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Advances in the Field of Thermal Procedures in Direct Combination with Thin-layer Chromatography

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The hitherto existing gap in the field of chromatographic methods has been filled by the direct coupling of a suitable oven (TAS-oven) with TLC. The sample to be examined is heated either isothermally or linearly within the temperature gradient of 50~450°C.

The volatile and/or thermolytically evolved substances are fractionated on the TLC-layer and subsequently chromatographed under standard conditions.

Transport mechanisms from the sample to the TLC-layer, applications of the TAS-procedure and further developments are discussed.

Thermofractography, developed from the TAS-procedure, is demonstrated on different groups of natural substances such as alkaloids, amino acids, nucleic acids. nucleosides, nucleotides, triglycerides and other lipids, pyrone glycosides and aglycon.

Experimental work and results on the thermolysis of macromolecular natural and synthetic substances, natural polyphenols, tanning agents and leather and the possibilities of differentiating various lignins, carbohydrate and synthetic polymers are reported.

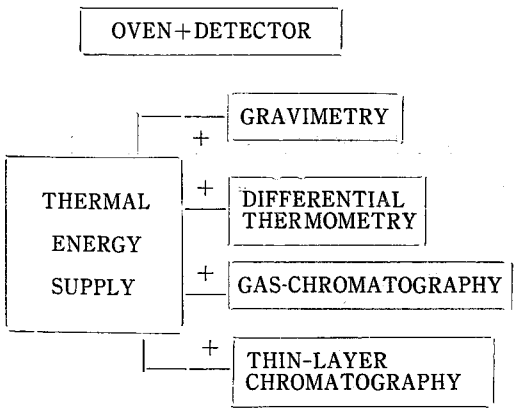
Further, it is shown that classical reactions in the microgram range, *e.g.* zinc dust distillation, sulphur-and selenium dehydrogenation and catalytic dehydrogenation, can be coupled directly with TLC.

Also described is a method which allows to investigate the gaseous compounds evolved during thermofractography in the range of up to 450°C.

Thermal procedures coupled with TLC open up the following new possibilities for chemical microanalysis: fractionated separation of distillable and sublimable components, fractionated thermolysis and carrying out of thermal reactions in the ultra micro range.

Introduction

Thermal procedures, in most cases coupling procedures, are gaining increasing use in the analytical field. The sample to be examined is hereby heated, and the resulting changes are registered. The following scheme (Fig. 1) summarizes the interesting possibilities, illustrates the parallels to GC, and clearly demonstrates that a hitherto existing gap has been filled by the TAS-procedure[15,18] and TFG[27] The TAS-procedure can be compared to the solid sample induction of GC, while it has the advantages of an all-glass system, rapid and easy exchange of sample, and immediate transfer of the volatile substances. The advantages of the TAS-procedure also apply to TFG, but TFG itself can only to a limited extent be compared to Pyrolysis-GC since working conditions are only in the range of up to 450°C. The sample is heated linearly in the temperature gradient of 50~450°C, and the evolving volatile compounds are



Name of the procedure	Abbreviation
=Thermogravimetric Analysis	TGA
=Differential Thermal Analysis	DTA
=Solid Sample Induction for GC Pyrolysis-GC Carbon Skeleton-GC	SSIGC PGC CSGC
=Thermomicro-, Transfer-, Separation- and Application Procedure	TAS
=Thermomicro-Fractionation in the Gradient, Thermo- fractography Carbon Skeleton-	TFG

Fig. 1. Thermal coupling procedures and their names.

collected continuously and separated on the TLC-layer. A "thermofractogram" shows the substances separated by temperature on the abscissa, and separated by their chromatographic behaviour on the ordinate. One single chromatogram registers the distillable and sublimable compounds of the starting mixture as well as the thermolytically evolved ones. During recent years a number of research investigations have proved these couplings with TLC to be a considerable analytical achievement. The following report summarizes our experimental work.

Transport mechanisms from the sample to the TLC-layer[28]

Some ideas, based on observations and quantitative evaluation, have been conceived for a better understanding of the procedures. They are illustrated in Fig. 2.

