UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY [Reports - Open file series]

Preliminary analytical results for a new U.S. Geological Survey Devonian Ohio Shale standard SDO-1

By

J. S. Leventhal, J. G. Crock, W. Mountjoy, J. A. Thomas, V. E. Shale, P. H. Briggs
J. S. Wahlberg, and M. J. Malcolm

Open-File Report 78-447
1978

This report is preliminary and has not
been edited or reviewed for conformity
with U.S. Geological Survey standards
and nomenclature.

Preliminary analytical results for a new U.S. Geological Survey Devonian Ohio Shale standard SDO-1

by

J. S. Leventhal, J. G. Crock, W. Mountjoy, J. A. Thomas, V. E. Shale, P. H. Briggs
J. S. Wahlberg, and M. J. Malcolm

LAYMANS SUMMARY

Using several analytical techniques, results of analysis of U. S. Geological Survey new standard SDO-1 are given for selected elements. The Devonian black shale shows an organic carbon content of approximately 10.3 percent, a sulfur content of approximately 5.6 percent, and a uranium content of approximately 56 ppm. Some elements show higher than average values for black shales: Mn, 389 ppm; Co, 57 ppm; Ni, 128 ppm; As, 104 ppm; and Hg, 0.19 ppm.

Preliminary analytical results for a new U.S. Geological Survey Devonian Ohio Shale standard SDO-1

by

J. S. Leventhal, J. G. Crock, W. Mountjoy, J. A. Thomas, V. E. Shale, P. H. Briggs
J. S. Wahlberg, and M. J. Malcolm

ABSTRACT

Using several analytical techniques, results of analysis of U. S. Geological Survey new standard SDO-1 are given for selected elements. The Devonian black shale shows an organic carbon content of approximately 10.3 percent, a sulfur content of approximately 5.6 percent, and a uranium content of approximately 56 ppm. Some elements show higher than average values for black shales: Mn, 389 ppm; Co, 57 ppm; Ni, 128 ppm; As, 104 ppm; and Hg, 0.19 ppm.

Table of Contents

Tables

Preliminary analytical results for a new U.S. Geological Survey Devonian Ohio Shale standard SDO-1

by

J. S. Leventhal, J. G. Crock, W. Mountjoy, J. A. Thomas, V. E. Shaw P. H. Briggs,
J. S. Wahlberg, and M. J. Malcolm

Introduction

Analytical data are presented here for the new USGS Devonian black shale standard SDO-1. The sample of Upper Devonian Ohio Shale was collected by Roy Kepferle, USGS, from a roadcut on Interstate 64 near Morehead in Rowan Co, Ky. The sample was crushed and split under the direction of F. J. Flanagan at a laboratory of the USGS in Reston. The sample, before it is ground, is an organic-rich, fissile, platy shale, brownish-black in color, containing flattened pyrite nodules up to 5 cm in diameter. Further information on the geology is available in Provo, Kepferle, and Potter (1977).

The sample was collected for the purpose of having an analytical reference for the many laboratories participating in the U.S. Department of Energy Eastern Gas Shales Project (administered from Morgantown Energy Research Center, W.Va.).

The sample is available as coarse and fine splits from F. J. Flanagan, USGS, Reston Va. The fine splits are for detailed chemical analysis, whereas the coarse material is for hand and microscopic as well as microfossil examination.

Analytical Methods

Carbon Determination

The wet oxidation technique was used for organic carbon. The sample ($\sim$0.2 g) is digested with 25 ml of 50% H_2SO_4 for 90 minutes at 150°C to remove carbonates. Approximately 3 of CrO_3 and 25 ml of concentrated H_2SO_4 are used as an oxidant at 220°C while the sample is flushed with CO_2-free air for 30 minutes. The CO_2 is collected on ascarite and weighed (Allison, 1956).

The Leco technique for total carbon consists of combustion at 1800°C of 0.3 g of sample with 3 g Cu metal accelerator; CO_2 is absorbed on molecular sieve pellets. CO_2 is then released by heating the sieve and measured by thermal conductivity (Leco, 1967).

