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UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

STATUS OF INVESTIGATIONS ON THE GEOCHEMISTRY AND MINERALOGY OF URANIFEROUS LIGNITES *

By

Irving A. Breger and Maurice Deul

December 1952

Trace Elements Investigations Report 284

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STATUS OF INVESTIGATIONS ON THE GEOCHEMISTRY AND MINERALOGY ON URANIFEROUS LIGNITES

by

Irving A. Breger and Maurice Deul

ABSTRACT

Detailed studies have been carried out on uraniferous lignite from the Mendenhall strip mine, Harding County, S. Dak.

By means of heavy-liquid separations, a mineral-free concentrate of the lignite containing 13.8 percent ash and 0.31 percent uranium in the ash was obtained. The minerals (gypsum 69 percent, jarosite 10 percent, quartz 2 percent, kaolinite and clay minerals 19 percent, and calcite trace) contain only 7 percent of the uranium in the original coal indicating an association of the uranium with the organic components of the lignite.

Preliminary batch extractions showed that 88.5 percent of the uranium could be extracted from the lignite by two consecutive treatments with boiling 1 N hydrochloric acid. Continuous extraction with hot 6 N hydrochloric acid removed 98.6 percent of the uranium.

Continuous treatment of columns of the coal (approximately 750 x 35 mm) with water, 1 N hydrochloric acid, or 6 N hydrochloric acid indicated the possibility that the uranium was held in the lignite by ion exchange. To investigate this further a solution of lanthanum nitrate was passed through a column of the coal to displace any base-exchanged uranium. This experiment

indicated that only 1.2 percent of the uranium in the coal is held by ion exchange. Furthermore, these elutriation experiments showed that the uranium is held in the coal as an organo-uranium compound or complex soluble at a pH of less than 2.18.

Because it is thought that certain phases of many organic geochemical problems may best be solved by correlation studies, equipment has been purchased and set up for the microchemical determination of carbon, hydrogen, nitrogen, sulfur, and oxygen in organic substances. Excellent carbon-hydrogen ratios have already been obtained with a standard sample. Equipment for microfunctional group analysis, that is, for acyl, alkoxyl, and alkimide groups, has also been obtained.

Details are given of conferences which were held with other investigators who are working with uraniferous lignites. A summary is also included of discussions held in Denver on general geochemical problems associated with the study of organic sediments.

Current ideas regarding the manner in which the uranium was brought into and retained by the lignite are discussed and future work is outlined.

INTRODUCTION

As early as 1946 A. L. Slaughter and J. M. Nelson (1946) reported the presence of uranium-bearing lignite in the Red Desert region of southern Wyoming. As a result of their work other areas were examined in 1948 and 1949 and uraniferous lignite was found in southwestern North Dakota (Wyant and Beroni, 1950) and in northwestern South Dakota (Beroni and Bauer, in

preparation). Further field work in these areas, in part supplemented by airborne radiometric surveys and by some core drilling, was done in 1950 and 1951 (Denson, Bachman, and Zeller, 1950; Wyant, Sharp, and Sheridan, 1951). Investigations in these areas as well as in many other areas in the western States have resulted in the discovery of many more uraniferous lignites (Denson, et al., 1952).

A laboratory program was established in 1951 to investigate problems of the origin, distribution, and occurrence of uraniferous lignites. A number of factors concerned with this program are economic: minability of the lignite, utilization of the energy from combustion of the lignite, chemical use of the lignite compatible with the recovery of its uranium, extraction of uranium from the ash of the lignite, and the investigation and extraction of trace elements from the lignite.

The purpose of the geochemical and mineralogic investigations is: (1) to study the distribution of uranium in the minerals and the organic material of the lower rank coals, (2) to determine the conditions under which the uranium can be extracted from the organic material and the manner by which uranium is held in the organic material, and (3) to establish the conditions under which the uranium could have been introduced into the coal so as to be found in its present state.

PERSONNEL

The work summarized in this report has been carried out by a small group of cooperating mineralogists and chemists with assistance, as required, for routine chemical analyses. Maurice Deul, who is responsible

for coordinating all information on the lignite program, is also directing the mineralogic investigations. He has been assisted by Samuel Rubenstein in this work since June 1952.

The chemical studies have been carried out by Irving A. Breger. Robert Meyrowitz has recently been assigned to assist Breger and is at present devoting his full time to the organization of an organic microanalytical laboratory.

Analytical assistance has been obtained, as required, from the staff of the Trace Elements Section Washington Laboratory. Mrs. Shirley Lundine has made most of the analyses for uranium. Many helpful suggestions on the chemical problems have been made by F. S. Grimaldi and Irving May. Charles Annell has performed most of the spectrographic analyses discussed in this report, and Edward Dwornik made the electron micrographs of the separates from the lignite. We acknowledge the cooperation and assistance of these people.

COLLECTION OF SAMPLES

Because of the wide scope of activities of the Geological Survey in the investigation of uraniferous lignites, it was agreed by all cooperating laboratories that samples for laboratory study should be collected by or with the aid of Survey field geologists. Most of the current investigations have been carried out on a large suite of samples collected in July 1952 from the Mendenhall strip mine, Harding County, S. Dak. These samples were collected by a group composed of Professors Spackman and Bates of the Pennsylvania State College, and N. M. Denson, H. D. Zeller

and R. Erickson of the Survey. Professors Spackman and Bates visited the uraniferous lignite deposit of South Dakota to examine field relationships and, at the suggestion of James Schopf of the Survey, collected a columnar sample of the upper part of the Mendenhall coal. In the course of exposing the columnar sample, samples were collected in 27 ten-gallon carbide cans, 3 cans from each of the three beds in each of three zones--front, middle, and back. Details of the sampling procedure are given by Bates and Spackman (1952).

The columnar sample from Harding County was sent to J. M. Schopf at the Survey's Coal Geology Laboratory, Columbus, Ohio, for standard description and preparation prior to distribution for analysis to the Trace Elements Section Washington Laboratory and to the U. S. Bureau of Mines, Pittsburgh. A split of the column was also sent to the Coal Petrology Laboratory at the Pennsylvania State College, and the remainder of the coal was retained at Columbus. Of the 27 carbide cans of samples, 18 were sent to the Trace Elements Section Washington Laboratory, and 9 were shipped to the Pennsylvania State College.

Work on the coal from Harding County, S. Dak., was undertaken because this was the first area containing uraniferous lignites to receive a detailed field examination. The Mendenhall strip mine is the only locality in this area where a thick sequence of lignite is exposed and therefore it was chosen for sampling.

The second area containing uraniferous lignites to receive a detailed field examination is in the Red Desert of Wyoming. Hence it became desirable to obtain a large sample of the low-rank coal from this locality so that

detailed laboratory investigation could be undertaken. It is essential that coals from several areas be studied and compared before arriving at any conclusions with regard to the geochemistry of uraniferous coals.

The Red Desert area was visited during October 1952 so that the general field relationships might be observed and a large sample of the uraniferous lignite collected. The coal was obtained from a good exposure of the Lumen No. 1 bed at the same place (NW1/4 sec. 28, T. 24 N., R. 95 W., Sweetwater County, Wyo.) where a sample had been collected for Dr. Keith Brown of the Oak Ridge National Laboratory. Core sampling by the Survey has been completed in Harding County, S. Dak., and at last report is continuing in the Red Desert of Wyoming. All cores are sent for processing to the Survey's Coal Geology Laboratory in Columbus, Ohio. As very little core material is available for mineralogic and chemical study, it is desirable that all such core material be collected at the Trace Elements Laboratory should the need arise for special chemical studies. Consequently, an effort will be made to recover any unused sample, if still available, from the Bureau of Mines.

MINERALOGIC STUDIES

Introduction

The purposes of the mineralogic studies are:

1. To determine how much of the uranium present in lignites is combined with minerals and to identify whatever uranium minerals may be present.

2. To determine whether any of the minerals, regardless of their uranium content, may be indicative of the presence of uranium in lignite.
3. To study the minerals in various lignites so that the mineralogic composition of "normal" lignite can be determined and definite criteria established for recognizing lignites after alteration by oxidation, weathering, and ground-water action.
4. To determine if a relationship exists between uranium and other minor and trace elements in ashed lignites.

To fulfill these purposes it is necessary to separate the minerals from the lignite, to identify the minerals, and to determine their radioactivity and uranium content. The separable minerals are only part of the total inorganic content of coal, inasmuch as there is always some inorganic material in combination with the plant material and some very fine grained mineral matter which may be incorporated in the coal and may be essentially inseparable. When coal is ashed the total inorganic material is represented by the ash. It is necessary to compare the analyses of mineral-free coal ash, ashed mineral separates, and the original coal ash so that the most significant trace-element and minor-element relationships can be evaluated.

Lignite fractions and separates

Separation and preparation

Several methods of mineral separation were tested and only float-sink separation in heavy liquid media has been found satisfactory for the

relatively large scale operations which are necessary. Froth flotation was attempted with the use of a modified laboratory flotation cell but was less efficient than float-sink. The modified flotation cell was also used as a vessel for float-sink separation to arrange a nearly continuously operating system. This was not practical because of excessive evaporation of the heavy liquid. Air elutriation of uniformly sized material in the Infrasizer was tried, but the continued drying of the lignite under steady air pressure caused further subdivision of the lignite so that no effective separation could be made.

Almost all of the detailed mineralogic separations were carried out on two similar samples, both from the Mendenhall strip mine, Harding County, S. Dak.

The first lignite used in these studies was representative of the entire top bed columnar sample and was a split of the -1/4 inch material prepared at the Coal Geology Laboratory for ultimate analysis and other standard tests by the Bureau of Mines Coal Analysis Section. The lignite was lightly rolled and crushed by hand to prevent formation of the large amount of fines that would be produced by grinding. This sample, which had been kept at original bed moisture, slacked into fines immediately upon air-drying. Oven-drying is not desirable because of the changes effected in both the organic matter and the hydrous minerals. Precise quantitative mineralogy was therefore not possible with this lignite because a material balance could not be maintained throughout a separation. The disaggregated sample, all of which passed a 25-mesh screen, was sieved to -25 +50, -50 +100, -100 +200, -200 +325, and -325 mesh fraction. Each of these

fractions was tested radiometrically, dried at 110 C, ashed, analyzed for uranium, and spectrographically analyzed.

The sieve fractions, except for the -325 fraction, were separated by float-sink in a liquid of 1.7 specific gravity in standard separatory funnels by modifying slightly the procedure reported by Clayton Ball (1935). The liquid was a mixture of carbon tetrachloride and bromoform.

Care was necessary to prevent the loss of organic material by the solvent action of the heavy liquids. Carbon tetrachloride and bromoform were satisfactory, but when such a mixture is used washing should be done with carbon tetrachloride. On one occasion acetone was used as a washing agent on about 30 g of mineral-free coal, and the filtrate showed immediate darkening. About 10 ml of the filtrate was collected in an evaporating dish and upon evaporation to dryness a resinous brown residue was obtained which hardened rapidly. A sample of the filtrate was collected for analysis, and the uranium content was determined to be 0.00447 mg/100 ml; the total solids in the sample were 0.32 g/100 ml. The uranium content of the extract, 0.0014 percent, shows that careful choice of liquids is essential to keep organic extraction to a minimum and to prevent loss of some uranium from the original sample.

The columnar sample from the Mendenhall strip mine furnished material for early experiments. This material was supplemented by 20 gallons of equivalent material which was homogenized and used for preparing further separates and to furnish material for additional experiments. This larger sample required faster means of separation. A preliminary separation was

possible by simple sink-float of -10 mesh lignite in a 5-gallon vessel. This was replaced by sink-float in 4-liter separatory funnels which emptied into large Buchner funnels where rapid filtration was possible with a minimum of evaporation. Pure carbon tetrachloride was used in this procedure and the change of specific gravity from 1.7 to 1.57 made little difference in the separation. The use of a pure liquid rather than a mixture of carbon tetrachloride and bromoform simplified the separations.

The fine sieve fractions offer a special problem in separation. Isolation of clay minerals from quartz is not successful even when -400 mesh material is used. Centrifugation helps somewhat, but quartz-free separates were not obtained.

The individual minerals were separated by heavy-liquid separation techniques. Mixtures of carbon tetrachloride and bromoform were used for separation of minerals with specific gravity as high as 2.7. No minerals with specific gravity over 3.2 were obtained, inasmuch as nothing sank in methylene iodide.

The separation of gypsum from clay minerals was greatly simplified by gently heating the clay-gypsum separate under an infrared heat lamp. As a result the gypsum alters to the hemihydrate and to anhydrite. The change of gypsum to the minerals of higher specific gravity permits the ready separation of the clay minerals in a liquid of specific gravity 2.4.

Analyses

The sieve fractions of the disaggregated lignite show no great variation in their analyses. The finer fractions generally have a lower ash

content and the finest fraction, -325 mesh, has the highest uranium content. This probably indicates that the organic matter is selectively concentrated in the finer fractions. Gypsum, the most abundant mineral, does not crush easily and therefore tends to remain on the coarser sieves.

Although the finer sieve fractions of unseparated lignite have a lower ash content, the reverse is true for the separated organic material with a specific gravity lower than 1.7. This is shown in table 1. The poor separation of minerals from the organic material in the finer fractions is reflected in the ash analyses of the B and C series of samples in this table. Series B consists mainly of organic material, series C mainly of minerals. It should be noted that the separates with a specific gravity over 1.7 were ashed to remove all the organic matter so that the uranium analyses could be made. In sample 1-C, for example there was probably less than 1 percent organic matter, and most of the loss in weight upon ashing results from the removal of water from the hydrous minerals.

The mineral separates show a marked disequilibrium. Although the equivalent uranium content of the mineral separates is generally higher than that of the organic fractions, the uranium content of the mineral separates is only one-fourth that of the organic fraction. The minerals which comprise about 20 percent of the air-dried lignite contain only about 7 percent of the total uranium in the lignite. The organic material, therefore, contains about 93 percent of the total uranium. Sulfate minerals commonly coprecipitate radium sulfate, an extremely insoluble compound, and it is rather certain that radium has been selectively concentrated in the sulfates and is the cause of the observed disequilibrium.

Table 1.--Percentage analyses of lignite, sieve fractions, and specific-gravity separates of sample from Mendenhall strip mine, Harding County, South Dakota.

Sample and mesh		Moisture	eU	Ash	Uranium in ash	Uranium in dry sample
Original lignite		42.0	0.018**	32.4	0.12	0.039
Sieved bulk lignite						
1-A	-25 +50	25.2	0.016*	32.2	0.104	0.033
2-A	-50 +100	20.1	0.026*	28.8	0.132	0.038
3-A	-100 +200	17.5	0.028*	27.9	0.120	0.033
4-A	-200 +325	15.9	0.026*	25.6	0.138	0.035
5-A	-325	13.6	0.027*	26.4	0.155	0.041
Sieved separate, specific gravity < 1.7 (mainly organic material)						
1-B	-25 +50	--	0.025	13.8	0.31	0.043
2-B	-50 +100	--	0.020	14.4	0.30	0.043
3-B	-100 +200	--	0.021	15.7	0.33	0.052
4-B	-200 +325	--	0.023	17.7	0.20	0.035
Sieved separate, specific gravity > 1.7 (mainly minerals)						
1-C	-25 +50	--	0.021	75.1	0.014	0.011
2-C	-50 +100	--	0.033	71.3	0.016	0.011
3-C	-100 +200	--	0.039	69.8	0.019	0.013
4-C	-200 +325	--	0.041	55.3	0.017	0.009

* Percent eU is determined on air dry material.
** Percent eU is determined on sample with original bed moisture. All other determinations based on samples dried at 110 C.