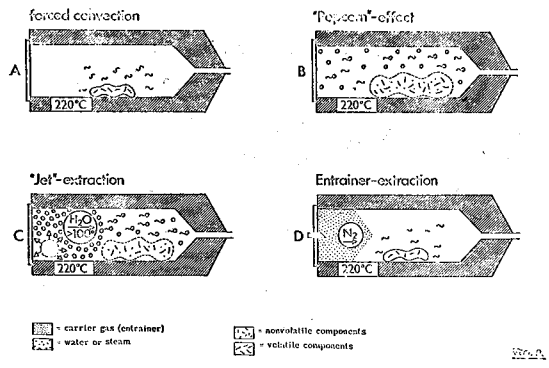


Fig. 2. Diagram of the four transport mechanisms of the TAS-procedure shown as a longitudinal section of the oven block with loaded cartridge.

A The transport of the components of water and solvent free samples is achieved by the increase of their vapor pressure and by the expansion of the air volume by *e.g.* 50% at 220°C, in the TAS-cartridge. Both effects of this *"forced convection"* only cause a very small stream of vapor to be directed on to the TLC-layer and thus "thermoextraction" is incomplete and the yields are low.

B Yields increase if the sample contains water, *e.g.* 10% in drugs. When heating rapidly, the sample puffs, the surface becomes enlarged and porous (*popcorn-effect*), and the vapour entrains the volatile components, thus considerably improving the transport to the start point of the TLC-layer. The process can be compraed to a "steam distillation", even though the water content is mostly too low and the evaporation too fast.

C An additional increase of the yields is achieved by adding so-called *"propellants"*. While in the oven they release water, which heats up on the hot walls of the TAS-cartridge, effecting so-called *"distillation with superheated steam"*. Thermogravimetric investigation proved that a spherical 4 Å molecular sieve charged with 25% of water yields the optimal amount of vapor. Suitable basic and acid propellants were tested in addition. Hexamminenickel chloride releases 6 mol of ammonia in two steps up to 350°C. Oxalic acid up to 210°C releases a stream of CO_2, CO, and water vapor, while malonic acid up to 210°C develops a stream of CO_2-acetic acid.

D. The transport of the molecules evaporated from

the sample can also be accomplished by means of a gas stream admitted from the outside. Nitrogen or preferably helium is used as an inert gas. This *carrier gas distillation* or *-sublimation* is the most suitable procedure in TFG. Using this, even substances with a high boiling range, *e.g.* fatty oils, can be transferred without decomposition to the TLC-layer. The effect is comparable to that of a vacuum distillation at below 0.1 mm Hg This phenomenon is being further investigated[40].

Experiments on the quantitative determination of the yields have also not been completed. In model experiments, close to 100% have been obtained under favourable conditions from 1—15μg amounts of volatile substances.

TAS-procedure, application and further developments

Applications: All new procedures in the beginning have to struggle with difficulties and are at first applied only to the fields in which preliminary experimental work has been done. With our own interest focusing mainly on the analysis of natural substances, drugs and foodstuffs, the TAS-procedure is applied chiefly to these fields, as Table I indicates. However, taking a closer look, one realizes that the TAS-procedure and especially TFG opens up numerous new possibilities in other diversified fields of microanalysis as well, *e.g.* forensic analysis, toxicological diagnosis of poisoning, criminology, chemical analysis in the field of archeometry, environmental analysis and metabolic studies. Looking at the widespread use TLC has gained during recent years, one can anticipate the TAS-procedure becoming more widely applicable than the corresponding coupling methods of GC.

Further instrumental development: During the investigation of numerous single samples, the idea of *simultaneous* transfer of the volatile compounds of several samples to the TLC-layer was conceived. As a result we developed the so-called *Multi-TAS-oven*, coupling 18 single ovens directly next to each other.

Already in 1971 we described a *prototype*[25], which in the meantime has been considerably improved. Evidently without knowing this, SITA, CHMELOVA-HLAVATA and CHMEL[13] recently described an

Table I. New Applications of Thermal Separation- and Application Procedures, Coupled with TLC.

