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Stability of Semi-Volatile Compounds in US EPA Method 8270 and Appendix IX Analytical Reference Materials

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Abstract

EPA method 8270 and Appendix IX contain over 150 commonly analyzed semi-volatile pollutants. The compounds include PAH's, chlorinated hydrocarbons, aldehydes, ketones, nitrosamines, phenols, anilines and benzidines. Preparing stable analytical reference materials for this extensive compound list is not trivial. Poorly formulated mixtures will give compound interaction over time in the flame sealed ampule that ultimately misrepresents the originally prepared target concentration leading to poor calibration data quality.

Data will be presented on the stability of many different semi-volatile analytical reference materials formulations. Incompatible compounds and their proposed reactions and products will be described. The role of solvent purity and specifications in good long term reference material will also be described.

Purpose

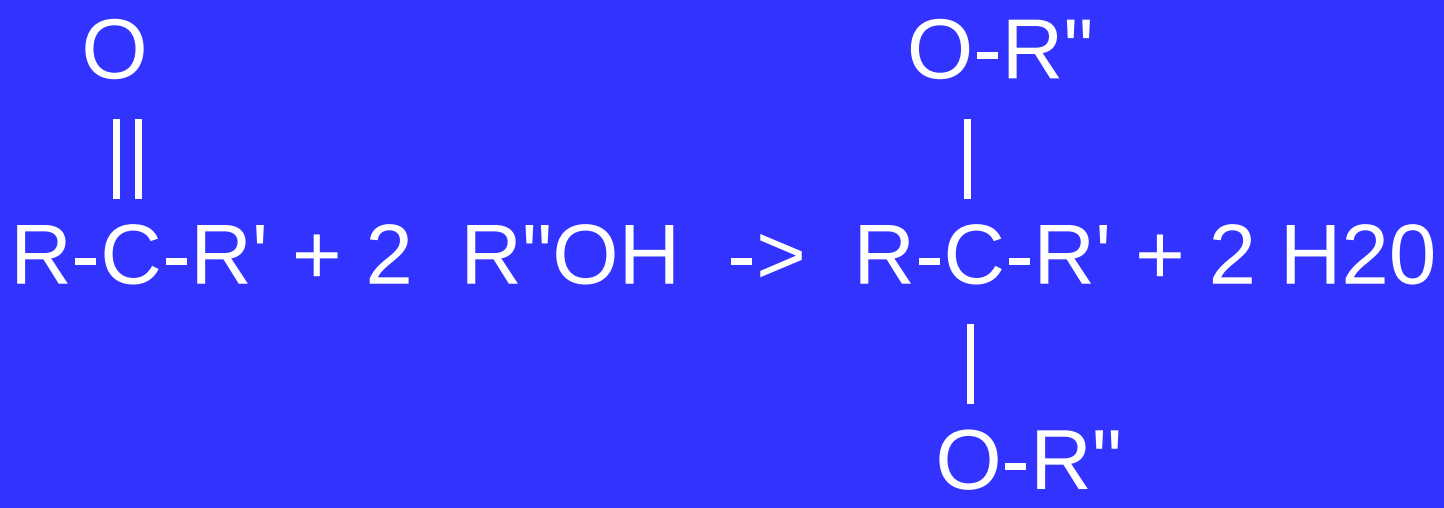
The purpose of this work was to identify the most commonly analyzed EPA 8270 and Appendix IX compounds and formulate these into a minimum number of stable, easily handled calibration stock mixtures.

Acid / Base Reactions

- Acids, such as phenols and benzoic acid will react with bases, such as anilines, benzidines, and nitrosamines. Most calibration standards prepared with these compounds together will only be usable for only about one week. These incompatible compounds were kept separate to ensure maximum shelf life of the ampulated stock solutions.
- Low response, tailing peaks, or complete loss of these compounds are signs of acid / base reactions in your calibration standards.

Ketone Addition Reaction with Alcohols

- Most ketones will form hemi-acetals and acetals in the presence of alcohols. The general reaction is as follows:



This reaction may be catalyzed by either acid or base

PAH Reactions in the Presence of Hexachlorocycopentadiene and Hexachlorobutadiene

- PAHs have been known to spontaneously chlorinate in the presence hexachorocyclopentadiene and hexachlorobutadiene. The reaction is a substitution reaction with chlorine for hydrogen on the PAH. The exact mechanism has not been determined at this time. No loss of hexachlorocyclopentadiene nor hexachlorobutadiene is seen in this reaction.