Mineral identifications

The minerals present in the lignite from the Mendenhall strip mine are gypsum, jarosite, quartz, kaolinite, calcite, and a clay mineral -- possibly allophane. All the minerals except the clays are easily identified by their optical properties as determined with the polarizing microscope. The gypsum exhibits its typical characteristics and can be recognized in hand specimen; once identified, the jarosite is readily recognized even in minute quantities by its characteristic yellow color. Quartz and calcite can best be identified by optical methods because they are almost always present as grains fine enough to pass a 50-mesh screen.

The mineral matter separable by a liquid of specific gravity 1.7 is 20 percent by weight of the air-dried lignite. As previously indicated this cannot be a precise determination but is as good a figure as can be obtained with the procedures followed. Starting with lignite of 42.0 percent bed moisture, each of the sieved fractions loses water at a different rate. The moisture of air-dried material ranges from 25.2 percent for -25 +50 mesh material, to the low of 13.6 percent for -325 mesh material. Oven drying for material to be used for quantitative mineral separation is unsatisfactory because gypsum dehydrates to the hemihydrate and to anhydrite, the characteristics of clay minerals are modified, and even the jarosite may lose some water at 110 C.

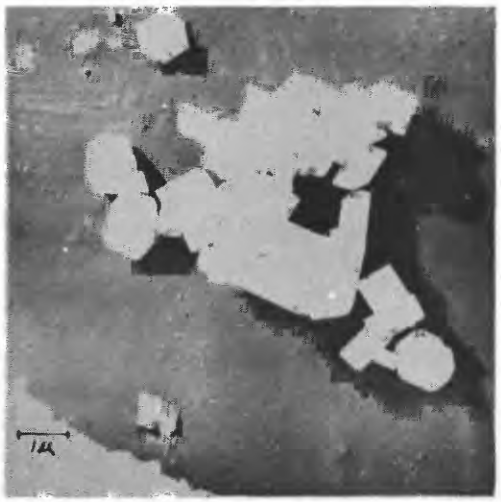
The distribution of the minerals in the columnar samples, as observed at the Coal Geology Laboratory in Columbus immediately after the sample was unpacked, showed great variation. Therefore, for the material from the

Mendenhall mine, only an average mineral composition can be given for the upper bed:

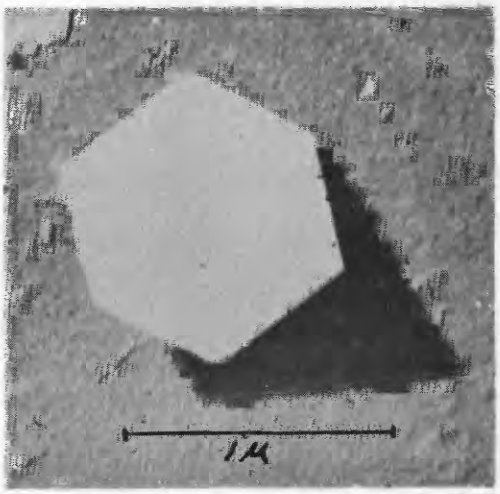
Gypsum	69 percent
Jarosite	10 percent
Quartz	2 percent
Kaolinite and other clay minerals (mostly "allophane")	19 percent
Calcite	< 1 percent
Only trace amounts of other minerals are present	

In the course of tests run to identify the clay minerals by X-ray diffraction, the presence of quartz, calcite, gypsum, jarosite, and kaolinite has been confirmed. Excellent X-ray spectrometer graphs for gypsum and other calcium sulfate hydrates were obtained indicating that changes in composition probably took place in the brief time necessary to separate the minerals. Eight electron micrographs of jarosite from the Mendenhall mine columnar sample have been made by E. J. Dwornik. These micrographs exhibit the perfect crystallinity of the jarosite, even in single discrete particles less than a micron in size. Hexagonal outlines of rhombohedral plates with well-developed pinacoids, and the pseudo-cubic rhombohedra so characteristic of jarosite are illustrated in figure 1.

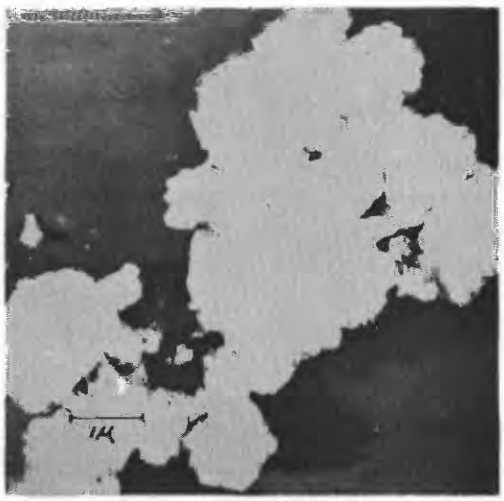
Many differential thermal analyses were made on a clay mineral separated from the lignite. It is now thought that this clay may be the mineraloid, allophane. It is a rather anomalous material and, although it cannot be completely separated from quartz and a small percentage of what is probably kaolinite, its isotropism is very definite. This so-called allophane has a higher index of refraction than that reported in the liter-



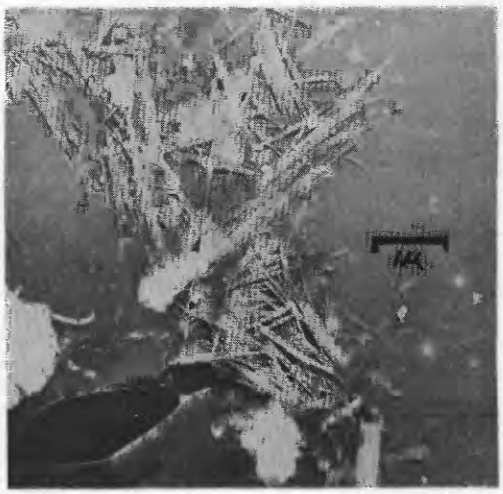
Jarosite



Jarosite



Clay
(Allophane ?)



Clay
(Attapulgite?)

Figure 1.–Electron Micrographs
(Chromium Shadowed)

ature, but it is believed that the higher index can be attributed to the presence of a ferric hydrate. We have not yet been able to determine if the high iron content of the clay rules out the likelihood of its identity as allophane. Electron micrographs of the material prepared by Dwornik (fig. 1) show only the irregular outlines of extremely small particles so typical of truly amorphous material; the complete absence of any well-defined recognizable shape rules out the possibility of this being kaolinite or any of the other well-crystallized clays of similar composition. Only silicon, aluminum, and iron are present in amounts greater than 1 percent, and some of the silicon represents the quartz which it has not been possible to separate from the clay. Because the allophane contains some organic material and also because of the difficulty of separating it from other minerals, the thermograms for this material are not diagnostic. This is true for the thermograms made on the portable non-automatic recording units in this laboratory, for thermograms made by Irving A. Breger at Massachusetts Institute of Technology, and for those obtained by George T. Faust at the Investigations Section Washington Laboratory of the Survey.

This particular clay-mineral separate contains 0.003 percent uranium--only about one-fourth that of any mineral separate. This is the mineral fraction containing the least uranium of any material yet separated from the lignite.

There has been another clay mineral identified from a lignite collected from the Medicine Pole Hills area, Bowman County, N. Dak. Electron micrographs of an ultra-fine fraction of the lignite from core hole no. 8

exhibit characteristic shapes and aggregates typical of attapulgite.

These same electron micrographs showed cubic particles, less than 1 micron in maximum dimension, which may be pyrite.

Alpha-plate studies

Six alpha plates of fine-grained material were made--two of the -165 mesh clay-quartz fraction, two of the -165 mesh material with specific gravity 2 to 2.4, and two of 80-165 mesh material with specific gravity 2 to 2.4 material. The material in the specific gravity range 2 to 2.4 is mostly gypsum, clay, and quartz, with some fine grains of jarosite. Very few alpha-particle tracks were observed but some definitely originate within mineral grains. There is no concentration of alpha-particle tracks, and judging from the track population, the uranium is sparsely disseminated through the mineral grains and might possibly be associated with occluded organic matter. There is no evidence that any of the mineral grains are uranium minerals or contain high concentrations of uranium.

Trace-elements studies

Every cored coal sample received for analysis in the Trace Elements Section Washington Laboratory has been ashed and spectrographically analyzed. This has permitted the comparison of the trace-element content of uraniferous lignites with that of nonuraniferous lignites.

Lignites have not been studied in as much detail as have the bituminous and sub-bituminous coals, and as a consequence most compilations of coal and coal-ash analyses make little or no reference to lignite. Gibson and

Selvig made a thorough review of the literature and in their Bureau of Mines Technical Paper 669, 1944, reported only two complete analyses of ashed lignite. It is fortunate that large suites of lignite samples from several localities were available for our current study. In all, some 325 samples have been analyzed and are considered in this discussion.

In preparation for the intensive study of the lignites six samples from Harding County, S. Dak., were selected for chemical and spectrographic analysis of the ash. These samples were chosen from the 435 samples collected by Denson, Bachman, and Zeller of the Survey during the 1950 field season. Table 2 shows the results of the spectrographic analyses and table 3 gives the chemical analyses of the six samples. Because the spectrographic analyses showed surprisingly high percentages of barium, strontium, nickel, cobalt, zirconium, and molybdenum, these elements were determined chemically, and the results confirmed the spectrographic data.

The method used in the semiquantitative spectrographic analysis for 68 elements in one exposure of a 10-mg sample was developed by C. L. Waring and C. S. Annell (1951, 1952) of the Geological Survey. Because the standard plates are prepared with elemental concentrations differing by a factor of 10 the analyses are reported in the percentage ranges listed below:

Over	-	10
1	-	10
0.1	-	1
0.01	-	0.1
0.001	-	0.01
0.0001	-	0.001

The standard sensitivities for the elements determined by the semiquantitative spectrographic method are given in table 4. Although all

Table 2.--Spectrographic analysis of selected samples of ashed lignite from Harding County, S. Dak. (in percentages) 1/

Sample no.	Lab. no.	Over 10	1 - 10	0.1 - 1.0	0.01 - 0.1	0.001 - 0.01	0.0001 - 0.001
SC-35	47933	Fe	Al Ca Na K Si	Mg Mo Sr Mn Zr	B Ti Ba Ni Pb Co Sc Ga V	Y Cr Cu	Yb
SC-36	47934	Al	Fe Si Ca Na	Mg K Sr Mo Mn Ba	B Ti Zr Ni Pb Co Sc	V Ga Y Cr Cu	Yb
F-95	42921	Fe Si Al	Ca Na	Mg Mn Ni Sr K Zr Co Ti	Ba Mo Pb Sc Y V Ga B	Cr Cu	Yb
F-84	42922	Fe Si Al	Na Ca	Mg K Mn Mo Ni Ti Zr	B Sr Ba Co Pb Sc Y V Ga	Cr Cu	Yb
C-18b	44269	--	Na Fe Mg Ca Al Si	K Sr Ba	Mo Zr Ti Mn Ni Pb Sc Ga B	V Cr Y Cu	Yb
S-29	45367	Fe	Al Na Si Ca K	Mg Mo Sr	B Mn Ti Ba Ni Pb Co Sc Ga	V Zr Y Cr Cu	Yb

1/ Analyst, Charles Annell

Table 3.--Chemical analysis of selected samples of lignite from Harding County, S. Dak.

Lignite ash 1/

Sample no.	SC-35	SC-36	F-95	F-84	C-18b	S-29
Lab. no.	47933	47934	42921	42922	44269	45367
LOI	3.32	5.62	2.10	7.80	2.30	7.30
SiO_2	9.54	21.76	32.18	28.46	11.58	15.20
Al_2O_3	14.75	23.80	21.85	19.60	12.90	17.65
Fe_2O_3	22.50	12.40	31.20	33.81	14.40	34.50
TiO_2	0.10	0.10	0.60	0.60	0.10	0.10
CaO	20.15	14.35	10.80	4.00	14.70	12.00
MgO	0.12	0.18	0.21	0.21	7.30	0.23
K_2O	1.11	1.11	0.82	0.82	0.92	1.54
Na_2O	3.14	3.45	1.90	3.55	24.88	4.38
MnO	0.26	0.48	1.01	0.26	0.05	0.14
SO_3 2/	29.00	22.82	1.35	4.68	13.40	9.23
BaO 3/					0.30	
SrO 3/					0.53	
NiO 3/			0.15			
CoO 3/			0.05			
ZrO_2 3/			0.27			
MoO_3 3/						0.23

Lignite

eU 4/	0.017	0.015	0.014	0.006	0.021	0.031
	0.016					
U 4/	0.027	0.014	0.012	0.005	0.018	0.030
	0.029					
U in ash 4/	0.116	0.056	0.035	0.033	0.053	0.12
Ash 4/	25.07	25.17	32.1	15.1	34.82	25.53

1/ Analyst, A. M. Sherwood.

2/ The sulfur is calculated as SO_3 although part of the sulfur is present as sulfide and possibly sulfite. Inasmuch as varying conditions of ashing would result in different losses of sulfur and in varying proportions of sulfide, sulfite, and sulfate residues, it was not considered necessary to determine the exact form of the sulfur. Summation to 100 percent is not possible.

3/ These determinations were made as spot checks only as listed.

4/ From other analytical reports, Trace Elements Section Washington Laboratory.

Table 4.--Standard sensitivities for the elements in lignite ashes determined by the semiquantitative spectrographic method (in percent)

Minor and trace elements

Ag	0.0001	Ge	0.001	Sn	0.01
As	0.1	La	0.01	Sr	0.01
B	0.001	Li	0.0001 (0.1)1/	Ti	0.001
Ba	0.0001	Mo	0.001	U	0.1
Be	0.0001	Mn	0.001	V	0.01
Co	0.01	Ni	0.01	Y	0.001
Cu	0.0001	P	0.1	Yb	0.0001
Cr	0.001	Pb	0.01	Zn	0.01
Ga	0.01	Sc	0.001	Zr	0.001

Major elements

Al	0.0001	Fe	0.001	Na	0.001 (0.1)1/
Ca	0.001	K	0.01 (1.0)1/	Si	0.0001
		Mg	0.0001		

Sensitivities of elements not detected

Au	0.01	Ho	0.01	Rh	0.01
Bi	0.001	In	0.001	Ru	0.01
Cd	0.01	Ir	0.1	Sb	0.01
Ce	0.1	Lu	0.01	Sm	0.1
Cs	0.1 (1.0)1/	Nb	0.01	Ta	0.1
Dy	0.01	Nd	0.01	Tb	0.01
Eu	0.01	Os	0.1	Te	0.1
Er	0.01	Pd	0.01	Th	0.1
F	0.1 2/	Pr	0.01	Tl	0.1
Gd	0.01	Pt	0.01	Tm	0.01
Hf	0.1	Rb	0.01 (10.0)1/	W	0.1
Hg	0.1	Re	0.1		

1/ A second exposure is required for the high sensitivity listed.
2/ A special exposure is required for the fluorine estimation.

