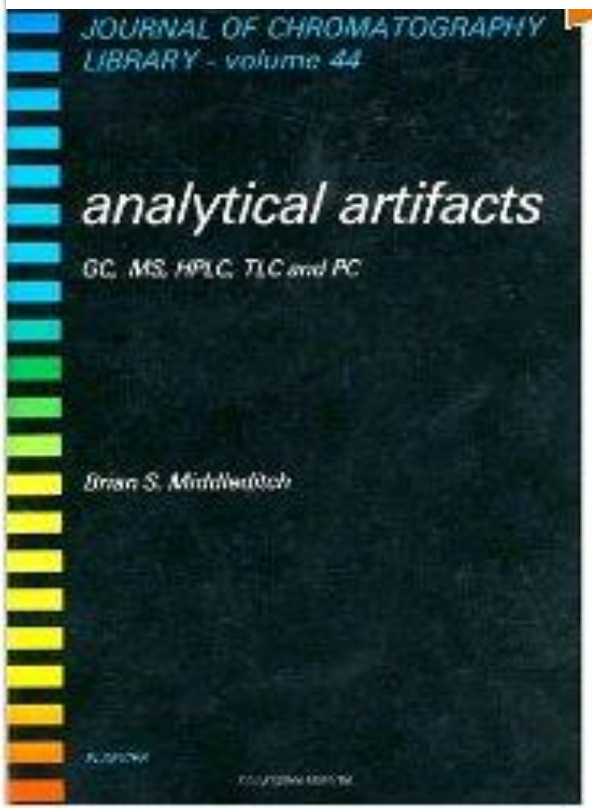
アーティファクト：文献紹介
Artifact or Artefact?

2012年6月8日
GC研究懇談会、薬業健保会館
（独）産業技術総合研究所
前田恒昭

紹介する文献の時代背景

Artifacts in Chromatography : An Overview, Brian S. Middleditch, Albert Zlatkis,
J. Chromatographic Sci. (1987) 547-551

Brian S. Middleditch “Analytical Artifacts” Elsevier (1989) Amazon.com　古本のみ



- 1975年　キャピラリーカラムを用いるGC/MSが登場
- 1979年　R.D.Dandeneau,E.H.Zerenner：
  溶融シリカキャピラリーカラムを開発
- 1976年から1986年：化学結合型固定相液相の研究
- 1980年代：キャピラリーカラム対応GC装置が一般化
  研究トレンド：High Resolution, Selectivity, Sensitivity & Speed)
- 1980年代：大量試料注入法の実用化
  PTV,クールオンカラム等試料導入系開発

キャピラリーカラムとGC/MSの普及、大量試料導入などで高分解能と感度化が進む。
利用分野が拡大、一般利用者に普及

www.gbv.de/dms/ilmenau/toc/183065425.PDF

J. Chromatographic Sci.での予告

不純物、汚染、副生成物やその他のアーティファクトについて注意すべきことは研究室で代々受け継がれてきた。しかし、訓練を受けていない新人が増え、文献に頼るようになり、情報の洪水に見舞われ、きちんとした支援が受けられずに質の悪い論文が多数発表されるようになった。

純度と安定化剤：安定化剤を加えていないクロロホルムは酸化されてホスゲンを生じる。含窒素薬（アンフェタミン、ノルコデインノルニコチン等）を水から抽出するとcarbamoyl chloridesを生じる。安定化剤としてエタノールを含むと残留ホスゲンと反応しクロロホルムの塩素化エチル化合物を生じ、含窒素薬のエチルカーバメート類を生じる。

高分子の安定化剤、添加剤、可塑剤：例えば、塩化ビニル樹脂の45%はフタル酸エステルの可塑剤が添加されている。プラスチック製シリンジや血液の採取道具は汚染等の問題を起こしやすい。

テフロンキャップライナー：電気陰性度の高い物質が溶け出したり、酢酸を吸収し、後にアセチル化反応を起こす等。

ガラス表面への吸着：Hydroxybenzoic acid, Hydroxycinnamic acidはソーダ石灰ガラスを使うと減少する。ステロイド類のメタノール溶液ではステロイド類が減少するが、エチルアセテート溶液では減少しない等。

人の手からの汚染：m/z400以上を見ていないとm/z69と81のイオンがスクアレンに由来することがわからない。シリンジの針の外側を手で触れるだけでこの汚染が検出される。

