Il mio viaggio attraverso la gascromatografia capillare



Koni Grob

Kantonales Labor Zürich

EFSA, Parma



Short CV

- born in 1949 (I'm soon 73)
- 1969-1975: study in chemistry
- 1977/78: thesis in plant physiology
- 1971-1974: teaching chemistry at gymnasium
- 1974: capillary GC analysis of cigarette smoke at BAT, Southampton, UK
- 1974-2014: Kantonales Labor Zürich, up to 1998 in part time, full time up to 2014
- 1980-2004: consultant for Carlo Erba Strumentazione, Rodano/Milano
- 1975-2010: teaching more than 200 courses on GC all over the world
- 1996-2004: personal consultant for EU legislator for food contact materials, Brussels
- 2006-2016: expert for the French food safety authority
- 2008-2021: expert for the German food safety authority
- 2004-today: expert in working groups of the European foods safety authority (EFSA)
- 2014-today: EFSA Panel member CEF, now called CEP panel

1961: my father starts analyzing cigarette smoke by GC



My father, Kurt, teacher in chemistry at gymnasium, run a laboratory in a dark room of the school house.

Task: identification of the substance(s) causing cancer and finding filters to remove them.

Left instrument: American, not suitable, sent back. Right Instrument: Carlo Erba Model B, start of collaboration

I'm 13 years old



Start in my fathers lab

ISOTHERMAL ANALYSIS ON CAPILLARY COLUMNS WITHOUT STREAM SPLITTING

THE ROLE OF THE SOLVENT

K. GROB and K. GROB, JR. GC-Laboratory, ETH Zürich, EAWAG, 8600 Dubendorf (Switzerland) (Received March 8th, 1974)



Experiments on solvent effects

ON-COLUMN INJECTION ON TO GLASS CAPILLARY COLUMNS
1977

1974

K. GROB
GC-Laboratory, ETH Zürich, EAWAG, 8600 Dübendorf (Switzerland)
and
K. GROB, Jr.
Inst. f. allg. Botanik/Pflanzenphysiologie, ETH Zürich, Sonneggstrasse 5, 8092 Zürich (Switzer (Received September 5th, 1977)

First on-column injector constructed in Zürich



GC technology, mainly 1978-1995







EVALUATION OF INJECTION TECHNIQUES FOR TRIGLYCERIDES IN CAPILLARY GAS CHROMATOGRAPHY

K. GROB, Jr.

Kantonales Laboratorium, P.O. Box, 8030 Zurich (Switzerland) (Received June 21st, 1979)

DEGRADATION OF TRIGLYCERIDES IN GAS CHROMATOGRAPHIC CAPILLARIES: STUDIES BY REVERSING THE COLUMN

K. GROB, Jr. Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland) (Received October 8th, 1980)

PEAK BROADENING OR SPLITTING CAUSED BY SOLVENT FLOODING AFTER SPLITLESS OR COLD ON-COLUMN INJECTION IN CAPILLARY GAS CHROMATOGRAPHY

K. GROB, Jr. Kantonales Labor, P.O.

Kantonales Labor, P.O. Box, CH-8030 Zurich (Switzerland, (Received March 31st, 1981)

"BAND BROADENING IN SPACE" AND THE "RETENTION GAP" IN CAP-ILLARY GAS CHROMATOGRAPHY

K. GROB, Jr. Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland) (Received October 6th, 1981)

1981: retention gap technology

SOME TECHNICAL ASPECTS OF THE PREPARATION OF A "RETENTION GAP" IN CAPILLARY GAS CHROMATOGRAPHY

K. GROB, Jr.* and R. MÜLLER Kantonales Labor, P.O. Box, CH-8030 Zurich (Switzerland) (Received March 17th, 1982)

> Peak splitting owing to flooding (2 μL acetone on PDMS; poor wettability)



well visible in edged (whitish) glass capillary columns



development of press-fit connectors



SOLVENT TRAPPING IN CAPILLARY GAS CHROMATOGRAPHY

TWO-STEP CHROMATOGRAPHY

K. GROB, Jr. Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland) (Received August 19th, 1982)

Solvent effects

1982



COUPLING OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH CAPILLARY GAS CHROMATOGRAPHY

1984

HPLC

190°c

K. GROB, Jr.*, D. FRÖHLICH, B. SCHILLING, H. P. NEUKOM and P. NÄGELI Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland) (Received March 6th, 1984)



1990: Carlo Erba (Fisons) brings an automated LC-GC instrument onto the market (Fausto Munari; "Dualchrom")

The first HPLC-GC application: colorant in a tooth paste. 50 m x 0.35 mm i.d. precolumn.