- The reaction is believed to be caused by free chlorine or chlorine radicals in certain lots of hexachlorocyclopentadiene and hexachlorobutadiene.

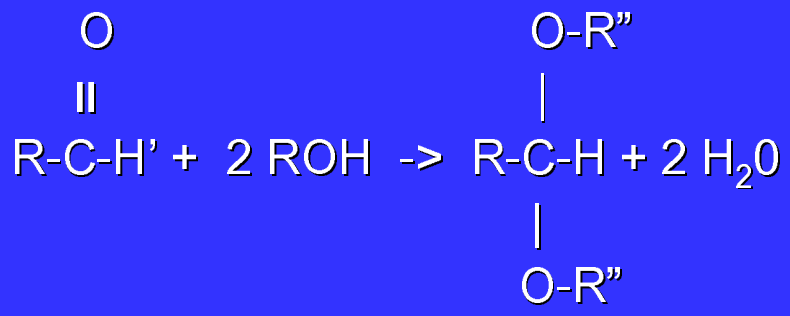
- Purification of hexachlorocyclopentadiene and hexachlorobutadiene by distillation prevents this reaction.

Aldehyde Adduct formation in the presence of alcohols

- Aldehydes will form adducts in the presence of alcohols. An example is benzaldehyde in the presence of methanol. This reaction may take place immediately or slowly over several months.

- Most brands and grades of methylene chloride contain methanol added at a concentration of about 500ppm as a stabilizer. This may or may not be listed on the bottle label. Methylene chloride can be quickly screened for added methanol by GC/FID on a non-polar column, such as the Rtx-5.

- The methylene chloride used for this study was amylene stabilized and contained no methanol.



This reaction may be catalyzed by either acid or base

Chorinated Triazine Herbicides

- Chlorinated triazine herbicides will substitute chlorine for OH or OR in the presence of water or alcohol.
- This reaction is catalyzed by light or acid.
- The reaction is very fast once started since the reaction product HCl is a catalyst.

Chlorinated Triazines include:

Atrazine

Cyanazine

Cyprozine

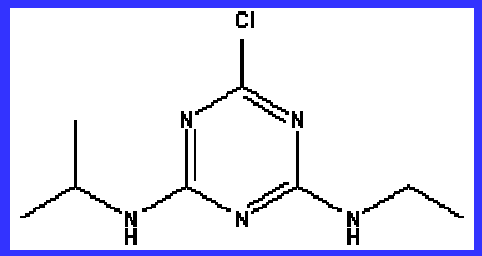
Procyazine

Propazine

Simazine

Terbuthylazine

Trietazine



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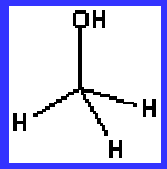

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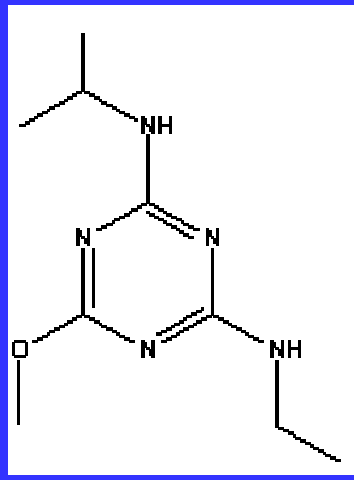

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Stability Testing

- Stability testing was based on flame sealed ampules stored at 4°C or –18°C under real-time conditions.
- Stored solutions where compared by GC/MS to newly prepared solutions.
- A stored solution was determined to be unusable if there was more than 5% difference in response for any one analyte.

Final Phenols Calibration Mixture

2,3,4,6-Tetrachlorophenol
2,4,5-trichlorophenol
2,4,6-Trichlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2,6-Dichlorophenol
2-Chlorophenol
2-Methylphenol (o-cresol)
2-Nitrophenol
3-Methylphenol (m-cresol)
4,6-Dinitro-2-methylphenol
4-Chloro-3-methylphenol
4-Methylphenol (p-cresol)
4-Nitrophenol
Benzoic acid
Dinoseb
Pentachlorophenol
Phenol

2000 ppm each in methylene chloride

This mixture is currently stable for 37 months at 4°C

Final Anilines / Nitrosamines Mixture #1

2-Nitroaniline
3,3'-dichlorobenzidine
3-Nitroaniline
4-Chloroaniline
4-Nitroaniline
Aniline
Benzidine
N-Nitrosodi-n-propylamine
N-Nitrosodimethylamine
Pyridine

2000 µg/ml in methylene chloride

This mixture is currently stable for 18 months at –18°C.

