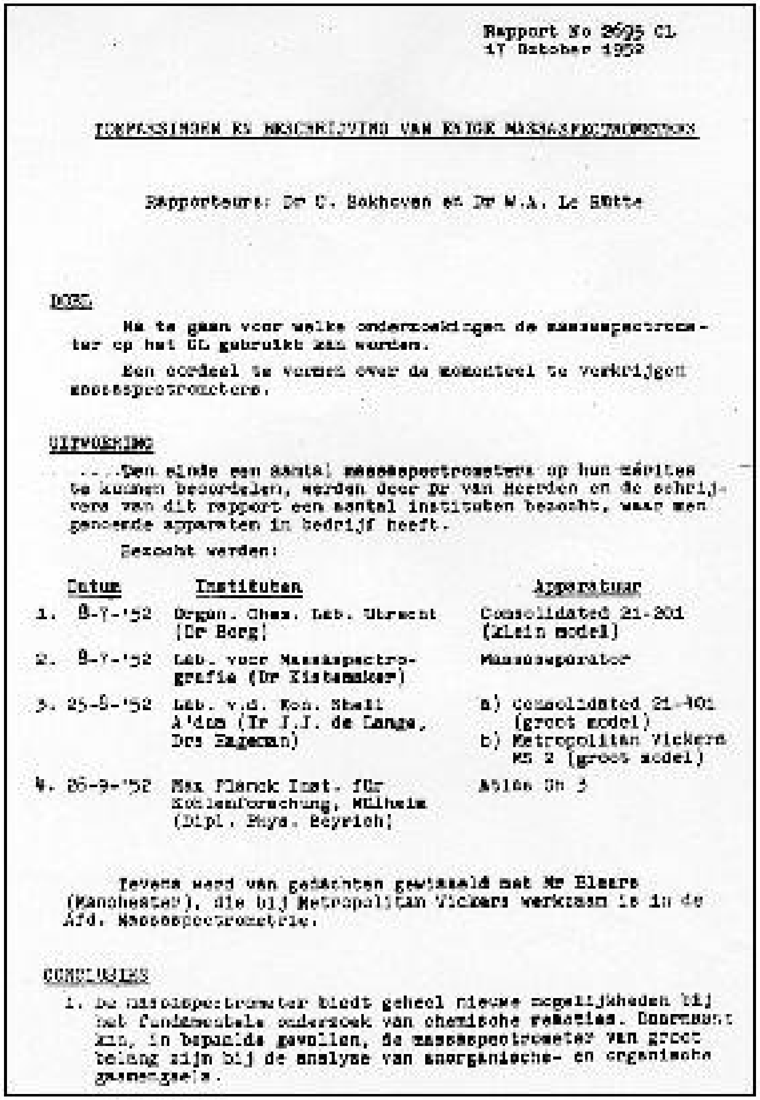
RAPPORT
No. 6

Onderwerp: Toepassingen en beschrijving van enige massaspectrometers

Rapporteurs: Dr C. Bokhoven en Dr W.A. Le Rütte

Datum: 17 October 1952

Datum	[illegible]	[illegible]	[illegible]	[illegible]
			CL: [illegible] [illegible]	1
			Hi van Krevelen	2
			Prof. de Boer	3
			Dr Dijkstra	4
			Dr van Heerden	5
			Dr Deinum	6
			Dr Le Rütte	7
			Dr Bokhoven	8
			Octrooibureau	9
			Reserve	10/11


Rapport No 2695 CL
17 October 1952

TOEPASSINGEN EN BESCHRIJVING VAN ENIGE MASSASPECTROMETERS

Rapporteurs: Dr C. Bokhoven en Dr W.A. Le Rütte

DOEL

Na te gaan voor welke onderzoekingen de massaspectrometer op het CL gebruikt kan worden.

Een oordeel te vormen over de momenteel te verkrijgen massaspectrometers.

UITVOERING

Ten einde een aantal massaspectrometers op hun merites te kunnen beoordelen, werden door Dr van Heerden en de schrijvers van dit rapport een aantal instituten bezocht, waar men genoemde apparaten in bedrijf heeft.

Bezocht werden:

	Datum	Instituten	Apparatuur
1.	8-7-'52	Organ. Chem. Lab. Utrecht (Dr Berg)	Consolidated 21-201 (klein model)
2.	9-7-'52	Lab. voor Massaspectrografie (Dr Kistemaker)	Massaseparator
3.	25-8-'52	Lab. v.d. Kon. Shell A'dam (Ir J.J. de Lange, Drs Hageman)	a) Consolidated 21-401 (groot model) b) Metropolitan Vickers MS 2 (groot model)
4.	26-9-'52	Max Planck Inst. für Kohlenforschung, Mülheim (Dipl. Phys. Beyrich)	Atlas CH 3

Tevens werd van gedachten gewisseld met Mr Blears (Manchester), die bij Metropolitan Vickers werkzaam is in de Afd. Massaspectrometrie.

CONCLUSIES

1. De massaspectrometer biedt geheel nieuwe mogelijkheden bij het fundamentele onderzoek van chemische reacties. Daarnaast kan, in bepaalde gevallen, de massaspectrometer van groot belang zijn bij de analyse van anorganische- en organische gasmengsels.

Massa-spectrometers	Prijs	Levertijd	Algemene toepassingen	"Scanning"	Meetmethode
Consolidated type 21-401	$ 35.000 / 150.000	1	gasanalysen (isotopen verh.)	automatisch of met de hand magnetisch	fotografische registratie van de uitslag van 4 galvanometers met verschillende gevoeligheden
Consolidated type 21-201	$ 12 à 15.000 / 60 à 80.000	?	isotopen verh.	met de hand + electrisch	galvanometer-uitslag methode compensatie-methode
Metropolitan Vickers type MS 2	£ 10.000 / 130.000	18 mnd.	gasanalysen isotopen verh.	automatisch of met de hand magnetisch	schrijvende meter en draaispoelmeter, uitslag methode compensatie methode
Metropolitan Vickers type MS 3	£ 3.500 / 46.000	18 mnd.	isotopen verh. gasanalysen	met de hand electrisch + magnetisch	draaispoelmeter, uitslag methode, compensatie-methode
Atlas type CH 3	D.M. 48.000 / 55.000	6 à 9 mnd.	gasanalysen (isotopen verh.)	magnetisch met de hand electrisch automatisch	draaispoelmeter, uitslag methode compensatie-methode en nauwkeurige verwijzing met oscillograaf

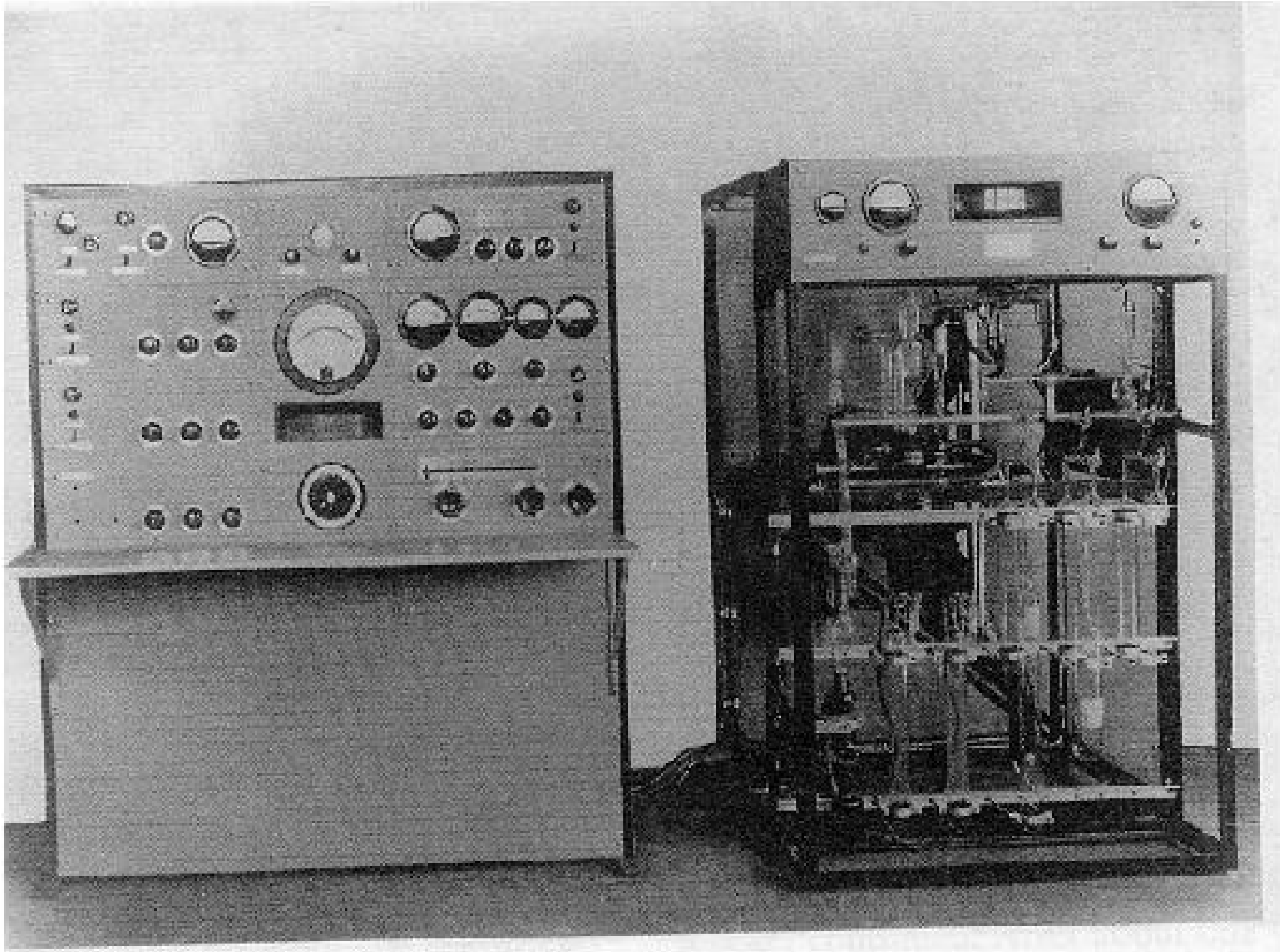
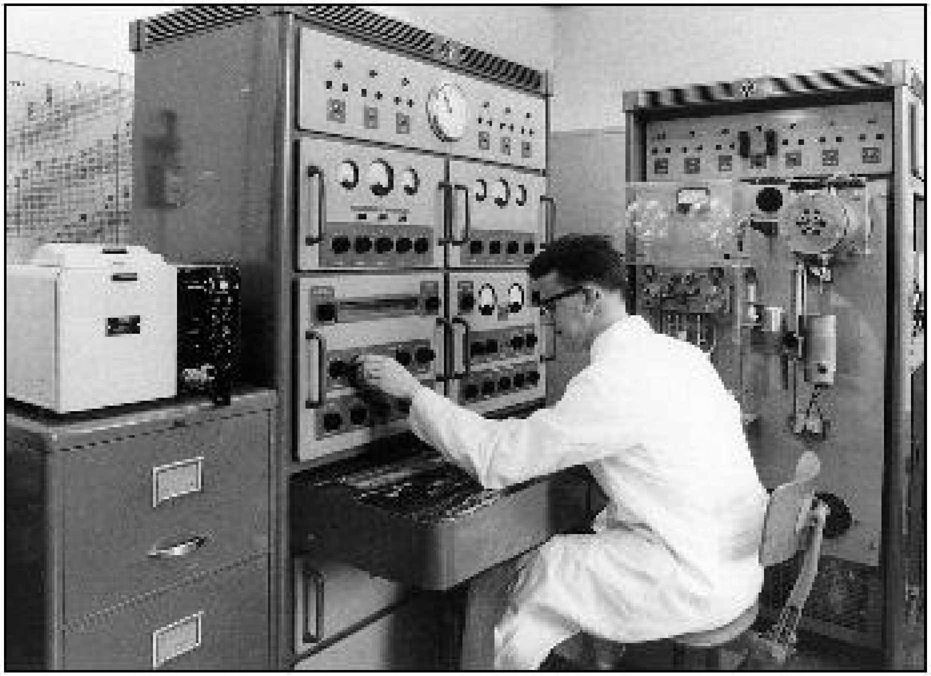
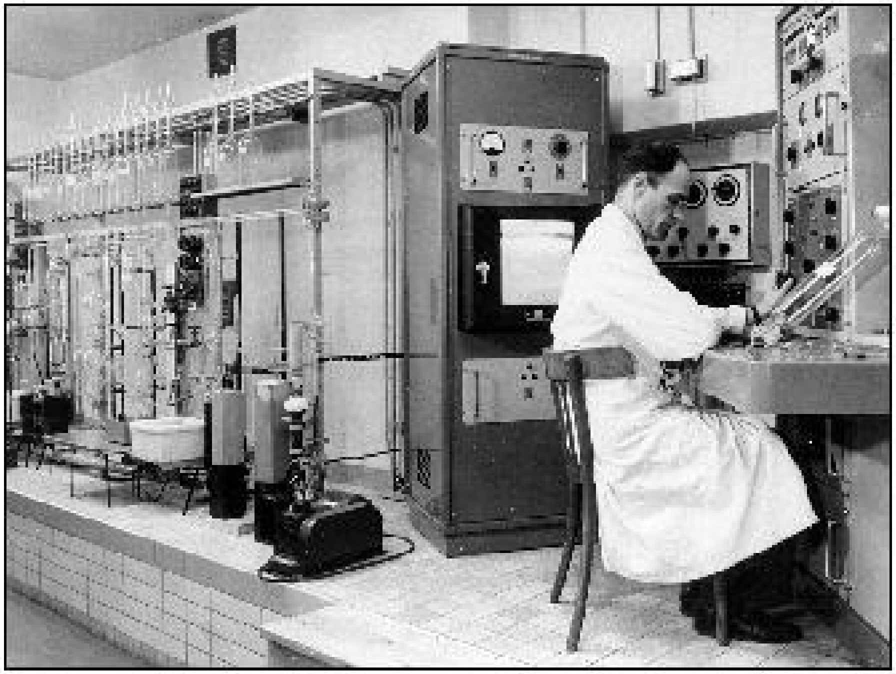


Figure 3. CH3 sector (1950).

Rapid Communications in Mass Spectrometry,

ATLAS CH3 Glass inlet system recording on galvanometer instruments (compensation method) manual or scanning magnet and no recorder jet! Mass range up to 300…





Here we see two AEI MS2 Mass Spectrometers in operation at DSM. It is obvious that this groups where among the first members of our MS Society. Chris de Koster is preparing a detailed paper on the MS History at wet DSM.

KSLA Amsterdam

At the Shell R&D Laboratory KSLA in Amsterdam there was also a group headed by Dr. L.A. Lauw and van Katwijk who were very actively exploring the application of Mass Spectrometry in the analysis of hydrocarbons, crude oil fractions etc. The exploration and production laboratory started GC/MS on a CH4 in 1962 with Dr. Engelhardt. Unfortunately I was not able to obtain more data from Shell because they destroyed their old archives a year ago.

