

METALS DISTRIBUTION IN SHALE OIL FRACTIONS

K. F. Jackson, J. E. Benedik and F. A. Birkholz
U.S. Department of Energy
Laramie Energy Technology Center
P. O. Box 3395, University Station
Laramie, WY 82071

ABSTRACT

This paper describes a study conducted by the Laramie Energy Technology Center to determine the metals distribution in shale oil and shale oil fractions. The shale oil was produced from the Rock Springs Site #9 field test and was fractionated by distillation. The shale oil fractions (oils, naphtha, light distillates, heavy distillates, and the residuum) were all digested for atomic absorption analysis. Flame and graphite furnace techniques were used to determine the distribution of the alkali earths and the transition metals in the shale oil and fractions.

INTRODUCTION

As shale oil production approaches reality as an industrial process, the upgrading of the crude product to useful liquid fuels is receiving more attention (1). An important aspect of shale oil upgrading which has received little coverage in the public literature is the trace metals content of the whole oil and its fractions which will make up the refinery feedstocks in shale oil country. Existing knowledge about the adverse role of trace metals in petroleum refining began to appear about 1950 and is still an active area of research. To date, substantive data on the undesirable effects of the following elements has been published: arsenic, chromium, copper, lead, nickel, sodium, and vanadium (2-6). This list is not intended to be all inclusive. In general, all of the metals listed act as catalyst deactivators or poisons. They tend to accumulate at the active sites of the catalyst, reducing their effectiveness.

This study was undertaken in the belief that the problems caused by trace elements during the refining of petroleum will also occur during the refining of shale oil products. This paper will present information on the trace element analysis of shale oil materials which simulate petroleum feedstocks to a refinery. Details will be given on the

laboratory schema used to prepare the shale oil materials and on the quality control procedures used to validate the chemical analysis. The authors are aware that popular wisdom indicates that elevated nitrogen levels in shale oils will be the major factor in the upgrading process. This paper was designed to provide data in a neglected area.

EXPERIMENTAL SECTION

In petroleum refineries the first processing step is normally a fractional distillation of the total crude. The actual boiling ranges of the fractions produced will vary to meet the plant capabilities and final product needs (7). For the purpose of this study, a sample of the shale oil produced during the Rock Springs, Site 9, true *in situ* field test (8) was distilled into four fractions: naphtha, b.p. 55-106°C/5.332 kPa, light distillate, b.p. 106-200°C/5.332 kPa, heavy distillate, 192-277°C/2.666 kPa, and residue.

Prior to the final distillation step, the straight run crude was centrifuged, dewatered and filtered to remove oil shale particles which are known to contain significant concentrations of trace elements (9). Generally the gravimetric dewatering step fails to remove the water which is intimately tied up in the shale oil, probably by a hydrogen-bonding mechanism. This bound water causes extensive bumping and foaming upon distillation. To circumvent this problem, it was necessary to remove this water in a preliminary distillation through a short path column to a final head temperature of approximately 150°C. The water/naphtha product which co-distilled was separated, the naphtha dried over anhydrous sodium sulfate, and the dried naphtha returned to the distillation pot. To prevent excessive coking due to long term heating of the oil, a rapid, short path distillation was carried out at 2.666 kPa to a final head temperature of 300°C and a final pot temperature of 330°C.

The resulting distillate was redistilled under vacuum through a 66 centimeter glass column packed with 0.31 centimeter stainless steel helices to yield the four fractions previously mentioned. The fractions produced from this second distillation were analyzed separately as was the primary pot residue from the original short path distillation. To obtain a complete picture of the quantity and quality of the fraction called pot residue, the weighted values from the two distillation pot residues were combined.

Two additional shale oil products were prepared for this study. A sample of the filtered, dewatered crude oil was coked at atmospheric pressure (77.98 kPa in Laramie, Wyoming). The oil was added to a 3 L coking vessel maintained at 482°C at a rate of 300 ml/hr. The product which distilled was condensed and collected as an atmospheric coker distillate and the residue remaining in the pot was collected as the atmospheric coker residue. This type of treatment may be used on crude shale oil at some future time.