Note: The standard plates are prepared with elemental concentrations differing by a factor of 10; hence, some elements can be detected below the sensitivities listed but not necessarily to the next lower value.

samples were analyzed for 68 elements, Si, Al, Fe, Ca, Na, K, and Mg are not of importance to this particular investigation because these elements are present in large amounts in almost every coal ash. Certain other elements were not detected and are so noted in table 4. Some elements can be detected far below the sensitivities listed but such determinations require far greater refinements and are not as rapid. Note that, even with the quick "one-shot" semiquantitative method used in this work, some elements are detected below the sensitivities listed.

The maxima for each of the 27 minor and trace elements present in ashed lignites from six areas are given in table 5.

The lignites from McKenzie County, N. Dak., are nonuraniferous and contain less than 0.0001 percent uranium in the ash. None of the lignites from Milam County, Texas, was sufficiently radioactive to warrant chemical uranium determinations. The Jefferson County, Colo., samples were cored samples taken from the vicinity of the Leyden mine where uranium had been found in what was reported to be a mineralized coal; none of the samples had more than 0.006 percent uranium in the ash, and most ashes contained 0.002 percent uranium or less.

The lignites from Bowman County, N. Dak., and Harding and Perkins Counties, S. Dak., have an extremely variable uranium content. In table 5 all the samples from these counties are from uranium-bearing series.

A set of histograms are presented to show the percentages of uranium, molybdenum, nickel, cobalt, lead, vanadium, zirconium, scandium, germanium, and tin (figs. 2-11) in the ashed lignites from the different areas. The trace-element data, as illustrated in the histograms, make no attempt to

Table 5.--Maximum percentages for elements detected in lignite ash from different areas

Locality	1-10	0.1 - 1.0	0.01 - 0.1	0.001 - 0.01	0.0001 - 0.001
Harding County, S. Dak., 149 samples		B Ba Sr P Mn Ti Mo Co Ni Zn As Pb Zr Be	Cu Cr V Li La Ga Ge Sc Y	Sn	Yb Ag
Perkins County, S. Dak., 59 samples		B Ba Sr P Ti Mo Zr	Cu Cr V Ni Co Pb Mn Ga Ge Zn La	Y Sc Sn	Be Yb Ag
Bowman County, N. Dak., 26 samples		B Ba Sr Mn Ti As Pb V Zr	Cu Cr Mo Ni Co Ga Ge	Y Sc Sn	Be Yb
McKenzie County, N. Dak., 4 samples		B Ba Sr Mn Pb	Ti V Cu Li Sn La Zr Co	Y Mo Ga Ge Ni Cr	Be Yb
Jefferson County, Colo., 35 samples		B Ba Sr Mn Ti Mo Y	Cu Cr V Ni Co Zr Pb Y	Sn Sc Ga Ge La Yb Be	
Milam County, Tex., 48 samples	P	B Ba Sr Mn Ti Ni Sn	Cu Cr V Co Pb Zr Zn Y	Mo Sc Ga Ge Be Yb	

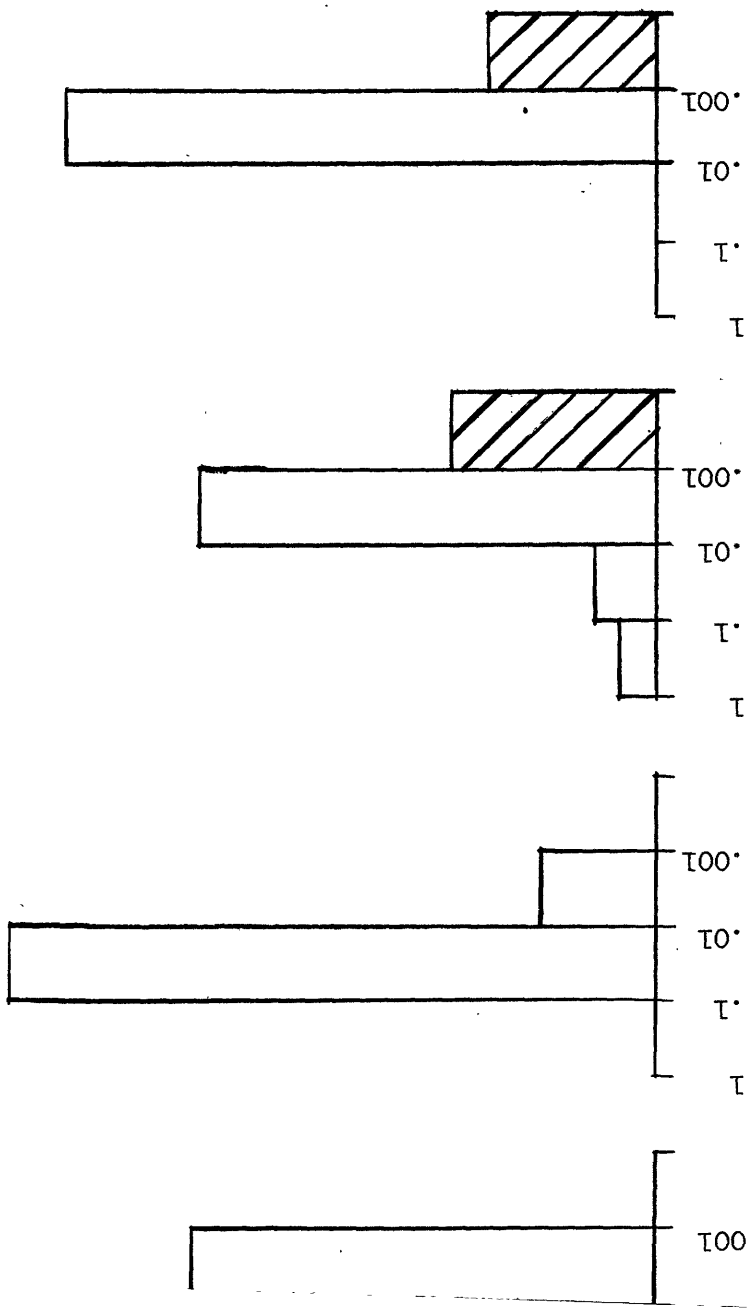


Figure 2.--Uranium in lignite ash.

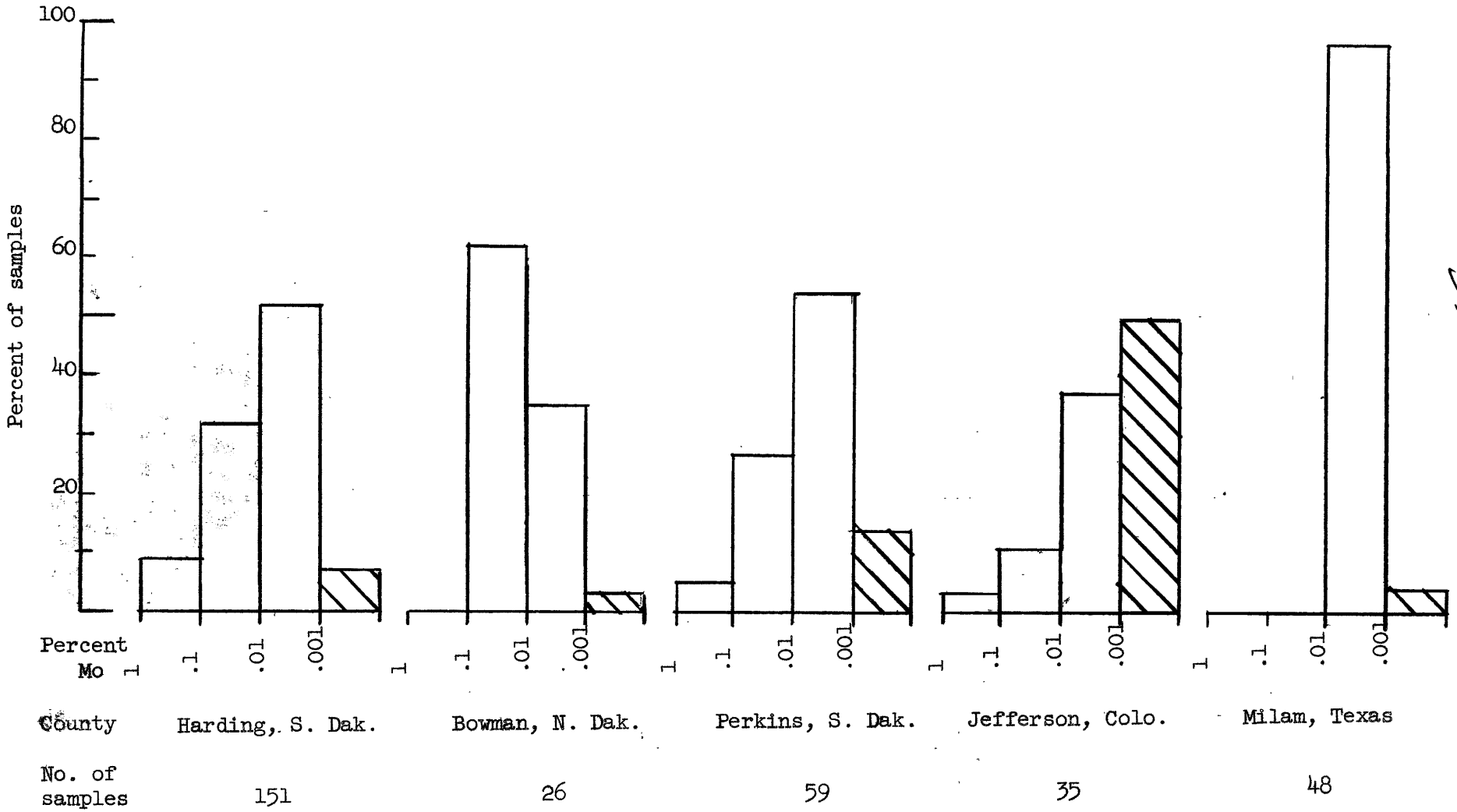


Figure 3.--Molybdenum in lignite ash (limit of detection, 0.001 percent)

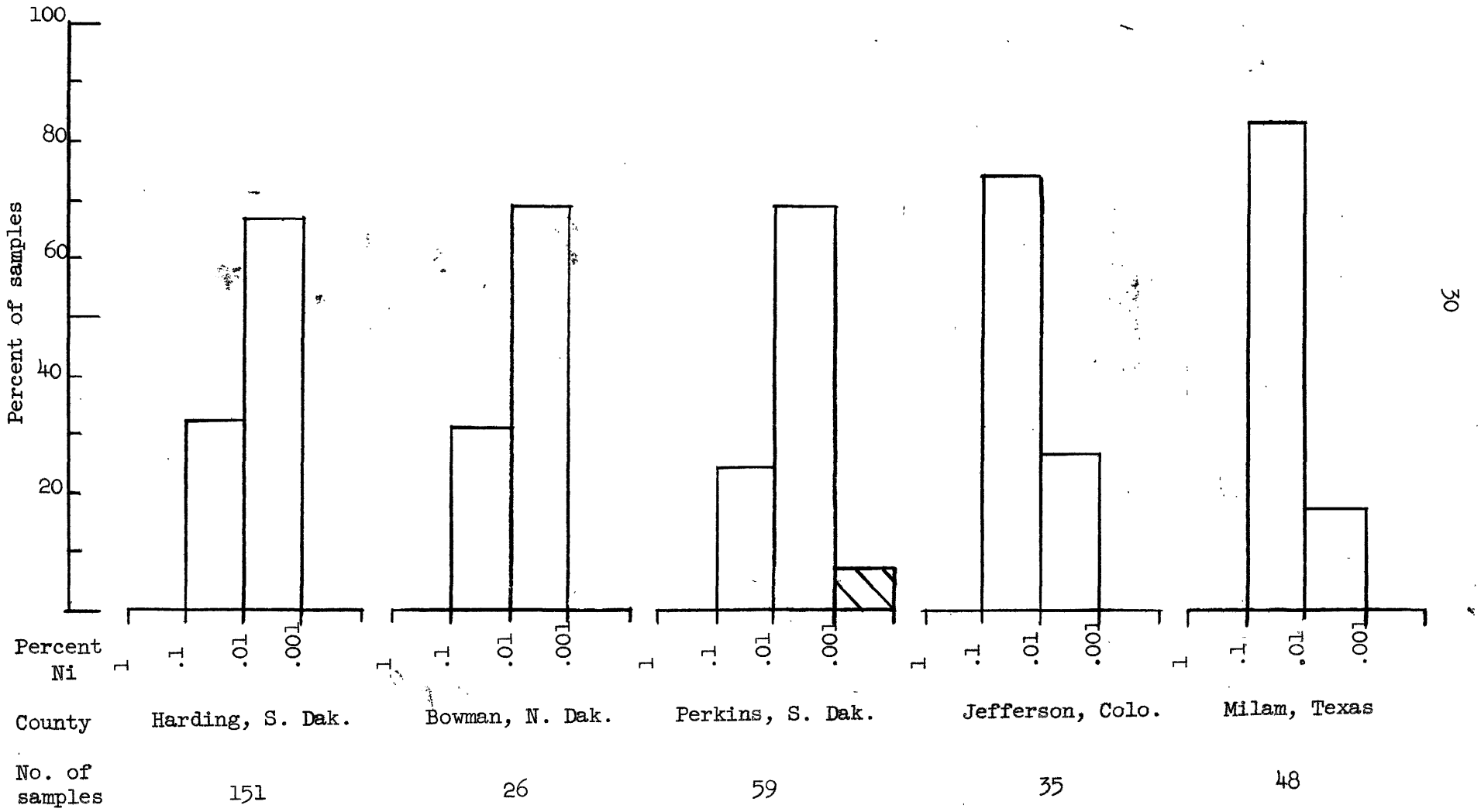


Figure 4.--Nickel in lignite ash (limit of detection, between 0.01 and 0.001 percent).