TU Eindhoven

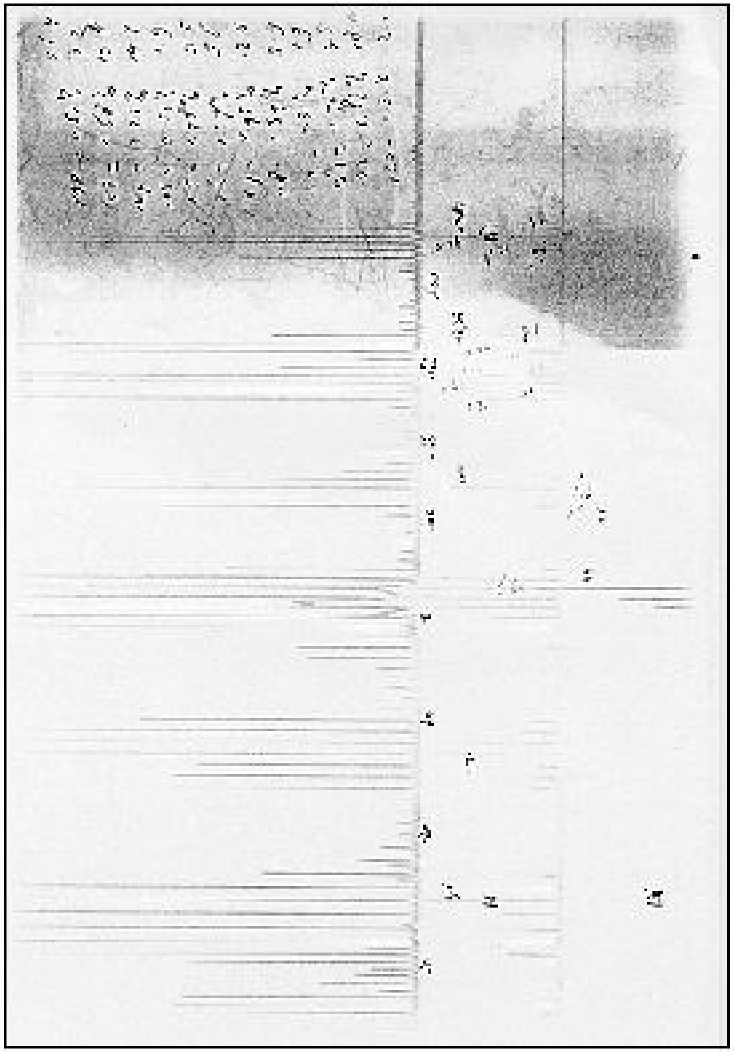
At the TU Eindhoven there was a group instrumental analyses headed by Prof. Keulernans. They were developing Gas Chromatography and wanted to combine this separation technique with Mass spectrometry. Below we observe the first Mass spectrmetrist of the group looking suspiciously at the ion source of an AIE MS2. They also performed science resulting in a PhD degree for Piet Leclerque. Here, he receives congratulations from his promoter Prof. Keulemans.

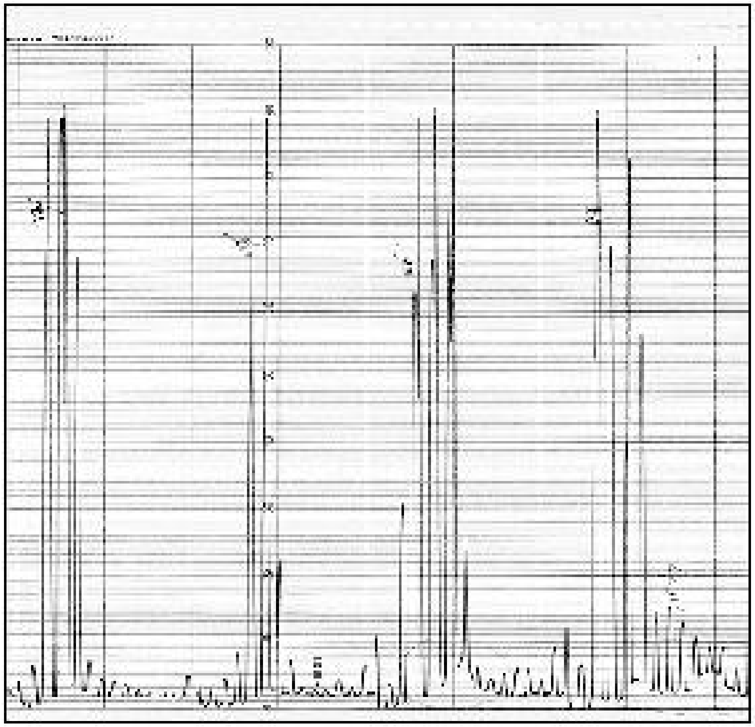
A.I.M. Keulemans

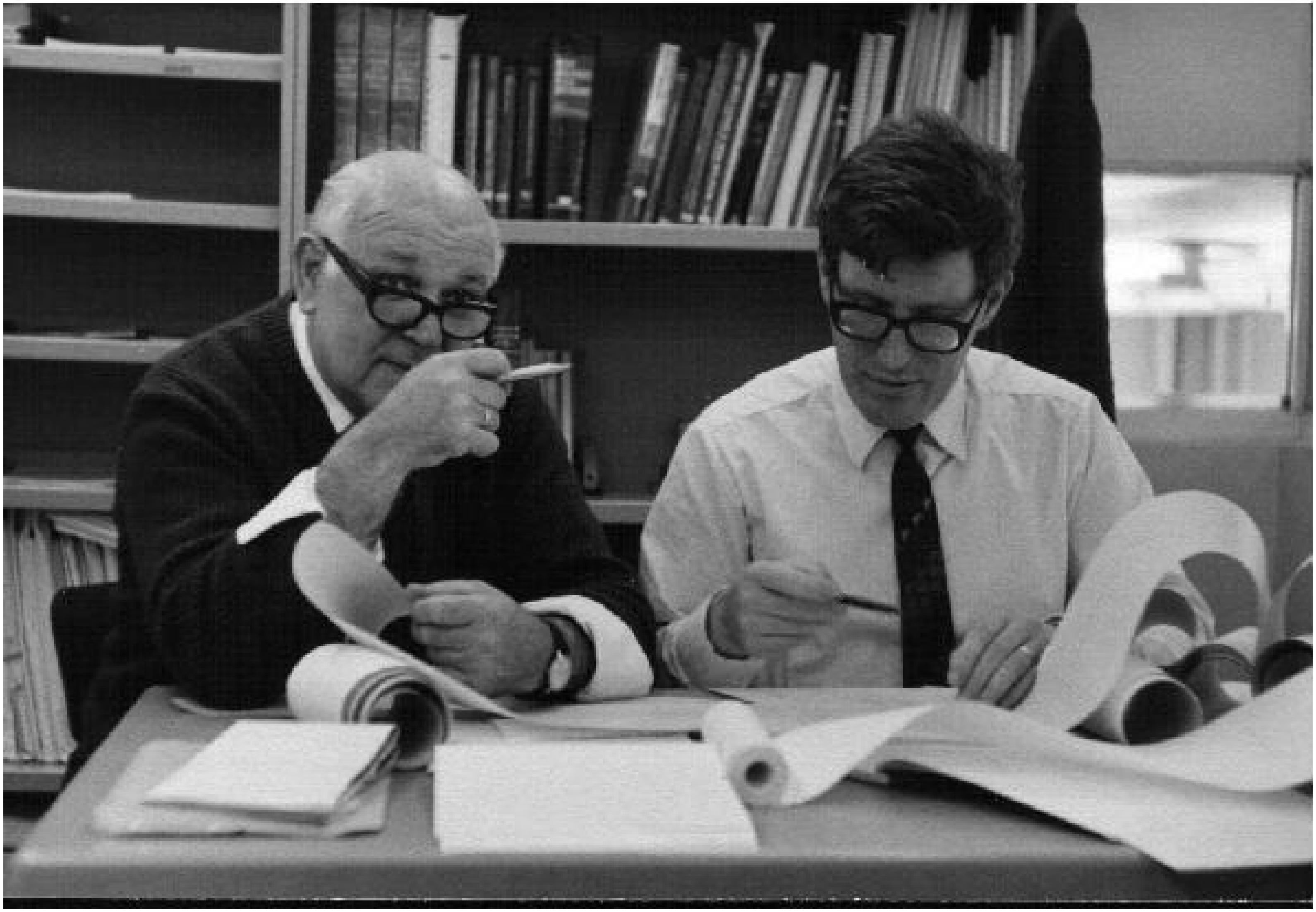
University of Amsterdam

Another famous group worked in Amsterdam, involved in more fundamental Mass spectrometric research; “Ion chemistry”, Ion physics, and Ionization methods. And that was the place where our society was founded. This enthusiastic group was headed and inspired by Prof. Nico Nibbering, one of the past chairmen of the NVMS.

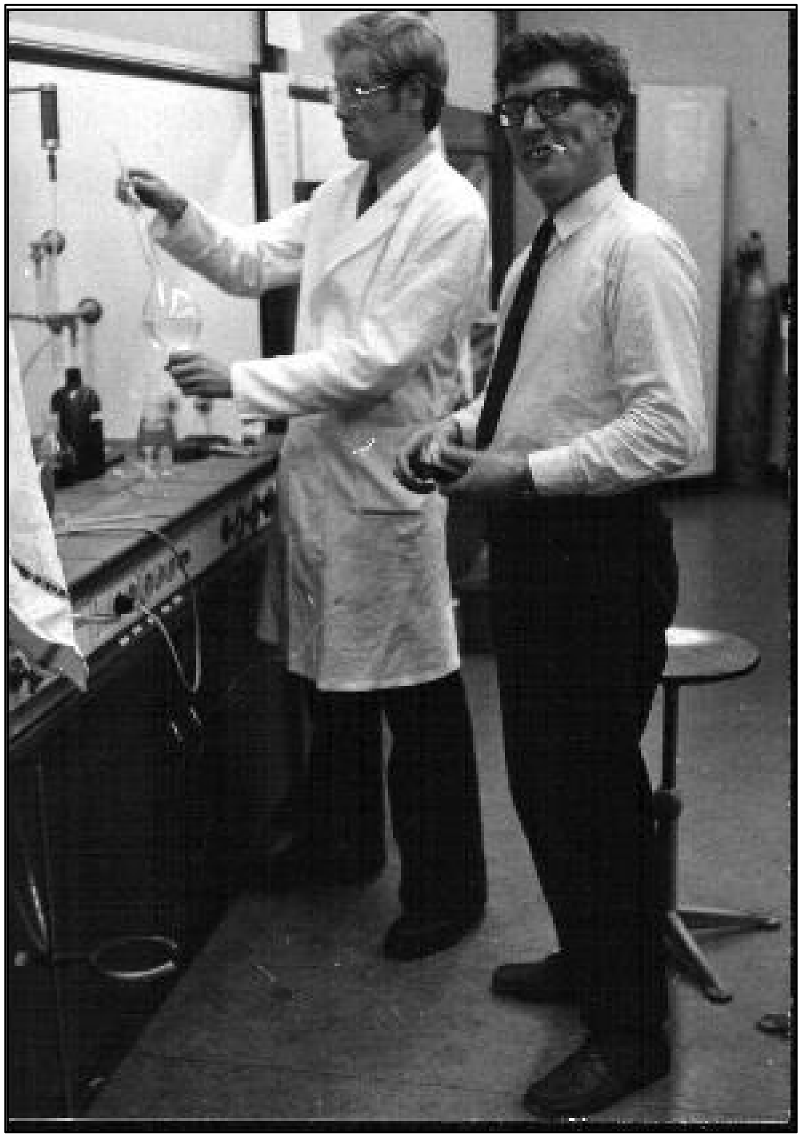
Spectra were recorded on paper or UV paper in those days. One of the problems was the assignment of the correct mass number to a certain mass peak. No mass markers or elegant software existed at that time.





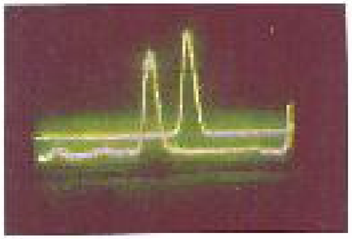


Here, we see the young Nico calibrating by hand, together with Mr. Rooselaar, some of the mass spectra obtained from the AEI MS9.

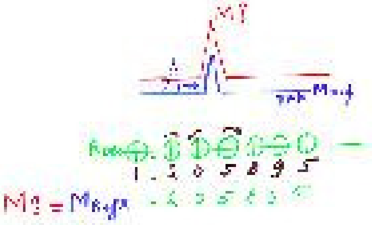


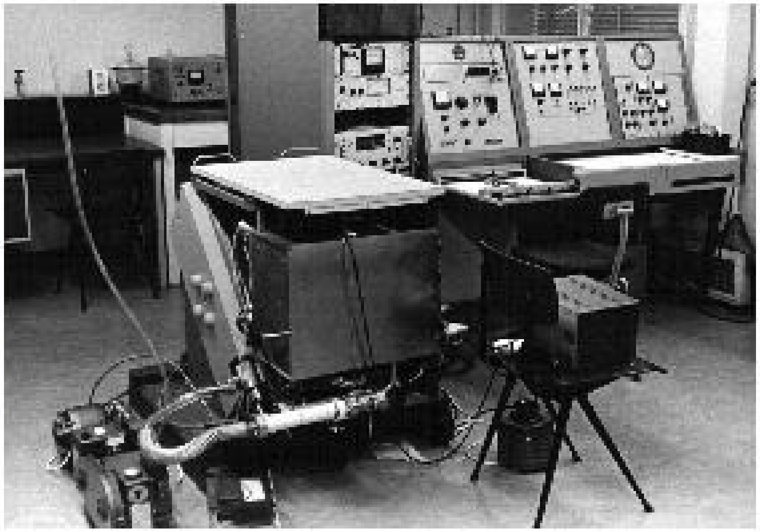
Here we see the proud professor with one of his promising young students Andries Bruins (trying to remember what he had done in his previous life).

In the following sheets I will quickly show some pictures of the Amsterdam Lab with their different instruments, including the Varian MAT 711 double focusing instrument (1969), the ZAB-2HF double focusing reversed geometry mass spectrometer (1983), the Varian Syrotron drift cell ion cyclotron resonance spectrometer (1971), the in one year in 1979/1980 constructed home-built Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer and the Bruker CMS 47 FT-ICR spectrometer (1986) which later on has been equipped with an external ion source (1988). (Tramway magnetic field distortion doing peak-match measurements, correction coil antenna, etc.)