Separated and Chromatographed			
Group	Substances	Samples	Literature
A	Analgesics, Sulfonamides	Tablets	Ia, 6
A	Methandiene+Hexachlorophene, Chlorobozoic acid+Salicylic acid	Ointments	Ia
A	Allobarbitone+Aminopyrine, Triple Sulfonamides	Suppositories	Ia
A,B	Capsaicine, and others	Adhesive plasters, Liniments, Drugs	22
A	Phenothiazines	Various Dosage Forms	24
B	Various Plant Active Substances	Drug material	26
B	Alkaloids and Fragments	Plant material and Pure Substances	5, 13, 33
B	Anthraquinones	Plant material and Pure Substances	13, 32
B	Components of Essential Oils	Fruits, Blossoms and Leaf-drugs	15, 16, 26
B	Essential Oils of Mentha hybrids	Plant material	2, (13)
B	Essential Oil of Satureia	Plant material	8
B	Azulene, Essential Oil	Chamomile flowers	20
B	Aromatics after dehydration	Sesquiterpenes, Diterpenes	36
B	Fragrances	Fungi	12
B	Glycoside cleavage Picrocin→Safranal	Saffron	19, 31
B	Naphthoqinone derivatives	Plant material	11
B	Fragmentation to Phenol derivatives	Wood, Lignin	29, 37
B,C	Fragmentation to Phenol derivatives	Tanning drugs, Leather	30

B	α-Pyrone derivatives	Plant material	11, 31, 39
B,A	Narcotics, Addictive drugs	Plant material, Pure Substances	3, 14
C	Antioxydants (MBT, PBN)	Rubber samples	7
C	Acetylacetonates	Pure Substances	35
C	Morphactines	Soil samples	17
C	Optical brighteners	Textile fabrics, Detergents	25
C	Pyrolysis products of synthetic material	Synthetics	9, 25, 34
D,C	Antioxidants	Fatty Oils and preparations	25, 40
C	Aromas	Toothpastes, Soaps	25
D	Caffeine, and others	Foodstuffs	23, 26
D	Gaseous compounds	Carbohydrates	38
D	Additives, Preservatives	Foodstuffs	21
D,C	Pesticides(DDT, HCH, Pyrethrines, 2,4 D etc.)	Foodstuffs	21
D,C	Plasticisers	Synthetic materials	25, 27
D	Sugar thermolysis products	Pure Substances	10

A : Pharmaceutical preparations
B : Plant drugs
C : Auxiliary agents
D : Foodstuffs and others

"Instrument for the simultaneous TFG-analysis of sample and standard or the simultaneous TAS-analysis of several samples and standards".

Using our instrument we have already investigated thousands of individual fruits of *Umbelliferae*-plants, and discovered that the composition of the volatile components can vary from fruit to fruit- even within one and the same *Umbelliferae-Plants* quantitatively[39]. We also discovered new "chemical races". Further developments are conveniently larger TAS-ovens for the preparative isolation of volatile compounds or thermolysis products. TAS-cartridges used for analytical purposes have a volume of 2ml., while the preparative version has a volume of 20 and 2000ml. The products evolved are retained in a special cooling trap system[40].

Thermofractography of low molecular natural substances

Alkaloids: It is not surprising that the steam-volatile tobaccoareca-, and hemlock alkaloids and similar ones can be transferred from the drug to the TLC-layer without decomposition.

Interesting though, is that the tropane alkaloids too can be transferred directly from the drug to TLC. Cinchona alkaloids may also be transferred without decomposition, but only as isolated substances and not from the drug, since they are seemingly bound so strongly to acids and tanning substances that influence of heat produces only cleavage products. These fluoresce light blue like the initial alkaloids and can therefore be used as fingerprint substances. The substances in question are 6-methoxyquinoline and 6-methoxylepidine derived from quinine and quinidine.

Quinoline and lepidine derived from cinchonine and cinchonidine have a dark blue fluorescence. A classical identity test in which the drug is pyrolysed in a test tube to yield a red condensate of characteristic light blue fluorescence was elucidated by our investigations[33]. Investigations on additional alkaloid drugs are being consinued.

Amino acids: Simple amino acids, such as glucine, alanine, valine, leucine and proline, are transferred without decomposition to the TLC-layer in a stream of nitrogen at 220°C.

Fragmentaton occurs only if additional functional groups are present. These reactions are presently being investigated[40].

Nucleic acids. nucleosides, nucleotides: BIELIG and SCHMITT[41] proved in preliminary tests that the bases adenine, cytosine, guanine, thymine, and uracil can be transferred to the TLC-layer without

decomposition in a stream of nitrogen, thus furnishing the conditions for a thermal cleavage of the corresponding nucleosides.

