Mercury

Occurrence in Crude Oil and Impact on Refineries

Presentation to:

Crude Quality Group
Houston, Texas
May, 2002

Mercury Technology Services

Outline

- **Hg in Hydrocarbons**
  - Chemical Properties
  - Operational Speciation
  - Chromatographic Speciation
  - Analysis of Total Mercury
  - Typical Concentrations
- **Mercury in Refineries**
  - Distillation
  - Products
  - Emissions
  - Catalysts
- **Regulatory Trends**
- **EPA – API – NPRA Mercury Study**

Mercury in Oil and Gas

Natural Gas

- Elemental Hg^0
- Organic RHgR, R = CH_3, C_2H_5

Oil and Condensate

- Elemental Hg^0
- Ionic $HgCl_2$
- Complexed HgK
- Organic RHgR, R = CH_3, C_2H_5
- Suspended HgS, HgX

Approximate Solubility
Mercury Compounds
25 C

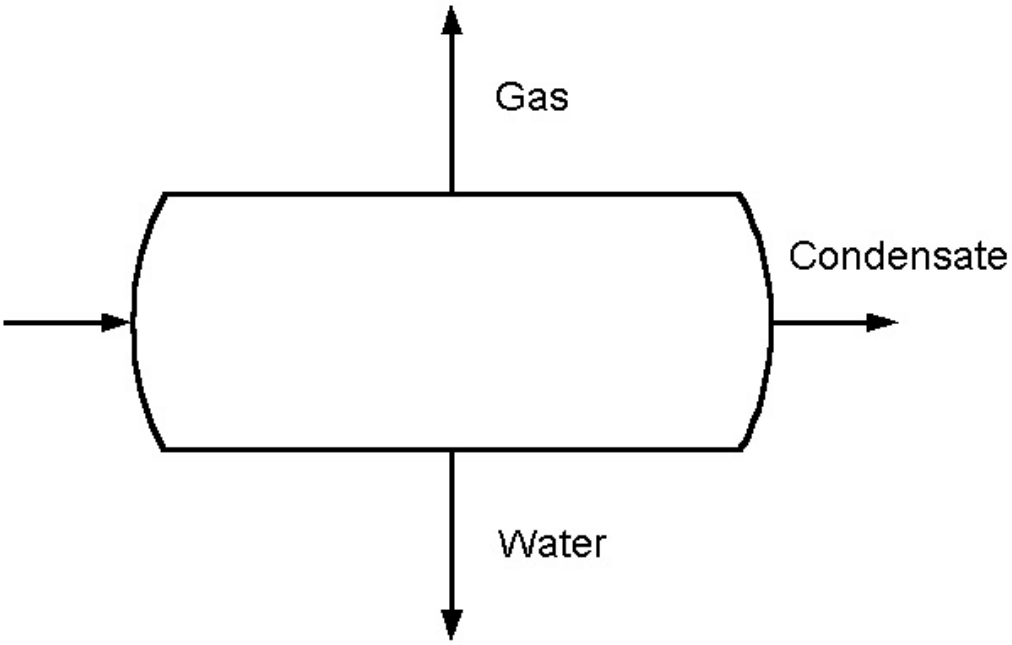
Species	Water (ppb)	Oil (ppb)	Glycol (ppb)
Hg^{O}	50	2,000	7,000
XHgX	<1000	infinite	>7,000
$HgCl_2$	70,000,000	>10,000	>50,000
HgS	<1	< 1	< 1
CH_3HgCl	very high	1,000,000	high

Solubilities and Volatilities of Mercury Compounds

Formula	State	Volatility	Hg Solubility in H_20; 25 C	Name
Hg^0	Liquid	Boiling Point 357 C Vapor Pressure 25 mg/m^3 (25 C)	50 ppb	Elemental
$HgCl_2$	Solid	Boiling Point 302 C	70 g/l	Mercuric chloride
$HgSO_4$	Solid	decomposes 300 C	0.03 g/l	Mercuric sulfate
HgO	Solid	decomposes 500 C	0.05 g/l	Mercuric oxide
HgS	Solid	Sublimes under vacuum; decomposes 560 C	- log Ksp(1) = 52	Mercuric sulfide
HgSe	Solid	Sublimes under vacuum, decomposes 800 C	- log Ksp ~ 100	Mercuric selenide
$(CH_3)_2Hg$	Liquid	Boiling Point 96 C	< 1 ppm	Dimethylmercury
$(C_2H_5)_2Hg$	Liquid	Boiling Point 170 C	< 1 ppm	Diethylmercury

