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

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Introduction

Mercury and other trace metals/metalloids in hydrocarbons can have significant impact on petroleum and related industries. The US Environmental Protection Agency mercury ruling in March 2005 regulates mercury emissions from coal-fired power plants.[1] It is also expected that the emission regulations will soon expand to include volatile arsenic, cadmium, nickel, selenium, and lead species. On top of regulatory concerns, trace metals in crude can effect process equipment; mercury can amalgamate with aluminum to create a more brittle alloy, which has been associated with structural failures.[2] Mercury is also known to poison catalysts used in refining processes, in one case reducing a 6-year, $500,000 palladium catalyst to 6 months of viable use. Trace metals/metalloids in crude oil can have significant environmental impact in wastewater, solid waste, or emissions that may have concentrations above regulated levels. They can also accumulate in equipment, causing health and safety concerns during operation and maintenance.[3]

Crude oil containing high levels of mercury and other trace metals are typically discounted at significant cost per barrel. However, estimated average concentrations of mercury in crude oil have been biased high due to the focus on high mercury crudes from locations such as Thailand, Argentina, and Croatia.[4] This problem is compounded as determination of low-level metals concentrations in hydrocarbons has been historically inaccurate, with insufficiently low detection limits. These limitations can often be directly associated with the difficulty to fully decompose the matrix.

Due to the relative inertness of hydrocarbons, common closed-vessel acid digestions result in incomplete dissolution and generate noxious nitro- and halogenated organic compounds that can interfere with analytical procedures. Perchloric acid bomb digestions can decompose hydrocarbons, but the method carries an explosion risk. Perchloric acid is also very costly and often impossible to obtain at sufficient purity levels required for ultra-trace analysis. Dry ashing can fully decompose a hydrocarbon matrix before acid digestion, but is difficult to employ without ignition and/or loss of volatile metals and organo-metallic compounds. Liquid/liquid extraction into hot oxidizing acids (HCl/BrCl or HNO_3) has been used for the extraction of total Hg and organo-Pb; however this method can only successfully be applied to low viscosity, highly saturated samples.

The use of high pressure, high temperature "wet" ashing overcomes these problems, allowing complete decomposition of even the most recalcitrant hydrocarbon matrices (tars, asphalts, waxes, and plastics). The sample matrices are decomposed to $CO_2 + H_2O$ in a simple matrix of dilute HNO_3, which is usually ideal for trace metals analyses by various means (ICP-MS, CVAFS, HG-AFS, ZGFAAS), with no loss of analyte.

Frontier Geosciences has recently completed optimization and MDL studies for metals of interest in the petroleum industry, utilizing the Anton-Paar High Pressure Asher (HPA) to digest samples. The technique digests the hydrocarbon sample with concentrated HNO_3 at 300°C and 130 bar. The resulting solution is directly analyzed for multiple metals, non-metals, and metalloids by a variety of analytical methods.

Experimental

Reagents

Reagent water was at least 18 MΩcm^{-1}. Concentrated Nitric acid (Fisher Scientific, Catalog #A509-212) was low trace-metals grade and tested to ensure minimal contamination.

Spiking standards for analytes were created by the respective dilutions, using reagent water, of Custom Grade standards (Inorganic Ventures, NJ). Mercury spiking standards were created by dilution, using reagent water, from certified standards (100033-1, High Purity Standards, SC and 54005, Absolute Standards, Inc., CT).

The certified samples used for digestion were NIST 1634c (Trace Elements in Fuel Oil, National Institute of Standards and Technology, MD), a custom oil standard made for this study (SPEX Certi-Prep, NJ) and an in-house manufactured Hg in Crude Oil standard (FGS Oil #4-03, 1500 ng/g Hg).

Instrumentation

Mercury was analyzed following a regulatory-approved, modified version of US EPA Method 1631 using a Tekran 2500 (Tekran, Inc., ON) cold vapor atomic fluorescence spectroscopy (CV-AFS) Mercury detector. Other trace metals concentrations were determined by an inductively coupled plasma mass spectrometer (ICP-MS) (Elan 6000, Perkin-Elmer, MA). Arsenic and Selenium were also analyzed by Hydride Generation-Atomic Fluorescence Spectroscopy (HG-AFS) using a Millenium Excalibur instrument and Millenium software (PS Analytical, Kent, UK), which offers lower detection limits for these metals.