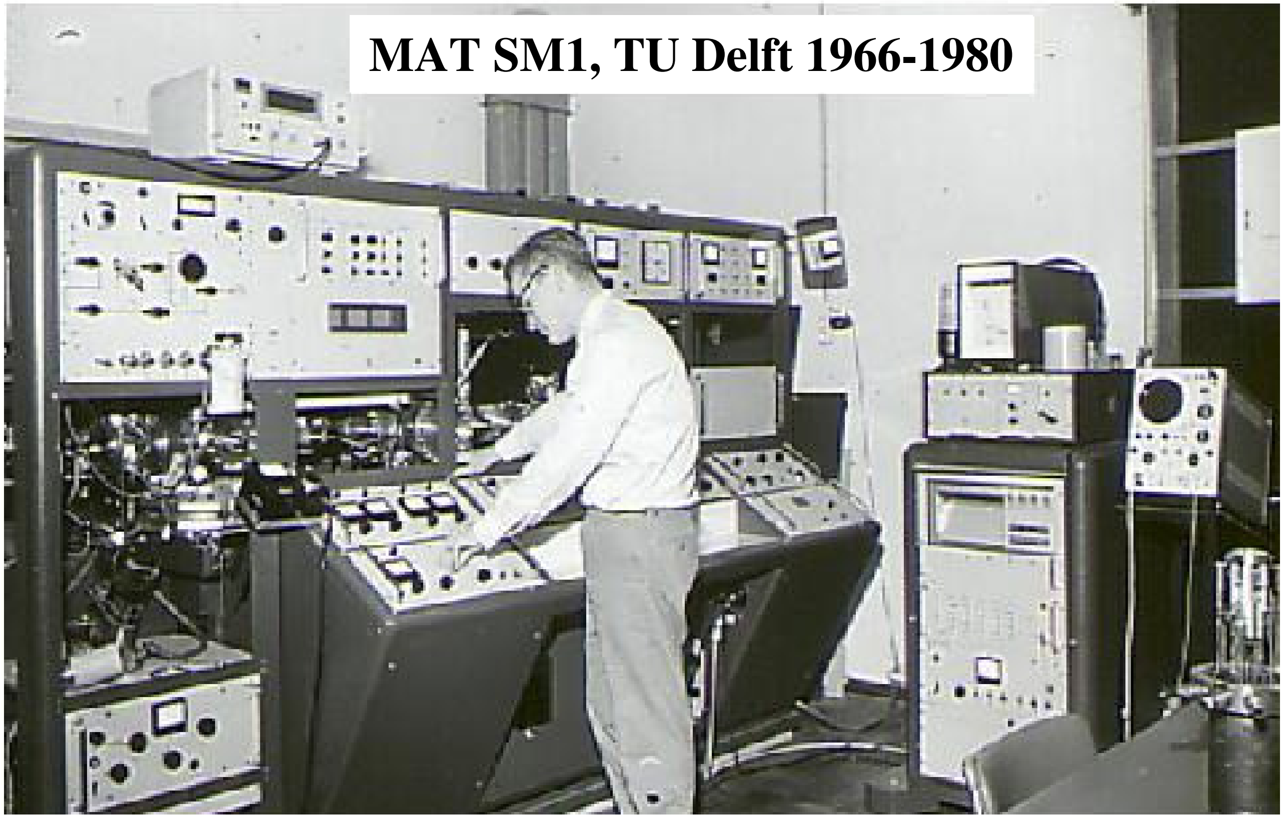
Peakshape traces on the MAT 711 screen





Here we see a young professor Nibbering enthusiastically lecturing about a new ionization method, manual ionization versus Field Desorption during the promotion of Jan van der Greef on this subject.

The TU Delft



MAT SM1, TU Delft 1966-1980

Some magic operation!!! by Bas van de Graaf, trying to adjust and channel the ion beam trough the complex SMI Analyzer, monitoring four indicators simultaneously.

Mass Spectrometers at the TU Delft

1965-1966 MAT CH4, MAT SM1
1972-1978 MAT1 Gnom
1980-1995 MAT 311
1974-1990 MAT44S
1990– VG70-SE

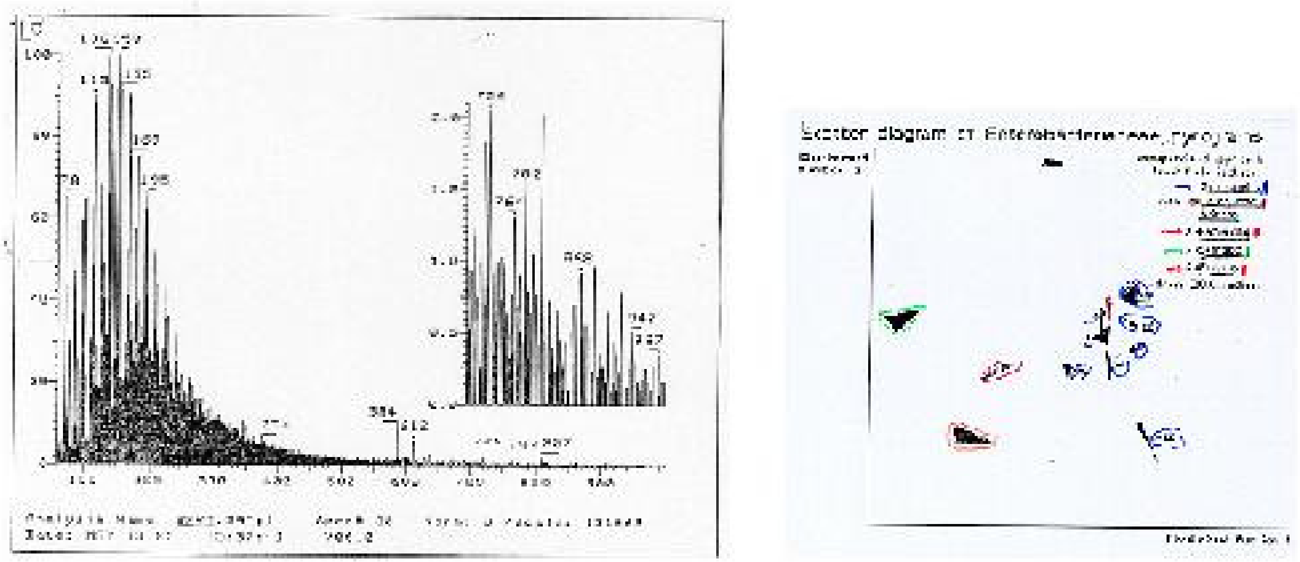
Some MAT benchmarks:

1969 MAT SM1	Mass range 1-1200	Res. 12000	Vac $4x10^{-8}$ mbar, 10 kV
1970 MAT 731	Mass range 1-1500	Res. 35000	Vac $4x10^{-8}$ mbar, 10 kV
1972 MAT 711	Mass range 1-1500	Res. 80000	Vac $4x10^{-8}$ mbar, 10 kV

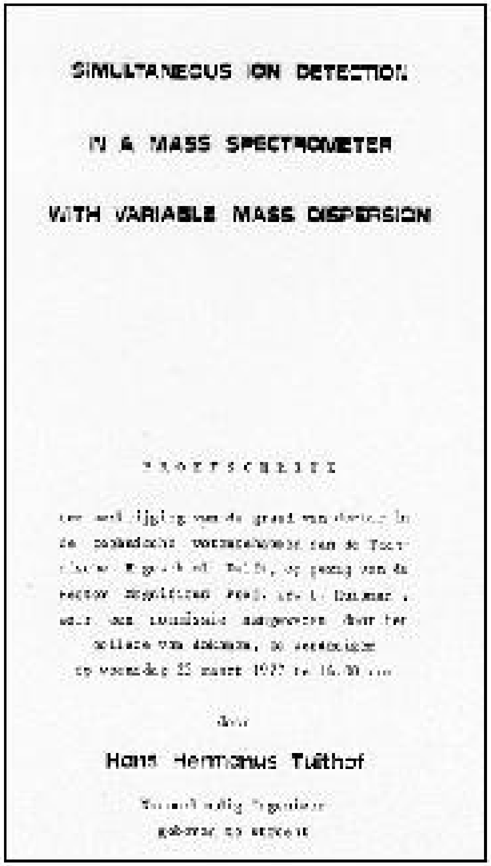
The FOM Institute in Amsterdam

The FOM Institute in Amsterdam was also a breeding ground of young mass spectrometric talents. They built their own innovative instruments, most of the time, and were specialists in ion optics (Henk Boerboom) and bizarre applications. They were the pioneers of pyrolysis mass spectrometry, pyrolyzing complete bacterial colonies in the ion source of a Mass Spectrometer (Curie-point pyrolysis, Henk Meuzelaar et al.). One can imagine that the spectra they obtained looked terrible and on first glance had no meaning at all. But by processing the spectra with specially developed mathematical methods (so-called multivariate analysis) W. Esshuis and ‘Willem ‘Windig were able to extract meaningful information from these spectra resulting in the characterization of different bacterial tribes.

The next step was to attempt to extract more information from the characteristic and discriminating masses by MSIMS methods. For that purpose they built a very special mass spectrometer 1977 with a big high-energy collision chamber and a fast integrating detection system necessary for the detection of these fast phenomena.



DCI in-source pyro1ysis ‚first. done‘ at TNO by A. Tas, J. v.d.Greef, and M.C.ten Noever de Brauw



SIMULTANEOUS ION DETECTION

IN A MASS SPECTROMETER

WITH VARIABLE MASS DISPERSION

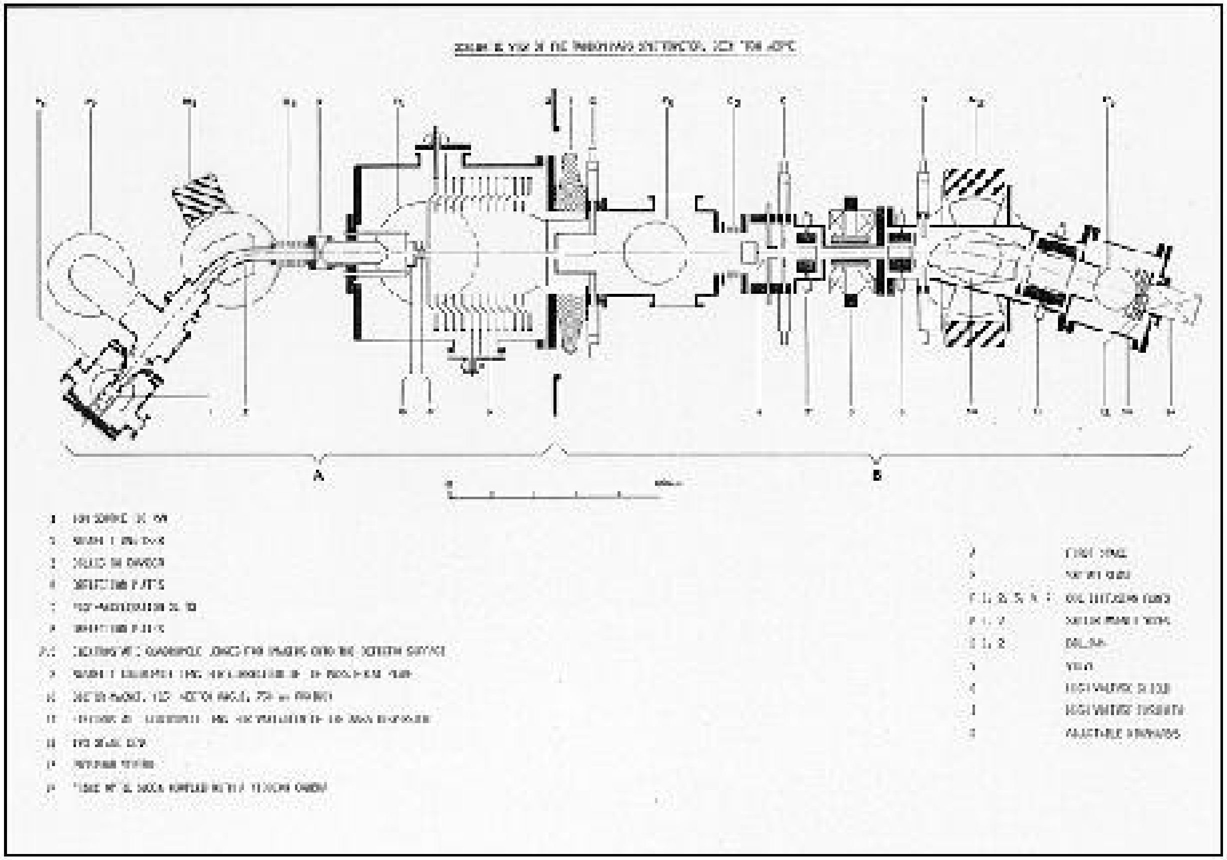
PROEFSCHRIFT

ter verkrijging van de graad van doctor in
de technische wetenschappen aan de Tech-
nische Hogeschool Delft, op gezag van de
rector magnificus prof. ir. L. Huisman ,
voor een commissie aangewezen door het
college van dekanen, te verdedigen
op woensdag 23 maart 1977 te 16.00 uur

