

ANALYTICAL METHOD VERIFICATION FOR THE DETERMINATION
OF WATER SOLUBLE COMPONENTS OF PETROLEUM COKE IN FRESHWATER USING
INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES)

WILDLIFE INTERNATIONAL, LTD. PROJECT NUMBER: 472C-105

GUIDELINE:

European Commission Working Document SANCO/3029/99 rev.4

AUTHORS:



STUDY INITIATION DATE: April 23, 2004

STUDY COMPLETION DATE: January 31, 2006

AMENDED REPORT DATE: April 10, 2007

Submitted to

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Page 1 of 115

AMENDED

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GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT

SPONSOR: American Petroleum Institute

TITLE: Analytical Method Verification for the Determination of Water Soluble Components of Petroleum Coke in Freshwater Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

WILDLIFE INTERNATIONAL, LTD. PROJECT NUMBER: 472C-105

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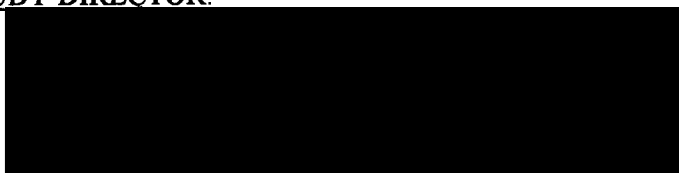
AMENDED REPORT DATE: April 10, 2007

This study was conducted in compliance with Good Laboratory Practice Standards as published by the U.S. Environmental Protection Agency in 40 CFR Parts 160 and 792, 17 August 1989 and OECD Principles of Good Laboratory Practice (ENV/MC/CHEM (98) 17) with the following exceptions:

Periodic analyses of well water for potential contaminants were performed using a certified laboratory and standard U.S. EPA analytical methods, but not under Good Laboratory Practice Standards.

The characterization of the test substance was not determined in accordance with Good Laboratory Practice Standards.

STUDY DIRECTOR:

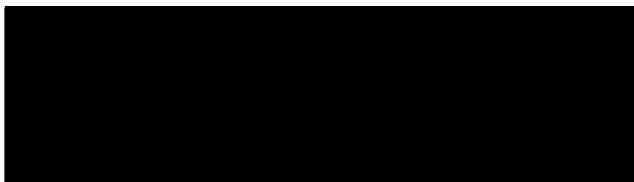


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April 10, 2007
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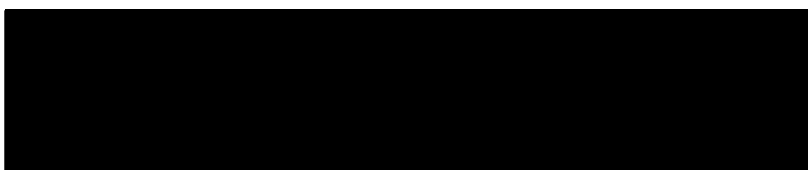
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QUALITY ASSURANCE STATEMENT

This study was examined for compliance with Good Laboratory Practice Standards as published by the U.S. Environmental Protection Agency in 40 CFR Parts 160 and 792, 17 August 1989 and OECD Principles of Good Laboratory Practice, (ENV/MC/CHEM (98) 17). The dates of all inspections and audits and the dates that any findings were reported to the Study Director and Laboratory Management were as follows:

ACTIVITY:	DATE CONDUCTED:	DATE REPORTED TO:	
		STUDY DIRECTOR:	MANAGEMENT:
Protocol	May 3, 2004	May 3, 2004	October 14, 2004
Sample Processing	October 14, 2004	October 14, 2004	October 18, 2004
Test Substance Preparation	October 29, 2004	October 29, 2004	November 9, 2004
Data and Draft Report	January 10-13, 2005	January 13, 2005	January 17, 2005
Final Report	January 30, 2006	January 31, 2006	January 31, 2006
Amended Report	March 30, 2007	March 30, 2007	April 10, 2007

All inspections were study-based unless otherwise noted.



4-10-07
DATE

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AMENDED REPORT APPROVAL

SPONSOR: American Petroleum Institute

TITLE: Analytical Method Verification for the Determination of Water Soluble Components of Petroleum Coke in Freshwater Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

WILDLIFE INTERNATIONAL, LTD. PROJECT NO.: 472C-105

This report was reviewed by the individuals involved in the conduct and management of the study, and was found to be an accurate reflection of the methods used, data collected and results of the study.

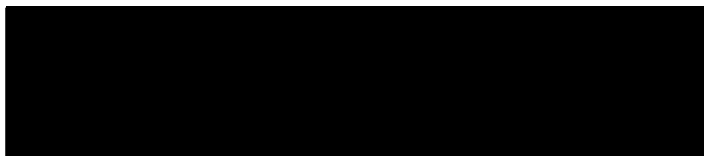
STUDY DIRECTOR:



Wildlife International, Ltd.

April 10, 2007
DATE

MANAGEMENT:



Wildlife International, Ltd.

4/10/07
DATE

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SUMMARY

SPONSOR: American Petroleum Institute

SPONSOR'S REPRESENTATIVE:

LOCATION OF STUDY, RAW DATA Wildlife International, Ltd.
AND A COPY OF THE FINAL Easton, Maryland 21601
REPORT:

WILDLIFE INTERNATIONAL, LTD.

PROJECT NUMBER: 472C-105

TEST SUBSTANCE: Petroleum Coke

STUDY: Analytical Method Verification for the Determination of Water Soluble Components of Petroleum Coke in Freshwater Using Inductively Coupled Plasma Atomic Emission Spectrometry

FORTIFIED TEST CONCENTRATIONS:	Element	LOQ level, µg/L	10x LOQ level, µg/L
	Arsenic 20.0		200
	Copper 20.0		200
	Iron 10.0		100
	Nickel 10.0		100
	Selenium 200		2000
	Sulfur 10,000		100,000
	Vanadium 0.400		4.00

TEST DATES: Experimental Start (OECD) – August 10, 2004
Experimental Start (EPA) – October 31, 2004
Experimental Termination – November 4, 2004

TEST SYSTEM: Freshwater

SUMMARY:

Instrumental detection limits for six metals (As, Cu, Fe, Ni, Se, V) and sulfur were established using Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). Freshwater matrix was screened for the seven elements. From these analyses, theoretical LOQs were established for each element based on the instrumental limits, matrix background level and/or environmental contamination.

Method verification samples containing the six metals and sulfur were fortified in freshwater at the LOQ and 10x LOQ levels. Samples were acidified and either further diluted in acidified freshwater or analyzed directly against metal and sulfur external standards also prepared in freshwater. Recovery samples and standards were analyzed by ICP-AES. The ICP system was configured for axial plasma viewing and ultrasonic nebulization sample introduction. The emission wavelengths selected to quantify As, Cu, Fe, Ni, Se, S and V were 188.979, 224.700, 239.562, 231.604, 196.026, 180.669 and 292.402 nm, respectively. Each element was quantified against external standards via linear regression analysis. Recoveries of each of the elements from freshwater are presented in Tables 2-8. Linear regression analyses of each of seven elements are presented in Figures 2-8. All elements were shown to recover quantitatively at the LOQ and 10x LOQ levels.

Water accommodated fractions (WAFs) were analyzed for the presence of the six metals and sulfur after mixing for 24, 48, 72 and 96 hours. Except for a trace of iron contamination in one test vessel, no metals were detected in any WAF samples. Sulfur was not detected above the background level in the freshwater used.

INTRODUCTION

Analytical trials were conducted to verify analytical methods for the determination of selected metals and sulfur (S) in water accommodated fraction (WAF) solutions made with petroleum coke and freshwater. The metals determined included arsenic (As), copper (Cu), iron (Fe), nickel (Ni), selenium (Se) and vanadium (V). The study was conducted by Wildlife International, Ltd. and identified as Project Number 472C-105. The study was performed based on procedures in *Residues: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, Section 4) and Annex III (Part A, Section 5) of Directive 91/414* (1). Details on the procedures followed in the conduct of the study are specified in the protocol and protocol amendments provided in Appendix I. A method for determination of selected metals and sulfur components of petroleum coke was verified by fortifying freshwater with reference standards of As, Cu, Fe, Ni, Se, V and S and determining the recoveries for the components. Limits of detection (LOD) and limits of quantitation (LOQ) also were established. All raw data generated by Wildlife International, Ltd. and a copy of the final report are filed under Project Number 472C-105 in archives located on the Wildlife International, Ltd. site.

OBJECTIVE

There were two objectives of this study. One was to verify an inductively coupled plasma atomic emission spectrometry (ICP-AES) method for determination of metals and sulfur in water accommodated fraction (WAF) solutions of petroleum coke. The second objective was to employ the method to determine the optimum WAF mixing time to achieve maximum leaching of metals and sulfur from the test substance matrix into freshwater.

EXPERIMENTAL DESIGN

Prior to performance of the method verification trial, an evaluation of the ICP-AES method was performed for each element to determine the limit of detection (LOD) at the instrument, determine background levels of the elements in water and establish a theoretical limit of quantitation (LOQ) in water. The LOQ was based on 10 times the LOD or 2 times the background level, whichever was higher.

The method verification trial was performed by fortifying freshwater with known standards (individual or mixed standards) of the seven elements of interest (Ni, V, Fe, Cu, S, As and Se) rather than with petroleum coke containing trace quantities of these elements. Concentrations of most of the elements of interest in petroleum coke were < LOQ or were present in trace quantities according to

information provided by the Sponsor. Fortifying with known concentrations using element standards verified the efficiency and accuracy of the ICP-AES method for analysis of the elements in water to be used for environmental effects testing. Fortification levels of each element included the calculated LOQ and 10X the LOQ to bracket the expected concentrations of each element in water to be used for environmental effects testing with petroleum coke. Reagent and matrix blanks were analyzed concurrently to evaluate potential analytical interferences. Calibration curves were prepared and analyzed with each series of matrix fortification samples.

A WAF trial was run for 96 hours to determine mixing time for preparation of WAF solutions. Analytical samples were taken at approximately 24, 48, 72 and 96 hours. Matrix blanks were analyzed concurrently to evaluate potential analytical interferences. Matrix fortification samples were also analyzed concurrently to evaluate method performance at each sampling interval.

MATERIALS AND METHODS

Test Substance

The test substance was green petroleum coke (CAS Number 64741-79-3). Petroleum coke was defined as the product formed by subjecting the heavy tar-like residue remaining following oil refining to high temperatures and pressures. It consists of primarily elemental carbon with considerably smaller amounts of hydrocarbons, sulfur and trace amounts of heavy metals. Analyses of selected components in petroleum coke are provided in Appendix 2. The test substance was received from EPL on October 7, 2003 and was assigned Wildlife International, Ltd. identification number 6485A. The test substance, black pellets, was identified as 2 mm Particle Size Petroleum Coke (aka Milled Pellets). The test substance was stored under ambient conditions. An expiration date was not provided. The stability of the test substance was performed concurrently during the method verification steps.

The identity, strength, purity, composition, and method of selection, synthesis, fabrication and/or derivation of each batch of the test substance and the maintenance of these records were the responsibility of the Sponsor (Appendix 2).

Reference Substances

Analytical standards for each of the seven elements of interest were received from Spex Industries (Metuchen, N.J. 08840) and were stored under ambient conditions. All of the materials were 1,000 mg/L Spex CertiPrep® plasma standards in 2% HNO₃, with the exception of the sulfur standards which were

1,000 mg/L and 10,000 mg/L preparations in water. Certificates of analyses for the reference substances are provided in Appendix 2. The following tabulation summarizes pertinent data for each analytical standard:

<u>Component</u>	<u>Test Substance Number</u>	<u>Lot/Batch</u>	<u>CAS Number</u>	<u>Date Received</u>	<u>Expiration Date</u>	<u>Description</u>
Arsenic	6543	10-06AS	7440-38-2	11/06/03	11/15/04	Clear liquid
Copper	6544	9-183CU	7440-50-8	11/06/03	11/15/04	Blue liquid
Iron	6545	9-184FE	7439-89-6	11/06/03	11/15/04	Clear Liquid
Nickel	6546	10-29NI	7440-02-0	11/06/03	11/15/04	Blue liquid
Selenium	6547	10-31SE	7782-49-2	11/06/03	11/15/04	Clear Liquid
Sulfur	6548	8-74S	7704-34-9	11/06/03	11/15/04	Clear Liquid
Sulfur	6890	S9-51S	7704-34-9	10/18/04	10/15/05	Liquid
Vanadium	6549	10-88V	7440-62-2	11/06/03	11/15/04	Yellow Liquid

Reagents and Solvents

Burdick & Jackson HPLC grade reagent water.

J.T. Baker, Baker Instra-Analyzed[®] concentrated nitric acid, ACS reagent grade, Lot No. Y33025.

Freshwater

The freshwater used for the method verification and the WAF trials was obtained from a well approximately 40 meters deep located on the Wildlife International, Ltd. site. The well water is characterized as moderately-hard water. The means and ranges of specific conductance, hardness, alkalinity and pH measurements of the well water during the four-week period immediately preceding the test are presented in Appendix 3.

The well water was passed through a sand filter to remove particles greater than approximately 25 µm, and pumped into a 37,800-L storage tank and aerated with spray nozzles. Prior to use, the water was filtered (0.45 µm) again to remove microorganisms and particles. The results of periodic analyses performed to measure the concentrations of selected organic and inorganic constituents in the well water are presented in Appendix 4.

Stock and Calibration Standard Preparations

For each phase of the study, a combined stock solution containing the seven elements of interest was prepared either directly from the procured Spex primary standards, or from single element secondary stock

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preparations. The combined stock solutions were used to prepare external calibration standards and matrix fortification samples. The preparation of the secondary stocks and combined stocks was as follows:

For the LOD experiment, single component secondary stocks for each element were prepared using volumetric flasks and calibrated micropipettors. For As, Cu, Fe, Ni and V, each primary standard was diluted by a factor of 1000 using 10% (v/v) nitric acid in reagent grade water (10:90 HNO₃: H₂O) dilution solvent. Each of these secondary stocks had a nominal concentration of 1.00 ng element/L. For Se and S, each primary standard was diluted by a factor of 100 using 10:90 HNO₃: H₂O dilution solvent. Each of these secondary stocks had a nominal concentration of 10.0 mg element/L. The single component stock solutions were used to prepare a single calibration standard in 10:90 HNO₃: H₂O dilution solvent using the following dilution scheme:

Element	Secondary Stock Concentration <u>mg/L</u>	Aliquot <u>(μL)</u>	Final Volume <u>(mL)</u>	Calibration Standard Concentration <u>(μg/L)</u>
As	1.00	1000		10.0
Cu	1.00	500		5.00
Fe	1.00	100	100	1.00
Ni	1.00	200		2.00
Se	10.0	200		20.0
S	10.0	200		20.0
V	1.00	100		1.00

For the freshwater matrix screen, a combined secondary stock in 10:90 HNO₃: H₂O dilution solvent was prepared as follows:

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Element	Primary Stock Concentration <u>mg/mL</u>	Aliquot <u>(mL)</u>	Final Volume <u>(mL)</u>	Secondary Stock Concentration <u>(mg/L)</u>
As	1.00	0.500		10.0
Cu	1.00	0.500		10.0
Fe	1.00	0.0500	50.0	1.00
Ni	1.00	0.0250		0.500
Se	1.00	5.00		100
S	1.00	1.25		25.0
V	0.001	10.0		0.200

This combined secondary stock solution was used to prepare a series of calibration standards, each in 10:90 HNO₃: H₂O dilution solvent and diluted to a 50-mL final volume, using the following dilution scheme:

Stock Aliquot:	0.0500 mL	0.125 mL	0.250 mL	0.375 mL	0.500 mL
Element	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>
As	10.0	25.0	50.0	75.0	100
Cu	10.0	25.0	50.0	75.0	100
Fe	1.00	2.50	5.00	7.50	10.0
Ni	0.500	1.25	2.50	3.75	5.00
Se	100	250	500	750	1000
S	25.0	62.5	125	188	250
V	0.200	0.500	1.00	1.50	2.00

For the method verification and WAF trials, a secondary vanadium stock was first prepared from a 10x dilution of the 1.00 mg/mL V primary standard using 2% (v/v) nitric acid in reagent grade water (2:98 HNO₃: H₂O) dilution solvent. The nominal concentration of the resultant vanadium stock was 0.100 mg V/mL. A combined secondary stock in 2:98 HNO₃: H₂O dilution solvent was then prepared as follows:

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Element	Primary Stock Concentration <u>mg/mL</u>	Aliquot <u>(mL)</u>	Final Volume <u>(mL)</u>	Secondary Stock Concentration <u>(mg/L)</u>
As	1.00	1.00	100	10.0
Cu	1.00	1.00		10.0
Fe	1.00	0.500		5.00
Ni	1.00	0.500		5.00
Se	1.00	10.0		100
S	1.00	10.0		100
V	0.100	0.200		0.200

This combined secondary stock solution was used to prepare two separate sets of calibration standards, each in 2% (v/v) nitric acid in Wildlife International, Ltd. freshwater (2:98 HNO₃: FW) dilution solvent and diluted to a 50-mL final volume, using the following dilution scheme:

Stock Aliquot:	0.0500 mL	0.125 mL	0.250 mL	0.375 mL	0.500 mL
Element	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>	Standard Concentration <u>µg/L</u>
As	10.0	25.0	50.0	75.0	100
Cu	10.0	25.0	50.0	75.0	100
Fe	5.00	12.5	25.0	37.5	50.0
Ni	5.00	12.5	25.0	37.5	50.0
Se	100	250	500	750	1000
S	100	250	500	750	1000
V	0.200	0.500	1.00	1.50	2.00

Two separate sets of sulfur calibration standards, each in 2:98 HNO₃: FW dilution solvent, were prepared from the 10.0-mg S/mL primary standard for use in the method verification and WAF trials using the following dilution scheme:

Stock Concentration <u>mg S/mL</u>	Aliquot <u>(μL)</u>	Final Volume <u>(mL)</u>	Standard Concentration <u>(mg S/L)</u>
10.0	25.0	50.0	5.00
10.0	50.0	50.0	10.0
10.0	125	50.0	25.0
10.0	175	50.0	35.0
10.0	250	50.0	50.0

Analytical Methods

The analytical method for each phase of the study generally consisted of acidification and/or dilution and direct injection into the ICP-AES system. Procedures specific to each phase are specified below. Concentrations of As, Cu, Fe, Ni, Se, S and V in the samples were determined using a Perkin-Elmer Optima 3000 DV ICP-AES configured in axial view mode and equipped with a Cetac U-5000AT⁺ Ultrasonic Nebulizer (sample introduction). For the detection limit determination and freshwater screen trials, simultaneous measurements were made for all seven elements. For the method verification and WAF trials, simultaneous measurements were made for six of the seven elements (As, Cu, Fe, Ni, Se and V). For sulfur, a single element method was employed due to the need for higher concentration-level calibration standards. Instrumental parameters for the analysis of the seven elements are summarized in Table 1 and a method flowchart applicable to the method verification and WAF sample analyses is provided in Figure 1.

For the LOD experiment, the specific analytical method consisted of calibration of the ICP-AES system with a single multi-element standard (as specified in previous section) followed by direct multiple injection ($n = 7$) and analysis of a neat blank sample consisting of acidified reagent water (10:90 nitric acid: reagent water). The response was monitored and the overall standard deviation was calculated from the replicate injections of the blank at the specified analytical wavelength for each of these seven (As, Cu, Fe, Ni, Se, S and V) elements (Table 1).

For the matrix water screen experiment, duplicate 9-mL aliquots of well water were filtered through a 0.45 μ m filter into centrifuge tubes and brought to final volume with concentrated nitric acid. The resultant solutions were 10% in nitric acid by volume. The duplicate preparations were further diluted 20x with 10:90 nitric acid: reagent water dilution solvent. Both initial and subsequent dilution samples were submitted for ICP-AES analysis. The instrument was calibrated with a set of multi-element

standards in 10:90 HNO₃: H₂O dilution solvent (as specified in previous section) and the samples were analyzed for the seven elements of interest.

The specific method used for the analysis of the method verification and WAF samples was based upon methodology developed by Wildlife International, Ltd. The analytical method consisted of acidifying the samples 2% by volume with concentrated nitric acid and, if required, further diluting the samples in acidified freshwater (2:98 HNO₃: FW dilution solvent) into the instrumental calibration range and analyzing by ICP-AES (Figure 1).

Calibration Curve and Limits of Quantitation (LOQ)

Multi-element calibration standards (as specified previously) were analyzed with the freshwater verification and WAF sample sets. The calibration standard series for each analysis was injected at the beginning and end of each analytical run. In addition, a standard was injected following a maximum of five sample analyses. For a given injection of a sample (including standards), the ICP-AES instrument integrated the steady-state emission signal at designated emission wavelengths for a method-specified period (read time). The net integrated intensity was then automatically corrected by subtraction of the mean corrected intensity of the calibration blank (determined at sequence initiation). The measurement cycle was automatically repeated two additional times during the sample injection (read replicates). The mean of the three measurements produced a mean corrected intensity for each monitored element in the sample. Linear regression equations for each monitored element were generated using mean corrected intensities versus the respective concentrations of the element in the calibration standards. Representative calibration curves for As, Cu, Fe, Ni, Se, S and V are presented in Figures 2 through 8. The concentrations of each of the seven elements in the water samples were calculated by substituting their mean corrected intensities into the applicable linear regression equation, and applying the appropriate dilution and unit conversion factors. Representative emission spectra of low- and high-level calibration standards are presented in Figures 9 through 11.

The limit of quantitation (LOQ) for each element during the method verification trials in freshwater was set as the product of the lowest calibration standard concentration for a given element and the dilution factor of the matrix blank samples (1.02).

Reagent and Matrix Blank Samples

Concurrent with the series of matrix fortification samples, two reagent blanks and two matrix blanks for each component were analyzed to determine possible interferences. No interferences were observed at or above the LOQ during the sample analyses (Tables 2 through 8). Representative emission spectra for each element of interest in reagent blank and matrix blank samples are presented in Figures 12 through 14.

Freshwater Method Verification Samples

Freshwater was fortified at the proposed LOQ and 10x LOQ levels for each element using stock solutions containing the elements of interest in 2%(v/v) nitric acid in reagent water. The proposed LOQ level for the WAF equilibration trial was defined as the concentration of the lowest fortification sample (MAS) of the element. To verify recoveries of each element at its proposed LOQ level, it was necessary to use a lower LOQ level for the method verification trial. Therefore, as shown in Tables 2 through 8, the LOQ used in the verification trial was calculated as the product of the concentration of the lowest standard and the dilution factor for the matrix blank samples (1.02). This enabled the quantification of the LOQ to be used for the WAF equilibration trial. Tables 2 through 8 present recoveries of the elements of interest at the proposed LOQ and 10x LOQ levels. Representative emission spectra of low and high-level freshwater fortifications are presented in Figures 12 through 14.

Example Calculations

The analytical result and percent recovery for sample number 472C-105-VMAS-8 for vanadium, nominal concentration of 0.400 µg/L in freshwater, were calculated using the following equations:

$$\text{Vanadium (}\mu\text{g/L) in sample} = \frac{\text{Mean Corrected Intensity} - (\text{Y-intercept})}{\text{Slope}} \times \text{Dilution factor}$$

Mean Corrected Intensity = 80.2

Y-intercept = 1.3227

Slope = 206.85

Dilution Factor = 1.02

$$\text{Concentration of Vanadium (}\mu\text{g/L) in sample} = \frac{80.2 - 1.3227}{206.85} \times 1.02$$

$$\text{Concentration of Vanadium in sample (}\mu\text{g/L)} = 0.389$$

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$$\text{Percent of nominal concentration} = \frac{0.389 (\mu\text{g/L})}{0.400 (\mu\text{g/L})} \times 100$$

$$\text{Percent of nominal concentration} = 97.3\%$$

Preparation of Test Concentrations for the WAF Trial

Petroleum coke was mixed directly with dilution water (well water) on a weight:volume basis. A WAF was prepared at a single high concentration of 1000 mg/L in two different size Pyrex® aspirator bottles with tubulation. For the first WAF, 12.0 grams of the test substance were transferred into 12,000 mLs of dilution water contained in a 13.2 L vessel. For the second WAF, 4.00 grams of test substance were transferred into 4000 mLs of dilution water contained in a 4 L vessel. Solutions were prepared by mixing the test solutions with Teflon®-coated stir bars to create a vortex depth of approximately 30% of the test solution height. After mixing, the WAFs were allowed to settle for 30 minutes to one hour. The test solutions were sampled following approximately 24, 48, 72 and 96 hours of mixing. Samples of each test solution were taken from mid-depth of the mixing vessels using graduated pipettes. Samples were processed for analysis following the verified methodology (Tables 9 through 15).