Carbonate carbon is determined by a modified Van Slyke method (Rader and Grimaldi, 1961). Carbon dioxide is liberated by the action of 1+1 hydrochloric acid on the sample. The volume of the liberated carbon dioxide plus the air present in the reaction flask is measured at a definite temperature and atmospheric pressure. The combined gases are then scrubbed free of carbon dioxide by passage through an alkali solution. The volume of the residual gases is again measured at the same temperature and pressure. The difference in the observed volumes, due to the volume of carbon dioxide, is calculated to standard conditions of temperature and pressure using the ideal gas relationships. The weight of carbon dioxide is then calculated from its volume at standard temperature and pressure.

See Table 1. for results

Atomic absorption spectroscopy

Copper, manganese, zinc, cadmium, and nickel are determined by the AA (atomic absorption) spectroscopy described by Swanson and Huffman (1976, p. 4-6), which follow the recommended procedures of Perkin-Elmer (Thomas and others, 1976).

Mercury, arsenic, vanadium, and cobalt are also determined by AA spectroscopy, but by specialized method. Vanadium is determined by the method of Stary (1963) and modified for AA by Mountjoy (1970). Cobalt is determined using a method described by Mountjoy (1970).

Arsenic is determined as described by Aruscavage (1977) and modified by J. G. Crock (USGS, Denver) as follows: 0.5 g of sample is digested with 15 ml conc. HNO_3, 13 ml conc. H_2SO_4, and 5 ml conc. $HClO_4$ and is then taken to SO_2 fumes by slowly heating to 200°C. The solution is transferred to a 65-ml culture tube. A mixture of 10 ml of 20% ascorbic acid, 10 ml H_2O and 5 ml 6N NaI, and 10 ml toluene is added and shaken together. A portion of the toluene layer is removed and back-extracted into 5% HCl. The HCl solution containing As is analyzed by AA using an Ar/H_2 flame with a three slot boling burner.

Mercury is determined by flameless AA spectroscopy (Huffman and others, 1972). Several tenths of a gram of ground shale are digested under oxidizing conditions (HNO_3-H_2SO_4-$HClO_4$). Mercury is reduced to its elemental state with stannous chloride and aerated from solution onto a silver screen placed in the vapor. The silver screen is subsequently heated and the mercury vapor is carried by an air stream to an absorption cell, where its concentration is determined by atomic absorption spectrometry.

See Table 1 for results of analysis

Other Methods

Molybdenum is determined by the technique described in Rader and Grimaldi (1961, p. A27). Molybdenum is isolated by precipitation with alpha-benzoinoxime, using vanadium as a collector. Molybdenum is determined colorimetrically as the thiocyanate after reduction with stannous chloride.

Sulfur is determined by the Leco combustion-iodometric titration method (leco, 1957). The 0.3 g sample is mixed with 1.5 g of Cu accelerator and 2 g of V_2O_5 oxidizer and combusted at 1800°C. The resulting sulfur oxides are determined by measurement of the HI formed.

Uranium is determined by the delayed-neutron method (Millard, 1976). Samples (6-10 g) are irradiated in a TRIGA reactor in a flux of 5×10^{12} neutron/cm^2-sec for 60 seconds. After a 20-second delay, the sample is counted for 60 seconds with BF_3 proportional counters.

See Table 1 for results.

X-Ray Fluorescence Spectroscopy

X-ray fluorescence methods, developed by James S. Wahlberg, are employed for the determination of Al, Ca, total Fe, K, Si, and Ti in the sample (table 2). In this method 0.800 g of sample is fused with 6 g of flux (mixture of 43 percent $Li_2B_4O_7$, 55 percent $Na_2B_4O_7$, and 2 percent NaBr) in a 20-ml platinum crucible. The NaBr is added to the fusion mixture to facilitate easy removal of the solidified button from the platinum crucible. This fused button is X-rayed and counted to determine the listed elements.

An automated, General Electric[1], vacuum spectrometer is used to determine the listed elements. The instrument parameters used are given in the following tabular form: (Swanson and Huffman, 1976)

Element	Crystal[1]	MA[2] on X-ray tube	X-ray tube target	2θ angle (degrees)
Al	PET	60	Cr	144.67
Ca	LiF	20	Cr	113.08
Total Fe	LiF	20	W	57.52
K	PET	60	Cr	50.64
P	PET	60	Cr	89.40
Si	PET	60	Cr	109.06
Total S	NaCl	60	Cr	144.53
Ti	LiF	60	Cr	86.13
Cl	NaCl	60	Cr	113.91

[1]PET, pentaerythritol. [2]MA, megaamperes.