Digestions were performed in 50mL pure quartz vessels in a High Pressure Asher (Anton-Paar, Graz, Austria).

Procedure

Approximately 0.3 g of hydrocarbon sample or CRM was weighed into a pre-cleaned 50mL pure quartz asher vessel containing 3 mL of concentrated nitric acid, and spiked as appropriate. Sample vessels were capped with PTFE tape and pure quartz lids. Sample vessels were loaded into the HPA and run through a digestion program that raised the temperature and pressure to 300°C and 130 bar, holding at these conditions for two hours to ensure complete dissolution of the samples. After removal from the HPA, samples were diluted to 20mL with reagent water before analysis.

A method detection limit (MDL) study based on the EPA method 40 CFR 136 (Appendix B)[5] was completed. It should be noted that this text is not intended to be a critique or supporting document for EPA method 40 CFR 136 (Appendix B), rather the procedure is being followed as one way of many procedures to determine the MDL values. This study consisted of 4 repetitions of "clean" pump oil (Maxima C Pump Oil, Fisher Scientific Catalog #01-158-42), 8 low-level spikes and 4-5 mid-level spikes of the same pump oil. Four or eight preparation blanks and repetitions of certified standards were prepared along with each digestion batch to monitor possible contamination and performance of the method.

All results were corrected based on instrument blanks and preparation blanks. An MDL for each analyte was calculated according to the following formula:[5]

MDL = Standard Deviation of Low-Level Spikes * Student's T Value

The student's T value used in this study, based on 8 repetitions (7 degrees of freedom) and a probability of 0.01, is 2.998. For an MDL value to be considered valid, the spiking level must be

2-10 times the calculated MDL value. If the spiking level was too high or too low, an ideal spiking level was calculated (ideal = 3*MDL) and another trial prepared with new spiking levels. This process was repeated as needed to determine acceptable MDL values for all analytes. Percent recoveries were calculated for the certified reference materials and mid-level spikes. Acceptable recoveries were between 75-125% of true value.

In certain cases, trials that needed repeating were modified; the initial MDL trial included 8 preparation blanks and 5 mid-level spikes (matrix spikes, or MSs), for the second set of trials it was determined that only 4 of each were necessary. The SPEX Custom Oil CRM was not available for the first MDL trials, therefore it was only run with later trials.

The second set of trials for mercury were performed using the same pump oil (using the background concentration to calculate the MDL) and with crude oil CRM NIST 2722 (Crude Oil (Heavy Sweet), National Institute of Standards and Technology, MD). These differed from the earlier trials as it included both spiked and non-spiked samples to calculate MDL values.

Results & Discussion

Tables 1-5 show the results and calculations made for the MDL study. Mean preparation blank (PB) concentrations and standard deviations from the latest MDL trial for each analyte are shown in Table 1. Sample concentrations were preparation blank corrected using these mean PB concentrations. High Fe concentrations in preparation blanks are likely due to interferences during ICP-MS analysis (ArO^+ is a recognized molecular interferent), and are likely not a contaminant incurred during the preparation procedure. The PB concentrations were below the calculated MDL values for all other analytes except for Ag (PB mean = 0.031 mg/kg, MDL = 0.006 mg/kg).

Table 1. Data from the analysis of preparation blanks (PBs) from MDL trials. The first MDL run included 8 preparation blanks, it was subsequently determined that this number of blanks was higher than necessary, and future runs included only 4 preparation blanks. For each analyte, the mean and standard deviation of the preparation blanks were calculated. Only the data from the run used for preparation blank correction of the final MDL values, as reported in this text, are shown here.

