

Determination of Elemental “Bad Actors” (As, Hg and Si) in Petrochemical Samples Using ICP-AES and ICP-MS

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The “Bad Actors”

- As
 - Catalyst poison, coking promoter in steam cracking, environmental toxin
- Hg
 - Steam cracking corrosive, environmental toxin
- Si
 - Catalyst poison, fuel contamination issues
- Parts per billion levels are of interest
- Samples may be naphthas, gas oils, crudes, finished fuels, almost any petrochemical material

Bad actors in the lab

- As, Hg and Si may exist in highly volatile forms
- Petrochemical samples range from LPG to solid resids
 - Matrix matching may be challenging
- Volatile element species concentrated in volatile petroleum fractions
 - Direct analysis methods challenged by matrix volatility
 - Traditional methods rely on destructive sample preparation [1]

Sample preparation is bad news

- Destructive sample preparation/analysis schemes are all subject to error from analyte loss/contamination:
 - Extraction – example HBr/Bromine extraction of As and Hg from naphtha
 - Extraction rendered ineffective by olefins, aromatics
 - Combustion – example oxygen calorimetric bomb combustion of oils
 - Sample dilution, contamination by quartz liner, bomb materials
 - Digestion – example oxidative acid digestion of oils for As, Hg
 - Open vessel - possibility of loss, closed vessel - limited sample size, incomplete digestion
- Analyte concentration for direct measurement (XRF) also subject to loss and contamination
- Si is easily contaminated in all lab handling

More bad news

- Analyte/standard matching limited
 - Available organic As, Hg and Si compounds/standards may not be similar to those naturally occurring
- Standard stability may be an issue
 - Part per billion level calibration standards and spikes may not be very stable
- Sample container may “get involved”
 - Analytes easily absorbed on walls, metal caps or cap liners

ICP Challenge

- The ICP Challenge is to introduce the As, Hg and Si species, whether volatile or not, together with the hydrocarbon matrix (be it light naphtha or tar) into the ICP and determine them accurately
- Direct analysis with minimum sample handling is clearly the best approach
- ICP-AES and ICP-MS have required sensitivity for part per billion level determinations

Direct Sample Introduction

- Direct aspiration of heavy oils into the ICP-AES became a standard practice early
 - Xylene dilution 1976
 - Accuracy improved with tetralin dilution 1986 [2]
- Volatile hydrocarbons (pentanes) analyzed directly using an ultrasonic nebulizer with microporous membrane desolvation (USN-MMD-ICP-AES) in 1993 [3]
 - Organic matrix removal >99%
 - Excellent detection limits and universal calibration but volatile element species were lost
 - Pb in gasoline determined by conversion to nonvolatile bromide

Microconcentric (MCN) nebulizer

- “Silicon crisis” in Houston 1996 handled with USN-MMD-ICP-AES
 - Troublesome effects attributed to volatile silicone gasoline contaminant
- Direct introduction of gasoline into ICP-AES achieved using MCN/chilled spray chamber in 1996
 - Detection limit for Si 9.5 wppb
 - Spray chamber matrix effects/memory noted
 - Difficulty pumping low flow rates (10-100 ul/min)

Direct injection nebulizer (DIN)

- Commercial DIN first used for introduction of volatile hydrocarbons (hexanes) in 1995 (3 sigma detection limits):

Element	Wavelength (m/e)	DIN-ICP-AES D.L.	DIN-ICP-MS D.L.
As	193.76nm (75)	>2 wppm	0.1 wppb
Hg	253.65nm (202)	0.02 wppm	0.8 wppb
Si	251.61nm	0.054 wppm	NA

DIN replaced by PFA nebulizer

- DIN used successfully until 2002 [4]
 - Naphthas analyzed routinely with excellent sensitivity
 - Equipment difficult to maintain and went out of production
- Low flow PFA nebulizer/cyclonic spray chamber replaced DIN
- Sample types expanded to include steam cracked naphthas and gas oils
 - DMF and even crudes run successfully with dilution
- QC program consisting of sample spikes maintained
 - Standard/spike stability evaluated