アルドリッチ社が公開している安定化剤（当時）の例

Table I. Commercial Stabilizers*

Stabilizer	Chemical
Butylated hydroxytoluene (I)	2,5-norbornadiene, 1-cyanovinyl acetate, cyclohexene, diethyl ether, furan, 2-methoxyethanol, α-methylene-γ-butyrolactone, 2-methyltetrahydrofuran, myrcene, tetrahydrofuran
p-tert-Butylcatechol (II)	5-ethylidene-2-norbornene, 4-fluorostyrene, isoprene, methylcyclopentadiene dimer, α-methylstyrene, styrene, 4-vinyl-1-cyclohexene, 2-vinylpyridine
Phosphoric acid	phenol
Polygard	tetrahydrofurfuryl alcohol
Potassium carbonate	2-bromo-2-methylpropane, 2-ethylhexyl bromide, 2-methoxypropene
Potassium fluoride	fluorosulfonic acid
Potassium hydroxide	1-vinyl-2-pyrrolidinone
Potassium metabisulfite	*N*-(4-hydroxyphenyl)glycine
Propylene oxide (XI)	benzyl chloride
Silver wool	4-bromo-2-methyl-2-butene

Artifacts in Chromatography : An Overview, Brian S. Middleditch, Albert Zlatkis, J. Chromatographic Sci. (1987) 547-551 より引用

analytical artifact

GC, MS, HPLC, TLC and PC

Brian S. Middleditch

Department of Biochemical and Biophysical Sciences, University of Hou
4800 Calhoun Road, Houston, TX 77004, U.S.A.

ELSEVIER
Amsterdam — Oxford — New York — Tokyo 1989

CONTENTS

Brian S. Middleditch “Analytical Artifacts” Elsevier (1989)

アーティファクト、副生成物、コンタミ、不純物

試料採取、試料処理、導入、分離、検出

1136項目を収録
物質以外の項目は123（吸着剤・捕集剤、容器・接液・接ガス部材、手法、汚染等）

前書きで一例として
・プラスチック容器よりガラス容器を用いたほうが良いが、洗剤はプラスチック製の洗瓶に入っており、これでガラス容器を洗うと可塑剤が残る可能性にはあまり気づいていない。

・最近の論文で雌犬から雄犬を誘惑するフェロモンが発見・同定されたが、これは広く用いられている抗菌剤であった。

・男性の友人が自分の額の皮膚油から女性ホルモン（エストロゲン）を検出して驚いたが、手を洗った後のハンドローション由来である事に気づいて安心した。

いろいろな間違いを犯さないよう、発表した後で恥ずかしい思いをしなくて良いように注意を喚起するものであり、続編への貢献を期待する。

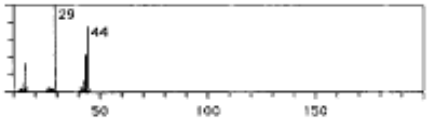
記載項目の説明(例:アセトアルデヒド)

Title

ACETALDEHYDE C_2H_4O (44)

The common name of the substance is given first. In this case it is acetaldehyde. For some entries, the choice of name to appear in the title is somewhat arbitrary since there are several commonly-used synonyms. The molecular formula and molecular weight are given at the right of the Title. For the convenience of mass spectroscopists the molecular weight is calculated from the integral atomic weight of the most abundant isotope of each element. Acetaldehyde is (2 x 12) + (4 x 1) + 16 = 44. Note that the atomic weight of the most abundant isotope of chlorine is 35, so that methylene chloride (CH_2Cl_2) is assigned a molecular weight of 12 + (2 x 1) + (2 x 35) = 84.

Mass Spectrum



Spectra were recorded in the author's laboratory or obtained from the published literature. All of the spectra were obtained by electron-impact ionization, with an electron energy of 70 eV. It should be noted that some of the spectra do not include ions with *m/z* values as low as 10 (some analysts scan from *m/z* 40 to avoid contributions from air peaks). If the molecular weight of a compound is greater than 200, the spectrum continues in one or more additional frames.

Structure

CH_3CHO

The only abbreviation employed in the structures is "Ph" for phenyl.

Chemical Abstracts Service Indexing Information

CAS: Acetaldehyde [75-07-0]

The most recent Chemical Abstracts Service name and registry number are provided. These may be employed both for manual searches of *Chemical Abstracts* and computer-assisted searches. The registry number is particularly useful, but is ignored by many scientists who do not understand it. The number itself does not contain any structural information. It is merely a number assigned by the Chemical Abstracts Service to an individual substance. Thus, it does not matter whether an author of a refers to acetaldehyde as "acetaldehyde", "ethanal", or one of the other synonyms; the Chemical Abstracts Service will always index it under the name "Acetaldehyde" and the registry number "75-07-0". The registry number should be used to conduct a comprehensive literature search.

