ORGANOCHLORINE RESIDUES, OECD PRELIMINARY STUDY 1966-67

METHODS OF ANALYSIS, AND EXAMPLES OF CHROMATOGRAMS

The method of analysis used in the Swedish programme is described in brief below.

1. Extraction

Homogenates: The homogenate (5 to 10 grams) was mixed with sodium sulphate and then extracted with n-hexane in a Soxhlet extractor. After evaporation, the fatty residue was weighed.

Individual muscles: A piece of muscle (sample size one gram) was placed in a test tube (8 ml) together with one ml of methanol and four mls of n-hexane. By means of a left-handed bore fixed on to a dental boring machine, the whole mixture was homogenized and centrifuged. The solvent was pipetted off and the procedure repeated. The hexane was evaporated in a stream of nitrogen at 40°C.

(All solvents used were checked to give acceptable blanks on EC).

2. Clean-up

The fatty residue was dissolved in methylene chloride so that 100 ul contained 10 mg of fat. 100 ul of this solution was applied as a band on a small thin layer plate (7,5 x 3,5 cm, 1 mm layer of silicagel). Methylene chloride was used as mobile phase and the layer above the fat front was scraped off and extracted in a short glass column with a mixture of n-hexane and diethyl ether 60-40 (v/v). Exactly one ml eluate was collected.

3. Gas-Liquid Chromatography

For quantitative analysis, 5 to 10 ul of the eluate was injected. Silanized glass columns were used throughout; length 180 cm, inner diameter 1,8 mm. Packing a) Gaschrom P AW/DMCS 100-120 mesh; sedimented in metanol in order to remove dust followed by application of the stationary phase, 4 % SF 96 (methyl silicone)

b) As above but stationary phase 8 % QF-1 (fluoro silicone).

4. Operating conditions for GLC

Instrument: Varian Aerograph 204

Temperatures: Injector: 207°C

Columns: (a) 201°C, (b) 182°C

Detector: 210°C

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Gas flow: Nitrogen adjusted to give pp-DDT a retention time of exactly 20,0 min.

Recorder: Speedomax H 1 mv, chart speed 15"/h
Detector: Electron-capture, tritium
Confirmations: After injection of two samples was injected a standard containing lindane, BHC, aldrin pp-DDE, dieldrin, pp-DDD and pp-DDT. The checking should give correct peak composition and rf values on both column (a) and column (b). Also a PCB standard was injected twice a day.

Further confirmation

Nitration method: A test tube containing an aliquot of the evaporated eluate, as above, was treated with a mixture of conc. sulphuric acid and conc. nitric acid (1:1, v/v) for 5 minutes at 0°C. After addition of crushed ice the mixture was extracted with n-hexane. 5 to 10 ul of the extract was injected into the GLC. - This method will leave the PCB, lindane and BHC unaffected.

Sulphuric acid method: The n-hexane extract of the one gram sample of tissue was concentrated to one ml, to which was added an equal volume of 90 % sulphuric acid. After shaking for several minutes and centrifuging at high speed the sulphuric acid phase was frozen, and the hexane layer decanted off and washed with water. After repeated freezing and decanting, the solution was injected into the GLC.

The sulphuric acid method is quantitative and rapid, but removes oxygen-containing compounds, including dieldrin, endrin and heptachlorepoxide. The method is especially suitable for the detection of small amounts of the volatile compounds, e.g. aldrin, lindane and BHC, since no steps of evaporation are applied. The sensitivity is as high as 0,001 ppm.

Discussion

It is usually assumed that pp-DDD and dieldrin are not present in Swedish samples. However, it is very difficult to state the absence of these compounds due to the interference of some of the PCB peaks. On SF-96 columns, the peaks of pp-DDD and dieldrin are covered by those of PCB no 7 and DDE, and in the case of QF-1 the interference is caused by the PCB-peaks nos 8 and 10.

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Relative retentions
(DDE, most often present in the samples, is taken as 1,0).

QF-1	SF 96	
0,35	0,22	Lindan
0,46	0,53	Aldrin
1,0	1,0	pp-DDE
1,48	1	Dieldrin
1,83	1,31	pp-DDD
2,0	1,79	pp-DDT
0,36	0,21	1
0,65	0,68	2
0,79	0,82	3
0,98	0,97	4
1,07	1,04	5
1,14	1,18	6
1,32	1,27	7
1,40	1,53	8
1,55	1,67	9
1,77	1,83	10
2,15	2,18	11
2,78	2,68	12
3,01	3,14	13
3,50	3,72	14