100°C

3°/mir

270 µl cyclohexane

270 µL

(2)

solvent evaporation at 80°C

الر 150

Our HPLC-GC instrumentation 1984-1989



HPLC with pressurized solvent for filling backflush loop



1989: Carlo Erba Instruments came out with the Dualchrom, designed by Fausto Munari

In the 1990es we run up to 5 of these machines



"Transparent injector" to investigate sample evaporation in vaporizing injectors





"Gooseneck"-liner does not stop the sample liquid!

3 µl chloroform/perylene, 200 °C oil temperature, 366 nm



Inability of unpacked gooseneck liners to stop the sample liquid after injection with band formation (fast sampler) into hot GC injectors. S. Bieri, Ph. Christen, M. Biedermann, K. Grob. Anal. Chem. 76 (2004) 165

1988: Mineral oil residues in hazel nuts from jute bags



Swiss chocolate!



Application to edible oil, mainly 1988-1996



Determination of Raffination of Edible Oils and Fats by Olefinic Degradation Products of Sterols and Squalene, Using Coupled LC-GC

By Konrad Grob, Anna Artho, and Carlo Mariani* Kantonales Labor Zürich, Switzerland, and Stazione Sperimentale per le Industrie degli Oli e Grassi, Milano, Italy





1992



On-Line LC-GC for the Analysis of the Minor Components in Edible Oils and Fats – The Direct Method Involving Silylation

By Anna Artho, Konrad Grob and Carlo Mariani* Kantonales Labor, Zürich, Switzerland, and Stazione Sperimentale per le Industrie degli Oli e dei Grassi, Milano, Italy



Recognition of Adulterated Oils by Direct Analysis of the Minor Components

Konrad Grob, Angelo Maria Giuffré, Ugo Leuzziand Biagio Mincione*

Kantonales Labor, Zürich, Switzerland, Istituto di Microbiologia e Tecnologia Agraria e Forestale, Reggio Calabria, Italy, and Dipartimento di Chimica Organica e Biologica, Universita di Messina, Italy



The Detection of Adulteration with Desterolized Oils



Detailed sterene analysis Rapeseed oil

Two silicagel HPLC columns in series

K. Grob, M. Biedermann, M. Bronz, and C. Mariani Riv. Ital. Sost. Grasse 72 (1995) 49-54. Maurus Biedermann · Konrad Grob · Carlo Mariani Joachim P. Schmidt

Detection of desterolized sunflower oil in olive oil through isomerized Δ 7-sterols



The analysis of the $\Delta 8/14$ -sterols is tricky since they are difficult to separate from the $\Delta 7$ -sterols in HPLC as well as in GC. Δ 7-Sterols are fairly specific for sunflower oil. They do not dehydroxylate, but isomerize to Δ 8/14-sterols.



On-line LC-UV-GC-FID for the determination of Δ^{7-} and $\Delta^{8(14)}$ -sterols and its application for the detection of adulterated olive oils

M. BIEDERMANN, K. GROB KANTONALES LABORATORIUM - ZÜRICH - SWITZERLAN C. MARIANI STAZIONE SPERIMENTALE PER LE INDUSTRIE DEGLI OLI E DEI GRASSI - MILANO

For an accurate transfer of the $\Delta 8/14$ -sterol fraction from HPLC, the Dualchrom offered the function of relative retention time, in this case used with the $\Delta 7$ sterols.

Recognition of mild deodorization of edible oils by the loss of volatile components

Konrad Grob¹, Maurus Biedermann¹, Marianne Bronz¹, Joachim P. Schmid²

¹ Kantonales Labor, P.O. Box, CH-8030 Zürich, Switzerland

² Givaudan-Roure Research Ltd, CH-8600 Dübendorf, Switzerland

Received December 20, 1993

HPLC-GC-FID

1993



On the origin of benzene, toluene, ethylbenzene and xylene in extra virgin olive oil

Maurus Biedermann¹, Konrad Grob¹, Gianni Morchio²

¹ Kantonales Labor, P. O. Box CH-8030 Zürich, Switzerland ² Oleificio Sasso-Nestlé, I-18100 Imperia, Italy

Maurus Biedermann · Konrad Grob · Gianni Morchio

On the origin of benzene, toluene, ethylbenzene, and the xylenes in virgin olive oil – further results

With tiny filters of charcoal and thermal desorption into GC we analyzed ambient air in the area of the olive trees as well as in the localities of storage of olives and the oil production. Ambient air is a source, but the main source was gasoline escaping from engines. 1995

Food contact materials: 1996 onwards

Bisphenol-A-Diglycidyl Ether (BADGE) in Edible-Oil-Containing Canned Foods: Determination by LC-LC-Fluorescence Detection

> Key words: Bisphenol-A-diglycidyl ether, BADGE, Canned foods, Epoxy coatings

Maurus Biedermann, Konrad Grob, Marianne Bronz, Raffaele Curcio, Matthias Huber and Fatima Lopez-Fabal Official Food Control Laboratory of the Canton of Zürich (Kantonales L

On analyzing an "olive oil" in a can of tuna for admixture of sunflower oil by the Δ8/14 stigmastenol method, a peak interfered in HPLC as well as in GC: bisphenol-Adiglycidyl ether (BADGE).