Several techniques of digesting the samples were tried and discarded before arriving at a satisfactory method. One method tried and found unsuitable was the wet digestion method recommended by the Environmental Protection Agency (EPA) (10). Regardless of the digestion times used, the oils and waxes could not be decomposed. Dry ashing was considered but rejected, due to the possible loss of both arsenic and selenium at the temperature required to ash the samples (10). The method proposed by Parr Instrument Company which utilizes their high temperature acid decomposition bomb was tried. The bomb consists of a 25 ml teflon sample container enclosed in a stainless steel jacket. For safety reasons, the method recommends using no more than 0.10 grams of an organic sample and 3 mls of concentrated nitric acid and a digestion temperature of 150°C. After an 18 hour digestion time, examination of the sample revealed that the sample wasn't completely digested. By using 1.5 mls of concentrated distilled nitric acid and 1.5 mls of distilled water, it was found that the sample could be completely decomposed under the same conditions. The digested sample was transferred to a 100 ml volumetric flask and diluted to volume. This concentration, 1 gram per liter, proved to be too dilute to allow the detection of the very low metals concentrations present in some of the sam-

ples. By acquiring the largest bomb available (125 ml) it was possible to increase the size of the organic sample to 0.5 grams and the amount of 50% nitric acid to 30 mls. This size sample required a reaction time of four hours at 180°C to assure complete digestion. This gave a solution equal to 5 grams of oil per liter when volumetrically diluted to 100 ml, enabling the detection of lower concentrations of the metals of interest.

The samples were analyzed using an atomic absorption spectrometer equipped with a graphite furnace. The analytical methods used for the analysis of the aqueous samples are those recommended by the EPA for the analysis of waters and waste waters. To assure high quality data in these rather complicated matrices, the necessary matrix modification procedures were used for each element analyzed and all determinations were carried out using the method of standard additions (10). In the matrix modification procedure, an additional reagent is added to the solution to be analyzed to suppress an unwanted interference during the analytical step. For example, for the determination of arsenic and selenium, a small amount of nickel nitrate is added to the sample to prevent the volatilization of the elements during the charring step. The standard addition technique utilizes the addition of a known amount of the element of interest in increasingly larger increments to aliquots of the sample prior to analysis. A graph is constructed by plotting instrument response versus the known incremental concentration of the element being analyzed and the value of the unknown (original) concentration is read from the plot at the measured instrument response for the unaltered sample.

As an additional quality control check, approximately 20% of all oil samples were digested in duplicate and analyzed separately. Another 20% of the oil samples were analyzed in triplicate with one sample of the set being spiked prior to digestion with an aqueous standard of all of the elements to be determined. The quantity of concentrated HNO₃ added to this spiked digestion was adjusted to maintain a 50% aqueous reaction media. As before, each digested sample was analyzed separately.

RESULTS AND DISCUSSION

The data from the metals analysis of the vacuum distillation fractionation scheme is shown in Tables 1 and 2. The results for the atmospheric distillation are shown in Table 3. Figures 1 and 2

TABLE 1
METALS CONCENTRATIONS IN SHALE OIL AND ITS VACUUM
DISTILLATION FRACTIONS, WEIGHT PERCENT

Element	Feed Stock		Naphtha	Light	Heavy	Pot
	Shale Oil	Mass Balance		Distillate	Distillate	Residue
	ppm	% Recovery	%	%	%	%
Arsenic	6.0	100.0	0.0	13.0	20.0	67.0
Chromium	7.2	123.0	22.0	58.0	27.0	16.0
Copper	13.6	111.0	2.0	32.0	22.0	55.0
Manganese	4.4	113.0	5.0	41.0	27.0	40.0
Nickel	10.5	60.0	3.0	15.0	10.0	32.0
Vanadium	4.0	104.0	1.0	32.0	24.0	27.0
Lead	8.0	229.0	28.0	40.0	125.0	15.0

Weight percent of the fractions is: naphtha 7.2%, light distillate 49.8%,
heavy distillate 37.7%, and pot residue 20.6%.