Analyte	**method**	**Units**	**n**	**PB mean**	**PB std dev**
Hg	CVAFS	μg/kg	8	0.245	0.109
Al	ICP/MS	mg/kg	8	0.184	0.156
Sb	ICP/MS	mg/kg	4	0.002	0.003
As	ICP/MS	mg/kg	4	0.009	0.013
As	HG-AFS	mg/kg	4	0.000	0.003
Ba	ICP/MS	mg/kg	4	0.001	0.000
B	ICP/MS	mg/kg	8	-0.090	0.047
Cd	ICP/MS	mg/kg	4	0.000	0.000
Cr	ICP/MS	mg/kg	8	-0.018	0.011
Co	ICP/MS	mg/kg	8	0.006	0.001
Cu	ICP/MS	mg/kg	8	0.002	0.004
Fe	ICP/MS	mg/kg	4	23.534	1.382
Pb	ICP/MS	mg/kg	8	0.000	0.001
Mg	ICP/MS	mg/kg	8	-0.017	0.013
Mn	ICP/MS	mg/kg	4	0.014	0.002
Mo	ICP/MS	mg/kg	8	-0.007	0.001
Ni	ICP/MS	mg/kg	8	0.006	0.003
K	ICP/MS	mg/kg	4	-2.640	1.511
Se	ICP/MS	mg/kg	4	-0.021	0.024
Se	HG-AFS	mg/kg	4	0.024	0.008
Sr	ICP/MS	mg/kg	8	0.000	0.000
Ag	ICP/MS	mg/kg	4	0.031	0.017
Sn	ICP/MS	mg/kg	4	0.049	0.030
Tl	ICP/MS	mg/kg	8	0.000	0.000
V	ICP/MS	mg/kg	8	-0.031	0.008
Zn	ICP/MS	mg/kg	4	0.010	0.019

The mean concentration of the four pump oil replicates (Table 2) establishes the ambient sample concentration used to calculate the percent recoveries for the MDL low-level spikes and matrix spike (MS) samples.

Table 2. Data from the analysis of pump oil replicates (n=4). The mean concentration calculated for each analyte is used in calculating the percent recovery of the MDL low-level spike values (Table 3) and mid-level spikes (Table 4). Pump oil concentrations were corrected using the mean of preparation blanks (Table 1).

Analyte	Method	Units	Pump Oil Mean	Pump Oil Std Dev
Hg	CV-AFS	µg/kg	0.600	0.369
Al	ICP-MS	mg/kg	0.434	0.111
Sb	ICP-MS	mg/kg	0.000	0.000
As	ICP-MS	mg/kg	0.007	0.012
As	HG-AFS	mg/kg	0.029	0.005
Ba	ICP-MS	mg/kg	0.001	0.001
B	ICP-MS	mg/kg	0.043	0.004
Cd	ICP-MS	mg/kg	0.001	0.001
Cr	ICP-MS	mg/kg	-0.022	0.007
Co	ICP-MS	mg/kg	-0.003	0.001
Cu	ICP-MS	mg/kg	0.715	0.008
Fe	ICP-MS	mg/kg	-13.638	0.431
Pb	ICP-MS	mg/kg	0.054	0.001
Mg	ICP-MS	mg/kg	0.039	0.046
Mn	ICP-MS	mg/kg	0.002	0.005
Mo	ICP-MS	mg/kg	0.031	0.001
Ni	ICP-MS	mg/kg	0.209	0.004
K	ICP-MS	mg/kg	3.223	1.180
Se	ICP-MS	mg/kg	-0.002	0.034
Se	HG-AFS	mg/kg	-0.016	0.006
Sr	ICP-MS	mg/kg	0.000	0.001
Ag	ICP-MS	mg/kg	-0.022	0.009
Sn	ICP-MS	mg/kg	0.023	0.086
Tl	ICP-MS	mg/kg	0.000	0.000
V	ICP-MS	mg/kg	-0.046	0.003
Zn	ICP-MS	mg/kg	0.677	0.060

The MDL replicates (Table 3) data includes the calculations for mean percent recovery, standard deviation, calculated MDL, and the ratio of spike level to MDL. The MDL for Boron is incomplete Boron was, inadvertently, not spiked in to the samples; therefore the calculated MDL value is based on the ambient concentration in the pump oil instead of low-level spikes. The MDL value for Boron will be repeated in a future study with MDL spiking at appropriate levels. The mean percent recoveries for most analytes were within an acceptable recovery range of 75-

125%, except for Sb, Ag and Sn. It is not expected that all recoveries will be within the acceptable range due to greater variability at low analyte concentrations; this is compounded as Ag and Sn may precipitate out of solution if halides are present. Some variability is also necessary for determining the MDL value—the spiking level must be less than ten times the calculated MDL value, which is calculated using the standard deviation of the replicates. If the variability (and hence the standard deviation) in the replicates is too low, the spiking level will be too high and the study will need to be repeated at a more appropriate (lower) spiking level.

