Memorandum

To: *Chicago Department of Public Health*

From: *Kent Whiting, LG*

Date: *December 5, 2014*

Subject: *Electron Microscopy Study Technical Memorandum*

1.0 Introduction

1.1 Objective

Electron microprobe (EMP) analyses were performed in order to identify the presence or absence of petcoke within residential dust samples collected downwind from the KCBX South storage facility in Chicago, Illinois.

1.2 Overview

Analyses on a single grain of soil or a single crystal of a precipitate were accomplished using an EMP. Not only can analyses be made on particles as small as 1 micron (μm), but the EMP also provides a visual picture of the soil at magnifications ranging from 40 to 300,000 times. The visual mode is referred to as the "backscatter mode." Information about the relative atomic number of the compounds can be obtained in the backscatter mode due to the contrast in brightness between the low atomic number compounds and the compounds with high atomic numbers. For example, iron compounds, which have high mean atomic numbers, tend to be bright white in backscatter mode, while silica compounds, with lower mean atomic numbers, are gray and carbon is nearly black. Direct visual inspection of the material also provides information on the associations, morphology, and any reaction rims on the particles; all of which provide insight into the source of the grains.

2.0   METHODOLOGY

2.1   Sample Preservation and Drying

Samples were received at the University of Colorado Laboratory for Environmental and Geological Sciences (LEGS), on September 26, 2014 (three dust samples) and October 13 (petcoke composite sample).

2.2   Sample Mount Preparation

A 1 gram split of each sample was used to prepare epoxy grain mounts. The procedure for preparing the mounts included pouring the sample into a 1-inch diameter mold and covering with a thin layer of air-cured epoxy. The grains were then blended with the epoxy using a disposable wood stirring rod and additional epoxy was added. After curing at room temperature, the mount was removed and ground flat, forming a cross sectional cut through the grains. Polishing of the mount was performed using successively finer grades of oil-based diamond paste. The final step in the preparation of the grain mounts was to apply a thin carbon coating to the surface of the mount or "puck" in order to allow proper conduction during microprobe analysis.

2.3   Operating Conditions

Operating conditions included a 15 KeV (15,000 electron volts), accelerating voltage, 17 NanoAmp cup current, and a 1 to 2 μm beam size. Certified pure element standards were used to determine phase compositions. Wavelength dispersive spectrometer (WDS) crystals PET for iron and sulfur and LDE1 for oxygen were used for the WDS analyses.

2.4   Analytical Procedure

Sample pucks were scanned for iron-containing minerals using backscattered electron images. The scanning was done manually by systematically traversing from left to right until the edge of the mount was reached. The puck was then moved up one field of view and scanned from right to left. This process was repeated until the whole mount was scanned.

Typically, the magnification used for scanning samples was 40-100X and 300-600X, depending on the individual sample's grain size distribution. The last setting allowed the smallest identifiable (1 to 2 μm) phases to be found. Once a candidate particle was identified, then the backscatter image was optimized to discriminate any different phases within the particle or its association. Identification of the iron-bearing phases was done using both energy-dispersive and wavelength-dispersive spectrometers set for analyses of sulfur, vanadium, and nickel. A macro was prepared to take into account the absorption of x-rays by elements such as iron using a "ZAF" (atomic number/absorption/fluorescence) correction (Sweatman and Long, 1969). The macro was set up to analyze for nickel (Ni), sulfur (S), vanadium (V), Silicon (Si), aluminum (Al), iron (Fe), calcium (Ca),

and magnesium (Mg), with carbon determined by difference (to get 100%). A direct analysis of carbon was not possible due to the carbon coating on the sample pucks.

2.5   Sample Collection and Preparation

2.5.1   Petcoke Samples

A total of 12 samples and 1 duplicate sample collected from the KCBX Petcoke site were submitted to the CDM Smith Denver Laboratory for drying, compositing, sieving, and homogenization prior to analysis by EMP and SW-846 Method 6010. Sulfur was analyzed using the "Sobek" total sulfur method (USEPA, 1978). A list of the samples received and the station location for each is provided in **Table 2-1**.

Table 2-1. Sample ID and Location Information

Sample ID	Station Location
S-1	1403001-01B
S-2	1403001-02B
S-3	1403001-03B
S-4	1403001-04B
S-5	1403001-05B
S-6	1403001-06B
N1	1403002-01B
N2	1403002-02B
N3	1403002-03B
N4	1403002-04B
N5	1403002-05B
N6	1403002-06B

Approximately 300 grams of each sample were received in 16 oz. glass jars. Approximately 150 grams of material were removed from each sample bottle and placed in a 12 inch round Teflon pan. The material was thoroughly mixed using a disposable plastic spoon, spread-out in the pan and placed in a fume hood to allow it to air dry for 2-days. After 2-days of air drying the material was transferred to a U.S. Sieve No. 100 (150 micron) stainless steel sieve equipped with a catch pan. The material that passed the 150 micron sieve (approximately 57 grams was then passed through a ¼ inch riffle splitter and split to 10 gram aliquots. One aliquot was submitted to Test America Denver for inorganic analyses and the other was submitted to the University of Colorado for EMP analysis.

2.5.2 Dust Samples

Three dust samples were collected by CDM Smith on September 19, 2014 from the area east of the KCBX facility. Dust samples were collected from flat, impervious surfaces (i.e., sidewalks) for electron microscopy analyses. The three sampling locations were located near the intersections of

South Buffalo Ave. and East 108th, 109th, and 110th Streets. The sampling locations are shown in Figure 2-1 and listed in Table 2-1.

The sampling locations were selected for a number of reasons. Overall, sampling locations were selected because they were distributed evenly northeast and east of KCBX South and within the residential neighborhood as close as possible to KCBX South. More specifically, sampling locations were based on being relatively unobstructed by structures or trees. The one exception to this was sampling location DST-03. At the original location selected for DST-03 on the east side of S. Buffalo Ave and E. 110th St., the resident informed CDM Smith personnel, while they were preparing to sample, that he had recently cut his lawn and used a leaf blower to remove yard debris from the sidewalk. CDM Smith surveyed several other locations in the immediate vicinity including two long-parked cars and the street, but determined the best location was the sidewalk directly across the street on the west side of S. Buffalo Ave., although it was partially obstructed by a tree.

Dust samples were collected from two to three sidewalk panels depending on how much area was needed to be swept in order to obtain approximately 1 cubic centimeter of dust. At each sampling location, dust was swept using a new, clean whisk broom. Dust on each panel was swept toward the middle of the panel and then collected using a new, clean dust pan. The dust was then transferred into laboratory-provided sample containers. Each sample container was labeled with the sampling location, date, and time. All sample containers were placed in a cooler and shipped to the University of Colorado Laboratory for Environmental and Geological Sciences (LEGS) in Boulder, Colorado.