The reproducibility of the thermal cleavage proved to be good. The thermofractograms obtained contain the initial base and the fingerprint of the ribose. As expected, the thermofractogram of ribonucleic acid (RNS from yeast) showed the four bases adenine, cytosine, guanine and uracil. Thermofractography of DNS as well as an analysis of cell fragments are still to be carried out. A publication on this subject is pending.

Triglycerides and other lipids: Preservatives, pesticides, and fragrances have hitherto been separated from lipid mixtures in the temperature range of 200—250°C by the TAS-procedure[25], but TFG has made it possible to transfer the triglycerides also without decomposition in the 325—400°C range. TFG-analysis of fatty oils performed then showed that fractional distillation is possible also in the ultra-micro range. Squalene, cholesterol, plasticisers and a series of non-identifiable products can be distinguished in this way, thus opening up new possibilities for the analysis of soaps, chocolates, detergents and numerous other lipid preparations[27,40].

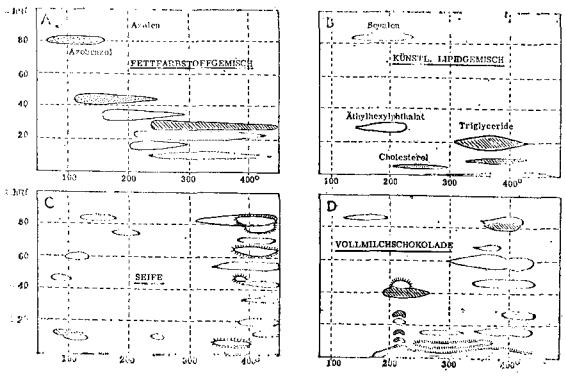


Fig. 3. Thermofractogram of complex lipophilic substance mixtures.

A : Mixture of fatdyes (Azobenzene, Azulene)
B : Artificial mixture of lipids(Squalene, Ethyl hexyl phtalate, Cholesterol, Triglycerides)
C : Soaf
D : Full-milkchocolate

Fig. 3 shows the corresponding thermofractograms.

Phyrone glycosides and aglycon: In previous transfer experiments with picrocrocin we found this glycoside is cleaved at 220°C within 60 seconds, yielding β-hydroxycyclocitral and safranal[19]. This result was checked by TFG of pyrone glycosides. A Study of the cleavage conditions for coumarin glycosides was made, including the behavior of free coumarins[31]. The "free" coumarins sublime at relatively low temperatures, whereas cleavage of all the glycosides examined takes place between 200 and 300°C. The expected aglycon is the main product, and also formed are very small amounts of the coumarin, containing one less hydroxyl group at the site of cleavage, and fragmentation products of the sugar. TFG of "coumarin drugs" thus indicates immediately whether "free" coumarin or a coumarin glycoside is present. The length of the zone gives additional information about the amount of substance. It was surprising to discover that the onset of sublimation of "free" coumarins is dependent on the carrier material; if, for instance, cellulose is used instead of quartz wool, sublimation starts almost 100°C higher.

The experiments are being continued with flavonoid- and anthraquinone glycosides, with the intention of studying the cleavage mechanisms of the aglycon.

So far we have found that flavonoid glycosides are split in the same way as the coumarin glycosides. The flavonoid aglycon formed are transferred largely undecomposed to the thermofractogram. Only the flavonols are fragmented completely. A common characteristic of flavonoid-fragmentation is the appearance of the corresponding phenol derivatives from rings A and B, the phenols from ring B clearly in the majority. The various flavonoid groups can be differentiated through their additional fragmentation products. Flavanones are identified by very distinct vinylphenol zones; these zones are only very weakly visible in fiavononones and entirely missing in all the other groups. Flavonols are characterized by newly formed "secondary flavonoid zones" which are located directly above the initial fiavonol. A sort of "fine structure analysis" is chromatographically feasible, based on the different degrees of hydroxylation of the

phenols formed. The experiments are being continued.

Thermofractography of high molecular natural and synthetic substances

Because of their extremely high polarity, numerous high molecular natural-and synthetic substances cannot be analyzed by chromatography. By reproducible degradation to defined low molecular compounds, the starting material can be identified by a "structural unit analysis". The best procedures are thermolysis (up to 500°C) and pyrolysis (500~1200°C) [38]. Thermolysis combined with TLC is the most suitable procedure since only very small amounts of gaseous and large amounts gaseous and large amounts of condensable products are yielded (see last paragraph).