Table 3. Data from the analysis of MDL value (low-level spike) replicates (n=8), prepared by spiking pump oil samples at a low concentration level. Sample concentrations are preparation blank corrected, using the mean blank concentrations in Table 1. The mean percent recoveries are included for informational purposes only—spike recoveries at low concentrations are expected to have more variability than those at higher concentrations. The expected recovery range is 75-125%.

Analyte	Method	Units	Pump Oil Mean (n=4)	Low-Level Spike TV	Low-Level Spike Mean Conc (n=8)	Std Dev	T Value	MDL	Spike Level/ MDL	Mean % recov
Hg	CV-AFS	µg/kg	0.600	2.928	3.664	0.155	2.998	0.465	6.5	104.7
Al	ICP-MS	mg/kg	0.434	1.6264	2.182	0.101	2.998	0.301	5.6	107.5
Sb	ICP-MS	mg/kg	0.000	0.4900	0.286	0.032	2.998	0.096	5.3	58.5
As	ICP-MS	mg/kg	0.007	0.9801	0.944	0.045	2.998	0.135	7.5	95.6
As	HG-AFS	mg/kg	0.029	0.9801	0.889	0.041	2.998	0.122	6.2	87.8
Ba	ICP-MS	mg/kg	0.001	0.4900	0.461	0.026	2.998	0.077	6.6	93.8
B	ICP-MS	mg/kg	0.043	ns	0.280	0.073	2.998	0.219	n/a	n/a
Cd	ICP-MS	mg/kg	0.001	0.1983	0.211	0.009	2.998	0.027	7.5	105.9
Cr	ICP-MS	mg/kg	-0.022	1.6264	1.506	0.057	2.998	0.172	9.8	94.0
Co	ICP-MS	mg/kg	-0.003	1.6264	1.618	0.057	2.998	0.171	9.9	99.6
Cu	ICP-MS	mg/kg	0.715	1.6264	2.596	0.070	2.998	0.211	8.0	115.6
Fe	ICP-MS	mg/kg	-13.638	69.4221	70.508	5.452	2.998	16.346	4.4	121.2
Pb	ICP-MS	mg/kg	0.054	3.2528	3.988	0.131	2.998	0.393	8.6	120.9
Mg	ICP-MS	mg/kg	0.039	1.6264	1.859	0.066	2.998	0.198	8.5	111.9
Mn	ICP-MS	mg/kg	0.002	0.4900	0.490	0.018	2.998	0.055	9.1	99.5
Mo	ICP-MS	mg/kg	0.031	1.6264	1.477	0.099	2.998	0.297	5.7	88.9
Ni	ICP-MS	mg/kg	0.209	1.6264	1.821	0.062	2.998	0.186	9.0	99.1
K	ICP-MS	mg/kg	3.223	9.8009	13.235	0.737	2.998	2.211	4.6	102.1
Se	ICP-MS	mg/kg	-0.002	0.9801	0.980	0.075	2.998	0.224	4.5	100.3
Se	HG-AFS	mg/kg	-0.016	0.9801	0.956	0.055	2.998	0.165	6.1	99.2
Sr	ICP-MS	mg/kg	0.000	1.6264	1.816	0.066	2.998	0.199	8.5	111.7
Ag	ICP-MS	mg/kg	-0.022	0.0198	-0.010	0.002	2.998	0.006	3.5	60.3
Sn	ICP-MS	mg/kg	0.023	0.0992	0.072	0.031	2.998	0.094	1.1	49.8
Tl	ICP-MS	mg/kg	0.000	1.6264	1.900	0.060	2.998	0.180	9.4	116.9
V	ICP-MS	mg/kg	-0.046	1.6264	1.384	0.073	2.998	0.219	7.7	87.9
Zn	ICP-MS	mg/kg	0.677	0.4900	1.159	0.029	2.998	0.088	5.7	98.3