Figure 2-1. Dust Sample Location Map

A summary of the samples analyzed is provided in **Table 2-1**.

Table 2-1. Samples Analysed

Sample Type	Sample ID	Description
Petcoke	Petcoke1	Composite of 12 samples shown in Table 2-1.
Dust	DST-01	Collected from near 10822/10816 S. Buffalo Ave.
	DST-02	Collected from near 10903 S. Buffalo Ave.
	DST-03	Collected from near 10952 S. Buffalo Ave.

2.6   Bulk Analyses

The petcoke composite sample was analyzed for target analyte list (TAL) metals, silica, sulfur, and phosphorous by EPA Method SW-846 6010.

3.0   Results

3.1   Petcoke Composite Sample

3.1.1   Petcoke Composite Raw Metals Analyses

The results of the bulk analysis for the petcoke composite sample is presented in **Table 3-1**.

Table 3-1. Bulk Petcoke Analyses (mg/kg)

Analyte	Result	Qualifier
Antimony	<1.5	
Arsenic	0.8	J
Barium	49	
Beryllium	0.28	J
Cadmium	0.13	J
Calcium	2700	
Cobalt	1.4	
Copper	4.8	B
Lead	5.5	
Magnesium	670	
Manganese	59	
Phosphorus	37	J
Potassium	67	J
Selenium	<1.3	
Silver	0.21	J
SiO2, Silica	320	
Sodium	340	J
Vanadium	560	
Zinc	58	
Aluminum	440	
Chromium	4.6	
Iron	1100	
Nickel	230	
Thallium	<1.2	
Sulfur	51,400	
Mercury	0.058	

J = Estimated value greater than the method detection limit, but less than the reporting limit

B = Estimated value above the calibration range

The results are consistent with previous petcoke analyses performed by CDM Smith, in which the major identified inorganic elements consisted of calcium, magnesium, aluminum, iron, vanadium, and nickel (sulfur concentrations were not previously determined).

### 3.1.2   Petcoke EMP Results

The petcoke particles had nearly the same backscatter intensity as the epoxy grain mount, which made them difficult to observe. However, once the contrast was adjusted the particles could be observed and analyzed. Under higher magnification, the epoxy partially melts in response to the energy of the backscatter electrons, resulting in a bubbled appearance within the photomicrographs (see Photomicrographs 1 and 2). The images were taken at magnifications of 370 times, as indicated in the lower left corner or the frames. The scale bar at the bottom left is in units of microns (μm), or millionths of a meter.

The petcoke grains had a uniform, smooth dark gray appearance within the backscatter images, due to the low atomic number of carbon (12). The light gray and white grains are aluminosilicate minerals (common dust) which have higher mean atomic numbers. The identification of the grains consists of the major element, in this case carbon ("C") along with the accessory constituent , in this case sulfur ("S") shown in parentheses.
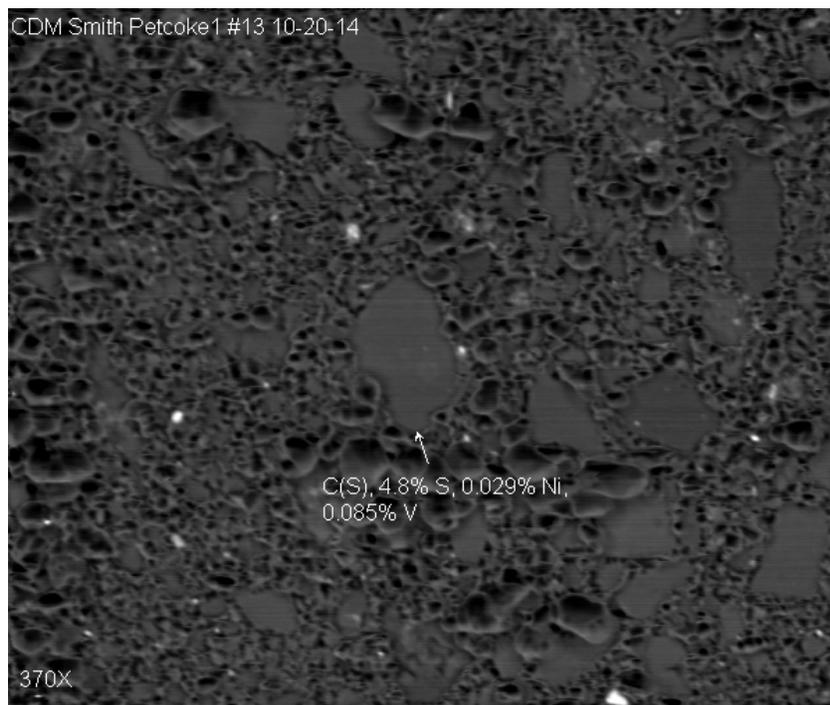
Photomicrograph 1 – Sample Petcoke1 showing multiple petcoke grains (uniform gray) within the epoxy matrix (porous).

CDM Smith Petcoke 1 #2 10-20-14

C(S), 5.4% S, 0.034%
Ni, 0.099% V

370X

50μm

BEI
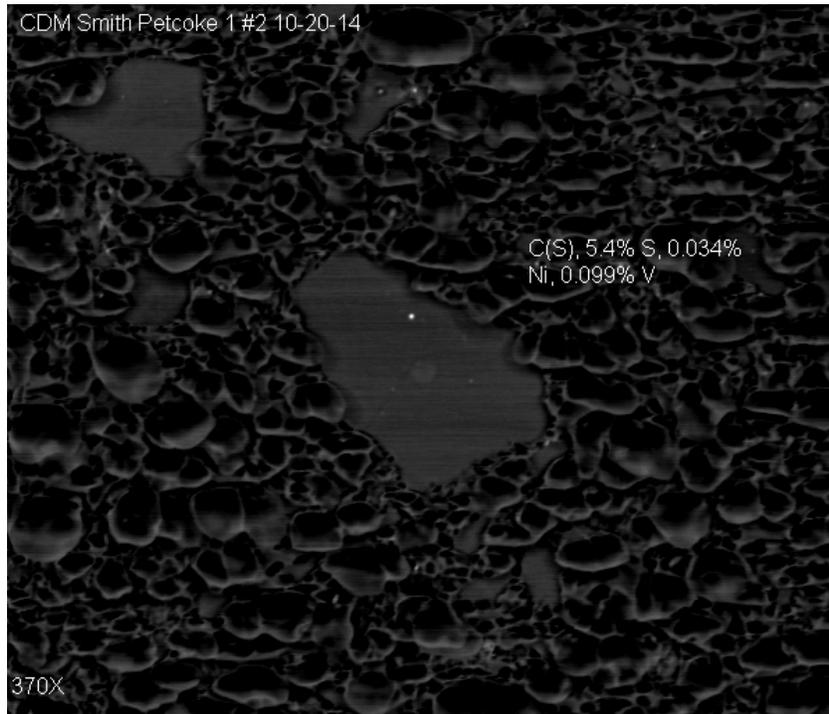
*Photomicrograph 2 – Sample Petcoke1 showing multiple
petcoke grains (uniform gray) within the epoxy matrix (porous).*