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Sept 14, 1967

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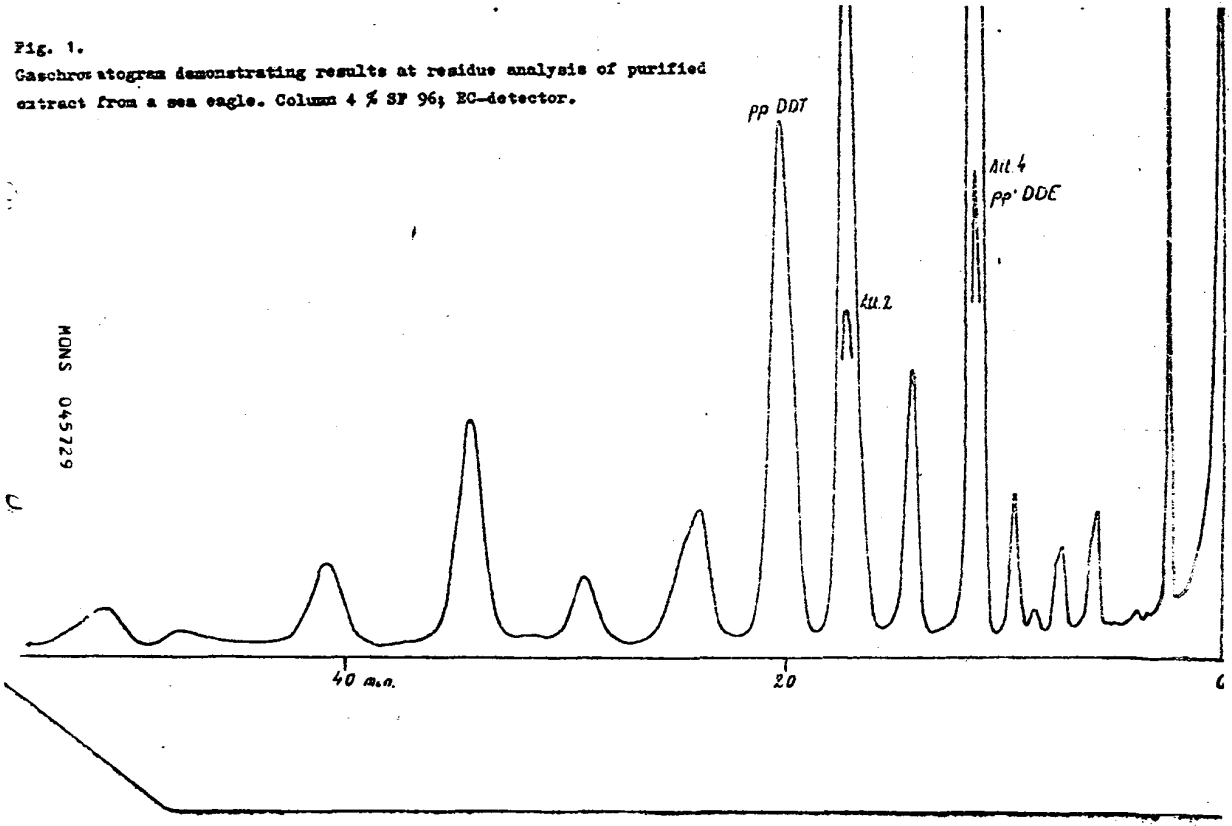
Fig. 1.
Gaschromatogram demonstrating results at residue analysis of purified extract from a sea eagle. Column 4 % SF 96; EC-detector.



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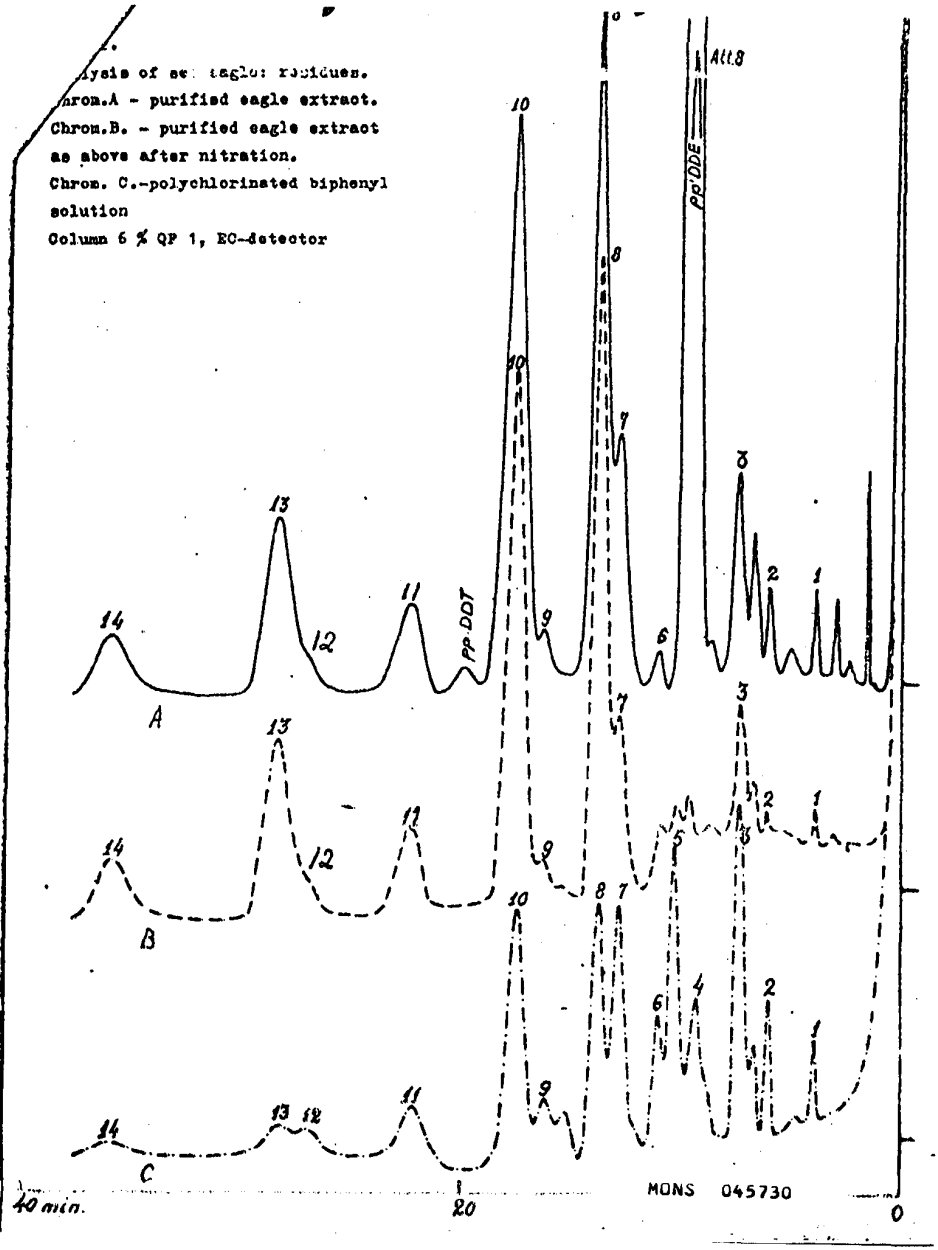