RESULTS AND DISCUSSION

The calculated instrumental detection limits for As, Cu, Fe, Ni, Se, S and V were 2.2, 1.9, 0.013, 0.11, 20, 5.6 and 0.035 µg/L, respectively. These values corresponded to theoretical sample LOQs of 22, 19, 0.13, 1.1, 199, 56 and 0.35 µg/L, respectively. These LOQ values were calculated from the product of 10 times the instrumental detection limit and the dilution factor for matrix blank samples (1.02). The background screen of the freshwater matrix revealed an appreciable background concentration of sulfur (approximately 5 mg/L). Therefore, the target LOQ for sulfur was raised to twice the background level, or 10 mg/L. In addition, the background screen analyses provided evidence for the need to matrix-match the calibration standards to be used in the subsequent verification and WAF trials. A final factor influencing the target LOQs was potential environmental contamination from sources such as dust particles in the lab or reagent background. Two of the elements typically adversely affected from these sources are iron and nickel. Therefore, the target LOQ levels were raised to 10 µg/L for both elements. Allowing for preparation at practical concentration levels, the overall target LOQs for As, Cu, Fe, Ni, Se, S and V were set at 20.0, 20.0, 10.0, 10.0, 200, 10,000 and 0.400 µg/L, respectively. These concentrations were used as the lowest fortification levels in the WAF equilibration trial.

The results of the verification trials for the seven elements of interest at LOQ and 10x LOQ fortification levels in freshwater were all within the acceptance range. The overall mean recovery for arsenic fortified into freshwater was $104 \pm 7.68\%$ of the nominal concentration (Table 2). The overall mean recovery for copper fortified into freshwater was $95.8 \pm 8.98\%$ of the nominal concentration (Table 3). The overall mean recovery for iron fortified into freshwater was $91.4 \pm 6.99\%$ of the nominal concentration (Table 4). The overall mean recovery for nickel fortified into freshwater was $97.3 \pm 8.05\%$ of the nominal concentration (Table 5). The overall mean recovery for selenium fortified into freshwater was $93.6 \pm 9.04\%$ of the nominal concentration (Table 6). The overall mean recovery for sulfur fortified into freshwater was $97.1 \pm 8.24\%$ of the nominal concentration (Table 7). The overall mean recovery for vanadium fortified into freshwater was $98.2 \pm 8.59\%$ of the nominal concentration (Table 8).

Water accommodated fractions (WAFs) were analyzed for the presence of the six metals and sulfur after mixing for 24, 48, 72 and 96 hours. Except for a trace of iron contamination in one test vessel, no metals were detected in any WAF samples. Sulfur was not detected above the background level in the freshwater used. Representative emission spectra for a WAF sample are presented in Figures 15-17. A blank and two quality control (QC) samples were prepared and analyzed at each interval. The QC samples were quantitative for all seven elements (Tables 9-15).

CONCLUSIONS

Instrumental detection limits for six metals (As, Cu, Fe, Ni, Se, V) and sulfur were established using Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). Freshwater matrix was screened for the seven elements. From these analyses, theoretical LOQs were established for each element based on the instrumental limits, matrix background level and/or environmental contamination.

Method verification samples containing the six metals and sulfur were fortified in freshwater at the LOQ and 10x LOQ levels. Samples were acidified and either further diluted in acidified freshwater or analyzed directly against metal and sulfur external standards also prepared in freshwater. Recovery samples and standards were analyzed by ICP-AES. The ICP system was configured for axial plasma viewing and ultrasonic nebulization sample introduction. The emission wavelengths selected to quantify As, Cu, Fe, Ni, Se, S and V were 188.979, 224.700, 239.562, 231.604, 196.026, 180.669 and 292.402 nm, respectively. Each element was quantified against external standards via linear regression analysis. Recoveries of each of the elements from freshwater are presented in Tables 2-8. Linear regression

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analyses of each of the seven elements are presented in Figures 2-8. All elements were shown to recover quantitatively at the LOQ and 10x LOQ levels.

Water accommodated fractions (WAFs) were analyzed for the presence of the six metals and sulfur after mixing for 24, 48, 72 and 96 hours. Except for a trace of iron contamination in one test vessel, no metals were detected in any WAF samples. Sulfur was not detected above the background level in the freshwater used.

REFERENCES

- 1 **European Commission.** 2002. *Residues: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, Section 4) and Annex III (Part A, Section 5) of Directive 91/414.* SANCO/3029/99 rev. 4, 11/07/00.

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Table 1

Typical ICP-AES Operational Parameters for the Analysis of
As, Cu, Fe, Ni, Se, S and V in Freshwater

Instrument:	Perkin-Elmer Optima 3000 DV Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)	
Sample Introduction System:	Cetac U-5000AT ⁺ Ultrasonic Nebulizer	
Analytical Wavelengths:	As	188.979 nm
:	Cu	224.700 nm
	Fe	239.562 nm
	Ni	231.604 nm
	Se	196.026 nm
	S	180.669 nm
	V	292.402 nm
Plasma:	Plasma Gas Flow:	15 L/min Ar
	Auxiliary Gas Flow:	0.5 L/min Ar
	Nebulizer Gas Flow:	0.7 L/min Ar
	RF Power:	1300 W
Pump:	Sample Flow Rate:	2.00 mL/min
	Sample Flush Time:	15 sec
	Wash Rate:	2.00 mL/min
	Wash Time:	60 sec
	Wash Frequency:	Between Samples
Spectrometer: View	Mode:	Axial
	Read Delay:	60 sec
	Read Time:	Min: 10.000 sec Max: 20.000 sec
	Read Replicates:	3
	Peak Algorithm:	Peak Area
	Points/Peak:	3
	Background Correction:	2-Point

Table 2

Method Verification Recoveries of Arsenic in Freshwater Analyzed by ICP-AES

Number (472C-105-)	Sample		Concentration (µg/L)		Percent Recovery ²	Mean Measured ¹ (µg/L)	Mean % Recovery Std. Dev. RSD(%)
	Type		Fortified	Measured ^{1,2}			
VREB-3	Reagent Blank		0.0	< LOQ	--	--	--
VREB-4	Reagent Blank		0.0	< LOQ	--		
VMAB-3	Matrix Blank	0.0		< LOQ	--	--	--
VMAB-4	Matrix Blank		0.0	< LOQ	--		
VMAS-6	Matrix Fortification	20.0		19.5	97.7	19.8	Mean = 99.2 Std. Dev. = 1.96 RSD = 1.97%
VMAS-7	Matrix Fortification		20.0	20.4	102		
VMAS-8	Matrix Fortification		20.0	19.9	99.4		
VMAS-9	Matrix Fortification		20.0	19.4	97.0		
VMAS-10	Matrix Fortification		20.0	20.0	99.8		
VMAS-16	Matrix Fortification		200	211	106	216	Mean = 108 Std. Dev. = 8.96 RSD = 8.30%
VMAS-17	Matrix Fortification		200	187	93.7		
VMAS-18	Matrix Fortification		200	221	110		
VMAS-19	Matrix Fortification		200	228	114		
VMAS-20	Matrix Fortification		200	233	116		
Mean =					104		
Std. Dev. =					7.68		
RSD (%) =					7.41%		
N =					10		

¹ The limit of quantitation (LOQ) was 10.2 µg/L, calculated as the product of the concentration of the lowest standard (10.0 µg/L) and the dilution factor of the matrix blanks (1.02).

² Results were generated using Excel 2000 in the full precision mode. Manual calculations may differ slightly.

Table 3

Method Verification Recoveries of Copper in Freshwater Analyzed by ICP-AES

Sample		Concentration (µg/L)		Percent Recovery ²	Mean Measured ¹ (µg/L)	Mean % Recovery Std. Dev. RSD(%)
Number (472C-105-)	Type	Fortified	Measured ^{1,2}			
VREB-3	Reagent Blank	0.0	< LOQ	--	--	--
VREB-4	Reagent Blank	0.0	< LOQ	--	--	--
VMAB-3	Matrix Blank	0.0	< LOQ	--	--	--
VMAB-4	Matrix Blank	0.0	< LOQ	--	--	--
VMAS-6	Matrix Fortification	20.0	20.6	103	18.2	Mean = 90.8 Std. Dev. = 7.27 RSD = 8.01%
VMAS-7	Matrix Fortification	20.0	18.0	90.0		
VMAS-8	Matrix Fortification	20.0	17.7	88.7		
VMAS-9	Matrix Fortification	20.0	16.9	84.3		
VMAS-10	Matrix Fortification	20.0	17.6	87.8		
VMAS-16	Matrix Fortification	200	186	93.2	202	Mean = 101 Std. Dev. = 8.14 RSD = 8.08%
VMAS-17	Matrix Fortification	200	182	91.0		
VMAS-18	Matrix Fortification	200	208	104		
VMAS-19	Matrix Fortification	200	215	108		
VMAS-20	Matrix Fortification	200	216	108		
Mean =				95.8		
Std. Dev.=				8.98		
RSD (%) =				9.37%		
N =				10		

¹ The limit of quantitation (LOQ) was 10.2 µg/L, calculated as the product of the concentration of the lowest standard (10.0 µg/L) and the dilution factor of the matrix blanks (1.02).

² Results were generated using Excel 2000 in the full precision mode. Manual calculations may differ slightly.

Table 4

Method Verification Recoveries of Iron in Freshwater Analyzed by ICP-AES

Number (472C-105-)	Sample Type	Concentration (µg/L)		Percent Recovery ²	Mean Measured ¹ (µg/L)	Mean % Recovery Std. Dev. RSD(%)
		Fortified	Measured ^{1,2}			
VREB-3	Reagent Blank	0.0	< LOQ	--	--	--
VREB-4	Reagent Blank	0.0	< LOQ	--	--	--
VMAB-3	Matrix Blank	0.0	< LOQ	--	--	--
VMAB-4	Matrix Blank	0.0	< LOQ	--	--	--
VMAS-6	Matrix Fortification	10.0	9.08	90.8	8.72	Mean = 87.2 Std. Dev. = 3.52 RSD = 4.03%
VMAS-7	Matrix Fortification	10.0	9.01	90.1		
VMAS-8	Matrix Fortification	10.0	8.76	87.6		
VMAS-9	Matrix Fortification	10.0	8.22	82.2		
VMAS-10	Matrix Fortification	10.0	8.53	85.3		
VMAS-16	Matrix Fortification	100	87.1	87.1	95.7	Mean = 95.7 Std. Dev. = 7.26 RSD = 7.59%
VMAS-17	Matrix Fortification	100	89.2	89.2		
VMAS-18	Matrix Fortification	100	97.2	97.2		
VMAS-19	Matrix Fortification	100	102	102		
VMAS-20	Matrix Fortification	100	103	103		
Mean =				91.4		
Std. Dev.=				6.99		
RSD (%) =				7.65%		
N =				10		

¹ The limit of quantitation (LOQ) was 5.10 µg/L, calculated as the product of the concentration of the lowest standard (5.00 µg/L) and the dilution factor of the matrix blanks (1.02).

² Results were generated using Excel 2000 in the full precision mode. Manual calculations may differ slightly.

Table 5

Method Verification Recoveries of Nickel in Freshwater Analyzed by ICP-AES

Sample		Concentration (µg/L)		Percent Recovery ²	Mean Measured ¹ (µg/L)	Mean % Recovery Std. Dev. RSD(%)
Number (472C-105-)	Type	Fortified	Measured ^{1,2}			
VREB-3	Reagent Blank	0.0	< LOQ	--	--	--
VREB-4	Reagent Blank	0.0	< LOQ	--	--	--
VMAB-3	Matrix Blank	0.0	< LOQ	--	--	--
VMAB-4	Matrix Blank	0.0	< LOQ	--	--	--
VMAS-6	Matrix Fortification	10.0	9.18	91.8	9.16	Mean = 91.6
VMAS-7	Matrix Fortification	10.0	9.40	94.0		Std. Dev. = 2.39
VMAS-8	Matrix Fortification	10.0	9.34	93.4		RSD = 2.61%
VMAS-9	Matrix Fortification	10.0	8.79	87.9		
VMAS-10	Matrix Fortification	10.0	9.11	91.1		
VMAS-16	Matrix Fortification	100	94.2	94.2	103	Mean = 103
VMAS-17	Matrix Fortification	100	95.1	95.1		Std. Dev. = 7.82
VMAS-18	Matrix Fortification	100	105	105		RSD = 7.60%
VMAS-19	Matrix Fortification	100	109	109		
VMAS-20	Matrix Fortification	100	111	111		
Mean =				97.3		
Std. Dev.=				8.05		
RSD (%) =				8.28%		
N =				10		

¹ The limit of quantitation (LOQ) was 5.10 µg/L, calculated as the product of the concentration of the lowest standard (5.00 µg/L) and the dilution factor of the matrix blanks (1.02).

² Results were generated using Excel 2000 in the full precision mode. Manual calculations may differ slightly.

Table 6

Method Verification Recoveries of Selenium in Freshwater Analyzed by ICP-AES

Sample		Concentration (µg/L)		Percent Recovery ²	Mean Measured ¹ (µg/L)	Mean % Recovery Std. Dev. RSD(%)
Number (472C-105-)	Type	Fortified	Measured ^{1,2}			
VREB-3	Reagent Blank	0.0	< LOQ	--	--	--
VREB-4	Reagent Blank	0.0	< LOQ	--	--	--
VMAB-3	Matrix Blank	0.0	< LOQ	--	--	--
VMAB-4	Matrix Blank	0.0	< LOQ	--	--	--
VMAS-6	Matrix Fortification	200	167	83.4	174	Mean = 86.9 Std. Dev. = 4.47 RSD = 5.15%
VMAS-7	Matrix Fortification	200	178	89.0		
VMAS-8	Matrix Fortification	200	186	93.2		
VMAS-9	Matrix Fortification	200	164	82.0		
VMAS-10	Matrix Fortification	200	174	86.8		
VMAS-16	Matrix Fortification	2000	1857	92.9	2005	Mean = 100 Std. Dev. = 7.18 RSD = 7.16%
VMAS-17	Matrix Fortification	2000	1842	92.1		
VMAS-18	Matrix Fortification	2000	2084	104		
VMAS-19	Matrix Fortification	2000	2107	105		
VMAS-20	Matrix Fortification	2000	2137	107		
Mean =				93.6		
Std. Dev.=				9.04		
RSD (%) =				9.66%		
N =				10		

¹ The limit of quantitation (LOQ) was 102 µg/L, calculated as the product of the concentration of the lowest standard (100 µg/L) and the dilution factor of the matrix blanks (1.02).

² Results were generated using Excel 2000 in the full precision mode. Manual calculations may differ slightly.

Table 7

Method Verification Recoveries of Sulfur in Freshwater Analyzed by ICP-AES

Sample Concentration		(mg/L)		Percent Recovery ²	Mean Measured ¹ (mg/L)	Mean % Recovery Std. Dev. RSD(%)
Number (472C-105-)	Type	Fortified	Measured ^{1,2}			
VREB-3	Reagent Blank	0.0	< LOQ	--	--	--
VREB-4	Reagent Blank	0.0	< LOQ	--	--	--
VMAB-3	Matrix Blank	0.0	< LOQ	--	--	--
VMAB-4	Matrix Blank	0.0	< LOQ	--	--	--
VMAS-21	Matrix Fortification	10.0	8.74	87.4	9.04	Mean = 90.4 Std. Dev. = 2.91 RSD = 3.22%
VMAS-22	Matrix Fortification	10.0	8.85	88.5		
VMAS-23	Matrix Fortification	10.0	8.91	89.1		
VMAS-24	Matrix Fortification	10.0	9.32	93.2		
VMAS-25	Matrix Fortification	10.0	9.38	93.8		
VMAS-26	Matrix Fortification	100	103	103	104	Mean = 104 Std. Dev. = 5.53 RSD = 5.33%
VMAS-27	Matrix Fortification	100	100	100		
VMAS-28	Matrix Fortification	100	109	109		
VMAS-29	Matrix Fortification	100	110	110		
VMAS-30	Matrix Fortification	100	97.1	97.1		
Mean =				97.1		
Std. Dev.=				8.24		
RSD (%) =				8.48%		
N =				10		

¹ The limit of quantitation (LOQ) was 5.10 mg/L, calculated as the product of the concentration of the lowest standard (5.00 mg/L) and the dilution factor of the matrix blanks (1.02).

² Results were generated using Excel 2000 in the full precision mode. Manual calculations may differ slightly.

Table 8

Method Verification Recoveries of Vanadium in Freshwater Analyzed by ICP-AES

Sample		Concentration (µg/L)		Percent Recovery ²	Mean Measured ¹ (µg/L)	Mean % Recovery Std. Dev. RSD(%)
Number (472C-105-)	Type	Fortified	Measured ^{1,2}			
VREB-3	Reagent Blank	0.0	< LOQ	--	--	--
VREB-4	Reagent Blank	0.0	< LOQ	--	--	--
VMAB-3	Matrix Blank	0.0	< LOQ	--	--	--
VMAB-4	Matrix Blank	0.0	< LOQ	--	--	--
VMAS-6	Matrix Fortification	0.400	0.362	90.5	0.371	Mean = 92.7 Std. Dev. = 5.70 RSD = 6.15%
VMAS-7	Matrix Fortification	0.400	0.390	97.4		
VMAS-8	Matrix Fortification	0.400	0.389	97.3		
VMAS-9	Matrix Fortification	0.400	0.378	94.6		
VMAS-10	Matrix Fortification	0.400	0.335	83.8		
VMAS-16	Matrix Fortification	4.00	3.73	93.2	4.15	Mean = 104 Std. Dev. = 7.66 RSD = 7.39%
VMAS-17	Matrix Fortification	4.00	3.92	97.9		
VMAS-18	Matrix Fortification	4.00	4.30	108		
VMAS-19	Matrix Fortification	4.00	4.35	109		
VMAS-20	Matrix Fortification	4.00	4.44	111		
				Mean =	98.2	
				Std. Dev. =	8.59	
				RSD (%) =	8.75%	
				N =	10	

¹ The limit of quantitation (LOQ) was 0.204 µg/L, calculated as the product of the concentration of the lowest standard (0.200 µg/L) and the dilution factor of the matrix blanks (1.02).

² Results were generated using Excel 2000 in the full precision mode. Manual calculations may differ slightly.

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Table 9

Matrix Blanks, Matrix Fortifications and Measured Concentrations of Arsenic in Samples Collected from a Water Accommodated Fraction (WAF) Equilibration Trial Analyzed by ICP-AES

Nominal Concentration (µg/L)	Sample Identification (472C-105-)	Sampling Interval (Hour)	Measured Concentration (µg/L) ¹	Percent of Nominal ¹
0.0	MAB-1	24	< 20.0	--
	MAB-2	48	< 20.0	--
	MAB-3	72	< 20.0	--
	MAB-4	96	< 20.0	--
20.0	MAS-1	24	23.8	119
	MAS-3	48	23.4	117
	MAS-5	72	23.4	117
	MAS-7	96	25.2	126
200	MAS-2	24	203	102
	MAS-4	48	198	98.9
	MAS-6	72	193	96.3
	MAS-8	96	214	107
1000000 ²	WAF-1 ³	24	< 20.0 ⁵	--
	WAF-2 ⁴	24	< 20.0	--
	WAF-3 ³	48	< 20.0	--
	WAF-4 ⁴	48	< 20.0	--
	WAF-5 ³	72	< 20.0	--
	WAF-6 ⁴	72	< 20.0	--
	WAF-7 ³	96	< 20.0	--
	WAF-8 ⁴	96	< 20.0	--

¹ Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

² Nominal petroleum coke test substance concentration.

³ Samples from a 13.2-L WAF bottle.

⁴ Samples from a 4-L WAF bottle.

⁵ All WAF sample results are the mean of duplicate analyses.

Table 10

Matrix Blanks, Matrix Fortifications and Measured Concentrations of Copper in Samples Collected from a Water Accommodated Fraction (WAF) Equilibration Trial Analyzed by ICP-AES

Nominal Concentration (µg/L)	Sample Identification (472C-105-)	Sampling Interval (Hour)	Measured Concentration (µg/L) ¹	Percent of Nominal ¹
0.0	MAB-1	24	< 20.0	--
	MAB-2	48	< 20.0	--
	MAB-3	72	< 20.0	--
	MAB-4	96	< 20.0	--
20	MAS-1	24	17.6 ⁵	88.1
	MAS-3	48	19.4	96.8
	MAS-5	72	18.6	93.1
	MAS-7	96	19.5	97.5
200	MAS-2	24	172	86.1
	MAS-4	48	182	91.1
	MAS-6	72	170	85.2
	MAS-8	96	188	93.9
1000000 ²	WAF-1 ³	24	< 20.0 ⁶	--
	WAF-2 ⁴	24	< 20.0	--
	WAF-3 ³	48	< 20.0	--
	WAF-4 ⁴	48	< 20.0	--
	WAF-5 ³	72	< 20.0	--
	WAF-6 ⁴	72	< 20.0	--
	WAF-7 ³	96	< 20.0	--
	WAF-8 ⁴	96	< 20.0	--

¹ Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

² Nominal petroleum coke test substance concentration.

³ Samples from a 13.2-L WAF bottle.

⁴ Samples from a 4-L WAF bottle.

⁵ Measured values greater than one-half the limit of quantitation (LOQ) in LOQ-level fortifications are reported.

⁶ All WAF sample results are the mean of duplicate analyses.

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Table 11

Matrix Blanks, Matrix Fortifications and Measured Concentrations of Iron in
Samples Collected from a Water Accommodated Fraction (WAF) Equilibration Trial
Analyzed by ICP-AES

Nominal Concentration (µg/L)	Sample Identification (472C-105-)	Sampling Interval (Hour)	Measured Concentration (µg/L) ¹	Percent of Nominal ¹
0.0	MAB-1	24	< 10.0	--
	MAB-2	48	< 10.0	--
	MAB-3	72	< 10.0	--
	MAB-4	96	< 10.0	--
10.0	MAS-1	24	9.69 ⁵	96.9
	MAS-3	48	10.2	102
	MAS-5	72	9.24	92.4
	MAS-7	96	10.1	101
100	MAS-2	24	89.1	89.1
	MAS-4	48	93.3	93.3
	MAS-6	72	84.0	84.0
	MAS-8	96	96.6	96.6
1000000 ²	WAF-1 ³	24	< 10.0 ⁶	--
	WAF-2 ⁴	24	< 10.0	--
	WAF-3 ³	48	< 10.0	--
	WAF-4 ⁴	48	11.3	--
	WAF-5 ³	72	< 10.0	--
	WAF-6 ⁴	72	-- ⁷	--
	WAF-7 ³	96	< 10.0	--
	WAF-8 ⁴	96	14.5	--

¹ Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

² Nominal petroleum coke test substance concentration.

³ Samples from a 13.2-L WAF bottle.

⁴ Samples from a 4-L WAF bottle.

⁵ Measured values greater than one-half the limit of quantitation (LOQ) in LOQ-level fortifications are reported.

⁶ All WAF sample results are the mean of duplicate analyses.

⁷ The measured value for the first replicate was <10.0 µg/L and was 11.5 µg/L for the second replicate.

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Table 12

Matrix Blanks, Matrix Fortifications and Measured Concentrations of Nickel in Samples Collected from a Water Accommodated Fraction (WAF) Equilibration Trial Analyzed by ICP-AES

Nominal Concentration (µg/L)	Sample Identification (472C-105-)	Sampling Interval (Hour)	Measured Concentration (µg/L) ¹	Percent of Nominal ¹
0.0	MAB-1	24	< 10.0	--
	MAB-2	48	< 10.0	--
	MAB-3	72	< 10.0	--
	MAB-4	96	< 10.0	--
10.0	MAS-1	24	9.01 ⁵	90.1
	MAS-3	48	9.96	99.6
	MAS-5	72	9.65	96.5
	MAS-7	96	9.93	99.3
100	MAS-2	24	86.4	86.4
	MAS-4	48	91.4	91.4
	MAS-6	72	85.1	85.1
	MAS-8	96	94.8	94.8
1000000 ²	WAF-1 ³	24	< 10.0 ⁶	--
	WAF-2 ⁴	24	< 10.0	--
	WAF-3 ³	48	< 10.0	--
	WAF-4 ⁴	48	< 10.0	--
	WAF-5 ³	72	< 10.0	--
	WAF-6 ⁴	72	< 10.0	--
	WAF-7 ³	96	< 10.0	--
	WAF-8 ⁴	96	< 10.0	--

¹ Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

² Nominal petroleum coke test substance concentration.

³ Samples from a 13.2-L WAF bottle.

⁴ Samples from a 4-L WAF bottle.

⁵ Measured values greater than one-half the limit of quantitation (LOQ) in LOQ-level fortifications are reported.

⁶ All WAF sample results are the mean of duplicate analyses.