The grains consisted of mostly carbon, but the amount could not be quantified due to the carbon coating used on the sample mount. The most important inorganic constituent was sulfur, as shown in the energy dispersive spectrograph in **Figure 3-1**.
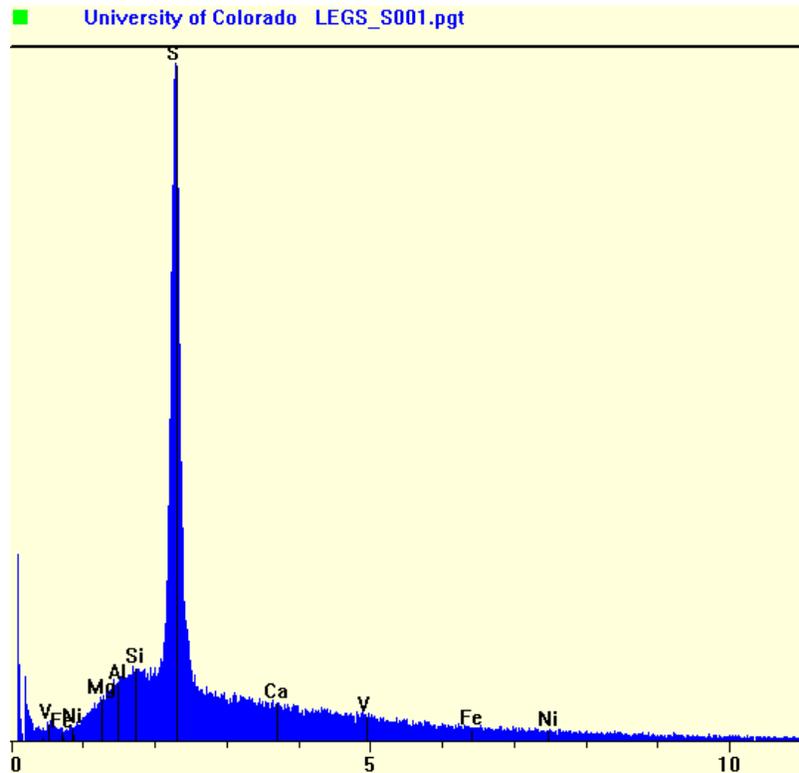
Figure 3-1. Energy dispersive spectrograph for a carbon-rich grain within sample Petcoke1

Analyses of 12 of the grains (see **Table 3-2**) showed that the sulfur concentrations ranged from 3.2 to 6.2% with a median value of 5.2%. These sulfur concentrations are consistent with petcoke analyses provided in the literature which indicate a sulfur content of a "typical" petcoke of 5.5%, although the concentrations can range up to 7% or more (Fan 2010).

Table 3-2. Summary of Analyses of Individual Petcoke Grains by EMP (Weight %)

| Sample	No	Weight %									V/Ni
		Ni	S	V	C[1]	Si	Al	Fe	Ca	Mg	
Petcoke1	3	0.032	5.00	0.092	94.85	0.002	0.009	0.013	0.008	0.001	2.90
	4	0.034	5.36	0.099	94.50	0.001	0.003	0.002	0.004	0.000	2.93
	5	0.044	6.15	0.113	93.69	0.001	0.000	0.002	0.002	0.001	2.56
	6	0.038	3.92	0.091	95.91	0.008	0.017	0.013	0.006	0.003	2.37
	7	0.021	5.92	0.061	93.98	0.004	0.010	0.002	0.000	0.000	2.84
	8	0.025	4.64	0.086	95.21	0.003	0.011	0.021	0.003	0.002	3.42
	9	0.031	4.88	0.068	95.01	0.004	0.004	0.000	0.000	0.000	2.16
	10	0.036	5.87	0.106	93.98	0.003	0.000	0.009	0.000	0.000	2.96
	11	0.037	6.07	0.100	93.76	0.001	0.010	0.020	0.003	0.001	2.68
	12	0.007	3.16	0.034	96.58	0.009	0.184	0.000	0.026	0.000	4.88
	25	0.035	6.20	0.100	93.62	0.006	0.003	0.019	0.016	0.001	2.86
	27	0.029	4.78	0.085	95.07	0.004	0.004	0.020	0.005	0.000	2.89
Minimum		**0.007**	**3.16**	**0.034**	**93.62**	**0.001**	**0.00**	**0.00**	**0.00**	**0.00**	**2.16**
Maximum		**0.044**	**6.20**	**0.113**	**96.58**	**0.009**	**0.184**	**0.021**	**0.026**	**0.003**	**4.88**
Average		**0.031**	**5.16**	**0.086**	**94.68**	**0.004**	**0.021**	**0.010**	**0.006**	**0.001**	**2.96**
Standard Deviation		**0.010**	**0.96**	**0.022**	**0.94**	**0.003**	**0.051**	**0.009**	**0.008**	**0.001**	**0.69**
Median		**0.033**	**5.18**	**0.091**	**94.67**	**0.003**	**0.007**	**0.011**	**0.004**	**0.00**	**2.88**

1. Determined by difference

Sulfur concentrations were consistent with the bulk petcoke analysis (5.14%, **Table 3-1**). Aluminosilicate grains were identified within the Petcoke1 sample during the EMP analysis. The grains appear white or gray in backscatter mode, as shown in Photomicrograph 1. Some areas of the sample mount contained abundant aluminosilicate grains, much more than appear in Photomicrograph 1.

Concentrations of vanadium and nickel were also elevated compared to other organic materials, with median values of 0.091% (910 mg/kg) and 0.033% (330 mg/kg), respectively. The vanadium to nickel ratio had a median value of 2.9. Concentrations of iron, calcium, aluminum, and magnesium were lower than for the bulk petcoke analysis due to the presence of some aluminosilicate grains within the petcoke samples (see white grains in Photomicrograph 1).

