MACHEREY-NAGEL

Derivatization reagents for GC



- Ultrapure
- Highly reactive
- Cost-effective

MACHEREY-NAGEL

www.mn-net.com





Useful MACHEREY-NAGEL chromatography products from sample preparation to subsequent analysis



SPE

- Concentration and clean-up of your target compounds
- CHROMABOND® and CHROMAFIX® columns and cartridges
- Flash columns, packing material and accessories



Sample filtration

- CHROMAFIL[®] and CHROMAFIL[®] Xtra syringe filters
- Protection of sensitive and expensive laboratory equipment
- Use our online FilterFinder on www.mn-net.com/filterfinder



Vials and caps

- For all common instruments and applications
- Vials from 0.1 mL up to 100 mL for analysis and for sample storage
- For cross-referencing use our VialFinder on www.mn-net.com/vialfinder



HPI C

- NUCLEOSIL® the original, one of the first spherical HPLC silicas
- NUCLEODUR® professional solutions by high purity spherical silica
- NUCLEOSHELL® highest efficiency with core-shell HPLC columns



TI C

- Quick, easy and cost-efficient separation
- Screening applications and routine analysis
- Glass plates, aluminium and polyester sheets as well as accessories



GC

- Highly inert and low-bleed OPTIMA® GC capillary columns
- GC columns for routine analysis and special separations
- More than 50 stationary phases

Content

A guide to derivatization reagents for GC	4
Silylation	6
Acylation	12
Alkylation	14
Derivatization procedures	16
Overview of important functional groups	20
General reaction mechanisms	22
Ordering information	24
Contact	26



A guide to derivatization reagents for GC

Regarding derivatization

Derivatization is one of the most common ways to prepare compounds for GC that are otherwise difficult to separate. Through derivatization, it is possible to improve the separation by replacing active hydrogens from the analyte with various groups that are easier to handle. Derivatization generally improves the following GC parameters:

- Chromatographic behavior
- Peak shape
- Thermal and chemical stability
- Detectability
- Volatility

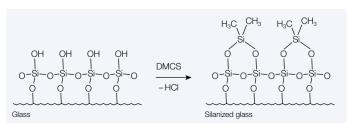
It is also important that all the instruments, e.g., laboratory glassware, will not interfere with the sample.

To make sure that no compounds containing -OH, -SH or -NH groups will be adsorbed by present Si-OH on the surface of the glass, a deactivation process may be necessary.

This is commonly achieved by rinsing the glass with a silvlating agent, e.g., DMCS or HMDS, hence masking all silanols with non adsorptive methyl groups.

To achieve a satisfying rate of derivatization, it is essential to keep the following requirements in mind:

- The derivatization reaction needs to be complete ≈ 100 %
- No loss of sample during derivatization
- The overall structure of the analyte will not be altered
- Produced derivative will be stable over time
- No interaction between the reagent and the chromatographic system



A guide to derivatization reagents for GC

Naturally, all other components of the sample preparation and handling process need to be contaminant-free and in top condition. Since water is, in most cases, a problem, it has to be removed from the derivatization process, e.g., by adding Na₂SO₄ to the reaction mixture. Like all reactions, derivatization takes time and a certain amount of heat to go to completion. As duration may vary greatly, dependent on the reactivity of the analyte, it is often necessary to screen several reagents for the best result. It is also important to realize that there is no such thing as the best derivatization method. There will always be several working solutions to a chromatographic problem with its own advantages and drawbacks, dependent on the equipment or on the approach of the chemist.

Derivatization reagents

There are many reagents in use today for derivatization. There are three categories they can be allocated to:

- Silvlation
- Acylation
- Alkylation (Methylation)



Silvlation is the most versatile method of derivatization in GC, i.e. more than 80 % of all derivatization reactions are actually silvlations. Usually the term silvlation in GC stands for replacement of active hydrogen atoms by a trimethylsilyl group (TMS derivative). Sometimes, however, trialkylsilyl groups or dimethylalkylsilyl groups with longer alkyl chains are used for derivatization. The trialkylsilyl group increases volatilitv and enhances thermal stability of the sample.

As with methylation, the replacement of an active hydrogen with a silyl group reduces the polarity of the compound. as well as hydrogen bonding.