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Table 13

Matrix Blanks, Matrix Fortifications and Measured Concentrations of Selenium in Samples Collected from a Water Accommodated Fraction (WAF) Equilibration Trial Analyzed by ICP-AES

Nominal Concentration (µg/L)	Sample Identification (472C-105-)	Sampling Interval (Hour)	Measured Concentration (µg/L) ¹	Percent of Nominal ¹
0.0	MAB-1	24	< 200	--
	MAB-2	48	< 200	--
	MAB-3	72	< 200	--
	MAB-4	96	< 200	--
200	MAS-1	24	166 ⁵	83.0
	MAS-3	48	185	92.6
	MAS-5	72	175	87.7
	MAS-7	96	180	89.8
2000	MAS-2	24	1656	82.8
	MAS-4	48	1801	90.1
	MAS-6	72	1742	87.1
	MAS-8	96	1974	98.7
1000000 ²	WAF-1 ³	24	< 200 ⁶	--
	WAF-2 ⁴	24	< 200	--
	WAF-3 ³	48	< 200	--
	WAF-4 ⁴	48	< 200	--
	WAF-5 ³	72	< 200	--
	WAF-6 ⁴	72	< 200	--
	WAF-7 ³	96	< 200	--
	WAF-8 ⁴	96	< 200	--

¹ Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

² Nominal petroleum coke test substance concentration.

³ Samples from a 13.2-L WAF bottle.

⁴ Samples from a 4-L WAF bottle.

⁵ Measured values greater than one-half the limit of quantitation (LOQ) in LOQ-level fortifications are reported.

⁶ All WAF sample results are the mean of duplicate analyses.

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Table 14

Matrix Blanks, Matrix Fortifications and Measured Concentrations of Sulfur in
Samples Collected from a Water Accommodated Fraction (WAF) Equilibration Trial
Analyzed by ICP-AES

Nominal Concentration (mg/L)	Sample Identification (472C-105-)	Sampling Interval (Hour)	Measured Concentration (mg/L) ¹	Percent of Nominal ¹
0.0	MAB-1	24	< 10.0	--
	MAB-2	48	< 10.0	--
	MAB-3	72	< 10.0	--
	MAB-4	96	< 10.0	--
10.0	MAS-1	24	9.61 ⁵	96.1
	MAS-3	48	9.27	92.7
	MAS-5	72	10.1	101
	MAS-7	96	9.64	96.4
100	MAS-2	24	88.2	88.2
	MAS-4	48	99.6	99.6
	MAS-6	72	98.7	98.7
	MAS-8	96	96.1	96.1
1000 ²	WAF-1 ³	24	< 10.0 ⁶	--
	WAF-2 ⁴	24	< 10.0	--
	WAF-3 ³	48	< 10.0	--
	WAF-4 ⁴	48	< 10.0	--
	WAF-5 ³	72	< 10.0	--
	WAF-6 ⁴	72	< 10.0	--
	WAF-7 ³	96	< 10.0	--
	WAF-8 ⁴	96	< 10.0	--

¹ Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

² Nominal petroleum coke test substance concentration.

³ Samples from a 13.2-L WAF bottle.

⁴ Samples from a 4-L WAF bottle.

⁵ Measured values greater than one-half the limit of quantitation (LOQ) in LOQ-level fortifications are reported.

⁶ All WAF sample results are the mean of duplicate analyses.

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Table 15

Matrix Blanks, Matrix Fortifications and Measured Concentrations of Vanadium in Samples Collected from a Water Accommodated Fraction (WAF) Equilibration Trial Analyzed by ICP-AES

Nominal Concentration (µg/L)	Sample Identification (472C-105-)	Sampling Interval (Hour)	Measured Concentration (µg/L) ¹	Percent of Nominal ¹
0.0	MAB-1	24	< 0.400	--
	MAB-2	48	< 0.400	--
	MAB-3	72	< 0.400	--
	MAB-4	96	< 0.400	--
0.400	MAS-1	24	0.380 ⁵	94.9
	MAS-3	48	0.388	97.1
	MAS-5	72	0.389	97.1
	MAS-7	96	0.390	97.5
4.00	MAS-2	24	3.48	86.9
	MAS-4	48	3.65	91.2
	MAS-6	72	3.50	87.4
	MAS-8	96	3.89	97.3
1000000 ²	WAF-1 ³	24	< 0.400 ⁶	--
	WAF-2 ⁴	24	< 0.400	--
	WAF-3 ³	48	< 0.400	--
	WAF-4 ⁴	48	< 0.400	--
	WAF-5 ³	72	< 0.400	--
	WAF-6 ⁴	72	< 0.400	--
	WAF-7 ³	96	< 0.400	--
	WAF-8 ⁴	96	< 0.400	--

¹ Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

² Nominal petroleum coke test substance concentration.

³ Samples from a 13.2-L WAF bottle.

⁴ Samples from a 4-L WAF bottle.

⁵ Measured values greater than one-half the limit of quantitation (LOQ) in LOQ-level fortifications are reported.

⁶ All WAF sample results are the mean of duplicate analyses.

**METHOD OUTLINE FOR THE DETERMINATION OF
As, Cu, Fe, Ni, Se, S and V IN FRESHWATER**

Rinse all glassware with 2% (v/v) nitric acid in reagent water solution.



Prepare quality control (QC) samples at each sampling interval as follows: Prepare matrix fortification samples by spiking the requisite volume(s) of the appropriate combined and/or individual element stock solution(s) directly into freshwater. Perform fortifications with calibrated micropipetors and graduated plastic centrifuge tubes. Bring to final volume with freshwater. The matrix blank consists of unfortified freshwater.



Partially fill a 15-mL plastic centrifuge tube with each sample. Using a calibrated micropipetor, fortify each QC and test sample with 200 μ L of concentrated nitric acid. Bring to final volume with the sample. Cap the centrifuge tubes and mix well with several repeat inversions. For samples not requiring further dilution into the calibration range of the ICP-AES methodology, submit for analysis.



For those samples requiring dilution into the calibration range of the ICP-AES methodology, perform dilutions using graduated plastic centrifuge tubes, calibrated micropipetor(s), and 2% (v/v) nitric acid in freshwater solution. Mix dilutions well and transfer into separate, labeled, 15-mL plastic centrifuge tubes. Submit for ICP-AES analysis.

Figure 1. Analytical method flowchart for the analysis of As, Cu, Fe, Ni, Se, S and V in freshwater analyzed by ICP-AES.

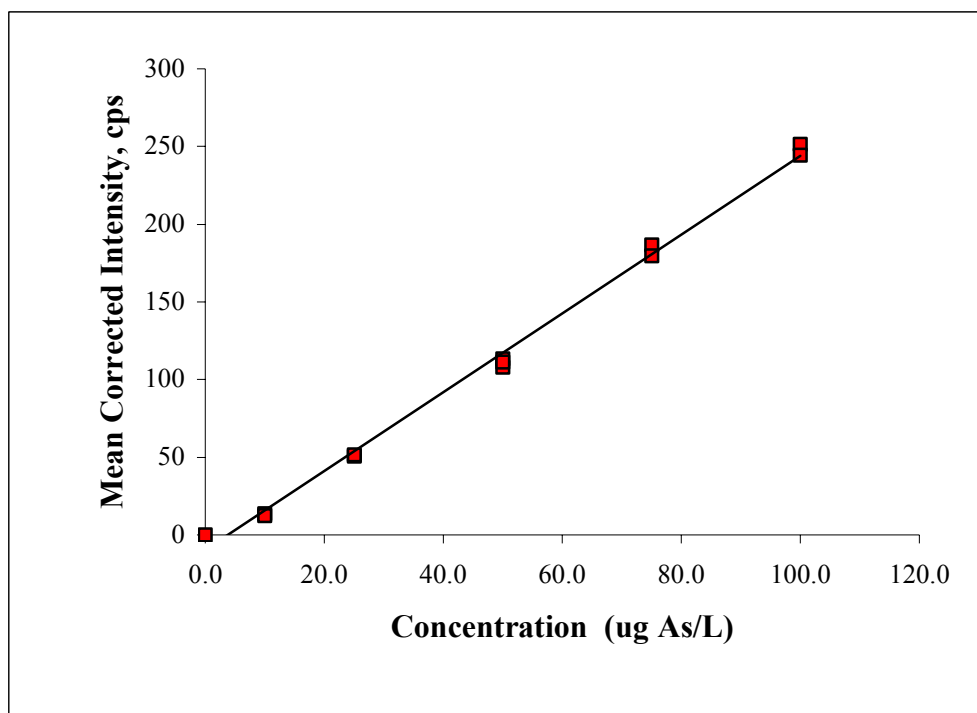


Figure 2. Representative calibration curve for arsenic analyzed by ICP-AES.
Slope = 2.5366; Intercept = -9.6221, $R^2 = 0.9958$.

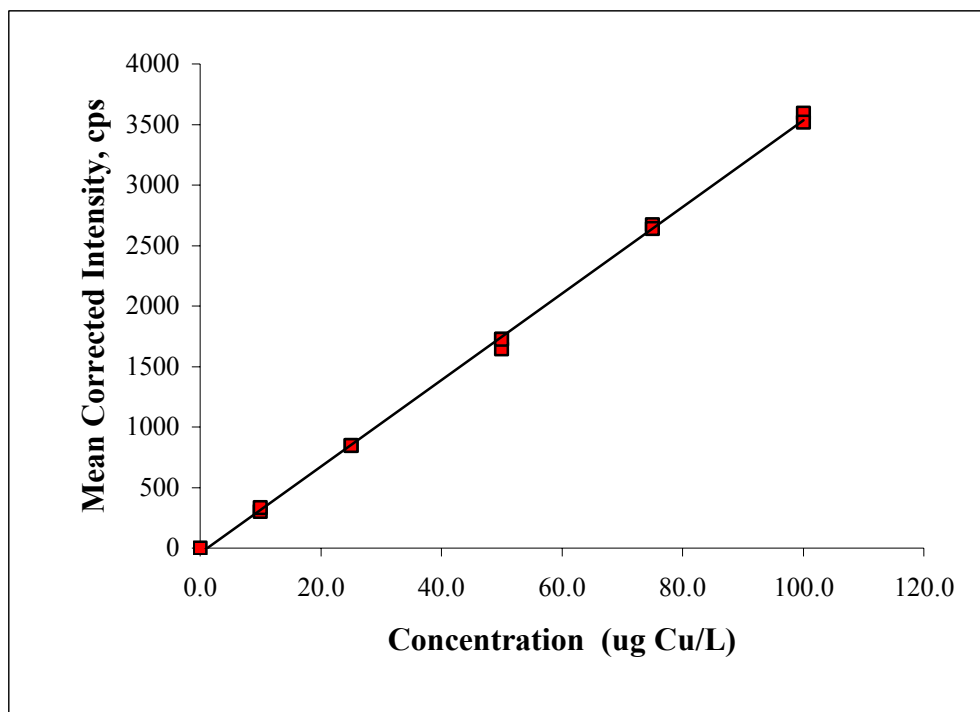


Figure 3. Representative calibration curve for copper analyzed by ICP-AES.
Slope = 35.749; Intercept = -41.605; $R^2 = 0.9991$.

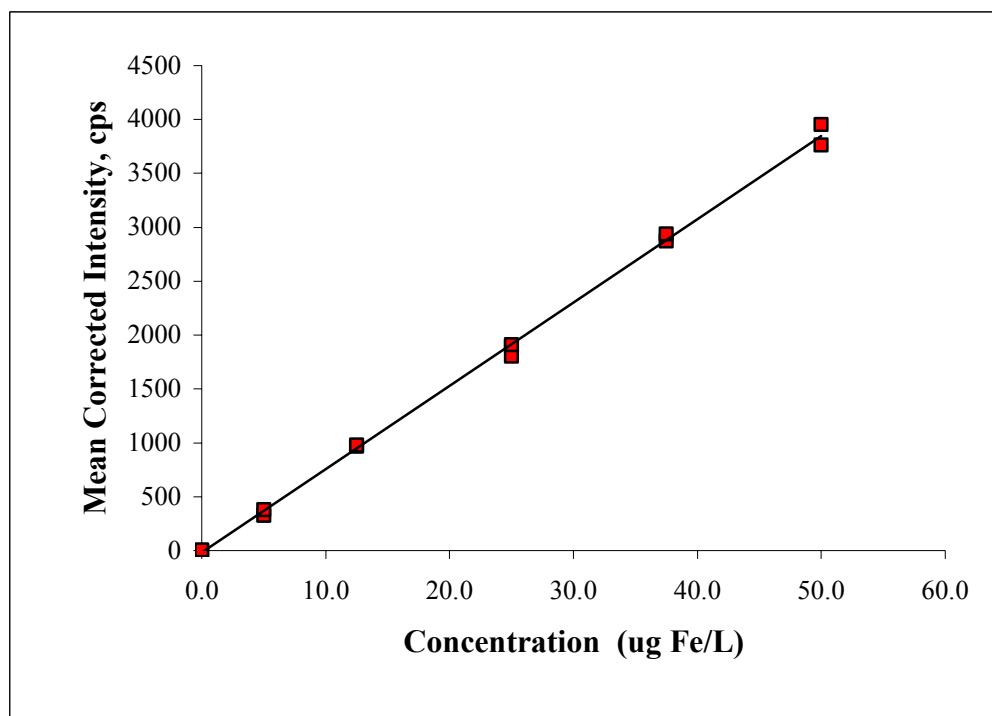


Figure 4. Representative calibration curve for iron analyzed by ICP-AES.
Slope = 77.377; Intercept = -19.151; $R^2 = 0.9983$.

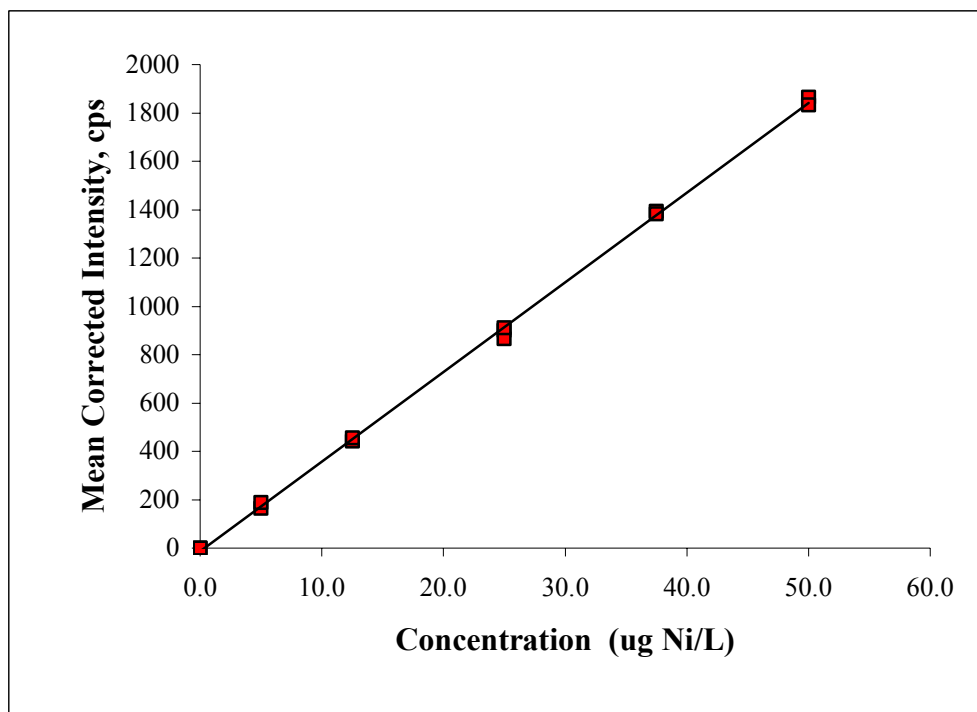


Figure 5. Representative calibration curve for nickel analyzed by ICP-AES. Slope = 37.044; Intercept = -11.989; $R^2 = 0.9992$.

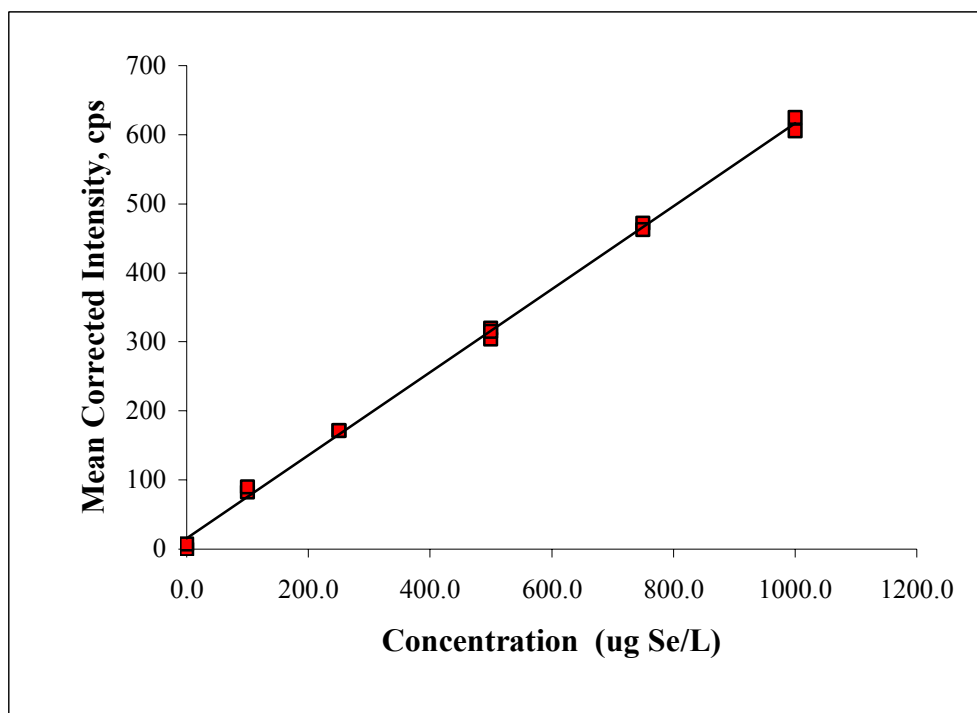


Figure 6. Representative calibration curve for selenium analyzed by ICP-AES.
Slope = 0.60112; Intercept = 15.386; $R^2 = 0.9982$.

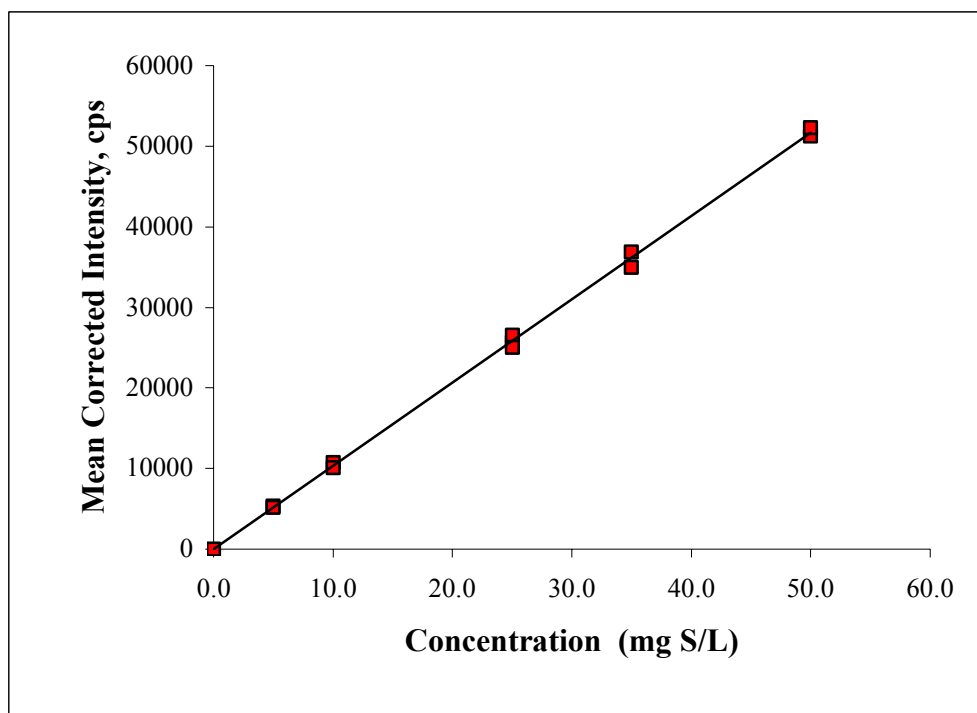


Figure 7. Representative calibration curve for sulfur analyzed by ICP-AES.
Slope = 1033.4; Intercept = -35.262; $R^2 = 0.9990$.

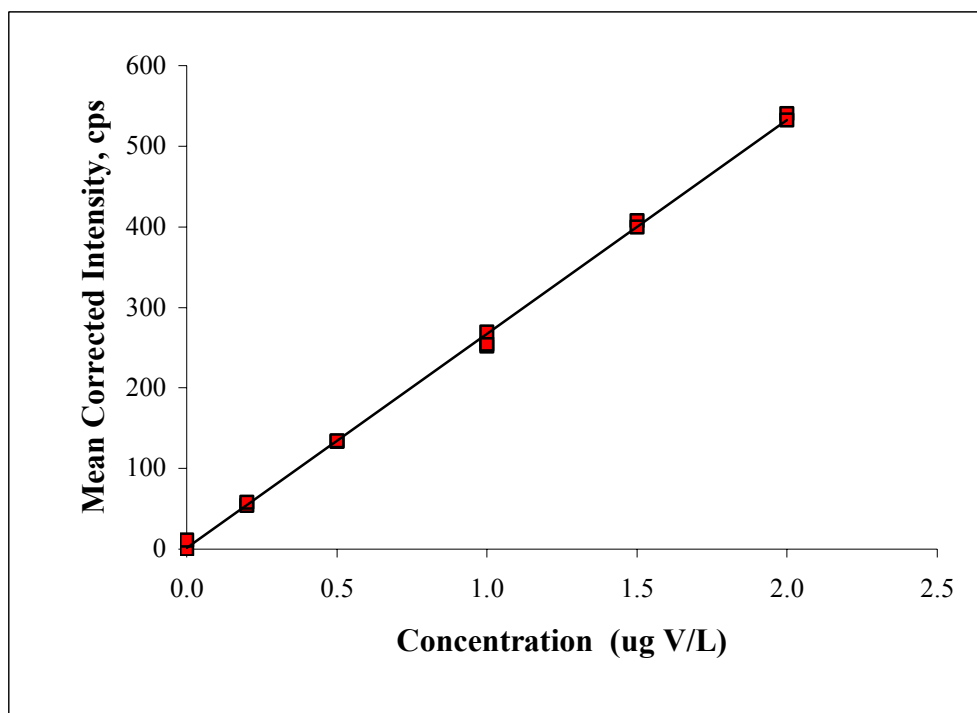


Figure 8. Representative calibration curve for vanadium analyzed by ICP-AES.
Slope = 265.72; Intercept = 1.4112; $R^2 = 0.9986$.

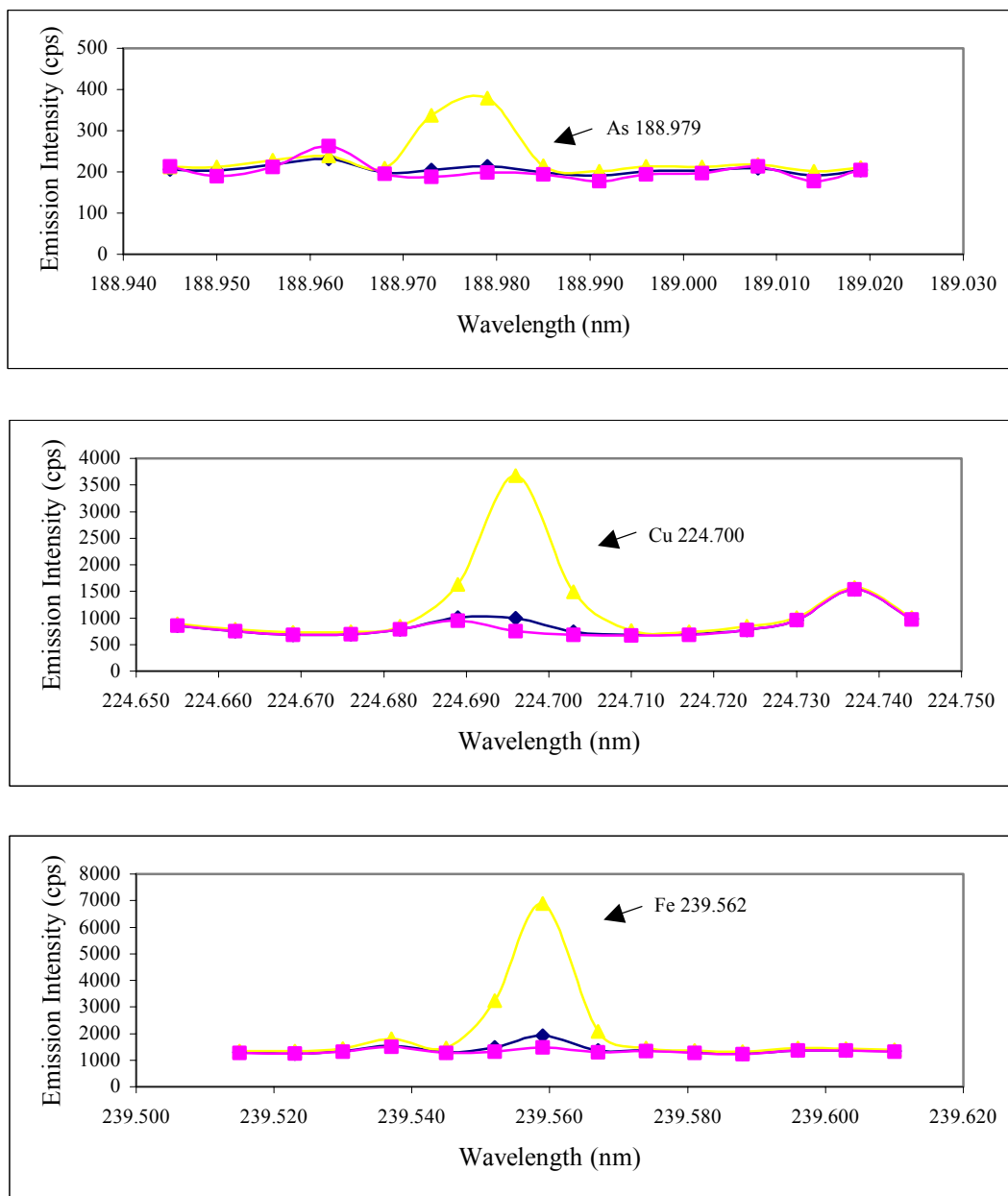


Figure 9. Representative emission spectra for arsenic (top), copper (middle) and iron (bottom) in low- and high-level calibration standards prepared in freshwater and analyzed by ICP-AES.