3.2   Dust Samples

3.2.1   Dust Sample EMP Results

Two types of vanadium- and nickel-bearing grains were found in the dust samples; one with high sulfur (see photomicrographs 3, 4, and 5) and little or no accessory elements and the other one with variable sulfur (photomicrograph 6) and percent levels of accessory elements such as calcium, aluminum, and iron. The high sulfur/low accessory element grains were identical in appearance and composition to the carbon-rich grains within the petcoke composite sample (petcoke1). The sulfur concentrations of the high sulfur grains which were consistent with petcoke ranged from 6.0 to 6.5%, while the variable sulfur/high accessory element grains had sulfur percentages ranging from 0.1% to 1.7% (with one outlier at 6.2% within sample DST-01).
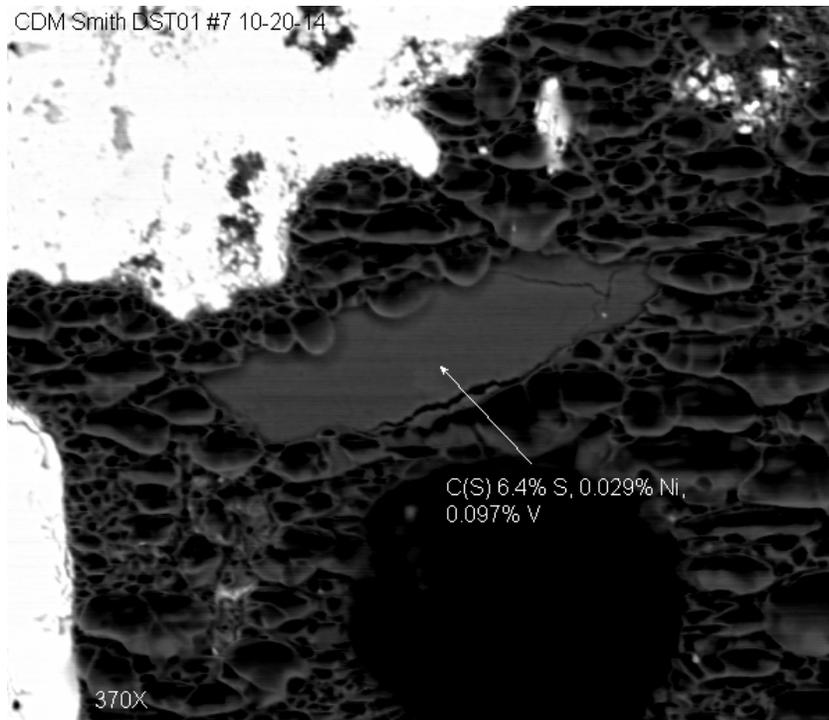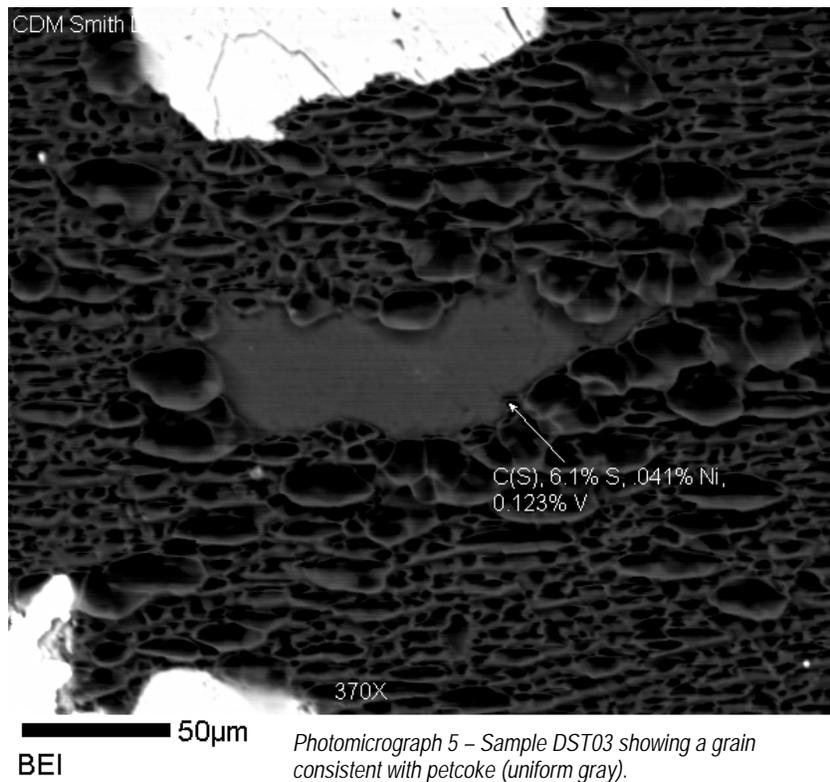

Photomicrograph 3 – Sample DST01 showing a grain consistent with petcoke (uniform gray).
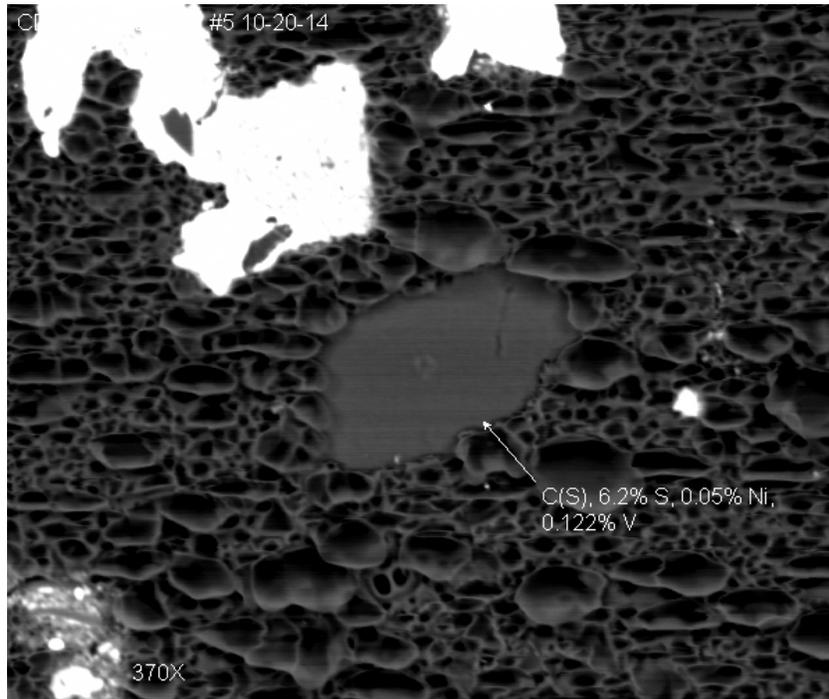
Photomicrograph 4 – Sample DST02 showing a grain consistent with petcoke (uniform gray).

Photomicrograph 5 – Sample DST03 showing a grain consistent with petcoke (uniform gray).