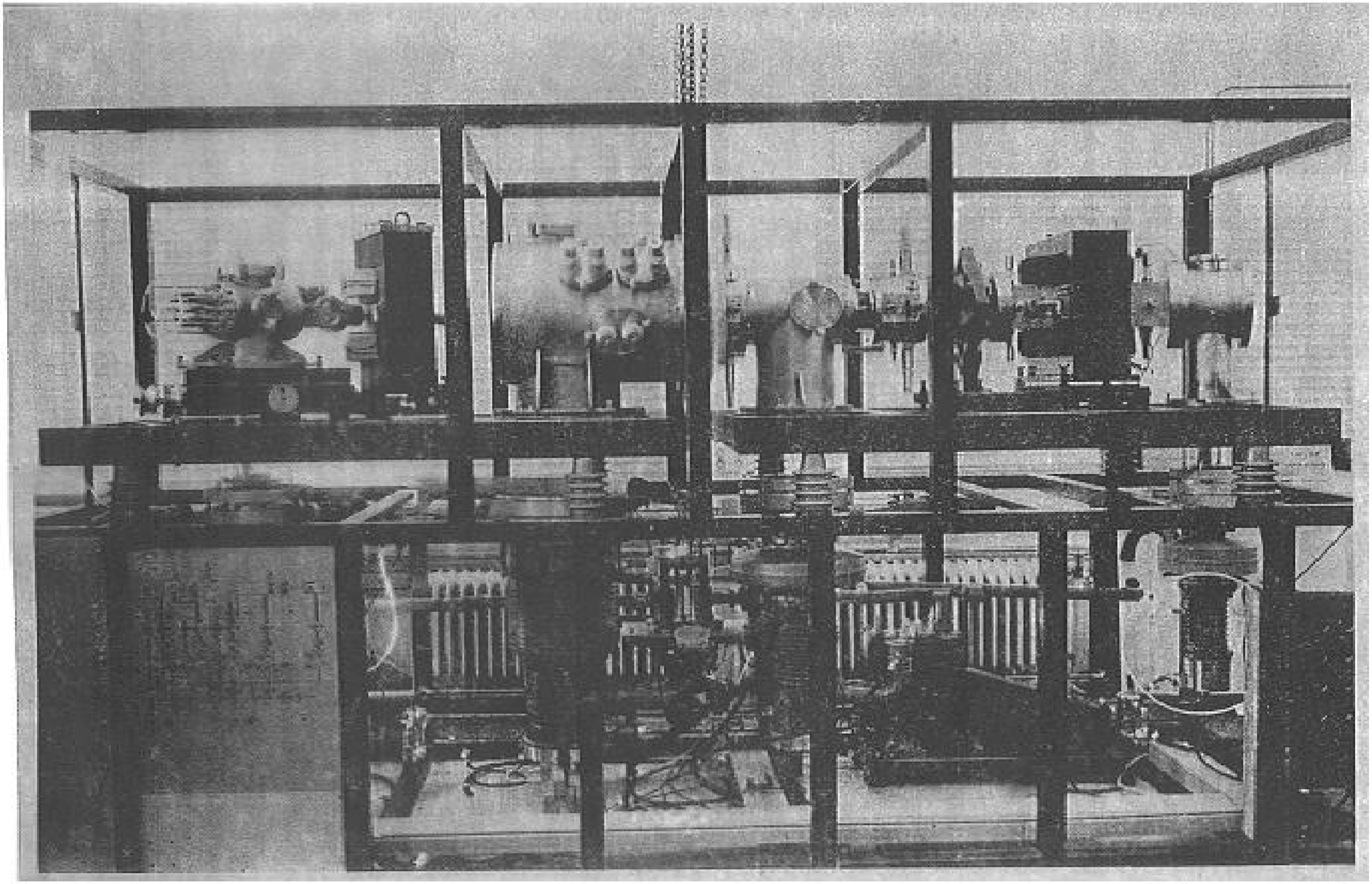
door

Hans Hermanus Tuithof

werktuigkundig ingenieur
geboren te Utrecht

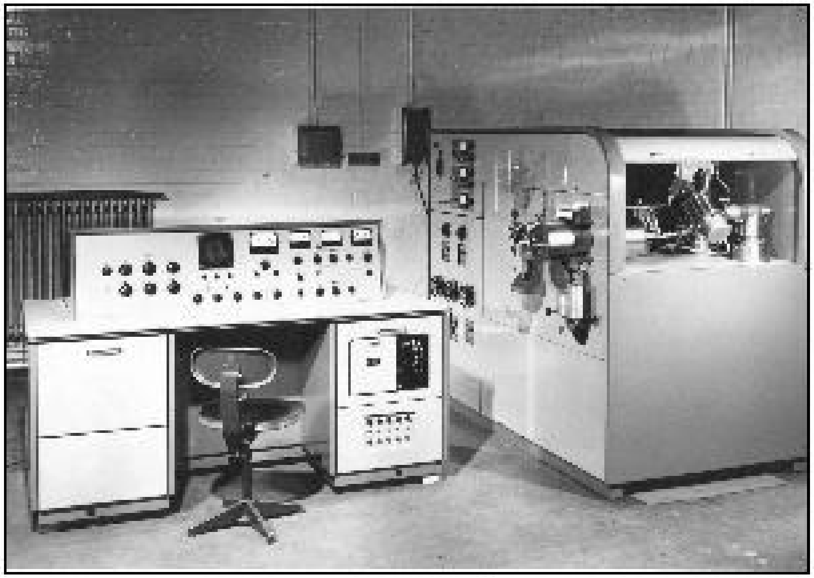


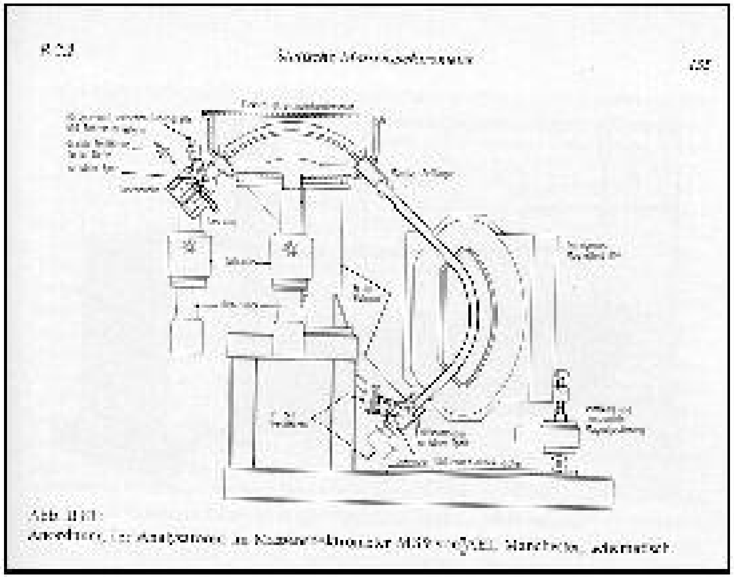
In the design phase there were lengthy discussions going on about where to put the 40 kV high voltage??! At the source, where Meuzelaar had to introduce the sample or shall we put the high voltage on the detector, the very sensitive channel plate, the great concern of Henk Boerboom? Finally they reached a typical Dutch compromise: - 10 kV on the source and 30 kV at the detector (The Polder model *avant la lettre*).
I remember being present at a small party, where the High voltage was switched on for the first time. There was a moment involving a lot of lightning, some kind of a disco effect, followed by a long dark period, the changing of all the transistors and other fragile electronic compounds.



Industrial Mass Spectrometry

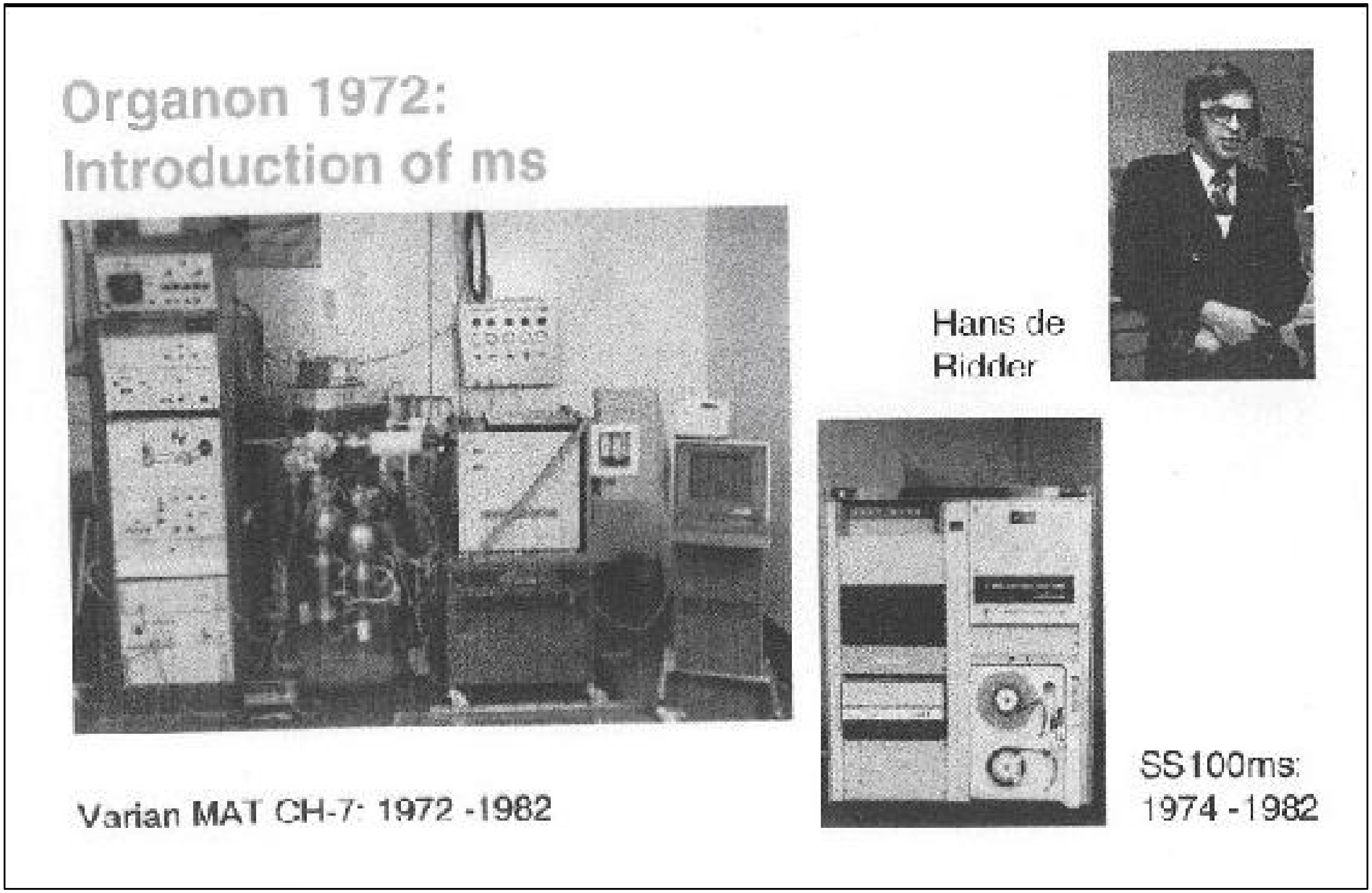
Duphar, Weesp





They started about 1965 with a high resolution MS AEI M89 to help the Duphar synthesis department to find out what compounds they had really produced in their retorts.

Organon, Oss



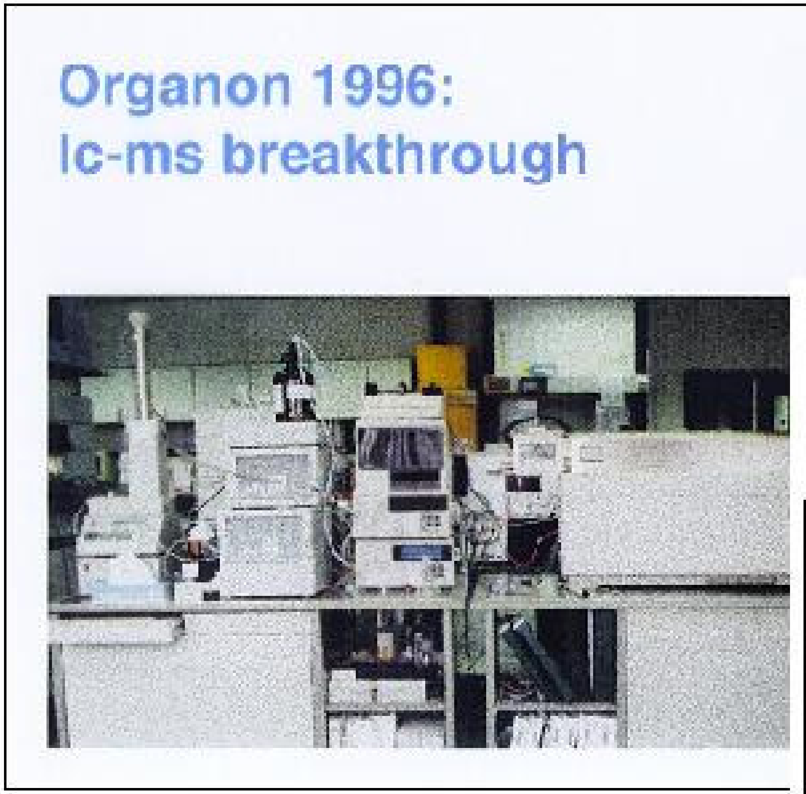
Organon 1972: Introduction of ms

Hans de Ridder

Varian MAT CH-7: 1972 -1982

SS100ms: 1974 -1982

The competition started in 1972 with GCIMS on a MAT CH7 complete with data system and a promising young scientist coming just from the MS group in Utrecht “Dr Hans de Ridder”.



Organon 1996:
lc-ms breakthrough

Organon 1982: removal of the Varian MAT-311a

1. Jan Vink
2. Gerrit Schmeits
3. Peter Jacobs

The 'Bremen' crew

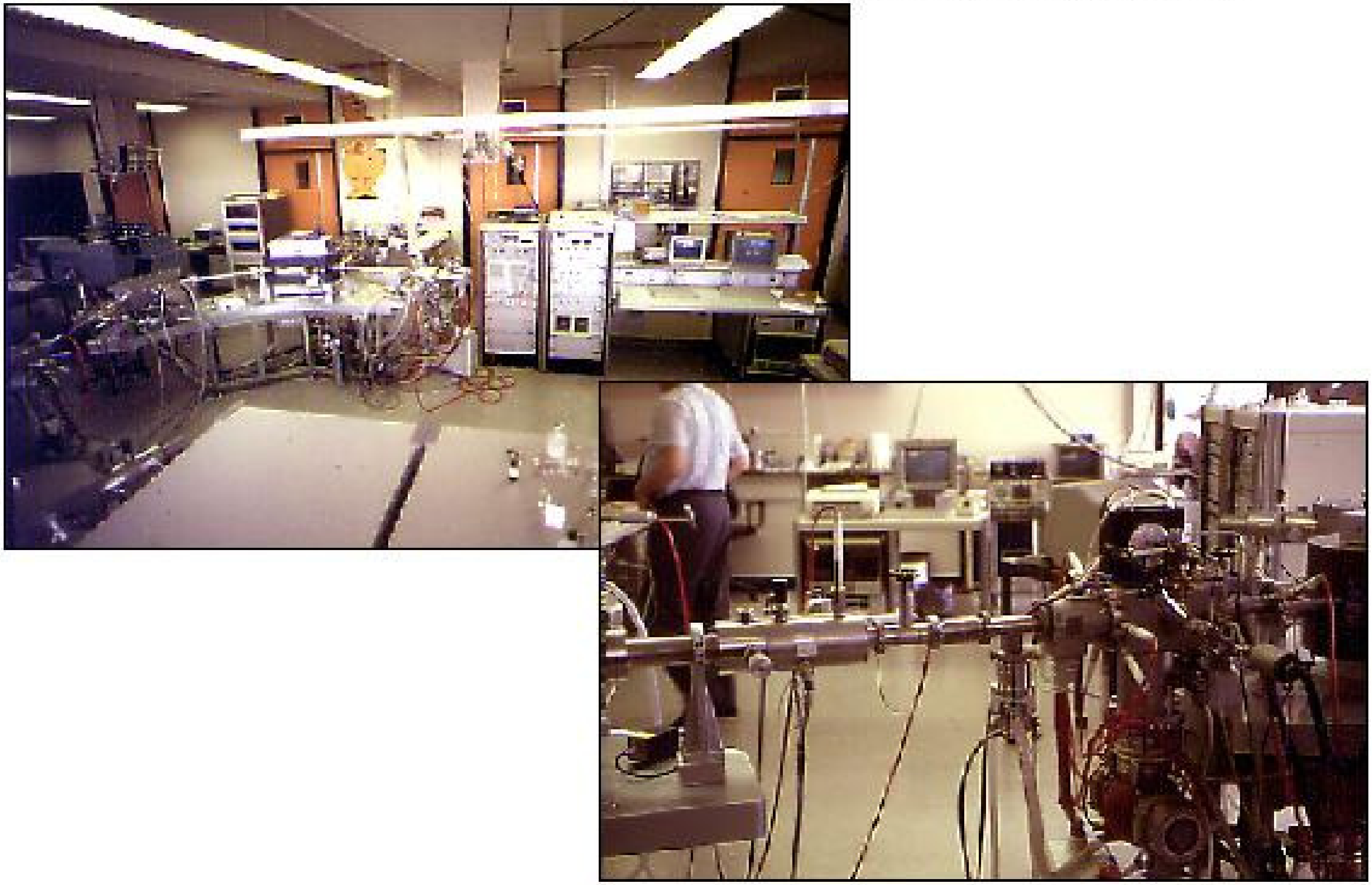
A new ms lab!

In 1982 Organon MS got a new lab and had to remove all the equipment from basements through narrow staircases. These images illustrate the heavy job. In 1996 Organon head their breakthrough in LC/MS when they obtained the Sciex API-300.

As we know, mass spectrometers are always installed at difficult places like the top floor at TNO Zeist.

Gist-Brocades

At Gist - Brocades Mass Spectrometers were used for process control, research and development of new products, identification of unknown compounds and characterization of chemical matrices using pattern recognition methods. A 4 sector AMD4 Mass Spectrometer was installed in their laboratory. This instrument could be easily operated as two independent mass spectrometers.



