Emerging Contaminants:

potentially hazardous physical, chemical, or biological agents posing new concern

Identifying Chemical Compounds of Concern
and
Addressing Adverse Effects

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- Emerging contaminants (ECs) include a subset of chemical compounds not monitored closely by regulatory agencies in the past but now determined to pose potential threat to human health and the environment.
- Little data are available about the health risks associated with ECs, even at higher concentrations, and little is known about EC persistence in environmental media.
- Ongoing technological advancements across industrial sectors continue to introduce new chemical agents posing unknown risks.
- This introduction of newly synthesized chemical compounds into our daily lives presents global concerns.(1)

- The U.S. Environmental Protection Agency (EPA) and other federal or state agencies recognize that more complete understanding of EC threats is needed to potentially regulate ECs and address associated site cleanups.

- One early approach to address ECs of concern was formulated in a 2003 joint request from the California Environmental Protection Agency (CalEPA) and State Water Resources Control Board to the U.S. Department of Defense (DoD).(2) DoD was requested to:

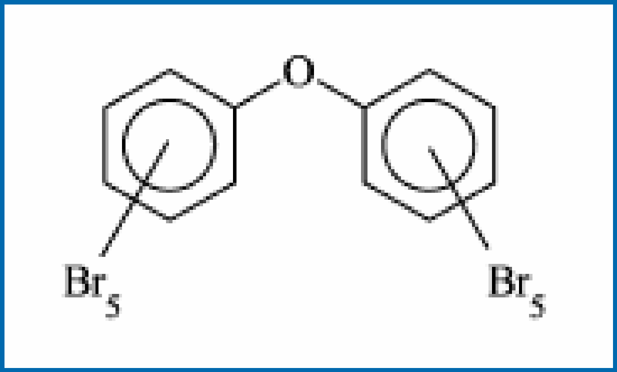
  - Address perchlorate and other ECs generated by military activities and potentially migrating offsite from military facilities.

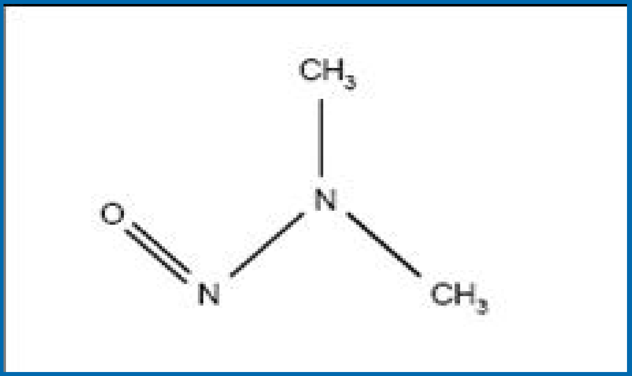
  - Coordinate with DoD service branches to identify specific ECs, conduct related site investigations, and complete associated cleanup of EC-contaminated media on these properties.

Contaminants of Particular Concern

- N-nitrosodimethylamine (NDMA)
- Polybrominated diphenyl ether (PBDE)
- Hexavalent chromium
- 1,2,3-Trichloropropane (TCP)
- Perchlorate
- Benzidine

Overviews of Selected ECs





PBDEs

NMDAs

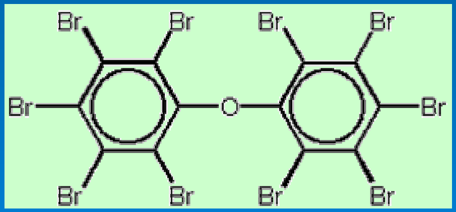
- Common industrial use
- Common locations of contamination
- Health effects
- Analytical detection methods

Polybrominated Diphenyl Ethers

Common industrial use of PBDEs

- PBDEs are a class of commercially produced flame-retardants added during the manufacturing of products ranging from clothing to electronic equipment.