Merck Index Reference

Merck Index: 31

The Merck Index is an excellent key to the literature. A reference is given to the Tenth Edition of the Merck Index for all substances which are listed in that volume. The Ninth Edition has a companion volume which lists entries in molecular weight order for the convenience of mass spectroscopists.

Synonyms

Acetic aldehyde, Aldehyde, Ethanal, Ethyl aldehyde

It is unfortunate that most chemicals have multiple names. Several groups have attempted to standardize systems of nomenclature over the years, but it is difficult to persuade scientists to abandon the names that are most familiar to them. The Chemical Abstracts Service uses a system of nomenclature designed for ease of indexing, and they revise this system with the publication of each collective index.

Brian S. Middleditch "Analytical Artifacts" Elsevier (1989)

Reported as a contaminant in chloroform, ethanol, ethyl acetate (Ende and Spiteller, 1982), and the antimicrobial agent dimethoxane (Woolfson and Woodside, 1976). Acetaldehyde is formed by interaction of ethylene oxide (a fumigant) with saline solutions (Shintani et al., 1981), oxidation of ethanol (a preservative in chloroform), and hydrolysis of ethyl acetate.

The accurate determination of acetaldehyde in blood is complicated by artifactual formation of acetaldehyde from ethanol during sample preparation. Several authors have described procedures for avoiding this problem (Christensen et al., 1981; Eriksson et al., 1982; Iversen and Damgaard, 1983; Pezzoli et al., 1984; Steenaart et al., 1985).

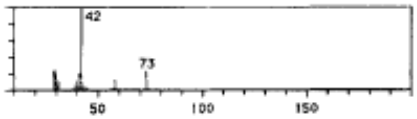
Nagy et al. (1985) have discussed the "disappearance" of acetaldehyde from human blood. While they did not determine the mechanism by which acetaldehyde is destroyed or bound to blood components, they found that the process could be inhibited by addition of hydrochloric acid immediately after the blood is collected. They also noted that it is important to take into consideration the artifactual formation of acetaldehyde from ethanol. Thus, the determination of acetaldehyde in blood is difficult to perform with any degree of accuracy.

Acetaldehyde can condense with β-phenylethylamines to afford tetrahydroisoquinolines and with tryptamines to yield tetrahydro-β-carbolines (Pictet and Spengler, 1911). During the 1970s it was believed that these psychoactive alkaloids were responsible for some of the behavioral problems associated with alcohol ingestion. It has now been demonstrated that they can be formed during the analysis if the solvents employed contain traces of acetaldehyde. We have used the Pictet-Spengler reaction to produce derivatives for the analysis of biogenic amines by gas chromatography and mass spectrometry (Middleditch, 1975b, 1976).

Acetaldehyde can also condense with diamines to produce perhydro 1,3-diazines.

ipectra of Derivatives

Mass spectrum of acetaldehyde *O*-methyloxime [C_3H_7NO (73), NBS 21*]:



Derivatives of artifacts are frequently encountered, so additional spectra are sometimes provided for the methyl esters, *O*-methyloximes, trimethylsilyl esters, and trimethylsilyl ethers, as appropriate. These may not be the derivatives of choice for the artifact, but they would be formed incidentally if the sample were treated with the corresponding reagents. The spectrum of the *O*-methyloxime of acetaldehyde is given in this monograph. Spectral data are included in the six-peak index, and the molecular formula is listed in the molecular formula index.

Cross-References

See also: CHLOROFORM, DIETHYL ETHER, DIMETHOXANE, ETHANOL, ETHYL ACETATE, ETHYLENE OXIDE, PARALDEHYDE, PERHYDRO 1,3-DIAZINES, TETRAHYDROISOQUINOLINES, TETRAHYDRO-β-CARBOLINES

Extensive cross-referencing has been employed to aid the reader in locating information and to minimize repetition of material in multiple monographs.