ICP-MS Operating Conditions/Calibration

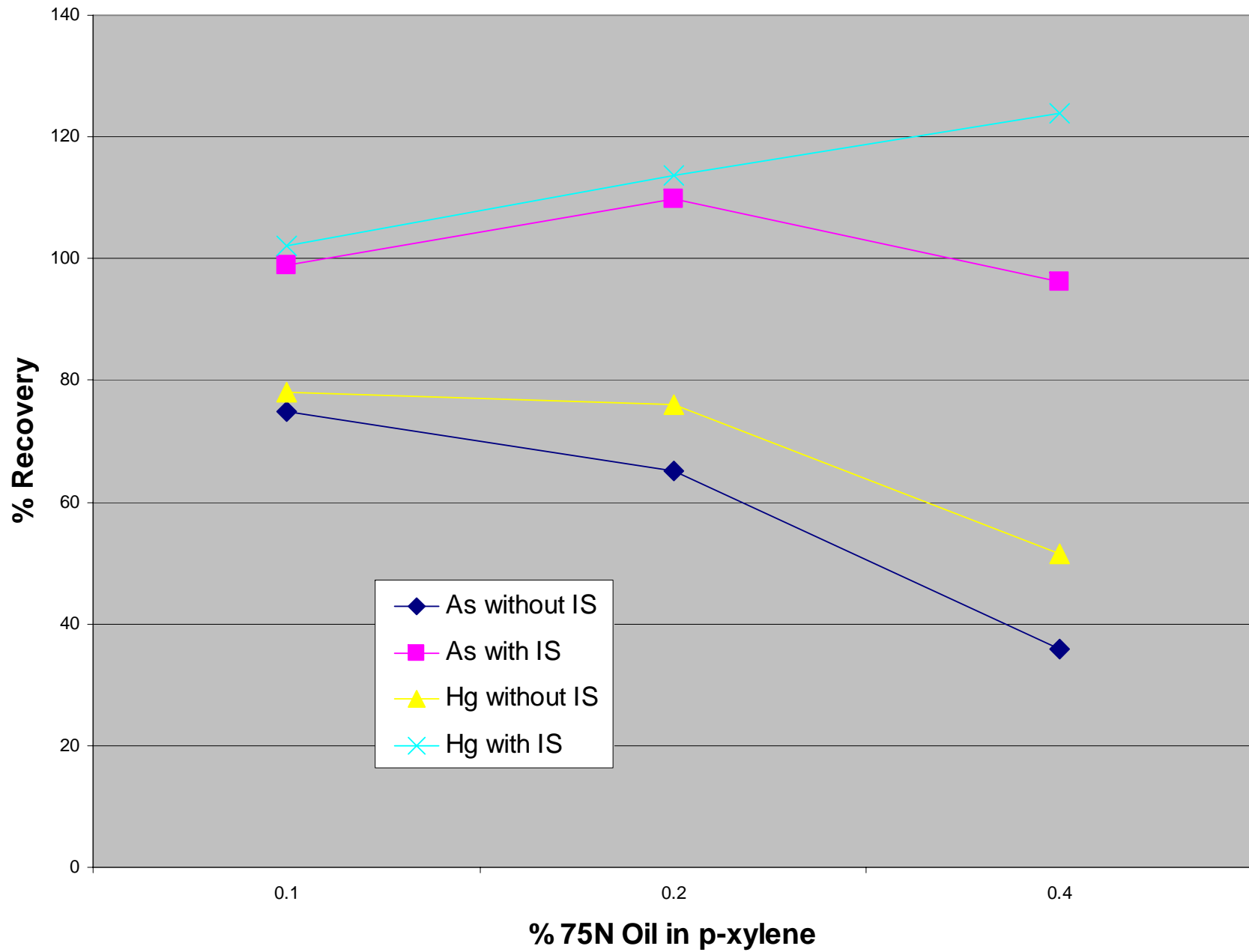
- ICP-MS - DIN
 - ICP Power 1500W
 - DIN nebulizer gas 50%Ar/50%O₂ 70 psig
 - DIN sample pump pressure 180 psig
 - DIN Aux. Neb. Gas 0.2 l/min Ar + 0.15 l/min O₂
- ICP-MS – PFA-20
 - ICP Power 1500W
 - Nebulizer gas 50%Ar/50%O₂ - 25 psig
 - Ar Carrier 0.2 l/min blended with 0.2 l/min O₂
- ICP-MS Calibration
 - Organo-metallic standards in p-xylene
 - Three internal standards cover mass range
 - Co (m/e= 59) for Na 23 - Zn 66
 - Y (m/e = 89) for As 75 - Sb 121
 - Bi (m/e = 209) for Hg 199 - Pb 208 (masses summed)
 - Samples diluted in p-xylene with internal standard mix added

