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

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

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

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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 violent. The decomposition rate is effectively retarded by the addition of HNO_3 and H_2SO_4 to the $HClO_4$ (by dilution and lower temperature of oxidation). Applications in the use of mixtures of $HClO_4$, H_2SO_4, and HNO_3 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 HNO_3. 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.

Sample	Uranium (percent)			
	Dry ashing		Wet ashing	
Chattanooga shale	0.0094	0.0093	0.0094	0.0095
Subbituminous coal	0.0026	0.0023	0.0023	0.0023
Coal from Chattanooga shale	--	0.0355	0.0347	0.0347
Swedish kolm	0.438	0.448	0.450	0.448
Chattanooga shale	0.0088	0.0087	0.0087	0.0086

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 $HClO_4$, 5 ml concentrated H_2SO_4, and 20 ml concentrated HNO_3 (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 HNO_3 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 HNO_3 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 HNO_3. 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.

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