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

By Frank Cuttitta and Jesse J. Warr, Jr.

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Trace Elements Investigations Report 683

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

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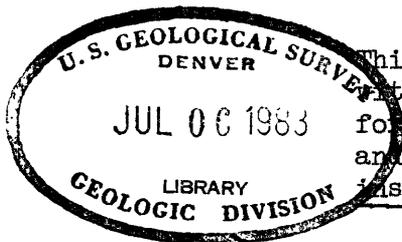
RETENTION OF LEAD DURING OXIDATIVE ASHING OF SELECTED  
NATURALLY OCCURRING CARBONACEOUS SUBSTANCES\*

By

Frank Cuttitta and Jesse J. Warr, Jr.

May 1957

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

## USGS - TEI-683

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RETENTION OF LEAD DURING OXIDATIVE ASHING OF SELECTED  
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ABSTRACT

The amount of lead retained in the ash of lead-bearing carbonaceous material is essentially independent of the method of ashing. Samples containing lead in the range of 0.00X to 0.X percent were ashed by ignition in a high-oxygen atmosphere and were also wet ashed. The lead in the ash was determined colorimetrically. Results were the same by both methods, but the time required is 3 to 10 times less for the dry-ashing method.

INTRODUCTION

The determination of geologic age by the lead-uranium or lead-lead methods (Stieff and others, 1953) is based on a knowledge of the  $Pb^{206}/U^{238}$ ,  $Pb^{207}/U^{235}$ , and  $Pb^{207}/Pb^{206}$  ratios. Errors in the chemical analyses for lead and uranium would introduce uncertainties in the computed age. In the quantitative isolation of milligram and submilligram amounts of lead from large amounts of mineral sample, special care must be exercised to prevent loss of lead. The isolation or the determination of lead in carbonaceous substances generally includes an oxidative ashing step. Previous experience indicates that lead may be lost by volatilization of elemental lead resulting from reduction by the large organic content of the ores during the ashing process (Vogel, 1951). As there are little or no

data regarding the loss of lead from carbonaceous substances during ashing, it was considered necessary to investigate the effects of oxidative ashing on the lead associated with selected uranium-bearing carbonaceous substances. To do this, comparison was made of the lead contents determined by dry ashing in a high-oxygen atmosphere and by wet-ashing techniques (Kahane, 1934; Smith, 1934, 1953; Smith and Sullivan, 1935) that would preclude loss of lead through volatilization.

The samples selected for this study were chosen from a series submitted for age determinations. Among the substances are coals, "asphaltites", woody extracts, and uraninites with admixed organic material. Data for samples containing lead in the range of 0.00X to 0.X percent, determined by both wet and dry techniques, are summarized in table 1.

#### EXPERIMENTAL METHODS

##### Dry ashing (direct combustion in high-oxygen atmosphere)

Samples weighing about 0.2 g were placed in a porcelain boat in a tubular furnace and the furnace temperature was gradually raised to 800° C. The heating was continued until the sample reached constant weight. The quartz combustion tube was continually swept free of combustion products by a mixture 1 part air and 2 parts oxygen at the rate of 5 ml per minute (5 psi pressure). The cooled residue was dissolved completely by treatment with distilled HF and HNO<sub>3</sub> acids. The lead content was determined colorimetrically with dithizone as described by Sandell (1950).

Table 1.--Results of lead determinations.

Sample no.	Nature of material	Lead (percent)		Calculated age (millions of years)	
		Dry ashing	Wet ashing	Dry ashing	Wet ashing
GS/146/55	Carbonaceous sandstone	0.024 0.026	0.023 0.022	185	175
GS/147/55	do.	0.0066	0.006 0.006	180	170
GS/151/55	Carbonaceous uranium-vanadium ore	0.009	0.008 0.008	150	130
GS/180/55	Carbonaceous uranium ore	0.069 0.066	0.061 0.062	150	140
GS/182/55	Carbonaceous sandstone	0.13 0.13	0.11	85	75
GS/375/55	do.	0.080	0.082 0.083	185	190
GS/417/55	Carbonaceous pellets	0.062 0.061	0.061	1700	1650
GS/424/55	do.	0.078 0.079	0.083 0.083	*	*
GS/445/55	Admixture of carbonaceous material with coffinite	0.020	0.018 0.018	*	*
GS/446/55	do.	0.079	0.091	*	*

\* Mass spectrometric data not available.

### Wet ashing

Samples of the carbonaceous material weighing about 0.2 g were treated in a 100-ml volumetric flask with 10 ml of 70 to 72 percent  $\text{HClO}_4$ , 5 ml concentrated  $\text{H}_2\text{SO}_4$ , and 20 ml concentrated  $\text{HNO}_3$  (all redistilled, lead-free reagents). The samples were digested at  $125^\circ$  to  $150^\circ$  C on an electric hot plate with condensation of vapors occurring about halfway up the neck of the flask. Decomposition required from several hours to several days for completion; digestion was stopped when the liquid became clear yellow in color. After cooling, the solution was transferred to a 100-ml platinum dish with 1+1  $\text{HNO}_3$  solution. Ten ml of distilled 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+2  $\text{HNO}_3$  was added to dissolve the salts. The solution was transferred to a volumetric flask and made up to volume. The final acidity was made to 1+4  $\text{HNO}_3$ . The lead content was then determined colorimetrically with dithizone as described by Sandell, (1950).

### ANALYSIS OF DATA

To determine if a difference exists between results of the two methods of ashing, the "t" test for the difference between two means was used (Dixon and Massey, 1951, p. 102). As a result of the test, a "t" value of 0.71 was obtained which is not significant when compared to the table value of  $t = 2.04$  for 30 degrees of freedom at the 95 percent confidence level.

The ages calculated using this lead data were compared by pairing the observations and taking differences (Youden, 1951, p. 28). The average

difference between the ages was not significantly different from zero at the 95 percent confidence level.

#### CONCLUSIONS

There is no significant difference in the lead content of the samples determined either by the dry- or wet-ashing techniques. The time involved in the wet-ashing procedure was from 3 to 10 times greater than that required in the dry-ashing procedure. When oxidative dry ashing of lead-bearing carbonaceous materials containing 0.00X to 0.X percent lead is carried out in a high-oxygen atmosphere, no significant loss of lead takes place.

This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

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