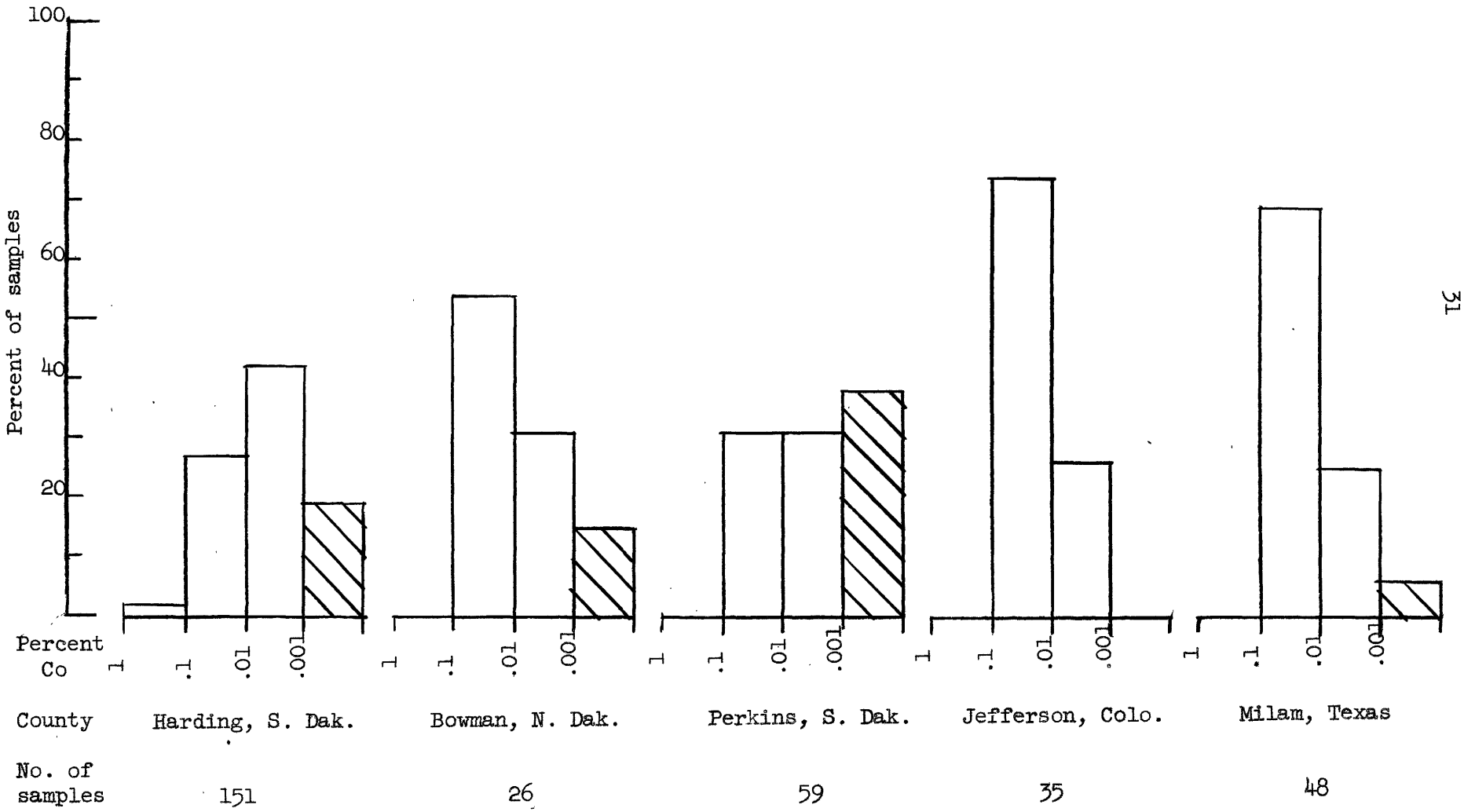


Figure 5.--Cobalt in lignite ash (limit of detection, between 0.01 and 0.001 percent).

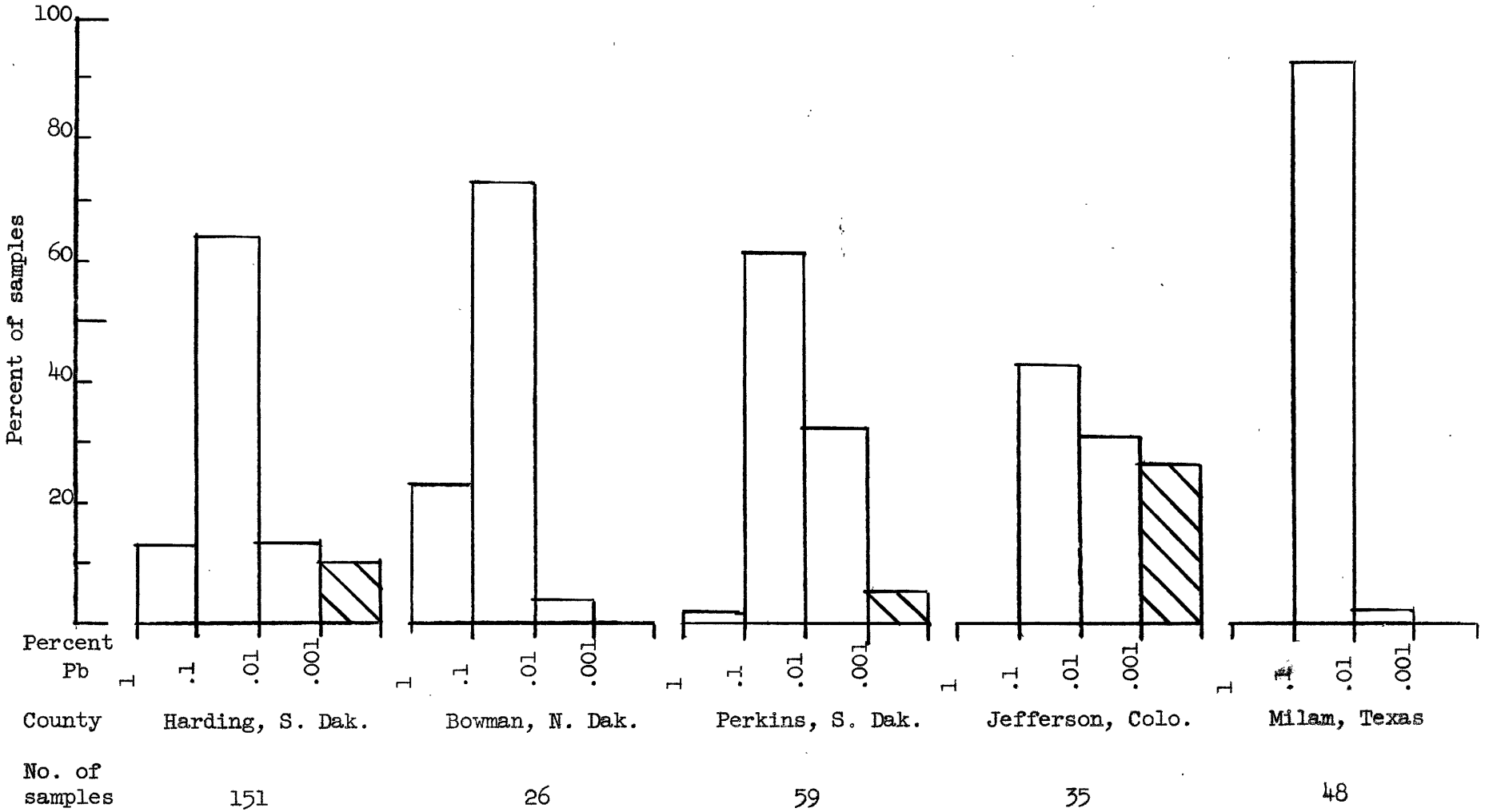


Figure 6.--Lead in lignite ash (limit of detection, between 0.01 and 0.001 percent).

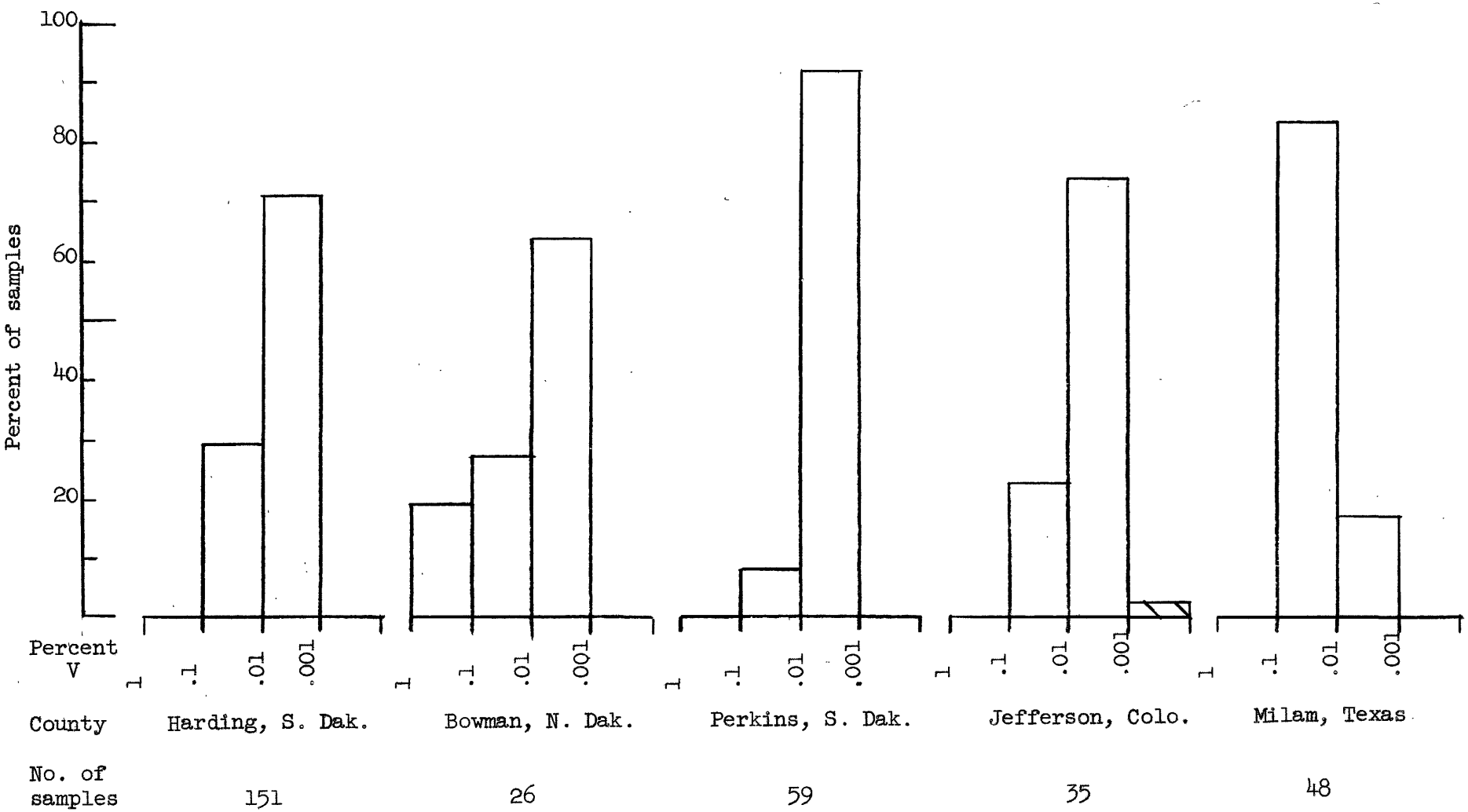


Figure 7.--Vanadium in lignite ash (limit of detection 0.001 percent).

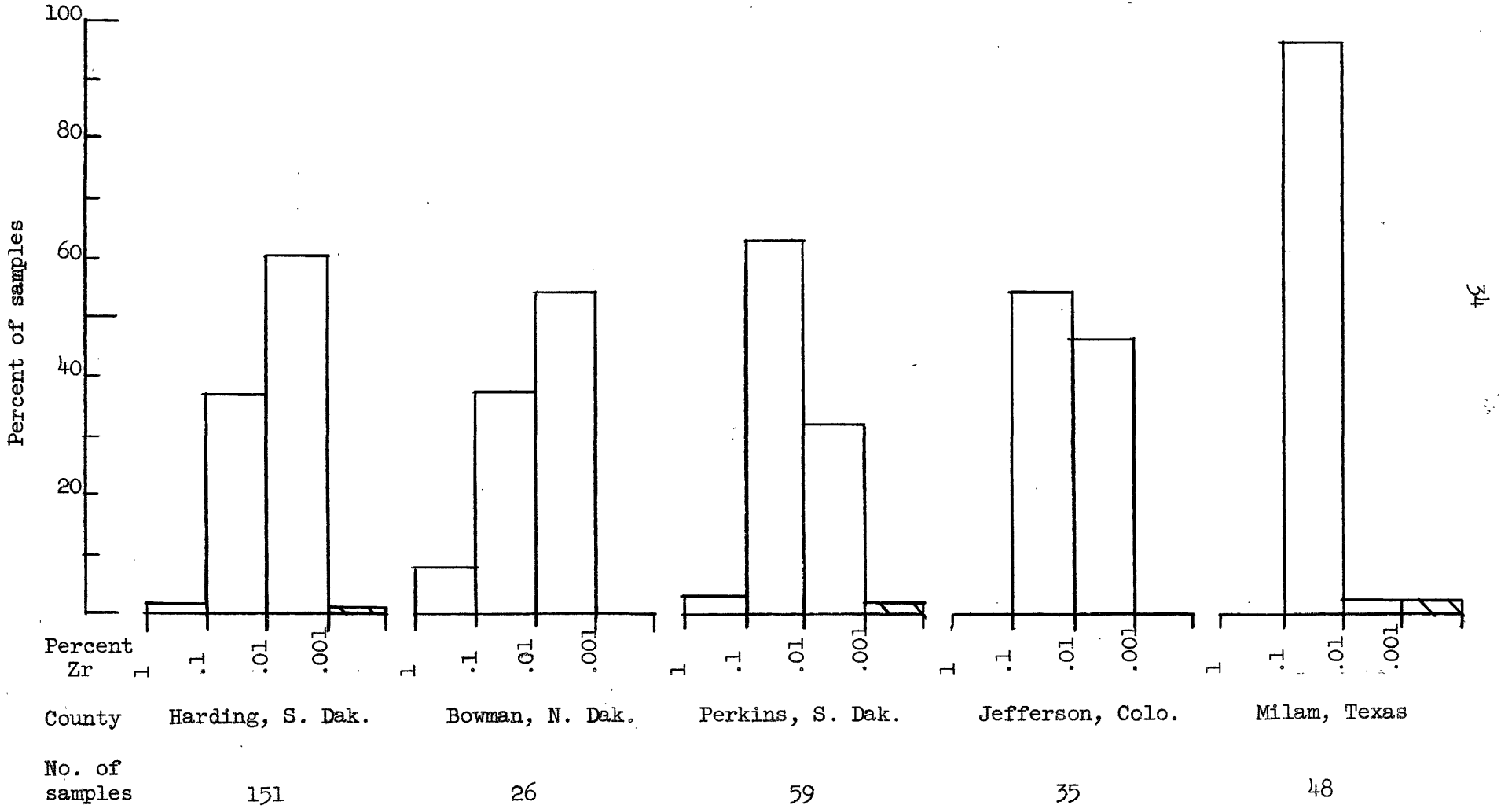


Figure 8.--Zirconium in lignite ash (limit of detection 0.001 percent)