- These compounds commonly provide the cheapest means for improving fire resistancy of products.



deca-BDE accounts for 75% of BDE production

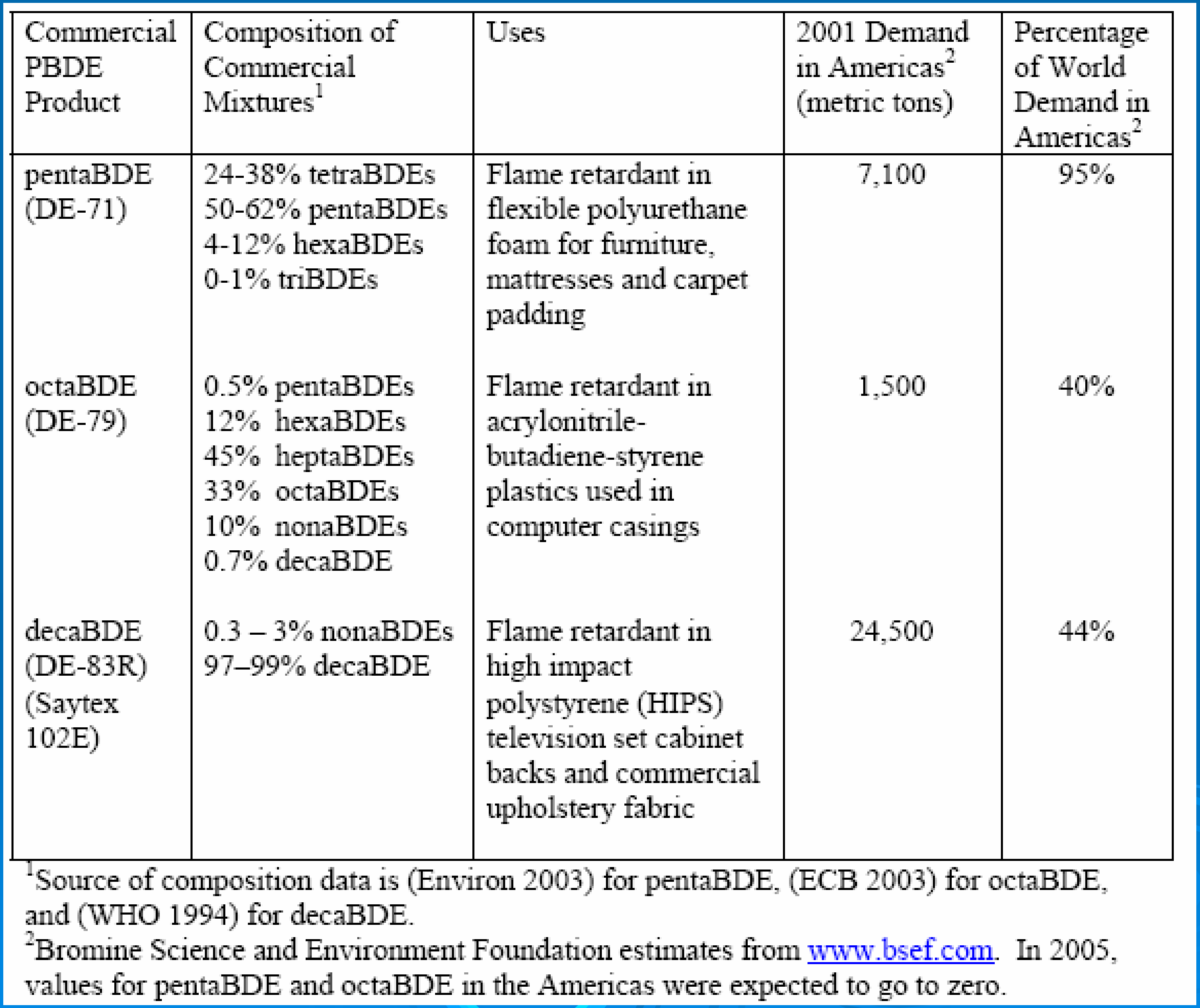
PBDE Applications

electronic circuit boards and wire and cable insulation

textiles containing non-covalently bound
additives released over product lifetime

various plastics posing additional
PBDE exposure during recycling

PBDE Applications



Commercial PBDE Product	Composition of Commercial Mixtures[1]	Uses	2001 Demand in Americas[2] (metric tons)	Percentage of World Demand in Americas[2]
pentaBDE (DE-71)	24-38% tetraBDEs 50-62% pentaBDEs 4-12% hexaBDEs 0-1% triBDEs	Flame retardant in flexible polyurethane foam for furniture, mattresses and carpet padding	7,100	95%
octaBDE (DE-79)	0.5% pentaBDEs 12% hexaBDEs 45% heptaBDEs 33% octaBDEs 10% nonaBDEs 0.7% decaBDE	Flame retardant in acrylonitrile-butadiene-styrene plastics used in computer casings	1,500	40%
decaBDE (DE-83R) (Saytex 102E)	0.3 – 3% nonaBDEs 97–99% decaBDE	Flame retardant in high impact polystyrene (HIPS) television set cabinet backs and commercial upholstery fabric	24,500	44%

[1] Source of composition data is (Environ 2003) for pentaBDE, (ECB 2003) for octaBDE, and (WHO 1994) for decaBDE.