Photomicrograph 6 – Low sulphur carbon-rich grain within sample DST-01.
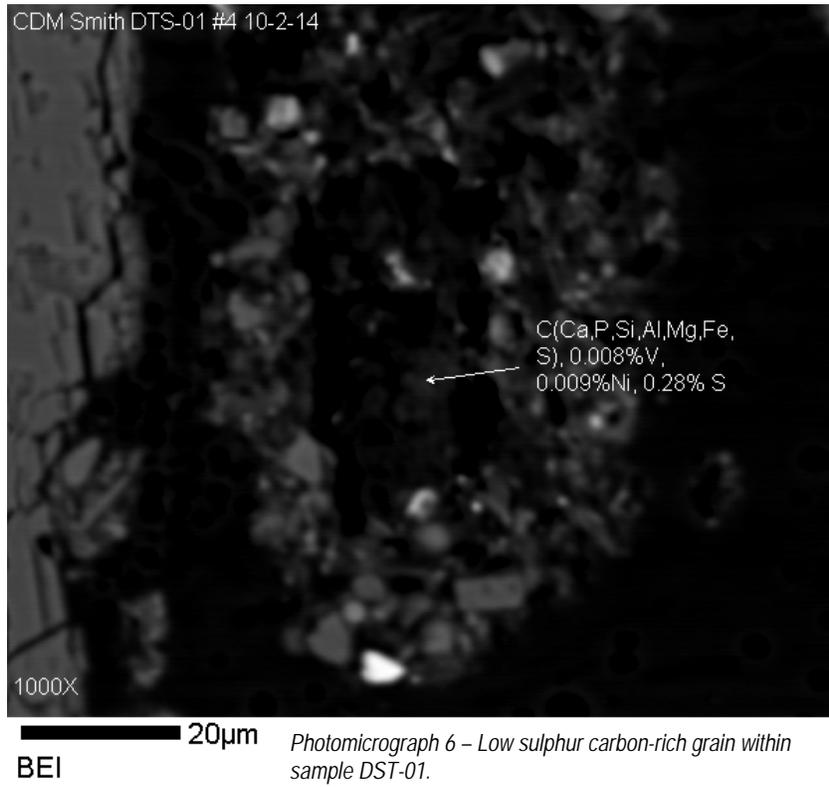
The high sulfur grains had identical spectrographs when compared to the grains within the Petcoke composite sample, as shown in **Figure 3-2**.
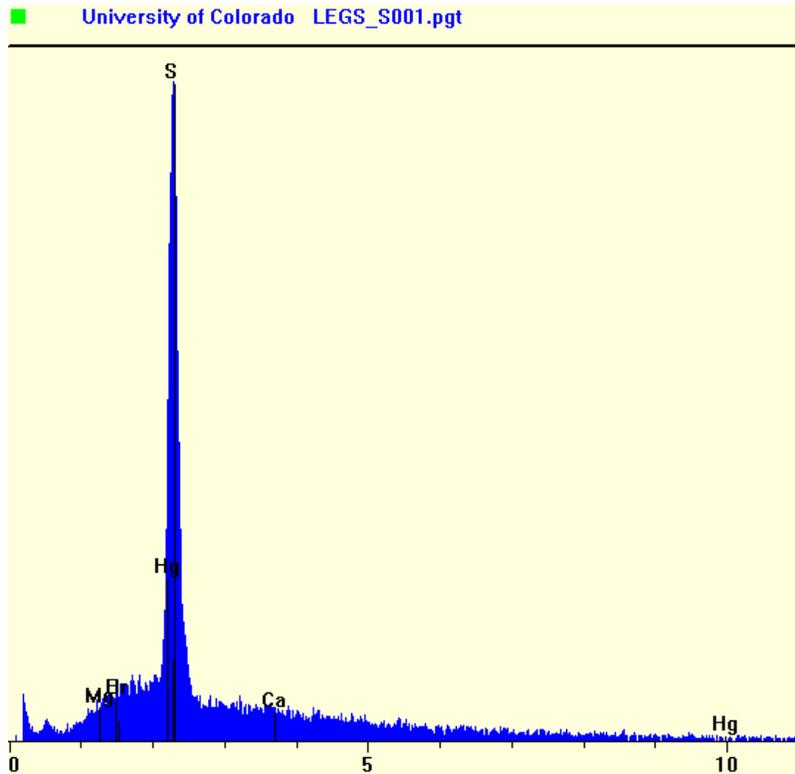
Figure 3-2. Energy dispersive spectrograph for a high-sulfur carbon-rich grain within sample DST-03

The variable sulfur grains had significant accessory elements such as calcium, phosphorous, silicon, and aluminum, as shown in the spectrograph presented in **Figure 3-3**.
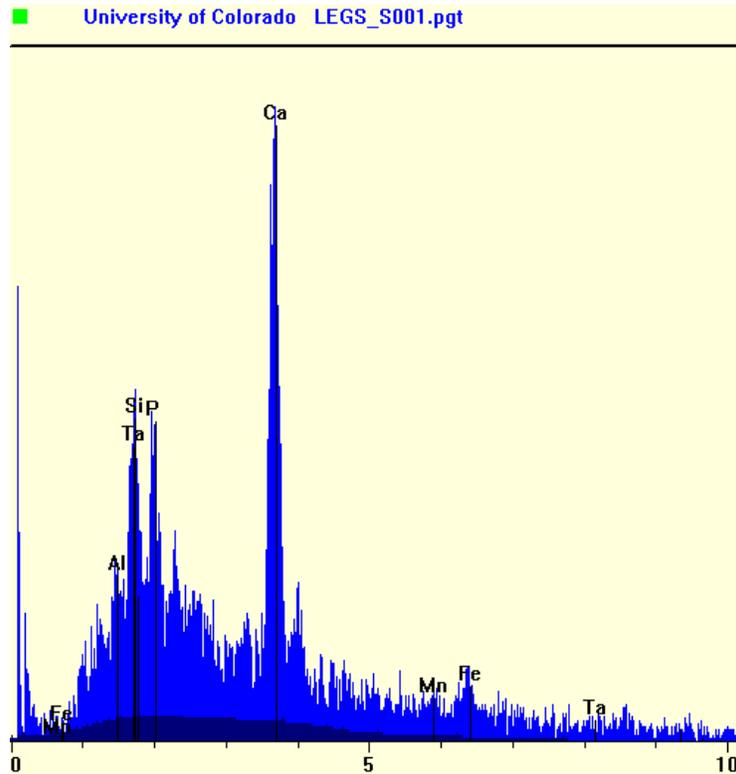

Figure 3-3. Energy dispersive spectrograph for a low-sulfur carbon-rich grain within sample DST-01

The analyses shown in **Tables 3-3** through **3-5** show that concentrations of vanadium and nickel as well as the vanadium:nickel ratio are higher for the non-mineral-accessory versus high-mineral-accessory grains.