Of the numerous substances considered here, the groups of natural tanning agents, lignins, and the presently most important plastics have been selected for TFG. Extensive preliminary experiments and chromatographic studies were necessary for each of these groups.

a) Natural polyphenols, tanning agents and leather[30]:

In TFG the free di- and triphenols are transferred without decomposition to the TLC-layer while the tan-agents based on them are fragmented in a reproducible in and hence characteristic way. Tanning agents of the gallotannin type stand out through an almost complete absence of the catechol and resorcinol zones. The two are the main zones in catechin tanning agents. The generally strongly defined pyrogallol zone is a common characteristic of both tanning agent groups. Based on these chromatographicall identifiable structural units, classification and statements as to the kind of linkage can be made. Further indications are that hydrogen bonds may be present. Just these results are important to us and are to be investigated more explicitly since they may be helpful in the structural elucidation of uniform compounds and furthermore give clues about bond formation in natural or artificial mixtures. Thermofractograms of tanning agents provided significant information about the "phlobaphenes" and their structure when compared to the extracts and extracted drugs. A type of "fine structure analysis" of the TFG of different extracts from tanning agents shows relatively large differences in the structure of the tanning agents. At the moment a classification into different groups of tanning agents is possible, but we have gained the impression that no truly uniform types of tanning agents are present in drugs but only mixtures with either the catechin- or the gallotannin type prevailing.

Subsequently, experiments with model, untreated and treated leathers proved it possible to detect and identify a vegetable tanning agent through typical phenol zones, even if the leathr was pre-tanned, pre-treated and dyed with chromium salts. Since the auxiliaries of the preparation also appear in the thermofractotogram, this method should be of great interest for the rapid analysis of leather. With the small sample amount of 2~5 mg. needed for analysis, the method should be interesting for criminological comparison of leather samples as well as for the food-chemist in investigating consumption goods made of leather(see Fig. 4 and 5).

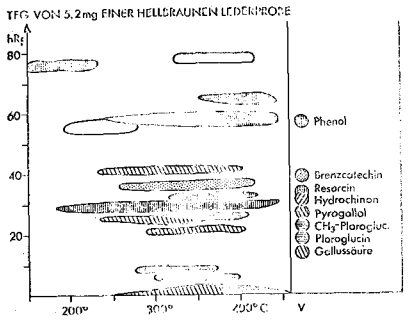


Fig. 4. TFG of 5.2 mg of a light brown leather sample.

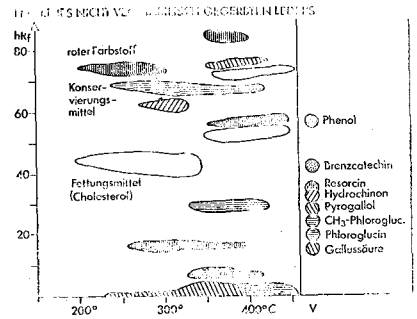


Fig. 5. TFG of a read leather tanned with an inorganic tanning agent.

TFG supplies the synthetical chemist in the field of organic tanning agents, auxiliaries and dyes with new information and thus enables him to classify and identify certain polymer products more accurately.

b) Lignins[20]: Lignins are divided into three major groups:

Softwood lignins consist mainly of guaiacylpropane units, hardwood lignins contain both guaiacyl- and syringylpropane units, the amount of the latter varying from species to species.

Grass lignins contain all three, guaiacyl-, syringyl-, and *p*-hydroxyphenylpropane units. The analytical procedures which have hitherto been used for characterization and classification are time consuming, require larger amounts of sample and are only of limited diagnostic value.

Corresponding preliminary experiments with model substances from the FREUDENBERG school indicated that thermal fragmentation in TFG leads to defined substances. The chromatogram of the lignins investigated showed as common structural units (fingerprint substances) guaiacol, 4-vinylguaiacol, vanillin, coniferylaldehyde and alcohol.

Additional syringyl derivatives, *e.g.* 4-vinylsyringyl, sinapaldehyde and alcohol are observed in the thermo fractograms of angiosperms. The possibilities of a further differentiation are interesting. In addition to syringaaldehyde only a faint blue zone was formed from poplar lignin, while no syringaaldehyde but a marked "blue" zone was formed from beech lignin. The TFG-procedure allowed us to clarify the controversial question whether the semi parasite, mistletoe, synthesizes the lignin of the host tree or its own: the latter is the case. This new kind of rapid lignin analysis will also facilitate investigation of the dissemination of lignins and to discover new types of lignins throughout nature.