[2] Bromine Science and Environment Foundation estimates from www.bsef.com. In 2005, values for pentaBDE and octaBDE in the Americas were expected to go to zero.

Common Locations of PBDE Contamination

- As persistent organic pollutants, PBDEs tend to accumulate in human and animal tissue and persist in environmental media for long periods.

Due to lipophilicity, PBDEs exist in tissue of many species of wildlife, including the body fat of Atlantic Ocean sperm whales.(3)

- These compounds easily adsorb onto solid particles of soil and sediment, which serves as a major contaminant sink in aquatic environments.
- Persistence of PBDEs in the environment is attributed to their resistance toward both acid and base compounds, heat, light, and reducing or oxidizing compounds. These characteristics provide PBDE utility, however, in products such as Teflon.®

PBDE Health Effects

- PBDEs have been identified in human breast milk, tissue, and blood samples.(4)(5)
- An examination of Swedish human milk samples collected in 1972-1997 showed exponential increases in PBDE levels with a doubling rate of about 5 years.(6)
- PBDEs are structurally similar to thyroid hormones and therefore may act as endocrine disruptors interfering with hormone homeostasis.(7)

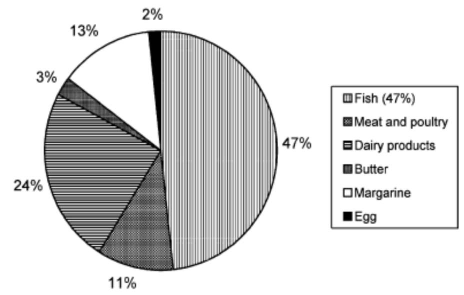
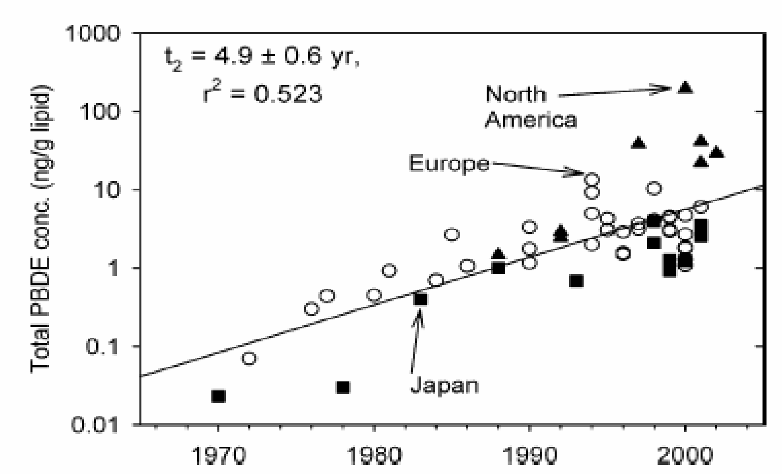
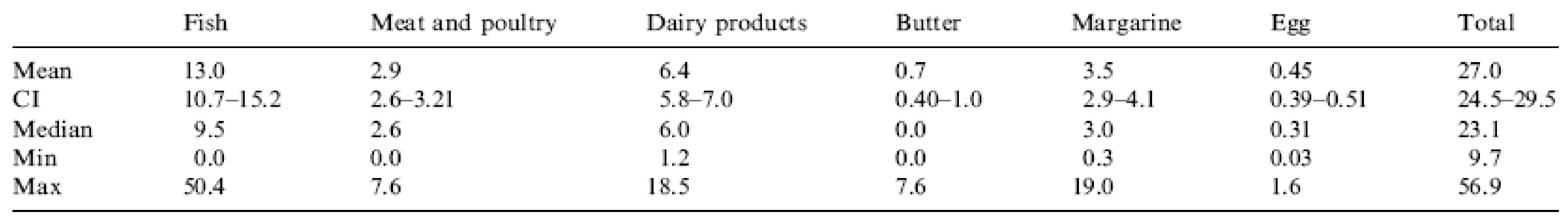


Fig. 2. The contribution of different food groups to the total estimated intake of PBDEs among primiparous women in Uppsala County, Sweden.