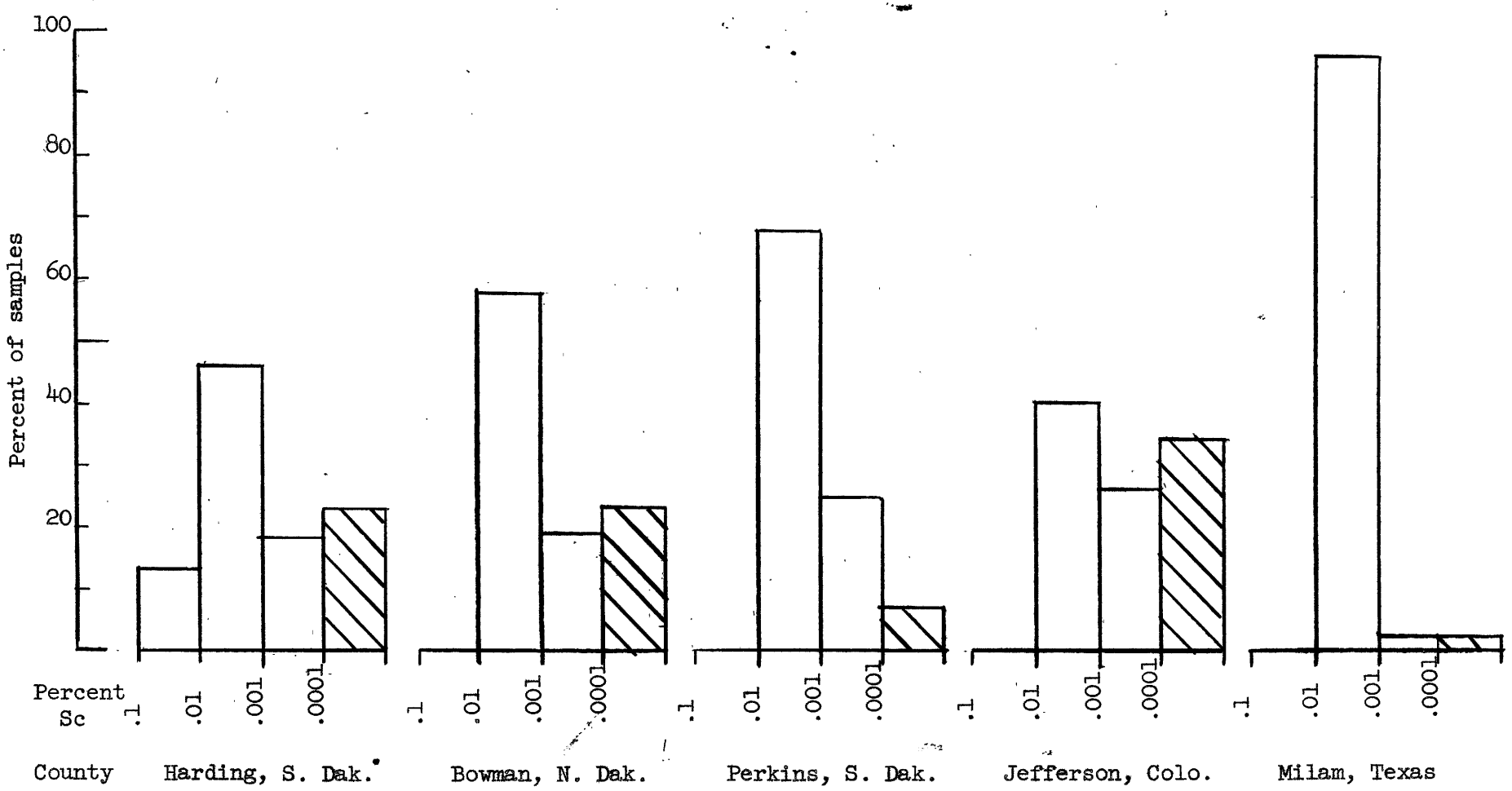


Figure 9.--Scandium in lignite ash (limit of detection, between 0.001 and 0.0001 percent).

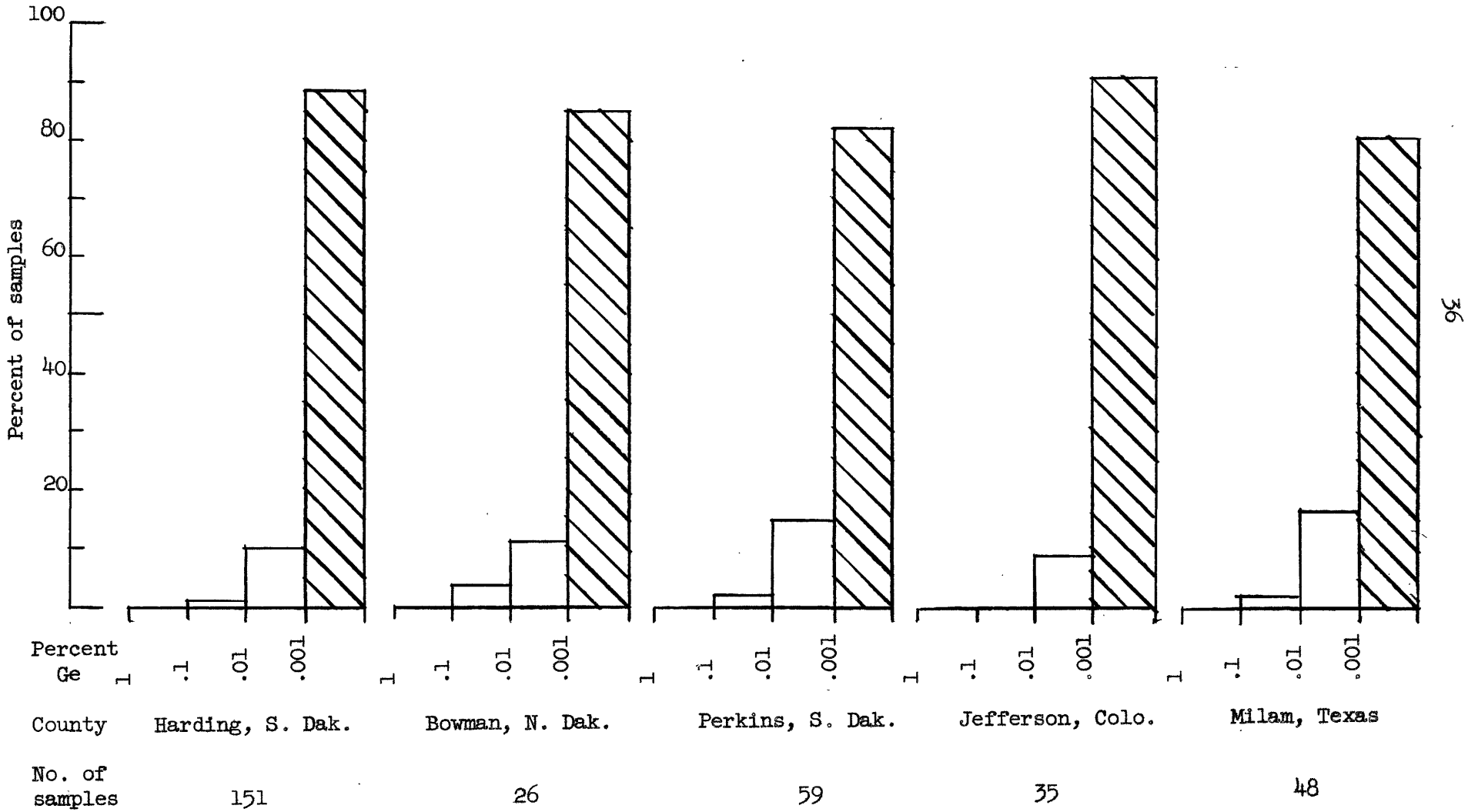


Figure 10.--Germanium in lignite ash (limit of detection, between 0.01 and 0.001 percent).

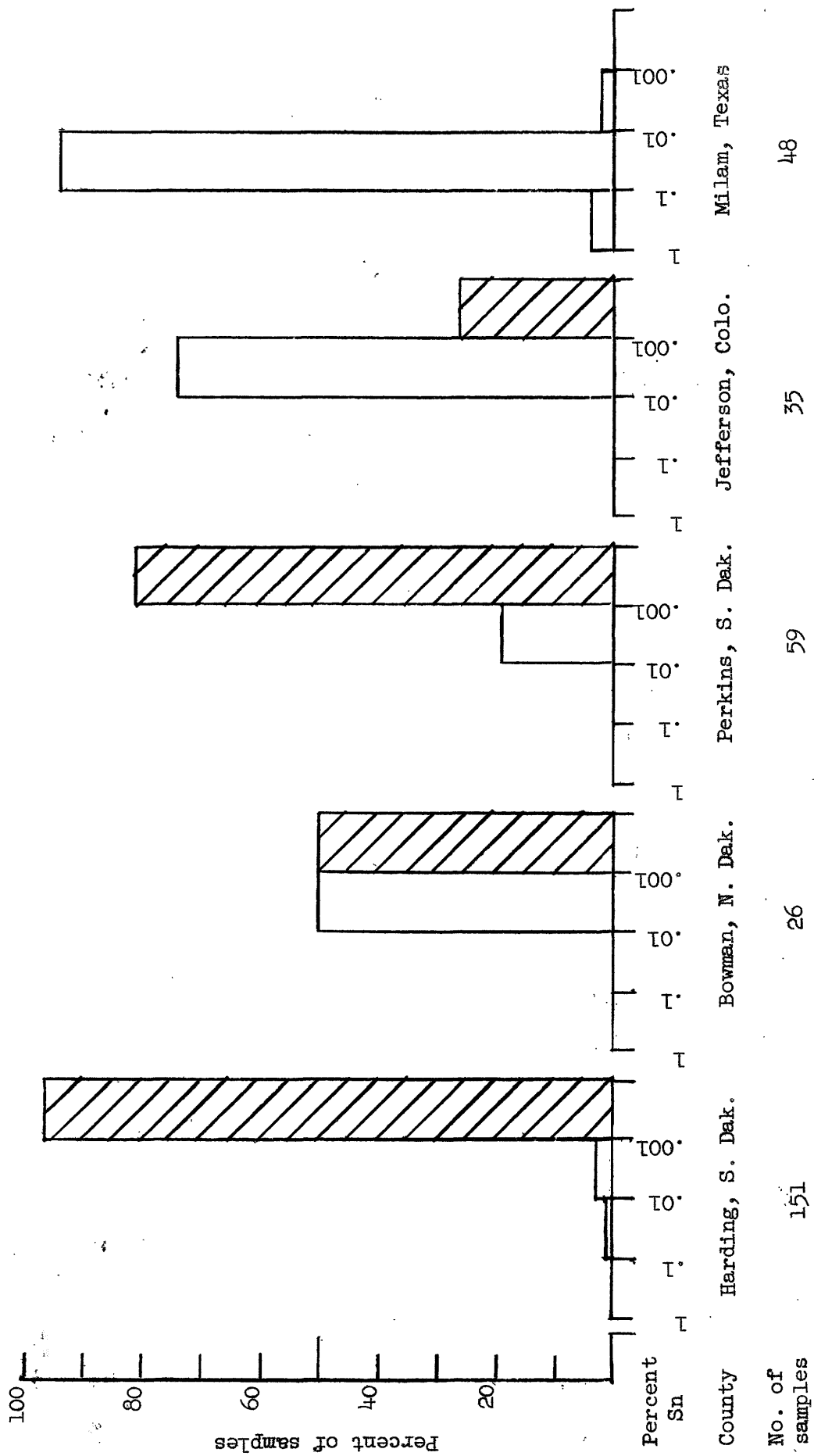


Figure 11.--Tin in lignite ash (limit of detection, between 0.01 and 0.001 percent).

correlate the elements within individual samples. This sample-to-sample comparison should be done in great detail by application of punched-card sorting methods so that all existing relationships can be observed and interpreted.

The histograms for uranium (fig. 2) and for molybdenum (fig. 3) show a general similarity. On a sample-to-sample comparison this similarity is not borne out in coals from Jefferson County, Colo., and from Bowman County, N. Dak. Here other factors must be considered. The arsenic concentration as determined spectrographically is unusually high in several samples from Bowman County. Arsenic may behave in quite the same manner as molybdenum, and thus it may be necessary to study the relationships of uranium to molybdenum and to arsenic. Special analyses for arsenic will be required because of its relatively low spectral sensitivity. It is unlikely that uranium molybdate or uranium arsenate minerals have formed because the arsenic and molybdenum tend to remain with the organic matter rather than with the mineral matter; this can be seen in table 6 where the analyses of organic matter and separated minerals are compared to the original bulk sample. There is a greater likelihood that the uranium-molybdenum association may be a fortuitous one and that in certain areas the molybdenum was present in the same solutions that carried the uranium. The Himus and Basak method (1949) for separating mineral matter from coal by extremely fine grinding may release any minerals still present in the coal separated by sink-float methods. This should permit the concentration of any molybdenum or arsenic minerals that may be intimately associated with the coal.

Table 6 --Associations of elements in ashed lignite and ashed sink-float separates from a sample from the upper bed, Meadenhall strip mine, Harding County, S. Dak. (in percent)

	Ash	Uranium in ash	>10	10 - 1	1 - 0.1	0.1 - 0.01	0.01-0.001	0.001-0.0001
Original coal	32.2	0.104	Al Si Fe	Ca Mg Na	Mo Ba B	Ti Sr As Mn Zr Ni Co Cr Cu Pb Zn	Ga V Y Sn Sc	Be Yb
Float, 1.7 specific gravity	13.8	0.31	Al Fe	Si Na Mg	Ca Mo Ti B Zr Ba Mn	As Cu Sr Ni Co Cr Zn	Ga V Y Sn Sc	Be Yb
Sink, 1.7 specific gravity	75.1	0.014	Si	Al Ca Fe	Na Mg Ba	Sr Ti Mo B Cu Mn Pb	Zr Ge Cr Ga V Sn Ni Y	Yb

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A sample of lignite from the Mendenhall strip mine in Harding County, S. Dak., was analyzed spectrographically as were its sink-float separates. These analyses are presented in table 6. The high ash content of the separated organic material suggests the need for further separation to determine if most of the ash represents finely divided minerals which floated with the coal or metallo-organic associations.

CHEMICAL STUDIES

Statement of problem

As stated in the Introduction, it was felt that the proposed laboratory investigations should contribute to an understanding of the manner in which the uranium was introduced into the coal, to the mechanism by which it is retained by the coal, and to means by which to extract it from the coal. It was recognized that none of these problems could be solved without close cooperation of chemists, mineralogists, and geologists. Plans were made to approach the chemical problems by application of the principles of organic chemistry.

At the time that the following studies were undertaken considerable information was available on the field relationships in North Dakota and Wyoming, where known uraniferous lignites occur, and on the composition of the ash from the uraniferous lignites. No work had been carried out on the chemical structure of the coal, nor had studies been undertaken to determine if the uranium in the coal was associated with its organic or mineral constituents. Because such studies would provide fundamental information with

regard to the relationship between the uranium and the coal, a joint program was organized for the mechanical isolation of the mineral constituents of the coal on the one hand, and for the study of the chemical character of the organic portion of the coal on the other hand. It has already been shown in the section on mineralogic studies that the greater part of the uranium seems to be associated with the organic constituents of the coal rather than with its minerals. This work emphasizes the importance for the study of the organic structure of the coal and has served as an impetus for the work which is described below.

Previous studies of the chemical structure of coal (Breger, 1951; Breger and Whitehead, 1951) had led to the belief that low-grade coals probably have well-developed ion-exchange properties. This consideration led to the desirability of the extraction of the uranium from the lignites in an effort to confirm the hypothesis that the uranium is held by ion-exchange. That uranium may be held in the coal in other forms, perhaps as a finely divided or colloidal oxide or salt, or as an organo-uranium compound or complex, was not overlooked.

Extraction studies

Batch extraction

Before detailed organic chemical studies could be initiated it was necessary to acquire the necessary laboratory equipment. In the meantime, however, a number of simple experiments were carried out to obtain some idea as to the relationship between the coal and its uranium.

To determine if uranium is held in lignite in a loose combination, perhaps by ion-exchange, a weighed amount of material from Hole 2, Harding County, S. Dak. (Lab. no. 63083) was refluxed for two hours with 500 ml of 1 N hydrochloric acid. After cooling, the suspension was filtered and the coal was returned to the flask for a second identical treatment. Each of the two filtrates was evaporated to dryness and along with the extracted residue, was weighed and analyzed for uranium. The flow sheet for this simple experiment is shown in figure 12 and related data are given in table 7. On the basis of the recovered extracts, this simple treatment with acid removed 73.7 percent of the uranium from the coal. Semiquantitative spectrographic analysis of the two extracts and of the original and residual coal indicated that vanadium, strontium, cobalt, chromium, nickel, manganese, boron, scandium, lithium, lanthanum, and silver are concentrated along with the uranium during the extraction, whereas there is no evident concentration of copper, lead, titanium, or gallium in the extract. Germanium seems to be concentrated in the residual coal. Spectrochemical data are given in table 8.