Additionally, silvlation improves volatility, so that many compounds that are normally considered nonvolatile or thermally instable, can be chromatographed easily. Introducing a silyl group may also enhance the GC-MS properties of the derivative, either through characteristic ions or more favorable diagnostic patterns for structure investigations.

Good to know

It is important to mention that silylated compounds should not be used with WAX or FFAP phases, as the OH groups of the stationary phase will definitely become derivatized by the silvlating reagent, and this will irreversible change selectivity of the column.



Amides

N.O-bis-trimethylsilyl-acetamide (BSA)

M: 203.4 a/mol Bp: 71-73 °C (35 mm Ha) density d20 °/4 ° = 0.83

$$H_3C-C = Si(CH_3)_3$$

 $N-Si(CH_3)_3$

BSA is a strong silvlation reagent that forms very stable TMS derivatives with a large variety of compounds, e.g., non-sterically hindered alcohols, carboxylic acids, phenols, enols, steroids, (biogenic) amines and alkaloids.

Not recommended for use with carbohydrates or very low molecular weight compounds.

Good solvent for polar compounds, but frequently used in combination with a solvent (pyridine, DMF etc.), with other silvlation reagents or catalysts such as TFA. HCI or TMBS.

Used in combination with DMF, BSA is the reagent of choice for derivatizing phenols.

N.O-bis-trimethylsilyl-trifluoroacetamide (BSTFA)

M: 257.4 a/mol Bp: 40 °C (12 mm Ha) density d20 °/4 ° = 0.96

$$F_3C-C$$
 $N-Si(CH_3)_3$

BSTFA is a powerful trimethylsilyl donor with approximately the same donor strength as the nonfluorinated analog BSA.

Advantage of BSTFA over BSA

Greater volatility of its derivatives (particularly useful for GC of some lower boiling TMS amino acids). BSTFA will generally react with all organic material present, but may not react with some amides, secondary amines and hindered hydroxyl groups. However, adding 1 % TMCS (SILYL-991) will solve that problem.



N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA)

M: 199.1 a/mol Bp: 70 °C (75 mm Ha) density d20 °/4 ° = 1.11 F3C-CO-N

MSTFA is the most volatile trimethylsilyl amide available.

MSTFA is a very strong TMS donor that does not cause any noticeable FID contamination even after long-time measuring series. It is one of the most important silvlating reagents. It can be used, to silvlate the hydrochloride salts of amines or amino acids directly.

The already good solution characteristics can be improved by adding submolar quantities of protic solvents (e.g., TFA for extremely polar compounds such as hydrochlorides) or pyridine (e.g., for carbohydrates).

Advantages

- Complete reaction with high reaction rates, even without a catalyst (1-2 % TMCS or TSIM)
- Bv-product of the reaction (N-methyltrifluoroacetamide) features high volatility and short retention time.

Reactivity of silvlation reagents (acc. to M. Donike)

TMS amides (e.g., BSA, MSTFA) > TMS amine = TSIM > Fnol-O-TMS ether > S-TMS ether > O-TMS ether > TMS-O-TMS

Stability of the TMS derivatives

O-TMS ether > S-TMS ether > Enol-O-TMS ether > TMS amine > TMS amide



N-methyl-N-trimethylsilyl-heptafluorobutyramide (MSHFBA)

M: 299.1 a/mol Bp: 148 °C (760 mm Ha)

MSHEBA is similar to MSTFA in reactivity and chromatography.

Used either alone or in combination with a catalyst (TMCS, TSIM) or another silvlation reagent with or without solvent.

By-product N-methylheptafluorobutyric amide has a lower retention time than the silylating reagent.

Especially useful for FID. because. due to the large 7:1 ratio of fluorine to silicon, the degradation of excess MSHFBA does not produce SiO2 but volatile, non-corrosive silicon compounds.



N-methyl-N-tert-butyldimethylsilyl-trifluoroacetamide (MBDSTFA)

M: 241.3 a/mol Bp: 168-170 °C (760 mm Ha) density d20 °/4 ° = 1.12

ty d20 °/4 ° = 1.12

$$CH_3$$

 $F_3C - CO - N$
 $Si(CH_3)_2 - C_4H_9$

MBDSTFA is a silvlation reagent that donates a tert-butyldimethylsilyl group (TBDMS) for derivatizing active hvdrogens in hydroxyl, carboxyl and thiol groups, primary and secondary amines, as well as in amino acids.