BADGE exceeded the then valid migration limit up to 8000 times (then considered genotoxic)!

Further investigations revealed that the migrants from can coatings that had not been assessed for safety!



Fluorescence

detector

Pump 1

This changed our focus for the years to come on food contact materials

LC on CN-column

LC on silica column

Migration from an epoxy-phenolic can coating

simulated migration for oily foods; NPLC, fluorescence detection





Comprehensive NPLC-GC

Cresol-phenol resin

Preseparation by NPLC, fractions separated by GC-FID.

2006



Migration from the (PVC) gaskets of lids into oily foods 2005-2008

PVC gasket tightening against glass jar





Swiss market survey June 2005

- •158 samples taken from the market
 - >3 % oil, non-emulsified (no mayonnaise)
 - contact with lids

•147 outside the limits (limit)

- 91 with ESBO >60 ppm (60 ppm), mean 216 ppm, max. 1170 ppm
- 17 with DEHP >3 ppm (1.5 ppm), 15 >180 ppm, max. 825 ppm
- 12 with **DIDP** >9 ppm (9 ppm), 7 >60 ppm, max. 740 ppm
- 9 with DINP >120 ppm (9 ppm), mean 175 ppm, max. 270 ppm
- 8 with **DEHA** >18 ppm **(18 ppm)**, max. 180 ppm
- 9 with **non-authorized** plasticizers

Another disaster for compliance!



2002-2007 Acrylamide



Rösti (hashbrowns)

Same potato lot, but..

Left

- Storage at 10 °C
- Red. sugars 0.2 g/kg
- Acrylamide 140 µg/kg

Right

- Storage at 4 °C
- Red. Zucker 3.1 g/kg
- Acrylamide 1020 µg/kg

Fatty acid methyl and ethyl esters as well as wax esters for evaluating the quality of olive oils

100 +Wax esters 24-18:X (mg/kg) 80 + + + + 40 Extra virgin Devaluated extra virgin Raffinate Preserve + * Preserve extra virgin 0 20 30 40 10 50 0 Wax ester 24-16:0 (mg/kg)

Fig. 5 Wax ester 24-16:0 against the wax esters 24-18:X for various types of olive oils



Fig. 4 Summed concentrations of the straight chain wax esters with C_{22} - C_{28} alcohols plotted against the sum of the methyl and ethyl oleate in 40 olive oils sold as extra virgin quality and three refined oils; limits suggested by Mariani [17]

Maurus Biedermann • Annette Bongartz • Carlo Mariani • Koni Grob

2008: Back to olive oil with Mariani



Wax ester fraction of edible oils: Analysis by on-line LC-GC-MS and GC \times GC-FID

Maurus Biedermann¹, Paul Haase-Aschoff² and Konrad Grob¹

2008

¹ Official Food Control Authority of the Canton of Zurich, Zurich, Switzerland ² Labor Dr. Haase-Aschoff, Bad Kreuznach, Germany



Safety assessment: 2006 onward

Two unassessed cases as examples

Trans-Diene and Triene Fatty Acids in Edible Oils from Deodorization

Key words: Trans-diene and triene fatty acids, Isomerized fatty acids, Deodorization of edible oils

1996

Konrad Grob, Beat Grolimund, Marianne Bronz, Martin Brunner and Rolf Etter Official Food Control Authority of the Canton of Zürich (Kantonales Labor), Zürich

Linoleic and linolenic acid are essential for humans

Up to almost 70 % of the linolenic acid isomerized with at least one trans double bond as a result of physical refining, including in infant products

Trans double bonds disturbing their function?

Was the effect of high temperature during deodorization checked?

Effect of high temperature deodoration of oils

FAME from commercial soybean oil



Decolorated oils

Hydrocarbons from the isomerization/degradation of squalene, sterols and carotenes.

Did somebody check for adverse effects on human health?

Concentrations 10 to >100 ppm. As migrating substances from packaging materials, much tox data would be required.

There is a problem of coherence!



Squalene

Palm oil

Isomerized squalene + sterenes

Isomerized carotenes

Overall...

Mastering of analytical technology was the great advantage in my professional life

- best when developed by oneself
- today: insufficient education in chromatography and interpreting of mass spectra of unknowns
 - a problem because of lacking teachers: universities focus on novel technologies

At my time, extended studies of literature were unnecessary, since most things were new

• science tends to lose knowledge elaborated in the past

The safety of foods, their industrial preparation and their domestic cooking are poorly investigated

 disturbing discrepancy between safety requirements, e.g. of food contact materials, food additives and food