Table 3-3. Summary of Analyses of Individual Grains from Sample DST01 by EMP (Weight %)

Sample	No	Weight %									V/Ni
		Ni	S	V	C	Si	Al	Fe	Ca	Mg	
DST01	1	0.000	0.66	0.016	99.33	-[1]	-	-	-	-	-
	2	0.005	0.49	0.007	99.50	-	-	-	-	-	1.33
	3	0.000	6.32	0.007	93.67	-	-	-	-	-	-
	4	0.009	0.28	0.008	99.70	-	-	-	-	-	0.90
	5	0.004	0.56	0.010	99.42	-	-	-	-	-	2.56
	13	0.000	1.04	0.011	98.90	0.009	0.000	0.027	0.011	0.000	-
	14	0.029	6.38	0.097	93.43	0.010	0.000	0.039	0.016	0.000	3.31
	15	0.043	6.13	0.101	93.61	0.011	0.005	0.078	0.024	0.000	2.36
	24	0.048	6.24	0.105	93.54	0.002	0.000	0.053	0.007	0.000	2.20
	26	0.035	6.27	0.113	93.48	0.005	0.000	0.094	0.000	0.000	3.24
Minimum*		0.029	6.13	0.097	93.43	0.002	0.000	0.039	0.000	-	2.20
Maximum*		0.048	6.38	0.113	93.61	0.011	0.005	0.094	0.024	-	3.31
Average*		0.039	6.26	0.104	93.52	0.007	0.001	0.066	0.011	-	2.78
Standard Deviation*		0.008	0.10	0.007	0.08	0.004	0.002	0.024	0.010	-	0.58
Median*		0.039	6.26	0.103	93.51	0.007	0.000	0.066	0.011	-	2.80

Shading indicates grain consistent with Petcoke

*Statistics on grains consistent with petcoke (shaded)

1. "-" indicates that the element was not analyzed

Table 3-4. Summary of Analyses of Individual Grains from Sample DST02 by EMP (Weight %)

Sample	No	Weight %									V/Ni
		Ni	S	V	C	Si	Al	Fe	Ca	Mg	
DST02	6	0.002	0.38	0.007	99.61	-[1]	-	-	-	-	3.43
	1	0.004	0.38	0.006	94.17	1.537	0.759	0.740	2.403	-	1.43
	2	0.015	1.65	0.060	98.21	0.010	0.002	0.048	0.009	-	4.00
	3	0.018	0.10	0.009	93.74	1.923	0.669	0.441	3.100	-	0.51
	4	0.000	0.27	0.008	96.83	0.112	0.029	0.040	2.718	-	-
	20	0.050	6.23	0.122	93.53	0.004	0.001	0.056	0.005	0.001	2.44
	21	0.039	6.11	0.114	93.69	0.011	0.003	0.005	0.028	0.001	2.93
	22	0.035	6.17	0.108	93.65	0.017	0.001	0.016	0.002	0.000	3.12
	23	0.039	5.99	0.091	93.82	0.008	0.001	0.033	0.015	0.001	2.32
Minimum*		**0.035**	**5.99**	**0.091**	**93.53**	**0.004**	**0.001**	**0.005**	**0.002**	**-**	**2.32**
Maximum*		**0.050**	**6.23**	**0.122**	**93.82**	**0.017**	**0.003**	**0.056**	**0.028**	**-**	**3.12**
Average*		**0.041**	**6.13**	**0.109**	**93.67**	**0.010**	**0.001**	**0.027**	**0.012**	**-**	**2.70**
Standard Deviation*		**0.007**	**0.10**	**0.013**	**0.12**	**0.006**	**0.001**	**0.022**	**0.012**	**-**	**0.38**
Median*		**0.039**	**6.14**	**0.111**	**93.67**	**0.010**	**0.001**	**0.024**	**0.010**	**-**	**2.68**

Shading indicates grain consistent with Petcoke

* Statistics on grains consistent with petcoke (shaded)

1. "-" indicates that the element was not analyzed

Table 3-5. Summary of Analyses of Individual Grains from Sample DST03 by EMP (Weight %)

Sample	No	Weight %									V/Ni
		Ni	S	V	C	Si	Al	Fe	Ca	Mg	
DST03	5	0.013	0.53	0.011	90.98	2.311	1.111	1.142	3.910	-[1]	0.83
	6	0.024	0.40	0.012	86.36	6.690	1.884	1.930	2.700	-	0.51
	7	0.010	0.79	0.007	98.73	0.033	0.004	0.030	0.402	-	0.71
	8	0.000	0.18	0.016	90.72	3.810	2.032	2.539	0.707	-	-
	16	0.038	6.46	0.113	93.36	0.007	0.001	0.012	0.009	0.000	2.95
	17	0.041	6.07	0.123	93.73	0.001	0.000	0.024	0.006	0.000	3.01
	18	0.038	6.29	0.095	93.48	0.006	0.000	0.086	0.002	0.000	2.52
	19	0.041	6.06	0.116	93.76	0.002	0.000	0.007	0.015	0.000	2.86
Minimum*		**0.038**	**6.06**	**0.095**	**93.36**	**0.001**	**0.000**	**0.007**	**0.002**	**-**	**2.52**
Maximum*		**0.041**	**6.46**	**0.12**	**93.76**	**0.007**	**0.001**	**0.086**	**0.015**	**-**	**3.02**
Average*		**0.039**	**6.22**	**0.11**	**93.58**	**0.004**	**0.000**	**0.032**	**0.008**	**-**	**2.84**
Standard Deviation*		**0.002**	**0.19**	**0.01**	**0.19**	**0.003**	**0.001**	**0.036**	**0.006**	**-**	**0.22**
Median*		**0.039**	**6.18**	**0.12**	**93.61**	**0.004**	**0.000**	**0.018**	**0.007**	**-**	**2.90**

Shading indicates grain consistent with Petcoke

* Statistics on grains consistent with petcoke (shaded)

1. "-" indicates that the element was not analyzed

The variable sulfur/high-accessory element particles appear to be coal grains (which are dominated by calcium) or possibly some other organic particle such as diesel soot or a combination of two or more carbon-rich materials. Coal is classified by sulfur content as follows (USGS, 1983):

- Low sulfur - ≤1% sulfur

- Medium sulfur – >1-<3% sulfur

- High sulfur - ≥3% sulfur

Of the 15 carbon-rich grains analyzed which were different from the grains within the petcoke composite sample, two would classify as medium sulfur coal, one as high sulfur and the balance as low sulfur. An example set of analyses for a bituminous coal using a very similar analysis technique is provided in **Table 3-6**.

Table 3-6 – ED-XRF Analyses of Nigerian Coal Samples in mg/kg (Adekola et al., 2012)

Element	Onyeama	Okpara	Okaba	Iva	Chikila	Lafia obi	Jankwa S.
S	3015	8614	7002	2996	7811	3503	4511
K	213	667	792	106	401	185	291
Ca	533	9751	8201	3852	1.604	355	5966
V	8.11	137	106.3	15	15.2	9	9.1
Mn	45.81	130.2	86	155.8	69	62.3	51.97
Fe (%)	7.11	5.02	5.585	7.771	7.1	9.07	8.72
Ni	87.1	1450.8	933	149.2	277	296	158
V/Ni	0.09	0.09	0.11	0.10	0.05	0.03	0.06

The most important inorganic components of the low sulfur Nigerian coal were sulfur, iron and calcium, giving a composition consistent with the variable sulfur, high accessory element carbon-rich grains within the dust samples. The V/Ni ratio for the Nigerian coal was lower than for the low sulfur carbon-rich grains within the dust samples. Analyses for some high sulfur coals within the Illinois Basin are provided in **Table 3-7**.