Fast reactions (typically 5-20 min) with high yields (> 96%). By-products are neutral and volatile.

TBDMS ethers are 104 times more stable than the corresponding TMS ethers. Chromatographic retention times are longer due to the large protecting group, which may improve some separations.

Very useful for GC-MS applications. because of a high molecular ion concentration at M⁺-57 applications.

Silanes / silazanes

Dimethyldichlorosilane (DMCS)

M: 129.06 a/mol Bp: 70 °C (760 mm Hg) density d20 °/4 ° = 1.07

DMCS is used to form dimethylsilyl (DMS) derivatives.

DMS derivatives are much more susceptible to hydrolysis than TMS derivatives. Therefore, strictly anhydrous conditions during the reaction are very important.

Hexamethyldisilazane (HMDS)

M: 161.4 a/mol

Bp: 126 °C (760 mm Ha) density d20 °/4 ° = 0.77

HMDS is a weak TMS donor. If used as sole reagent, it is slow and not very effective. After addition of catalytic quantities (e.g., 1%) of TMCS or as a mixture with TMCS, it is a fast and quantitative reagent for trimethylsilylation of organic compounds.

Aprotic solvents, e.g., acetonitrile, pyridine, dimethylformamide, carbon disulfide and dimethylacetamide are recommended for use with HMDS.

Trimethylchlorosilane (TMCS)

M: 108.7 g/mol

Bp: 57 °C (760 mm Hg) density d20 °/4 ° = 0.86

TMCS is often used as a catalyst with other trimethylsilyl reagents. Without additives it can be used for preparing TMS derivatives of organic acids.

Together with methanol, TMCS can be used for Methylation.

Silvlation reagent mixtures

SILYL-271 BSA - HMDS - TSIM (2:7:1)

SILYL-271 will derivatize all hydroxyl groups in any position. Useful in multiderivatization schemes involving hydroxyl or amine groups.

SILYL-1139 TSIM - pyridine (11:39)

Recommended application: alcohols, phenols, organic acids, steroids, hormones, glycols, nucleotides and narcotics.

Silvlation

SILYL-21 HMDS - TMCS (2:1)

SILYL-21 will derivatize amides and many secondary amines and hindered hydroxyls that would not be completely derivatized by HMDS alone. It can be used without solvent

SILYL-2110 HMDS - TMCS - pyridine (2:1:10) SILYL-319 HMDS - TMCS - pvridine (3:1:9)

SILYL-2110 and SILYL-319 will derivatize alcohols, bile acids, phenols, most steroids, sterols, and sugars that would not be completely derivatized by HMDS alone. SILYL-2110 and SILYL-319 are fast and easy to use, and can be used without solvent.

SILYL-991 BSTFA - TMCS (99:1)

BSTFA is a powerful trimethylsilyl donor. For silylating of fatty acid amides, hindered hydroxyls and other compounds that are difficult to silvlate, e.g., secondary alcohols and amines, we recommend BSTFA + 1 % TMCS. available under the designation SILYL-991.



- Reactions only in aprotic solvents possible
- The presence of water does not interfere with SII YI -1139.

Imidazoles

N-Trimethylsilvl-imidazole (TSIM)

M: 140.3 a/mol Bp: 94-96 °C (760 mm Ha) density d20 °/4 ° = 0.96

TSIM is the strongest hydroxyl silylator, the reagent of choice for carbohydrates and most steroids (even highly hindered steroids).

The reagent is unique in that it reacts quickly and smooth with hydroxyl (even tert. OH) and carboxyl groups, but not with amines. This characteristic makes TSIM particularly useful in multi-derivatization schemes for compounds with different functional groups that are to be derivatized differently, e.g., -O-TMS/-N-HFB derivatives of catecholamines.

Summary silylation

- Silvlation can be applied on many compounds
- Silylating reagents are easily prepared
- Large variety of reagents available

Acvlation / Benzovlation

Generally, acylation involves the introduction of an acyl group into a molecule with a replaceable hydrogen, or across a double bond. Acvlation is used to convert compounds like alcohols, amines and thiols into their respective esters, amides and thioesters. Additionally, they enhance the detectability of the compounds by adding halogenated carbon to the compounds. This is achieved through the reaction with fluorinated acvl halides, anhydrides or bisacvlamides. While the corresponding acidic by-products of the reactions with acyl halides and anhydrides need to be removed from the system by a suited base, e.g., pyridine, to prevent column damage. By-products of bisacylamides are not acidic and normally do not interfere with the subsequent analysis. Hence, they are favorable reagents for acylations.