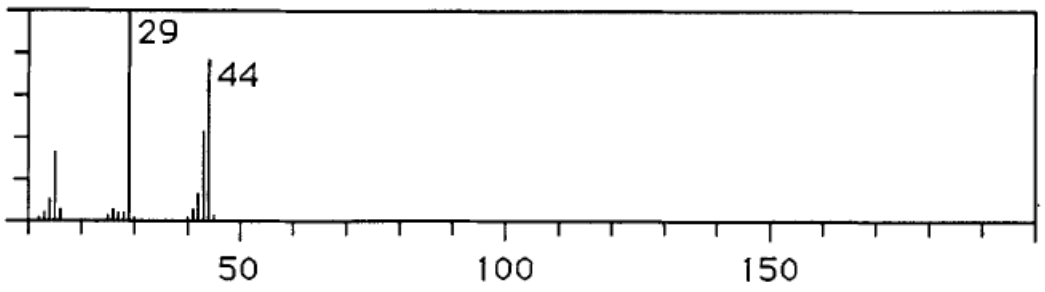
References

Complete literature references are provided, so that the reader will have a good indication of the content of a publication before consulting it. Nothing is more frustrating than waiting a month or more for an obscure article to be located by an interlibrary loan service, only to find that it is of marginal relevance.

Brian S. Middleditch "Analytical Artifacts" Elsevier (1989)

実際の記載

ACETALDEHYDE C_2H_4O (44)



CH_3CHO

CAS: Acetaldehyde [75-07-0]

Merck Index: 31

Mass spectrum: NBS 3978, Atlas 12*

e and Spiteller, 1982),
1976). Acetaldehyde
solutions (Shintani et
d hydrolysis of ethyl

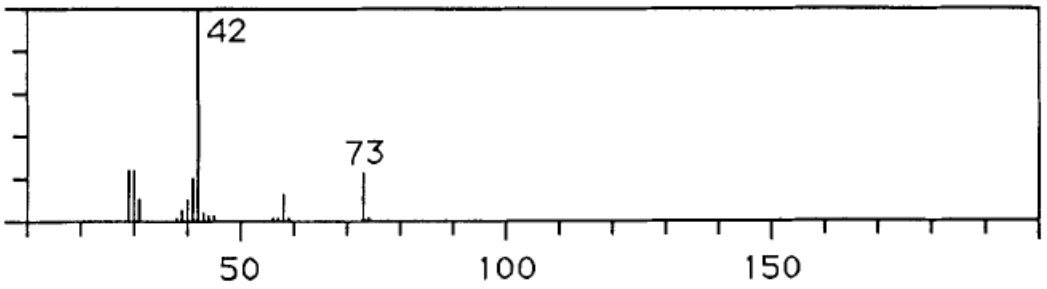
y artifactual formation
uthors have described
Eriksson et al., 1982;
985).

de from human blood. While they did not determine the mechanism by which acetaldehyde is destroyed or bound to blood components, they found that the process could be inhibited by addition of hydrochloric acid immediately after the blood is collected. They also noted that it is important to take into consideration the artifactual formation of acetaldehyde from ethanol. Thus, the determination of acetaldehyde in blood is difficult to perform with any degree of accuracy.

Acetaldehyde can condense w
and with tryptamines to yield t
the 1970s it was believed that
the behavioral problems associ
that they can be formed during
aldehyde. We have used the Pi
of biogenic amines by gas chr
1976).

Acetaldehyde can also condens

Mass spectrum of acetaldehyde *O*-methyloxime [C_3H_7NO (73), NBS 21*]:



See also: CHLOROFORM, DIETHYL ETHER, DIMETHOXANE, ETHANOL, ETHYL ACETATE, ETHYLENE OXIDE, PARALDEHYDE, PERHYDRO 1,3-DIAZINES, TETRAHYDROISOQUINOLINES, TETRAHYDRO-β-CARBOLINES

Brian S. Middleditch “Analytical Artifacts” Elsevier (1989)

