



UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

Page

JAN 18 1955

AEC-544/5

Mr. Robert D. Nininger, Acting Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEM-864, "Observations on the wet ashing of oils and asphaltenes," by Herbert M. Ezekiel, January 1955.

We are asking Mr. Hosted to approve our plan to make TEM-864 part of a larger report and to submit the larger report for publication in *Geochimica et Cosmochimica Acta*.

Sincerely yours,

for *John H. Eric*
W. H. Bradley
Chief Geologist

*
(200)
TL67mm

Chemistry

This document consists of 10 pages.
Series A.

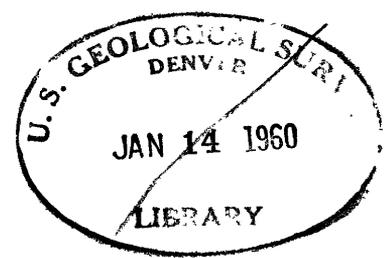
UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

OBSERVATIONS ON THE WET ASHING OF OILS AND ASPHALTENES*

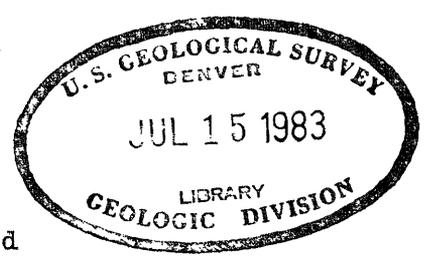
By

Herbert M. Ezekiel

January 1955



Trace Elements Memorandum Report 864



This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

USGS - TEM-864

CHEMISTRY

<u>Distribution (Series A)</u>	<u>No. of copies</u>
Argonne National Laboratory	1
Atomic Energy Commission, Washington	2
Battelle Memorial Institute, Columbus	1
Carbide and Carbon Chemicals Company, Y-12 Area	1
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Butte	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Douglas	1
Division of Raw Materials, Hot Springs	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Phoenix	1
Division of Raw Materials, Richfield	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Washington	3
Dow Chemical Company, Pittsburg	1
Exploration Division, Grand Junction Operations Office	1
Grand Junction Operations Office	1
National Lead Company, Winchester	1
Technical Information Service, Oak Ridge	6
Tennessee Valley Authority, Wilson Dam	1
U. S. Geological Survey:	
Fuels Branch, Washington	2
Geochemistry and Petrology Branch, Washington	20
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	1
E. H. Bailey, Menlo Park	1
A. L. Brokaw, Grand Junction	1
J. R. Cooper, Denver	1
N. M. Denson, Denver	1
C. E. Dutton, Madison	1
W. L. Emerick, Plant City	1
L. S. Gardner, Albuquerque	1
M. R. Klepper, Spokane	1
A. H. Koschmann, Denver	1
R. A. Laurence, Knoxville	1
D. M. Lemmon, Washington	1
J. D. Love, Laramie	1
P. C. Patton, Denver	1
J. F. Powers, Salt Lake City	1
J. M. Schopf, Columbus	1
Q. D. Singewald, Beltsville	1
J. F. Smith, Jr., Denver	1
A. E. Weissenborn, Spokane	1
TEPCO, Denver	2
TEPCO, RPS, Washington, (Including master)	2

CONTENTS

	Page
Abstract	4
Introduction	4
Samples	5
Experimental methods	6
Discussion	8
Literature cited	10

OBSERVATIONS ON THE WET ASHING OF OILS AND ASPHALTENES

By Herbert M. Ezekiel

ABSTRACT

The wet ashing of oils and asphaltenes by sulfuric acid, perchloric acid, and nitric-sulfuric acid techniques is discussed and compared. A simple sulfuric acid-nitric acid technique which has been found to be satisfactory for these substances is described.

INTRODUCTION

Investigations of the association of uranium and other elements with naturally occurring carbonaceous substances usually necessitate the preparation of ash for subsequent analysis. A number of techniques for the dry or wet oxidative ashing of organic materials have been published in recent years, but none of these methods has been found to be entirely satisfactory for petroleum oils.

Dry ashing of petroleum by combustion has been a common practice for many years (ASTM D-482-46). Morgan and Turner (1951) have indicated, however, that dry ashing can lead to the following sources of error: (1) loss of inorganic material during the preliminary stages of heating, (2) loss by volatilization during combustion, and (3) loss by mechanical entrainment during both stages of ignition. To eliminate these sources of error, a number of wet oxidation techniques have been developed and published. In one such method (Milner et al., 1952) sulfuric acid is used to decompose the organic material and convert metallic constituents in the petroleum to the respective sulfates. A second technique

(Kahane, 1934; Smith, 1953) uses mixed nitric and perchloric acids for wet combustion of oils and other organic materials.