Additional indicators of method performance (for digestion preparation and analysis) include the preparation of Certified Reference Materials (CRMs) and Matrix Spikes (MSs). Three CRMs were prepared over the course of the MDL study. NIST 1634c, a fuel oil certified for several metals, was used in the initial MDL run along with an internal crude oil standard with a known Hg concentration, FGS Oil #4-03. After the initial MDL run, a custom-made oil standard certified for many metals was implemented (Spex Custom Oil Standard). Replicates of this standard were also after the MDL trials for validation purposes. Mean concentrations, true values (TVs), and mean percent recoveries for all three CRMs are found in Table 4. Data for the Spex Custom Oil Standard from the validation studies is also included, giving mean recoveries for replicates for most analytes.

Most of the mean percent recoveries are within acceptable limits (75-125%). All recoveries for certified analytes in 1634c were acceptable except for Se, which was low (69.1%) when analyzed by HG-AFS but acceptable by ICP-MS analysis (107.5%). This variability is due to the low true value (0.102 mg/kg), which is below the calculated MDL values (0.160 mg/kg by HG-AFS analysis, 0.217 mg/kg by ICP-MS analysis). Recoveries from the Spex Custom Oil Standard were more varied. The As recovery by ICP-MS analysis was acceptable (92.3%); however the recovery was low by HG-AFS analysis (36.6%). This is probably due to the species of As present in the CRM, since some forms of As are not accessible by the HG-AFS method. This under further investigation. The Sb recoveries were very low from the SPEX CRM (7.4%), for unknown reasons. Sb recoveries were low from the MDL spikes (58.5%) and pump oil and crude oil MSs (3.1% and 1.8%, respectively). Fe was not recovered (-130.4%) from the SPEX CRM, as the TV for Fe is below the MDL value, in addition to the high blanks incurred from ICP-MS molecular interferences. The TV for K in the SPEX CRM is also low, less than three times the MDL value, which likely accounts for its high recovery (184.1%).

Table 4. Data from CRMs analyzed as part of MDL trials. All concentrations are in mg/kg. Datapoints from validation studies are included for the Spex Custom Oil CRM. "nc" is not certified, "nd" is not determined, and "n/a" is not analyzed.