(1) Ksp = solubility product

Primary Separation



Gas	**Hg^0 >> RHgR**
Water	**HgS, Hg^{2+} >> Hg^0**
Condensate	**Hg^0, HgS > $HgCl_2$**

Mercury in Liquid Hydrocarbons
Operational Speciation

$$\text{Total Hg} = Hg^0 +$$

$$(RHgR + HgK) +$$

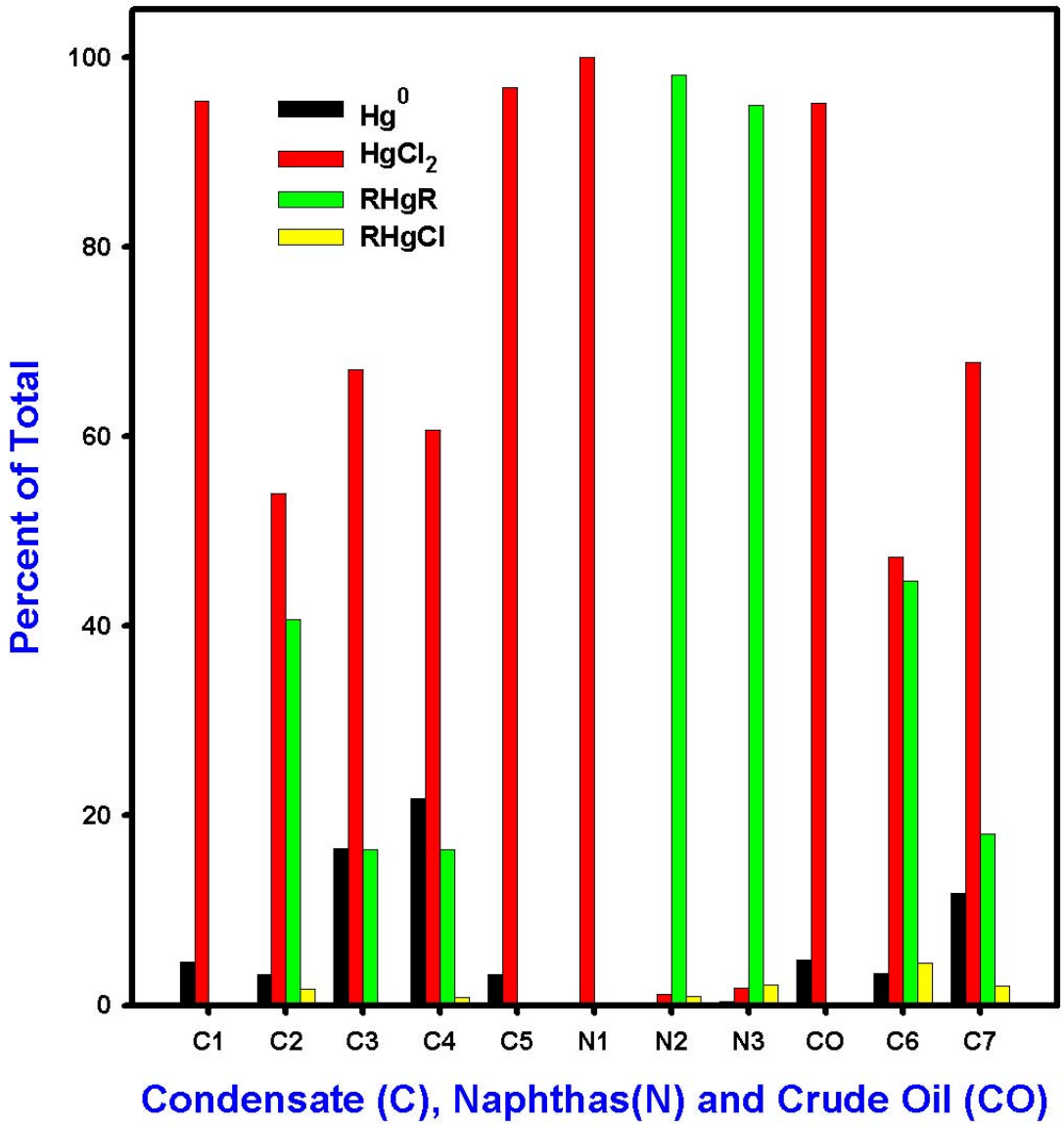
$$(HgCl_2 + RHgCl) +$$

$$(HgS + HgX)$$

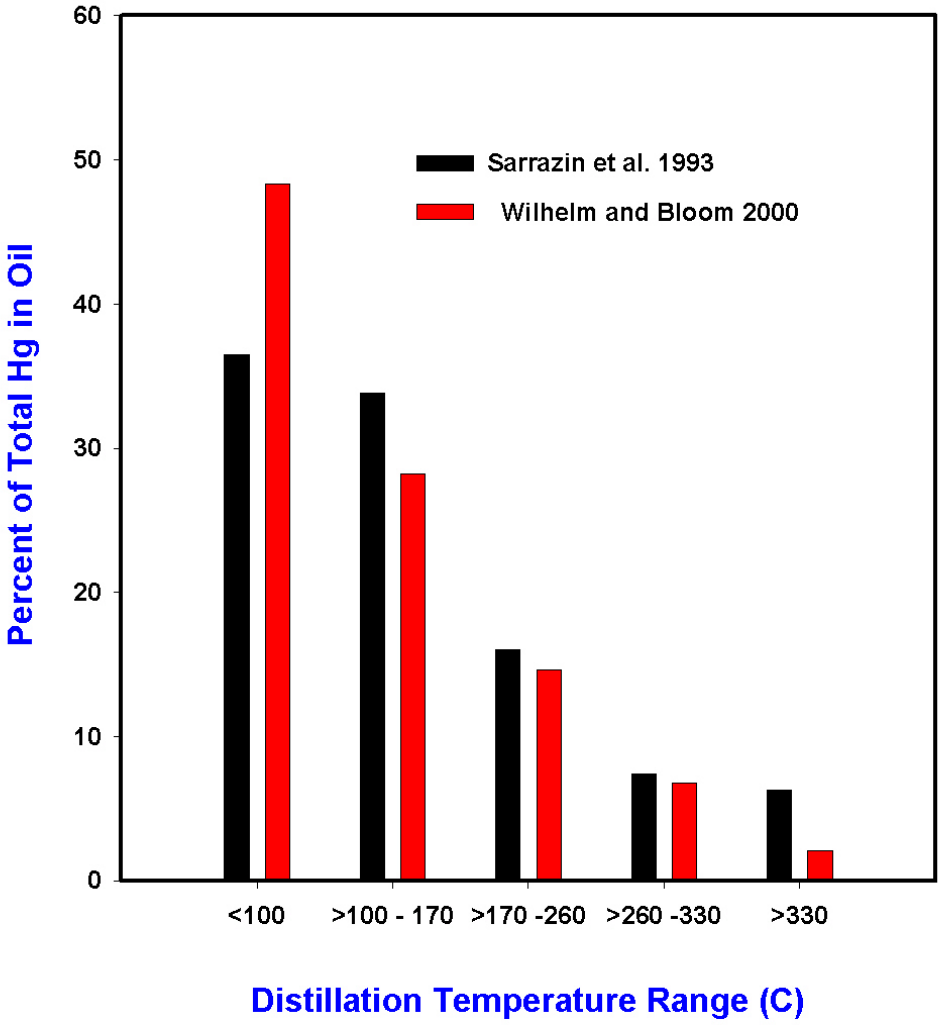
$$Hg^0 + O_2 \rightarrow Hg^{2+}$$

$$RHgR + HgCl_2 \rightarrow 2\ RHgCl$$