The majority of wet-ashing procedures incorporates the use of perchloric acid. Southwick (1951), in a study of the inorganic constituents of crude oils, used the following acid mixtures: nitric acid-perchloric acid, perchloric acid-sulfuric acid, and nitric acid-perchloric acid-sulfuric acid. Southwick reported that nitric acid alone destroys much of the organic matter, that the addition of sulfuric acid retards this action, and that perchloric acid is required to complete the oxidation.

One purpose of this report is to summarize observations on the sulfuric acid (Milner et al., 1952) and perchloric acid-nitric acid (Smith, 1953) wet-ashing techniques. These procedures were chosen after a critical review of the literature indicated them to be the most satisfactory methods of many which have been published (Bourget and Tanner, 1953; Keith and Downing, 1953; Wahlin, 1953).

A second purpose of this report is to outline a simple method, using only nitric and sulfuric acids, which has been found to be satisfactory. This information may be helpful to other chemists faced with the problem of wet ashing oils.

This work is part of a program undertaken by the Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission.

SAMPLES

Oil 1.--Oil collected from an oil seep in the Shinarump conglomerate in the A. E. C. no. 5 mine, North Mesa area, Temple Mountain, Emery

County, Utah. This oil was carefully filtered to free it of entrained solid matter. A portion of the original oil was diluted with pentane to precipitate asphaltenes which were isolated, washed, and recovered. Pentane was removed from the asphaltene-free oil which was then also recovered.

Oil 2.--An oil-impregnated sandstone from the Shinarump conglomerate in the A. E. C. no. 4 mine, North Mesa area, Temple Mountain, Emery County, Utah, was Soxhlet-extracted with benzene, alcohol, and ether for several days, after which the extract was evaporated to remove the solvents. The residual oil was treated as above to isolate the asphaltenes. Complete data on the extraction and isolation techniques used for oils 1 and 2 will appear in another report.

Oil 3.--Duo-Seal high vacuum pump oil was obtained from the W. M. Welch Scientific Company, Chicago, Ill., and was used for test purposes because of its relatively high viscosity.

EXPERIMENTAL METHODS

Milner sulfuric acid technique.--The technique recommended by Milner (1952) was employed with only minor modifications. A 100-ml platinum crucible containing 3 to 10 g of oil was placed on a silica triangle bent so that the crucible was suspended above a hot plate. Concentrated sulfuric acid (0.5 ml per gram of oil) was added and a metal shield placed around the triangle and crucible. The temperature of the mixture was gradually raised to the maximum attainable by means of an infrared lamp suspended above the crucible and was then further increased by means of the hot plate at a rate that led to steady evolution of fumes. When fuming stopped at the maximum temperature

obtainable in this fashion (8 to 40 hours), the crucible was placed in a furnace at 500° C under a slow stream of oxygen. After organic matter was completely removed, the temperature of the furnace was raised to 800° C. The crucible was then heated to constant weight at this temperature.

G. Frederick Smith nitric acid-perchloric acid technique.--This procedure was used with only minor modification in an attempt to wet ash the asphaltenes and asphaltene-free oils from oil samples 1 and 2. The asphaltenes (0.8 to 2 g) or oil (4 to 7 g) samples were placed in 100-ml round bottom flasks fitted with 100-mm air condensers to prevent loss of sample or oxidizing mixture by vaporization. Each sample was boiled with 15 to 25 ml of 1:1 nitric acid for approximately 2 hours after which the samples were cooled and 3 to 5 ml of 70 to 72 percent perchloric acid was added. The samples were again heated to boiling. After several hours one asphaltene sample reacted explosively without warning. Use of this technique was, therefore, discontinued.

Sulfuric acid-nitric acid technique.--Oil sample 3 and the asphaltenes and asphaltene-free oil from oil sample 2 were used in this work. Approximately 0.5 g of sample was placed in a 100-ml round bottom flask fitted with a 500-mm air condenser. Sulfuric acid (approximately 3 ml) was added and the mixture heated vigorously until the sample was charred. Concentrated nitric acid (approximately 3 ml) was next added and the mixture was refluxed, with additions of nitric acid as required, until a clear red or brown-red solution resulted. The acid mixture was concentrated by replacing the 500-mm air condenser with a 100-mm air condenser and boiling the solution vigorously. Additions of concentrated nitric acid were repeated until the final concentrated

solution was light greenish-yellow to colorless.