			NIST 1634c			**Spex Custom Oil**				**FGS Oil #4-03**		
Analyte	**Analysis method**	**Calc MDL**	**mean conc**	**TV**	**mean % recov**	**mean conc**	**n=**	**TV**	**mean % recov**	**mean conc**	**TV**	**mean % recov**
Hg	CVAFS	0.000465	0.121	*nc*	***nd***	4.437	3	5.0	**88.7**	1.509	1.5	**100.6**
Al	ICP/MS	0.301	4.007	*nc*	***nd***	*n/a*	*n/a*	*nc*	***nd***	0.164	*nc*	***nd***
Sb	ICP/MS	0.096	0.013	*nc*	***nd***	0.370	4	5.0	**7.4**	0.072	*nc*	***nd***
As	ICP/MS	0.135	0.161	0.143	**112.8**	4.616	4	5.0	**92.3**	2.480	*nc*	***nd***
As	HG-AFS	0.122	0.127	0.143	**89.4**	1.830	1	5.0	**36.6**	*n/a*	*nc*	***nd***
Ba	ICP/MS	0.077	1.978	1.800	**109.9**	4.492	4	5.1	**88.1**	0.029	*nc*	***nd***
Cd	ICP/MS	0.027	0.003	*nc*	***nd***	4.876	4	5.0	**97.5**	0.000	*nc*	***nd***
Cr	ICP/MS	0.172	0.045	*nc*	***nd***	5.052	3	5.0	**101.0**	-0.127	*nc*	***nd***
Co	ICP/MS	0.171	0.132	0.151	**87.3**	5.218	3	5.0	**104.4**	0.024	*nc*	***nd***
Cu	ICP/MS	0.211	0.679	*nc*	***nd***	5.462	3	5.0	**109.2**	0.014	*nc*	***nd***
Fe	ICP/MS	16.346	32.595	*nc*	***nd***	-6.522	1	5.0	**-130.4**	-14.456	*nc*	***nd***
Pb	ICP/MS	0.393	0.717	*nc*	***nd***	5.108	3	5.0	**102.2**	0.011	*nc*	***nd***
Mg	ICP/MS	0.198	2.993	*nc*	***nd***	4.740	3	5.1	**92.9**	0.104	*nc*	***nd***
Mn	ICP/MS	0.055	0.335	*nc*	***nd***	5.118	4	5.0	**102.4**	-0.009	*nc*	***nd***
Mo	ICP/MS	0.297	0.140	*nc*	***nd***	4.009	3	5.0	**80.2**	0.028	*nc*	***nd***
Ni	ICP/MS	0.186	15.288	17.540	**87.2**	5.329	3	5.0	**106.6**	0.193	*nc*	***nd***
K	ICP/MS	2.211	7.447	*nc*	***nd***	9.203	1	5.0	**184.1**	-7.898	*nc*	***nd***
Se	ICP/MS	0.224	0.110	0.102	**107.5**	4.666	4	5.2	**89.7**	3.053	*nc*	***nd***
Se	HG-AFS	0.165	0.071	0.102	**69.1**	5.386	1	5.2	**103.6**	*n/a*	*nc*	***nd***
Sr	ICP/MS	0.199	0.633	*nc*	***nd***	*n/a*	*n/a*	*nc*	***nd***	0.038	*nc*	***nd***
Ag	ICP/MS	0.006	-0.001	*nc*	***nd***	3.982	3	5.0	**79.6**	0.000	*nc*	***nd***
Tl	ICP/MS	0.180	0.003	*nc*	***nd***	5.192	3	5.0	**103.8**	0.000	*nc*	***nd***
V	ICP/MS	0.219	25.531	28.190	**90.6**	*n/a*	*n/a*	*nc*	***nd***	0.118	*nc*	***nd***
Zn	ICP/MS	0.088	3.421	*nc*	***nd***	5.151	4	5.0	**103.0**	0.033	*nc*	***nd***