lysis of se eagle residues.
hrom.A - purified eagle extract.
Chrom.B. - purified eagle extract
as above after nitration.
Chrom. C.-polychlorinated biphenyl
solution
Column 6 % QF 1, EC-detector
Att.8
pp'DDE
pp·DDT
A
B
C
40 min.
20
0
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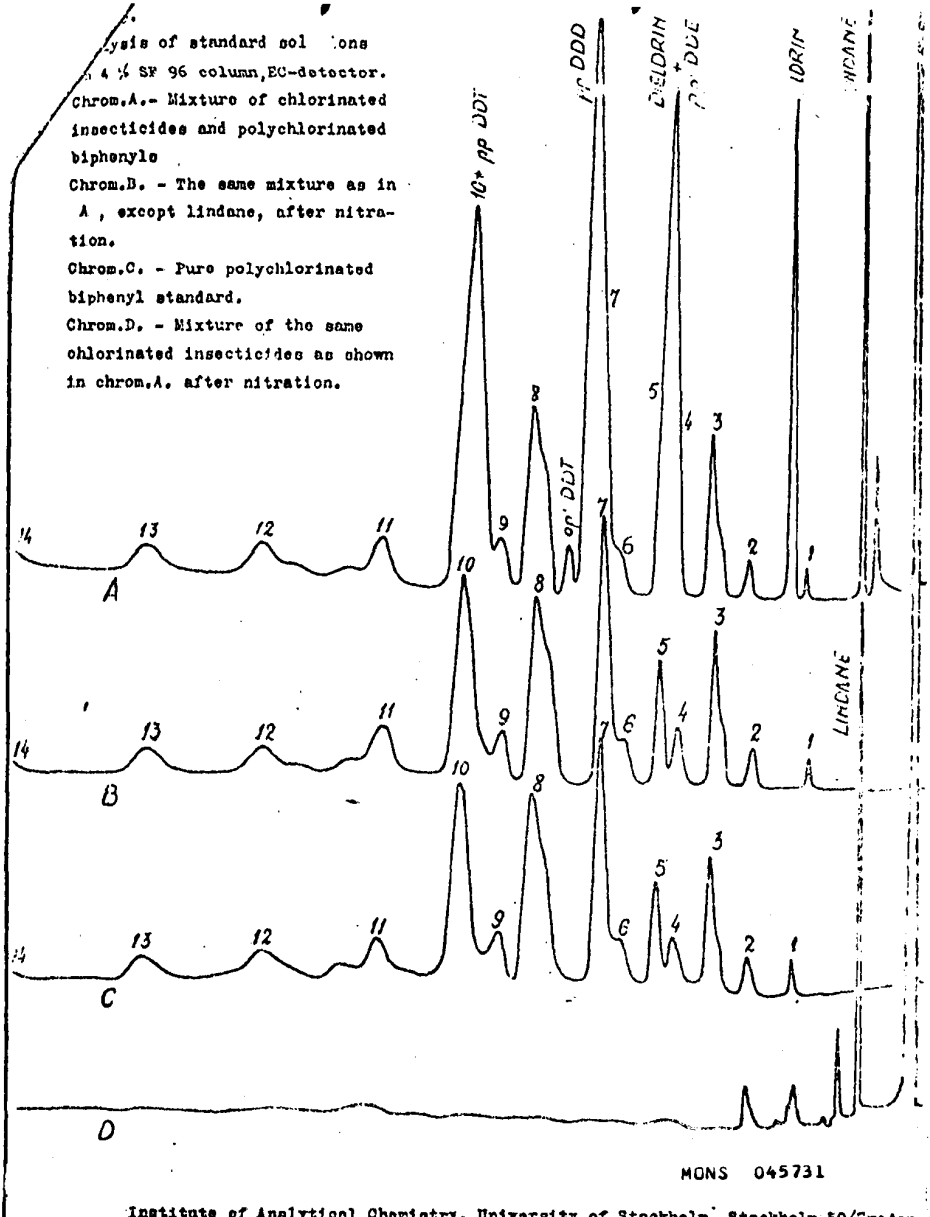