Final Chlorinated Compounds Mix

1,2,4,5-Tetrachlorobenzene
1,2,4-trichlorobenzene
1,2-dichlorobenzene
1,3-Dichlorobenzene
1,3-Dinitrobenzene
1,4-Dichlorobenzene
2-Chloronaphthalene
4-Bromophenyl phenyl ether
4-Chlorophenyl phenyl ether
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl) ether
bis(2-chloroisopropyl)ether [2,2'-oxylbis-(1-chloropropane)]
Chlorobenzilate
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachloropropene
Isodrin
Kepone
Pentachlorobenzene
Pentachloronitrobenzene
Aramite

2000 ppm each in methylene chloride

This mixture is currently stable for 12 months at –18°C. More stability testing is in progress.

Final Neutral Compound Mixture

1,3,5-Trinitrobenzene
1,4-Naphthoquinone
2,4-Dinitrotoluene
2,6-Dinitrotoluene
4-Nitroquinoline-1-oxide
Acetophenone
azobenzene
Benzyl alcohol
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
DI-n-octyl phthalate
Dibenzofuran
Diethyl phthalate
Dimethyl phthalate
Ethyl methanesulfonate
Isophorone
Isosafrole (cis & trans)
Methyl methanesulfonate
Nitrobenzene
Phenacetin
Safrole

2000 ppm each in methylene chloride

This mixture is currently stable for 24 months at –18°C. More Stability testing is in progress.

Final PAH Mixture

1-methylnaphthalene
2-Methylnaphthalene
3-Methylcholanthrene
Acenaphthene
Acenaphthylene
Anthracene
Benz(a) anthracene
Benzo(a) pyrene
Benzo(b) fluoranthene
Benzo(g,h,i) perylene
Benzo(k) fluoranthene
Chrysene
Dibenz(a,h) anthracene
Fluoranthene
Fluorene
Ideno(1,2,3-cd) pyrene
Naphthalene
phenanthrene
Pyrene

2000 ppm each in methylene chloride

This mixture is currently stable for 37 months at 4°C.

Final Organophosphorus Mixture

0,0,0-Triethyl phosphorothioate
Diallate (cis or trans)
Dimethoate
Disulfoton
Famphur
Methyl parathion
Parathion
Phorate
Pronamide
Thionazine

2000 ppm each in methylene chloride

This mixture is currently stable for 11 months at 4°C.

Final Organochlorine Pesticide Mixture

4,4'-DDD
4,4'-DDE
4,4'-DDT
Aldrin
alpha-BHC
Alpha-chlordane
beta-BHC
delta-BHC
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
gamma-BHC (Lindane)
Gamma-chlordane
Heptachlor
Heptachlor epoxide
Methoxychlor

200 ppm each in 1:1: hexane/toluene

Currently stable for 37+ months at 4°C.

Final Anilines / Nitrosamines Mix #2

1,4-Phenylenediamine
1-Naphthylamine
2-Acetylaminofluorene
2-Naphthylamine
2-Picoline
3,3'-Dimethylbenzidine
4-Aminobiphenyl
5-Nitro-o-toluidine
a,a,-Dimethylphenethylamine (free base)
Methapyrilene (free base)
N-Nitrosodibutylamine
N-Nitrosodiethylamine
N-Nitrosomethylethylamine
N-Nitrosomorpholine
N-Nitrosopiperidine
N-Nitrosopyrrolidine
o-Toluidine
p-Dimethylaminoazobenzene

This mixture is currently stable for 18 months at –18°C.

2000 ppm each in methylene chloride

Conclusions

- Stable stock calibration mixtures can be prepared by carefully considering potential chemical interactions between target analytes, impurites, solvents, and solvent stabilizers.
- Solvents must be carefully chosen and screened to obtain good shelf life of stock solutions.
- Stock solution storage plays a role in shelf life. Amber glass ampules will prevent reactions caused by light. While refrigerator storage is generally recommended for semivolatile standards, freezer storage will improve stability for certain mixtures, especially anilines and benzidines.