Squares = freshwater matrix blank (I.D.: 472C-105-MAB-3); Diamonds = low-level standard (I.D.: 472C-105-VALCAL-11); Triangles = high-level standard (I.D.: 472C-105-VALCAL-15). Nominal concentrations for As, Cu and Fe = 10.0, 10.0 and 5.00 µg/L and 100, 100 and 50.0 µg/L, in the low- and high-level standards, respectively.

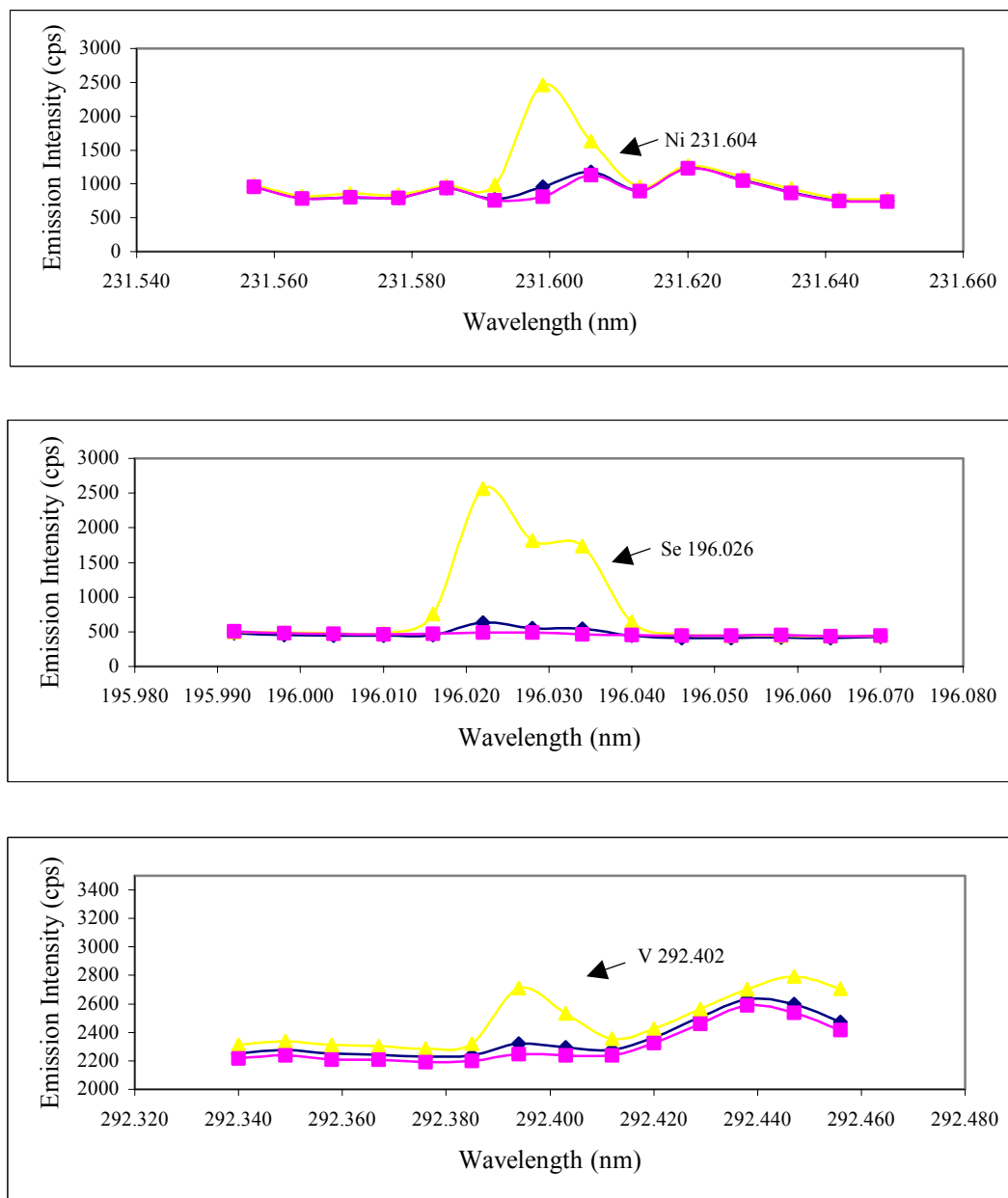


Figure 10. Representative emission spectra for nickel (top), selenium(middle) and vanadium(bottom) in low- and high-level calibration standards prepared in freshwater and analyzed by ICP-AES.

Squares = freshwater matrix blank (I.D.: 472C-105-MAB-3); Diamonds = low-level standard (I.D.: 472C-105-VALCAL-11); Triangles = high-level standard (I.D.: 472C-105-VALCAL-15). Nominal concentrations for Ni, Se and V = 5.00, 100 and 0.200 µg/L and 50.0, 1000 and 2.00 µg/L, in the low- and high-level standards, respectively.

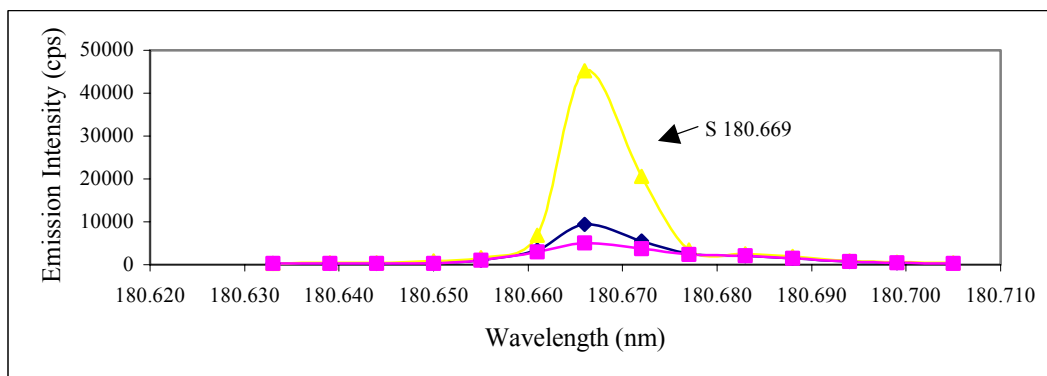


Figure 11 Representative emission spectra for sulfur in low- and high-level calibration standards prepared in freshwater and analyzed by ICP-AES.

Squares = freshwater matrix blank (I.D.: 472C-105-MAB-S-3); Diamonds = low-level standard (I.D.: 472C-105-S-6); Triangles = high-level standard (I.D.: 472C-105-S-10). Nominal concentrations for S = 5.00 and 50.0 mg/L in the low- and high-level standards, respectively.

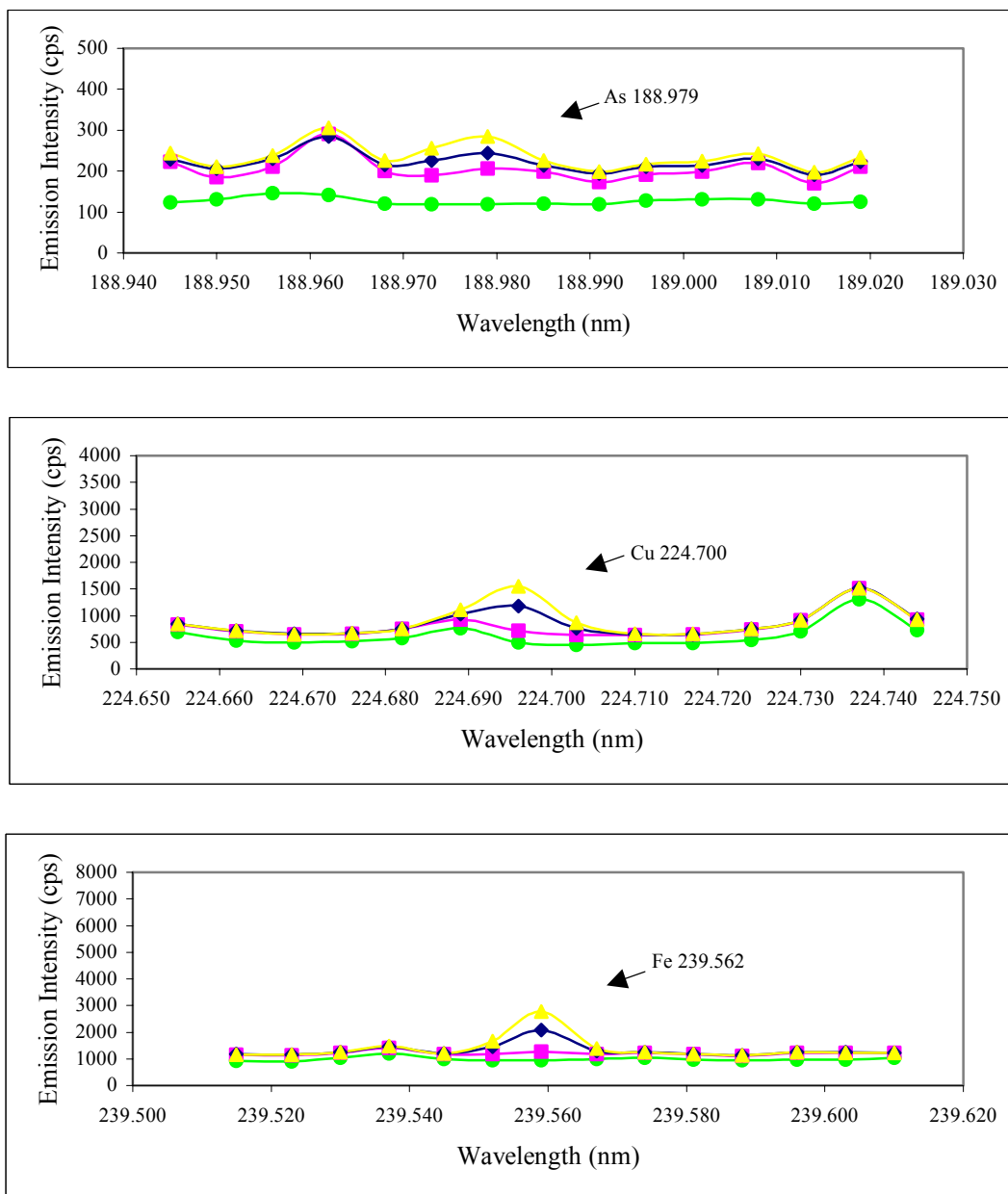


Figure 12. Representative emission spectra for arsenic (top), copper (middle) and iron (bottom) in reagent and matrix blank samples and low- and high-level matrix fortification samples prepared in freshwater and analyzed by ICP-AES.

Circles = reagent blank (I.D.: 472C-105-VREB-3, $D_f = 1.02x$); Squares = freshwater matrix blank (I.D.: 472C-105-VMAB-3, $D_f = 1.02x$); Diamonds = low-level matrix fortification (I.D.: 472C-105-VMAS-6, $D_f = 1.02x$); Triangles = high-level matrix fortification (I.D.: 472C-105-VMAS-16, $D_f = 5.00x$). Nominal concentrations for As, Cu and Fe = 20.0, 20.0 and 10.0 $\mu\text{g/L}$ and 200, 200 and 100 $\mu\text{g/L}$, in the low- and high-level matrix fortifications, respectively.

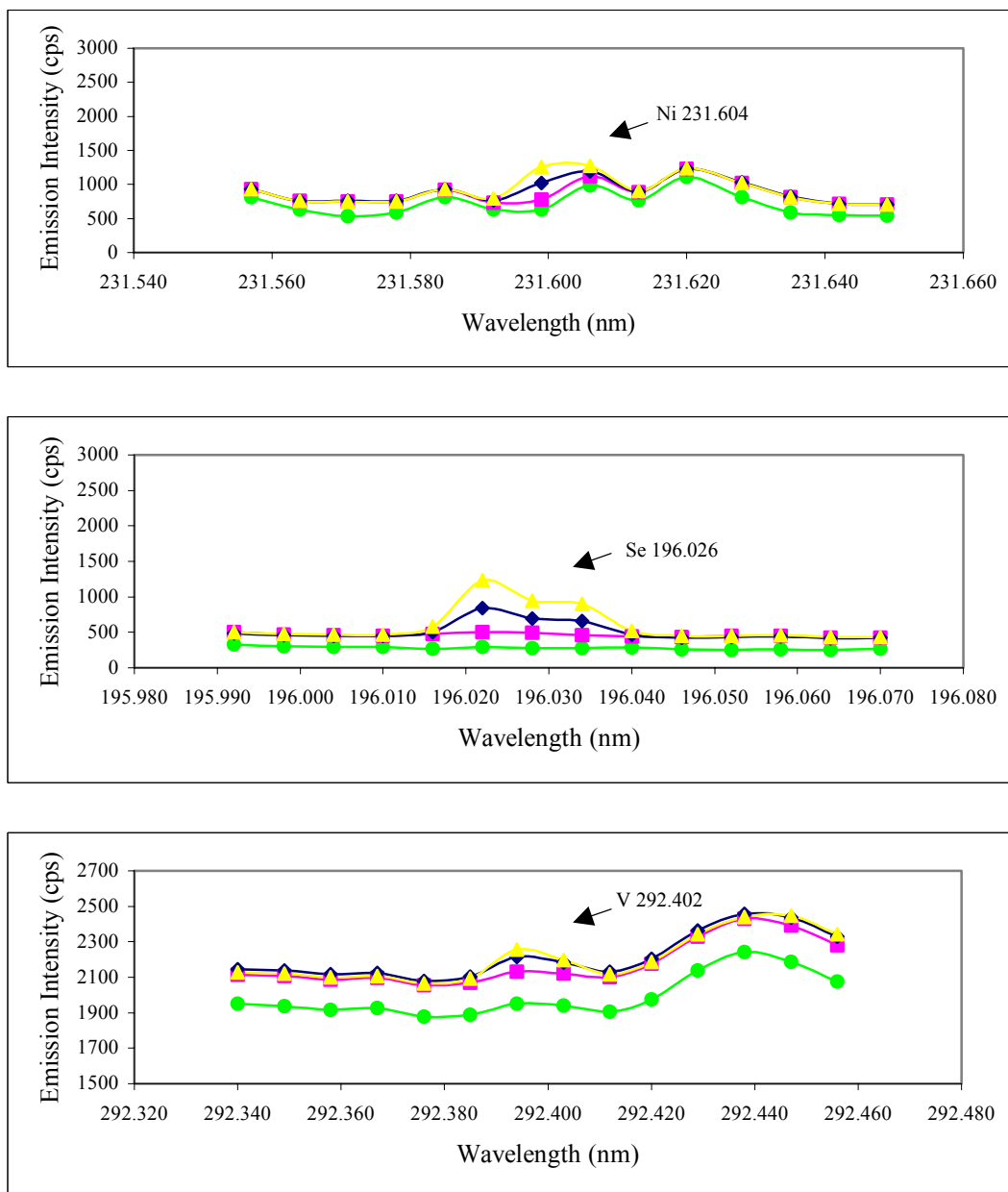


Figure 13. Representative emission spectra for nickel (top), selenium (middle) and vanadium (bottom) in reagent and matrix blank samples and low- and high-level matrix fortification samples prepared in freshwater and analyzed by ICP-AES.

Circles = reagent blank (I.D.: 472C-105-VREB-3, $D_f = 1.02x$); Squares = freshwater matrix blank (I.D.: 472C-105-VMAB-3, $D_f = 1.02x$); Diamonds = low-level matrix fortification (I.D.: 472C-105-VMAS-6, $D_f = 1.02x$); Triangles = high-level matrix fortification (I.D.: 472C-105-VMAS-16, $D_f = 5.00x$). Nominal concentrations for Ni, Se and V = 10.0, 200 and 0.400 $\mu\text{g/L}$ and 100, 2000 and 4.00 $\mu\text{g/L}$, in the low- and high-level matrix fortifications, respectively.

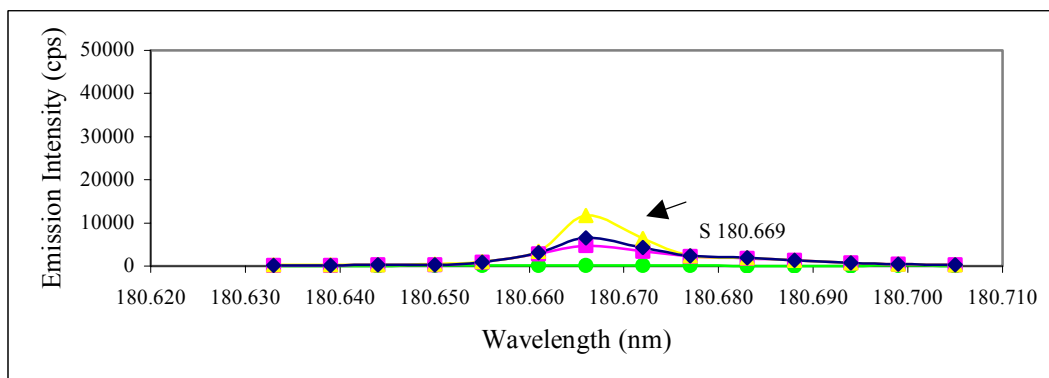


Figure 14. Representative emission spectra for sulfur in reagent and matrix blank samples and in low- and high-level matrix fortification samples prepared in freshwater and analyzed by ICP-AES.

Circles = reagent blank (I.D.: 472C-105-VREB-3, $D_f = 1.02x$); Squares = freshwater matrix blank (I.D.: 472C-105-VMAB-3, $D_f = 1.02x$); Diamonds = low-level matrix fortification (I.D.: 472C-105-VMAS-21, $D_f = 1.02x$); Triangles = high-level matrix fortification (I.D.: 472C-105-VMAS-26, $D_f = 5.00x$). Nominal concentrations for S = 10.0 and 100 mg/L in the low- and high-matrix fortifications, respectively.

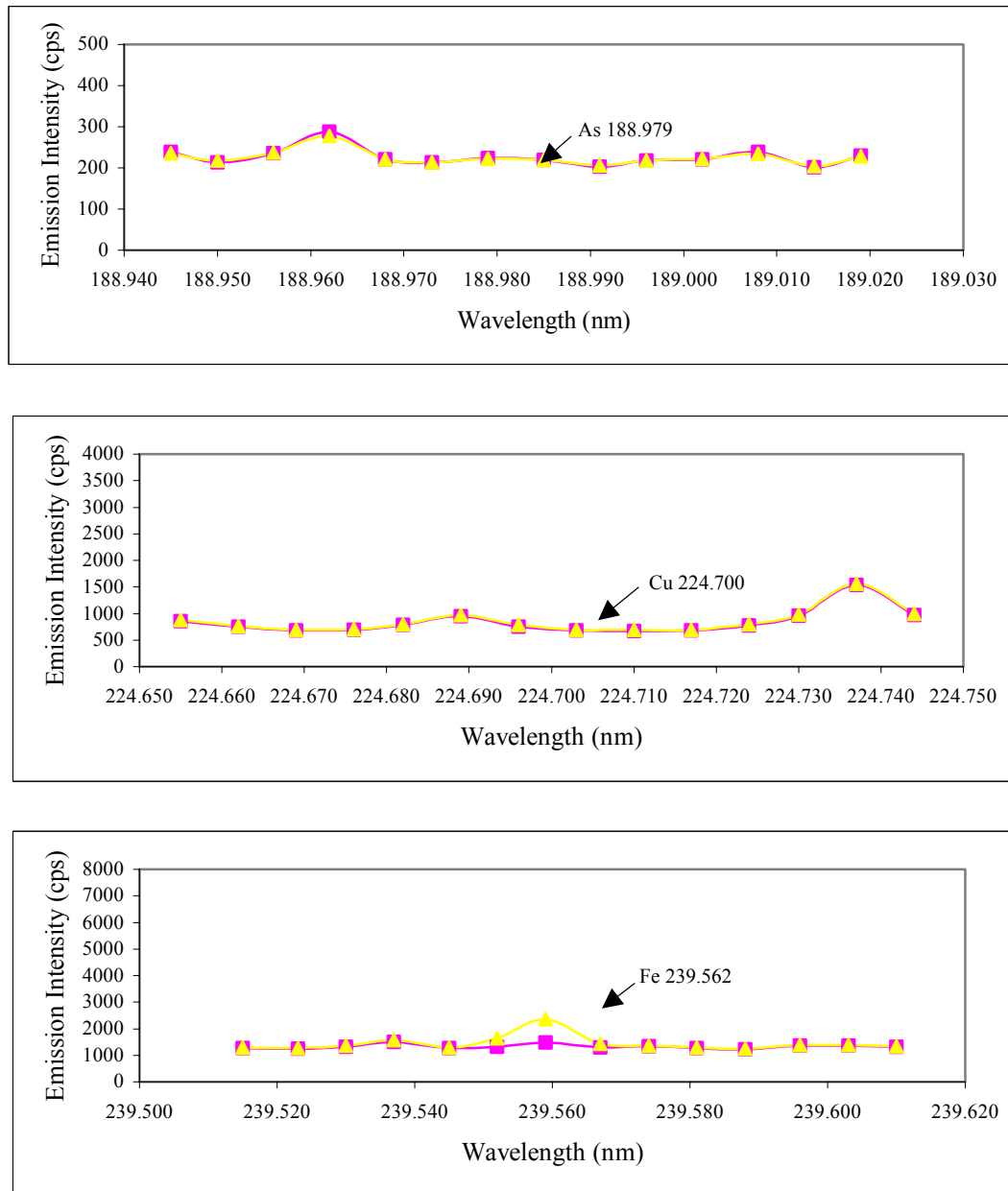


Figure 15. Representative emission spectra of arsenic (top), copper (middle) and iron (bottom) in a test sample (472C-105-5A, 1.00 mg/mL petroleum coke nominal concentration) from the WAF trial analyzed by ICP-AES.

Squares = freshwater matrix blank (I.D.: 472C-105-MAB-3, $D_f = 1.02\times$); Triangles = 72 hour WAF test sample. The arrows indicate expected wavelength for each element response. Note: the trace of iron was attributed to test chamber contamination.