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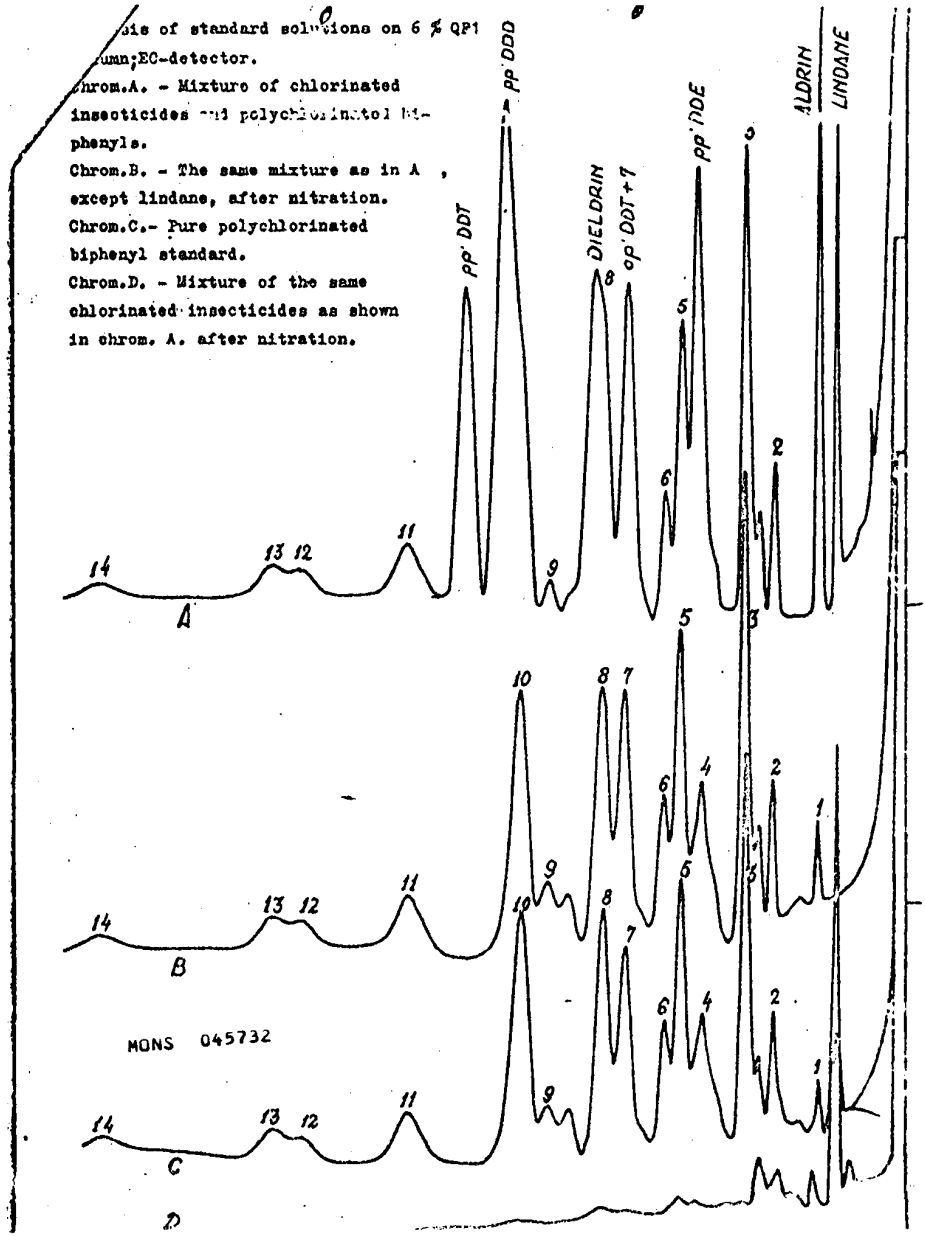
...sis of standard solutions on 6 % QF1
...umn;EC-detector.
...hrom.A. - Mixture of chlorinated
insecticides and polychlorinated bi-
phenyls.
Chrom.B. - The same mixture as in A ,
except lindane, after nitration.
Chrom.C.- Pure polychlorinated
biphenyl standard.
Chrom.D. - Mixture of the same
chlorinated insecticides as shown
in chrom. A. after nitration.
pp' DDT
pp' DDD
DIELDRIN
op' DDT+7
pp' DDE
ALDRIN
LINDANE
A
B
C
D
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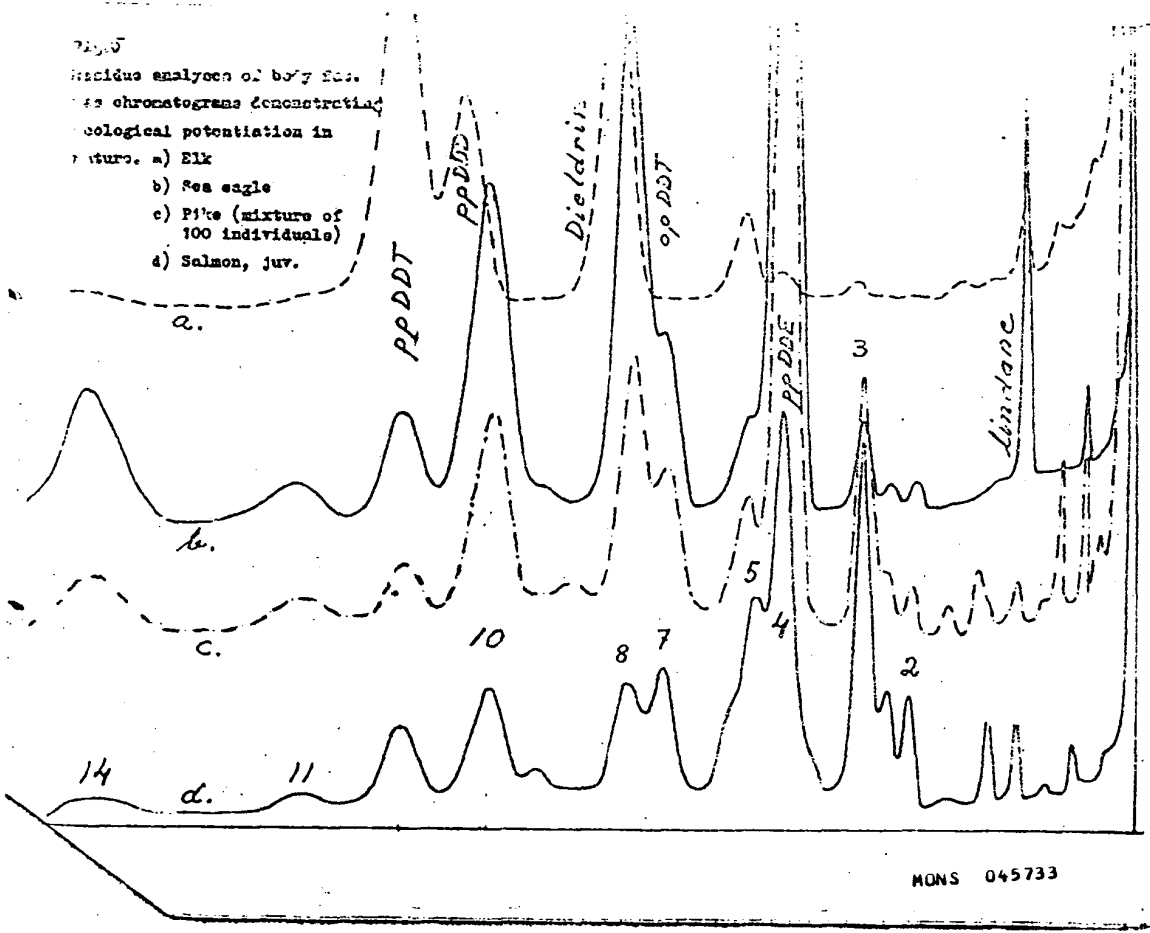