The calculated intake of ΣPBDE (ng/day) from food among primiparous women in Uppsala County, Sweden ($N = 87$)

	Fish	Meat and poultry	Dairy products	Butter	Margarine	Egg	Total
Mean	13.0	2.9	6.4	0.7	3.5	0.45	27.0
CI	10.7–15.2	2.6–3.21	5.8–7.0	0.40–1.0	2.9–4.1	0.39–0.51	24.5–29.5
Median	9.5	2.6	6.0	0.0	3.0	0.31	23.1
Min	0.0	0.0	1.2	0.0	0.3	0.03	9.7
Max	50.4	7.6	18.5	7.6	19.0	1.6	56.9

Actions Limiting PBDE Production and Use

- In 2002, the European Parliament adopted a ban on marketing and use of penta-BDE and octa-BDE throughout the European Union.
- In July 2003, the State of California adopted a ban on the manufacture or distribution in commerce of any product containing penta-BDE or octa-BDE.
- EPA has proposed a “significant new use rule” requiring prior notification to EPA by any manufacturer or importer intending to reintroduce penta-BDE or octa-BDE in the U.S.
- EPA is reviewing available toxicology data and preparing toxicological profiles for tetra-BDE, penta-BDE, hexa-BDE and deca-BDE congeners under its Integrated Risk Information System (IRIS) program.

PBDE Analytical Detection Methods

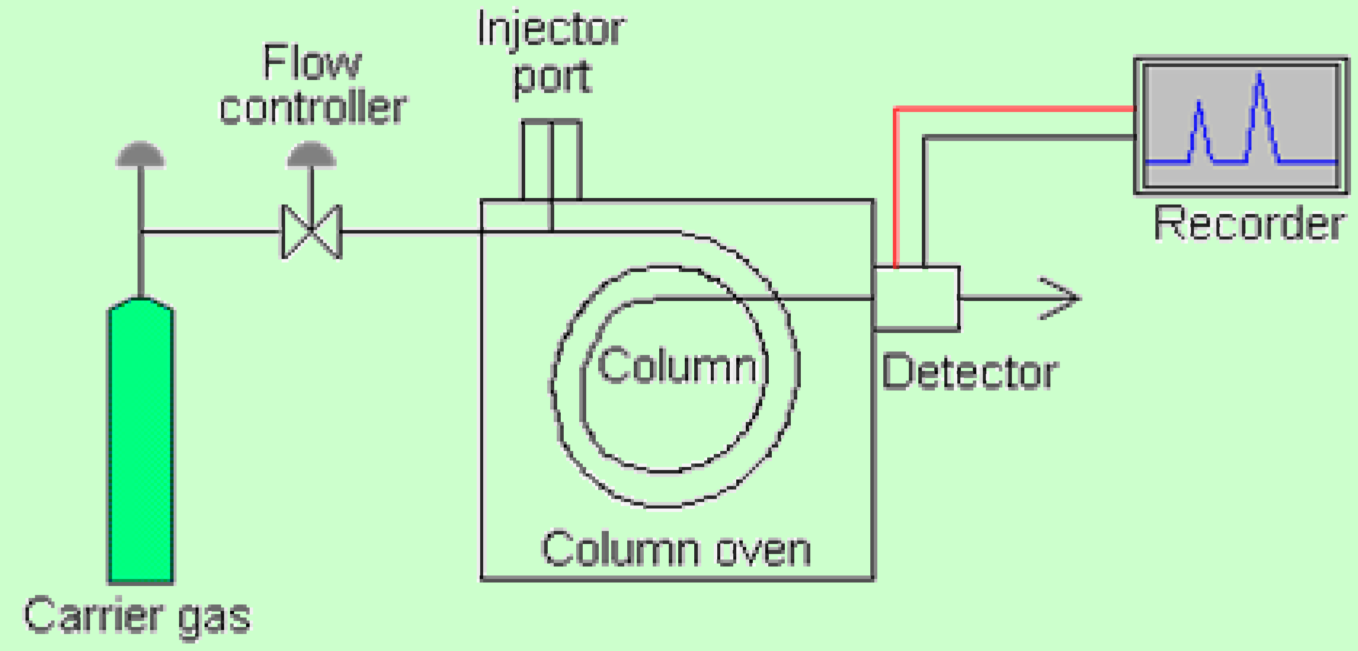
- EPA Draft Method 1614

Description	Method	Detection Limit	Cost/sample	Matrix Addressed	Holding Time	Date Released
For determination of brominated diphenyl ether (BDE) congeners in water, soil, sediment, biosolids, tissue, and other sample matrices.	high resolution gas chromatography combined with high resolution mass spectrometry (HRGC/HRMS)	MDL: 20-50 pg/L ML: 50-200 pg/L	$500-900	aqueous, solid, tissue, and multi-phase matrices	up to a year	August 2003 patterned after EPA Method 1668A