Acvl halides

Pentafluorobenzovl chloride (PFBC)

R= C₆F₆, X=CI

M: 230.52 a/mol

Bp: 158-159 °C (760 mm Hg) density d20 °/4 ° = 1.60



PFBC will react with hydroxyls, primary and secondary amines, amides and thiols

Anhydrides

Trifluoroacetic acid anhydride (TFAA)

R=CF₃

M: 210.04 a/mol

Bp: 39.5-40.5 °C (760 mm Ha) density d20 °/4 ° = 1.49

Heptafluorobutyric acid anhydride (HFBA)

R=C₂F₇

M: 410.06 a/mol

Bp: 106-107 °C (760 mm Hg) density d20 °/4 ° = 1.665



Acylation with fluorinated acid anhydrides can be used for alcohols, phenols, carboxylic acids, amines, amino acids and steroids forming volatile, stable derivatives suited for FID as well as for ECD detection.

Acvlation

Bisacylamides

N-methyl-bis(trifluoroacetamide) (MBTFA)

R=CF₂

M: 223.08 a/mol Bp: 123-124 °C (760 mm Hg) density d20 °/4 ° = 1.55

N-methyl-bis(heptafluorobutyramide) (MBHFBA)

R=C₃F₇

M: 423.1 a/mol

Bp: 165-166 °C (760 mm Hg) density d20 °/4 ° = 1.67

Acylation with fluorinated acid amides is recommended for alcohols, primary and secondary amines as well as for thiols under mild, neutral conditions. MBTFA also forms very volatile derivatives with carbohydrates.



 Reaction products (acidic by-products) often have to be removed before analysis

Summary acylation

- Addition of halogenated carbons enhances detectability by ECD
- Derivatives are hydrolytically stable
- Increased sensitivity by adding molecular weight

Alkylation (methylation) / esterification

Alkylation is a derivatization method used to replace an acidic hydrogen with an alkyl or methyl group. It is generally restricted to amines or hydroxy groups like in amino or carboxvlic acids. The resulting derivatives are ethers, esters, methylamines or -amides and less polar than the original compounds. Therefore, less hydrogen bonding occurs. The acidity of the hydrogen to be replaced significantly determines the conditions needed to perform the alkylation. The less acidic, the more vigorous the conditions.

Methylation reagents

Dialkylacetals

N.N-dimethylformamide dimethylacetal (DMF-DMA)

M: 119.17 a/mol

Bp: 106-107 °C (760 mm Ha) density d20 °/4 ° = 0.89

DMF-DMA is recommended for sterically hindered carboxylic acids, aldehydes, phenols and amines.

Trimethylsulfonium compounds

Trimethylsulfonium hydroxide (TMSH, 0,2 M in methanol)

M: 94.06 g/mol

$$\begin{bmatrix} H_3C \\ H_3C \end{bmatrix} \overline{S} - CH_3 \end{bmatrix} \stackrel{\bigoplus}{OH} \stackrel{\bigoplus}{OH}$$

Methylation with TMSH is recommended for free acids, chlorophenoxycarboxylic acids, their salts and derivatives as well as for phenols and chlorophenols. Lipids or trialvcerides can be converted to the corresponding fatty acid methyl esters (FAMEs) by a simple transesterification.

This reaction is very elegant and convenient, because it is just necessary to add the reagent (0.2 M in methanol) to the sample solution. Removal of excess reagent is not required, since in the injector of the gas chromatograph. at 250 °C, pyrolysis to volatile methanol and dimethylsulfide will occur. Due to the high reactivity, complete derivatization is often obtained at ambient temperature. However, heating

(e.g., 10 min at 100 °C) in a closed sample vial may be necessary to complete

the reaction.

Alkylation

Esterification reagents

Methylation with methanol /TMCS

An 1M solution of TMCS in methanol is suited for the esterification of free carboxylic acids and transesterification of glycerides. Formation of HCl catalyzes the reaction. TMCS and silvl ether remove water and thus drive the reaction to completion. The mixture should be freshly prepared.