Upon the completion of this experiment the following conclusions could be drawn:

1. The uranium is associated with the lignite in a rather loose fashion, perhaps by ion-exchange.

2. The uranium can be stripped from the lignite by simple treatment with dilute acid. Complete removal of the uranium was deemed possible and was effected, as shown below, when a continuous extraction procedure was employed.

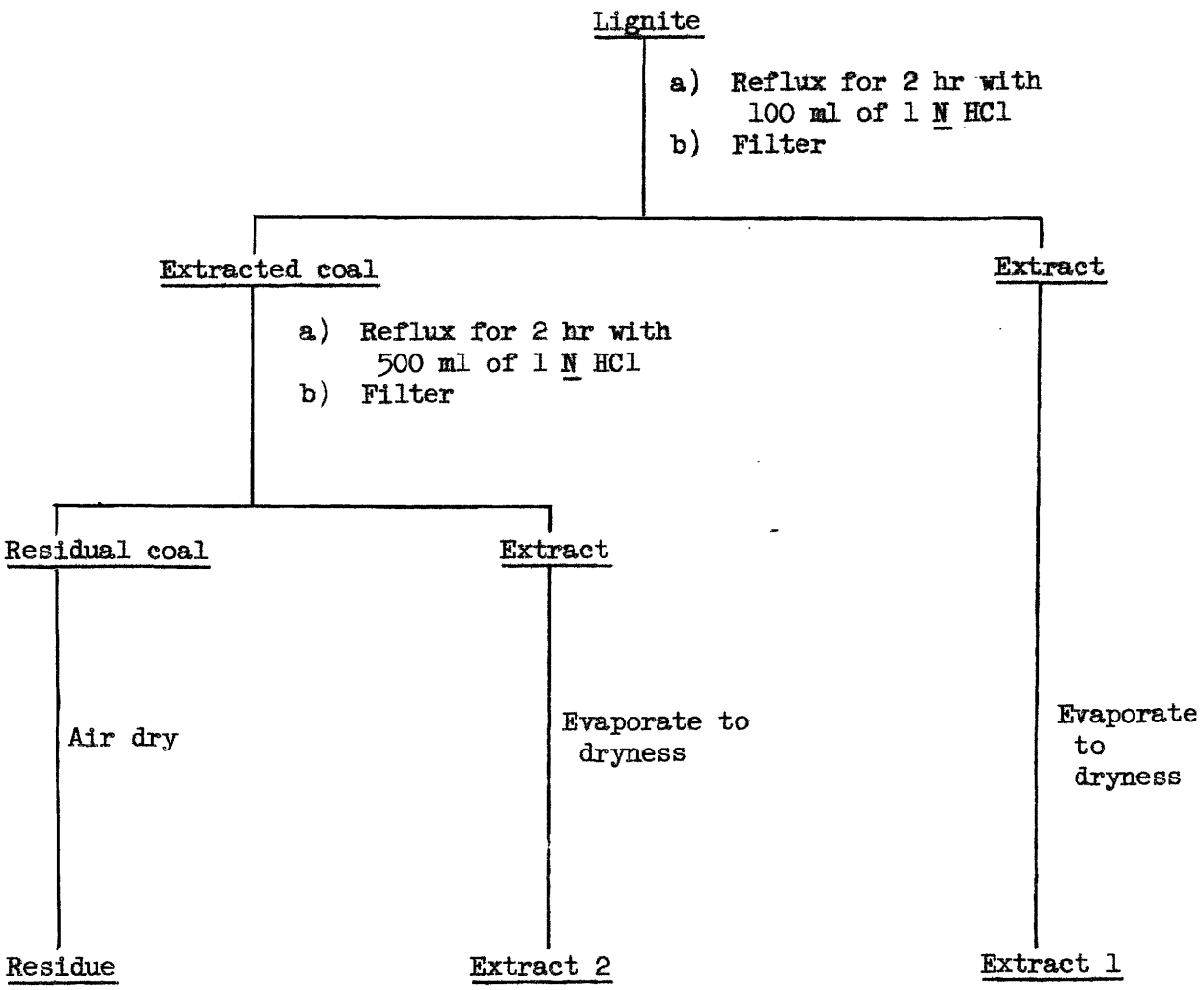

Figure 12.--Extraction of uranium from lignite by 1 N hydrochloric acid

Table 7.--Extraction of lignite with 1 N hydrochloric acid.

	1 Loss at 105 C (percent)	2 Ash in dry sample (percent)	3 Uranium in dry sample (percent)	4 Uranium in dry ash (percent)	5 Weight of dry sample (g)	6 Uranium in dry sample 1/ (mg)
Original coal	--	27.45	0.038	0.138	27.1	10.3
Extract 1	4.68	57.6	0.14	0.24	4.01	6.4
Extract 2	22.1	60.3	0.002	0.39	0.48	1.2
Residual coal	3.75	17.1	0.002	0.009	--	--

1/ Calculated from columns 3 and 5

Table 8.--Spectrographic analyses of ashes from extracts and residual coal (Hole 2, Harding County, S. Dak.) after treatment with 1 N hydrochloric acid, in percent.

Sample	Over 10	1 - 10	0.1 - 1	0.01 - 0.1	0.001 - 0.01	0.0001 - 0.001
Original coal	Si Al Fe	Na Ca Mg	Mo Ba B	Ti Sr Mn Co V Cr Zn Pb Ni Cu Zr	Ga Y	Be Yb
Residual coal	Si Fe	Al	Na Ca Mg Mo Ti	Zr B Cu Pb Ba Mn Ge	Co Cr Sr Ga Ni V	Yb
Extract 1	Fe	Al Mg Na Ca Si	Mn Ba Sr B	Mo Co Cu V Li Ti Cr Ni Zn	Y Ga	Sc Yb Be
Extract 2	Al Si	Fe Mg Ca Na	Mo B Ba Ti	Mn Sr Pb Cr Ni Cu Co V Li Zn Ga	La Y Sc	Be Ag Yb

3. A number of important trace elements of possible economic interest are stripped from the coal and concentrated along with the uranium by the simple procedure employed.

4. The extracts from the coals contain a high percentage of inorganic material. This is reflected by a decrease of nearly 40 percent in the ash content of the original coal.

At about the time that this preliminary experiment was being completed, a large bulk sample of lignite from the Mendenhall strip mine, Harding County, S. Dak., was received in Washington. To investigate the extractability of the uranium from this uraniferous lignite, an experiment similar to that just described was carried out using 50 g of the coal and 1 N hydrochloric acid as before. The data for this experiment are shown in table 9. As in the previous work, a material balance indicates that most of the uranium in the lignite, in this case 88.5 percent, was extracted by the 1 N acid.

The complete extractability of the uranium from the Mendenhall lignite was demonstrated by treating 80.0 g of the coal in the Soxhlet extractor with the condensed vapors from boiling 6 N hydrochloric acid. Under these conditions of continuous extraction with warm, approximately 6 N acid, 98.6 percent of the uranium was removed from the coal.

It should be pointed out that the choice of hydrochloric acid for this work was governed by the ease of its recovery through the distillation of its azeotrope. Although the economics of the recovery of uranium were of no immediate interest at this preliminary stage of the investigation, the low cost of hydrochloric acid was also taken into consideration. Inasmuch as

Table 9.--Extraction of lignite from the Mendenhall strip mine with 1 N hydrochloric acid.

	1 Loss at 105 C (percent)	2 Ash in dry sample (percent)	3 Uranium in dry sample (percent)	4 Uranium in dry ash (percent)	5 Weight of dry sample (g)	6 Uranium in dry sample 1/ (mg)
Original coal	41.96	32.43	0.039	0.12	29.0	11.3
Extract 1	3.02	59.1	0.083	0.140	10.84	9.0
Extract 2	5.66	32.8	0.096	0.292	1.05	1.0
Residual coal	23.3	14.4	0.0005	0.004	--	--

1/ Calculated from columns 3 and 5

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the hydrochloric acid was chosen purely as a source of hydrogen ions, however, there is no reason to believe that any other acid would not serve equally well for effecting the extraction.

Columnar extractions

The results from batch-extraction experiments indicated the possible retention of uranium in the coal by ion exchange. An elution experiment was designed to investigate further this possibility. An undried and unground sample of the Mendenhall bulk lignite (49.52 g) was mixed intimately with 12.38 g of a commercial brand of diatomaceous earth (Celite). A glass tube was loosely packed with this mixture to form a column 17 x 550 mm. The coal-Celite mixture was supported by a plug of Pyrex wool, and a small glass stopcock was sealed to the base of the column so that the rate of flow of effluent could be adjusted. To attain equilibrium conditions and saturate and wash the column, 200 ml of distilled water was passed through the coal. The rate of flow of the water through the column was increased by connecting a rubber tube between the top of the glass tube and the low pressure side of a reducing valve that was attached to a cylinder of compressed nitrogen. A pressure of 7.5 psi of nitrogen was found to be sufficient to give a reasonable rate of flow. The effluent was collected from the bottom of the column in 25-ml fractions. Following the disappearance of the last of the 200 ml of water at the top of the column, 325 ml of 1 N hydrochloric acid was added. The collection of fractions was then continued until 510 ml of effluent had been obtained. The effluent, prior to the break-through of the acid, had a pH of about 2.7;

at the break-through the pH dropped to 0.56, the same as that of 1 N hydrochloric acid. The water effluent was light yellow in color and acicular crystals of gypsum, identified microscopically, separated out on standing. At the break-through the color of the effluent changed abruptly to dark reddish brown, and consecutive fractions then became progressively lighter brown. Each fraction was evaporated to dryness on a steam bath and the residues were then analyzed to determine the loss at 105 C, percent ash, and percent uranium in the ash. The data so obtained are reported graphically in figure 13.

Inspection of figure 13 shows that, regardless of the shape of the curves, the uranium in the ash varies inversely with the total amount of the ash for the series of fractions. Because in any fraction there is a mixture of inorganic and organic constituents, the curves seem to indicate that the uranium must vary directly with the organic constituents of the fractions. The association of uranium with organic substances, either in compounds or complexes, is suggested.

A small amount of uranium is probably soluble in the water effluent (pH 2.7), but at the break-through of acid the amount of uranium which is eluted increases sharply. The reason for the sharp dip and rise in the curves following the elution of about 350 ml of water and acid is unknown. It is thought that a very irregular acid front, combined with some lack of equilibrium in the column due to excessively rapid flow of liquid, may have contributed to this feature. Slow attainment of equilibrium was noted in the work described below.

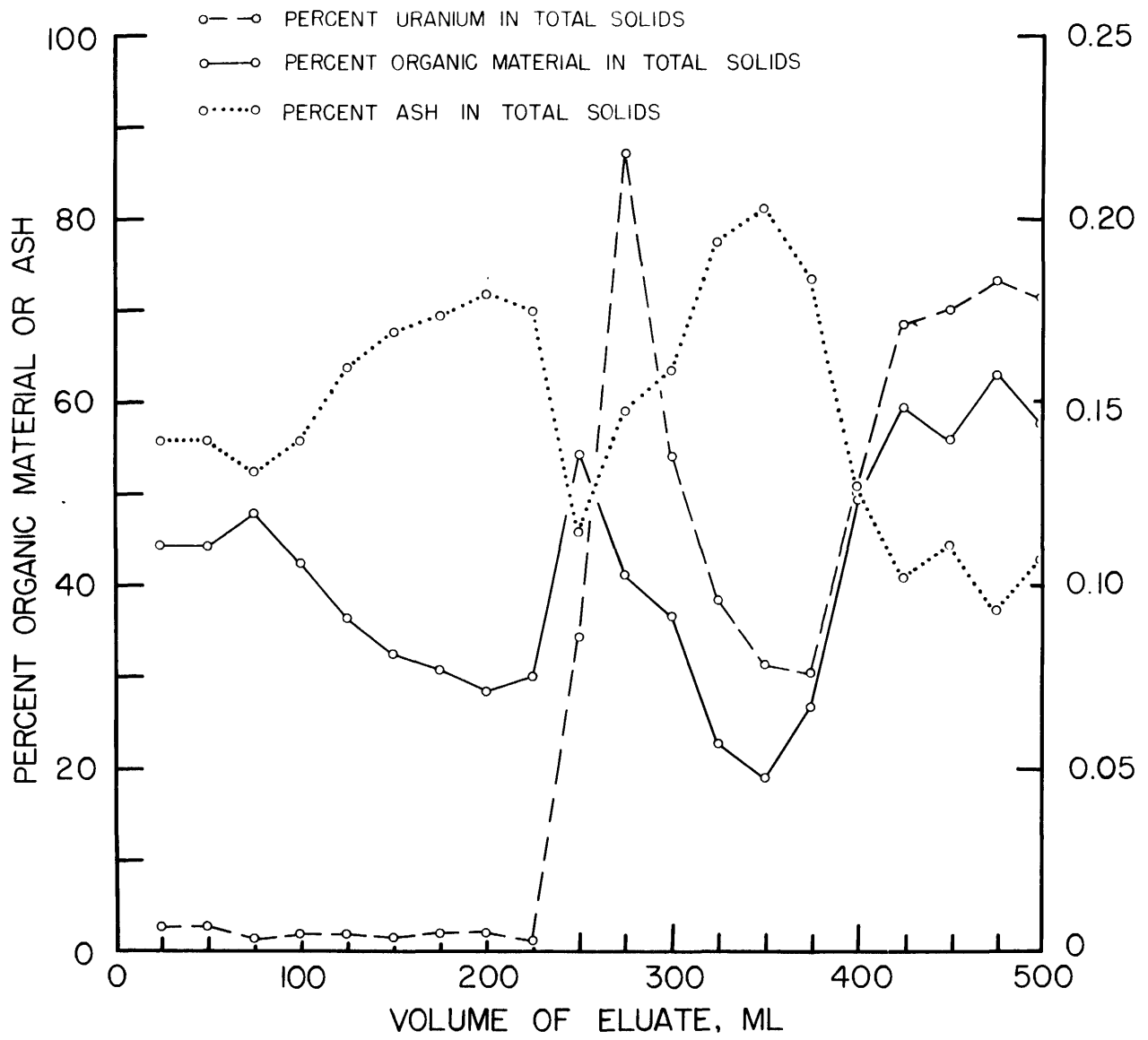


FIGURE 13. — ELUTION OF URANIUM FROM LIGNITE BY 1 N HCl: RATIOS

A factor other than ion exchange was indicated by this work to account for the association of the uranium with the organic materials. This factor may be the existence of an organo-uranium compound or complex that is insoluble at pH 2.7 but soluble at pH 0.5.

In deciding the course of further investigations it was necessary to take into account the rather large amount of effort and time involved in the analysis of the fractions obtained from elution experiments. Continuing on the assumption that a column of uraniferous lignite may be similar to a column of ion-exchange resin on which uranium had been adsorbed, a new large-scale elution experiment was chosen using the previous technique but replacing the 1 N hydrochloric acid by 6 N hydrochloric acid. This procedure was used in an effort (1) to attempt to reproduce the previous work under more favorable conditions, and (2) to determine if all the uranium could be elutriated just prior to the break-through of the descending acid front. If this were found to occur, then it was believed that by simple treatment of the coal it might be possible to bring about a tremendous concentration of the uranium.