The question arose whether the applied conditions of thermolysis lead to secondary reactions like in mass spectrometry. The problem was examined in an additional experiment[37], on the formation of conif eryl aldehyde and alcohol. TFG of defined model substances (dilignols and artificial polymer mixtures) and spruce lignin as well as supplementary experiments demonstrated that the free and/or preformed aldehyde- and alcohol groups of the structural units of lignin remain practically unchanged under the conditions of TFG. The procedure has the advantage that the fragmentation products yielded are diluted immediately with the inert gas, transferred to the cool TLC-layer and fixed here until separation.

c) Carbohydrates[40]: The emphasis of the experiments was on cellulose and sugar. However, simple saccharides were examined in addition for comparative reasons. The ranges of thermolysis shift from mono- to di-to polysaccharides from 200 to 350°C.

Of the already known substances we found amongst others: furfural 5-methylfurfural, 5-hydroxymethylfurfural and small amounts of 2-hydroxymethyl furylketone. Noticeable in addition were two substances which reacted with fast blue salt to give a blue or red color respectively. The first substance was identified as cyclopentane-1,2 dione and the second one as 3-methylcyclopentane-1,2-dione. Cyclopentane-1,2-dione is formed in smallar or larger amounts during the thermolysis of all carbohydrates investigated. However, additional zones which may serve for characterization are formed from different carbohydrates. Thermolysis of cellulose ethers and esters takes place analogously to the starting compound. Some textile fibers and mixed textile fabrics were tested practically[27]. In each case identification of cellulose and its derivatives was achieved even with very small amounts of sample. Identification of polyester and polyacrylonitrile-and polyamide fibers in mixed textile fabrics is to be achieved by subsequen investigations of polymers on the thermofractogram.

d) Synthetic polymers: The rapid analysis of polycondensates (polyester, polyamide, polyurethane), of phenolic resins and of vinylpolymers(polystyrenes, acrylates)as well as of stabilizing agents, plasticisers and dyes is of practical interest.

Our experiments in the field of TFG of polycondensates have been completed[34].

Polycondensates: A TFG is carried out for preliminary orientation, *i.e.* group analysis. Based on this thermofractogram it can be determined whether the polycondensate belongs to the group of the polyamides

of the nylon-or perlon type, or whether a polyester or polyurethane on polyester basis is present. For "fine structure analysis" an alkali fusion in a nickel-boat is carried out in the TAS-cartridge, and the corresponding bases and neutral compounds are chromatographed following the direct transfer. To analyze the salt-forming compounds, the sample is acidified and the free glycols and acids are carried over and chromatographed. The different polycondensates can thus be analytically distinguished. Further, minor modifications in the polymer chains may be recognized, something which has hitherto not been possible by means of chemical analysis.

Possibilities of rapid analysis of phenolic resins and vinylpolymers by TFG are at present under investigation. We can already state that a differentiated analysis with very small amounts of sample is possible.

Fig. 6 shows the thermofractogram of 5 mg. of a technical grade 4-t-butylphenol-formaldehyde resin. The free phenols appear in the range of 200~300°C and the fragmentation products of the condensate (1 and 1'=4-t-butylphenol) in the 350~450°C range. Fast blue salt was used as detecting agent.

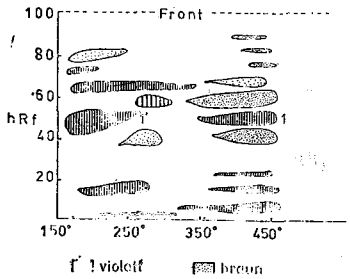


Fig.6. Thermofractogram of a technical grade phenolic resin. Sample weight: 5mg., Heating rate: 16°C /min., Speed: 5.5 mm/min., N_2: 15 ml/min., Layer: Silica gel HF_{254}, Benzene-Methanol(98 : 2), CS, 2×12cm., (additional details see text)

Results in our opinion are much more conclusive than those obtained with the thermal analytical procedures hitherto used.

Coupling of classical thermal reactions in the μg-range with TLC

Still today one utilizes gladly the classical thermal methods for establishing the skeleton in structural elucidation of natural substances. However, the small amounts of sample available, often prevent application of these procedures. The idea of combining classical thermal procedures directly with TLC was conceived when first testing the TAS-procedure[18].