Summary alkylation (methylation)

- Methylation derivatives are generally stable
- Wide range of reaction conditions (from strongly acidic to strongly basic)
- Some reactions can be achieved. with water present

Good to know



- Reactions are limited to acidic hydrogens or amines
- Reaction conditions may be extreme



Silvlation

with BSA, BSTFA or SILYL-991 (BSTFA + 1 % TMCS) BSA MN Appl. No. 213091 · BSTFA MN Appl. No. 213092 · SILYL-991 MN Appl. No. 213093

Add 0.5 mL of the silylation reagent to 1-10 mg sample; if necessary, add some solvent (normally pyridine or DMF [dimethylformamide]). Heat to 60-80 °C for 20 min to increase the reaction rate, 1-2 drops of TMCS (trimethylchlorosilane) or TSIM will also speed up the reaction.

with BSA in combination with other silvlation reagents · MN Appl. No. 213100

BSA alone silvlates all sterically unhindered hydroxyl groups of the steroid skeleton: addition of TMCS will enable reaction of moderately hindered OH groups (reaction time 3-6 h at 60 °C). After addition of TSIM even strongly hindered hydroxyl groups will react (reaction time 6-24 h at 60 °C).

with MSTFA. MSHFBA or MBDSTFA MSTFA MN Appl. No. 213111 · MSHFBA MN Appl. No. 213112 · MBDSTFA MN Appl. No. 213113

Dissolve 10-15 mg sample in 0.8 mL solvent, then add 0.2 mL of the silvlation reagent. The reaction mixture can be heated to 60-70 °C for up to 1 h and can be analyzed directly. If TFA is used as a solvent, proceed as follows [20]: dissolve 1-2 mg sample in 100 uL TFA. Dropwise add 0.9 mL of the silvlating reagent. After cooling the sample can be chromatographed directly.

with TSIM or SILYL-1139 (TSIM - pyridine 11:39) TSIM MN Appl. No. 213121 SILYL-1139 MN Appl. No. 213122

Dissolve 10-15 mg sample in 0.8 mL solvent, then add 0.2 mL of the silvlation reagent. The reaction mixture can be heated to 60-70 °C for up to 1 hour and can be analyzed directly. Recommended solvent is pyridine. When using SILYL-1139, the presence of water does not interfere.

Silvlation

with SILYL-21 or SILYL-2110 or SILYL-319 · SILYL-21 MN Appl. No. 213131 · SILYL-2110 · MN Appl. No. 213132

Carefully add SILYL-21, SILYL-2110 or SILYL-319 to 1-10 mg of the sample. Precipitated ammonium chloride does not interfere. If the sample should not dissolve within 5 min. heat to 75-85 °C. If no mutarotation is to be expected. you may dissolve the sugar in warm pyridine first and then add the silvlation reagent. In some cases it may be advantageous to use a different solvent instead of pyridine. For derivatization of 3-ketosteroids we recommend to use DMF (dimethylformamide).

O-trimethylsilylation with MSTFA followed by N-trifluoroacetylation with MBTFA MN Appl. No. 213140

Completely silylate 2 mg of the sample with 0.3 mL MSTFA. After addition of 0.3 mL MBTFA the N-trimethylsilyl group is replaced by the N-trifluoroacetyl group. The mixture can be analyzed directly.



Acylation

with fluorinated acid anhydrides TFAA MN Appl. No. 213041 · HFBA MN Appl. No. 213042

Dissolve 0.1 to 1 mg sample in 0.1 mL solvent, add 0.1 mL of the anhydride and heat to 60-70 °C for 1-2 h. If the sample needs not be concentrated prior to the analysis and if there is no danger of catalytically induced side reactions, pyridine is used as solvent. The reaction solution can be injected directly into the gas chromatograph. Otherwise, use a volatile solvent and evaporate solvent, excess reagent and free acid in a stream of nitrogen. Dissolve residue in 50 µL hexane, chloroform etc. and inject aliquot portions.

with fluorinated acid amides MBTFA MN Appl. No. 213051 · MBHFBA MN Appl. No. 213052

Add 0.5 mL MBTFA or MBHFBA to about 2 mg sample. If there is no reaction at ambient temperature, heat the reaction mixture to 120 °C. Compounds difficult to dissolve, can be trifluoroacetylated in suitable solvent mixtures. It is recommended to use a ratio of solvent to MBTFA or MBHFBA of 4:1. The reaction mixture is chromatographed directly.