Most of these elements are conventionally reported as oxides. The lower limits of determination in the ash are:

Element[1]	Sample Weight (g)	Lower limit (percent)
Al_2O_3	0.8	0.2
CaO	.8	.02
Total Fe (as Fe_2O_3)	.8	.02
K_2O	.8	.02
P_2O_5	.8	.1
SiO_2	.8	.2
Total S (as SO_3)	.8	.04
TiO_2	.8	.02
Cl	.8	.1

[1]MgO, Na_2O, and MnO, as determined by atomic absorption method, are also included in tables showing major-oxide composition of ash.

---

1. Use of a specific trade name does not necessarily constitute endorsement of a product by the U.S. Geological Survey.

Emission Spectroscopy

A six-step semiquantitative optical emission spectrographic method developed by Myers, Havens, and Dunton (1961) and by Myers and Havens (1970) is used to look for 63 elements. In this method, 1 part sample is mixed with 1.15 parts of a mixture of 9 parts quartz (SiO_2) and 1 part Na_2CO_3. Ten milligrams of the resulting mixture is in turn mixed with 20 mg of pure graphite powder. This final mixture is burned in a d-c arc for 120 seconds, and the spectra are collected on photographic plates. The resulting spectra are visually compared with reference standards. The element determinations are identified with geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, and so forth, but are reported as midpoints of these brackets: 1., 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, and so forth; there are thus six brackets to the decade. The precision of a reported value is approximately plus-or-minus one bracket at the 68-percent confidence level. More details are given in Swanson and Huffman (1976). Results are given on table 3 only for elements that have not been determined at a higher precision (given on tables 1 and 2).

Table 1. Results for selected elements in SDO-1 using high-precision techniques
Fines Split 0051. Job QA61-D196766

Element	Content[a]	Technique	Error[b]	Lower Limit
		Whole Sample		
C, total %	10.36±.05	Leco combust	±3%	.05 %
C, carbonate %	0.28± 02	HCℓ gasmetric	±5%	.05 %
C, organic %	10.08±.06	by difference	±3%	.1 %
C, organic %	10.44±.03	wet oxidation	±3%	.05 %
C, total %	10.80±.04	wet oxidation	±3%	.05 %
C, carbonate %	0.36±.04	by difference	±10%	.1 %
S, total %	5.56±.05	Leco combust iodometric	± 3%	.05 %
As, ppm	104 ±1	Atomic absorption (AA)	± 5%	10 ppm
Hg, ppm	0.19±.01	wet oxid, flameless AA	± 5%	.01 ppm
V, ppm	161± 1	AA	± 7%	10 ppm
U, ppm	55.6	delayed neutrons	± 2%	.05 ppm
Mo, ppm	122 ± 6	Colorimetric	± 10	4 ppm
% Ash	82.1 ±.1	525°C gravimetric	± 1%	
		Ashed Sample		
Mn, ppm	389± 1	AA	±7%	5 ppm
Co, ppm	57± 1	AA	±5%	1 ppm
Zn, ppm	76± 0	AA	±5%	5 ppm
Cd, ppm	< 1	AA	±5%	1 ppm
Cu, ppm	74± 0	AA	±4%	5 ppm
Ni, ppm	128± 0	AA	±4%	20 ppm

a. ± based on replicates.

b. Based on splits, duplicates, or analytical precision.

2. Results for selected elements in SDO-1 by X-ray fluorescence

Whole sample by X-ray fluorescence

Component	Value (%)	Precision (%) *
Al_2O_3	12.	± 10
SiO_2	49.	± 3
CaO	0.90	± 10
TiO_2	0.60	± 10
Fe_2O_3	9.3	± #
K_2O	3.0	± 10

Written communication from F. J. Flanagan, USGS, Reston, by atomic absorption.
* Average based on results from 5 pairs of analyses.

3. Results for selected elements in SDO-1 using emission spectroscopy

Semiquantitative Emission Spectrographic Analysis

(on the ash)

Element	Value (ppm)	Error
Cr	70	± 33 %
La	50	*
Pb	20	*
Sc	15	*
Sr	150	*
Y	50	*
Zr	150	*
Ga	20	*
Na	0.5%	± 33%
Yb	3	*

The error is based on results from three pairs of samples: The * denotes the same result; the Cr and Na showed the quoted error in two of the three pairs.