TABLE 2
METALS CONCENTRATIONS IN SHALE OIL AND ITS VACUUM
DISTILLATION FRACTIONS, WEIGHT PERCENT

Element	Feed Stock		Naphtha	Light	Heavy	Pot
	Shale Oil	Mass Balance		Distillate	Distillate	Residue
	ppm	% Recovery	%	%	%	%
Aluminum	16.0	118.0	7.0	35.0	42.0	34.0
Cadmium	1.0	95.0	11.0	20.0	45.0	19.0
Cobalt	1.6	117.0	6.0	40.0	22.0	49.0
Molybdate	5.0	114.0	7.0	17.0	30.0	60.0
Selenium	<0.1	--	--	--	--	--
Tin	28.0	104.0	4.0	4.5	33.0	22.0
Sodium	0.18	84.0	2.0	24.0	10.0	48.0

Weight percent of the fractions is: naphtha 7.2%, light distillate 49.8%,
heavy distillate 37.7%, and pot residue 20.6%.

TABLE 3
METALS CONCENTRATIONS IN SHALE OIL AND ITS
ATMOSPHERIC DISTILLATION FRACTIONS, WEIGHT PERCENT

Element	Shale Oil	Mass Balance	Distillate	Coke
	ppm	% Recovery	%	Residue %
Aluminum	16.0	120	64	60
Arsenic	6.0	65	56	9
Chromium	7.2	82	78	5
Cobalt	1.6	105	0	105
Copper	13.6	44	22	20
Manganese	4.4	76	63	13
Molybdate	5.0	107	74	33
Nickel	10.5	90	28	62
Selenium	>0.1	---	--	--
Tin	28.0	95	92	3
Vanadium	4.0	107	100	7
Lead	8.0	---	---	--
Sodium	0.18	76	34	42

Weight percent of the two fractions is distillate 93% and coke 2.2%.