Alkylation (Methylation)

with TMSH · MN Appl. No. 213060

Dissolve 100 mg sample (e.g., butter) in 5 mL of a solvent (e.g., tert.-butyl methvl ether). Add 50 uL reagent to 100 uL of this solution. The mixture is injected directly. The temperature of the injector must be at least 250 °C.

with DMF-DMA · MN Appl. No. 213070

Add 1 mL of a mixture of DMF-DMA and pyridine (1:1) to 1-50 mg fatty acids. The sample can be injected as soon as a clear solution has formed. It is recommended, however, to heat the solution to 60-100 °C for 10-15 min.

with methanol - TMCS · MN Appl. No. 213080

Add 1 mL methanol - TMCS to about 50 mg carboxylic acid or glyceride and heat. Then evaporate in a stream of nitrogen and dissolve again for injection in, e.a., n-heptane.



Overview of important functional groups

Functional Group	Silylation*	Acylation / Benzoylation	Alkylation
Primary alcohols	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	TFAA, HFBA, MBTFA, MBHFBA, PFBC	TMSH
Secondary alcohols	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	TFAA, HFBA, MBTFA, MBHFBA, PFBC	TMSH
Tertiary (and sterically hin- dered) alcohols	TSIM, BSTFA, SILYL-991	TFAA, HFBA, PFBC	
Thiols	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	MBTFA, MBHFBA, HFBA, TFAA	TMSH
PhenoIs	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	TFAA, HFBA, MBTFA, MBHFBA, PFBC	DMF-DMA, TMSH
Glycols	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	TFAA, HFBA, MBTFA, MBHFBA, PFBC	TMSH
Aldehydes	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	TFAA, HFBA, MBTFA, MBHFBA, PFBC	DMF-DMA, TMSH, MeOH/TMCS
Ketones	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	TFAA, HFBA, MBTFA, MBHFBA, PFBC	DMF-DMA, TMSH, MeOH/TMCS
Carboxylic acids	BSA, MSTFA, MSHFBA, TSIM, SILYL-2110, SILYL-319, SILYL-21, SILYL-1139	TFAA, HFBA, MBTFA, MBHFBA, PFBC	DMF-DMA, TMSH, MeOH/TMCS
Carbohy- drates /Sugars	MSTFA, TSIM, SILYL-2110, SILYL-319, SILYL-991, HMDS	TFAA, MBTFA, PFBC	
Acid anhydrides			MeOH/TMCS
α-hydroxy acids	MSTFA	MBTFA	

Overview of important functional groups

Functional Group	Silylation*	Acylation / Benzoylation	Alkylation
Primary amines	BSA, MSTFA, MSHFBA, SILYL-991	TFAA, HFBA, MBTFA, MBHFBA, PFBC	DMF-DMA
Secondary amines	BSA, MSTFA, MSHFBA, SILYL-991	TFAA, HFBA, MBTFA, MBHFBA, PFBC	DMF-DMA
Amides	Silylamides are not stable	TFAA, HFBA, MBTFA, MBHFBA, PFBC	
Amino acids	BSA, BSTFA, MSTFA, MSHFBA	TFAA, HFBA, MBTFA, MBHFBA, PFBC	MeOH/TMCS, TMSH
Amino sugars	BSA, MSTFA, MSHFBA, SILYL-991	TFAA, HFBA, MBTFA, MBHFBA, PFBC	
Imino acids	BSA, MSTFA, MSHFBA, SILYL-991	TFAA, HFBA, MBTFA, MBHFBA, PFBC	
Carbamides	Silylamides are not stable	TFAA, HFBA, MBT- FA, MBHFBA	
Alkylamides	Silylamides are not stable	PFBC	
Amino alcohols	MSTFA	MBTFA	

^{* (}Avoid polar stationary phases containing active protons, e.g., WAX or FFAP)

General reaction mechanisms

Silylation

$$\begin{array}{ccc} CH_3 & CH_3 \\ Analyte-X-H+H_3C-Si-Y & \longrightarrow & Analyte-X-Si-CH_3+HY \\ CH_3 & CH_3 & CH_3 \end{array}$$

X = e.g., O, S, COO, etc.