Table 3-7 – Median Inorganic Constituent Concentrations within Coal Samples from the Illinois Basin in mg/kg (USGS, 2002)

Element	Danville Coal	Baker Coal in KY	Herrin Coal in IL	Springfield Coal	Nonassessed Coal in the Illinois Basin
S	31,000	36,000	32,000	33,000-35,000	36,000
K	2300	1700	1500	1500	1400
Ca	3700	2700	4200	4000	650
V	20	25	18	19	17
Mn	48	36	39	34	22
Fe (%)	1.7	2.5	1.6	1.8	1.9
Ni	27	31	13	10	25
V/Ni	0.74	0.81	1.4	1.9	0.68

The concentrations of iron and the V/Ni ratio within the Illinois coal samples, are consistent with the low sulfur carbon-rich grains within the dust samples, while the calcium and sulfur concentrations appear to be different. The two examples of coal analyses illustrate the high variability among different types of coal from different locations. The low carbon-rich grains within the dust samples appear to be consistent with coal, although this cannot be confirmed without performing EMP analyses on site-specific coal sources.

3.3   Comparisons

Petcoke grains within sample petcoke1 were compared to the high sulfur/low accessory element carbon-rich grains within the dust samples. The results are shown within the box plots in **Figure 3-4** through **3-6,** for sulfur, vanadium, and nickel, respectively. The tops of the boxes represent the 75th percentile, the bottoms represent the 25th percentile, and the red square represents the 50th percentile (the median). The region between the green diamonds represents the range.

Sulfur (Weight Percent)

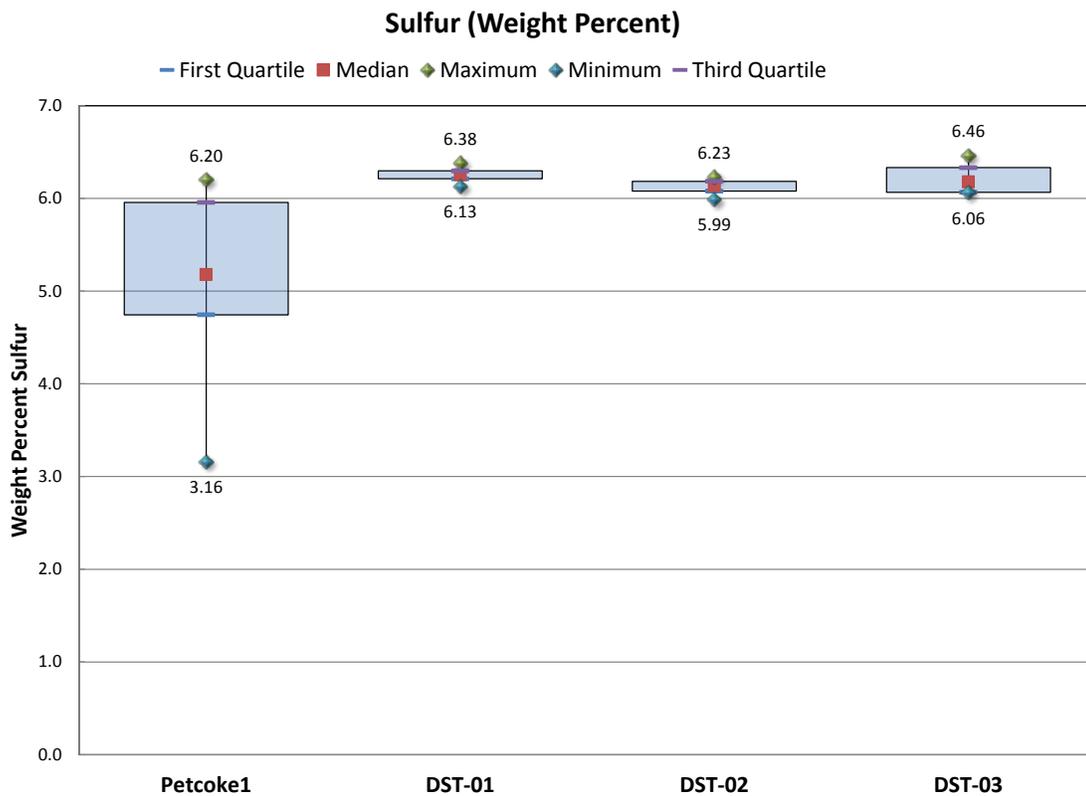─ First Quartile ■ Median ◆ Maximum ◆ Minimum ─ Third Quartile