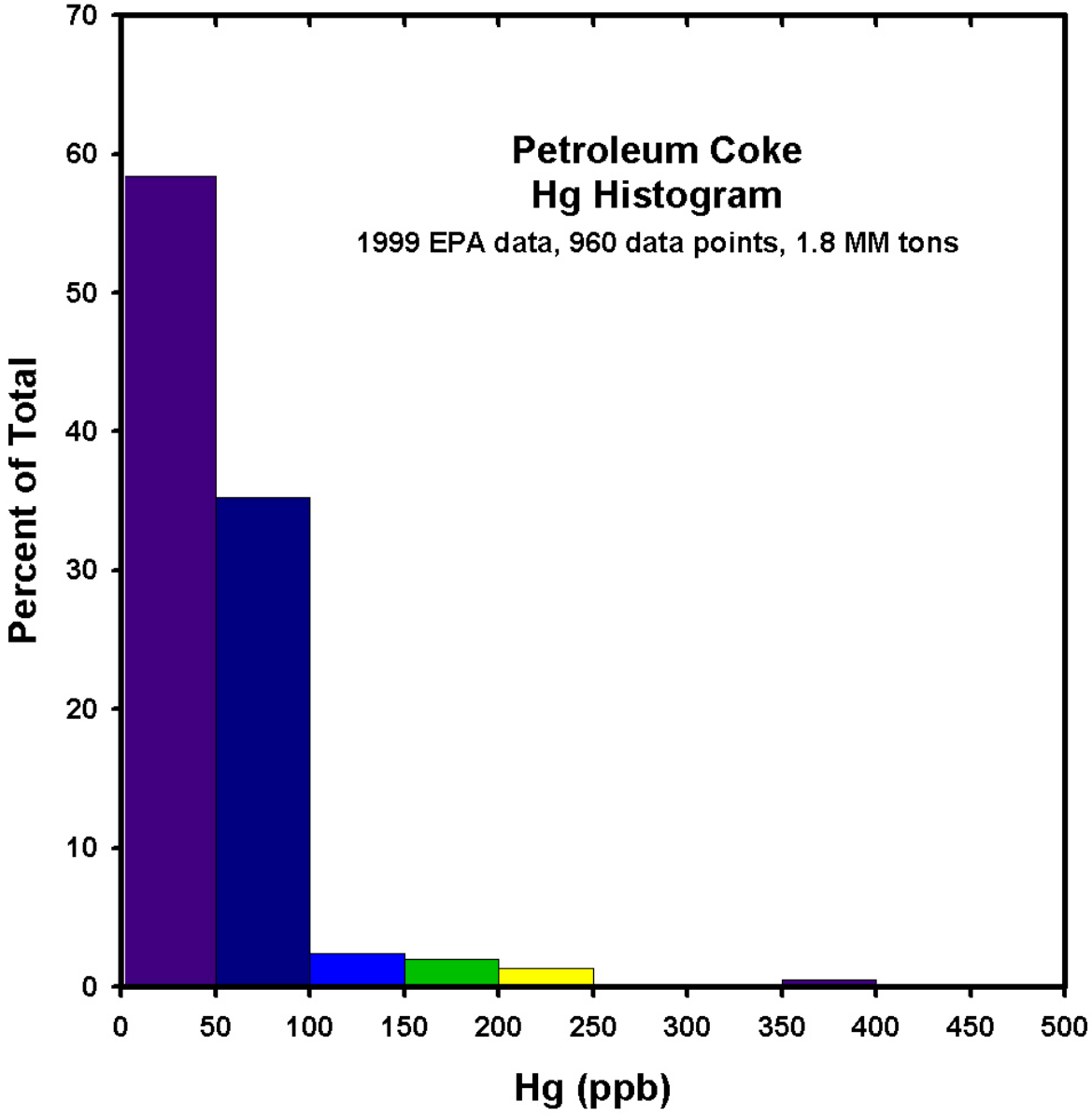
$$Hg^0 + HgCl_2 \rightarrow Hg_2Cl_2\downarrow$$



Chromatographic Separation



Mercury (Total) in Distilled Products



Mercury in Petroleum Coke

Analysis of Total Mercury in Crude Oil

- **Combustion/CVAF**
- **Neutron Activation Analysis**
- **Digestion CVAA**
- **Digestion CVAF**

Sampling

- **Samples must be fresh**
- **Must account for all Hg (container walls)**
- **Avoid loss of volatile Hg**

Hg in Hydrocarbon Liquids

THg in Alberta Crude Oils *(9)*

Stratigraphic Era	Number of Samples	Number Above DL	High (ppb)	Low (ppb)	Mean* (ppb)	Median (ppb)	SD	Detection Limit (ppb)
Upper Cretaceous	21	11	202	DL	17.6	2.5	46.0	2
Lower Cretaceous	18	7	138	DL	17.1	1	38.1	2
Jurassic	3	0	1	DL	1	1		2
Triassic	4	2	6	DL	3	2.5	2.4	2
Carboniferous	8	4	19	DL	5	1.5	6.3	2
Devonian	36	13	399	DL	36	1	92.5	2
Total	86	38	399	DL	21.9	1	63.6	