Using a column with an outside diameter of 32 mm, a mixture of 400 g of the Mendenhall lignite (-50 mesh, 36.6 percent H_2O) and 100 g of Celite-545 (a high grade of diatomaceous earth) was made into a slurry with 800 ml of distilled water and poured into the column. Elutriation was begun after the column had remained undisturbed overnight. In all, 1700 ml of water were elutriated through the column and this was followed by the addition and elutriation of about 1000 ml of 6 N hydrochloric acid. Most of the fractions were 50 ml in volume. The break-through of acid was detected by pH measure-

ments of the fractions and could also be observed by the sudden darkening of the color of the fraction at the break-through. At the suggestion of Irving May of the Geological Survey, the fractions, as obtained, were submitted for chemical analysis, and after considerable investigation a new procedure was devised for the determination of uranium in the samples. The data from this experiment are presented graphically in figures 14 and 15. In figure 14 the break-through of acid, with the consequent sudden increase of total dry solids, ash, and uranium in each fraction, is evident. The total solids and ash increase gradually as the pH drops from 2.79 to 2.18, probably because of the increased solution of gypsum from the coal at the lower pH. There is no great elutriation of uranium even at pH 2.18 indicating that the critical acidity must be below this value. That all the uranium is not elutriated in one fraction, as had been hoped, is evident from the gradual sloping off of the curve for uranium. By means of the following material balance it was shown that only about 75 percent of the uranium was recovered by elutriation with 6 N acid.

Uranium in coal	=	88.76 mg
Uranium in fractions	=	66.53 mg
Uranium left in coal	=	13.55 mg
Uranium elutriated	=	75.0 percent
Total uranium recovered	=	86.8 percent
Loss	=	13.2 percent

If the uranium were held in the coal by ion exchange, then the uranium should have been elutriated in a greater sudden concentration. The gradual decrease in the content of uranium in fractions subsequent to the break-through is suggestive of something other than ion exchange.

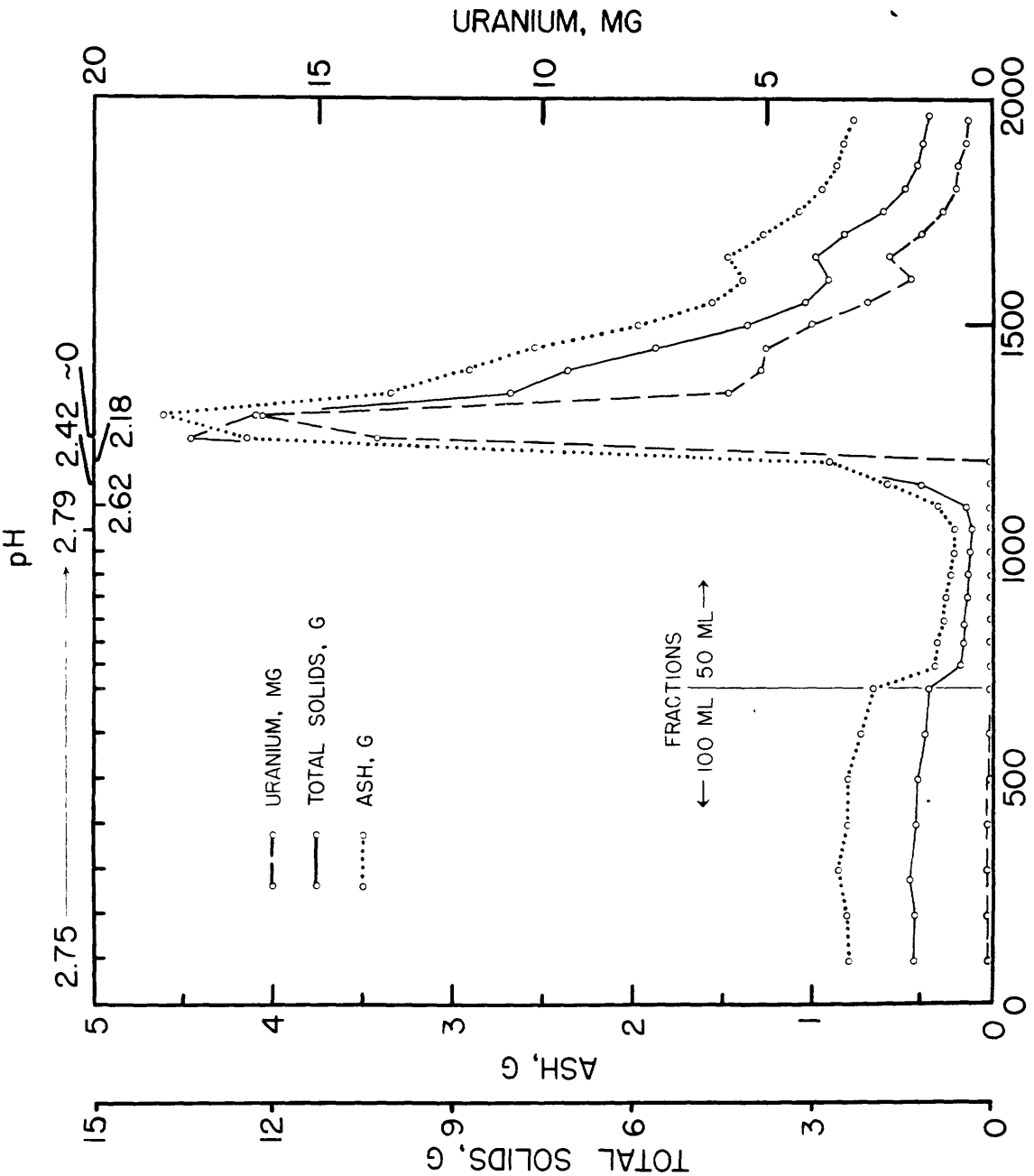


FIGURE 14.—ELUTION OF URANIUM FROM LIGNITE BY 6N HCl: DATA

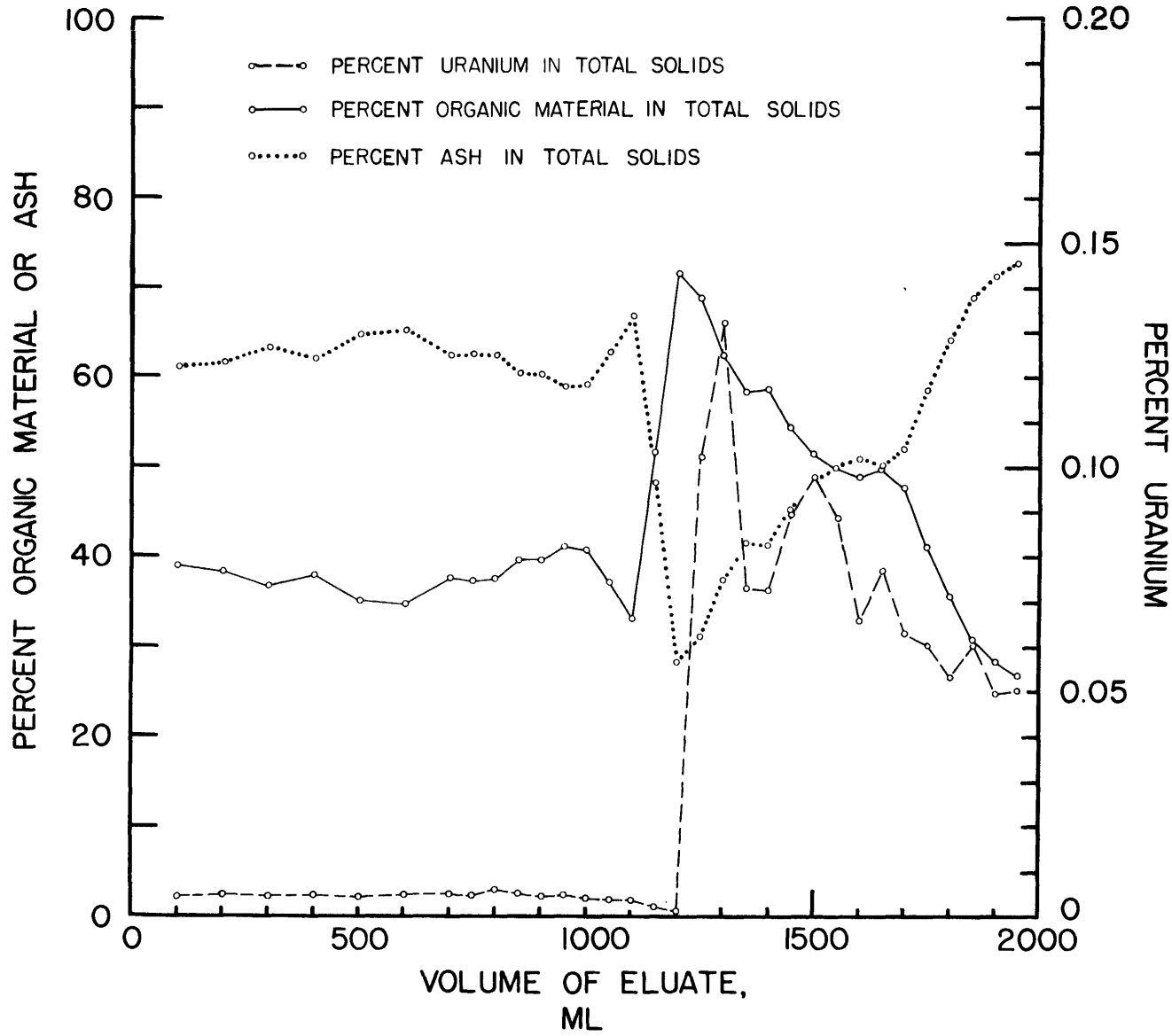


FIGURE 15. — ELUTION OF URANIUM FROM LIGNITE BY 6 N HCl : RATIOS

The data used to compile figure 14 were recalculated on the basis of the total solid material, both organic and inorganic, elutriated and recovered from each fraction. These recalculated data are plotted in figure 15. In figure 15 one curve represents the ash content of each fraction; another curve represents the uranium content of each fraction. As the ash represents the inorganic constituents, 100 percent minus percent ash must represent the organic material elutriated from the column by the water or acid during its passage through the coal. Because of the analytical procedure, 100 percent minus percent ash must also include a small amount of water not driven off at 105 C and other minor losses which may occur if some inorganic compound decomposes during the ashing procedure. Consideration of figure 15 leads to the same conclusion as that reached from figure 13, which represents an experiment using 1 N acid. Again in figure 15 the acid break-through is accompanied by increase in uranium and a relative decrease in the proportion of inorganic matter in the fraction. From the curves it is evident that the uranium follows the organic material rather than the inorganic material. Again, therefore, an association between the organic extract and the uranium is strongly suggested by this work.

To complete the study of the possible retention of uranium in the coal by ion exchange, a new experiment was devised and carried out. In this experiment a glass column made from 32-mm Pyrex tubing was loaded with a slurry containing 200 g of the Mendenhall lignite (-50 mesh) and 66.7 g of Celite-545 in 500 ml of distilled water. After allowing the column to stand overnight an additional 500 ml of water was passed through the column while

fractions of the percolate, first 50 ml and then 25 ml in volume, were taken. Following passage of the water through the coal, 925 ml of a solution containing 100 g/liter of $La(NO_3)_3 \cdot 6H_2O$ was added. The choice of lanthanum as a displacing ion was governed to a large extent by its relatively low cost, its valence of three, and its inertness during the analysis for uranium. As the lanthanum solution had a pH of 4.43, there was no possibility of the removal of uranium from the coal by the solution of an organo-uranium compound or complex. This possibility existed when hydrochloric acid had been used. The lanthanum ion was, therefore, expected to replace any ion-exchanged uranium or other elements in the coal, with its effectiveness purely a function of concentration and valence. In this work it was assumed that any ionized uranium was probably present in the coal in the form of the uranyl ion, UO_2^{++}. In all, a total of 47 fractions representing 1275 ml of percolate were removed from the bottom of the column and analyzed. The curves in figure 16 summarize the analytical data obtained in this experiment, and the curves in figure 17 represent, for each fraction, the percent ash and the percent uranium in the total dry solids and, by difference, the percent of "organic material" in the dry solids recovered from each fraction. In order to check this work and also to have a blank determination for comparison, a duplicate column was operated simultaneously with the one just described with the exception that only water was percolated through the coal. Within close limits the data for the blank and test columns were similar until the break-through of the lanthanum occurred.

