Determination of Mercury and Other Trace Metals in Hydrocarbons using the Anton-Paar High Pressure Asher (HPA)

Deborah L. Cussen

Carl E. Hensman, Ph.D.

Frontier Geosciences, Inc.
414 Pontius Ave N.
Seattle, WA 98109
www.FrontierGeosciences.com

Project Background

- Metals are present in fossil fuels at varying concentrations
- Knowledge of metals levels are important for:
  - Emissions regulations
  - Employee exposure during processing & maintenance
  - Environmental impacts of waste and spills
  - Structural integrity issues
  - Effects on catalysts
- Low-level analysis of metals - historically difficult
  - Goal of developing improved digestion technique

Why, Historically, has Analysis of Metals in Hydrocarbons been Difficult?

- Relatively inert matrix
  - Incomplete digestions
  - Generation of noxious fumes
- Closed-vessel digestions
  - Explosion hazard
  - Costly reagents
  - Difficult to obtain reagents at required level of purity
- Dry Ashing
  - Ignition hazard
  - Loss of volatiles
- Liquid/liquid extractions
  - Difficult for high viscosity or low concentration samples

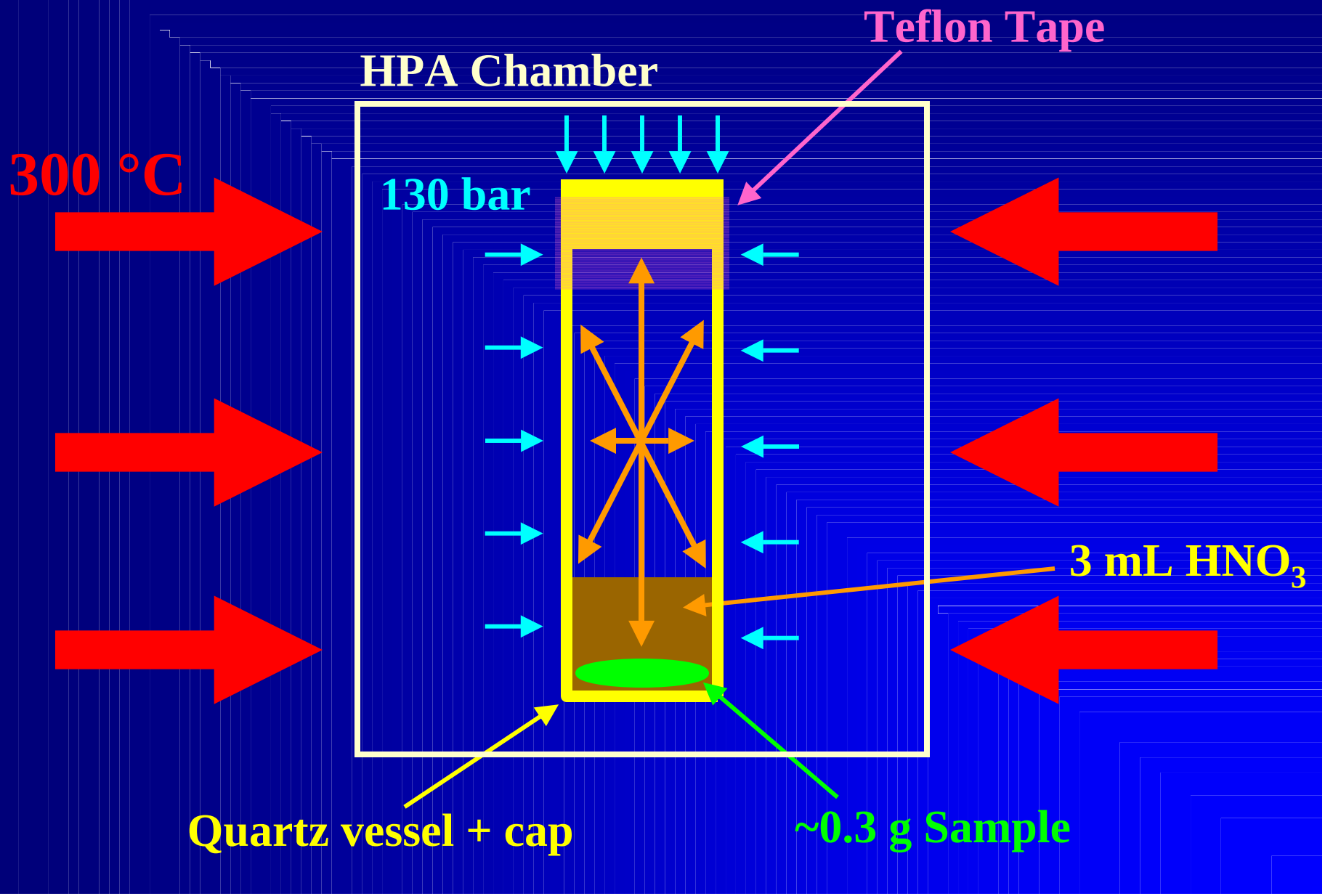
Is Wet Ashing Better?