ICP-MS Detection Limits

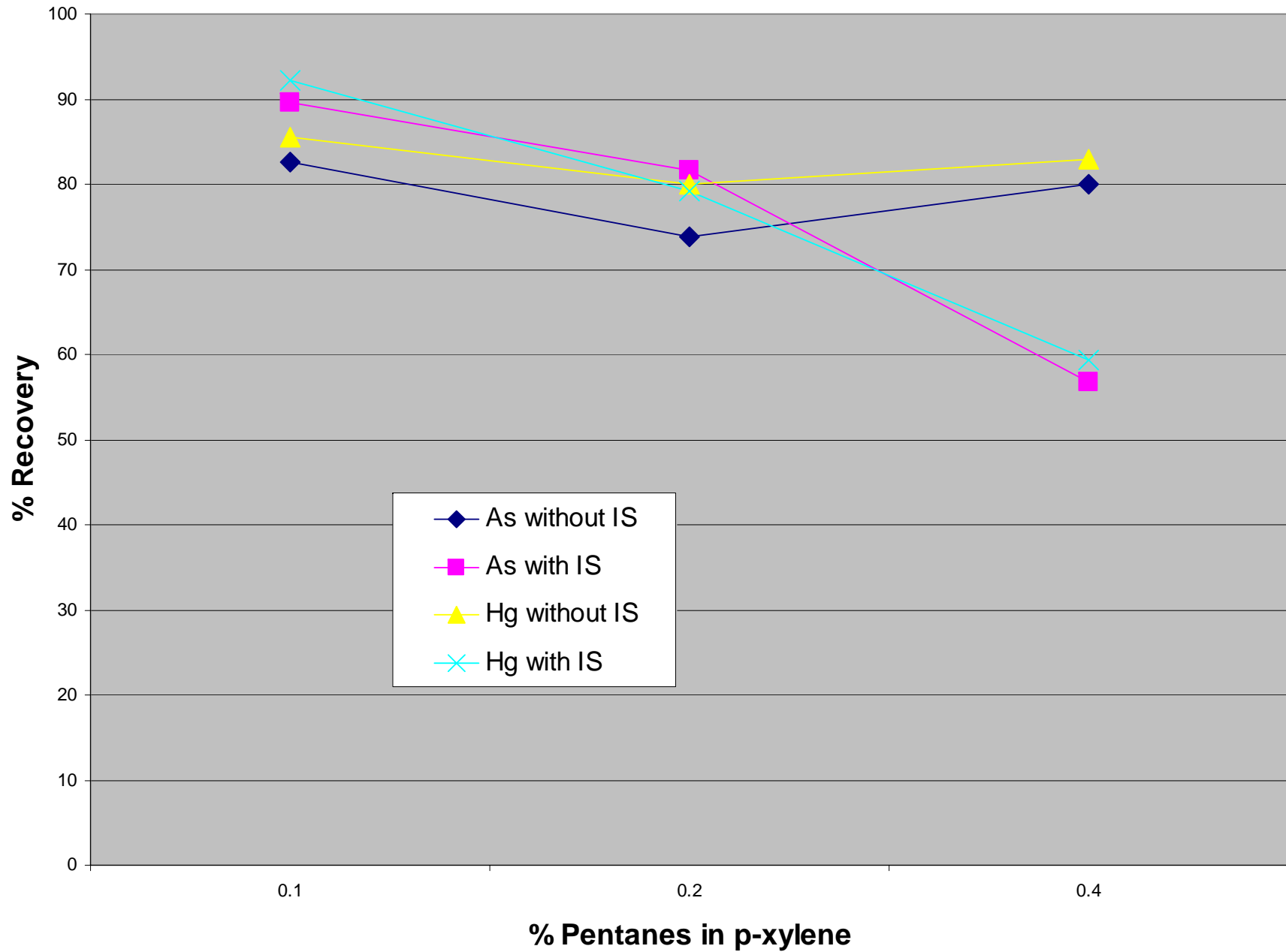
Xylene matrix, three sigma, ng/g

<u>Element (m/e)</u>	<u>Internal Standard (m/e)</u>	<u>DIN Internal Stds</u>	<u>PFA-20 No Internal Stds</u>	<u>PFA-20 Internal Stds</u>
Na (23)	59	2.0	0.8	0.7
PO (47)	59	20	2.0	2.0
Ti (47)	59	0.2	0.5	0.3
V (51)	59	3.8	2.8	4.0
Mn (55)	59	0.5	2.4	1.7
Fe (57)	59	5.0	50	11
Ni (60)	59	2.0	0.4	0.1
Cu (63)	59	0.2	0.04	0.03
Zn (66)	59	0.6	0.8	0.3
As (75)	89	0.2	0.4	0.9
Se (82)	89	2.8	0.6	0.6
Mo (95)	89	0.1	0.1	0.03
Cd (111)	89	2.0	0.1	0.1
Sn (118)	89	0.1	0.04	0.2
Sb (121)	89	0.03	0.1	0.04
Hg (199-202)	109	0.4	1.7	0.7
Pb (206-208)	109	0.3	0.2	0.2