物質以外の例（全体）

	page	Monograph
1	28	Air leaks
2	31	Amberlite XAD-2
3	32	Amberlite XAD-4
4	32	Ambersorb XE-340
5	33	Ambersorb XE-348
6	33	Animals
7	45	Artifact or artefact?
8	48	Autoxidation
9	49	Axillary volatiles
10	85	Blender contaminants
11	85	Blood alcohol determination
12	85-87	Blood collection devices
13	89	Bottle caps
14	90	BSTFA additional products
15	129	Carbon black
16	140	Chacoal
17	164	Coelution
18	164	Coextractives
19	164	Column adsorption
20	165-7	Column bleed
21	168	Column reagents
22	198	Dedradation in the GC-MS interface
23	199	Degradation and dehydrogenation
24	302	Direct aquenous injection
25	311	Drug interference
26	312	Drying agents
27	313	Electrophores
28	363	Expired blood contaminants
29	363,4	Extraction column contaminants
30	365	Filter paper contaminants
31	366	Florisil contaminants
32	370	Freeze drying artifacts
33	370	Frying oil artifacts
34	376	Ghost peaks
35	378	Glass lined steel tusing
36	378	Glassware adsorption
37	379	Glassware cleaning
38	380	Glass wool contaminants
39	402	Heroin analysis
40	414	Hop constituents
41	416	Hydrysis of trimethylsilyl derivatives
42	448	Isotope memory effect
43	453	Laminated plastic food packaging
44	456	Legionnaire's nickel
45	459	Lidocaine artifact
46	464	Leiterature survays
47	464	Lubricants
48	465	Lunar samples
49	467	[M+11] peaks
50	474	Mesh size
51	476	Metal column
52	479	Methoxylation artifacts
53	481	Methylation artifacts
54	494	Metylformamide artifacts
55	494	Methyl α -D-galactonurate artifacts
56	504	O-Methyloxime degradation
57	521	Molecular sieve artifacts
58	530	Ninhidrin-positive artifacts
59	531	Nitrile formation
60	534	Nitrosamine analysis
61	558	Oxygen isotope formation
62	561	Paper chromatography
63	561	Parafilm
64	562	Pasteur pipette contaminants
65	574	Pesticide persistence
66	574	pH
67	579	Phenolic artifacts
68	593	Photochemical reactions
69	600	Pink beards and black spots
70	602	Plankton nets
71	603	Plastic tubing adsorption
72	606	Polygard
73	606	Polypropylene contaminants
74	608	Porapak oxidation
75	613	Propoxphene degradation
76	620	Protein binding
77	620	Purine oxidation
78	620	Purple artifact
79	627	Rat peaks
80	627	Reaction time
81	627	Red specks
82	628	Retention index values
83	629	Reviews
84	630	Rubber glove contaminants
85	634	Saliva
86	634	Sample collection and storage
87	634	Sample-loop volume
88	637	Saniticizer
89	637	Selective ion monitoring
90	638	Septum rinsing
91	639	Shipboard contaminants
92	639	Silicagel contaminants
93	640	Silicate anlysis
94	640	Silicate analysis
95	640	Silicones
96	640	Siloxanes
97	648	Solvent impurities
98	649	Soxlet thimbles
99	650	Spirocyclic indole derivaives
100	651	Spot splitting
101	652	Stabilizers
102	653	Steam distillation
103	657	Straw
104	660	Sulfate artifact
105	661	Sulfoxide degradarion
106	663	Syn/anti isomers
107	663,4	Syringe contaminants
108	665,6	Talcum powder contaminants

109	667	Teflon
110	668	Teflon FEP
111	668,9	Tenax artifacts
112	670	Terpene artifacts
113	690	Thiamine artifact
114	691	Thin-layer chromatography artifacts
115	699	Transfer efficiency
116	726	Trimethylsilyl derivative decomposition
117	736	Tryptophan degradation
118	740	Urethan
119	743	Vitamin D analysis
120	744	Viton artifacts
121	744	Volatilization artifact
122	745	Wash bottle contaminants
123	745	Water
124	751	Zechmeister's artifacts

特徴
・全ての事がわかっているわけではない
・自分の研究室や文献紹介例を収録
・留意すべき点を挙げており参考になる

物質以外の収録項目例の分類

吸着剤・捕集材	容器・接液・接ガス部材	手法	汚染
Amberlite XAD-2	Blood collection devices	Blood alcohol determination	Air leaks
Amberlite XAD-4	Bottle caps	Coelution	Axillary volatiles
Ambersorb XE-340	Column reagents	Coextractives	Blender contaminants
Ambersorb XE-348	Glass lined steel tusing	Column adsorption	Column bleed
Carbon black	Glassware adsorption	Nitrosamine analysis	Expired blood contaminants
Chacoal	Glassware cleaning	Paper chromatography	Extraction column contaminants
Molecular sieve artifacts	Laminated plastic food packaging		Filter paper contaminants
Porapak oxidation	Metal column		Florisil contaminants
	Parafilm		Glass wool contaminants
	Pasteur pipette contaminants		
	Plankton nets		
	Plastic tubing adsorption		
	Polygard		
	Polypropylene contaminants		
	Rubber glove contaminants		

AIR LEAKS

Air leaks are a continual problem for mass spectroscopists. They tend to raise the pressure in the ion source and defocus the instrument, and they may also obscure low-mass ions. A severe leak might oxidize the filament or even burn it out. We have on occasion observed the mass spectra of rhenium oxides due to air-oxidation of a rhenium filament.