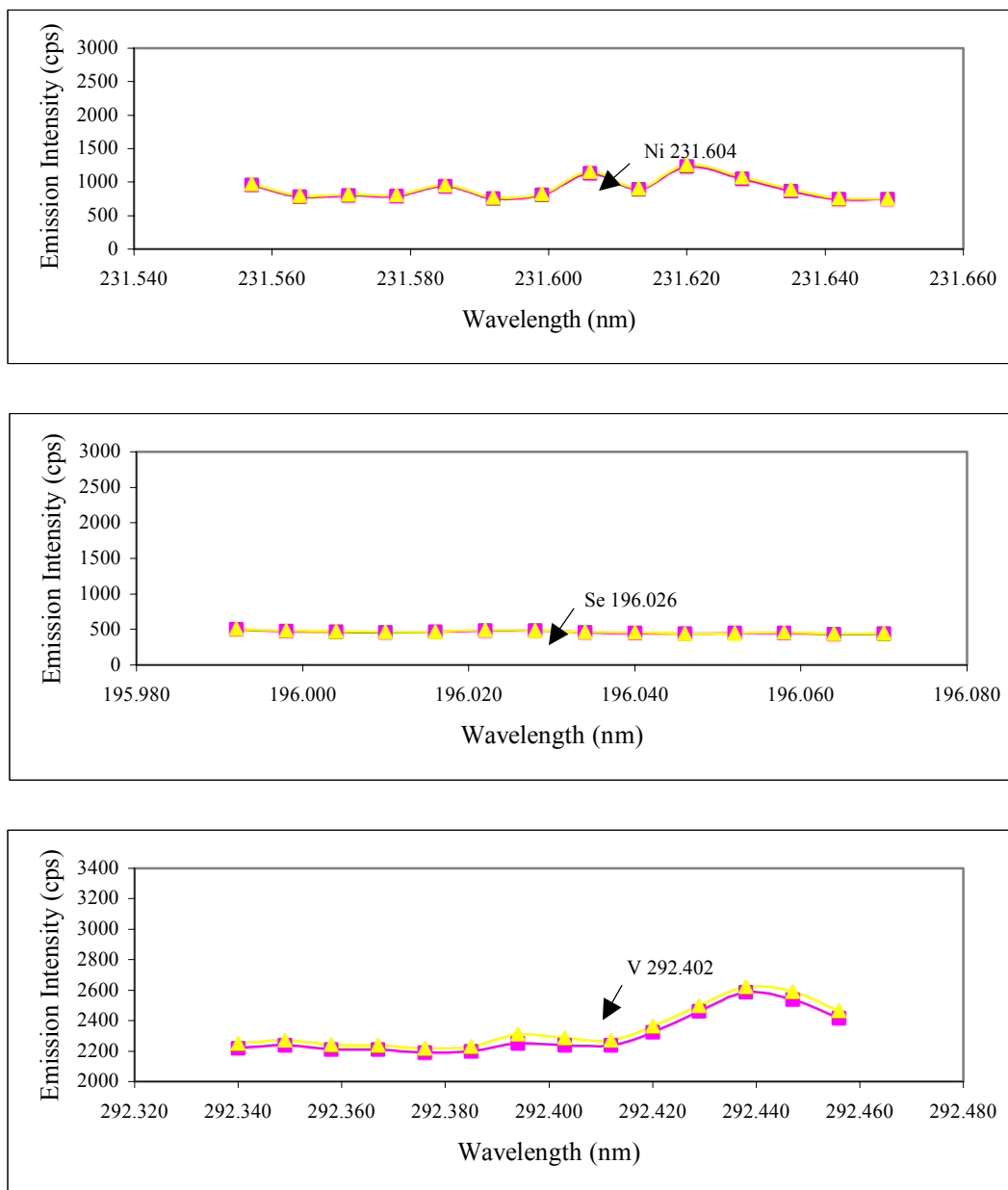


Figure 16. Representative emission spectra of nickel (top) selenium (middle) and vanadium (bottom) in a test sample (472C-105-5A, 1.00 mg/mL petroleum coke nominal concentration) from the WAF trial analyzed by ICP-AES.

Squares = freshwater matrix blank (I.D.: 472C-105-MAB-3, $D_f = 1.02\times$); Triangles = 72 hour WAF test sample. The arrows indicate expected wavelength for each element response.

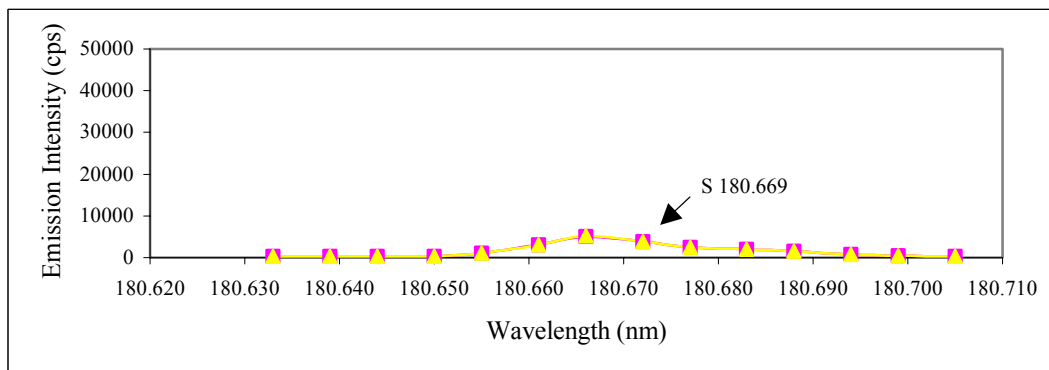


Figure 17. Representative emission spectra of sulfur in a test sample (472C-105-5A, 1.00 mg/mL petroleum coke nominal concentration) from the WAF trial analyzed by ICP-AES.

Squares = freshwater matrix blank (I.D.: 472C-105-MAB-3, $D_f = 1.02\times$); Triangles = 72 hour WAF test sample. The arrow indicates expected wavelength for sulfur response.

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Appendix 1

Protocol and Protocol Amendments

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P R O T O C O L

ANALYTICAL METHOD VERIFICATION FOR THE DETERMINATION
OF WATER SOLUBLE COMPONENTS OF PETROLEUM COKE IN FRESHWATER USING
INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES)

European Commission Working Document SANCO/3029/99 rev. 4

Submitted to

American Petroleum Institute
1220 L Street, N.W.
Washington, DC 20005

Wildlife International, Ltd.

8598 Commerce Drive
Easton, Maryland 21601
(410) 822-8600

March 30, 2004

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ANALYTICAL METHOD VERIFICATION FOR THE DETERMINATION
OF WATER SOLUBLE COMPONENTS OF PETROLEUM COKE IN FRESHWATER USING
INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES)

SPONSOR:

American Petroleum Institute
1220 L Street, N.W.
Washington, DC 20005

SPONSOR'S REPRESENTATIVE:

[REDACTED]

SPONSOR'S TECHNICAL STUDY MONITOR:

[REDACTED]

TESTING FACILITY:

Wildlife International, Ltd.
8598 Commerce Drive
Easton, Maryland 21601

STUDY DIRECTOR:

[REDACTED]
Wildlife International, Ltd.

LABORATORY MANAGEMENT:

[REDACTED]
Wildlife International Ltd.

FOR LABORATORY USE ONLY

Proposed Dates:	
Experimental	Experimental
Start Date: _____	Termination Date: _____
Project No.: 472C-105	Test Concentrations: _____
Test Substance No.: 6485	Reference Substance No.(if applicable): _____

PROTOCOL APPROVAL

[REDACTED]

4/23/04
DATE

4/23/04
DATE

01 April, 2004
DATE

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INTRODUCTION

Wildlife International, Ltd. will conduct analytical trials to verify the performance of methods for the determination of metals and sulfur in water accommodated fraction (WAF) solutions made with petroleum coke and freshwater. The study will be performed at the Wildlife International, Ltd. analytical chemistry facility in Easton, Maryland. Petroleum coke is defined as the product formed by subjecting the heavy tar-like residue remaining following oil refining to high temperatures and pressures. It consists of primarily elemental carbon with considerably smaller amounts of hydrocarbons, sulfur and trace amounts of heavy metals. The study will be performed based on procedures in *Residues: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, Section 4) and Annex III (Part A, Section 5) of Directive 91/414 (1)*. The method will be verified by fortifying freshwater with the test substance and determining the recoveries. Raw data for all work performed at Wildlife International, Ltd. and a copy of the final report will be filed by project number in archives located on the Wildlife International, Ltd. site, or at an alternative location to be specified in the final report.

OBJECTIVE

There are two objectives to this study. One is to verify an inductively coupled plasma atomic emission spectrometry (ICP-AES) method for determination of metals and sulfur in water accommodated fraction (WAF) solutions of petroleum coke. The second is to employ the method to determine the optimum WAF mixing time to achieve maximum leaching of metals and sulfur from the test substance matrix into freshwater.

EXPERIMENTAL DESIGN

Wildlife International, Ltd. freshwater will be fortified at three different concentrations and analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES). Modifications to the methodology will be made as necessary to achieve quantitation of the components of petroleum coke in the freshwater matrix. Matrix and/or reagent blanks will be analyzed concurrently to evaluate potential analytical interferences. Quantitation will be performed with external standards of the components of petroleum coke using concentrations that bracket the concentrations of samples. One or more calibration curves will be generated from analyses of standard solutions of test substance to be analyzed with each series of matrix fortification samples.

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MATERIALS AND METHODS

Test Substance

The test substance is green coke (CAS Number 64741-79-3) sieved to approximately 2 mm particle size. Information on the characterization of test, control and reference substances is required by Good Laboratory Practice Standards (GLP), 40 CFR Parts 160.31 and 792. The Sponsor is responsible for providing Wildlife International, Ltd. written verification that the test substance has been characterized according to GLPs prior to its use in the study. If written verification of GLP test substance characterization is not provided to Wildlife International, Ltd., it will be noted in the compliance statement of the final report.

The Sponsor is responsible for all information related to test and reference substances and agrees to accept any unused test or reference substance and/or test or reference substance containers remaining at the end of the study.

Reagents and Solvents

All solvents used in the method or procedure will be HPLC grade or equivalent. All reagents will be ACS reagent grade or higher quality. Nanopure water will be used. The solvents and reagents are not expected to contain contaminants capable of interfering with the purpose of this study.

Freshwater

Freshwater to be used for the method verification will be obtained from a well approximately 40-meters deep located on the Wildlife International, Ltd. site. The water will be passed through a sand filter and pumped into a 37,800-L storage tank where the water will be aerated with spray nozzles. Prior to use, the water will be filtered to 0.45 µm in order to remove fine particles. The resulting water is characterized as moderately hard. Typical values for hardness, alkalinity, pH and specific conductance are approximately:

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Hardness, mg/L as CaCO ₃	145
Alkalinity, mg/L as CaCO ₃	190
pH	8.1
Specific Conductance, µmhos/cm	330

Hardness, alkalinity, pH and specific conductance will be measured weekly to monitor the consistency of the well water. Means and ranges of the measured parameters for the four-week period preceding the test will be provided in the final report. Analyses will be performed at least once annually to determine the concentrations of selected organic and inorganic constituents of the well water. Results of these analyses will be summarized in the final report. Specifications for acceptable levels of contaminants in well water have not been established. However, there are no known levels of contaminants reasonably expected to be present in the well water that are considered to interfere with the purpose or conduct of the test.

Fortification Stock Solution(s)

Freshwater will be fortified with a stock solution(s) of the test substance. Each stock solution will be assigned a unique identification code that will be recorded on a stock preparation log sheet.

Reference Stock Solution(s), Calibration Standards and Curves

A primary stock solution(s) will be prepared from appropriate reference substances, when available. Calibration standards will be prepared by appropriate dilution of this primary stock solution(s). A minimum of five concentrations of calibration standards will be prepared and analyzed along with each analysis set of verification samples. The calibration standard series will be injected at the beginning and end of the analytical run with, in addition, a minimum of one standard injected following every five samples. One or more calibration curves will be derived from regression analysis of the instrumental responses of the standards.

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Method

The analytical methods to be used will be based upon ICP-AES procedures. The method may be modified to yield a method capable of determining the test substance in freshwater. Samples will be analyzed for the components of petroleum coke listed in Table 1, if possible. The method used will be described in the final report.

Verification Analyses - Method Performance

Matrix fortifications (fortified wellwater), prepared at known concentrations of the test substance, will be analyzed to determine recovery and to evaluate method performance. The anticipated verification series will consist of the following analyses:

SUMMARY OF PROPOSED VERIFICATION ANALYSIS SCHEME

Analysis Type	Concentration	Number of Samples
Reagent Blank	0 (Control)	2
Matrix Blank	0 (Control)	2
Matrix Fortifications	Level 1 – Low ¹	5
	Level 2	5
	Level 3 – High	5
Total Number of Analyses		19
¹ Matrix fortifications will be prepared at three concentrations, the lowest and highest of which will bracket the anticipated treatment range for environmental effects studies.		

Matrix fortifications will span the range of concentrations that are anticipated to be used in subsequent environmental effects tests and will be selected in consultation with the Sponsor. Individual fortification samples (identified by project number and a unique sample identification number) will be prepared and analyzed.

If difficulties arise in the validation process (e.g., low recoveries or interferences), the Sponsor will be notified and the need for additional validation and/or method development will be determined through discussions with the Sponsor. Upon completion of the method verification, the Sponsor will review the results and authorize the use of the methodology for analysis of samples, or will authorize further method development trials. Recovery values in the range of 80 to 120% will be used as criteria for method acceptability.

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Evaluation of Interferences

Matrix and reagent blanks, if applicable, will be analyzed to assess the presence of potential interferences. Matrix and reagent blanks will consist of freshwater and/or reagent without addition of test substance.

Data Analysis

One or more calibration curves for each analytical run will be derived from the instrumental responses of test substance standards of known concentration using regression analysis. The concentrations of fortified samples will be determined by substituting the respective instrumental response into the regression equation.

If the fortification range and calibration curve standard concentrations are significantly higher than method capabilities for quantitation, the limit of quantitation (LOQ) will be defined as the concentration equivalent to the lowest standard accounting for dilutions and other manipulations in the method for matrix blanks. If the fortification range is near the method capability for accurate quantitation of the analyte, the LOQ will be determined from the responses of replicate control samples. The mean (S_b) and standard deviation (σ) of responses will be determined for the replicate control sample and converted to ppm equivalents using a standard curve and method dilution factors. The LOQ will be expressed as the concentration equivalent of $S_b + 10 \sigma$. The limit of detection (LOD), defined as the lowest concentration of analyte which can be injected and produce a measurable response above background, will be expressed as the amount equivalent to $S_b + 3 \sigma$.

Precision and Repeatability

The precision of the method will be reported as the RSD of repeatability at each fortification level and the overall RSD will be reported. In general, the RSD should be $\leq 20\%$.

Determination of Mixing Time for the Preparation of WAF Solutions

Petroleum Coke will be mixed directly with dilution water on a weight:volume basis. A water accommodated fraction (WAF) will be prepared at a single high concentration of 1000 mg coke/L in 13.2L and 4L Pyrex® aspirator bottles with tubulation (Fisher Catalog Numbers 02-972-2 and 02-972F). Solutions will be prepared by mixing the test solutions with a vortex depth of

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approximately 30% of the test solution height and then allowing settling before sampling. A WAF equilibration test will be performed with analysis of test solutions after approximately 24, 48, 72 and possibly 96 hours of mixing. Sampling intervals may be modified by the Study Director based upon the analytical results. The length of the mixing time required to achieve approximately stable concentration in the WAF will be evaluated and used in aquatic toxicity testing. Analysis of WAF solutions for the analytes listed in Table 1 will be performed using the ICP-AES.

RECORDS TO BE MAINTAINED

Records, to be maintained for data generated by Wildlife International, Ltd., will include:

1. A copy of the signed protocol.
2. Identification and characterization of test and reference substances, if provided by the Sponsor.
3. Dates of initiation and termination of the test.
4. Storage conditions for test and reference substances, and samples.
5. Test and reference substance use logs.
6. Concentration calculations and records of solution preparation.
7. Instrument operating conditions and chromatograms.
8. Statistical calculations.
9. A copy of the final report.

FINAL REPORT

The report will summarize the findings of the verification, the fortification recoveries obtained, and method(s) and instrumentation employed. Upon receipt of these findings, the Sponsor will review the methods and results, and evaluate the results for acceptability. The final report will include, but not be limited to, the following:

1. Name and address of the facility performing the study.
2. Dates on which the study was initiated and completed.
3. A statement of compliance signed by the Study Director addressing any exceptions to Good Laboratory Practice Standards.

Wildlife International, Ltd.

4. Objectives and procedures stated in the approved protocol, including any changes in the original protocol or deviations from the protocol.
5. Identification of test and reference substances, including name, chemical abstract number or code number, strength, purity, composition, date of receipt, lot number, storage conditions, physical characteristics, stability and method of preparation of test concentrations, if provided by the Sponsor.
6. A brief summary of the analytical methodology to include, where applicable, a description of the experimental measurements, example calculations, sample preparation (sample weights and/or dilutions), instrumentation employed, reagents used, purity of reagents and solvents, and any major modifications to the method.
7. A description of any circumstances that may have affected the quality or integrity of the data.
8. The name of the Study Director, the names of other scientists or professionals, and the names of all supervisory personnel involved in the study.
9. A description of the transformations, calculations, or operations performed on the data.
10. The signed and dated reports of each of the individual scientists or other professionals involved in the study, if applicable.
11. The location where raw data and final report are to be stored.
12. A statement prepared by the Quality Assurance Unit listing the dates that study inspections and audits were made and the dates of any findings reported to the Study Director and Management.

CHANGES TO PROTOCOL

Planned changes to the protocol will be in the form of written amendments signed by the Study Director and approved by the Sponsor's Representative. Amendments will be considered as part of the protocol and will be attached to the final protocol. Any other changes will be in the form of written deviations signed by the Study Director and filed with the raw data. All changes to and deviation from the protocol will be indicated in the final report.

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GOOD LABORATORY PRACTICES

This study will be conducted in accordance with Good Laboratory Practice Standards for EPA (40 CFR Part 160 and/or 792) and OECD Principles of Good Laboratory Practices (ENV/MC/CHEM (98) 17). Each study conducted by Wildlife International, Ltd. is routinely examined by the Wildlife International, Ltd. Quality Assurance Unit for compliance with Good Laboratory Practices, Standard Operating Procedures and the specified protocol. A statement of compliance with Good Laboratory Practices will be prepared for all portions of the study conducted by Wildlife International, Ltd. The Sponsor will be responsible for compliance with Good Laboratory Practices for procedures performed by other laboratories.

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REFERENCES

1. **European Commission.** 2000. *Residues: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, Section 4) and Annex III (Part A, Section 5) of Directive 91/414.* SANCO/3029/99 rev. 4, 11/07/00

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Wildlife International, Ltd.

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Table 1.

Analytes of Interest in Petroleum Coke

Metals and Sulfur
Nickel
Vanadium
Iron
Copper
Selenium
Arsenic
Sulfur

Project Number 472C-105

Wildlife International, Ltd.

Page 1 of 2

AMENDMENT TO STUDY PROTOCOL

STUDY TITLE: Analytical Method Verification for the Determination of Water Soluble Components of Petroleum Coke in Freshwater Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

PROTOCOL NO.: 472/033004/MVFW-ICP/SUB472

AMENDMENT NO.: 1

SPONSOR: American Petroleum Institute

PROJECT NUMBER: 472C-105

EFFECTIVE DATE: 5 August 2004

Add to Page 5 – Method

Prior to performance of the method verification trial, an evaluation of the ICP method will be performed for each analyte to determine the limit of detection (LOD) at the instrument, determine background levels of the analytes in water and establish a theoretical limit of quantitation (LOQ) in water. The LOQ will be based on 10 times the LOD or 2 times the background level, whichever is higher.

REASON:

At the request of the Sponsor, the steps to be taken to establish the theoretical LOQ were specified in the protocol.

Add and Revise Page 6 – Verification Analysis – Method Performance:

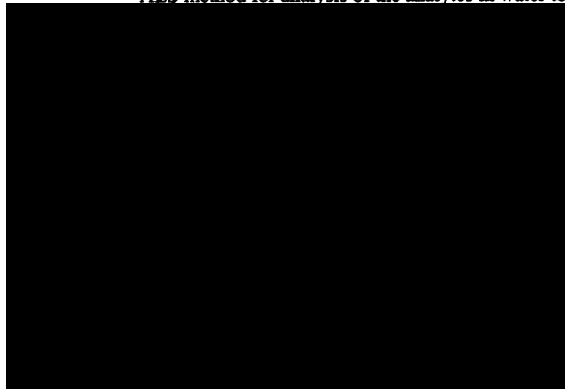
The method verification trial will be performed by fortifying freshwater with known concentrations of analytical standards of the seven analytes of interest (Ni, V, Fe, Cu, S, As and Se) rather than with petroleum coke containing trace quantities of these analytes. Portions of the protocol that refer to fortifying water with petroleum coke are effectively changed to fortifying water with known standards (individual or mixed standards) of the seven analytes of interest.

Fortification levels of each analyte will include the calculated LOQ and 10X the LOQ to bracket the expected concentrations of each analyte in water to be used for environmental effects testing with petroleum coke. If expected levels of an analyte are above 10X the LOQ, additional fortification levels for that analyte will be added at the appropriate concentration(s).

REASON:

Concentrations of most of the analytes of interest in petroleum coke are < LOQ or are present in trace quantities according to information provided by the Sponsor. Fortifying with known

concentrations using analyte standards will verify the efficiency and accuracy of the ICP-AES method for analysis of the analytes in water to be used for environmental effects testing.



8/10/04
DATE

8/10/04
DATE

August 6, 2004
DATE

AMENDMENT TO STUDY PROTOCOL

STUDY TITLE: Analytical Method Verification for the Determination of Water Soluble Components of Petroleum Coke in Freshwater Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

PROTOCOL NO.: 472/033004/MVFW-ICP/SUB472

AMENDMENT NO.: 2

SPONSOR: American Petroleum Institute

PROJECT NUMBER: 472C-105

EFFECTIVE DATE: 5 August 2004

Add to Page 2 – Reference Substance Numbers

6543, 6544, 6545, 6546, 6547, 6548 and 6549.

REASON:

Specification of analytical standards for ICP-AES measurements of arsenic, copper, iron, nickel, selenium, sulfur and vanadium, respectively. The standards will be used for instrument calibration, detection limit determination and matrix fortifications.

Add to Page 2 – Proposed Dates

Experimental Start Date: August 10, 2004
Experimental Termination Date: October 24, 2004

REASON:

Information required to complete the protocol.

Page 4 – Reagents and Solvents

Delete second sentence "Nanopure water will be used."

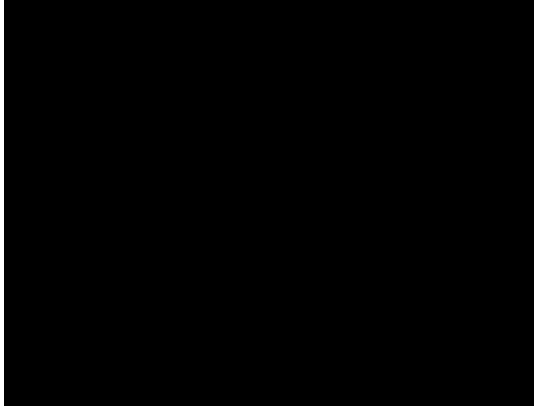
REASON:

HPLC grade reagent water is preferred and will be used.

Project Number 472C-105

Wildlife International, Ltd.

Page 2 of 2



9/29/04
DATE

9/29/04
DATE

10/1/04
DATE

Project Number 472C-105

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Page 1 of 1

AMENDMENT TO STUDY PROTOCOL

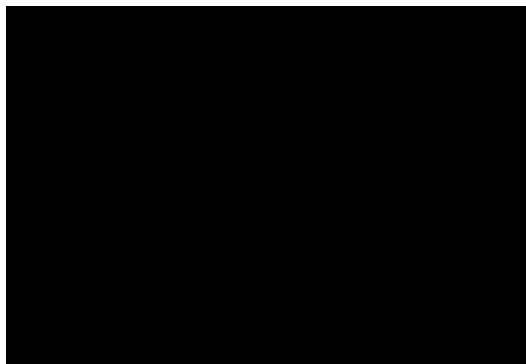
STUDY TITLE: Analytical Method Verification for the Determination of Water Soluble Components of Petroleum Coke in Freshwater Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

PROTOCOL NO.: 472/033004/MVFW-ICP/SUB472**AMENDMENT NO.:** 3**SPONSOR:** American Petroleum Institute**PROJECT NUMBER:** 472C-105**EFFECTIVE DATE:** 1 October 2004**Add to Page 2 – Concentrations to be verified:**

Element	LOQ level, µg/L	10x LOQ level, µg/L
Arsenic	20.0	200
Copper	20.0	200
Iron	10.0	100
Nickel	10.0	100
Selenium	200	2000
Sulfur	10,000	100,000
Vanadium	0.400	4.00

REASON:

Provides the levels of elements to be measured in the method verification trial.



10/05/04
DATE

10/5/04
DATE

10/5/04
DATE

Project Number 472C-105

Wildlife International, Ltd.

Page 1 of 1

AMENDMENT TO STUDY PROTOCOL

STUDY TITLE: Analytical Method Verification for the Determination of Water Soluble Components of Petroleum Coke in Freshwater Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

PROTOCOL NO.: 472/033004/MVFW-ICP/SUB472

AMENDMENT NO.: 4

SPONSOR: American Petroleum Institute

PROJECT NUMBER: 472C-105

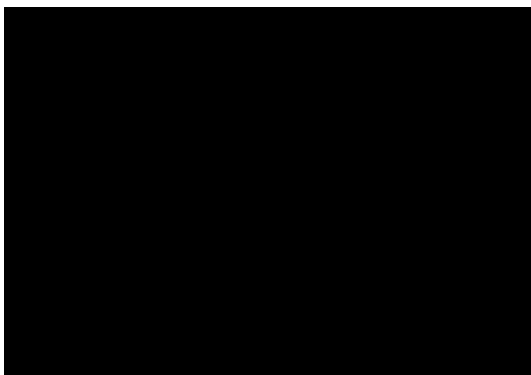
EFFECTIVE DATE: 18 October 2004

Add to Page 2 –

Reference Substance Number 6890.