Figure 3-4. Box and whiskers plot comparing the sulfur content of the petcoke composite sample to each of the three dust samples (Petcoke1 n = 12, DST-01 n=4, DST-02 n = 4, DST-03 n = 4)
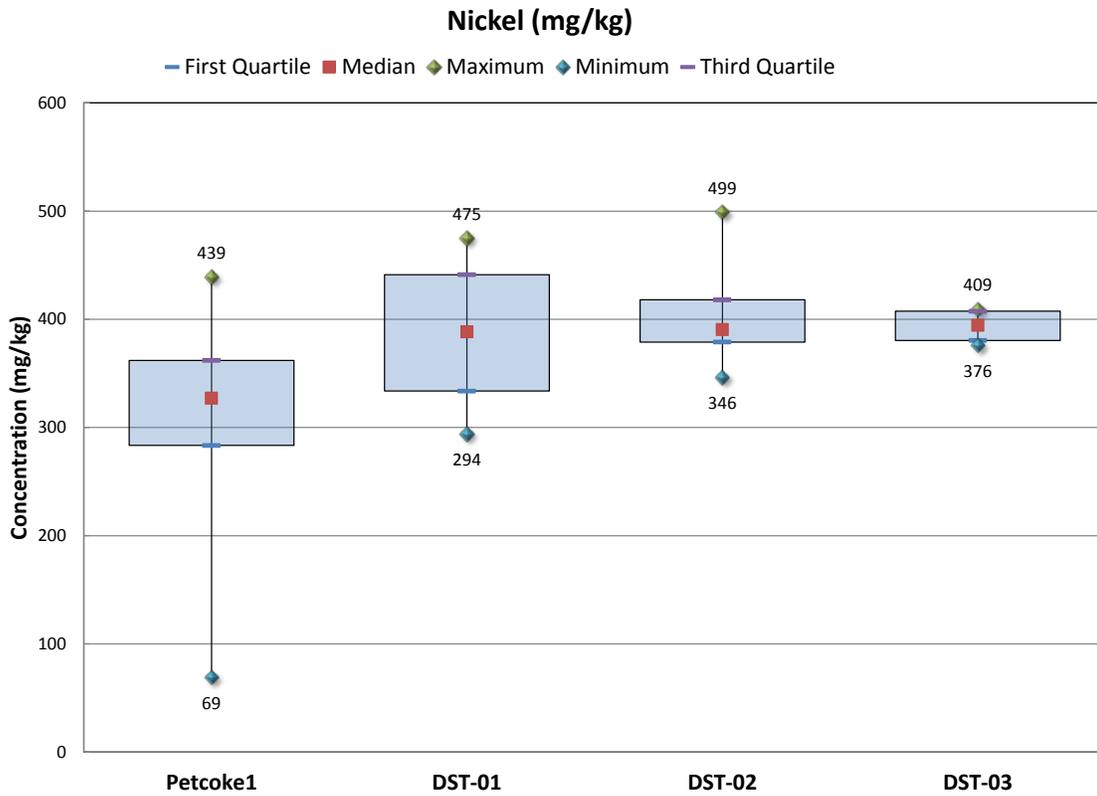
Figure 3-5. Box and whiskers plot comparing the nickel content of the petcoke composite sample to each of the three dust samples (Petcoke1 n = 12, DST-01 n=4, DST-02 n = 4, DST-03 n = 4)
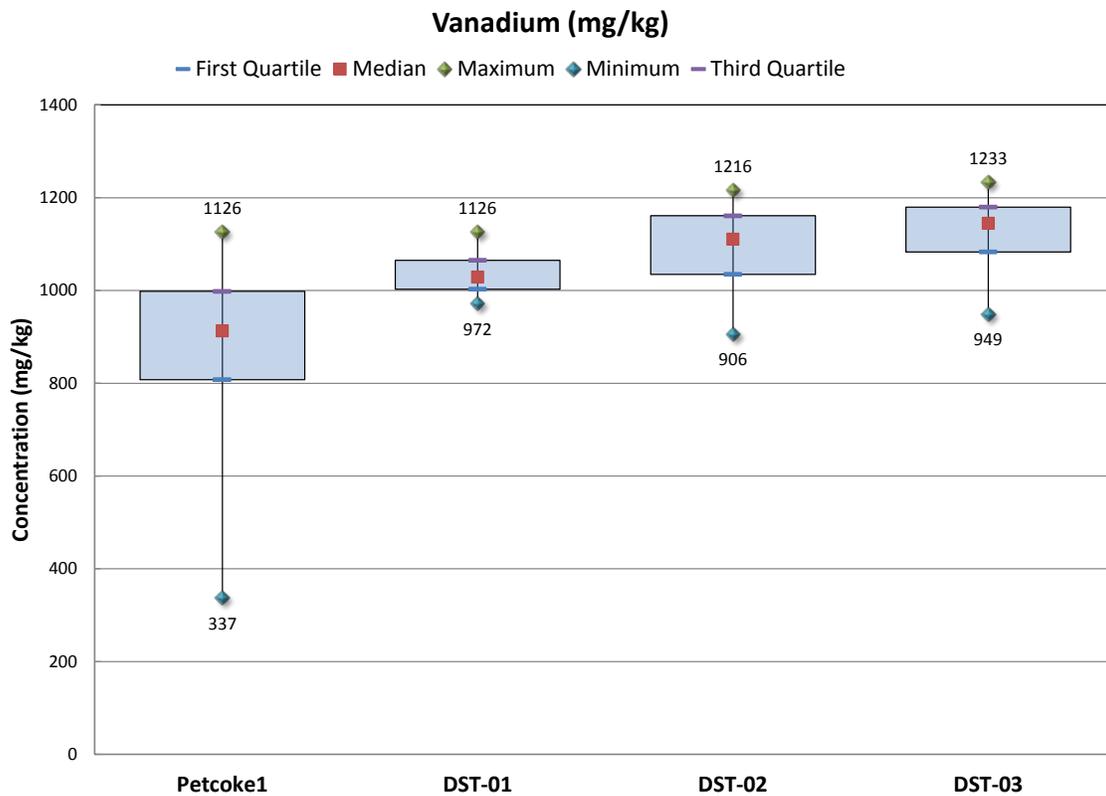
Vanadium (mg/kg)

Figure 3-6. Box and whiskers plot comparing the vanadium content of the petcoke composite sample to each of the three dust samples (Petcoke1 n = 12, DST-01 n=4, DST-02 n = 4, DST-03 n = 4).

In general, the concentrations of sulfur vanadium, zinc and nickel for the dust samples were within or slightly above the upper end of the range for the petcoke composite. The concentrations of these elements within the high sulfur/low accessory element carbon-rich particles are consistent with the petcoke1 particles and the analyses for bulk petcoke found in the literature (see **Tables 3-7** and **3-8**).

Table 3-7. Major element analysis for a typical petcoke (Fan, 2010)

Constituent	Content (weight %)
C	86
S	5.5
H	3.6
O	1.7
N	1.8

Table 3-8 - Trace element analyses for petcoke (Fan, 2010)

Constituent	Average	Minimim	Maximum
V	1160	330	2500
Ni	250	200	500
Si	150	100	500
Ca	230	100	300
Fe	90	200	650
Na	40	100	300

4.0   Conclusions

The high sulfur/low accessory element carbon rich grains within all three dust samples were consistent with the petcoke composite sample grains, in terms of morphology, backscatter intensity, and composition. The low sulfur carbon-rich grains are consistent with coal or possibly diesel soot, or both.

5.0   References

Adekola, F.A., Baba, A.A., and S. Buhari. 2012. Physico-chemical characterization and speciation of sulphur of Nigerian coal samples. *Journal of Minerals and Materials Characterization and Engineering*, v. 11, p. 965-969.

Fan, Xiaofei. 2010. *The Fates of Vanadium and Sulfur Introduced with Petcoke to Lime Kilns.* University of Toronto MS thesis.

Sweatman, T.R. and J.V.P. Long. 1969. Quantitative electron-probe microanalysis. *Journal of Petrology*. v. 10, p. 332-379.

United States Environmental Protection Agency (USEPA). 1978. *Field and Laboratory Methods Applicable to Overburdens and Minesoils*. EPA-600/2-78-054. March 1978.

United States Geological Survey (USGS), 1983. *Coal Resource Classification System of the U.S. Geological Survey.* By Gordon H. Wood, Jr., Thomas M. Kehn, M. Devereux Carter, and William C. Culbertson. Geological Survey Circular 891.

USGS, 2002. *Resource Assessment of the Springfield, Herrin, Danville, and Baker Coals in the Illinois Basin.* By J.R. Hatch, R.H. Affolter. U.S. Geological Survey Professional Paper 1625–D.