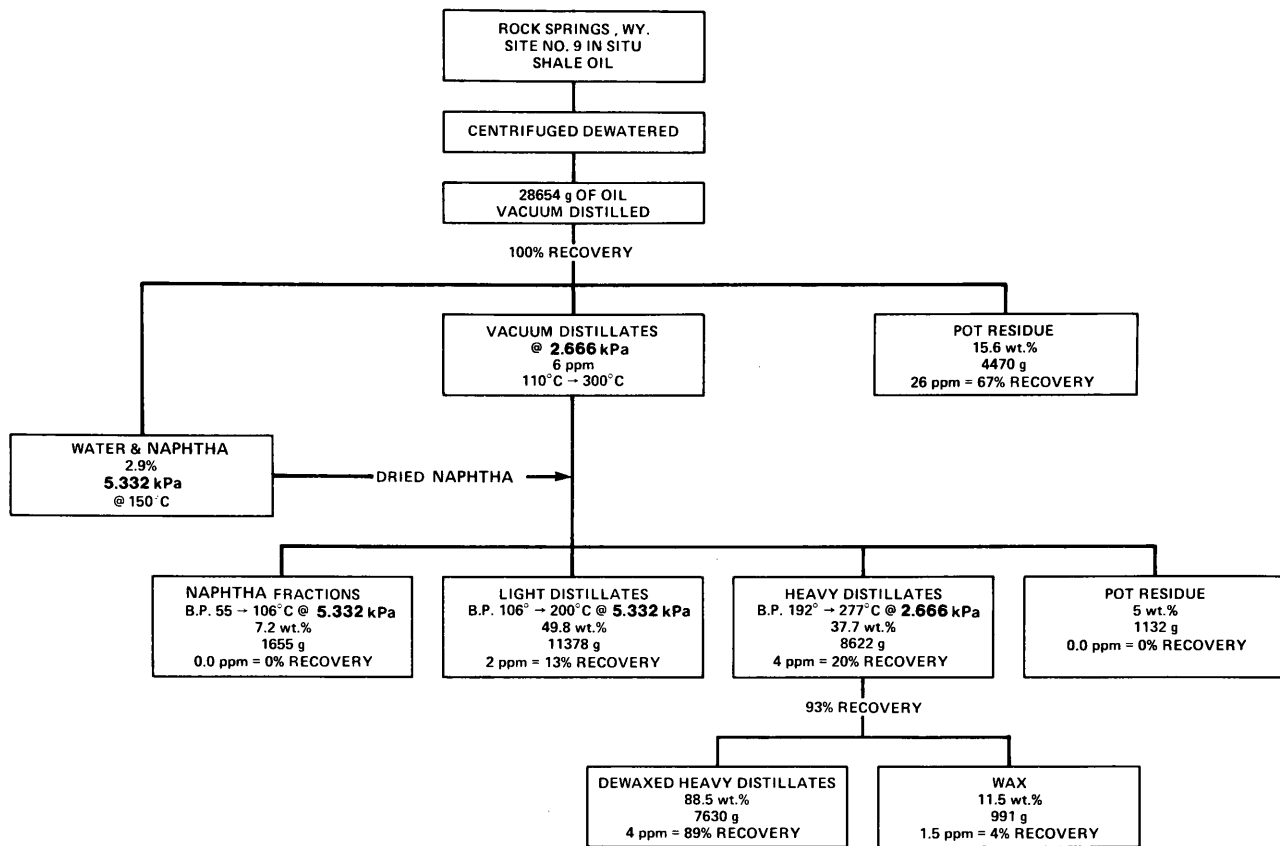


Figure 1. Arsenic Distribution in the Fractions from the Vacuum Distillation

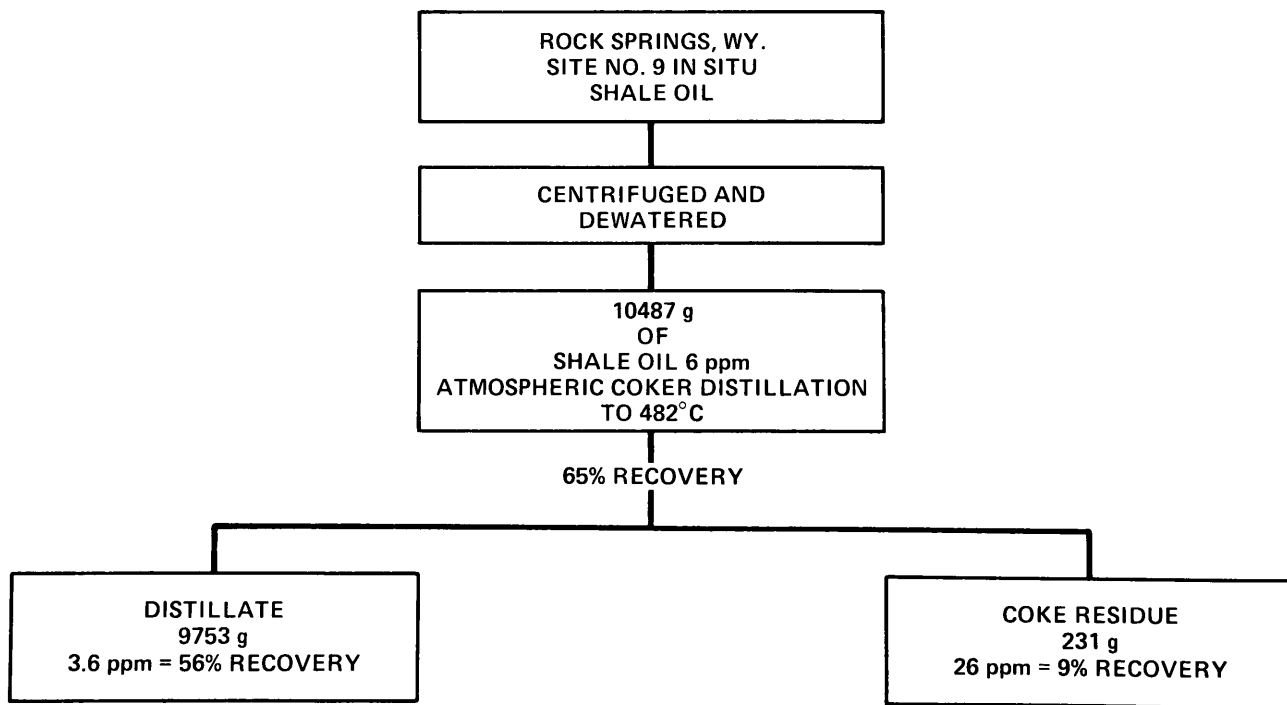


Figure 2. Arsenic Distribution in the Fractions from the Atmospheric Coker Distillation.