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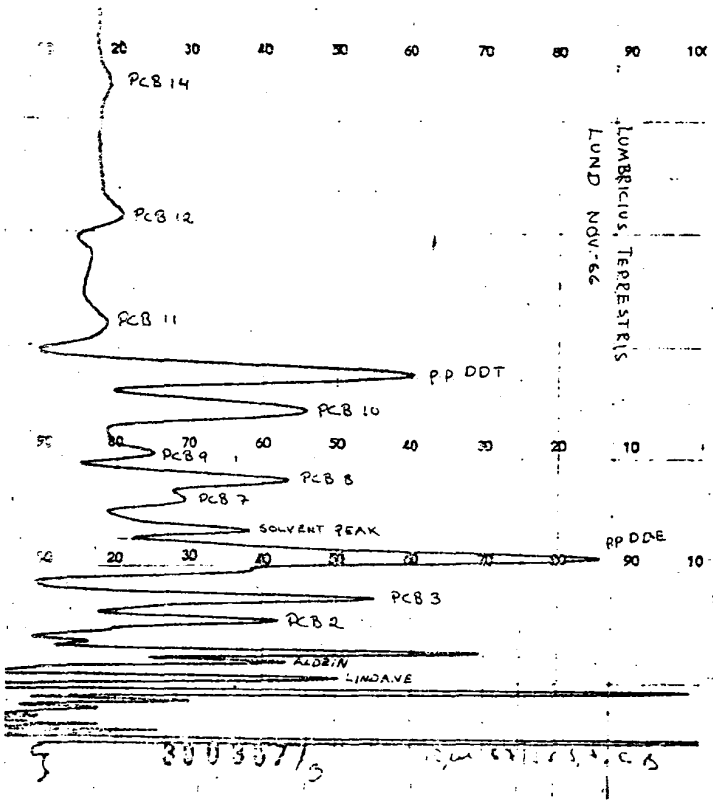