ICP-MS Spike Recoveries using PFA-20 nebulizer



ICP-MS Spike Recoveries using PFA-20 nebulizer



ICP-MS Spike Recovery Comparison DIN vs. PFA20

Spike % recoveries (and sigma) for light paraffinic naphtha

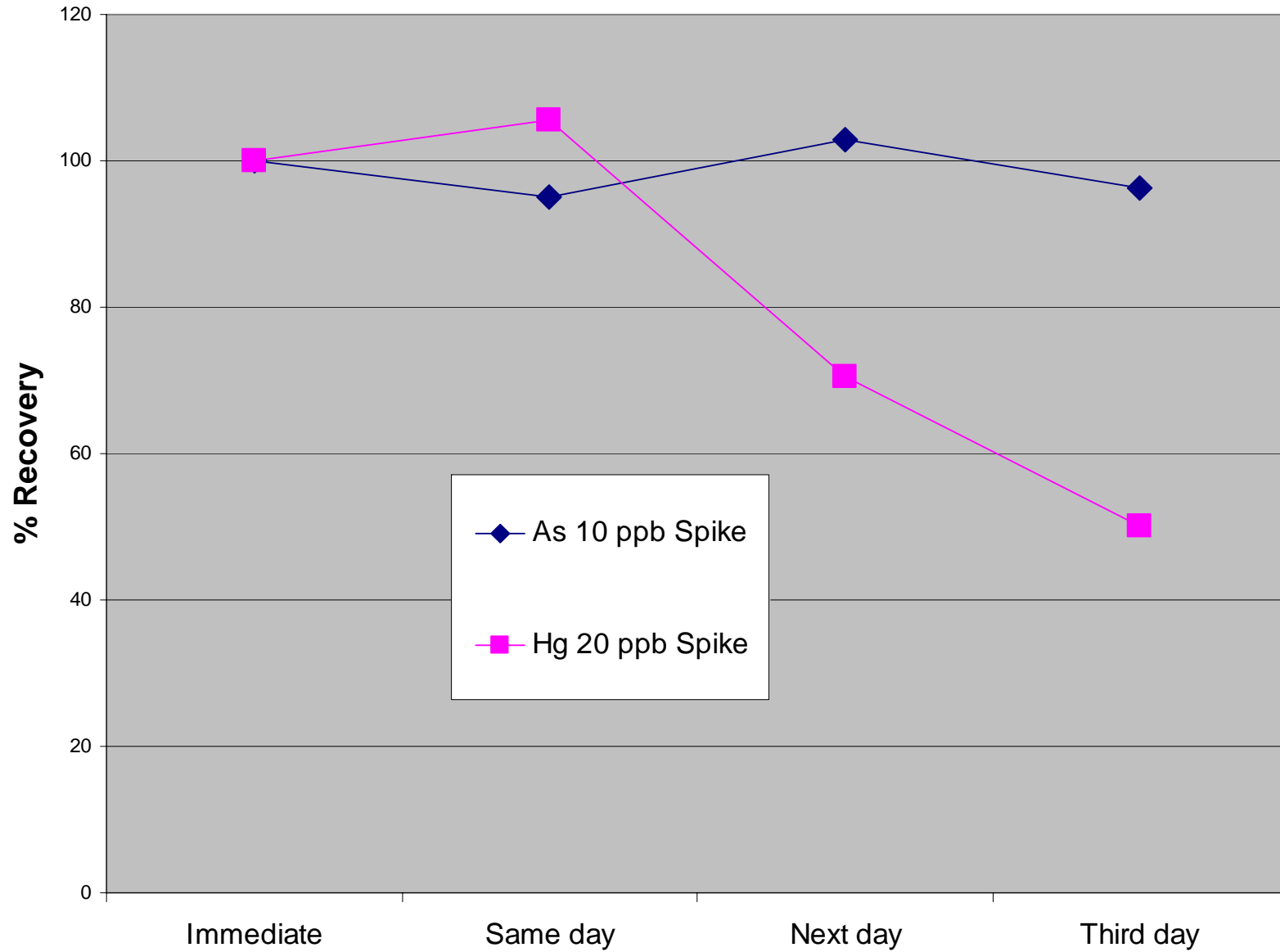
<u>Element (m/e)</u>	<u>Spike Level</u> <u>ng/g</u>	<u>DIN - IS</u> <u>Dilution 1:5, n=14</u>	<u>PFA20 - NO IS</u> <u>Dilution 1:5, n=11</u>	<u>PFA20 - IS</u> <u>Dilution 1:5, n=6</u>
Na (23)	10	65 (35)	90 (11)	94 (8.4)
PO (47)	100	90 (27)	90 (14)	94 (12)
Ti (47)	10	96 (18)	89 (12)	98 (4.4)
V (51)	10	99 (24)	87 (10)	109 (7.1)
Mn (55)	10	99 (19)	90 (10)	96 (5.4)
Fe (57)	100	92 (17)	90 (9.6)	101 (9.4)
Ni (60)	10	96 (16)	96 (13)	97 (4.9)
Cu (63)	10	117 (22)	87 (9.7)	93 (5.3)
Zn (66)	10	96 (13)	93 (8.5)	97 (6.6)
As (75)	10	93 (12)	91 (8.2)	92 (15)
Se (82)	10	91 (11)	88 (13)	85 (16)
Mo (95)	10	97 (15)	90 (8.5)	99 (2.8)
Cd (111)	10	127 (37)	89 (13)	106 (9.0)
Sn (118)	10	97 (17)	88 (11)	103 (5.6)
Sb (121)	10	95 (17)	95 (11)	102 (10)
Hg (199-202)	4 (25 PFA)	91 (15)	158 (43)	86 (13)
Pb (206-208)	10	115 (23)	95 (17)	100 (3.9)
	Overall mean	97 (20)	94 (13)	97 (8.1)