The matrix spike data are found in Table 5. Antimony recoveries were all significantly low, as seen previously. The Fe recovery from the crude oil MS is slightly low (73.0%), likely due to the spike level being just below the MDL value (unfortunately the MDL value was not known prior to the spiking of the solution). Mo is under the recovery limit (74%) for the pump oil MS. The high recovery of K in the crude oil MS is suspected to be operator error (possibly due to the spike being 10-fold greater than desired), however, even assuming this error it would be over the acceptable limit at 127.3%. The mean Ag recovery from the MDL low-level spikes was under the acceptable limit (60.3%), which is likely due to precipitation induced by a small amount of halides in the matrix.

Table 5. Data from spiked samples analyzed as part of MDL trials. MDL spikes are low level spikes (see Table 3 for full MDL data). Matrix spikes are higher in the instrument calibration range than MDL spikes, ideally 3-5 times the ambient sample concentration or in the middle of the instrument calibration range. "nc" is not certified, "nd" is not determined, and "n/a" is not analyzed.

					Pump Oil MDL Spikes			**Pump Oil Matrix Spikes**			**Sweet Crude Oil Matrix Spikes**			
Analyte	**Analysis method**	**Units**	**MDL Value**	**Pump Oil Mean**	**TV**	**Mean Conc.**	**Mean % Recov.**	**TV**	**Mean Conc.**	**Mean % Recov.**	**Mean Amb. Conc**	**MS TV**	**MS Mean Conc.**	**MS Mean % Recov.**
Hg	CVAFS	µg/kg	0.465	0.600	2.928	3.664	104.7	322.673	338.297	104.7	-0.130	327.254	339.211	103.7
Al	ICP/MS	mg/kg	0.301	0.434	1.626	2.182	107.5	15.974	18.148	110.9	0.717	16.201	19.875	118.3
Sb	ICP/MS	mg/kg	0.096	0.000	0.490	0.286	58.5	5.085	0.158	3.1	0.000	16.201	0.290	1.8
As	ICP/MS	mg/kg	0.135	0.007	0.980	0.944	95.6	10.171	10.083	99.1	0.154	16.201	15.479	94.6
As	HG-AFS	mg/kg	0.122	0.029	0.980	0.889	87.8	10.171	10.093	98.9	*n/a*	*nc*	*n/a*	*nd*
Ba	ICP/MS	mg/kg	0.077	0.001	0.490	0.461	93.8	5.085	4.945	97.2	7.740	16.201	24.127	101.2
Cd	ICP/MS	mg/kg	0.027	0.001	0.198	0.211	105.9	1.989	2.078	104.4	0.001	16.201	17.418	107.5
Cr	ICP/MS	mg/kg	0.172	-0.022	1.626	1.506	94.0	15.974	14.603	91.6	-0.100	16.201	14.697	91.3
Co	ICP/MS	mg/kg	0.171	-0.003	1.626	1.618	99.6	15.974	15.326	96.0	0.102	16.201	15.513	95.1
Cu	ICP/MS	mg/kg	0.211	0.715	1.626	2.596	115.6	15.974	18.988	114.4	0.024	16.201	18.460	113.8
Fe	ICP/MS	mg/kg	16.346	-13.638	69.422	70.508	121.2	696.155	799.473	116.8	-4.702	16.201	7.117	73.0
Pb	ICP/MS	mg/kg	0.393	0.054	3.253	3.988	120.9	31.948	38.263	119.6	0.019	32.401	40.013	123.4
Mg	ICP/MS	mg/kg	0.198	0.039	1.626	1.859	111.9	15.974	18.889	118.0	0.536	16.201	20.081	120.6
Mn	ICP/MS	mg/kg	0.055	0.002	0.490	0.490	99.5	5.085	5.107	100.4	0.064	16.201	16.119	99.1
Mo	ICP/MS	mg/kg	0.297	0.031	1.626	1.477	88.9	15.974	11.858	74.0	0.055	16.201	12.284	75.5
Ni	ICP/MS	mg/kg	0.186	0.209	1.626	1.821	99.1	15.974	15.516	95.8	0.304	16.201	15.643	94.7
K	ICP/MS	mg/kg	2.211	3.223	9.801	13.235	102.1	101.709	114.250	109.2	-7.116	16.201	199.177	1273.4
Se	ICP/MS	mg/kg	0.224	-0.002	0.980	0.980	100.3	10.171	10.038	98.7	0.087	16.201	17.783	109.2
Se	HG-AFS	mg/kg	0.165	-0.016	0.980	0.956	99.2	10.171	10.130	99.8	*n/a*	*nc*	*n/a*	*nd*
Sr	ICP/MS	mg/kg	0.199	0.000	1.626	1.816	111.7	15.974	17.706	110.8	0.186	16.201	18.432	112.6
Ag	ICP/MS	mg/kg	0.006	-0.022	0.020	-0.010	60.3	0.199	0.163	93.0	-0.001	*nc*	-0.001	*nd*
Tl	ICP/MS	mg/kg	0.180	0.000	1.626	1.900	116.9	15.974	18.767	117.5	0.002	16.201	19.136	118.1
V	ICP/MS	mg/kg	0.219	-0.046	1.626	1.384	87.9	15.974	14.492	91.0	-0.051	16.201	14.672	90.9
Zn	ICP/MS	mg/kg	0.088	0.677	0.490	1.159	98.3	5.085	5.975	104.2	0.456	16.201	16.031	96.1

A comparison of calculated MDL values with those from other methods (Table 6) shows that digestion in the HPA yields a lower MDL than digestions of soils or tissues for most analytes.

Table 6. A comparison of MDL values calculated (based on 40 CFR)[5] for Oil in HPA versus other solids preparation methods. All MDL concentrations are in mg/kg.