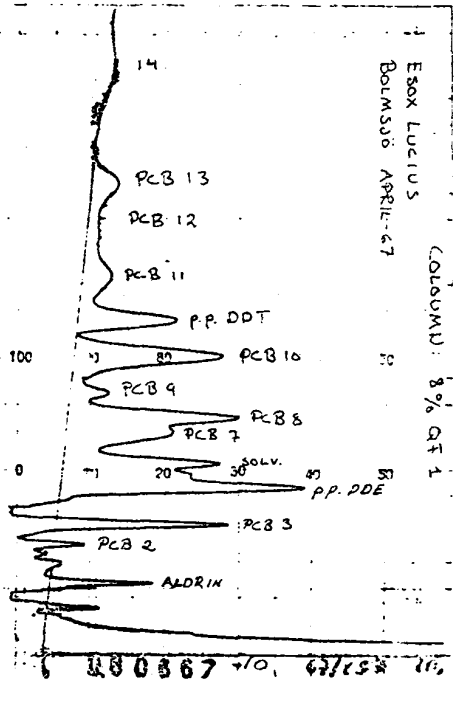

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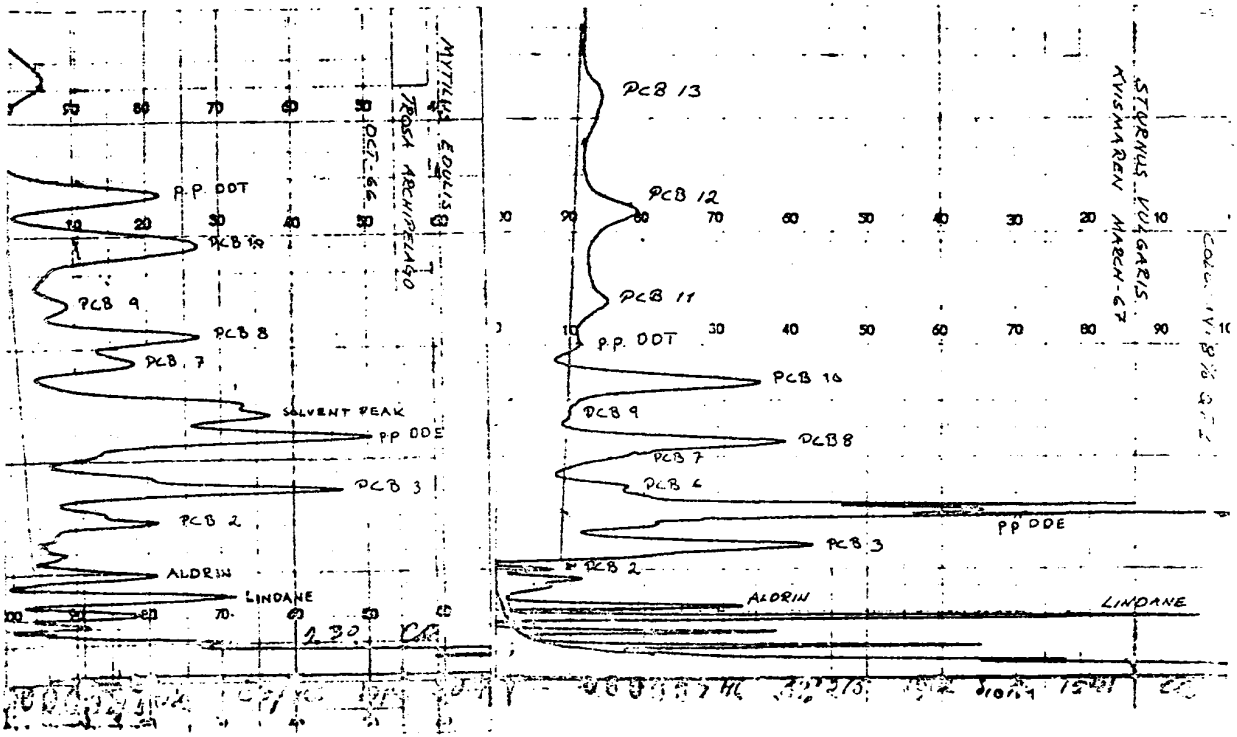
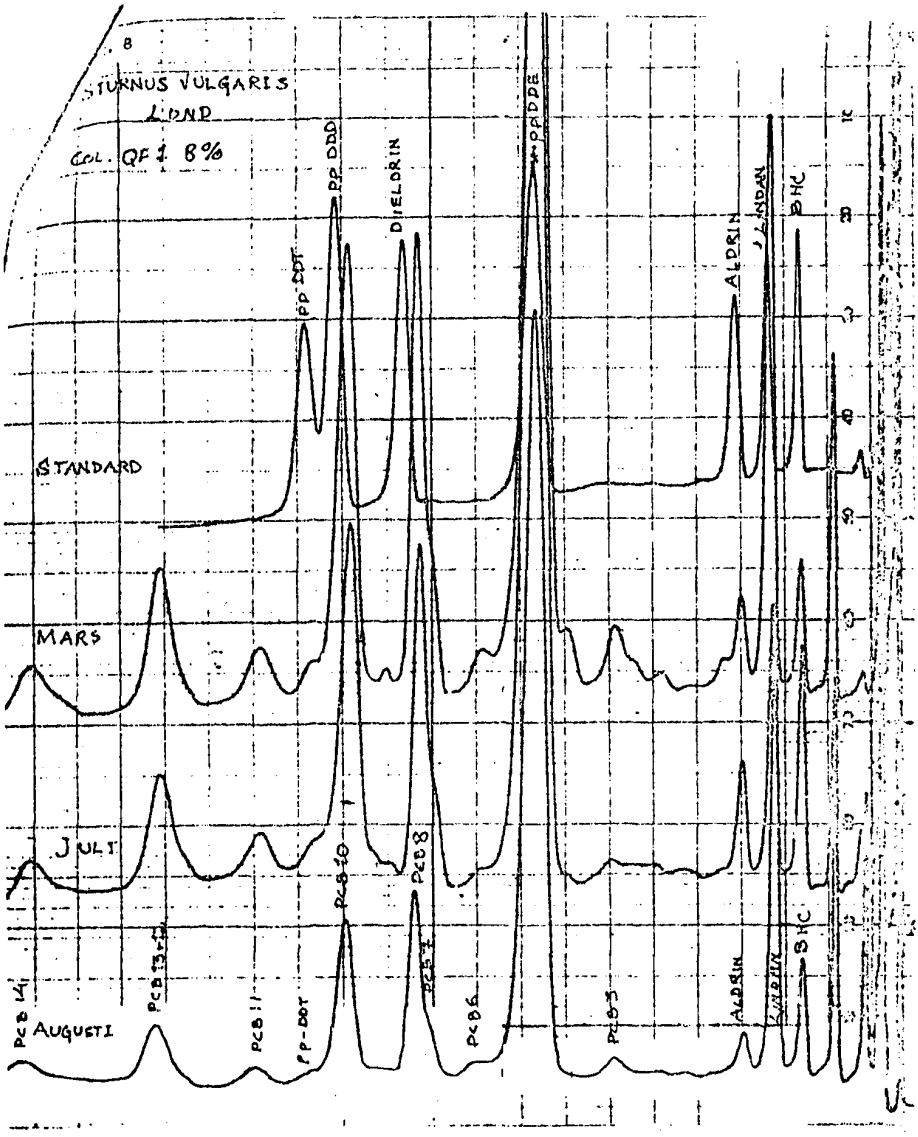

MYTILUS EDULIS
TROSA ARCHIPELAGO
PCB 66
P.P. DDT
PCB 10
PCB 9
PCB 8
PCB 7
SOLVENT PEAK
PP DDE
PCB 3
PCB 2
ALDRIN
LINDANE
STURNUS VULGARIS
KVISMAREN MARCH-67
PCB 13
PCB 12
PCB 11
P.P. DDT
PCB 10
PCB 9
PCB 8
PCB 7
PCB 6
PP DDE
PCB 3
PCB 2
ALDRIN
LINDANE



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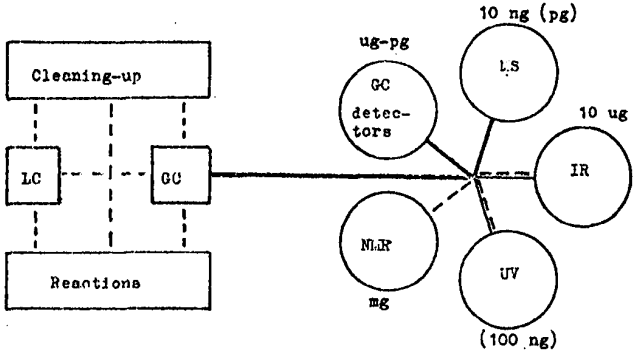
Exempel på system för separation och identifiering