Discussion

Some elements in SDO-1 show higher than average (Vine and Tourtelot, 1970) values for black shales: organic carbon, uranium, manganese, cobalt, nickel, arsenic and mercury.

Several results need to be discussed. The organic carbon determination was done two ways. They are not in agreement in terms of the stated precision, but do overlap in the accuracy for the method (± 3%). It is possible that volatile, hydrolyzable, or soluble organic carbon is lost in either of the methods. Loss of volatile organics would tend to make the Leco total value low. Loss of volatile or hydrolyzable organic carbon would tend to make the wet oxidation value low.

The results are given either on an ashed or a whole sample (unashed) basis depending on the requirements of the analytical method. Since the ash content is 82.1 percent whole sample numbers can be multiplied by 1.22 to get a corresponding ashed value, or the ashed values can be divided by 1.22 to get the whole sample value.

Many elements were below detectability of the methods employed. Except for Cd, these are not reported.

We recommend that the coarse sample <u>not</u> be used for analytical determinations because of splitting problems, which are especially related to the sulfide nodules.

Allison, L.E., 1965, Organic Carbon, in Methods of Soil Analysis. Ed. by C.A. Black, Am. Soc. Agron, Madison, Wisconsin Monog. No. 9, p. 1367-78.

Aruscavage, P., 1977, Determination of As, Sb, and Se in coal by atomic absorption spectrometry with graphite tuve atomizer. U.S. Geol. Survey, Journal of Research. v.5, p. 405-408.

Huffman, Claud, Jr., Rahill, R.L., Shaw, V.E., and Norton, D.R., 1972, Determination of mercury in geologic materials by flameless atomic absorption spectrometry in Geological Survey research, 1972: U.S. Geol. Survey Prof. Paper 800-C, p. C203-C207.

Leco, 1957, Instructions for sulfur determinations with Leco no 532.

Leco, 1967, Leco Corp. St. Joseph Michigan, Instruction manual for 763-200 and WR-12 carbon determinator 761-200.

Millard, H.T. Jr., 1976, Determination of uranium and thorium in USGS standard rocks by the delayed neutron method: F.J. Flanagan, ed. Descriptions and analyses of eight new USGS rock standards. U.S. Geol. Survey Prof. Paper 840, p. 61-65.

Mountjoy, W., 1970, Determination of cobalt in geologic materials by solvent extraction and atomic absorption spectrometry. U.S. Geol. Survey Prof. Paper 700B, p. B174-B176.

Myers, A.T., and Havens, R.G., 1970, Spectrochemistry applied to geology and geochemistry by the U.S. Geological Survey in the Rocky Mountain Region-Proceedings of the Second Seminar on Geochemical Prospecting Methods and Techniques Applicable in the Humid Tropic Environment: UN ECAFE, Mineral Resources Development Series 38, New York, p. 286-291.

Myers, A.T., Havens R.G., and Dunton, P.J., 1961, 1961, A spectrochemical method for the semiquantitative analysis of rocks, minerals and ores: U.S. Geol. Survey Bull. 1084-I, p. 207-229.

Provo, L., Kepferle, R, Potter P.E., 1977, Three back bed; useful stratigraphic marker in upper devonian shale in E. Ky. Morgantown Energy Research Center, MERC-CR-77-2. p. 6-8.

Rader, L.F., and Grimaldi, F.S., 1961, Chemical analyses for selected minor elements in Pierre Shale: U.S. Geol. Survey Prof. Paper 391-A, 45 p.

Stary, J., 1963, Systematic study of the solvent extraction of metal oxinates: Analyt, Chim. Acta, v. 28, p. 132-149.

Swanson, V.E. and Huffman, C., Jr., 1976, Guidelines for sample collecting and analytical methods used in the U.S. Geological Survey for determining chemical composition of Coal. U.S. Geol. Survey Circ. 735, 11 p.

Thomas, J.A., Mountjoy, W., and Huffman, C. Jr., 1976, Copper, lithium, manganese, strontium, zinc, sodium, potassium, and manganese contents of eight new USGS standard rock samples, in U.S. Geol. Survey Prof. Paper 840, p. 119-122.

Vine, J.D. and Tourtelot E.B., 1970, Geochemistry of black shale deposits, a summary: Econ. Geol. v. 65, p. 253-272.