Y = rest of silylation reagents; stuctures see page 7-11

Acylation

X = e.g., O, S, NH, etc.

Y = rest of acylation reagents; stuctures see page 12, 13

General reaction mechanisms

Alkylation (Methylation) · example TMSH

$$\label{eq:Analyte} \text{Analyte} - \text{X} - \text{H} + \left[\text{TMSH} \right]^+ \text{OH} \xrightarrow{} \quad \text{Analyte} - \text{X} - \text{CH}_3 + \overset{\text{CH}_3}{\text{S}} \\ \text{CH}_3 \\ \end{array} \\ + \text{H}_2 \text{O}$$

X = e.g., O, S, COO, etc.

Alkylation reagents; stuctures see page 14

References

- 1. MN Chromatography catalog
- 2. Blau, K., Halket, J., Handbook of Derivatives for Chromatography, Second Edition; John Wiley & Sons; Chichester, 1993
- 3. Knapp, D.R. Handbook of Analytical Derivatizations Reactions; John Wiley & Sons; New York, 1979
- Butte, W., J. Chromatogr, A. 261, 1983

Ordering information

Substance	Packing unit 10 x 1 mL	20 x 1 mL	1 x 10 mL	5 x 10 mL
Silylation reagents*				
BSA			701210.110	701210.510
BSTFA		701220.201	701220.110	701220.510
DMCS**				
HMDS				701240.510
TMCS**		701280.201		
TSIM		701310.201	701310.110	701310.510
MSHFBA		701260.201	701260.110	701260.510
MSTFA		701270.201	701270.110	701270.510
MBDSTFA	701440.101	701440.201		
SILYL-271 (BSA – HMDS – TSIM 2:7:1)		701450.201	701450.110	701450.510
SILYL-1139 (TSIM – pyridine 11:39)		701460.201		
SILYL-21 (HMDS – TMCS 2:1)		701470.201		
SILYL-2110 (HMDS – TMCS – pyridine 2:1:10)		701480.201		
SILYL-319 (HMDS – TMCS – pyridine 3:1:9)		701241.201		
SILYL-991 (BSTFA - TMCS 99:1)		701490.201		
Acylation reagents*				
HFBA		701110.201	701110.110	701110.510
MBTFA		701410.201	701410.110	701410.510
MBHFBA	701420.101	701420.201		
PFBC	701120.101			
TFAA			701130.110	701130.510
Alkylation reagents*				
DMF-DMA		701430.201	701430.110	
TMSH	701520.101	701520.201	701520.110	701520.510

Due to their purpose, derivatization reagents are very reactive chemicals. For this reason, they should be stored cool and protected from moisture. For easy access with a syringe, our derivatization reagents are supplied in vials with crimp caps. Vials with pierced sealing disks have limited stability and should be used up soon.

Ordering information

1 x 50 mL	6 x 50 mL	1 x 100 mL	6 x 100 mL	12 x 100 mL
		·	·	·
701210.150				
	701230.650			
	701240.650			
	701280.650			
		701260.1100	701260.6100	
	701270.650	701270.1100	701270.6100	701270.12100
701490.150		701490.1100		
701400.100		701400.1100		

^{*} These products contain harmful chemicals which must be specially labeled as hazardous. For detailed information please see SDS.

^{**} Vials with screw caps. Further screw caps on request.

Contact

MACHEREY-NAGEL GmbH & Co. KG

Neumann-Neander-Str. 6–8 \cdot 52355 Düren \cdot Germany

DE/International:

Tel.: +49 24 21 969-0 Fax: +49 24 21 969-199 E-mail: info@mn-net.com

CH:

Tel.: +41 62 388 55 00 Fax: +41 62 388 55 05 E-mail: sales-ch@mn-net.com

FR:

Tel.: +33 388 68 22 68 Fax: +33 388 51 76 88 E-mail: sales-fr@mn-net.com

US:

Tel.: +1 484 821 0984 Fax: +1 484 821 1272 E-mail: sales-us@mn-net.com

www.mn-net.com

MACHEREY-NAGEL

www.mn-net.com





1-800-267-8103 • www.chromspec.com • tech@chromspec.com