show the different fractions obtained by the two distillation schemes and their arsenic concentrations, in parts per million, as well as their relationship to the total concentration of the arsenic in the sample. It should be noted that the calculated mass balance for the vacuum distillation results in 100% recovery. The atmospheric distillation, on the other hand, resulted in only a 65% recovery. This difference can be attributed to the much higher temperature used in the atmospheric distillation, 482°C as compared to 330°C for the vacuum distillation. At this higher temperature, the arsenic may have been converted to arsine gas or other noncondensable forms and may have been lost in the distillation process. Comparison of the elemental mass balances between the two different processing conditions shows that less material can be accounted for in the coker distillation process than in the vacuum distillation. As with arsenic, it is likely that volatile forms of the metals are produced at the higher temperatures reached in the coking operation. This would imply that stricter off-gas control technology may be required for coker operation to assure minimum loss of undesirable products.

Table 1 shows the results for vanadium, nickel, chromium, copper, lead, manganese and arsenic. Examination of the vanadium and nickel data shows concentrations of 4 ppm and 10.5 ppm respectively. The vanadium behavior is similar to that of arsenic, in that 27% of the total vanadium ends up in the pot residue from the vacuum distillation and only 8% is contained in the pot residue from the atmospheric coker distillation. Calculation of the mass balance for vanadium also indicates complete recovery. The concentration of nickel in the feedstock was 10.5 ppm, but unlike arsenic and vanadium, nickel exhibited entirely different behavior under the two different processing conditions. The pot residue from the vacuum distillation contained 30% of the total nickel concentration present in the feedstock while the pot residue for the atmospheric coker distillation contained 62% of the total nickel in the feedstock. Nickel was also the only element on which less than 90% of the total elemental concentration present in the feedstock could not be accounted for in the vacuum distillation fractions. Chromium and manganese react differently from the other metals in that the greater portion of both of these metals are found in the light distillate fraction after vacuum distillation.

Comparison of the results obtained in this study with results obtained by previous investigators indicates that the level of metals found in this study are generally within the range of the earlier studies. This is shown in Table 4. Poulson (9) reported the values for metals obtained for

TABLE 4
COMPARISON OF METALS CONCENTRATIONS
IN SHALE OILS AND PETROLEUMS

Element	This Study	Poulson &	
	Shale Oil	Jackson Shale Oil	Smith et. al. Petroleum
	ppm	ppm	ppm
Aluminum	16.0	0.1 - 19	---
Arsenic	6.0	0.5 - 53	0.05 - 1.1
Cadmium	1.0	0.1	
Chromium	7.2	0.02 - 0.3	0.001 - 0.01
Cobalt	1.6	0.6 - 7.2	0.03 - 12.7
Copper	13.6	0.08 - 0.5	0.13 - 6.3
Manganese	4.4	0.01 - 1.1	0.63 - 2.5
Molybdenum	5.0	0.4 - 14	0.008 - 0.05
Nickel	10.5	0.4 - 55	49.1 - 344.5
Selenium	<0.1	0.1 - 0.5	0.026 - 1.4
Tin	28.0	0.6 - 7.2	
Vanadium	4.0	0.3 - 9.0	4.0 - 298
Lead	8.0	0.09 - 1.1	0.17 - 0.31
Sodium	0.18	<0.7 - <71	

eight different retorting methods with shale from different sources. Jackson (11), on the other hand, reports values on shale oils obtained by the standard Fischer Assay of segments of a single core sample which represent different depths. Six of the fourteen metals reported show significantly higher concentrations in this study. It may be that this sample is truly different. However, as pointed out by Poulson (8), the in situ produced oils would be expected to show lower levels of metals because they are essentially water-washed by the native groundwater and co-produced water during their production. This is very analogous to the desalting procedures normally used in refineries to reduce metal levels in contaminated crudes (7). Since the data from the two studies (9), (11) were produced in this laboratory five years ago, the higher levels of some metals in the current study may reflect improved analytical techniques as experience was gained over time.

Table 4 also shows the metal concentrations in petroleum crude oils as reported by Smith et al (12). In both products the nickel is present in greater concentration than the vanadium. Only very general comparisons will be of use due to the wide variation in sample characteristics of crudes and shale oils, depending on the locations from which they were obtained.

As noted, major emphasis was placed on quality assurance in the design of this project. The result of this is manifested by a comparison of the relative standard deviation for this study, (4.5%) with the results obtained for the analyses of petroleum by other investigators. Filby and Shah (12) reported a 6.6% relative standard deviation when using neutron activation analysis. McCoy (2) found the reproducibility for emission spectroscopy to be in the range of 20 to 30%. Hofstader (13) data shows an average coefficient of variation of 13%.