Ions characteristic of an air leak include *m/z* 14 ($N^{+\cdot}$ or N_2^{2+}), 16 ($O^{+\cdot}$ or O_2^{2+}), 17 (HO^+), 18 ($H_2O^{+\cdot}$), 20 (Ar^{2+}), 28 ($N_2^{+\cdot}$), 32 ($O_2^{+\cdot}$), 40 ($Ar^{+\cdot}$) and 44 ($CO_2^{+\cdot}$) (Spiteller and Spiteller, 1973). Old-time mass spectroscopists (before the days of computers and electronic mass markers) will remember using the air peaks for calibrating the low end of the mass scale. The relatively broad peak at *m/z* 40 (representing $Ar^{+\cdot}$ of *m/z* 39.95 and $C_3H_4^{+\cdot}$ of *m/z* 40.03—separated by 0.08 atomic mass units) was particularly useful.

Leak detection may be tackled at any of several levels. If the leak is small enough to allow the filament to be turned on, one can tune the mass spectrometer to *m/z* 43 (CH_3CO^+) and spray potential trouble spots with acetone to locate the leak. Air may be heard to "hiss" through large leaks. Leaks of intermediate size are more troublesome. The best method of locating them is to systematically isolate the various components of the vacuum system. If there is a leak in a gas chromatograph attached to a mass spectrometer it may be possible to detect it with a soap solution. This approach is not recommended for capillary columns; methanol is a reasonable alternative.

GC/MSの負圧部分のリークを調べるにはアセトンを用いると良い（現在使用している方法）。

架橋して化学結合型のカラムになればブリードの問題は解決するとの期待が込められているが、実際にはブリードや分解の問題は未解決のままである。

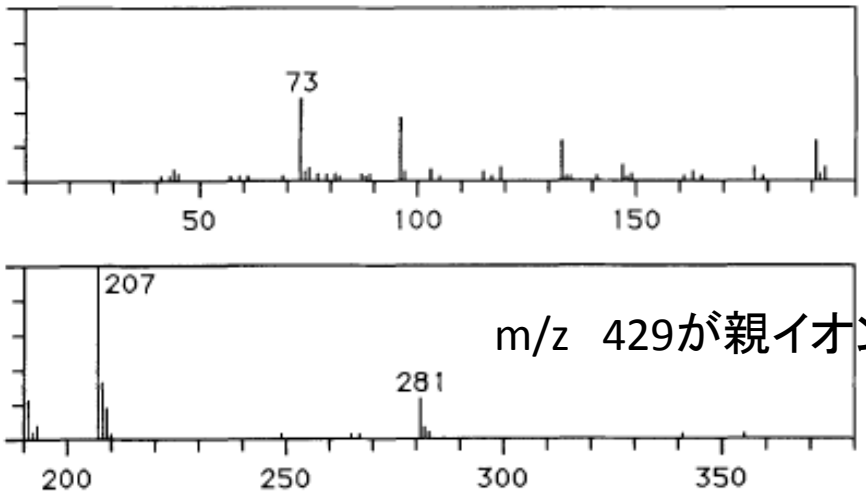
記載例

COLUMN BLEED

At one time column bleed was accepted as an inevitable phenomenon in gas chromatography. It was particularly troubling for those of us who were developing methods for trace analysis by combined gas chromatography – mass spectrometry since we has to select mass numbers for selective ion monitoring which did not coincide with "bleed" peaks (Brooks and Middleditch, 1971). The only positive feature of column bleed is that it helped us to calibrate the mass scale of a spectrum before the days of mass markers and computerized data systems.

With the introduction of bonded-phase columns, column bleed is no longer a problem. However, no book on analytical artifacts would be complete without spectra of column bleed from the more popular stationary phases. Those which are reproduced here are taken from a Finnigan Corporation Applications Tip (Taylor, 1974).

Bleed spectrum of OV-101, a methylsilicone:



m/z　429が親イオン

Brian S. Middleditch "Analytical Artifacts" Elsevier (1989)

TENAX TAが開発された当時の例

TENAX ARTIFACTS

Tenax-GC, a porous polymer of 2,6-diphenyl-*p*-phenyl oxide, was initially used as a packing material for gas-solid chromatography. It was later discovered that it could be employed as a trapping agent for the concentration of organic vapors for trace analysis (Zlatkis et al, 1973b). More recently a specially-prepared grade of polymer (Tenax-TA) has been introduced specifically for use as a trapping agent. It contains fewer contaminants (MacLeod and Ames, 1986).