** calculated assuming < DL = 1 ppb*

Reported Total Hg Concentration in Crude Oil Processed in New Jersey Refineries

Type	THg (ppb)	Notes
	mean	
Angola	2.7	Palanca
Angola	1.5	Soyo
Arab	5.7	
Columbia	12.3	
Columbia	2	
Congo	1.8	Kitina
Dubai	2.9	Nemba
Gabon	1.8	Rabi
Mexico	2.7	
Mexico	0.1	
Mixed	3.1	
Newfoundland	1.9	
Nigeria	1.0	Escravos
North Sea	3.4	
North Sea	9.3	Ecofisk
North Sea	2.5	Gullfaks
North Sea	4.7	Norne
Venezuela	4.8	light
Venezuela	5.1	
Venezuela	0.8	
Venezuela	6	
West Africa	3.2	
West Africa	1.5	light
Mean	3.5	

Mercury Estimates in Crude Oil and Refined Products

IN

	Type (U.S. DOE 2000)	Barrel/y (U.S. DOE 2000)	kg/y	THg	Estimated Total
		(10^9)	(10^{11})	ppb	kg/y
Crude Oil (d=0.85)					
Domestic (40%)	Alaska (18%)	0.4	0.5	<10	500
	GOM (20%)	0.5	0.7	<10	700
	Other (62%)	1.5	2.0	<10?	*2,000?*
Imported (60%)	Canada (15%)	0.5	0.7	<10?	*700?*
	Mexico (15%)	0.5	0.7	<10	700
	Middle East (20%)	0.8	1.1	<10	1,100
	Other (50%)	1.8	2.4	<10?	*2,400?*
Total (IN)		6.0	8.1		8,100

Mercury Estimates in Crude Oil and Refined Products

OUT

	Type (U.S. DOE 2000)	Barrel/y (U.S. DOE 2000)	kg/y	THg	Estimated Total
Refined Products		6.2	7.9		7,000
d = 0.75	Motor fuels (60%)	3.7	4.4	<3?	*1,200?*
d = 0.80	Naphthas (5%)	0.3	0.4	<5	200
d = 0.85	Residual fuel oil (5%)	0.3	0.4	<5	200
d = 0.85	Distilled fuel oil (21%)	1.3	1.8	<5	900
d = 1.10	Petroleum coke (3%)	0.2	0.3	50	1,500
d = 0.90	Heavy oils (3%)	0.2	0.3	50	1,500
d = 0.55	Still Gas (3%)	0.2	0.3	<30?	*1,000?*
Wastewater (U.S.EPA 1982)		1.5	2.5	1	250
Solid waste (U.S. EPA 1996)			0.3	50?	*1,500?*
Air (Table 7.4)	(from fuels included in refinery totals)				*(1,500)**
Air (fugitive)					250?
Total (OUT)					8,500

Petroleum Contribution

- **Global (anthropogenic to air) - 2,000,000 kg/y (US EPA)**
- **US (waste + fuel combustion) - 125,000 kg/y (US EPA)**
- **US Coal - 75,000 kg/y (US EPA)**
- **US Fuel Oil - 10,000 kg/y (US EPA)**
- **US Oil <8,000 kg/y (MTS)**
- **US Fuel Oil - 1,100 kg/y (MTS)**
- **US Refineries (air) <1,500 kg/y (MTS)**

Mercury In Petrochemical Processes

- Catalysts
- Equipment
- Contamination
- Environmental concerns
- Health and safety
- Waste
- Wastewater

Mercury Removal from Oil ??

- **Precipitation**
- **Conversion**
- **Sorbents**
- **Filtration**

Regulatory Issues

Water

- **Clean Water Act (CWA, Section 304)**
- **Total Maximum Daily Load (TMDL)**

Air

- **Clean Air Act of 1990 (CAA, Section 112)**
- **National Emission Standards for Hazardous air Pollutants (NESHAP)**
- **Maximum Available Control Technology (MACT)**

Solid Waste

- **Resource Conservation and Recovery Act (RCRA)**

Toxic Release Inventory (TRI)

- **Emergency Planning and Community Right-to-Know Act (EPCRA)**
- **Persistent Bioaccumulative Toxics (PBT)**
- **Report threshold - Mercury 10 lbs.**
- **Elimination of the de minimis exemption**

EPA – API – NPRA
Mercury Study

- **Analytical Issues**
- **Variation in Concentration**
- **Sample Stability**
- **Survey Crude Oils Processed in the U.S.**
- **Blind Study**

smw@hgtech.com