- Uses common, high-purity reagent (HNO_3)
- High temperature & pressure
- Complete decomposition of organics
- Simple final matrix applicable for many types of metals analysis (ICP-MS, CV-AFS, HG-AFS, ZGF-AAS) that typically requires no further manipulation beyond dilution
- Anton-Paar High Pressure Asher (HPA) and consumables readily available (Perkin Elmer)

HPA Digestion Method Summary

- 0.3 g hydrocarbon sample
- 3 mL Nitric Acid (Trace-Metals Grade)
- Prepared in 50 mL pure quartz asher vessel (pre-cleaned)
- Subjected to 300º C and ~130 bar
- Diluted with ultra-pure reagent water prior to analysis

Wet Ashing Conditions



Matrix Before & After Wet Ashing

Before

After Wet Ashing

After Dilution

Method Detection Limit Procedure

- 40 CFR Part 136, Appendix B
  - Minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte
  - MDL = Standard Deviation of Low-Level Spikes * Student's T Value

Method Detection Limit Trials

- Preparation Blanks (n = 4-8)
- Pump Oil Reps (n = 4)
- Low-Level Spikes (n = 8)
- Mid-Level Spikes (n = 4-5)
- CRMs ($n \geq 1$)

Method Detection Limits (mg/kg)

Analyte	Analysis method	Calc. MDL	Analyte	Analysis method	Calc. MDL
Hg	CVAFS	0.000465	Mg	ICP/MS	0.198
Al	ICP/MS	0.301	Mn	ICP/MS	0.055
Sb	ICP/MS	0.096	Mo	ICP/MS	0.297
As	ICP/MS	0.135	Ni	ICP/MS	0.186
As	HG-AFS	0.122	K	ICP/MS	2.211
Ba	ICP/MS	0.077	Se	ICP/MS	0.224
Cd	ICP/MS	0.027	Se	HG-AFS	0.165
Cr	ICP/MS	0.172	Sr	ICP/MS	0.199
Co	ICP/MS	0.171	Ag	ICP/MS	0.006
Cu	ICP/MS	0.211	Tl	ICP/MS	0.180
Fe	ICP/MS	16.346	V	ICP/MS	0.219
Pb	ICP/MS	0.393	Zn	ICP/MS	0.088

SPEX CRM (mg/kg)

Analyte	n	Mean Conc.	Cert. Value	% Rec.	Analyte	n	Mean Conc.	Cert. Value	% Rec.
As (ICP/MS)	4	4.616	5	92.3	Mg	3	4.74	5.1	92.9
As (HG-AFS)	1	1.83	5	36.6	Mn	4	5.118	5	102.4
Ba	4	4.492	5.1	88.1	Mo	3	4.009	5	80.2
Cd	4	4.876	5	97.5	Ni	3	5.329	5	106.6
Co	3	5.218	5	104.4	Se (ICP/MS)	4	4.666	5.2	89.7
Cu	3	5.462	5	109.2	Se (HG-AFS)	1	5.386	5.2	103.6
Cr	3	5.052	5	101.0	Ag	3	3.982	5	79.6
Hg	3	4.437	5	88.7	Tl	3	5.192	5	103.8
Pb	3	5.108	5	102.2	Zn	4	5.151	5	103.0

NIST 1634c – Fuel Oil (mg/kg)

Analyte	Measured	Certified Value	Recovery (%)
As (ICP/MS)	0.161	0.143	112.8
As (HG-AFS)	0.127	0.143	89.4
Ba	1.978	1.800	109.9
Ni	15.288	17.540	87.2
V	25.531	28.190	90.6

FGS-Oil #4-03 (mg/kg)