Tenax-GC is generally stable to 350°C, but some batches have been reported to decompose at lower temperatures (Budde and Eichelberger, 1979), and contaminants can be obtained during solvent extraction (Johnson et al., 1986).

Degradation products of Tenax-GC which have been identified include acetophenone, benzaldehyde, benzoic acid, ethylene oxide, α-hydroxyacetophenone, and phenol (Pellizzari et al., 1984). Neher and Jones (1977) have reported that contact with acid (especially SO_2 and sulfuric acid) may result in cleavage of Tenax-GC to 2,6-diphenylhydroquinone, which is further oxidized in air to 2,6-diphenylbenzoquinone.

Atlas et al. (1985) have suggested the use of amber-coated 5-mL Kimax pipettes as sorbent tubes. They claim that the amber coating minimizes photooxidation of Tenax-GC. After Soxhlet extraction with methanol and petroleum ether, Tenax-GC (60-80 mesh) was packed into the volumetric bulb of the pipette and was held in place by plugs of silanized glass wool. Prior to sampling, Tenax tubes were conditioned for a minimum of eight hours at 320°C under nitrogen flow. Excellent blanks could be obtained with unused Tenax tubes; however, artifacts became apparent after sampling. In addition to oxidation products normally reported an unidentified high-molecular weight material was encountered.

See also: ACETIC ACID, ACETOPHENONE, BENZALDEHYDE, BENZENE, BENZOIC ACID, BENZOPHENONE, BIPHENYL, 2-CHLOROCYCLOHEXANOL, CHLOROSTYRENE, CYCLOHEXADIENE, CYCLOHEXENE, *p*-DICHLOROBENZENE, DICHLOROCYCLOHEXANE, DICHLOROSTYRENE, 2,6-DIPHENYLBENZOQUINONE, 2,6-DIPHENYLHYDROQUINONE, DODECANE, ETHYLBENZENE, ETHYLENE OXIDE, 1-ETHYLNAPHTHALENE, FURFURAL, HEXAMETHYLCYCLOTRISILOXANE, α-HYDROXYACETOPHENONE, 1-METHYLNAPHTHALENE, NAPHTHALENE, NITRATED AROMATIC HYDROCARBONS, *N*-NITROSODIMETHYLAMINE, *N*-NITROSODIPROPYLAMINE, *N*-NITROSOMORPHOLINE, *N*-NITROSOPIPERIDINE, *N*-NITROSOPYRROLIDINE, OCTAMETHYLCYCLOTETRASILOXANE, PHENOL, STYRENE, TETRADECANE, TETRAMETHYLBENZENES, TOLUENE, 1,1,1-TRICHLOROETHANE, TRIDECANE, *m*-XYLENE

Degradation products encountered when Tenax GC is exposed to nitric oxide or nitrogen dioxide include 2,6-diphenylbenzoquinone, 2,6-diphenylhydroquinone, and several unidentified compounds which are C_3H_7CO or C_5H_{10} adducts of these two substances (Hanson et al., 1981).

Pellizzari and Krost (1984) have conducted extensive studies of the reactions which may take place in Tenax-GC sampling tubes when used for sampling air containing chlorine, ozone, or oxides of nitrogen. Under these conditions cyclohexene could be converted to benzene, 2-chlorocyclohexanol, cyclohexadiene, two dichlorocyclohexane isomers, and three substances with molecular formula $C_6H_{10}O$. Styrene was converted to benzaldehyde, two chlorostyrenes, and a dichlorostyrene. Zielinska et al. (1986) have shown that fluoranthene can be converted to 2-nitrofluoranthene in cartridges containing Tenax-GC through which N_2O_5 is drawn.

Hampton et al. (1982) found acetic acid, difluorodimethylsilane, fluorotrimethylsilane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, 1,1,1-trichloroethane, trichlorofluoromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane in control cartridges packed with Tenax-GC, but it is not clear whether they derived from the resin itself or were added during cleanup, processing, and transport.