Collision chamber and connecting device between the two AMD Mass Spectrometers

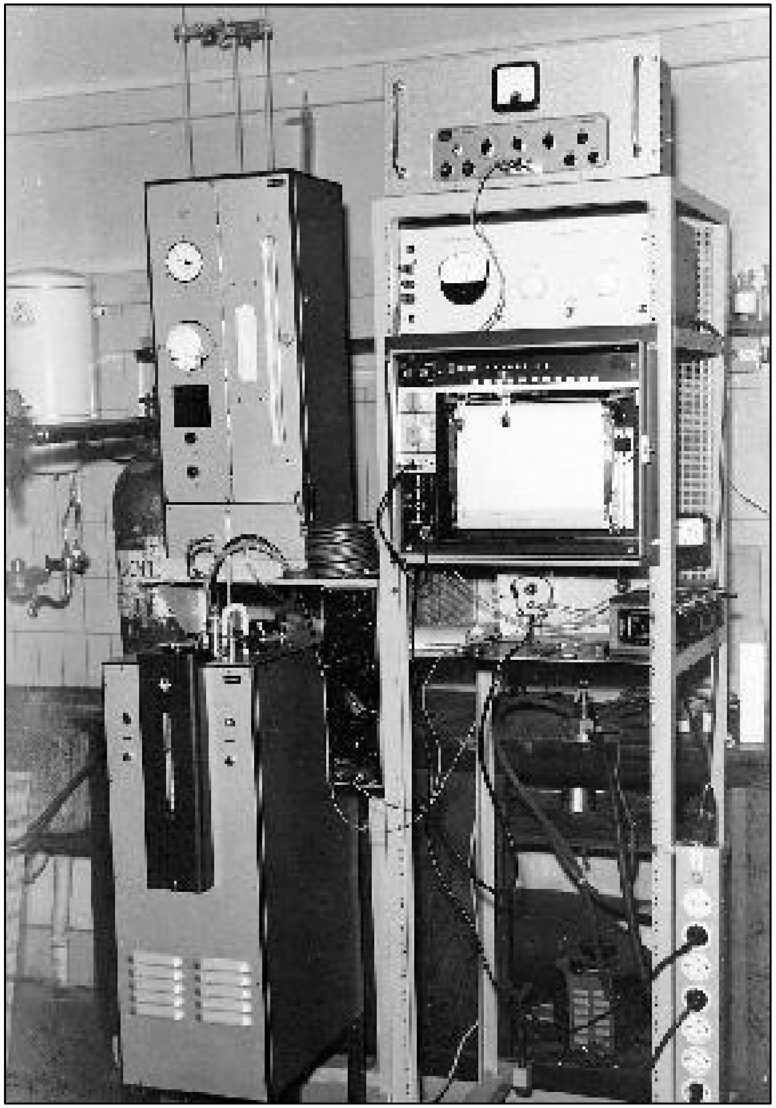
RIVM, Utrecht/Bilthoven

In the catacomb's of RIVM Utrecht, resided a physicist who was always trying to improve instruments, Didi Freudenthal. Such as there were a MAT73l used with photoplate detection a CH5 and CH7 GCIMS solving all kinds of environmental questions. Later the group moved to the new building in Bilthoven taking the opportunity to replace all the old instruments, resulting in a big new ms lab under de guidance of Henk van't Klooster and Ad de Jong. They installed the first JEOL 4 sector mass spectrometer.

Jan ten Hove

NIZO

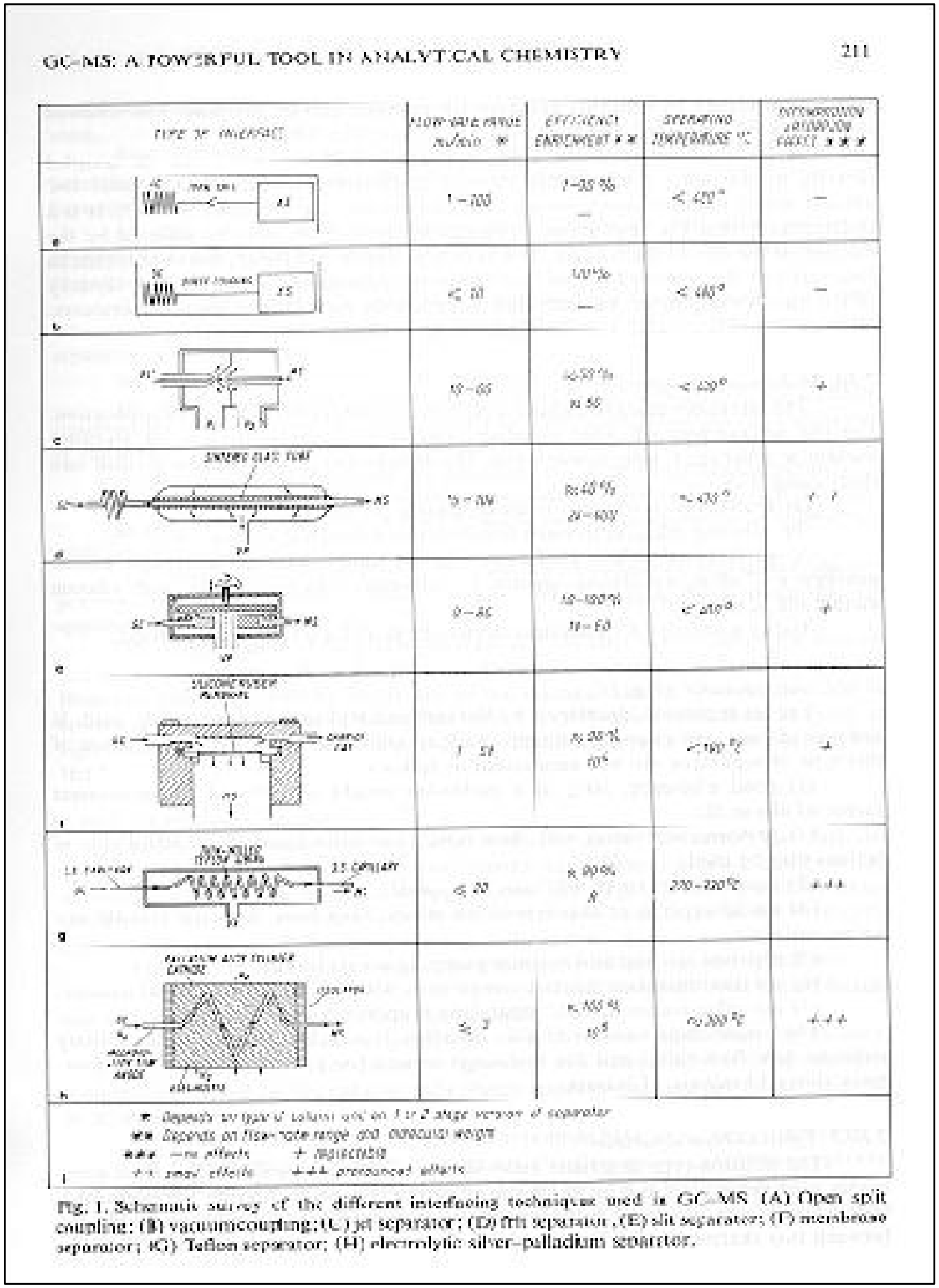
This image shows Rowald Neeter, one of our honorable Chairmen, with his modem GC/MS. He started with a CH5 GC/MS system counting endless spectrum photo ro1l’s trying to identify the flavor components of Milk and Cheese.



I will now talk a little bit about the beginning of GC/MS. In the beginning GC's were big instruments with big packed columns as shown in this image from one of the old GC's of the TU Delft.

It was obvious that these complementary methods GC&.MS should be connected, in order to avoid the terrible and time consuming, inefficient trapping of compounds eluting from the GC column and introduce them afterwards into the mass spectrometer. The only problem was to combine and connect these two to make a perfect Marriage!!

One needed an interface to overcome the problems of a GC operating at atmospheric pressure and a Mass Spectrometer operating under vacuum. Many Interfaces have been developed and this history repeated itself with the introduction of LCMS and it's many interfaces and special ionization methods. Next sheet provides an overview of some GC MS interfaces.



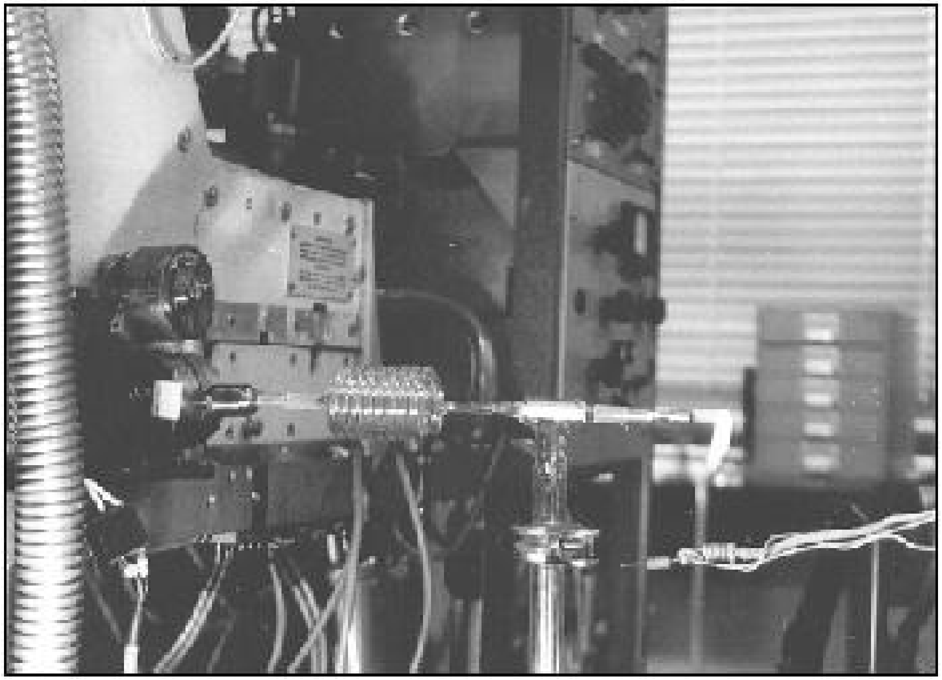
GC-MS: A POWERFUL TOOL IN ANALYTICAL CHEMISTRY 211

Fig. 1. Schematic survey of the different interfacing techniques used in GC–MS. (A) Open split coupling; (B) vacuumcoupling; (C) jet separator; (D) frit separator; (E) slit separator; (F) membrane separator; (G) Teflon separator; (H) electrolytic silver–palladium separator.

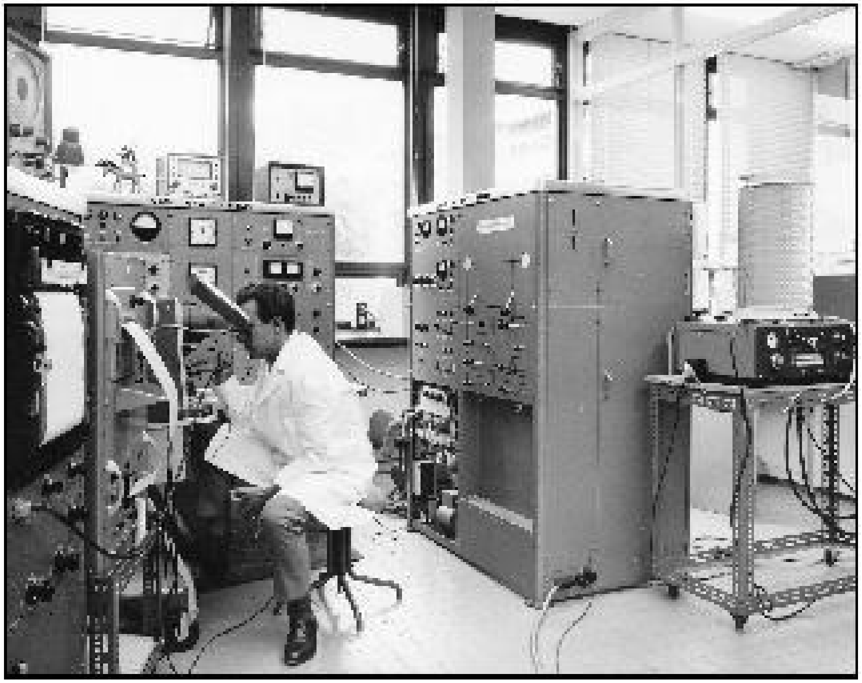
The main job of these interfaces was to separate the compounds from the carrier gas and transferring it with a minimum loss into the ion source, while at the same time not affecting the properties of the GC, mass spectrometer, and compound (with respect to resolution and decomposition). The same problems occurred later on in the development of LCIMS.

Dr. C. Engel, director of CIVO-TNO recognized the great potential of this technique in flavor research for the identification of unknown compounds. He started in 1962 in the instrumental analysis department, buying the first commercial available GC/MS, the ATLAS MAT CH4.

Dr. C. Engel

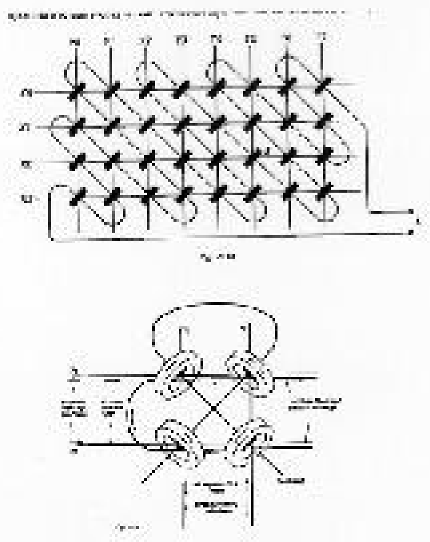


Experimental setup fritte separator



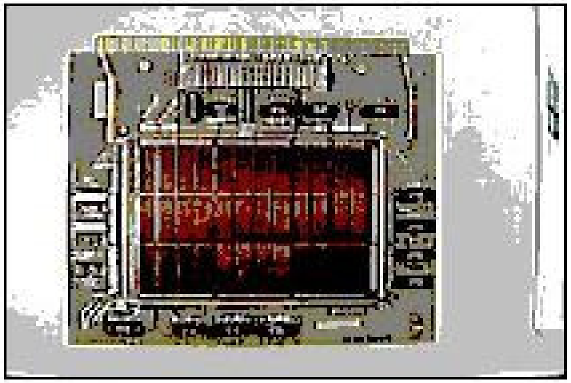
ATLAS MAT CH4 GC/MS at CIVO TNO Zeist, mass range 1-800 resolution 1000, scope and galvanometer recorder etc.

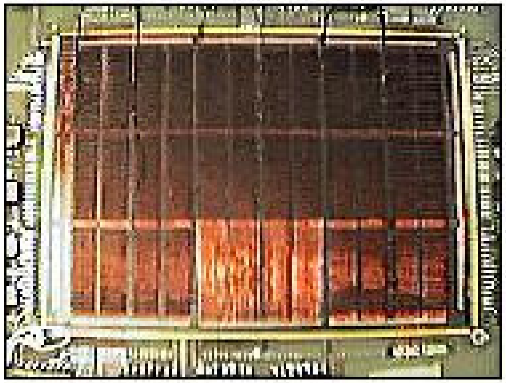
In the early work with GC/MS we were overloaded with avalanches of data or mass spectra which had to he looked at and interpreted. One needed almost l persons to perform such an analysis, one looking in a scope, one focusing on the total ion current chromatogram and the 3rd, catching the spectra on the UV paper, shooting out of the galvanometer recorder at a speed of 1 meter per second! This person had to number the spectra corresponding with the number of the eluting GC peak. If it was a complex GC capillary chromatogram it became sometimes quite messy. Very often one had to repeat the whole GC analysis because at the moment supreme when an important component eluted from the column, the galvanometer recorder runs out of UV paper, following Murphy's Law.....