Analyte	Measured	True Value	Recovery (%)
Hg	1.509	1.5	100.6

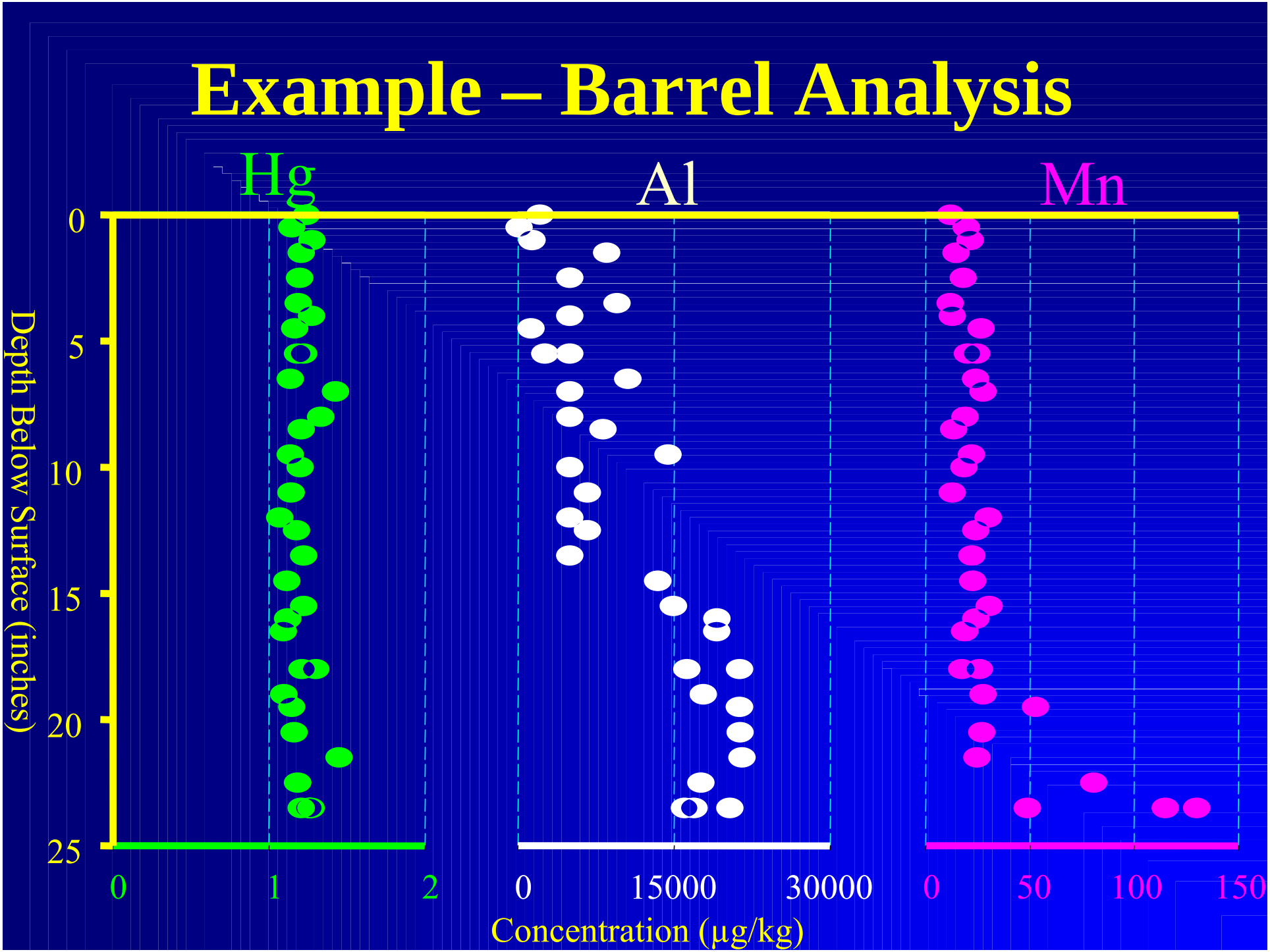
HPA Method Limitations

- Low sample throughput
  - 7 vessels per run
  - ~4 hours from start-up to cool down per run
- Sample Handling
  - Similar to other digestions; possible sample contamination and/or loss
  - Small sample size increases homogeneity issues
- Cost
  - HPA ~$50K
  - Method requires training & expertise

HPA Method Applications

- Wet ashing followed by analysis is equivalent to direct measurement of Hg in crude
  - Current intercomparison studies with combustion cell methods for hydrocarbons
- Glassy carbon vessels allow HF digestion
- Simple matrix after digestion allows analysis of multiple metals by many methods
  - Investigation of a barrel of crude oil: metals profiles

Example – Barrel Analysis



Summary & Conclusions

- Wet ashing safely and completely breaks down complex hydrocarbon matrices
- Simple, common final matrix
  - Different sample types can be batched and share QC
  - Analysis of various metals by different methods