ICP-MS Spike Recoveries using PFA20 nebulizer

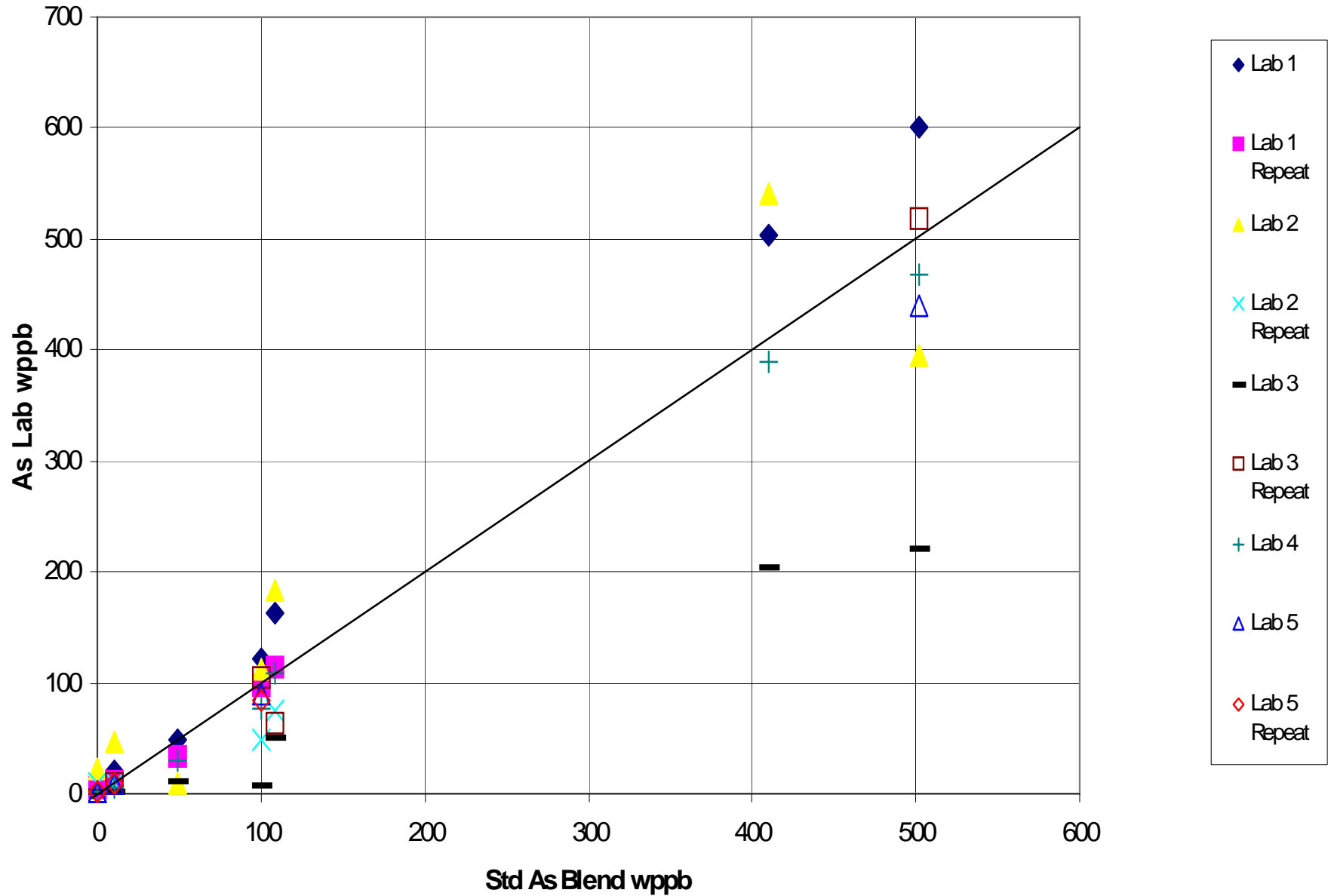
Spike % recoveries (and sigma) for light steam cracked naphtha and gas oils

<u>Element (m/e)</u>	<u>Spike Level</u> <u>ng/g</u>	<u>SCN - No IS</u> <u>Dilution 1:5, n=14</u>	<u>SCN - IS</u> <u>Dilution 1:5, n=6</u>	<u>Gas Oil - IS</u> <u>Dilution 1:5, n=6</u>
Na (23)	10	88 (16)	94 (10)	94 (8.4)
PO (47)	100	90 (11)	95 (5.5)	94 (12)
Ti (47)	10	88 (12)	97 (6.5)	98 (4.4)
V (51)	10	85 (10)	98 (16)	109 (7.1)
Mn (55)	10	89 (10)	96 (5.9)	96 (5.4)
Fe (57)	100	87 (11)	99 (6.9)	101 (9.4)
Ni (60)	10	93 (15)	93 (5.4)	97 (4.9)
Cu (63)	10	89 (8.7)	93 (3.7)	93 (5.3)
Zn (66)	10	90 (9.3)	97 (6.1)	97 (6.6)
As (75)	10	89 (7.5)	92 (5.7)	92 (15)
Se (82)	10	92 (15) n=11	87 (6.9)	85 (16)
Mo (95)	10	87 (9.8)	101 (4.9)	99 (2.8)
Cd (111)	10	91 (13)	104 (6.6)	106 (9.0)
Sn (118)	10	87 (11)	101 (5.4)	103 (5.6)
Sb (121)	10	87 (11)	105 (5.1)	102 (10)
Hg (199-202)	25	131 (64)	93 (7.9)	86 (13)
Pb (206-208)	10	90 (19)	102 (3.6)	100 (3.9)
	Overall mean	91 (15)	97 (6.6)	97 (8.1)