A parallel in GC is the "Carbon Skeleton Chromatography" of BEROZA *et al.*[1], which our own instruments, using the TAS-cartridge as reaction vessel and the TAS-oven as source of heat.

Detailed investigations showed that the zinc dust distillation with 20~200μg of starting material can be rapidly and easily performed under controlled conditions and coupled with TLC. The sample is heated in the TAS-cartridge on copper-activated zinc for several minutes up to 350~450°C and the evolving oxygen-free aromatic or stable heterocyclic components are carried by a stream of nitrogen of 15ml./min. directly on the start point of a TLC layer. The reaction products are then identified after chromatography. The optimal temperature ranges were determined by thermofractography; they depend on the compound class.

The procedure was tested on naphtalene-, anthracene-, phenanthrene-, tetracene- and indol derivatives. Results and experimental details have in the meantime been published[32].

Further, it has been shown that a coupled dehydr ation snd sulphur- or selenium dehydrogenation can be carried out with 50~300μg of starting material in direct combination with TLC. The sample together with a potassium hydrogen sulfate- sulphur- or selenium mixture is heated up to the pre-selected temperature of between 160~400°C for several minutes in the TAS-cartridge. The resulting aromatic compounds are transferred by a stream of nitrogen to the start point of the TLC-layer. The reaction products are identified and in part quantiatively determined after chromatography.

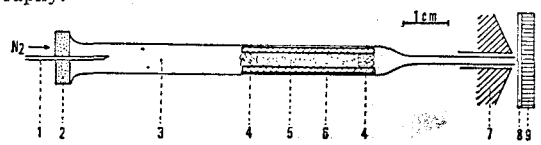


Fig. 7. Loading of TAS-cartridge for sulphur- or selenium dehydrogenation.

1 : canula
2 : silicone membrane
3 : cartridge made of PYREX-glass
4 : quartz wool
5 : dehydrogenation mixture with substance
6 : V 4 A insertion
7 : oven block tip
8 : TLC layer
9 : TLC plate

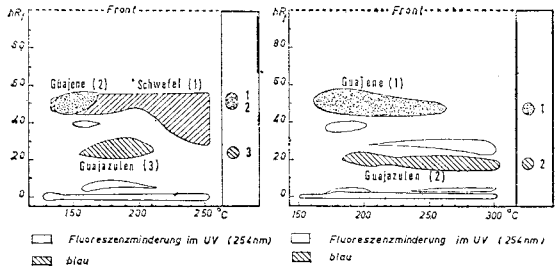


Fig. 8. TFG, comparing a sulphur dehydrogenation (left) to a selenium dehydrogenation (right) of guajol.
Besides the dehydration products (guajenes), the blue guajazulene is visible as de hydrogenation product.
Additional interpretations are given in the original paper [36].

The procedure was tested on samples of the sesquiterpene diterpene-and steroid groups [36].

We also investigated catalytic dehydrogenation in the microgram-range. Palladium on barium sulfate or calcium carbonate was found to be especially useful as catalyst. Here, in contrast to the previously mentioned proedures, the highest yields are gained if the dissolved substance is squirted in very small portions on to the catalyst [40]. The following table summarizes the experimental conditions for the thermal reduction and dehydrogenation in coupling with TLC.

Table II. Directive Values for "Thermal Reactions and Dehydrogenations" Coupled with TLC.

	Sample	Reaction Partner or Catalyst	Temperature
Zine dust distillation	5— 50μg	200~300mg Cu-activated zinc dust	350—450°C
Sulphur-dehydrogenation	50—100μg	10mg S-dehydrogenation mixture	160—220°C
Selenium-dehydrogenation	100—200μg	20~30mg Se-dehydrogenation mixture	250—320°C
Catalytic dehydrogenation	20—100μg	25mg Pd-$BaSO_4$ (10 percent)	250—350°C

The optimal conditions in the given ranges vary from substance to substance.

Investigation of the gaseous products of thermal separation and thermolysis produres[38]

Since only substances condensed on the layer are detected when coupling the previously described methods with TLC, investigation of the corresponding non-condensable *i.e.*of the gaseous compounds is of immediate interest. Little was known whether in the "low temperature range", *i.e.* the temperature range of up to 500°C the nature and amount of the compounds formed are also dependent on the existing temperature grades.