Magnetic core memory

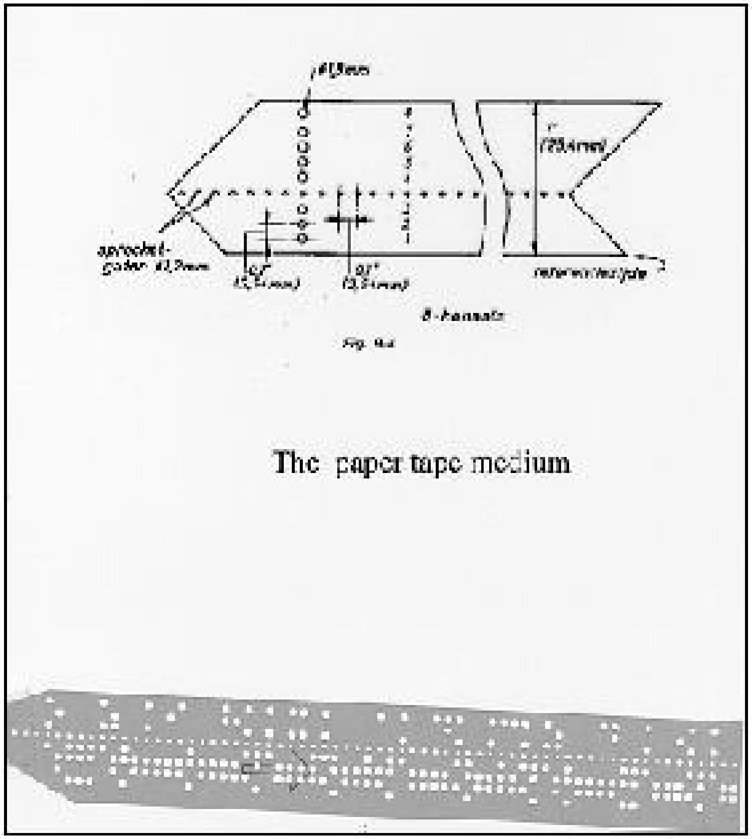
Memories……



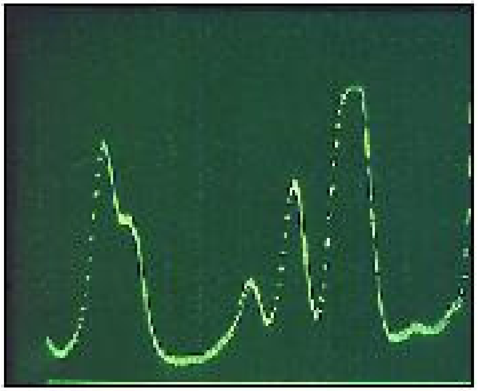


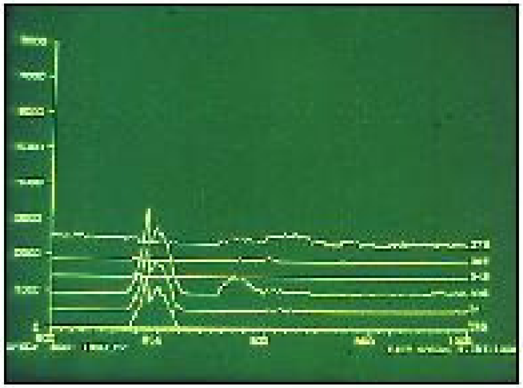
In 1970 we got the first data system; a Varian 620i ss100 to help us out of our misery. These systems were really a great help. Now all the GC and MS data could be stored via the computer on a big magnetic tape and later evaluated wher1 the GC/MS analysis was completed. These systems were primitive and large, when you compare them with your PC at home today. The software was written in machine language and was loaded from paper tape. The process memory was 8k, 16 byte, two blocs of 4k magnet core memory (your PC has 32 MB memory). The left image shows the principle of such a core memory, consisting of thousands of small magnets. Ferrite rings which can be polarized in two directions indicating a zero or a one 0-1. The right images show such a memory board where you could actually see the ferrite rings with a magnifying glass. Costs in 1970: HFl.14000,=. So, much has been changed over the last 30 years.

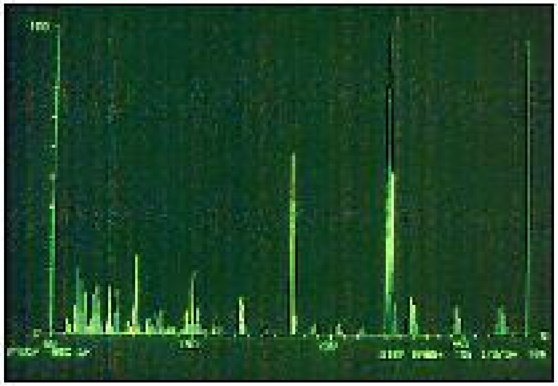
This sheet shows the data system SS100 complete with exhausted operator, tape plotter and memory scope.



The paper tape medium

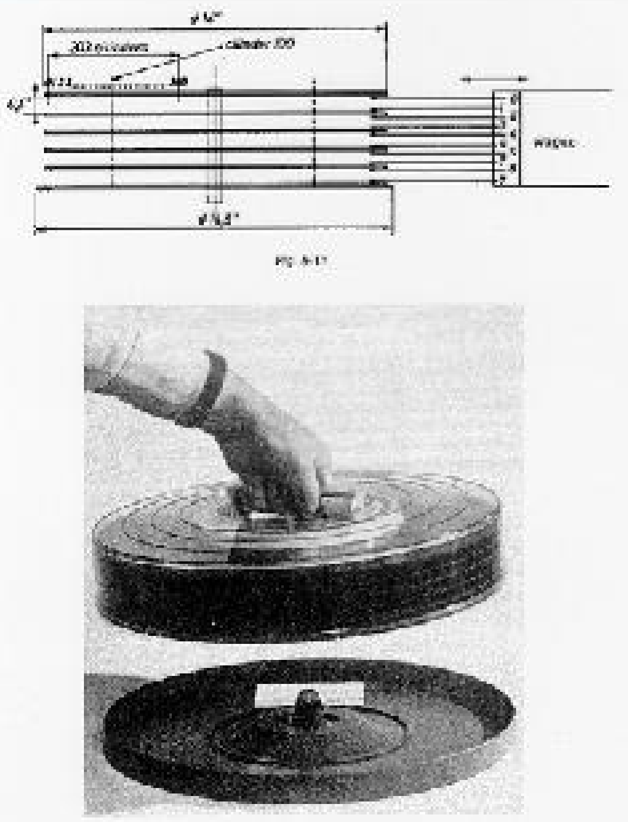






Here we see 3 images of an early GC/MS analysis of a cormorant liver extract injected on a packed column. Displayed are the total ion current, a mass fragment gram of three characteristic masses of octa CL styrene and the mass spectrum, which could also be corrected for interfering compounds by spectrum subtraction.

The storage of data, however, was still primitive; it was paper tape and/or magnetic tape at first, and then we got the first disc drives with removable discs having the astounding capacity of 5, 10, 28 MB shown here.

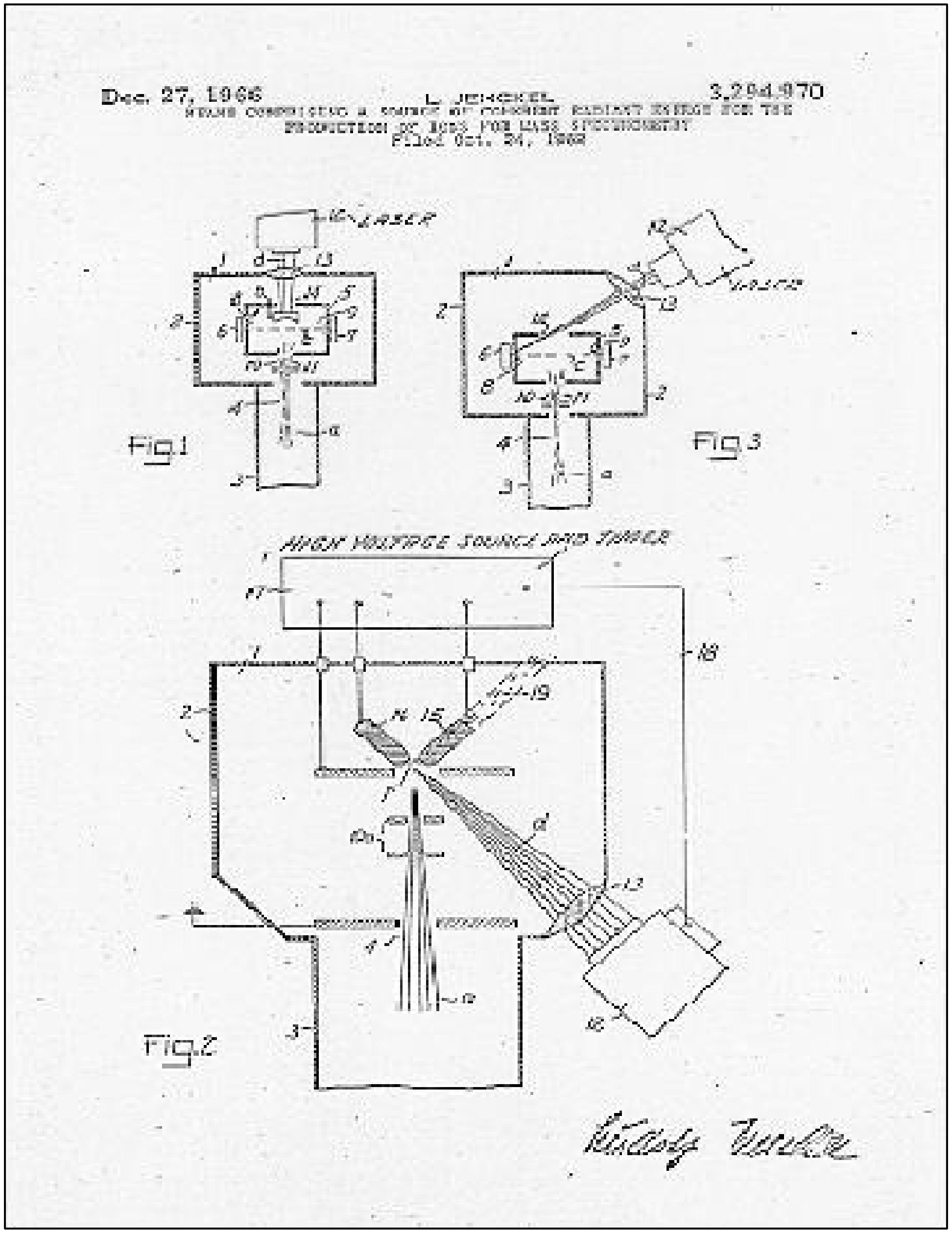


Removable disc 28 MB. 1971

Here we see Jaap Bouman changing a 10 MB disc on the SS300 system (RKU7 with the dimensions of a dish washer!!)

Today; 20 years later, your PC has a hard disc of 10 Gigabytes (you can put in your pocket) and you run around with zip disc's in your pocket or CD's haying a storage capacity of 100-600 MB. The storage needed for the Software, however, has grown considerably compared to the machine language written Software in 1970.

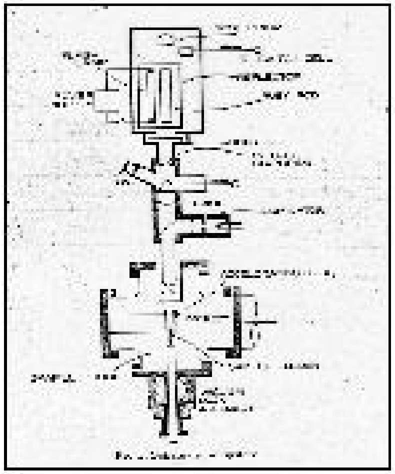
I leave the computer business for what it is and will now talk a little bit about a few MS applications!

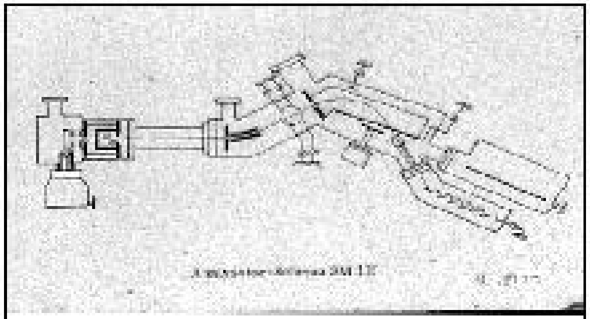


At TNO we had a broad spectrum of analytical problems to solve and that of course also goes for many other laboratories. So we explored many different techniques. There were problems for example 'with the ionization of non-volatile organic compounds.

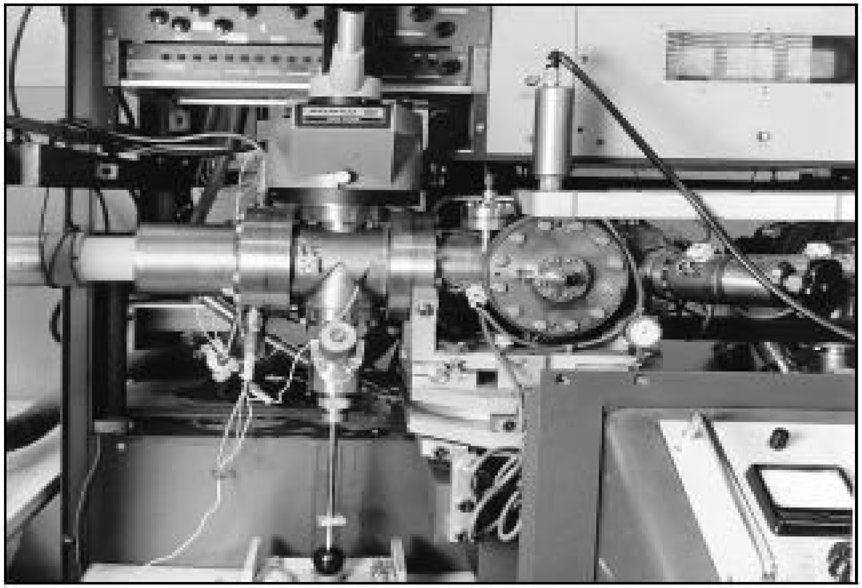
In the mid sixties there were already scientists envisaging the application of lasers for fast evaporation and ionization of non volatile compounds in a mass spectrometer. Dr. Jenkel, the founder of MAT, applied already in 1966 for a patent covering all kind of laser applications in MS. In such applications we have to deal with very fast processes which brought about the need for a very fast or integrating detector. Mass Spectrometers with photo plate detection or TOF's were the only instruments in those years. Later on channel plates and array detectors became available making life much easier.