ICP-MS Spike Recoveries in Steam Cracked Naphtha - Three day aging study

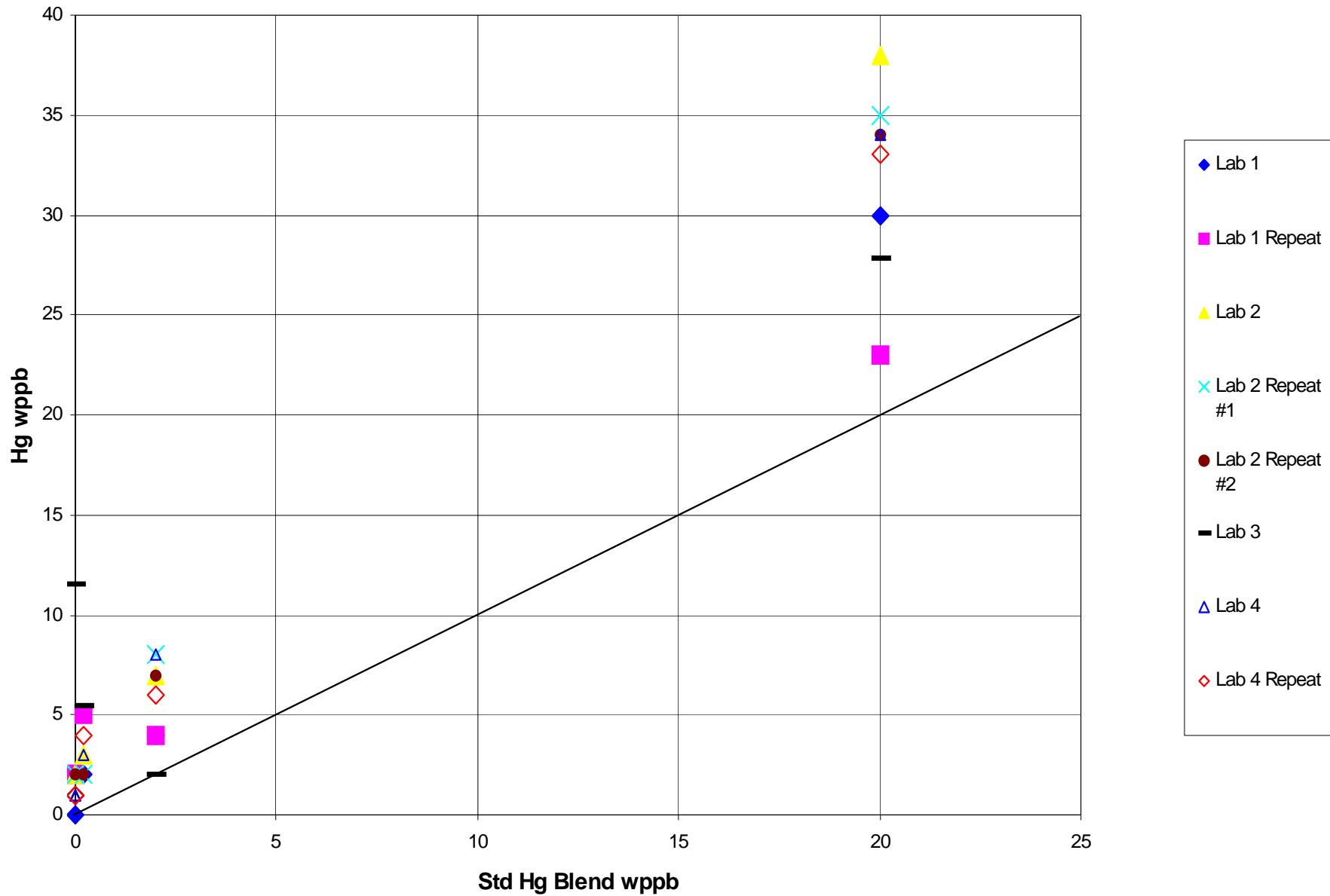


Arsenic Interlaboratory Crosscheck Data (wppb)