SEPARATION - IDENTIFICATION

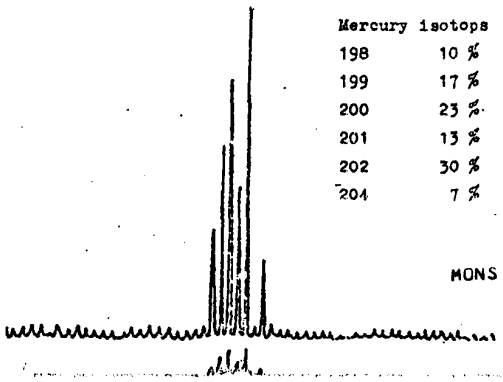
(confirmation - quantitation)



Problem: Treatment of multi-information

SCANNING MASS SPECTROMETRY; GC - MS

Isotopic distribution CH_3Hg (15 + Hg)



Mercury isotops	
198	10 %
199	17 %
200	23 %
201	13 %
202	30 %
204	7 %

MONS 045737

Litteratur ang utveckling i analytisk kemi

Analytical Chemistry publicerar varje år, i april, ett separat häfte som enligt nedanstående rubriker ger en sammanställning av utvecklingen inom analytisk kemi. Vartannat år redogörs för nyheter inom olika användningsområden (Applications), udda årtal, och jämna årtal behandlas metoder (Fundamental). Analytical Chemistry anlitar högt kvalificerade experter för dessa oöverträffade sammanställningar.

1966 (Fundamental)

Biochemical Analysis 19R
Chromatography 61R
Ion Exchange Chromatography 79R
Distillation Analysis 87R
Electroanalysis and Coulometric Analysis 88R
Electrophoresis 99R
Extraction 131R
Fluorometric Analysis 155R
Gas Analysis 166R
Ion Exchange 176R
Inorganic Microchemistry 180R
Organic Microchemistry 186R
Chemical Microscopy 197R
Electron Microscopy 209R
Polarographic Theory, Instrumentation, and Methodology ...261R
Electrochemical Relaxation Techniques 270R
Organic Polarography 278R
Emission Spectrometry 297R
Infrared Spectrometry 311R
Light Absorption Spectrometry ..317R
Nuclear Magnetic Resonance Spectrometry 331R
Mass Spectrometry 350R
Electron Paramagnetic Resonance 371R
Mössbauer Spectrometry 382R
Raman Spectrometry 393R
Ultraviolet Spectrometry 404R
X-Ray Absorption and Emission ..416R
Statistical Methods in Chemistry440R
Thermal Analysis 443R
Amperometric Titrations 452R
Potentiometric Titrations 467R
Volumetric and Gravimetric Analytical Methods for Inorganic Compounds 469R
Volumetric and Gravimetric Analytical Methods for Organic Compounds 479R
Titrations in Nonaqueous Solvents..485R
X-Ray Diffraction 493R
Magnetic Susceptibility: Trends in Instrumentation, Research and Applications 501R
Kinetic Aspects of Analytical Chemistry 513R
Light Scattering 517R
Use of Enzymes in Analytical Chemistry 572R

1967 (Applications)

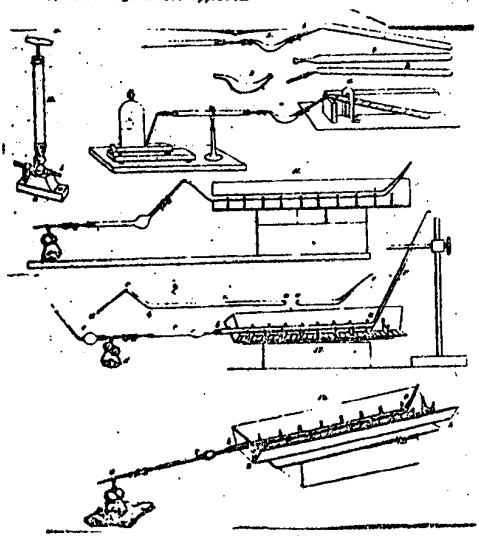
Air pollution 10R
Clinical Chemistry 22R
Coatings 42R
Essential Oils 48R
Fertilizers 69R
Food 75R
Ferrous Metallurgy 92R
Nonferrous Metallurgy I. Light Metals 102R
Nonferrous Metallurgy, II. Zr, Hf, V, Nb, Ta, Cr, Mo and W 110R
Simultaneous Determination of Oxygen and Nitrogen in Metals by Carrier-Gas Fusion Extraction 133R
Pesticide Residues 142R
Petroleum 157R
Pharmaceuticals 191R
Rubber 239R
Solid and Gaseous Fuels 248R
Water Analysis 261R

MONS 045738

Exempel på utvecklingen av förbränningsmetoder för elementaranalys

TIDIGASTE APPARATER FÖR ELEMENTARANALYS

1-6 enl Berzelius
11 enl Liebig-Mitscherlich
17-18 Liebigs äldsta apparatur



Principskiss för modern mikroförbränningsapparatur

C–H Elementaranalys

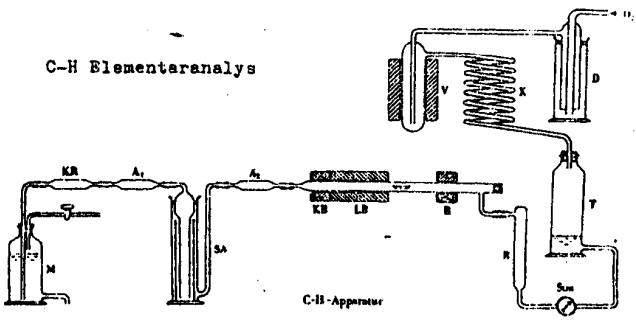


Abb. 1

D	Druckregler	R	Reinigungsrohr	A_1	Kohlendioxydabsorptionsrohr
V	Vorverbrennungsrohr	B	Bewegl. Brenner	SA	Stickoxydabsorption
K	Kühlspirale	LB	Langbrenner	KR	Kontrollrohr
T	Trockenturm	KB	Kurzbrenner	M	Mariotte'sche Flasche
Stm	Stabilisierungsmesser	A_2	Wasserabsorptionsrohr		