- EPA Method 527 (8)

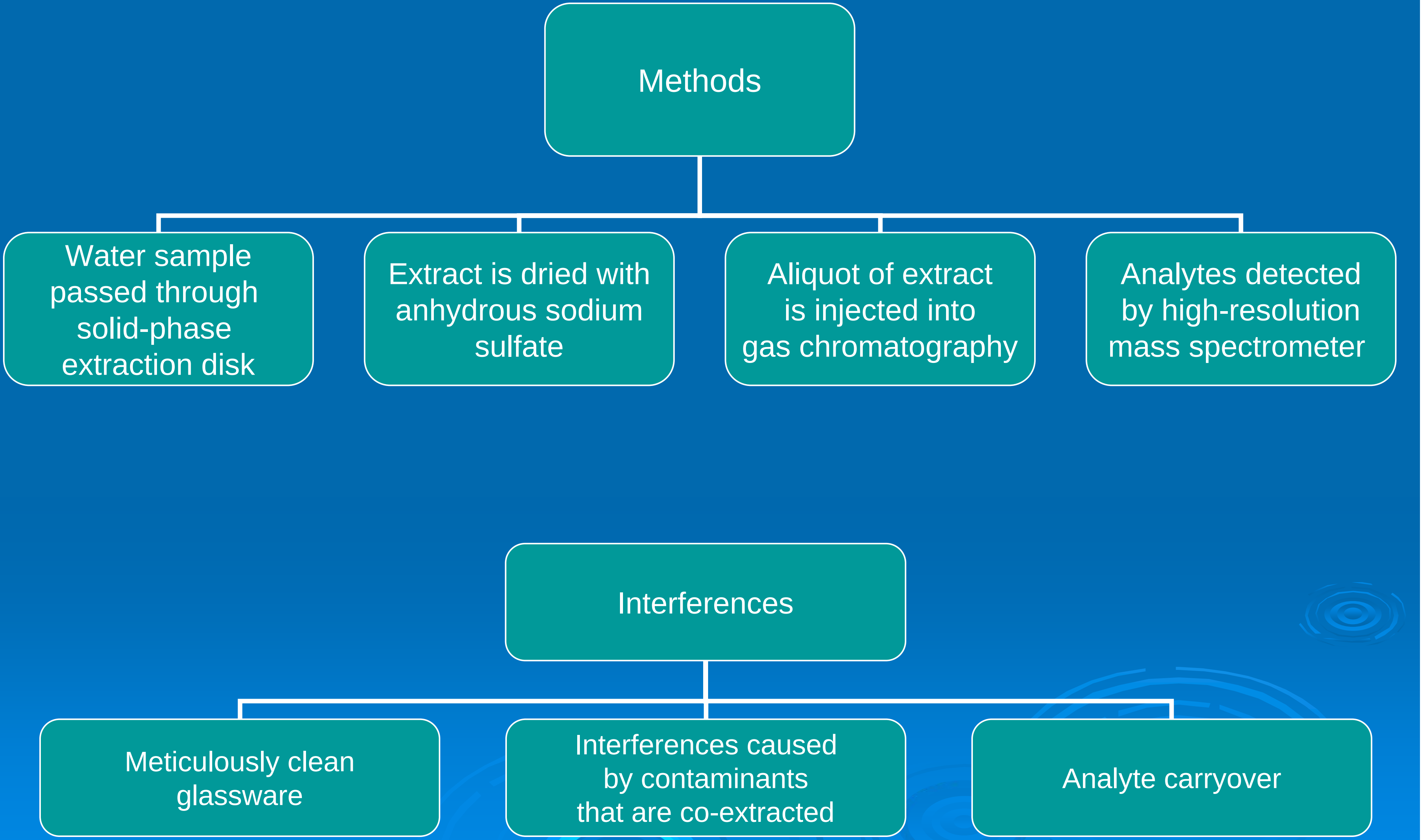
Description	Method	Detection Limit	Cost/sample	Matrix Addressed	Holding Time	Date Released
Determination of selected pesticides and flame retardants in drinking water by solid phase extraction and capillary column gas chromatography / mass spectrometry (GC/MS)	solid phase extraction, injection is made into a GC equipped with a high-resolution fused silica capillary column that is interfaced to a MS.	DL: 0.051 - 0.097 ug/L	$500-900	drinking waters	extraction within 28 days	April 2005

Gas Chromatography for Detecting PBDE



Gas chromatography (GC) involves injection of a sample and vaporization onto the head of a GC column. The sample is transported through the column by the flow of inert gas in mobile phase.