Analyte	**Analysis Method**	**Hydrocarbons in Asher (HNO_3) 40 CFR MDL**	**Tissue Digest (HNO_3) 40 CFR MDL[6]**	**Sediment Digest (HNO_3/HF) 40 CFR MDL[7]**
Hg	CV-AFS	0.000465	0.0028	n/a
Al	ICP/MS	0.301	1.1	112
As	ICP/MS	0.135	0.07	0.72
As	HG-AFS	0.122	n/a	n/a
Ba	ICP/MS	0.077	0.030	0.75
Cd	ICP/MS	0.027	0.003	0.14
Cr	ICP/MS	0.172	0.14	0.47
Co	ICP/MS	0.171	0.02	0.13
Cu	ICP/MS	0.211	0.04	0.44
Fe	ICP/MS	16.346	3.9	43
Pb	ICP/MS	0.393	0.006	0.2
Mg	ICP/MS	0.198	n/a	10.3
Mn	ICP/MS	0.055	0.14	1.4
Mo	ICP/MS	0.297	0.04	0.15
Ni	ICP/MS	0.186	0.02	0.21
K	ICP/MS	2.211	n/a	100
Se	ICP/MS	0.224	0.22	14
Se	HG-AFS	0.165	0.1	n/a
Sr	ICP/MS	0.199	n/a	n/a
Ag	ICP/MS	0.006	0.007	0.13
Tl	ICP/MS	0.180	0.003	0.5
V	ICP/MS	0.219	0.06	1.1
Zn	ICP/MS	0.088	0.4	0.9

Further investigations of Hg MDL value in hydrocarbons show consistency with previous trials, Table 7. The certified value of NIST 2722 (0.129 µg/kg) is lower than the previously established MDL value (0.465 µg/kg) and the concentrations of the preparation blanks from both

MDL trials. The calculated MDL value from the unspiked NIST 2722 repetitions is lower than the established MDL value at 0.329 µg/kg, however the ratio of the certified concentration to MDL value is too low (0.196) to render this MDL value reliable.

The ratio of sample Hg concentration to MDL value is within the acceptable range for the trials using spiked NIST 2722 and unspiked Pump Oil (2.707 and 2.598, respectively). The MDL value calculated with the spiked NIST 2722 repetitions is consistent with the previous MDL value determined (0.456 µg/kg) and has a mean analyte recovery of 83.2%. The MDL value calculated from the unspiked pump oil data is lower at 0.250 µg/kg. However, the pump oil is a cleaner, less complicated matrix than the crude oil. Using the "worst-case" higher MDL value is more analytically reliable.

Table 7. MDL studies for Hg in hydrocarbons using NIST 2722 (spiked and not spiked) and Pump Oil (not spiked). The pump oil was the same used in the previously discussed MDL studies. All Hg data is in µg/kg.

	rep#	Hg
PBO's	1	0.202
	2	0.202
	3	0.143
	4	0.399
	Mean	**0.236**

	rep#	Hg	% recov
NIST 2722	1	-0.030	-23.2
	2	-0.053	-41.4
	3	-0.013	-10.2
	4	0.005	3.7
	5	0.186	144.0
	6	0.042	32.5
	7	0.140	108.9
	8	0.240	186.2
	Mean	0.065	50.1
	Std Dev	0.110	
	T Value	2.998	
	Calculated MDL	0.329	
	Conc/MDL	0.196	
	Cert Value	0.129	
	mean % recovery	50.1	

	rep#	Hg	TV	% recov
NIST 2722 spiked (MDL) samples	1	1.287	1.143	112.6
	2	1.059	1.231	86.0
	3	1.144	1.329	86.0
	4	1.039	1.187	87.5
	5	1.066	1.238	86.1
	6	0.833	1.194	69.8
	7	1.210	1.316	91.9
	Mean	1.091	1.234	83.2
	Std Dev	0.145		
	T Value	3.143		
	Calculated MDL	0.456		
	Spike Level/MDL	2.707		
	Mean TV	1.234		
	mean % recovery	83.2		

	rep#	Hg
Pump Oil Reps	1	0.771
	2	0.551
	3	0.701
	4	0.652
	5	0.611
	6	0.523
	7	0.694
	8	0.698
	Mean	0.650
	Std Dev	0.083
	T Value	2.998
	Calc MDL	0.250
	Conc/MDL	2.598

Conclusions

The digestion of hydrocarbons at high temperature and pressure with concentrated nitric acid in the Anton-Paar High Pressure asher provides a clean matrix that is easy to analyze for mercury and other trace metals by several analytical methods. The digestion method completely decomposes all organic samples into a common final matrix. Therefore samples of different types (hydrocarbons, plastics, chemicals, coal, biota) can be processed in the same analytical batch, allowing the economy of shared QA/QC. This study provides method detection limits for many analytes of interest by several analytical methods.

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