To analyze the gaseous products, we developed a procedure coupling a TAS-oven directly with a gas chromatograph.

The TAS-oven was adjusted so as to allow the TAS-cartridge with extra long capillary to reach directly into the injection port through a septum. The sample remained for 90 seconds at 250 or 300°C; the gaseous products were then transferred by a stream of helium of 1ml./min. as carrier gas to the column. Fig. 9 illustrates the coupling.

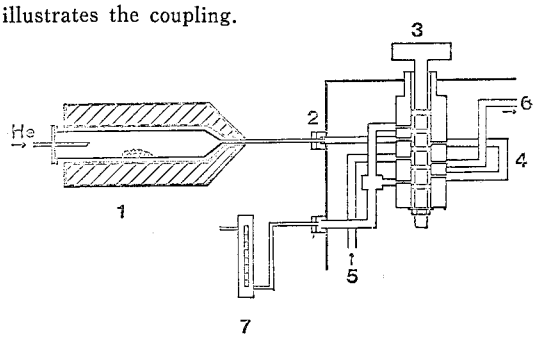


Fig. 9. Diagram of the coupling of a TAS-oven with the gas control valve of a gas chromatograph.
1 : TAS-oven with extra long cartridge and sample
2 : gas control valve inlet
3 : sample rod
4 : gas loop
5 : carrier gas inlet
6 : connection path to GC-column
7 : flow meter for intermediate control

Table III. Thermolysis of Carbohydrates with the TAS-oven.

Peak number		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pyrolysis products / Substance		Methane	Ethylene	Ethane	Propylene	Propane	Methanol-Formaldehyde	Acetaldehyde	Ethanol	Acrolein	Acetone, Furane, Propionaldehyde	n-Propanol	2-Methylfurane Butyraldehyde	Valeraldehyde	Furfural
Cellulose	250°C	−	−	−	−	−	−	−	−	−	−	−	−	−	−
	300°C	##	##	(+)	+	(+)	(+)	###	+	+	###	+	###	+	(+)
Cellobiose	250°C	+	−	−	−	−	(+)	##	###	(+)	###	−	+	−	−
Glucose	250°C	−	−	−	−	−	(+)	−	−	−	+	−	+	−	+
	300°C	##	##	(+)	−	−	(+)	##	(+)	(+)	###	−	(+)	−	(+)
Potato	250°C	−	−	−	−	−	−	−	−	−	−	−	−	−	(+)
starch	300°C	###	+	+	##	(+)	(+)	###	+	+	###	+	###	+	+
Apple pectin	250°C	(+)	(+)	−	##	##	###	##	−	−	###	−	##	−	−
Inulin	250°C	(+)	(+)	−	−	−	###	+	−	−	+	−	+	−	(+)

Since the results of detailed TFG-experiments with regard to the condensable fragmentation products of carbohydrates were already available they were examined at first. The results are listed in Table III.

It was thus confirmed that gaseous products evolve from carbohydrates only on reaching a temperature range of ca. 300°C. Additional experiments proved the amounts to be relatively small compared to the condensable products. With increasing temperature the gaseous products increase at the cost of the condensable ones, as experiments with the Pyrolysis-GC instrument, used for comparative reasons, indicated. Summing up the results one can state that mainly condensable products arise from carbohydrates in the usual range of TFG. Details and results compared to those of thermogravimetric analysis and the inductor-GC-system are described and listed in the original paper[38].

Additional experiments with natural and synthetic substances have been begun and are to bring conclusive information.

Summary

A distinct gap in the area of chromatographic methods was filled by the direct coupling of a suitable oven (TAS-oven) with TLC. The samples to be examined are heated either isothermally or linearly within the temperature gradient of 50~450°C. The volatile and/or thermolytically evolved substances are fractionated along the starting line of the TLC-plate and subsequently chromatographed under standard conditions. This procedure, called Thermofractography (TFG), has proved to be successfully applicable to the rapid analysis of complex samples such as chewing gum, plant material, detergents, shoe polish, synthetic mixtures, and similar products. TFG is also suited for the investigation of the thermal fragmentation of defined individual substances. By using the TAS-cartridge as reactor, zinc dust distillation, sulphur-and selenium dehydrogenation, as well as the catalytic palladium-dehydrogenation can be coupled with TLC in the ultramicro-range. A total of nearly 40 publications represents the scientific knowledge gathered so far in this area.

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