Similarities Between Methods 1614 and 527



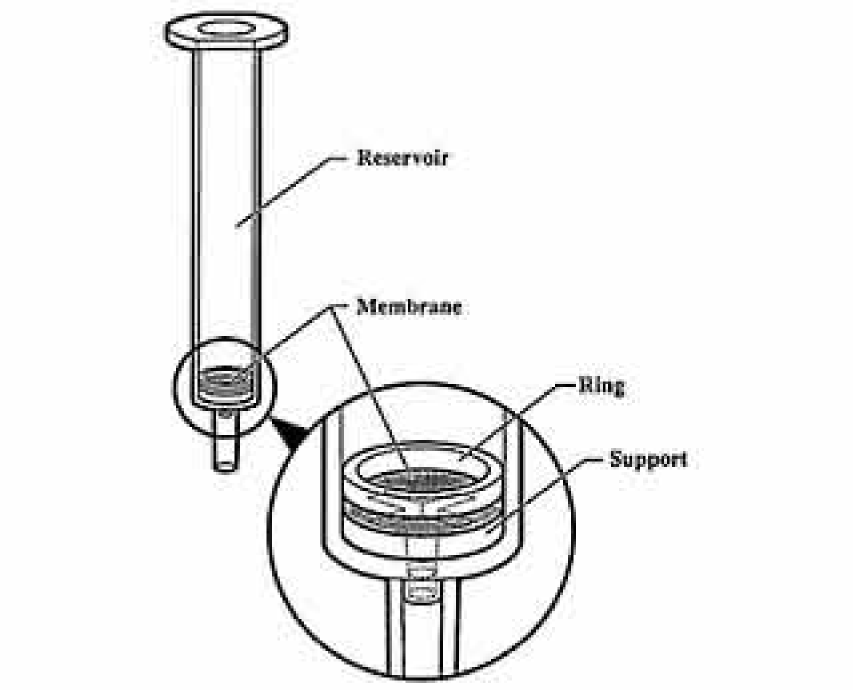
Methods

- Water sample passed through solid-phase extraction disk
- Extract is dried with anhydrous sodium sulfate
- Aliquot of extract is injected into gas chromatography
- Analytes detected by high-resolution mass spectrometer

Interferences

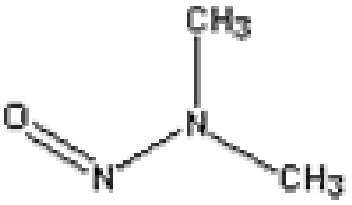
- Meticulously clean glassware
- Interferences caused by contaminants that are co-extracted
- Analyte carryover

Solid-Phase Extraction for Detecting PBDE



Solid-phase extraction (SPE) is a method that uses a solid phase and a liquid phase to isolate one, or one type, of analyte from a solution. It is usually used to clean up a sample before using a chromatographic or other analytical method.

N-Nitrosodimethylamine

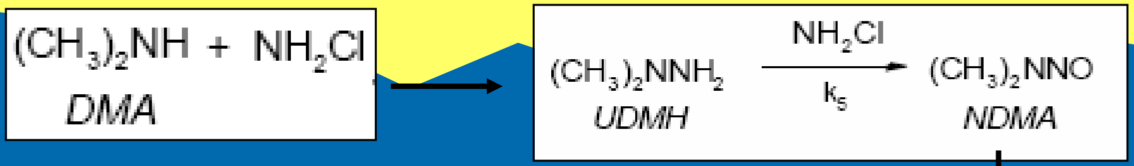


Common industrial use of NDMA

- NDMA is used as an intermediate compound to produce 1,1-dimethylhydrazine for liquid rocket fuel.
- NDMA also is used as a nitrification inhibitor in soil, additive for lubricants, and plasticizer.

Common Locations of NDMA Contamination

- As a byproduct of wastewater chlorination:
  - Recent studies have found N-nitrosamines, particularly NDMA, in drinking water throughout the U.S. due to chlorination and chloramination processes used at water treatment facilities.