REASON:

Specification of an additional analytical standard for ICP-AES measurements of sulfur. A reference standard containing a higher sulfur concentration (10 mg/mL) was required to minimize the solvent volume for the relatively high sulfur verification levels in freshwater (10 and 100 mg/L).



11/3/04
DATE

11/3/04
DATE

11/03/04
DATE

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Appendix 2

Certificates of Analysis

Certificate of Analysis for 1000 mg/L Arsenic

SPEX TM Certificate of Reference Material					
Catalog Number: PLAS2-2X/2Y/2T			Lot No. 10-06AS		
Description: 1000 mg/L Arsenic					
Matrix: 2% HNO ₃					
This ASSURANCE[®] certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.					
Certified Value: 1000 mg/L					
Uncertainty Associated with Measurement: +/- 3.0 mg/L					
Certified Value is Traceable to: NIST SRM 3103a.					
The CRM is prepared gravimetrically using high purity Orthoarsenic Acid Lot# 01021C. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis.					
Refer to side 2 for details of measurement uncertainties.					
Classical Wet Assay: 1000 mg/L					
Method: Precipitation using Silver Nitrate. Filter and weigh as Ag ₃ AsO ₄ .					
Instrumentation Analysis By ICP spectrometer: 1000 mg/L					
Uncertified Properties:					
Density: 1.010 @ 23.7 Degrees Celsius					
Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:					
Element	mg/L	Element	mg/L	Element	mg/L
Al	0.004	Fe	0.010	Re	<0.001
Ag	<0.001	Ga	<0.001	Rb	<0.001
B	<0.003	In	<0.001	Sr	<0.001
Ba	<0.001	K	0.055	Sb	0.001
Be	<0.001	Li	<0.001	Si	0.05
Bi	<0.001	Mn	<0.001	Ti	<0.001
Cd	<0.001	Mo	<0.001	Tl	<0.001
Cu	<0.001	Mg	<0.001	V	<0.001
Co	<0.001	Na	0.009	Zr	<0.20
Ca	0.020	Ni	<0.001	Zn	0.008
Cr	<0.002	Pb	0.001		
Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.					
Date of Certification: NOV '03			Certifying Officer: <i>N. Kocherakota</i>		

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Certificate of Analysis for 1000 mg/L Copper

SPEXcertificate™ <i>Certificate of Reference Material</i>					
Catalog Number: PLCU2-2X/2Y/2T			Lot No. 9-183CU		
Description: 1000 mg/L Copper					
Matrix: 2% HNO ₃					
This ASSURANCE® certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.					
Certified Value: 999.5 mg/L					
Uncertainty Associated with Measurement: +/- 3 mg/L					
Certified Value is Traceable to: NIST SRM 3114					
The CRM is prepared gravimetrically using high purity Copper Metal Lot# 05021D. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis					
Refer to side 2 for details of measurement uncertainties.					
Classical Wet Assay: 1000 mg/L					
Method: EDTA titration using PAN as indicator. EDTA standardized against Pb(NO ₃) ₂ NIST SRM #928.					
Instrumentation Analysis By ICP spectrometer: 999 mg/L					
Uncertified Properties:					
Density: 1.011 @ 23.5 Degrees Celsius					
Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:					
Element	mg/L	Element	mg/L	Element	mg/L
Al	0.002	Fe	0.008	Pb	0.001
As	<0.001	Ga	<0.001	Re	<0.001
Ag	<0.002	In	<0.001	Rb	<0.001
B	<0.002	K	0.06	Sr	<0.001
Ba	0.002	Li	<0.001	Sb	<0.001
Be	<0.001	Mn	<0.001	Si	0.03
Bi	<0.001	Mo	<0.001	Ti	<0.001
Ca	0.07	Mg	<0.001	Tl	<0.001
Cr	<0.001	Na	0.005	V	<0.001
Cd	<0.001	Ni	<0.001	Zr	<0.001
Co	<0.001			Zn	0.04
Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.					
Date of Certification: NOV '03			Certifying Officer: <i>N. Kocherakota</i>		

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Certificate of Analysis for 1000 mg/L Iron

SPEXertificateTM

Certificate of Reference Material

Catalog Number: PLFE2-2X/2Y/2T**Lot No.** 9-184FE**Description:** 1000 mg/L Iron**Matrix:** 2% HNO₃

This ASSURANCE[®] certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.

Certified Value: 1000 mg/L**Uncertainty Associated with Measurement:** +/- 3 mg/L**Certified Value is Traceable to:** NIST SRM 3126a

The CRM is prepared gravimetrically using high purity Iron Metal Lot# 02011B. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis. Refer to side 2 for details of measurement uncertainties.

Classical Wet Assay: 1000 mg/L**Method:** Precipitation using Ammonium Hydroxide. Filter, ignite, and weigh as Fe₂O₃.**Instrumentation Analysis By ICP spectrometer:** 1000 mg/L**Uncertified Properties:****Density:** 1.012 @ 23.2 Degrees Celsius**Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:**

Element	mg/L	Element	mg/L	Element	mg/L
Al	<0.002	Cu	0.001	Pb	0.001
As	<0.001	Ga	<0.001	Re	<0.001
Ag	<0.001	In	<0.001	Rb	<0.001
B	<0.008	K	0.002	Sr	<0.001
Ba	<0.001	Li	<0.001	Sb	<0.001
Be	<0.001	Mn	0.01	Si	<0.001
Bi	<0.001	Mo	<0.001	Ti	<0.001
Ca	0.013	Mg	<0.001	Tl	<0.001
Cr	<0.002	Na	0.001	V	<0.001
Cd	<0.001	Ni	0.002	Zr	<0.001
Co	0.02			Zn	0.008

Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.

Date of Certification: NOV 83 Certifying Officer: N. Kocherakula

Certificate of Analysis for 1000 mg/L Nickel

SPEXertificateTM
Certificate of Reference Material

Catalog Number: PLN12-2X/2Y/2T **Lot No.** 10-29NI

Description: 1000 mg/L Nickel

Matrix: 2% HNO₃

This ASSURANCE[®] certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.

Certified Value: 999 mg/L
Uncertainty Associated with Measurement: +/-3.0mg/L
Certified Value is Traceable to: NIST SRM #3136

The CRM is prepared gravimetrically using high purity Nickel Metal Lot# 02021B. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis.

Refer to side 2 for details of measurement uncertainties.

Classical Wet Assay: 999 mg/L

Method: EDTA titration using Murexide as indicator. EDTA standardized against Pb(NO₃)₂ NIST SRM #928.

Instrumentation Analysis By ICP spectrometer: 998 mg/L

Uncertified Properties:

Density: 1.011 @ 22.6 Degrees Celsius

Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:

Element	mg/L	Element	mg/L	Element	mg/L
Al	<0.001	Cu	<0.001	Pb	0.002
As	0.005	Fe	0.005	Re	<0.001
Ag	<0.001	Ga	<0.001	Rb	<0.001
B	<0.003	In	<0.001	Sr	<0.001
Ba	<0.001	K	<0.09	Sb	<0.001
Be	<0.002	Li	<0.001	Si	0.014
Bi	<0.001	Mg	<0.001	Ti	<0.002
Ca	0.008	Mn	<0.001	Tl	<0.001
Cr	<0.001	Mo	<0.001	V	<0.001
Cd	<0.001	Na	0.003	Zr	<0.001
Co	0.002			Zn	0.007

Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.

Date of Certification: NOV '03 **Certifying Officer:** N. Kochavakota

Certificate of Analysis for 1000 mg/L Selenium

SPEXertificate™

Certificate of Reference Material

Catalog Number: PLSE2-2X/2Y/2T **Lot No.** 10-31SE
Description: 1000 mg/L Selenium
Matrix: 2% HNO₃

This ASSURANCE® certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.

Certified Value: 1000.5 mg/L
Uncertainty Associated with Measurement: +/- 3.0 mg/L
Certified Value is Traceable to: NIST SRM #3149

The CRM is prepared gravimetrically using high purity Selenium Metal Lot# 05891Z. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis. Refer to side 2 for details of measurement uncertainties.

Classical Wet Assay: 1001 mg/L

Method: Precipitation using Sulfurous Acid. Filter, dry, and weigh as Selenium.

Instrumentation Analysis By ICP spectrometer: 1000 mg/L

Uncertified Properties:

Density: 1.011 @ 22.5 Degrees Celsius

Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:

Element	mg/L	Element	mg/L	Element	mg/L
Al	0.002	Cu	0.001	Pb	0.001
As	0.002	Fe	0.004	Rb	<0.001
Ag	<0.001	Ga	<0.001	Re	<0.001
B	<0.002	In	<0.001	Si	<0.005
Ba	<0.001	K	<0.01	Sr	<0.001
Be	<0.001	Li	0.001	Sb	0.001
Bi	<0.001	Mg	<0.001	Ti	<0.001
Ca	0.012	Mn	<0.001	Tl	<0.001
Cr	<0.003	Mo	<0.001	V	<0.001
Cd	<0.001	Na	0.007	Zr	<0.001
Co	<0.001	Ni	<0.001	Zn	0.02

Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.

Date of Certification: NOV '03 **Certifying Officer:** N. Kocherakota

Certificate of Analysis for 1000 mg/L Sulfur

SPEXTM
Certificate of Reference Material

Catalog Number: PLS9-2X/2Y/2T **Lot No.** 8-74S

Description: 1000 mg/L Sulfur

Matrix: H₂O

This ASSURANCE[®] certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.

Certified Value: 1003 mg/L
Uncertainty Associated with Measurement: +/- 3 mg/L
Certified Value is Traceable to: NIST SRM 3154

The CRM is prepared gravimetrically using high purity Ammonium Sulfate Lot# 05891M. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis. Refer to side 2 for details of measurement uncertainties.

Classical Wet Assay: 1003 mg/L
Method: Precipitation using barium chloride, filter, ignite and weigh as BaSO₄.

Instrumentation Analysis By ICP spectrometer: 1003 mg/L

Uncertified Properties:

Density: 1.007 @ 23.6 Degrees Celsius

Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:

Element	mg/L	Element	mg/L	Element	mg/L
Al	<0.001	Cu	<0.001	Pb	0.002
As	<0.001	Fe	0.008	Rb	<0.001
Ag	<0.001	Ga	<0.001	Re	<0.001
B	<0.004	In	<0.001	Sn	<0.001
Ba	<0.001	K	<0.001	Sr	<0.001
Be	<0.001	Li	<0.001	Sb	<0.001
Bi	<0.001	Mg	0.005	Ti	<0.002
Ca	0.009	Mn	<0.001	Tl	<0.001
Cr	<0.004	Mo	<0.001	V	<0.001
Cd	<0.001	Na	0.02	Zr	<0.001
Co	<0.001	Ni	<0.001	Zn	0.0075

Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.

Date of Certification: NOV 03 **Certifying Officer:** N. Kocherakota

Certificate of Analysis for 10,000 mg/L Sulfur

SPEXertificateTM

Certificate of Reference Material

Catalog Number: PLS9-3X/3Y Lot No. S9-51S

Description: 10,000 mg/L Sulfur

Matrix: H₂O

This ASSURANCE[®] certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.

Certified Value: 9961 mg/L

Uncertainty Associated with Measurement: ± 30.0 mg/L

Certified Value is Traceable to: NIST SRM #3154

The CRM is prepared gravimetrically using high purity Ammonium Sulfate Lot# 05891M. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis.

Refer to side 2 for details of measurement uncertainties.

Classical Wet Assay: 9,960 mg/L

Method: Precipitation using Barium Chloride. Filter, ignite and weigh as BaSO₄.

Instrumental Analysis by ICP spectrometer: 9962 mg/L

Uncertified Properties:

Density: 1.021 @ 22.7 Degrees Celsius

Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:

Element	mg/L	Element	mg/L	Element	mg/L
Al	0.002	Cu	0.004	Pb	<0.001
As	<0.007	Fe	0.14	Rb	<0.001
Ag	<0.004	Ga	<0.001	Re	<0.001
B	<0.005	In	<0.001	Si	0.01
Ba	<0.001	K	<0.10	Sr	<0.001
Be	<0.003	Li	<0.004	Sb	<0.004
Bi	<0.001	Mg	0.07	Ti	<0.008
Ca	0.057	Mn	<0.02	Tl	<0.001
Cr	<0.007	Mo	<0.001	V	<0.004
Cd	<0.001	Na	0.24	Zr	<0.001
Co	0.002	Ni	<0.002	Zn	<0.005

Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to $\pm 0.5\%$ of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.

Date of Certification: OCT - - 2004 Certifying Officer: *N. Kocherakota*

Certificate of Analysis for 1000 mg/L Vanadium

SPEXertificate™
Certificate of Reference Material

Catalog Number: PLV2-2X/2Y **Lot No.** 10-88V

Description: 1000 mg/L Vanadium

Matrix: 2% HNO₃

This ASSURANCE® certified reference material, CRM, is intended primarily for use as a calibration standard or quality control standard for inorganic spectroscopic instrumentation such as ICPOES, DCP, AA, ICPMS, and XRF. It can be employed in USEPA, ASTM and other methods relevant to the certified properties listed below.

Certified Value: 1003 mg/L
Uncertainty Associated with Measurement: +/-3.0mg/L
Certified Value is Traceable to: NIST SRM #3165

The CRM is prepared gravimetrically using high purity Ammonium Vanadate Lot# 06021B. The certified value listed is the average of values obtained by classical wet assay and ICP spectrometer analysis. Refer to side 2 for details of measurement uncertainties.

Classical Wet Assay: 1003 mg/L
Method: Evaporate to dryness. Fume with Nitric Acid. Ignite and weigh as V₂O₅.

Instrumental Analysis by ICP spectrometer: 1003 mg/L

Uncertified Properties:
Density: 1.010 @ 22.6 Degrees Celsius

Trace Metallic Impurities in the Actual Solution via ICP / ICPMS Analysis:

Element	mg/L	Element	mg/L	Element	mg/L
Al	0.02	Cu	0.001	Pb	0.002
As	<0.003	Fe	0.016	Rb	0.001
Ag	<0.001	Ga	<0.001	Re	<0.001
B	<0.006	In	<0.001	Si	0.15
Ba	<0.001	K	0.014	Sr	<0.001
Be	<0.001	Li	<0.001	Sb	0.001
Bi	<0.001	Mg	0.001	Ti	0.001
Ca	0.013	Mn	0.001	Tl	<0.001
Cr	<0.003	Mo	<0.001	Zr	<0.001
Cd	<0.001	Na	0.02	Zn	0.02
Co	<0.001	Ni	<0.001		

Balances are calibrated regularly with weight sets traceable to NIST #32856, #32857 and others. This CRM is guaranteed stable to +/-0.5% of the certified concentration inclusive of uncertainty of measurements and other effects, such as transpiration losses, for a period of one year from the date of certification. This guarantee is valid only when the material is kept tightly capped and transported and stored under laboratory conditions.

Date of Certification: NOV 03 **Certifying Officer:** N. Kocherakota

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Test Article Selection

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THE PACE CONSULTANTS INC.
Post Office Box 53473 Houston, Texas 77052 853/351-7800 Fax 853/351-7887
A Member of Jacobs Engineering Group

February 22, 2001

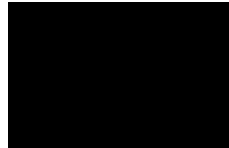


American Petroleum Institute
1220 L Street, NW
Washington, D.C. 20005-4070

Attached is Pace's report covering Task 1 and 2 entitled "U.S. Delayed Coker Petroleum Coke Quality Survey 1998-1999."

We would be pleased to answer any questions concerning this work for API. Please contact me at 832/351-7811 or email [REDACTED]

For PACE



Attachment

AMENDED

U.S. DELAYED COKER PETROLEUM COKE QUALITY SURVEY 1998-1999

INTRODUCTION

In 1998 the United States Environmental Protection Agency (EPA) challenged chemical producers and importers to provide voluntarily basic toxicity information on their high production volume (HPV) chemicals, defined as those chemicals which are produced in or imported to the U.S. in amounts greater than 1 million pounds per year. The goal of the HPV Challenge Program is to ensure that the American public has access to basic information about the hazards associated with chemicals manufactured and used in the greatest quantities in the United States. It is designed to generate the complete hazard screening data for HPV commercial chemicals.

The American Petroleum Institute (API) serves as administrator of the Petroleum HPV Testing Group, a consortium made up of 72 member companies from API, the National Petrochemical & Refiners Association (NPRA), the Gas Producers Association (GPA) and the Asphalt Institute. These companies represent 92% of the nation's refinery capacity. The Petroleum HPV Testing Group has sponsored 396 substances produced and used by the nation's petroleum industry to meet the EPA's HPV challenge.

Pace was retained by the API HPV Testing Group to assist in identifying potential sources of U.S. petroleum coke samples that could be used in the HPV testing program. As the first step in this process, Pace undertook a review of its quarterly petroleum coke production data to help characterize current U.S. petroleum coke production qualities. Pace has now completed the review of its 1998 and 1999 quarterly petroleum coke production data for all U.S.-based delayed cokers. The results of this review are discussed below.

METHODOLOGY

Pace's petroleum coke production database was used to determine quality characteristics of petroleum coke produced by U.S. refineries. Pace has conducted a survey of U.S. petroleum coker production on a quarterly basis since the second quarter of 1983. Refineries provide the bulk of the data, but some data are also gathered from other market participants. These data are maintained in a database from which the 1998 and 1999 quarterly data were extracted for this study. It was decided that data analysis would concentrate on delayed cokers (excluding needle cokers) since for 1999 our delayed coker data set includes 92+% of all the petroleum coke produced in the United States. Accordingly, fluid and Flexicokers¹ were removed from the data set.

Needle cokers were removed from the delayed coker database because needle cokers represent a special subset of delayed coking production. Needle coke differences include:

¹ Flexicoke is a proprietary coking process developed by Exxon. It involves partially gasifying fluid coke.

1. Needle coke quality is much higher than other delayed coke
2. Needle coke is produced using different feedstock & coking operational procedures because it is a product, not a by-product like other delayed cokes
3. The quantity of needle coke produced is very small
4. Needle coke is handled very carefully due to its high price (typically > \$350/metric ton)

SUMMARY AND DATA ANALYSIS

These data were analyzed to determine the ton-weighted average petroleum coke qualities of sulfur (wt%), nickel (ppm), vanadium (ppm), and volatile material (wt%). All data are presented on a dry basis. The results are presented in Table 1 below.

TABLE 1

U.S. DELAYED PETROLEUM COKE QUALITY SUMMARY TON-WEIGHTED QUARTERLY AVERAGES								
Quarter	Sulfur, Wt%		Nickel, ppm		Vanadium, ppm		Vol. Mat., Wt%	
	1998	1999	1998	1999	1998	1999	1998	1999
1Q	4.15	4.11	286	275	758	801	10.9	10.5
2Q	4.22	4.22	277	283	811	821	10.8	11.0
3Q	4.21	4.21	277	282	811	857	10.9	10.9
4Q	4.21	4.22	282	276	854	852	10.7	10.9
Ton-Wt Avg	4.20	4.19	280	279	809	833	10.8	10.8

Ton-weighted average qualities for each quarter were calculated in the following manner:

$$\frac{\sum (\text{quality value})_{\text{delayed coker}} * (\text{quarterly production})_{\text{delayed coker}}}{\text{Total quarterly production}}$$

Where:

quality value = sulfur, vanadium, nickel or volatile content of petroleum coke produced by each delayed coker

quarterly production = petroleum coke produced by that delayed coker

Pace next reviewed the data to determine a ton-weighted frequency distribution for each of the qualities listed. The results of this analysis are presented in Table 2 and in Figures 1 through 4.

TABLE 2

U.S. DELAYED PETROLEUM COKE QUALITY SUMMARY BY PRODUCTION QUARTILE								
Cumulative Production	Sulfur, Wt%		Nickel, ppm		Vanadium, ppm		Vol, Wt%	
	1998	1999	1998	1999	1998	1999	1998	1999
min.	0.90	0.50	50	5	45	45	7.0	4.0
25%	3.20	3.10	180	185	400	445	10.0	10.0
50%	4.45	4.60	250	250	650	675	10.7	10.7
75%	5.34	5.30	360	400	1205	1200	12.0	12.0
100%	6.90	6.30	568	568	1900	2000	14.0	14.0

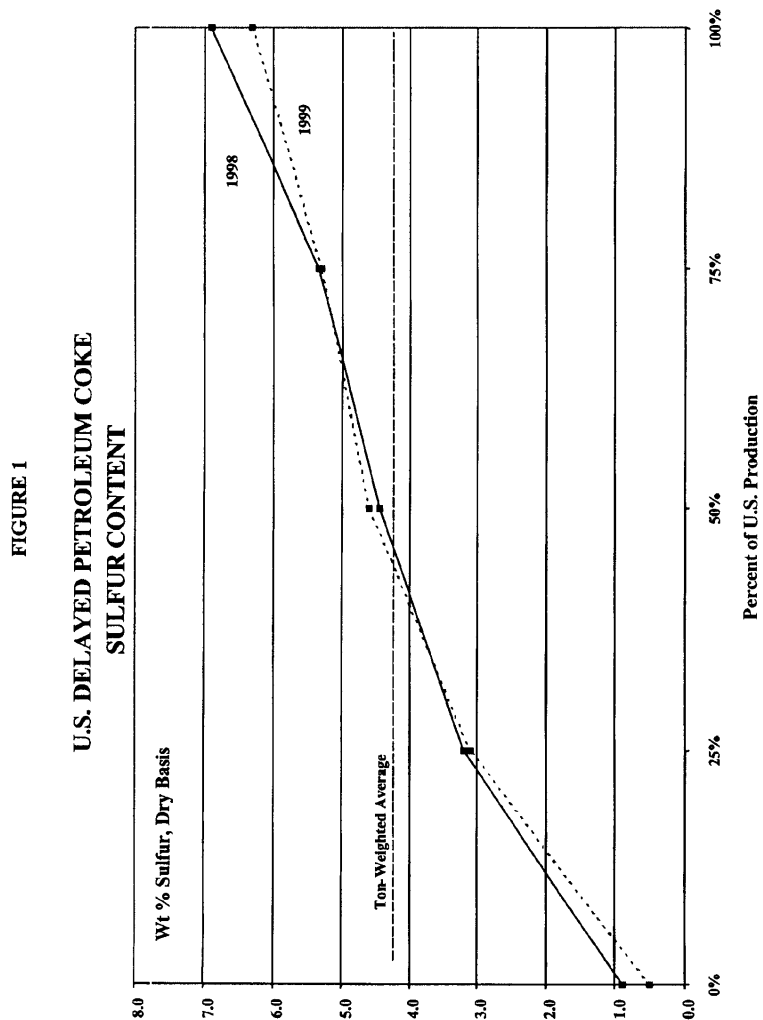
Quality quartiles for each year were calculated in the following manner:

Annual data were sorted according to each specific quality value (e.g., sulfur, vanadium, nickel, and volatile content) and the cumulative production of petroleum coke by delayed coker was calculated. Quartiles were then calculated for the annual production total, and the quality value at the cumulative total that equaled each quartile was used to determine the quality for that quartile.