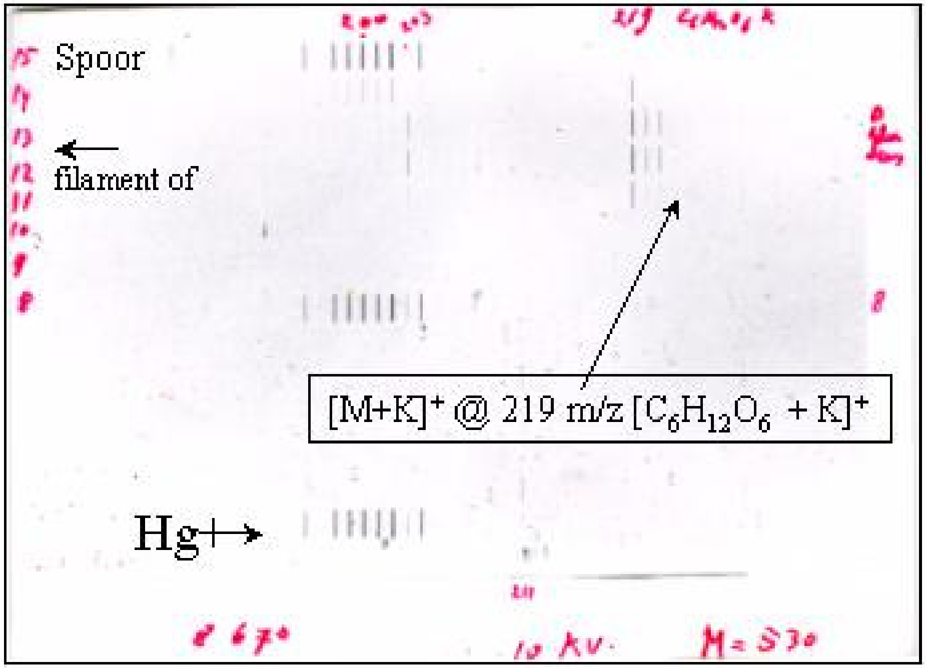
At TNO we modified our SMI ion source and made some promising measurements using a Neodymium-Glass pulsed laser 1.06 μ wavelength. The drawings provide a schematic of the modified SM1. The machine and its operator are shown in action below. (TNO-CIVO Zeist Atlas MAT SM1)





Scematic ATLAS MAT SM 1H

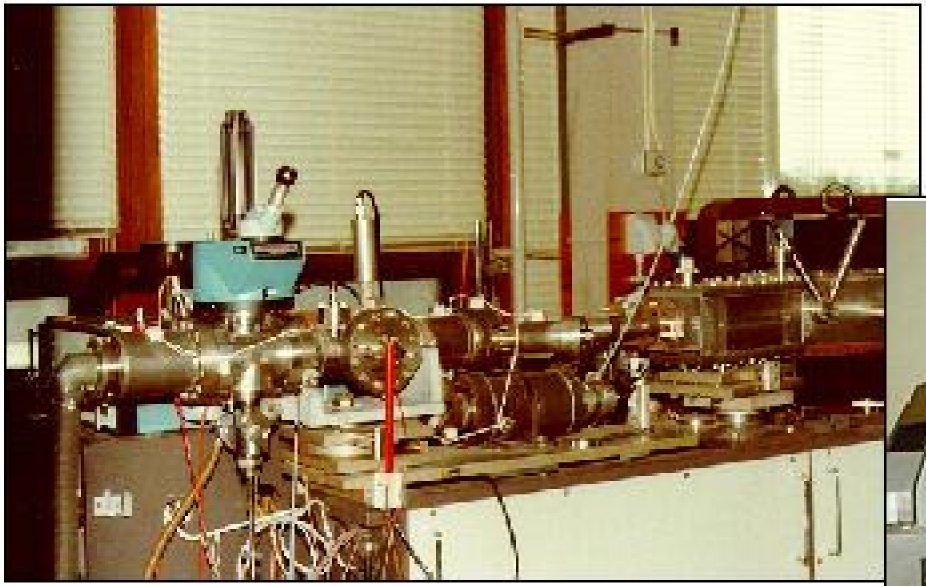




Photoplaat detectie sporen.

ATLAS SM1 en 1.06u Laser ion source.
(TN0 1970)

The figure on the left shows the photo plate spectrum of a laser desorption and ionization experiment performed in 1970 with filament on showing the mercury Hg lines, filament out produced for the first time the $[M+K]^+$ ion of glucose, saccharose, and some nucleotides. On the MAT 7'31 with Laser Source 4 laser shots per minute was the maximum. These experiments were sometimes very frustrating. You could not exactly see what you were doing, Only in the darkroom when developing your plate one could see if there was a result, Sometimes you measured all morning finding out later that the photo plate was put with the wrong side up, in the mass spectrometer, yielding in a clan plate ‘without any lines. Or the plate dropped right out of your fingers In the dark room!!!! Later on with the channel-plates combined with a vidicon, you could immediately see what was going on, if you had a result.

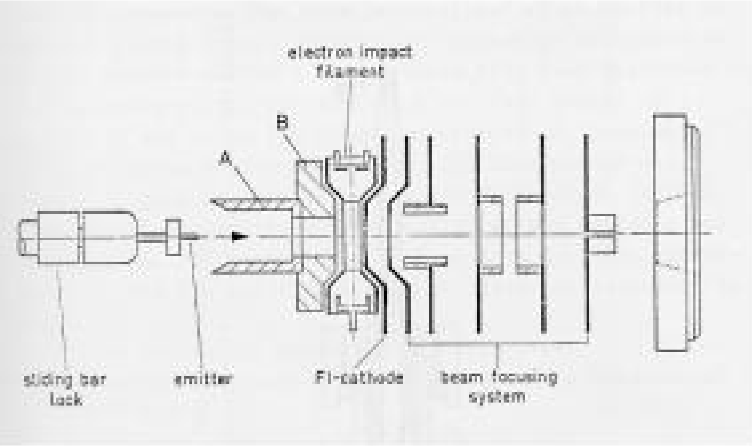


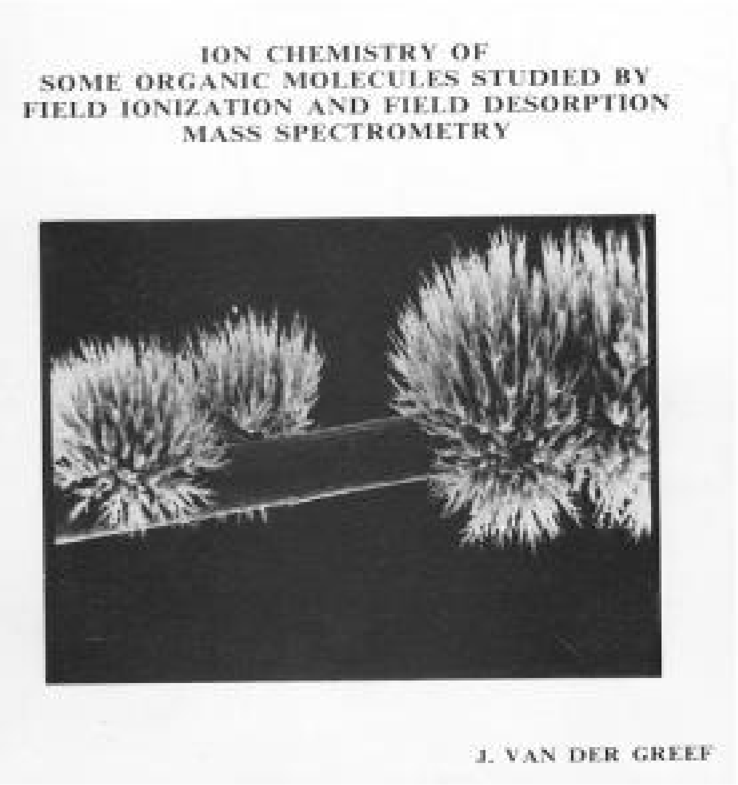
MAT 731 with Laser Source

Computer controlled Leitz comparator

It was also possible to measure very accurately the distances between the mass lines (ref-unknown) and calculate their ct masses and element composition. To do this also very sophisticated equipment was needed. The right figure shows such equipment; the computer controlled Leitz comparator. At TNO Rijswijk and RIVM where similar instruments in use. The project faded away for a certain time as the laser, small Mass range, and lack of money existed as limiting factors.

Hillenkamp and Karras started applying matrices and sophisticated lasers on time of flight mass spectrometers and made the great breakthrough 17 years later. At TNO the method is again in use and we now have our Sonja Jespersen who just obtained her PHD on the subject!



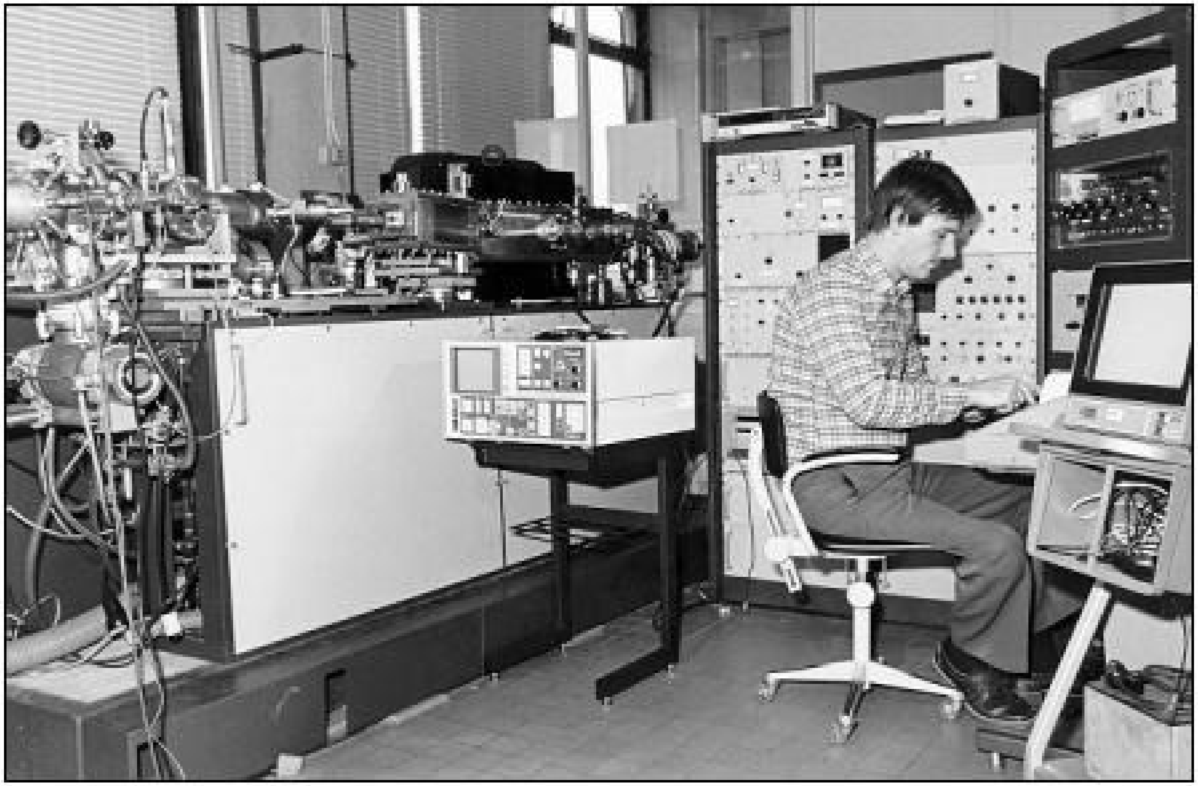

ION CHEMISTRY OF
SOME ORGANIC MOLECULES STUDIED BY
FIELD IONIZATION AND FIELD DESORPTION
MASS SPECTROMETRY

J. VAN DER GREEF

Field desorption

An other interesting ionization method for non-volatile and insatiable compounds was Field Desorption, a method developed in 1969 By Prof. Beckey and his group in Bonn. This method was also practiced at the Univ. of Amsterdam in Nico Nibberings group, at the RIVM and at TNO. It is hardly in use anymore because it is not a robust method and requires extremely skilled people to do it.

The sample was deposited on a very thin special prepared wire (5 µ). On these wires crystals are grown with very sharp needle whiskers. This was the critical pan. of the experiment, namely the preparation of the so-called field emitters. Lauretz Gramberg and Jan van der Greef were really the magicians able to do this job. These emitters are put on a very high voltage (10 kV) creating around these sharp needles Whiskers a field strength of several hundred thousand volts/cm pulling out an electron of the molecule, through tunneling effects. This resulted in a molecular ion which is accelerated into the mass spectrometer, producing that way, a nice molecular ion peak.
The method however, is tricky and requires magic fingers and nowadays FD is superseded by more robust and efficient methods like Electrospray ionization (ESI).



Here we observe a young enthusiastic researcher hammering on his TTY trying to restart the data system after one of the many crashes caused by high voltage sparks. Jan van der Greef is always very positive about the application of Mass Spectrometry in many different disciplines. He became a Professor at the University of Leiden at the faculty of bio-pharmaceutical sciences. One of his favorite statements is:

"In mass spectrometry there are no problems, only challenges!!!!!"

We see him here preaching!

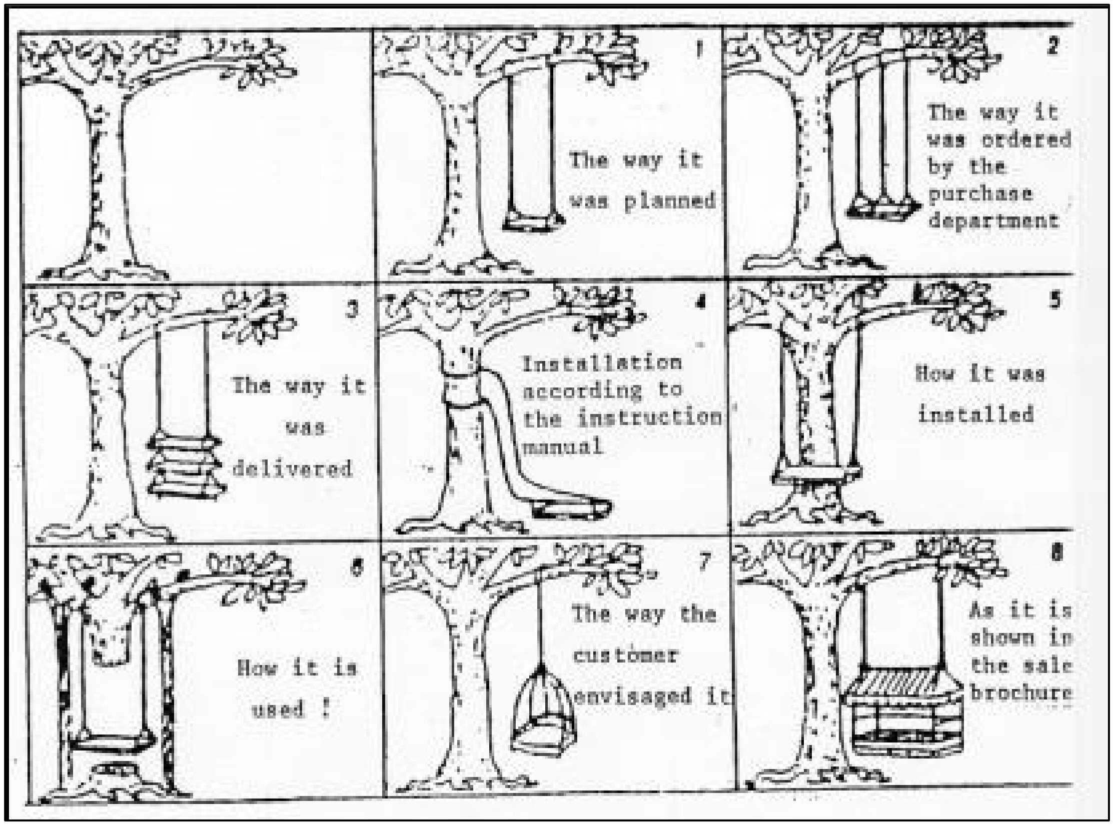
The TNO group dream team

1983

1999

Buying equipment

There is one aspect of our Mass Spectrometry community that I want to mention and that is “Buying Equipment”. This was always a nice opportunity to travel around the world visiting different countries and manufactures. One of the favorites was the Japanese JEOL company. It was a pity that there were no factories in Hawaii (that problem was however solved by organizing some Congresses). Below an illustration is shown of the different phases of a mass spectrometer purchase which one had to endure. The way it was planned, the way it was ordered by the purchase department (if possible avoid that department), then you had the way it was delivered, installation according to the instruction manual by a service engineer who himself saw the instrument for the first time at your site, how it was relay installed, the way it was finally used, how the customer envisaged it and last but not last how it looked in the brochure.