Lewis and Williams (1980) heated *unconditioned* Tenax-GC in a stream of nitrogen and examined the volatiles that were produced. A gas chromatogram of the volatiles contained 60 peaks. Components which were positively identified were acetophenone, benzaldehyde, benzophenone, biphenyl, ethylbenzene, 1-methylnaphthalene, 2-methylnaphthalene, naphthalene, styrene, and toluene. "Less conclusive" identifications were made for 1,4-diphenylbutane, phenol, 1,2,3,4-tetramethylbenzene, and two xylenes, while "tentative" identifications were made for an aliphatic hydrocarbon, a dichlorobenzene, a dimethylacetophenone, diphenyl oxide, four dodecanes, 5-ethyl-2-methylfuran, 1-ethylnaphthalene, 2-ethylnaphthalene, an ethyltoluene, furfural (which coeluted with an ethyldimethylbenzene), an octane, a tetradecane, a tridecane, and two undecanes. Mass spectral data were provided for each of these substances and for the 23 gas chromatographic peaks that were not identified. The authors noted that many of these compounds would not be found in conditioned Tenax-GC.

Walling (1984) noted that artifacts associated with the use of Tenax-GC can be recognized if multiple samples of greatly different volumes are taken simultaneously using a series of cartridges. Acetophenone, benzaldehyde, and benzonitrile always displayed corrupted behavior, and it was suggested that Tenax-GC not be used to determine these compounds in air (Walling et al., 1986).

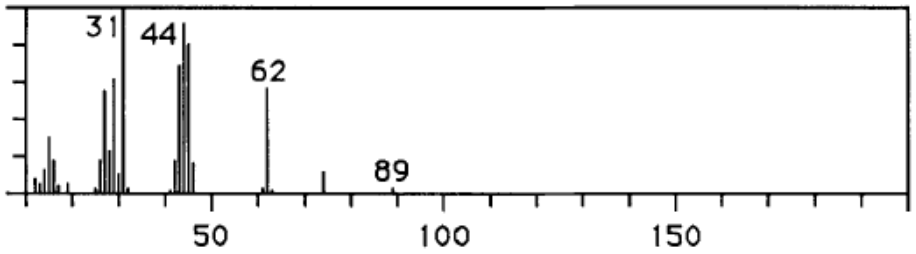
Blok et al. (1983) concluded that Tenax-GC was too heavily contaminated to be suitable for the trace analysis of organics from water.

Porapackの酸化分解の例（P608)もある

Brian S. Middleditch “Analytical Artifacts” Elsevier (1989)

URETHAN

$C_3H_7NO_2$ (89)



$H_2NCO.OCH_2CH_3$

CAS: Carbamic acid, ethyl ester [51-79-6]

Merck Index: 9681

Mass spectrum: NBS 3996, Registry 59, Atlas 172*

Retention index: 838 (Ardrey et al., 1985)

Ethyl carbamate, Ethyl urethan, Leucothane, NSC 746, Pracarbamin, Uretan, Urethane

It has been suggested that this carcinogen is a reaction product of ammonia and amines with diethyl dicarbonate, which was formerly used as an additive in wines and other beverages. Indeed, the use of diethyl dicarbonate was discontinued because of this possibility. However, Ough (1976a,b) has determined that urethan is a natural constituent of most fermented beverages (up to 5.8 ppm), and is present in concentrations as high as 192 ppm in a commercial sake.

See also: AMMONIA, DIETHYL CARBONATE

文献から紹介した例

試料の接ガス部分に金属がつかわれない理由
（ガラスライニング又はガラスインサートの使用）

METAL COLUMNS

Copper, stainless steel, and aluminum columns were compared with quartz columns by Beckman and Bevenue (1963) for the analysis of DDD, DDE, *p,p'*-DDT, technical DDT, dichloran, endrin, and heptachlor. In all cases, the results obtained for quartz were significantly better than for the metal columns. Losses of DDT, dichloran, and heptachlor on copper and stainless steel columns were particularly pronounced. It was recommended that metal injection ports be lined with quartz tubes.

Ziegler and Günther (1971) compared glass and metal columns for the analysis of citrus oils. They found that the use of glass columns resulted in a higher recovery of alcohols and esters due a reduction in artifact formation.

See also: *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, DICLORAN, ENDRIN, HEPTACHLOR, POLY-CHLORINATED BIPHENYLS

Brian S. Middleditch “Analytical Artifacts” Elsevier (1989)

アーティファクト：分析結果をそのまま受け入れてよいのか？
疑うことが初めの一歩

アーティファクト、副生成物、不純物、分解などの情報はどこにある？

同じ経験や失敗をいっぱいしているかもしれないが失敗例は公表されない？

論文にならないので公表されない？

特定分野では常識だが他の分野では未知（無知）？

一人で悩んでいないでいろいろな人に相談しては +++++だれと、いつ？

GC研究懇談会に情報を集めませんか