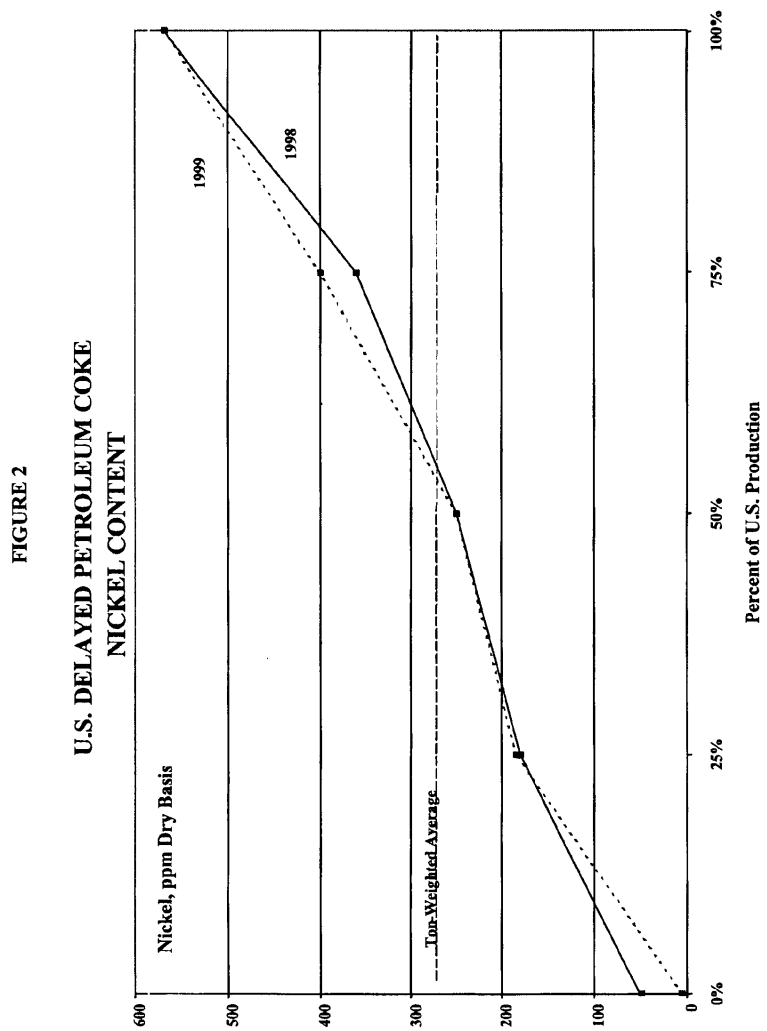
TRENDS

Comparing the ton-weighted averages to the 50% production quartile (i.e., the median) reveals the following trends:

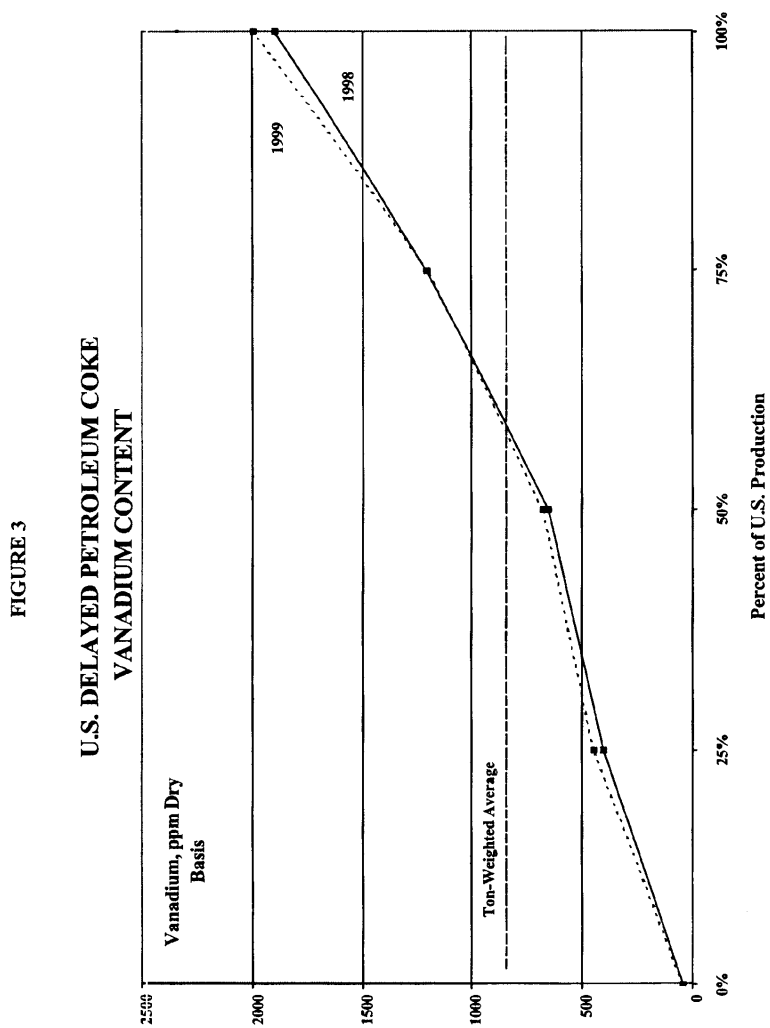
- The weighted average nickel and vanadium content of U.S. delayed petroleum coke is higher than the median. This is a direct result of the increasing amount of heavy crudes, particularly Mexican and Venezuelan crudes, processed by U.S. refineries. Because these crudes produce petroleum cokes with nickel and vanadium contents that are significantly above the median, they skew the weighted average away from the median.
- Ton-weighted sulfur content is slightly below the median because some cokers produce petroleum cokes that are well below the median sulfur content (i.e., anode-grade coke which is calcined and primarily used to make anodes for the aluminum smelting industry).



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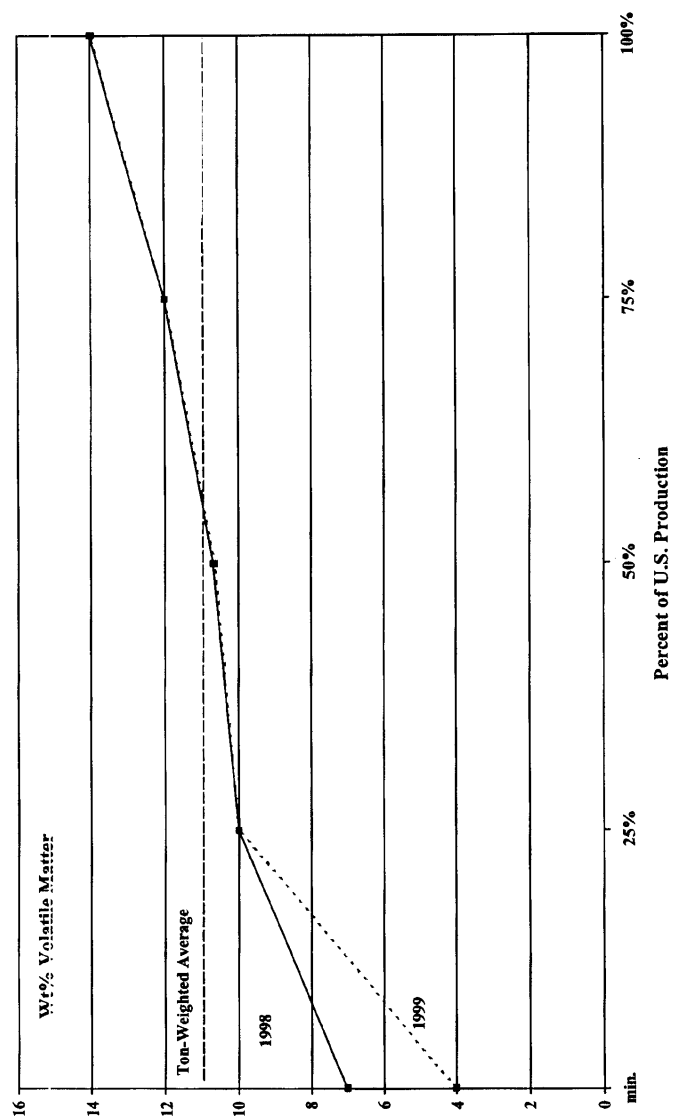


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FIGURE 4
U.S. DELAYED PETROLEUM COKE VOLATILE MATTER CONTENT



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- The sulfur content at the upper and lower ends of the quality spectrum was better in 1999 than in 1998. We believe the lower sulfur content in 1999 was a result of crude production cut-backs by OPEC (Organization of Petroleum Exporting Countries) and other crude oil producers. These producers preferentially reduced the production of their lower quality crude oils in order to minimize the production reductions of their higher quality (i.e. higher priced) crude oils. We see 1999 as an aberration in the general trend of increasing sulfur content in U.S. petroleum cokes.
- We expect the metals content and sulfur content of U.S. petroleum coke will deteriorate beginning in 2001 as new U.S. cokers scheduled to begin operations in the 2000-2002 time frame start up.
- The average volatile matter content is essentially equal to the median.

RECOMMENDATIONS

Pace identified candidate refineries for sampling based on the quality data from the third quarter of 2000, which is the most recent quarter for which data are available. It should be noted that these data may vary slightly from the 1998-1999 averages as increasing amounts of heavy crude are processed. Based on these data, Pace recommends the following candidates for sampling in support of the Petroleum HPV Testing Program:

PETROLEUM HPV TESTING PROGRAM DELAYED PETROLEUM COKE SAMPLE CANDIDATES						
	Candidate A		Candidate B		Candidate C	
	Value	Percentile	Value	Percentile	Value	Percentile
Sulfur, Wt%	6.00	93	5.75	86	5.50	80
Nickel, ppm	500	90	300	58	250	50
Vanadium, ppm	1,500	84	1,200	75	1,000	65
Volatiles, Wt%	10.00	25	12.00	75	13.00	88

PETROLEUM HPV TESTING PROGRAM DELAYED PETROLEUM COKE SAMPLE CANDIDATES						
	Candidate D			Candidate E		
	Value	Percentile		Value	Percentile	
Sulfur, Wt%	4.20	43		5.50	80	
Nickel, ppm	250	50		350	67	
Vanadium, ppm	1,500	84		1,100	70	
Volatiles, Wt%	15.00	100		10.00	25	

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Our analysis indicates that some compromises will have to be made in obtaining a sample for the HPV program since no refinery's petroleum coke is in the upper 75th percentile in all four quality parameters we have evaluated. Additionally, we have spent some time and effort trying to find petroleum cokes which are sampled with automatic sampling equipment that has been bias tested and is operated by an independent laboratory. Unfortunately, we have found that the locations with the best sampling systems have petroleum cokes of generally better quality. Therefore, we do not believe that we will be able to find a "perfect" candidate petroleum coke.

While the sampling at the candidate refineries may not be ideal, the sampling and analysis data have been used for commercial transactions. Substantial quantities of petroleum coke from each of the candidate refineries have been sold in the petroleum coke market. Commercial transactions have relied on the laboratory results for determining quality bonus and penalties and conformance with contract quality specifications. Thus, the samples taken for the HPV study would conform to generally accepted industry sampling practice.

The sampling plan would be to have the sample analyzed for the quality parameters used in this screening analysis (i.e. sulfur, vanadium, nickel, volatile matter) as well as four other commonly tested quality parameters—gross calorific value (Btu/lb), moisture (%), ash (%), and Hardgrove Grindability Index (HGI)—to verify that the sample obtained is similar to the anticipated quality characteristics. This plan would assure that the sample submitted for detailed HPV testing conforms to our quality expectations.

We may not be able to receive authorization from a refinery to use a sample of their petroleum coke for the HPV test. Our present plan would be to approach Refineries B and C regarding obtaining a sample. In the event that these two refineries choose not to participate, then the choice would be either refinery A or E, which have high sulfur and metals but low volatile content or refinery D, which has high vanadium and volatile matter but low sulfur content. (note: each of the five candidate refineries has a different corporate owner).

Pace requests that the HPV Committee confirm Pace's recommended plan to approach refineries B and C regarding obtaining an HPV sample. It is not necessary for the HPV committee to decide now on the preferred refinery to contact in the event that refineries B and C do not wish to participate in the program. However, we would suggest that the committee begin to think about this issue so that decisions can be made expeditiously in the event that refineries B and C choose not participate.

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Chevron Metals Analyses

From:
Sent:
To:
Cc:
Subject:

Found your results.

3030999 PETROLEUM COKE 2NM YCJ58009 REGULAR SERVICE *micronized*
REPORTED 06/13/2003 Marked-up: 06/12/2003 by [REDACTED] at 50-1118
[REDACTED] (474/0) Prj Id: GLOBETECH

Test code Test Name/Element/Result Test Status Analyst Status date Test Cost

30258 MICROWAVE DIGST/ICP PLUS REPORTED [REDACTED] 06/13/2003 \$200.00
AL 300.200 PPM AS <29.61 PPM B <29.61 PPM
BA <29.61 PPM BE <14.805 PPM BI <29.61 PPM
CA 121.600 PPM CD <14.805 PPM CO <14.805 PPM
CR <14.805 PPM CU <17.766 PPM FE 247.000 PPM
K <44.414 PPM LI <14.805 PPM MG 60.850 PPM
MN <29.61 PPM MO <29.61 PPM NA 114.600 PPM
NI 351.700 PPM P 30.300 PPM PB <29.61 PPM
S 58060.000 PPM SB <74.024 PPM SE <29.61 PPM
SI 554.600 PPM SN <44.414 PPM TI <14.805 PPM
V 1805.000 PPM ZN <14.805 PPM

3030251 PETROLEUM COKE YCJ58009 REGULAR SERVICE *2mm*
REPORTED 06/09/2003 Marked-up: 06/09/2003 by [REDACTED] at 50-1118
[REDACTED] (474/0) Prj Id: [REDACTED]

Test code Test Name/Element/Result Test Status Analyst Status date Test Cost

30258 MICROWAVE DIGST/ICP PLUS REPORTED [REDACTED] 06/09/2003 \$200.00
AL 321.000 PPM AS <19.279 PPM B <19.279 PPM
BA <19.279 PPM BE <9.639 PPM BI <19.279 PPM
CA 178.000 PPM CD <9.639 PPM CO <9.639 PPM
CR <9.639 PPM CU <11.567 PPM FE 310.000 PPM
K <28.918 PPM LI <9.639 PPM MG 77.370 PPM
MN <19.279 PPM MO <19.279 PPM NA 133.000 PPM
NI 367.100 PPM P <19.279 PPM PB <19.279 PPM
S 73920 PPM SB <48.197 PPM SE <19.279 PPM
SI 743.200 PPM SN <28.918 PPM TI 12.910 PPM
V 1938.000 PPM ZN 12.010 PPM

-----Original Message-----
From:

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Lancaster Laboratory PAH Analyses

AUG. 18. 2003 10:47AM CRTC THRA

Analysis Report NO. 2755 P. 2



ANALYTICAL RESULTS

Prepared for:

Chevron Products Company
940 Hensley St. Bldg. 210

Richmond CA 94801
510-242-8191

Prepared by:

Lancaster Laboratories
2425 New Holland Pike
Lancaster, PA 17605-2425

SAMPLE GROUP

The sample group for this submittal is 857532. Samples arrived at the laboratory on Friday, June 27, 2003.
The PO# for this group is 99011184 and the release number is BEATTY.

Client Description

Pet Coke 2mm Solid Sample
Pet Coke Micronized Solid Sample

Lancaster Labs Number

4073301
4073302

1 COPY TO Lancaster Laboratories
1 COPY TO Chevron CRTC

Questions? Contact your Client Services Representative
Alison M O'Connor at (717) 656-2300.

Respectfully Submitted,

MEMBER
Lancaster Laboratories, Inc.
2425 New Holland Pike
PO Box 12425
Lancaster, PA 17605-2425

AMENDED

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AUG. 18. 2003 10:47AM CRTC THRA

NO. 2755 P. 3
Analysis Report

Page 1 of 2

Lancaster Laboratories Sample No. SW 4073302

Collected: 06/26/2003 00:00

Account Number: 10863

Submitted: 06/27/2003 10:40

Chevron Products Company

Reported: 07/09/2003 at 11:42

940 Hensley St. Bldg. 210

Discard: 08/09/2003

Pet Coke Micronized Solid Sample

Richmond CA 94801

Cost Center# ENG-4066

HPV Petroleum Cake

MICPC

CAS No.	Analysis Name	CAS Number	As Received Result	As Received Method Detection Limit	Units	Dilution Factor
07804	PAHs in Soil by GC/MS					
01191	Acenaphthene	83-32-9	N.D.	1,000.	ug/kg	10
01195	Pyrene	129-00-0	8,600.	J 1,000.	ug/kg	10
02751	1-Methylnaphthalene	90-12-0	10,000.	1,000.	ug/kg	10
03761	Naphthalene	91-20-3	11,000.	1,000.	ug/kg	10
03765	Acenaphthylene	208-96-8	N.D.	1,000.	ug/kg	10
03768	Fluorene	86-73-7	1,500.	J 1,000.	ug/kg	10
03775	Phenanthrene	85-01-8	7,800.	J 1,000.	ug/kg	10
03776	Anthracene	120-12-7	3,300.	J 1,000.	ug/kg	10
03779	Fluoranthene	206-44-0	1,400.	J 1,000.	ug/kg	10
03781	Benzo(a)anthracene	56-55-3	7,100.	J 1,000.	ug/kg	10
03782	Chrysene	218-01-9	9,400.	J 1,000.	ug/kg	10
03786	Benzo(b)fluoranthene	205-99-2	3,800.	J 1,000.	ug/kg	10
03787	Benzo(k)fluoranthene	207-08-9	N.D.	1,000.	ug/kg	10
03788	Benzo(a)pyrene	50-32-8	11,000.	1,000.	ug/kg	10
03789	Indeno(1,2,3-cd)pyrene	193-39-5	3,500.	J 1,000.	ug/kg	10
03790	Dibenz(a,h)anthracene	53-70-3	4,100.	J 1,000.	ug/kg	10
03791	Benzo(g,h,i)perylene	191-24-2	8,700.	J 1,000.	ug/kg	10
04694	2-Methylnaphthalene	91-57-6	26,000.	1,000.	ug/kg	10

Due to sample matrix interferences observed during the extraction, the normal reporting limits could not be obtained.

Due to the sample matrix an initial dilution was necessary to perform the analysis. Therefore, the reporting limits for the GC/MS semivolatiles compounds were raised.

State of California Lab Certification No. 2116

Laboratory Chronicle

CAT No.	Analysis Name	Method	Trial#	Analysis Date and Time	Analyst	Dilution Factor
07804	PAHs in Soil by GC/MS	SW-846 8270C	1	07/02/2003 18:34	Susan L Scheuring	10



Lancaster Laboratories, Inc.
2425 New Holland Pike
PO Box 12425
Richmond, CA 94801-0425

AMENDED

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AUG. 18. 2003 10:47AM CRTG THRA

NO. 2755 P. 4
Analysis Report



Page 2 of 2

Lancaster Laboratories Sample No. SW 4073302

Collected: 06/26/2003 00:00

Account Number: 10863

Submitted: 06/27/2003 10:40

Chevron Products Company

Reported: 07/09/2003 at 11:42

940 Hensley St. Bldg. 210

Discard: 08/09/2003

Pet Coke Micronized Solid Sample

Richmond CA 94801

Cost Center# ENG-4066

HPV Petroleum Cake

MICPC

07806 ENA Soil Extraction

SW-846 35508

1 06/30/2003 20:00 Sally L Appleyard

1



Lancaster Laboratories, Inc.
2415 New Holland Pike
PO Box 12425
Lancaster PA 17604-7425

AMENDED

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AUG. 18. 2003 10:48AM CRTG THRA

NO. 2755 P. 5
Analysis Report

Page 1 of 1

Lancaster Laboratories Sample No. SW 4073301

Collected: 06/26/2003 00:00

Account Number: 10863

Submitted: 06/27/2003 10:40

Chevron Products Company

Reported: 07/09/2003 at 11:42

940 Hensley St. Bldg. 210

Discard: 08/09/2003

Pet Coke 2mm Solid Sample

Richmond CA 94801

Cost Center# ENG-4066

HPV Petroleum Cake

2MMPC

CAT No.	Analysis Name	CAS Number	As Received Result	As Received Method Detection Limit	Units	Dilution Factor
07804	PAHs in Soil by GC/MS					
01191	Acenaphthene	83-32-9	N.D.	330.	ug/kg	10
01195	Pyrene	129-00-0	1,300.	J 330.	ug/kg	10
02751	1-Methylnaphthalene	90-12-0	2,700.	J 330.	ug/kg	10
03761	Naphthalene	91-20-3	3,600.	330.	ug/kg	10
03765	Acenaphthylene	208-96-8	N.D.	330.	ug/kg	10
03768	Fluorene	86-73-7	340.	J 330.	ug/kg	10
03775	Phenanthrene	85-01-8	690.	J 330.	ug/kg	10
03776	Anthracene	120-12-7	N.D.	330.	ug/kg	10
03778	Fluoranthene	206-44-0	N.D.	330.	ug/kg	10
03781	Benzo(a)anthracene	56-55-3	580.	J 330.	ug/kg	10
03782	Chrysene	218-01-9	880.	J 330.	ug/kg	10
03786	Benzo(b)fluoranthene	205-99-2	520.	J 330.	ug/kg	10
03787	Benzo(k)fluoranthene	207-06-9	N.D.	330.	ug/kg	10
03788	Benzo(a)pyrene	50-32-6	1,800.	J 330.	ug/kg	10
03789	Indeno(1,2,3-cd)pyrene	193-39-5	340.	J 330.	ug/kg	10
03790	Dibenz(a,h)anthracene	53-70-3	490.	J 330.	ug/kg	10
03791	Benzo(g,h,i)perylene	191-24-2	1,100.	J 330.	ug/kg	10
04694	2-Methylnaphthalene	91-57-6	11,000.	330.	ug/kg	10

Due to the sample matrix an initial dilution was necessary to perform the analysis. Therefore, the reporting limits for the GC/MS semivolatiles compounds were raised.

State of California Lab Certification No. 2116

Laboratory Chronicle

CAT No.	Analysis Name	Method	Trial#	Analysis Date and Time	Analyst	Dilution Factor
07804	PAHs in Soil by GC/MS	SW-846 8270C	1	07/02/2003 15:41	Susan L Schouering	10
07806	DNA Soil Extraction	SW-846 3550B	1	06/30/2003 20:00	Sally L Appleyard	1



Lancaster Laboratories, Inc.
2425 New Holland Pike
PO Box 12425
Richmond, CA 94801-0425

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- 100 -

AUG. 18. 2003 10:48AM CRTC THRA

NO. 2755 P. 6
Analysis Report

Page 1 of 2

Quality Control Summary

Client Name: Chevron Products Company
Reported: 07/09/03 at 11:42 AM

Group Number: 857532

Laboratory Compliance Quality Control

Analysis Name	Blank Result	Blank MDL	Report Units	LCS <u>USEC</u>	LCS <u>USEC</u>	LCS/LCSD <u>Limits</u>	RPD	RPD Max
Batch number: 03181SLA026	Sample number(s): 4073301-4073302							
Acenaphthene	N.D.	33.	ug/kg	91		76-109		
Pyrene	N.D.	33.	ug/kg	89		71-110		
1-Methylnaphthalene	N.D.	33.	ug/kg	87		76-101		
Naphthalene	N.D.	33.	ug/kg	87		73-103		
Acenaphthylene	N.D.	33.	ug/kg	94		73-106		
Fluorene	N.D.	33.	ug/kg	93		66-115		
Phenanthrene	N.D.	33.	ug/kg	88		70-107		
Anthracene	N.D.	33.	ug/kg	86		71-107		
Fluoranthene	N.D.	33.	ug/kg	90		69-107		
Benzo(a)anthracene	N.D.	33.	ug/kg	93		74-107		
Chrysene	N.D.	33.	ug/kg	89		72-109		
Benzo(b)fluoranthene	N.D.	33.	ug/kg	95		71-113		
Benzo(k)fluoranthene	N.D.	33.	ug/kg	97		75-112		
Benzo(a)pyrene	N.D.	33.	ug/kg	94		79-111		
Indeno(1,2,3-cd)pyrene	N.D.	33.	ug/kg	88		74-113		
Dibenz(a,h)anthracene	N.D.	33.	ug/kg	95		81-118		
Benzo(g,h,i)perylene	N.D.	33.	ug/kg	92		74-114		
2-Methylnaphthalene	N.D.	33.	ug/kg	90		70-102		

Sample Matrix Quality Control

Analysis Name	MS	MSD	MS/MSD	RPD	MS	DUP	DUP	DUP
	<u>USEC</u>	<u>USEC</u>	<u>Limits</u>	<u>RPD</u>	<u>MAX</u>	<u>Conc</u>	<u>Conc</u>	<u>RPD</u>
Batch number: 03181SLA026	Sample number(s): 4073301-4073302							
Acenaphthene	107	93	48-132	14	30			
Pyrene	82	68	28-144	12	30			
1-Methylnaphthalene	75	67*	72-100	5	30			
Naphthalene	77	61	38-132	9	30			
Acenaphthylene	108	91	46-128	18	30			
Fluorene	88	75	39-137	14	30			
Phenanthrene	88	74	29-143	13	30			
Anthracene	101	85	35-138	17	30			
Fluoranthene	81	72	19-148	11	30			
Benzo(a)anthracene	89	75	26-144	14	30			
Chrysene	101	90	23-150	9	30			
Benzo(b)fluoranthene	90	74	32-140	16	30			
Benzo(k)fluoranthene	103	88	36-143	16	30			
Benzo(a)pyrene	90	72	23-154	13	30			
Indeno(1,2,3-cd)pyrene	92	78	13-155	15	30			
Dibenz(a,h)anthracene	110	88	19-163	19	30			
Benzo(g,h,i)perylene	99	83	17-152	13	30			
2-Methylnaphthalene	38	19*	32-133	6	30			

*- Outside of specification

- (1) The result for one or both determinations was less than five times the LOQ.
- (2) The background result was more than four times the spike added.

MEMBER
Lancaster Laboratories, Inc.
2425 New Holland Pike
PO Box 12425
Lancaster, PA 17606-2425

AMENDED

- 101 -

AUG. 18. 2003 10:48AM CRTG THRA

NO. 2755 P. 7
Analysis Report

Page 2 of 2

Quality Control SummaryClient Name: Chevron Products Company
Reported: 07/09/03 at 11:42 AM

Group Number: 857532

Sample Matrix Quality Control

Analysis Name	MS	MSD	MS/MSD	RPD	MRG	DUP	DUP	Dup
	4REC	4REC	Limits	RPD	MRG	Conc	RPD	Max

Surrogate Quality ControlAnalysis Name: PAHs in Soil by GC/MS
Batch number: 031818LA026

	Nitrobenzene-d5	2-Fluorobiphenyl	Terphenyl-d14
4073301	101	108	92
4073302	101	99	84
Blank	87	85	83
LCS	94	92	93
MS	105	107	88
MSD	90	90	78
Limits:	47-128	55-123	39-128

*- Outside of specification

- (1) The result for one or both determinations was less than five times the LOQ.
- (2) The background result was more than four times the spike added.