The Mass Spectrometrist

Mass Spectrometrists are also a peculiar breed of human beings. A definition of such a person I once heard was:

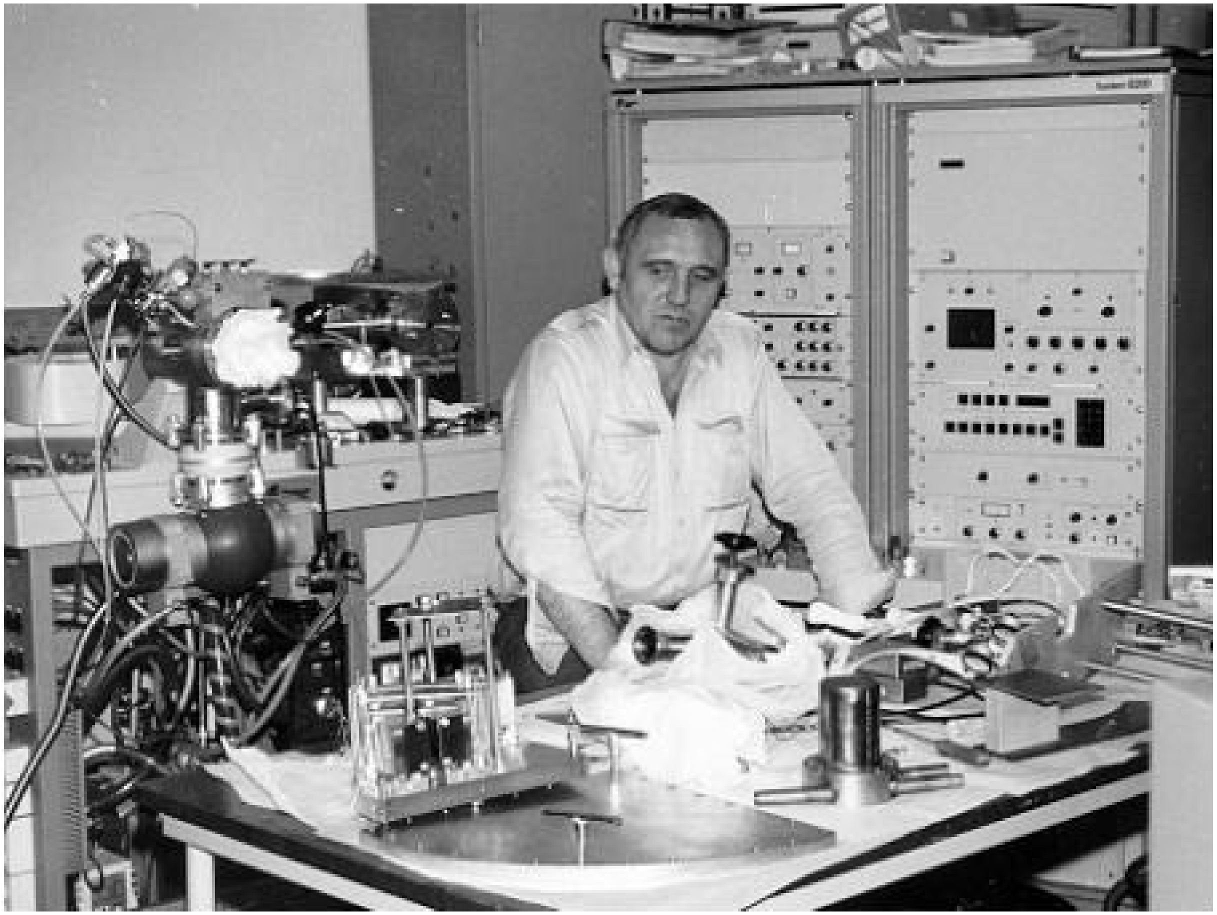
> *"A Mass Spectrometrist is a person who talks to a chemist about physics, to a physicist about chemistry and with a colleague about sex".*

So the sales people of the MS industry found a way to distract our attention a little bit from the real problems when you had to make up your mind choosing an instrument. One of these seductive methods are shown below.

Presentation MAT44

and customer TU Delft

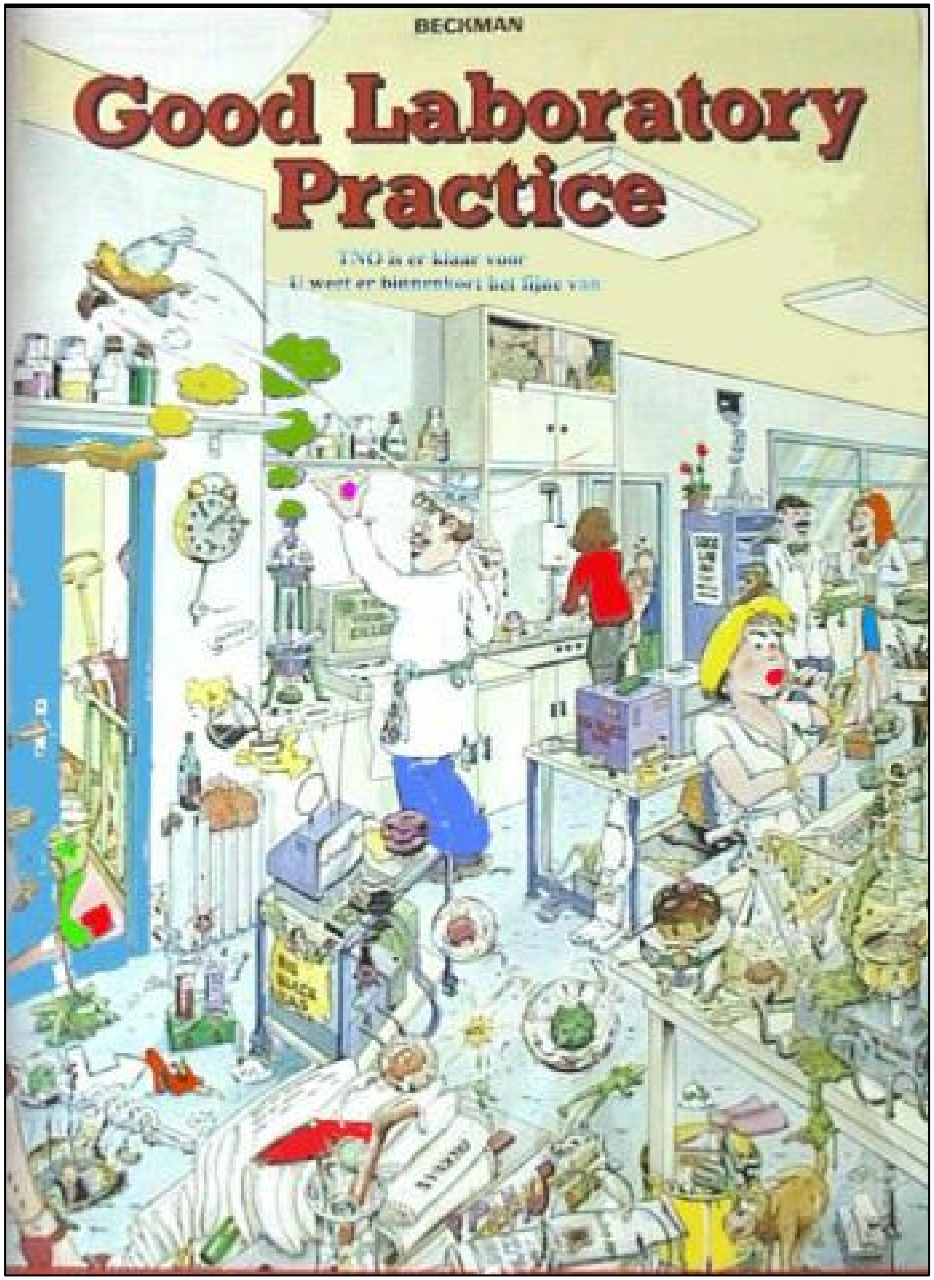
There is one person of the Dutch sales force that I want to memorize and that is our late Fred van Loenen. I worked with and knew him for more than 30 years. Everybody from our MS society had somehow the privilege of dealing with him. It was said that you bought your instrument not from a certain from but you bought it from Fred van Loenen. This thesis proved to be true when Fred left Finnigan MAT and went to Fisons. Their sales figures increased rapidly while those from Finnigan MAT dropped. Fred had the ability to defend the customers' needs and the manufacturer's interests in an honest and balanced way. He was a very good interface between the two parties, and the manufacturer had to be aware that what sales had promised, sometimes put the engineer in a very difficult position! As is shown in the next sheet of Mr. H. Katenkamp.



How do I get the instrument on specification promised by the sales department? Hr H. Katenkamp MAT8200

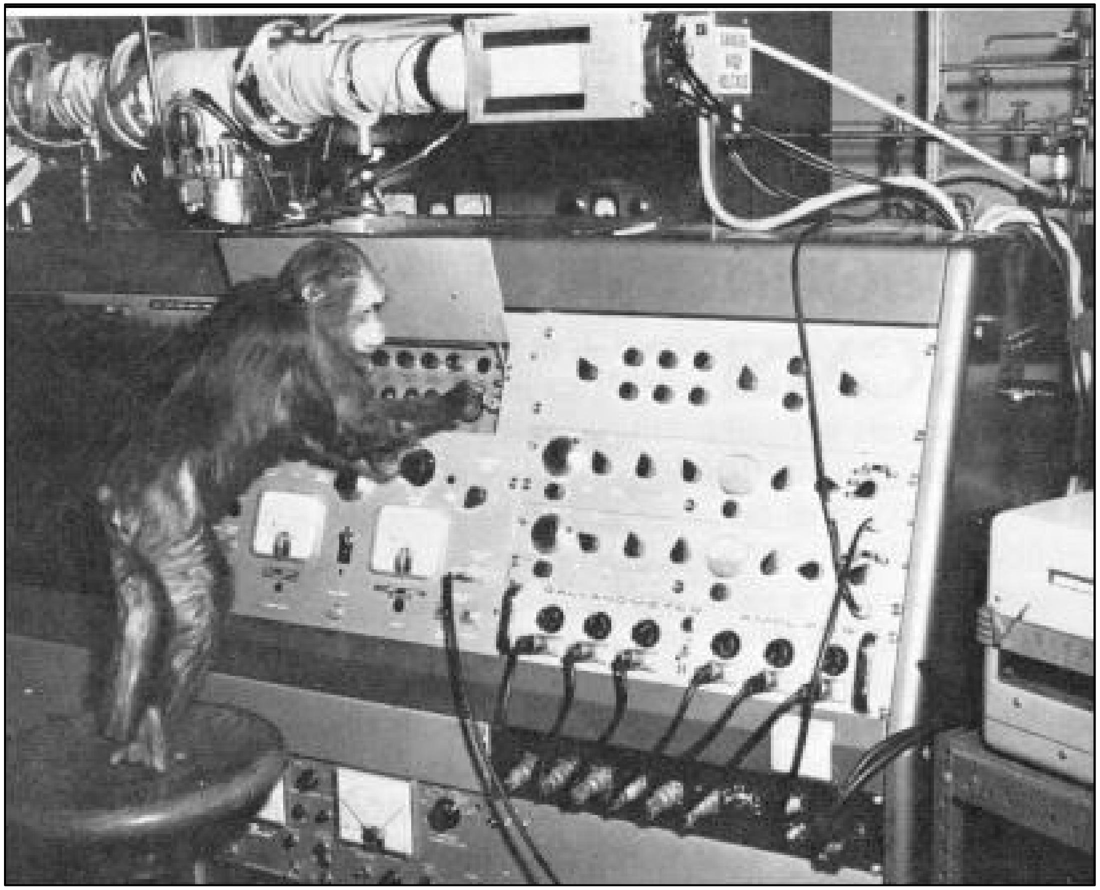
There is one highlight I almost forgot to mention and that was the organization of the 12th IMSC in 1991 in Amsterdam (1500 attendance) which is still a record to day. The right picture shows the organizing committee with our chairman Nico Nibbering. On the left we see the audience of the 3rd IMSC held in Brussels in 1970.

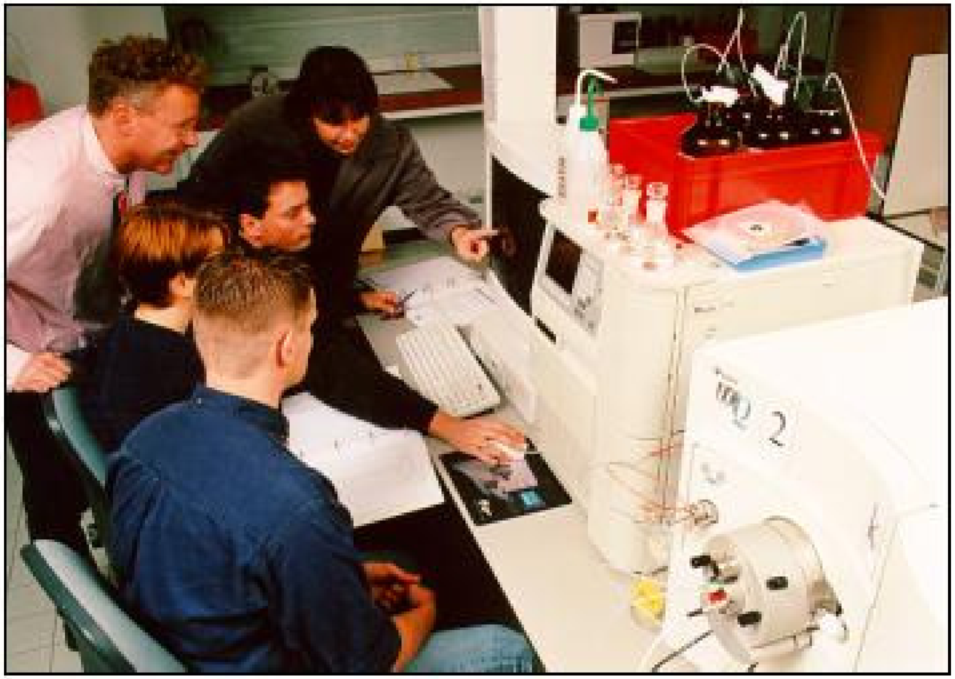
I am coming now to the end of my story. We have seen mass spectrometers evolve into highly sophisticated analytical tools. They started, as we saw, as desktop models, evolved to very big machines, and shrunk back again to tabletop models having perhaps a 100-fold increase in analytical power. It is almost impossible to do your work without them. The quality and user friendliness has been greatly improved, no buttons, switches etc. needing skilled physicists and operators to optimize the instrument, only a keyboard, a computer and a good analysis protocol giving you access to the mass spectrometer. The computer even performs the optimization of the instrument. There is, however, a black side to this fast development and increase in applications. Where do we get good mass spectrometrists, keeping up with the demand from the market? The universities are reducing their capacity to deliver well educated new mass spectrometrists, so they have to be trained on the job. The modern computer-controlled systems always produce plenty of data and these data have to be interpreted and evaluated backed up by experience and intelligence. GLP procedures do not overcome these problems!!!!!



The young generation is hardly given any time in order to grow into the field of analytical mass spectrometry and therefore it is necessary that there are good training facilities where they learn how to look at the obtained data and interpret them showing them all the pitfalls and interpretation errors you can encounter. These courses should have a good theoretical and practical part. Bill Mac Fadden, a GC/MS pioneer in the flavor research (and also the father of the moving Belt present at our exhibition), already had problems getting skilled personnel in the late 60s. Here we can see how he solved that problem:

He extended his human resources to the annex animal house!!!!!





Well, such training courses and workshops can be a lot of fun and very beneficial when people from different laboratories meet each other. Talking about their different problems and building their own user network for the future. On the left we see enthusiastic students at an LC/MS course. The only complaints are the costs involved. Management having a more long-term view can save a lot of money, much more than the course expenses, having a good-trained work force avoiding costly mistakes.

And I wish the coming generation all the success they need, enjoy your work, because it is still a really challenging time exploring new fields. We A started with mass ranges up to mass 100 and nowadays we surpass the 300,000 and the end is not yet in sight.....

I wish you all the best and thank you for your patience and attention!!!!