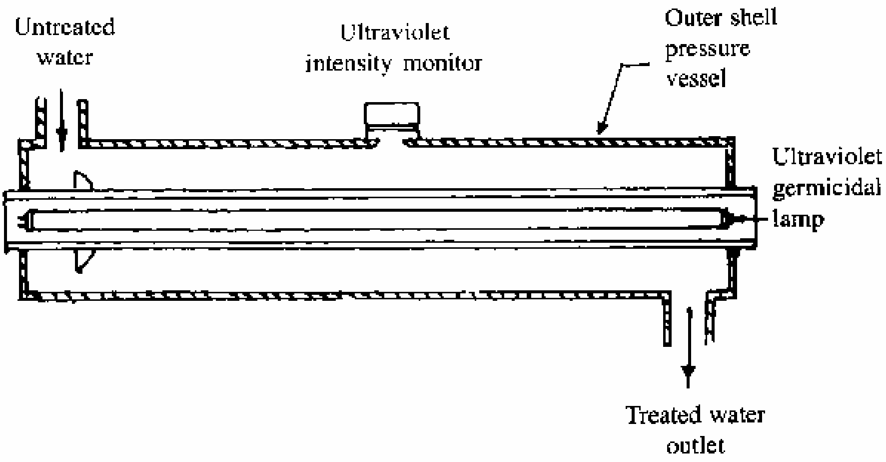
$(CH_3)_2NH + NH_2Cl$

DMA

$$(CH_3)_2NNH_2 \xrightarrow[k_5]{NH_2Cl} (CH_3)_2NNO$$

UDMH *NDMA*

- As an industrial agent:
  - Production began in the mid-1950s throughout the U.S. for its use in manufacturing 1,1-dimethylhydrazine (rocket fuel).
  - Commercial NDMA was last produced in the U.S. in 1976.



Health Effects of NDMA

- Sufficient evidence for the carcinogenicity of N-nitrosodimethylamine exists:
  - EPA lists NDMA as a possible human carcinogen based on sufficient evidence of carcinogenicity in experimental animals.(9)
  - The State of California lists NDMA on its Proposition 65 Chemical List.(10)
- NDMA administration in rodents resulted in an abundance of cancers formed in the esophagus, nose, and liver.(11)

Actions Limiting NDMA Production and Use

- In April 1998, the California Department of Health Services (CDHS) established a drinking water action level (notification level) of 10 ng/L for NDMA.

- Since few laboratories offer analytical capabilities for NDMA detection at that concentration, CDHS considers any detectable quantity of NDMA to be exceeding the action level.(12)

- In February 2006, CalEPA’s Office of Environmental Health Hazard Assessment released a draft public health goal of 3 ng/L for NDMA.

- In the absence of a maximum contaminant level for NDMA, CDHS’s notification level continues to be used as a tool for informing local agencies and consumers of NDMA presence in California drinking water.

NDMA Analytical Detection Methods

EPA Method 1625 (13)

Description	Method	Detection Limit	Cost/sample	Matrix Addressed	Holding Time	Date Released
This method is designed to determine the semivolatile toxic organic pollutants associated with the 1976 Consent Decree and additional compounds amenable to extraction and analysis by capillary column gas chromatography-mass spectrometry (GC/MS).	Stable isotopically labeled analogs of the compounds of interest are added to a 1-L wastewater sample. The sample is extracted at pH 12-13, then at pH <2 with methylene chloride using continuous extraction techniques. The extract is dried over sodium sulfate and concentrated to a volume of 1 mL. An internal standard is added to the extract and the extract is injected into the GC. The compounds are separated by GS and detected by MS. The labeled compounds serve to correct the variability of the analytical technique.	ML: 50 ug/L	Greater than $400	waste water	sample extraction within seven days of collection, and analyze all extracts within 40 days of extraction	current edition