The percent recovery of the added spikes for arsenic (105%), vanadium (99%) and nickel (140%) are typical of the percent recovery of all spikes analyzed in this study.

There are some notable differences in trace metal content between shale oils and petroleum which may be significant to the refining of the shale oil products. Firstly, the concentration of nickel plus vanadium is considerably lower for the shale oil products, a maximum of 64 ppm compared to a maximum of 642 ppm (a factor of 10). Petroleum refineries frequently judge the catalyst deactivation capacity of a feed by this sum (3). It follows then that shale oils will not deactivate catalysts as rapidly as petroleum via this mechanism. If the Ni+V values for shale oils may be considered favorable when compared to petroleum, this is certainly not the case with several other catalyst poisons. Chromium is more prevalent by a factor of 350 (Cr, X350). The other metals and their factors are: Cu, (X2), Mn (X2), Mo (X100), and Pb (X25). Quantitative data on the magnitude of the adverse effects of these metals is generally lacking and their combined deleterious effects may far outweigh any benefits resulting from the low Ni+V.

SUMMARY

This paper has presented new data on the distribution of trace metals in shale oil products. Some details of the type of digestion procedures,

analytical techniques, and quality controls necessary to produce data of known reliability were given. Limited comparison between petroleum and shale oils were made and the potential effects of the differences in trace metal contents between the two products on their upgrading were pointed out.

REFERENCES

1. Lander, H. R., Jet Fuel Loops to Shale Oil: 1980 Technolgy Review, Conference Report, U.S. Air Force Wright Aeronautical Laboratories, Fuels Branch of the Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Cincinnati, Ohio, Nov., 1980.
2. McCoy, J. W. The Inorganic Analysis of Petroleum, Chemical Publishing Company, Inc., New York, 1962.
3. Dale, G. H. and D. L. McKay. Passivate Metals in FCC Feeds, Hydrocarbon Processing, V. 56, Sept. 1977, pp. 97102.
4. Cimbalo, R. N., R. L. Foster and S. J. Wachtel. Deposited Metals Poison FCC Catalyst, OGJ, 70 (20), May 15, 1972, pp. 112-120.
5. Conner, J. E. Jr., J. J. Rothrock, E. R. Birkhimer and L. N. Leum. Some Fundamental Aspects of Metals Contamination, IEC, 49(2), February 1957, pp. 276282.
6. Magee, J. S., R. E. Riher and L. Rheume. Hydrocarbon Processing, 58(9) September 1979, pp. 123130.
7. Gary, J. H. and G. E. Handwerk. Petroleum Refining Technology and Economics, Marcel Dekker, Inc., New York, 1975.
8. Long, A. Jr., N. W. Merriam, C. G. Mones and L. J. Romanowski. Evaluation of an In Situ Oil Shale Retorting Experiment in Wyoming, Preprints, 28th Annual Technical Meeting of Petrol Society of CIM, Edmonton, Alberta, Canada, 12 pp.
9. Poulson, R. E., J. W. Smith, N. B. Young, W. A. Robb and T. J. Spedding. Minor Elements in Oil Shale and Oil-Shale Products, DOE Report of Investigation 77/1, 1977, 17 pp.
10. U. S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Waste, EPA, March 1979.
11. Jackson, L. P., J. R. Morandi and R. E. Poulson. Compositional Variation of Retorted Shale Oils with Stratigraphy: Wyoming Core, Northern Green River Basin, Preprints, Div. of Fuel Chem., ACS, V.22, No. 3, 1977, pp. 6674.
12. Filby, R. H. and K. R. Shah. "Neutron Activation Methods for Trace Elements in Crude Oils", in The Role of Trace Metals in Petroleum, Yen, T. F., Ed., Ann Arbor Science, Ann Arbor, Michigan, 1975, p. 89.
13. Fofstader, R. A., Milner, O. I. and Runnels, J. H. Analysis of Petroleum for Trace Metals, Gould, R. F. Ed., Advances in Chemistry Series 156, American Chemical Society, Washington, D.C. 1976 p. 4.