MEMBER
LABORATORYLancaster Laboratories, Inc.
2425 New Holland Pike
PO Box 12425
Lancaster, PA 17602-0425

AMENDED

- 102 -

Aveka, Inc. Milling Particle Size Analysis

AVEKA, Inc.

PARTICLE PROCESSING & CUSTOM RESEARCH

Date: May 29, 2003

Make Order #: 5369

Company Name: API

Contact Person: [REDACTED]

Material: Green Petroleum Coke

Objective: Task 1: Hammermill, Ball-mill and Classify Petroleum Coke to a mean particle size less than 3.6 microns. Task 2: Crush and Classify petroleum coke to a mean particle size of 2 mm.

Equipment: Homoloid JT Hammermill (SN # JT-694) with 0.0093 screen
5 Gallon Ball-mill with 0.25 inch alumina media
Majac A-12 classifier
Horiba LA-910 Laser Light Scattering Particle Sizer
Marcy 4"x 6" Jaw Crusher
Gilson Sonic Sieve

Receipt: Approximately 80 lbs. of material was received 3-19-03 from Federal Express. Confirmation of receipt (EPL Project Identification 1203-001) was returned upon delivery.

Storage: Petroleum coke was stored at room temperature in sealed polyethylene bags when the material was not being processed.

Processing Procedure:

The green petroleum coke showed high moisture content upon inspection. The high moisture content was indicated by condensation on the inside of the received petroleum coke bags. After consulting with Deborah Herron and Jacobs Consultancy, the material was dried according to ASTM D 3302-00 (Standard Test Method for Total Moisture in Coal).

Task 1

All processes were run at room temperature. The dried petroleum coke was then run through a Homoloid JT Hammermill (SN # JT-694) equipped with a 0.0093 screen.

The resulting hammermilled powder was loaded into 5-gallon ball mills loaded with 0.25 inch ceramic (alumina) media. The loading level in the ball mill was 27 lbs. of media with 5.5 lbs. of petroleum coke.

AVEKA, Inc.

PARTICLE PROCESSING & CUSTOM RESEARCH

The mills were rotated at 36 rpm for 17.25 hours. The resulting powder had a mean particle size of 9.56 microns (Attech 1) when tested with the Horiba LA-910 in water.

The oversized petroleum coke material was removed using a Majac A-12 Classifier. The Majac was run at 1800 RPM and 8.5 cfm. The resulting particle size of the petroleum coke was a 3.3 micron mean (Attech. 2) when tested with the Horiba LA-910 in water. The Horiba LA-910 test method for the petroleum coke samples is outlined in Attech. 3.

The final yield of product was 10.5 kg of powder.

Task 2

All processes were run at room temperature. An 18" Sweco Screener was set-up with a 7 mesh (2.8 mm) top-screen and a 14 mesh (1.4 mm) bottom-screen. Petroleum coke was fed through the screener and 2-mm material was collected from between the top and bottom screen. Oversized petroleum coke was jaw crushed with a Marcy 4"x 6" Jaw Crusher and rescreened. A Gilson Sonic Sieve particle size analysis (Attech. 4) was run on the screened petroleum coke and the results showed 99.4 % of the material between 1.4 mm - 2.8 mm. Final yield was 3.3 kg of 2 mm Petroleum Coke.

Shipping

All samples were shipped UPS Ground. The following is a summary of the sample disposition.

<u>Sample/Amount</u>	<u>Address</u>	<u>Person</u>
200 grams of 2-3 micron particle size sample	ChevronTexaco Energy Research and Technology Corp. 100 Chevron Way Richmond, CA 94802 Tel: 510-242-7037	Richard Dutta

- 105 -

AVEKA, Inc.**PARTICLE PROCESSING & CUSTOM RESEARCH**

<u>200 grams</u> of 2 mm particle sample	ChevronTexaco Energy Research and Technology Corp. 100 Chevron Way Richmond, CA 94802 Tel: 510-242-7037	Richard Dutta
<u>10.5 kg</u> of 2-3 micron particle size sample	EPI Archives, Inc. 45610 Terminal Drive Sterling, Virginia 20166 703/435-8780 ext 201	Sam Busey
Remainder (slightly less than <u>3 kg</u> of 2 mm particle size sample)	EPI Archives, Inc. 45610 Terminal Drive Sterling, Virginia 20166 703/435-8780 ext 201	Sam Busey
<u>Leftover petroleum coke material</u> , i.e., that material not used in samples	EPI Archives, Inc. 45610 Terminal Drive Sterling, Virginia 20166 703/435-8780 ext 201	Sam Busey

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Attch 1

HORIBA LA-910**PARTICLE SIZE DISTRIBUTION DATA TABLE Standard 04/23/03**

File Name: 5369001.DAT Sample Name: Ballmilled 17.25 Hours

ID No: **/04/23-350

Dist. Form: STANDARD R.R. Index: co.rj□

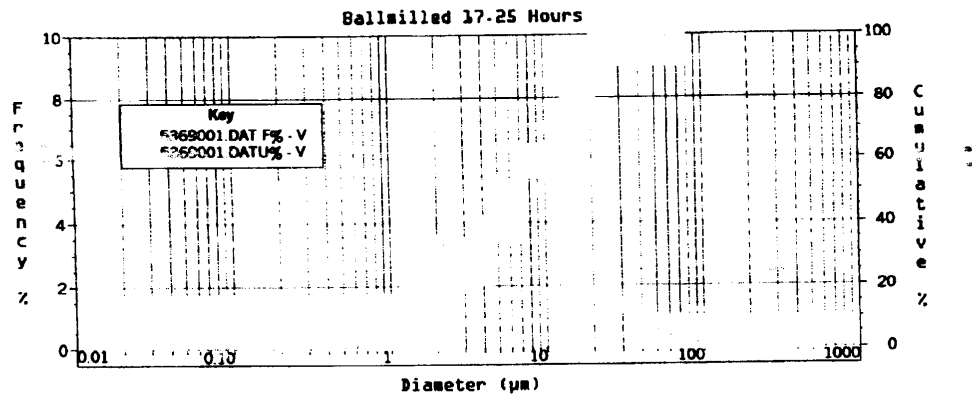
Dist. Mode: VOLUME Laser: 65.128 % Lamp: 61.185 %

Circulation: 2 Agitation: 7 U.Sonic ** (min)

Material: Petroleum Coke Source: American Petroleum

Lot No: MO5369

Test No: 5369001



				SIZE (µm)	FREQ%	UNDR%	No.	SIZE (µm)	FREQ%	UNDR%
(1)	0.020	0.0	0.0	(28)	0.766	0.5	(55)	29.907	1.5	95.4
(2)	0.022	0.0	0.0	(29)	0.877	0.8	(56)	34.255	1.2	96.6
(3)	0.026	0.0	0.0	(30)	1.005	1.2	(57)	39.234	0.9	97.5
(4)	0.029	0.0	0.0	(31)	1.151	1.6	(58)	44.938	0.7	98.2
(5)	0.034	0.0	0.0	(32)	1.318	2.0	(59)	51.471	0.5	98.8
(6)	0.039	0.0	0.0	(33)	1.510	2.3	(60)	58.953	0.4	99.2
(7)	0.044	0.0	0.0	(34)	1.729	2.6	(61)	67.523	0.3	99.5
(8)	0.051	0.0	0.0	(35)	1.981	2.9	(62)	77.340	0.2	99.7
(9)	0.058	0.0	0.0	(36)	2.269	3.0	(63)	88.582	0.2	99.9
(10)	0.067	0.0	0.0	(37)	2.599	3.2	(64)	101.460	0.1	100.0
(11)	0.076	0.0	0.0	(38)	2.976	3.5	(65)	116.210	0.0	100.0
(12)	0.087	0.0	0.0	(39)	3.409	3.7	(66)	133.103	0.0	100.0
(13)	0.100	0.0	0.0	(40)	3.905	4.0	(67)	152.453	0.0	100.0
(14)	0.115	0.0	0.0	(41)	4.472	4.3	(68)	174.616	0.0	100.0
(15)	0.131	0.0	0.0	(42)	5.122	4.6	(69)	200.000	0.0	100.0
(16)	0.150	0.0	0.0	(43)	5.867	5.1	(70)	229.075	0.0	100.0
(17)	0.172	0.0	0.0	(44)	6.720	5.5	(71)	262.376	0.0	100.0
(18)	0.197	0.0	0.0	(45)	7.697	5.9	(72)	300.518	0.0	100.0
(19)	0.226	0.0	0.0	(46)	8.816	6.0	(73)	344.205	0.0	100.0
(20)	0.259	0.0	0.0	(47)	10.097	5.8	(74)	394.244	0.0	100.0
(21)	0.296	0.0	0.0	(48)	11.565	5.4	(75)	451.556	0.0	100.0
(22)	0.339	0.0	0.0	(49)	13.246	4.8	(76)	517.200	0.0	100.0
(23)	0.389	0.0	0.0	(50)	15.172	4.2	(77)	592.387	0.0	100.0
(24)	0.445	0.0	0.0	(51)	17.377	3.5	(78)	678.504	0.0	100.0
(25)	0.510	0.0	0.0	(52)	19.904	2.9	(79)	777.141	0.0	100.0
(26)	0.584	0.1	0.1	(53)	22.797	2.3	(80)	890.116	0.0	100.0
(27)	0.669	0.2	0.3	(54)	26.111	1.9	(81)	1019.510	0.0	100.0

Median : 6.533 (µm) Mean: 9.561 (µm) Mode: 8.237 (µm)
 Std. Dev.: 10.531 (µm) Span: 10.623
 Coef. Var: 110.14% Spec. Area: 15308 (cm2/cm3)

AMENDED

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Attch. 2

HORIBA LA-910**PARTICLE SIZE DISTRIBUTION DATA TABLE** Standard 05/15/03

File Name: 5369011.DAT Sample Name: Fines

ID No: **/04/30-566

Dist. Form: STANDARD R.R. Index: co.mj□

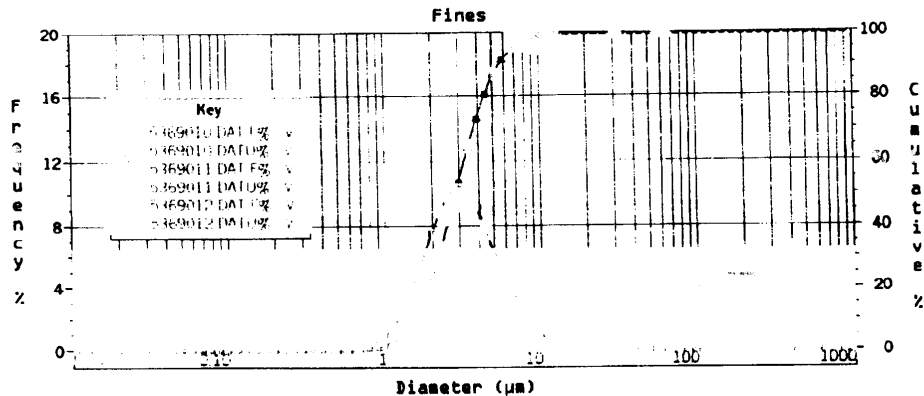
Dist. Mode: VOLUME Laser: 85.118 % Lamp: 86.338 %

Circulation: 3 Agitation: 7 U.Sonic OFF (min)

Material: Petroleum Coke Source: American Petroleum

Lot No: MO5369

Test No: 5369004



No.	SIZE (μm)	FREQ%	UNDR%	No.	SIZE (μm)	FREQ%	UNDR%	No.	SIZE (μm)	FREQ%	UNDR%
(1)	0.020	0.0	0.0	(28)	0.766	0.2	0.2	(55)	29.907	0.0	100.0
(2)	0.022	0.0	0.0	(29)	0.877	0.5	0.7	(56)	34.255	0.0	100.0
(3)	0.026	0.0	0.0	(30)	1.005	1.0	1.7	(57)	39.234	0.0	100.0
(4)	0.029	0.0	0.0	(31)	1.151	1.7	3.5	(58)	44.938	0.0	100.0
(5)	0.034	0.0	0.0	(32)	1.318	2.8	6.3	(59)	51.471	0.0	100.0
(6)	0.039	0.0	0.0	(33)	1.510	4.3	10.6	(60)	58.953	0.0	100.0
(7)	0.044	0.0	0.0	(34)	1.729	5.9	16.5	(61)	67.523	0.0	100.0
(8)	0.051	0.0	0.0	(35)	1.981	7.6	24.1	(62)	77.340	0.0	100.0
(9)	0.058	0.0	0.0	(36)	2.269	9.0	33.0	(63)	88.582	0.0	100.0
(10)	0.067	0.0	0.0	(37)	2.599	10.1	43.1	(64)	101.460	0.0	100.0
(11)	0.076	0.0	0.0	(38)	2.976	10.6	53.7	(65)	116.210	0.0	100.0
(12)	0.087	0.0	0.0	(39)	3.409	10.2	63.8	(66)	133.103	0.0	100.0
(13)	0.100	0.0	0.0	(40)	3.905	9.0	72.9	(67)	152.453	0.0	100.0
(14)	0.115	0.0	0.0	(41)	4.472	7.6	80.4	(68)	174.616	0.0	100.0
(15)	0.131	0.0	0.0	(42)	5.122	6.0	86.5	(69)	200.000	0.0	100.0
(16)	0.150	0.0	0.0	(43)	5.867	4.6	91.1	(70)	229.075	0.0	100.0
(17)	0.172	0.0	0.0	(44)	6.720	3.4	94.5	(71)	262.376	0.0	100.0
(18)	0.197	0.0	0.0	(45)	7.697	2.3	96.8	(72)	300.518	0.0	100.0
(19)	0.226	0.0	0.0	(46)	8.816	1.5	98.3	(73)	344.205	0.0	100.0
(20)	0.259	0.0	0.0	(47)	10.097	0.9	99.1	(74)	394.244	0.0	100.0
(21)	0.296	0.0	0.0	(48)	11.565	0.5	99.6	(75)	451.556	0.0	100.0
(22)	0.339	0.0	0.0	(49)	13.246	0.2	99.9	(76)	517.200	0.0	100.0
(23)	0.389	0.0	0.0	(50)	15.172	0.1	100.0	(77)	592.387	0.0	100.0
(24)	0.445	0.0	0.0	(51)	17.377	0.0	100.0	(78)	678.504	0.0	100.0
(25)	0.510	0.0	0.0	(52)	19.904	0.0	100.0	(79)	777.141	0.0	100.0
(26)	0.584	0.0	0.0	(53)	22.797	0.0	100.0	(80)	890.116	0.0	100.0
(27)	0.669	0.0	0.0	(54)	26.111	0.0	100.0	(81)	1019.510	0.0	100.0

Median : 2.840 (μm) Mean: 3.289 (μm) Mode: 2.781 (μm)

Std. Dev.: 1.844 (μm) Span: 2.780

Coef. Var: 56.08% Spec. Area: 23790 (cm²/cm³)

AMENDED

Attd. 3

TEST METHOD FOR API PETROLEUM COKE

Sample Preparation

May 15, 2003

Mix 0.15 – 0.2 grams of petroleum coke with 5-6 grams distilled water. Add TX-100 surfactant to aid dispersion. Mix thoroughly until no large concentrations of sample are evident.

LA-910 Preparation

Fill the test chamber to capacity with 140 ml distilled water. Add 3-4 drops of TX-100 surfactant from a 10% concentrate source, resulting in approximately a .1% diluted total. Select the relative refractive index appropriate for this material (1.61-3.02i). Circulate the solvent using a pump speed of 2-3, subtract the background. Add the sample drop by drop until the laser transmission falls into the acceptable range (70 – 95)% transmittance. Activate the sonicator to aid dispersion, cease sonication when sample is completely dispersed.

Sample Test

Measure the sample three times. Save each measurement. Overlay the three measurements on a graph. If they appear stable, the test is complete. If not, investigate. A steady increase in the laser transmission rate indicates more particles are present from pass to pass. That indicates the sample was not completely dispersed yet. A steady decrease in the laser transmission rate indicates the sample is agglomerating, settling, or dissolving.

Report

Using the Display module, graph the three test runs over one another. A stable test will appear as one line, an unstable condition will clearly show all three runs, indicating instability. If stable, select a run (typically the middle run) and print the complete data table along with the graph.

Author: T.J. Roberts
Lab Manager
Aveka, Inc.
(651) 714-4293 ext 208

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Atch. 4

MO5368a.xls

5/29/03

Sieve Analysis

Sample ID: American Petroleum Institute
2mm Pet Coke

US Standard Mesh Size	Mesh Opening (Microns)	Sieve Weight (Grams)	Sieve Weight + Sample (g)	Weight of Sample (g)	Sample Above Sieve	Sample Under Sieve
7	2800	50.951	50.975	0.024	0.31	39.69
8	2360	50.741	52.146	1.405	18.18	31.51
10	2000	48.772	51.024	2.252	29.14	32.37
12	1700	47.324	50.173	2.849	36.86	15.51
14	1400	48.450	49.624	1.174	15.19	0.32
catch	0	220.018	220.043	0.025	0.32	0.00
Totals:				7.729	100.00	

Notes/Comments:

AMENDED

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Appendix 3

Specific Conductance, Hardness, Alkalinity and pH of Well Water Measured
During the 4-Week Period Immediately Preceding the Freshwater Verification Test

	Mean	Range
Specific Conductance ($\mu\text{mhos/cm}$)	310 (N = 4)	310 – 310
Hardness (mg/L as CaCO_3)	131 (N = 4)	128 – 136
Alkalinity (mg/L as CaCO_3)	181 (N = 4)	180 – 182
pH	8.2 (N = 4)	8.0 – 8.3

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Appendix 4Analyses of Pesticides, Organics and Metals in Wildlife International, Ltd. Well Water¹

Pesticides and Organics			
Component	Measured Concentration (µg/L) Component		Measured Concentration (µg/L)
Aldrin	< 0.0099	Heptachlor Epoxide	< 0.0099
Alpha BHC	< 0.0099	Malathion	< 2.0
Beta BHC	< 0.040	Merphos	< 2.0
Bolstar	< 2.0	Methoxychlor	< 0.099
Chlordane	< 0.50	Methyl Parathion	< 2.0
Coumaphos	< 3.0	Mevinphos	< 2.0
Delta BHC	< 0.0099	Mirex	< 0.050
Demeton-O	< 2.0	Naled	< 3.0
Demeton-S	< 2.0	o,p-DDD	< 0.020
Diazinon	< 2.0	o,p-DDE	< 0.020
Dichlorvos	< 2.0	o,p-DDT	< 0.020
Dieldrin	< 0.020	p,p-DDD	< 0.020
Disulfoton	< 2.0	p,p-DDE	< 0.020
Dursban (Chlorpyrifos)	< 2.0	p,p-DDT	< 0.025
Endosulfan I	< 0.0099	PCB-1016	< 0.50
Endosulfan II	< 0.042	PCB-1221	< 1.2
Endosulfan Sulfate	< 0.020	PCB-1232	< 0.89
Endrin	< 0.020	PCB-1242	< 0.50
EPN	< 4.0	PCB-1248	< 0.50
Ethion	< 2.0	PCB-1254	< 0.50
Ethoprop	< 2.0	PCB-1260	< 0.50
Ethyl Parathion	< 2.0	Phorate	< 2.0
Famphur	< 2.0	Ronnel	< 2.0
Fensulfothion	< 4.0	Stirophos	< 2.0
Fenthion	< 2.0	Telodrin	< 0.0099
Gamma BHC – Lindane	< 0.0099	Tokuthion	< 2.0
Guthion (Azinphos-methyl)	< 4.0	Toxaphene	< 0.99
HCB	< 0.099	Trichloronate	< 2.0
Heptachlor	< 0.0099	Trithion	< 2.0

¹Analyses performed by Lancaster Laboratories on samples collected on December 22, 2004.

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Appendix 4 (Continued)Analyses of Pesticides, Organics and Metals in Wildlife International, Ltd. Well Water¹

Metals			
Component	Measured Concentration (mg/L) Component		Measured Concentration (mg/L)
Aluminum <	0.200	Magnesium	12.7
Antimony	< 0.0200	Manganese	< 0.0050
Arsenic	< 0.0100	Mercury	< 0.00020
Barium	< 0.0050	Nickel	< 0.0100
Beryllium	< 0.0050	Nitrate Nitrogen	< 0.50
Bromide	< 2.5	Nitrite Nitrogen	< 0.50
Cadmium <	0.0050	Potassium	6.64
Calcium 31.1		Selenium	< 0.0100
Chloride 6.9		Silver	< 0.0050
Chromium <	0.0050	Sodium	19.7
Cobalt <	0.0050	Sulfate	5.5
Copper	< 0.0100	Thallium	< 0.0200
Fluoride	< 0.50	Vanadium	< 0.0050
Iron	< 0.200	Zinc	< 0.0200
Lead <	0.0200		

¹Analyses performed by Lancaster Laboratories on samples collected on December 22, 2004.

- 113 -

Appendix 5

Personnel Involved in the Study

The following key Wildlife International, Ltd. persons were involved in the conduct or management of this study:

1. [REDACTED]
2. [REDACTED]
3. [REDACTED]
4. [REDACTED]

- 114 -

Appendix 6

Report Amendment

- | | | |
|----|-------------------------------------|---|
| 1. | Original Report:
Amended Report: | Title Page
The amended report date was added. The total number of pages was changed from 102 to 115. |
| | Reason: | To indicate that the report was amended and note change in pagination. |
| 2. | Original Report:
Amended Report: | Page 2
The amended report date was added and new signatures and dates were added. |
| | Reason: | To show the amended report date and to provide new signatures and dates for the amended report. |
| 3. | Original Report:
Amended Report: | Page 3
The audit dates for the amended report were added and a new signature and date were added. |
| | Reason: | To show the amended report audit dates and to provide a new signature and date for the amended report. |
| 4. | Original Report:
Amended Report: | Page 4
New signatures and dates were added. |
| | Reason: | To provide new signatures and dates for the amended report. |
| 5. | Original Report:
Amended Report: | Page 8
The Table of Contents was updated to show the addition of the Test Article Selection section in Appendix 2 and to add the Report Amendment appendix (Appendix 6). |
| | Reason: | The Sponsor requested that the Test Article Selection section be added to Appendix 2. |
| 6. | Original Report:
Amended Report: | Page 12
The method of selection was added to the Test Substance Section. |
| | Reason: | The Sponsor requested that the method of selection be added to the final report. |
| 7. | Original Report:
Amended Report: | Page 84
Test Article Selection was added to Appendix 2. |
| | Reason: | The Sponsor requested that the Test Article Selection section be added to Appendix 2. |

AMENDED

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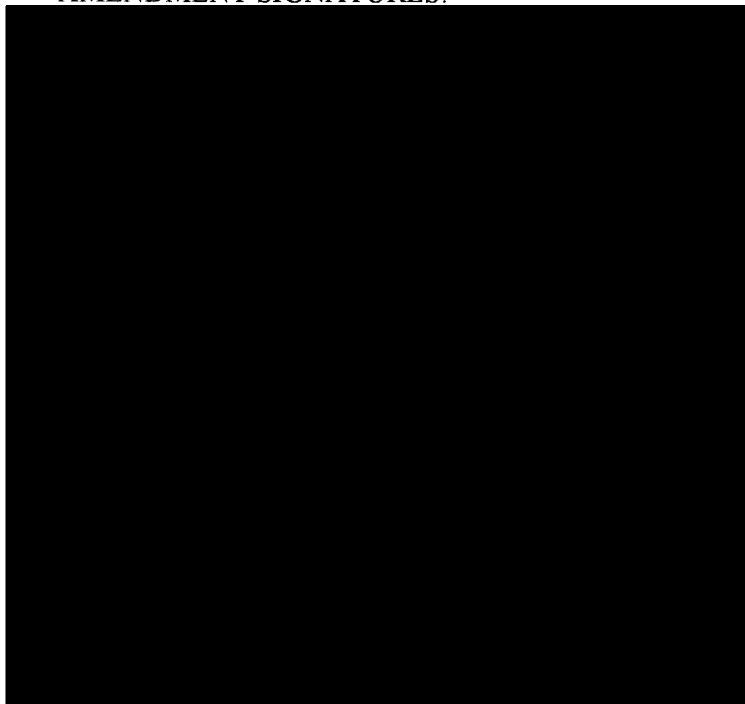
Appendix 6

(continued)

Report Amendment

- | | | |
|----|-------------------------------------|---|
| 8. | Original Report:
Amended Report: | Pages 84-102
The Test Article Selection section was added to Appendix 2, therefore all pages thereafter were renumbered. |
| | Reason: | The Sponsor requested that the Test Article Selection section be added to Appendix 2. |

AMENDMENT SIGNATURES:



April 10, 2007
Date

4/10/07
Date

4-10-07
Date

AMENDED