Mercury

Interlaboratory CrossCheck Data (wppb)



Si in Naphtha by ICP-AES

- Si in Naphtha performed using PFA-20 nebulizer, Peltier cooled spray chamber [5]
 - Samples containing mainly pentanes may be analyzed
- Calibration with octaphenylcyclotetrasiloxane or commercial standards
- Mo internal standard compensates for effects due to sample matrix volatility
 - Samples diluted 1:5 in toluene with Mo added
- Ongoing QC shows accurate spike recoveries in diverse naphtha types

Si Spike Recoveries in Naphtha

1.00 ppm level

	Si 212.4 nm	Si 251.6 nm
N	55 (5 rejected)	55 (5 rejected)
Mean % Recovery	101.6	101.2
% RSD	9.6	10.9
D.L (3 sigma) ug/g	0.02	0.006

Effect of Volatile Si Compounds

Spiked with tetramethylsilane (TMS) b.p. 26.5 deg. C or
hexamethyldisiloxane (HMS) b.p. 101 deg. C - Mo internal standard

Toluene (neat)	% Spike Recovery		Sigma (n)
	Si 212.4 nm	Si 251.6 nm	
TMS	175	174	4.8 (6)
HMS	146	139	6.9 (6)

20.0% Naphtha in toluene

TMS	214	214	26 (8)
HMS	176	177	6.6 (8)

Interlaboratory comparison of Si in naphtha suggests contamination

Element/Sample	Lab 1	Lab1	Lab 2	Lab 2	Lab 3	Lab 3	Lab 4
	Result 1	Result 2	Result 1	Result 2	Result 1	Result 2	Result 1
As/1	15 ppb	15 ppb	<5 ppb	<5 ppb	6 ppb	6 ppb	NA
As/2	<10 ppb		<5 ppb		1 ppb		4 ppb
Hg/1	<2 ppb	<2 ppb	2 ppb	<2 ppb	<1 ppb	1 ppb	NA
Hg/2	<2 ppb		<2 ppb		<1 ppb		<2 ppb
Si/1	<10 ppb	<10 ppb	3260 ppb	2669 ppb	847 ppb	1121 ppb*	NA
Si/2	<10 ppb		618 ppb		<50 ppb	* Lab 1 retain	<50 ppb

Present status

- As
 - Confident to about 20 ppb level in naphthas, gas oils
 - Effect of species more volatile than triphenylarsine unknown
 - Interlaboratory comparison data shows good trend but too much scatter
- Hg
 - Accuracy at low ppb levels dependent on careful blank/washout control
 - Accurate spike recoveries with relatively non-volatile organic mercury
 - Effect of elemental Hg and other highly volatile species unknown
 - Interlaboratory comparison data shows positive bias, scatter
- Si
 - Accurate determinations for non-volatile forms in naphtha to 1 ppm
 - Determinations at ppb level problematic
 - Volatile forms cause up to factor of three enhancement
 - Interlaboratory comparison data very scattered

Future work

- Further improvement may be possible with mini-spray chamber, in-torch nebulizer or DIHEN
 - Initial test of in torch nebulizer failed by plugging
 - Tiny capillaries necessary to restrict flow may not permit analysis of “real” samples
- Work with laboratories in circuit to standardize techniques, tighten comparisons
- Determine best containers to use for samples
 - Minimize incidental contamination

References

- [1] R. I. Botto, Sample preparation for crude oil, petroleum products and polymers, Chapter 23 in *Comprehensive Analytical Chemistry*, D. Barcelo, ed., Vol. XLI "Sample Preparation for Trace Element Analysis", Z. Mester and R. Sturgeon eds., Elsevier, Amsterdam (2003).
- [2] R. I. Botto, *Spectrochim Acta*, **42B**, 181 (1987).
- [3] R. I. Botto and J. J. Zhu, *J. Anal. At. Spectrom.*, **11**, 675 (1996).
- [4] R. I. Botto, *Can. J. Anal. Sci. Spectrosc.*, 47, 1 (2002).
- [5] R. I. Botto, Paper M-01, ICP Winter Conference on Plasma Spectrochemistry 2004, Ft. Lauderdale, FL (January 2004).