DEPARTMENT OF THE INTERIOR

TEI-461

RETENTION OF URANIUM DURING OXIDATIVE ASHING OF SELECTED NATURALLY OCCURRING CARBONACEOUS SUBSTANCES

By

Frank Cuttitta
Edward Brittin

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

September 1954
United States Geological Survey
Washington, D. C.

42202

UNITED STATES ATOMIC ENERGY COMMISSION
Technical Information Service, Oak Ridge, Tennessee
Subject Category, CHEMISTRY.

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

Issuance of this document does not constitute authority for declassification of classified material of the same or similar content and title by the same authors.

This report has been reproduced with minimum alteration directly from manuscript provided the Technical Information Service in an effort to expedite availability of the information contained herein.

Printed in USA, Price 10 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.
CONTENTS

Abstract ................................................................................. 4
Introduction ................................................................................ 4
Experimental methods ............................................................... 5
Conclusions ................................................................................. 7
Literature cited ............................................................................. 7

TABLE

Table 1. Results of duplicate uranium determinations by dry- and wet-ashing techniques ................................. 6
RETENTION OF URANIUM DURING OXIDATIVE ASHING OF SELECTED
NATURALLY OCCURRING CARBONACEOUS SUBSTANCES

By Frank Cuttitta and Edward Brittin

ABSTRACT

Data are presented to show that no appreciable loss of uranium occurs when uranium-bearing carbonaceous materials undergo oxidative ashing under routine conditions and with routine care.

INTRODUCTION

The routine determination of uranium in naturally occurring carbonaceous substances generally includes an oxidative ashing step. It has been assumed that uranium is not lost from the sample during oxidative ashing. However, during the course of a recent geochemical investigation on uraniferous coals and shales, it was suggested that uranium may be lost from the sample during ashing.

As no formal data had been obtained regarding the loss of uranium from carbonaceous substances during oxidative ashing, it was considered important to investigate the effects of oxidative ashing on the uranium associated with selected carbonaceous substances. After careful consideration, we decided to compare uranium contents obtained through dry-ashing and wet-ashing techniques.

At high temperatures, perchloric acid is an energetic oxidizing agent and can be advantageously employed (3) in the oxidation of organic material previous to the determination of the mineral constituents. In some experiments the rate of oxidation is excessive and may become
The decomposition rate is effectively retarded by the addition of HNO₃ and H₂SO₄ to the HClO₄ (by dilution and lower temperature of oxidation). Applications in the use of mixtures of HClO₄, H₂SO₄, and HNO₃ in the oxidation of both organic and inorganic substances have been contributed by many investigators (3, 4, 5, 6). The wet-ashing technique can be carried out at low temperatures and where care is taken to prevent evaporation of liquid or volatile material from the reaction mixture. It was considered that the uranium values obtained by this procedure would serve as a basis for comparing uranium values obtained by standard oxidative ashing procedures.

The samples selected for this report were those studied by Breger, Meyrowitz, and Deul (1) to determine if volatilization of uranium took place during reductive distillation of certain naturally occurring carbonaceous substances. The samples, ranging in uranium content from approximately 0.002 percent to 0.4 percent, were analyzed by both dry-ashing and wet-ashing techniques. Each sample was analyzed in duplicate by each method.

EXPERIMENTAL METHODS

The following techniques were used to obtain the data shown in table 1.

**Dry ashing (direct combustion).**—Samples weighing approximately 0.2 g were ignited to constant weight in an electric furnace at 850 C. Residual material was dissolved by treatment with HF and HNO₃. Complete solution was effected in all cases. The uranium content was then determined fluorimetrically as described by Grimaldi (2).
### Table 1—Results of duplicate uranium determinations by dry- and wet-ashing techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uranium (percent)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry ashing</td>
<td>Wet ashing</td>
<td></td>
</tr>
<tr>
<td>Chattanooga shale</td>
<td>0.0094</td>
<td>0.0094</td>
<td>0.0095</td>
</tr>
<tr>
<td>Subbituminous coal</td>
<td>0.0026</td>
<td>0.0023</td>
<td>0.0023</td>
</tr>
<tr>
<td>Coal from Chattanooga shale</td>
<td>--</td>
<td>0.0355</td>
<td>0.0347</td>
</tr>
<tr>
<td>Swedish kolm</td>
<td>0.438</td>
<td>0.448</td>
<td>0.450</td>
</tr>
<tr>
<td>Chattanooga shale</td>
<td>0.0088</td>
<td>0.0087</td>
<td>0.0086</td>
</tr>
</tbody>
</table>

Wet ashing—Samples (0.2000 g) of the coal in a 100-ml volumetric flask were treated with 10 ml of 70 to 72 percent HClO₄, 5 ml concentrated H₂SO₄, and 20 ml concentrated HNO₃ (sp. g. 1.42). The samples were digested at a moderate temperature (125-150°C) on an electric hot plate. The temperature of the digestion was so adjusted that the solution simmered gently but vigorously enough to result in condensation of vapors about halfway up the neck of the flask. As the destruction of organic matter progressed, the temperature of the reaction medium increased. Heavy brown fumes of oxides of nitrogen appeared and the decomposition required several hours' treatment. The completion of the digestion is recognized when the digestion liquid becomes a clear yellow. The reaction mixture was cooled and the solution transferred quantitatively to a 100-ml platinum dish using a 1:1 HNO₃ wash solution. Ten milliliters of HF was added to the solution, the digestion was continued, and the temperature was gradually raised until heavy fumes appeared in the dish. Fuming was continued to incipient dryness.
Sufficient 1:1 HNO₃ is added to effect complete solution of the salts. The solution was transferred to a volumetric flask and made up to volume. The final acidity was made to 7 percent v/v HNO₃. The uranium content was then determined fluorimetrically as described by Grimaldi (2).

A blank determination was carried out exactly as above, but with the carbonaceous sample omitted.

CONCLUSIONS

The results of the uranium determinations are given in table 1. The data show that there is no significant difference between the uranium content in the samples as determined by the dry-ashing or the wet-ashing techniques.

It appears from the data, therefore, that when oxidative ashing of uranium-bearing carbonaceous materials is carried out under routine conditions and with routine care, no appreciable losses of uranium from samples take place.

LITERATURE CITED