DISCUSSION

The Milner technique for wet-ashing with sulfuric acid seems to give acceptable results, but the procedure is very slow and requires considerable attention over a period of days for proper control of decomposition temperature. A trace of moisture in the sample can also lead to splattering during the early stages of heating.

The perchloric acid-nitric acid technique is not only slow but is considered unsatisfactory because violent reactions may occur during the oxidation of organic matter. These reactions, in which the reaction mixture suddenly bursts into flame, are identical in appearance to those which may occur when perchloric acid alone is used (Smith, 1953). When the procedure is modified to eliminate the possibility of violent reactions, the first stage of oxidation may require as much as 80 hours of heating with considerable attention.

It has been suggested by Smith that this uncontrollable reaction takes place in the vapor phase and is the result of the reaction between hot perchloric acid vapors and the vapors of partly oxidized oil. The oils and asphaltenes do not mix with the acid solution and, consequently, are oxidized very slowly. In both cases the initial flash of flame occurs above the liquid. It appears that not only oils but also asphaltenes form breakdown products of such volatility that complete oxidation fails to take place in the liquid phase. Thus the presence of nitric acid cannot moderate the oxidation as it does in the oxidation of many other organic materials.

A major advantage of the sulfuric acid-nitric acid technique is that the oils or asphaltenes are broken down during the first stage of oxidation into substances which mix readily with the oxidizing medium. Further attack by the oxidants can then occur in the liquid phase at moderate temperatures.

Although the sulfuric acid-nitric acid technique is slow, the experiments require attention only during the initial charring and final concentration processes. It is possible, therefore, to carry out a large number of such oxidations simultaneously if necessary. Experiments have shown that the reactions proceed smoothly and that there is no danger of explosion. The constant evolution of fumes which may carry entrained inorganic material in the Milner technique is eliminated in the nitric acid-sulfuric acid method. Solid materials which can be wet by the sulfuric acid, such as the asphaltenes, char rapidly and require only short oxidation periods.

On the basis of this work it is recommended that the sulfuric acid-nitric acid technique be used in wet ashing oils and other carbonaceous substances. The suggested procedure is as follows:

In a 100-ml round bottom flask fitted with a 500-mm air condenser place approximately 1 gram of sample and 6 ml of concentrated sulfuric acid. Heat the flask until the oil has become thoroughly charred and a black slurry has formed. After cooling, add 6 ml of concentrated nitric acid through the condenser and reflux the acid mixture. Further additions of nitric acid should be made as necessary. When a clear red solution is formed, the long condenser may be replaced by one approximately 100 mm in length. The solution is then heated vigorously to reduce its volume and further additions of nitric acid are made, as

necessary, until a greenish-yellow or colorless solution results. This solution can then be transferred to a crucible or beaker and, after drying, be used for an ash determination or for other determinations as required.

LITERATURE CITED

- ASTM D-482-46, Am. Soc. of Testing Materials Standards, Philadelphia, Pa.
- Bourget, S. J., and Tanner, C. B., 1953, Removal of organic matter with sodium hypobromite for particle-size analysis of soils: Canadian Jour. Agr. Sci., v. 33, p. 579-585.
- Kahane, E., 1934, L'action de l'acide perchlorique sur les matières organiques. I. Généralités, 48 p.; II. Applications: 124 p., Paris, Herman et Cie.
- Keith, F. W., Jr., and Downing, F., 1953, Measurement of ash content in residual fuel oil: Diesel Power and Diesel Transportation, v. 31, no. 9, p. 44-46.
- Milner, O. L., Glass, J. R., Kirchner, J. P., and Yurich, A. N., 1952, Determination of trace metals in crude and other petroleum oils: Anal. Chemistry, v. 24, p. 1728-1732.
- Morgan, L. O., and Turner, S. E., 1951, Recovery of inorganic ash from petroleum oils: Anal. Chemistry, v. 23, p. 978-979.
- Smith, G. F., 1953, The wet ashing of organic matter employing hot concentrated perchloric acid: Acta Anal. Chim., v. 8, p. 397-421.
- Southwick, S. H., 1951, Inorganic constituents of crude oil, Massachusetts Institute of Technology, Ph. D. thesis, 93 p.
- Wahlin, E., 1953, Polarographic determination of trace metals in organic material: Acta Chem. Scand., v. 7, p. 956-968.