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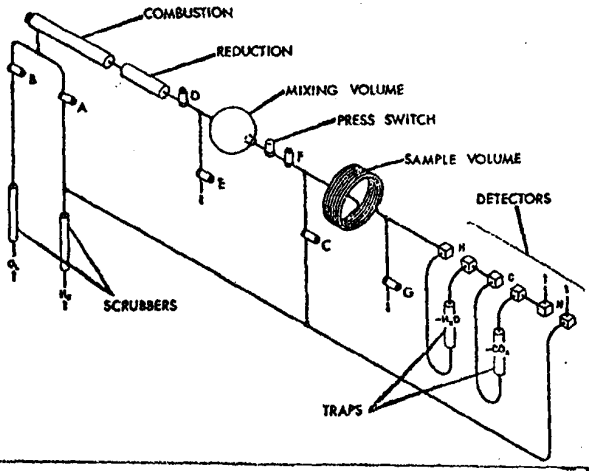
Elementaranalys enl gaskromatografisk teknik

(Principskiss för instrument från Perkin-Elmer; jfr liknande instrument från Technicon och F and M)



Elementaranalys enligt masspektrometrisk metodik; för enkelupplösande instrument, system "Peak-Matching"

jfr Ragnar Ryhage

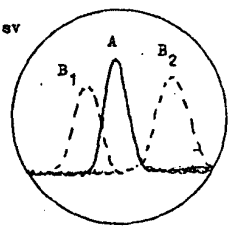
Omkopplare

Läge A för peak från prov
Läge B för peak från match-substans
vanligen C_nF_m

B_1 för V_1; B_2 för V_2 osv



$$\frac{m}{e} = \frac{r^2 \cdot H^2}{2V}$$



Oscilloscopbild

m = jonens massa
e = jonens laddning
r = avböjningsradie
B = magnetflöde
V = accelerationsspänning

C	H	N	O	$\Delta M \cdot 10^{-3}$
17	32	3	2	110,5
19	34	0	3	109,1
22	32	1	0	106,5
18	34	2	2	97,9
23	34	0	0	93,9
19	36	1	2	85,3
18	36	3	1	74,1
20	38	0	2	72,8
19	38	2	1	61,5
20	40	1	1	48,9
19	40	3	0	37,7
21	42	0	1	36,4
20	42	2	0	25,1
21	44	1	0	12,6
22	46	0	0	0

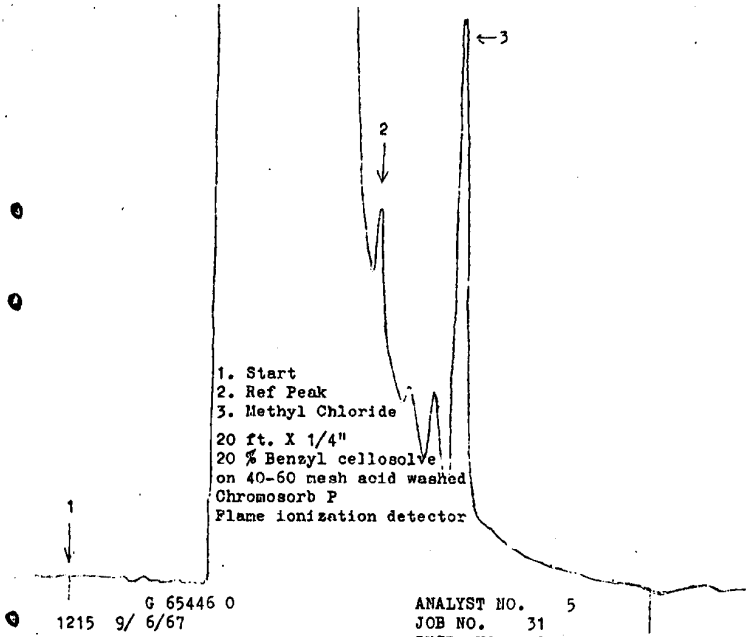
(Saturated hydrocarbon)

$C_{22}H_{46}$ M = 310

MONS 045740

Exempel på datamaskinbehandlat resultat från gaskromatografisk analys av metylklorid i propan (taget från IBM:s exempelsamling)

METHYL CHLORIDE IN COMMERCIAL PROPANE



G 65446 0 ANALYST NO. 5
1215 9/ 6/67 JOB NO. 31
INST. NO. 8

UNKNOWN	ELUTION TIME	PEAK AREA
	221	0.5508108E 08
	234	0.1015468E 09
	247	0.8287650E 09
	279	0.6560846E 08
	285	0.1869463E 09
	292	0.1110860E 09
	315	0.3255085E 09
	365	0.1819579E 08
	415	0.3481068E 07
	514	0.5104004E 06
	553	0.5764698E 06

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PERCENT OF TOTAL AREA UNKNOWN = 99.86

COMPONENT	RESULTS	UNITS	ELUTION TIME	PEAK AREA
REFERENCE PEAK	-0.000		465	0.1284736E 07
CHLORIDE ION	38.063	P.P.M.	590	0.9103201E 06

JOB COMPLETE