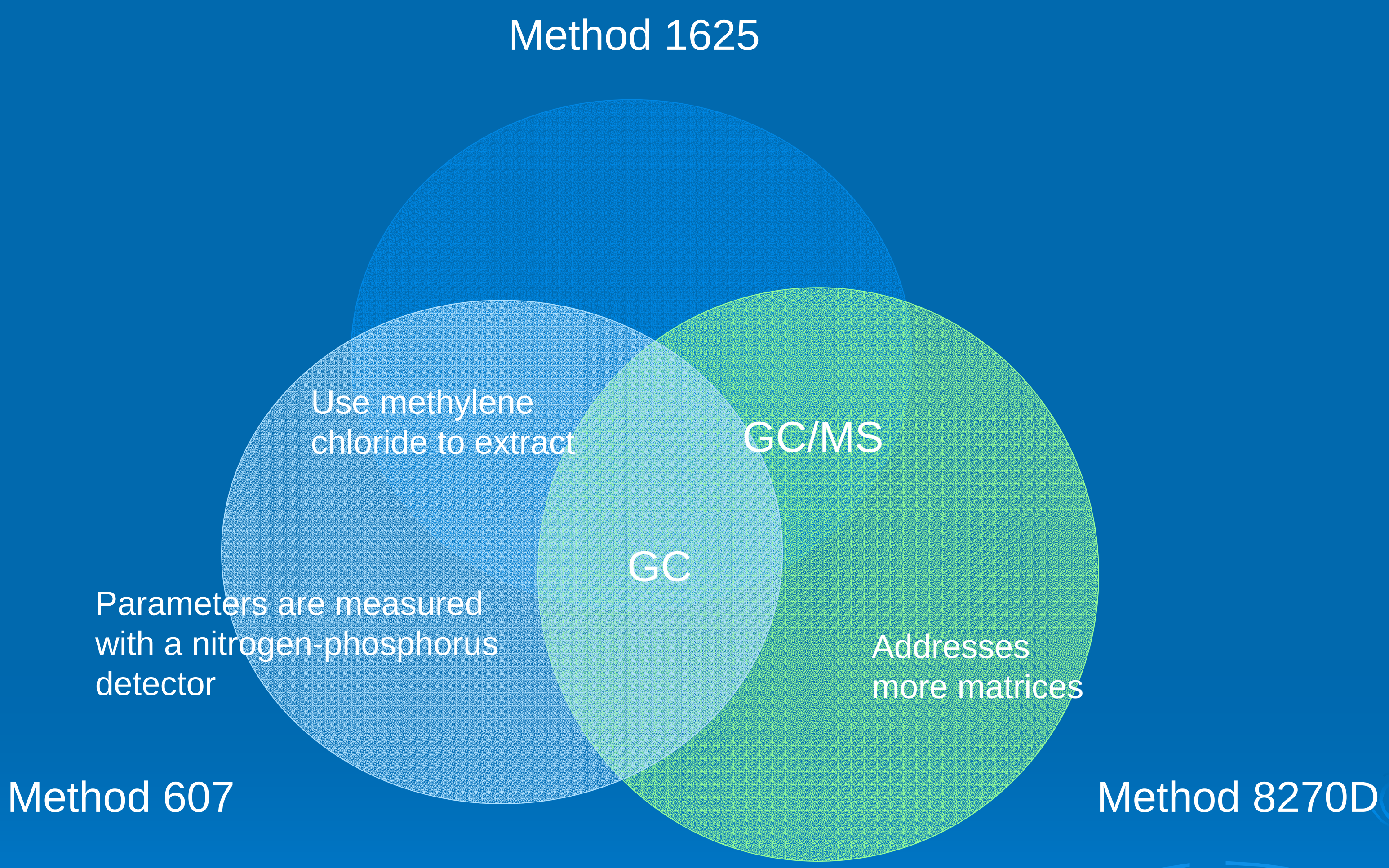
EPA Method 607 (13)

Description	Method	Detection Limit	Cost/sample	Matrix Addressed	Holding Time	Date Released
This is a gas chromatographic (GC) method applicable to the determination of N-Nitrosodimethylamine, N-Nitrosodiphenylamine, and N-Nitrosodi-n-propylamine in municipal and industrial discharges as provided under 40 CFR 136.1.	A measured volume of sample is extracted with methylene chloride. The methylene chloride extract is washed with dilute HCl and concentrated to a volume of 10 mL or less. After the extract has been exchanged to methanol it is separated by GC and the parameters are measured with a nitrogen-phosphorus detector.	MDL: 0.15 ug/L	$201 to $400	waste water	sample extraction within seven days of collection, and analyze all extracts within 40 days of extraction	current edition

EPA Method 8270D (SW-846) (14)

Description	Method	Detection Limit	Cost/sample	Matrix Addressed	Holding Time	Date Released
To determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications.	The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph. Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection.	?	$201 to $400	various solid waste matrices: soils, air and water		revision 4 1/1/1998

Similarities and Differences Between 1625, 607, 8270D



Method 1625

Method 607

Method 8270D

Use methylene chloride to extract

GC/MS

GC

Parameters are measured with a nitrogen-phosphorus detector

Addresses more matrices

The nitrogen phosphorus detector (NPD) is a highly sensitive but specific detector that gives a strong response to organic compounds containing nitrogen and/or phosphorus.

References

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