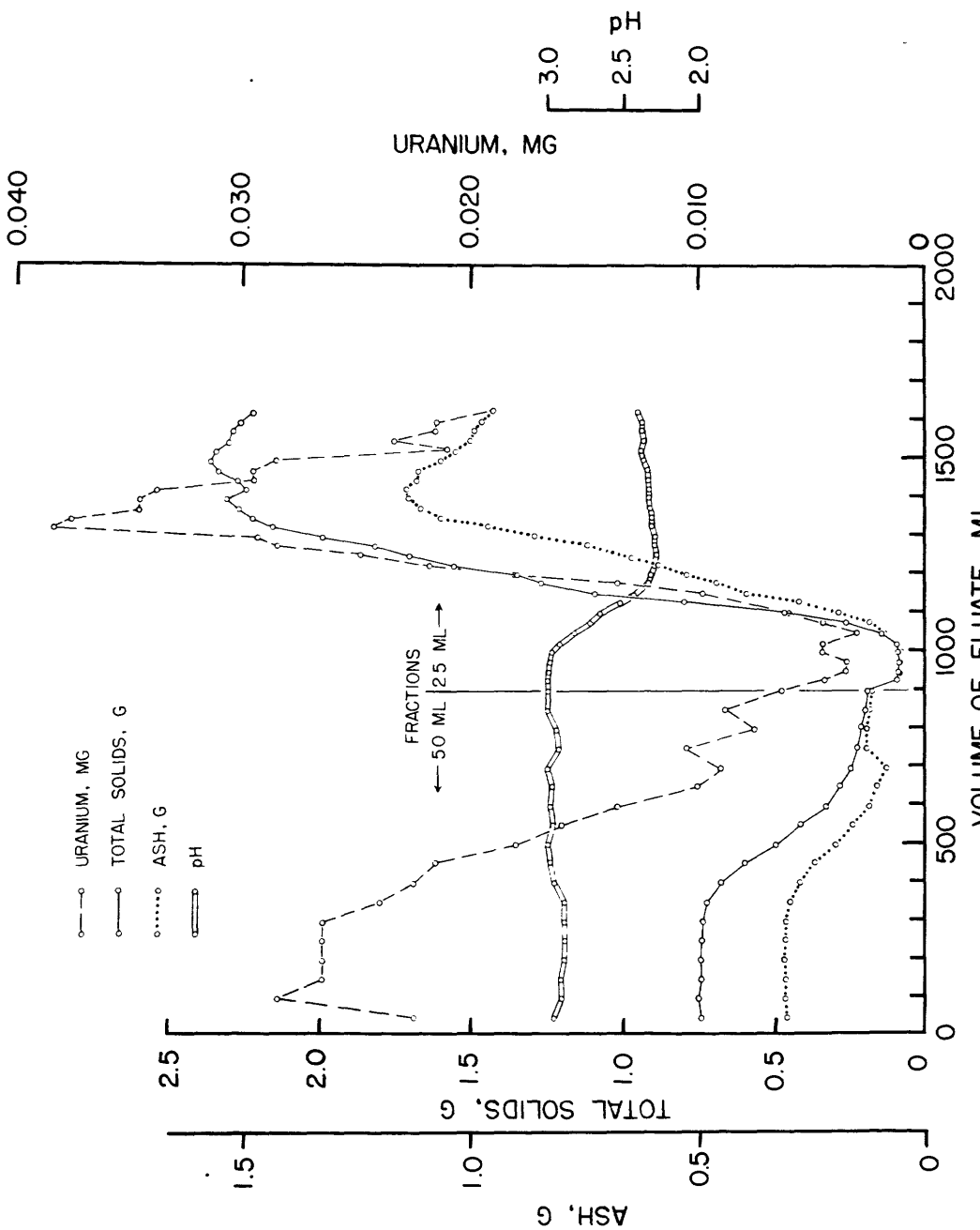


FIGURE 16.—ELUTION OF URANIUM FROM LIGNITE BY $La(NO_3)_3$: DATA

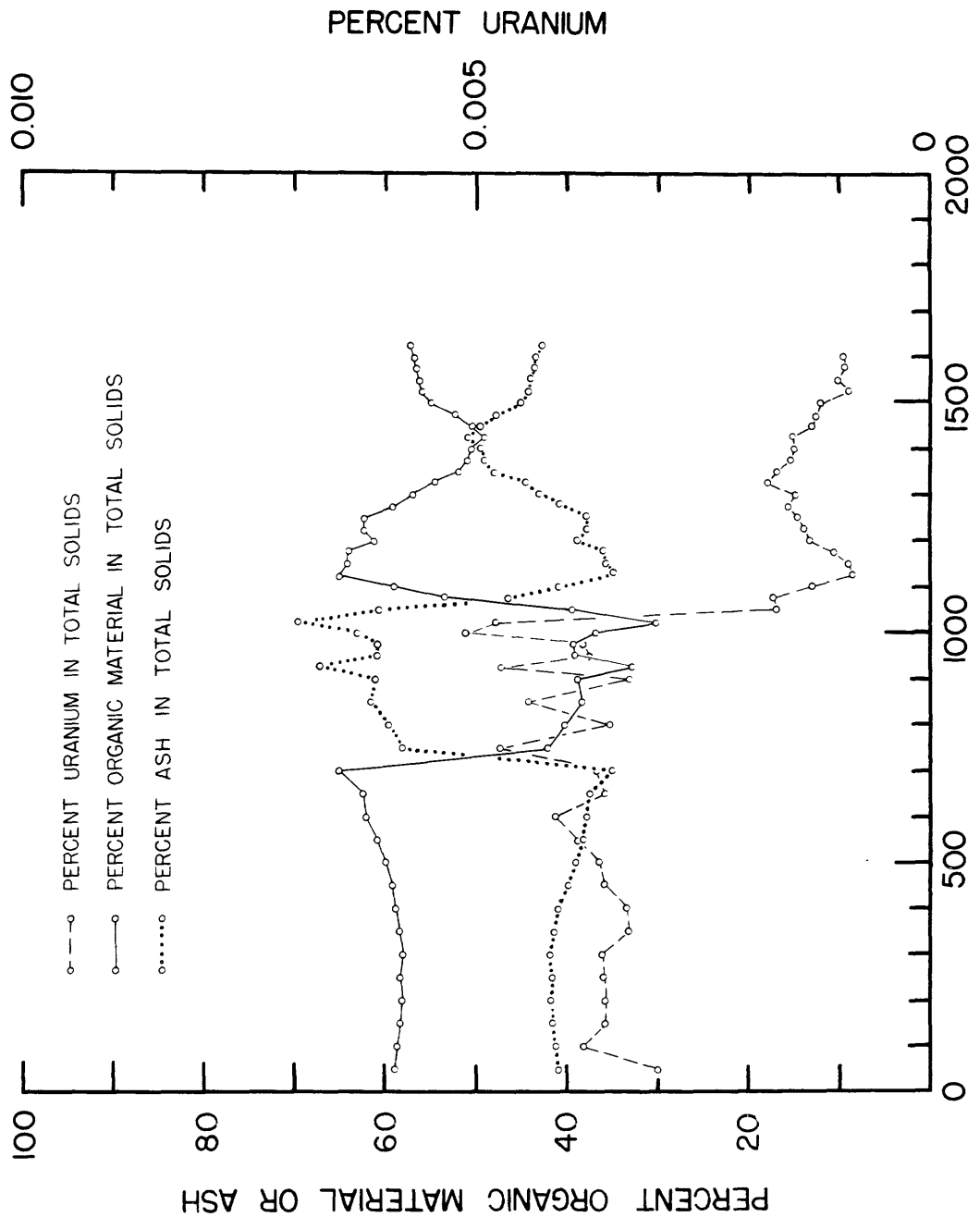


FIGURE 17.—ELUTION OF URANIUM FROM LIGNITE BY $La(NO_3)_3$;

In figure 17 the curve showing the elutriation of the uranium is rather straight until the break-through of lanthanum occurs following the collection of 1000 ml of percolate. The variability in the points of the curve between about 600 and 1000 ml of percolate is a reflection merely of the size of sample taken for the uranium determination. All these points are within the limits of error of the analytical procedure used. After the percolation of about 1000 ml of liquid through the column a very sharp apparent decrease in the concentration of uranium takes place because of dilution by lanthanum. That there is no real change in the concentration of elutriated uranium is evident from figure 16 where no sharp break occurs in the curve at this point. That section of the curve for uranium following the break-through of the lanthanum will be discussed below.

Referring now to the curve of figure 17 that indicates the ash content of the solid material elutriated from the column, it can be seen that the curve is quite regular until 700 ml of water were passed through the coal. At this point, before the addition of lanthanum, there is a sudden and very sharp increase in the ash recovery followed by a leveling off of the curve. This sharp break, which is reproduced exactly in the blank column, was due to the fact that the columns remained overnight at this point during the experiment. The sharp break seems to infer, therefore, that the rate of percolation of water had been too rapid, and that during the period of standing equilibrium conditions were probably reached. The very sharp and large loss of weight of the solid extracts from the fractions collected at the point where lanthanum breaks through the column probably results from two

causes. First, $La(NO_3)_3 \cdot 6H_2O$ decomposes at 126 C. This means that as lanthanum is collected in the fractions, the nitrate loses its water of crystallization on ashing, and apparently only loses part of this water, if any, on drying at 105 C for three hours. Secondly, $La(NO_3)_3$ is known (Kolthoff and Elmquist, 1931) to decompose as shown below, at 800 C with the elimination of NO_2 and O_2 which contribute to the loss of weight on ashing. Following the break-through of the lanthanum in equilibrium

$$2La(NO_3)_3 \xrightarrow{800^\circ C} La_2O_3 + 6NO_2 + 1\ 1/2\ O_2$$

quantity, the curve for percentage ash should reach a new level and remain reasonably constant.

Those sections of the curves following the break-through of lanthanum are of particular importance and will be considered together. Returning now to the curve showing the elutriation of uranium, it is evident that the break-through of lanthanum is accompanied by first a lowering and then an increase in the pH of consecutive fractions. There can be no doubt but that this trend in pH indicates that the coal structure has an ion-exchange capacity which is not saturated. The displacement of hydrogen ions by lanthanum and the subsequent concentration and elutriation of the hydrogen ions results in a simultaneous lowering in the pH of the fractions of percolate so effected. With the lowering of pH it can be seen from figure 17 that not only does the percentage of uranium in the recovered percolate increase, but also that the percentage of ash increases.

Inasmuch as no appreciable ion exchange of uranium or other elements by lanthanum can be expected until just before or after the break-through of the lanthanum, it is evident that only those portions of the curves in figures 16 and 17 which represent the removal of more than 1000 ml of percolate are significant in this study. Comparison of the elutriation of uranium and inorganic substances beyond this point indicates that the elutriation of uranium is directly related to the displacement of inorganic matter from the column and is inversely related to the displacement of organic material. This result is the opposite of that found when elutriation of uranium was carried out with either 1 N or 6 N hydrochloric acid in previous studies.

The fact that the uranium is not leached even at a pH as low as 2.18 and the fact that the uranium does not vary directly with the organic content of the percolate indicate that uranium shown in figure 17 which was displaced after the elutriation of about 1125 ml of solution was truly ion-exchanged uranium. The information obtained from this experiment indicates that the uranium held in the coal by ion exchange probably amounts to about 1.2 percent of the total uranium in the coal.

To check the possible displacement by lanthanum of other ion-exchanged elements besides uranium, the ashes from 35 fractions were analyzed spectrographically. The data show that none of the following elements is held in the coal by ion exchange: Mn, Sr, Fe, Ni, Co, Be, Mo, Ti, Li, Pb, V, Zr, Cr, Sn, Be, Mg. There is evidence that the following elements may be held in the coal to some extent by ion exchange: Na, Cu, Zn, Y, Ba, and Si.

These last elements are concentrated during the elutriation, but it must be remembered that bracketed values (1-10 percent, 0.1-1 percent, 0.01-.1 percent, etc.) are being compared and that the concentration of some elements may not be recognized from the data.

Organization of organic chemical laboratory

Following the decision to undertake organic chemical studies on the uraniferous lignites, it was necessary to organize a laboratory with the facilities and equipment suitable for this type of research. A great deal of time was spent choosing and arranging for the purchase of special items such as fractionating columns and extractors, besides the usual glassware which had not been required for previous work in the laboratory and was therefore not available. To assure the proper supply of organic reagents, all organic chemicals, dyes, and indicators in the laboratory have been collected and indexed in a card file. The available stock of chemicals has been enlarged by the purchase of a wide variety of supplementary solvents and reagents.

Inasmuch as it is thought that many of the problems associated with organic sediments may not be solved by a direct approach, the need for correlation studies of uranium with other elements such as carbon, hydrogen, nitrogen, sulfur, and oxygen was recognized. Consequently, much time and effort has been spent in the selection and purchase of the necessary microchemical equipment for this work. Robert Meyrowitz, who has had experience with inorganic microchemical analytical techniques, has been placed in full charge of this work.

Two microchemical combustion furnaces have been purchased for the determination of carbon, hydrogen, and nitrogen. For the direct determination of oxygen, an Unterzaucher analytical train with the necessary furnaces, controllers, and timing devices has been purchased. Although micro-bombs are available for the determination of sulfur, the Carius procedure for this analysis may be preferable. For this reason the purchase of a Carius tube furnace is now being considered.

Besides this equipment for ultimate analysis, analytical apparatus has also been acquired for the determination on a micro-scale of percent acyl, alkimide, and alkoxyl. Functional group analyses have proved invaluable in previous organic geochemical research on the origin and structure of coal.

In the short time that Meyrowitz has been associated with this work he has made excellent progress in setting up the equipment. Following the calibration of one of our two available microbalances and a set of weights, he has set up and placed in operation the train for carbon and hydrogen analyses and is now setting up the equipment for the determination of nitrogen and the direct determination of oxygen. Using a sample of benzoic acid obtained from the National Bureau of Standards (No. 140) he has obtained the ten analyses shown in table 10. The theoretical and determined percentages of carbon and hydrogen are tabulated as follows:

Percent carbon	
Theoretical	68.84
Found	69.09 ± 0.27*
Percent hydrogen	
Theoretical	4.95
Found	5.43 ± 0.24*

* Mean and standard deviation from the mean.

The slightly high results represented by the above data will undoubtedly drop somewhat when a preheater for the purification of the oxygen is placed in the system and also as the analytical train "ages". In any case the results already obtained are excellent when compared to those summarized in a recent article by Kirsten (1951). In figures 18 and 19 are plotted the analytical data of table 10. It is evident that the accuracy of the analyses improves as the sample increases in size from micro (approximately 5 mg) to semimicro (10-15 mg). Figures 18 and 19 indicate that it takes, under present conditions, a sample weighing 15.5 mg to obtain accurate hydrogen analyses, and that 10 mg of sample are required for accurate carbon analyses. As indicated above, these sample requirements should drop considerably with improvement of the analytical train. Meyrowitz is now acquiring larger absorption tubes which will enable him to use semimicro-samples with the micro-equipment whenever sufficient material is available. The slopes of the curves of figures 18 and 19 are similar to those reported by other micro-analysts.

A great deal of time has been spent recently in consideration of the possible use of infrared absorption analysis for the determination of the structure of organic separates and extracts from coals and other sediments. In the past, infrared analysis has proved to be an invaluable analytical tool (Breger, 1951). With the conclusion that the uranium in lignite probably exists in the form of organo-uranium compounds or complexes, it is now essential to employ every possible means for the analysis of any organic substances that will be isolated. Recent publications on the use of infrared

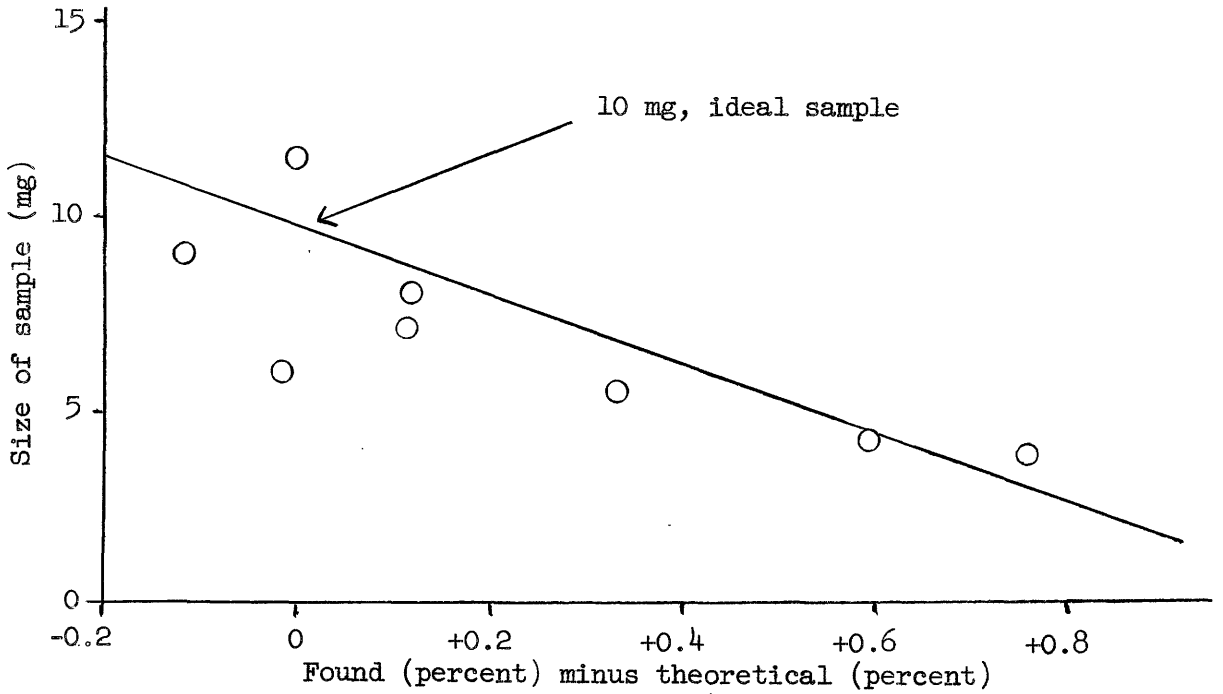


Figure 18.--Dependence of carbon analyses upon sample size

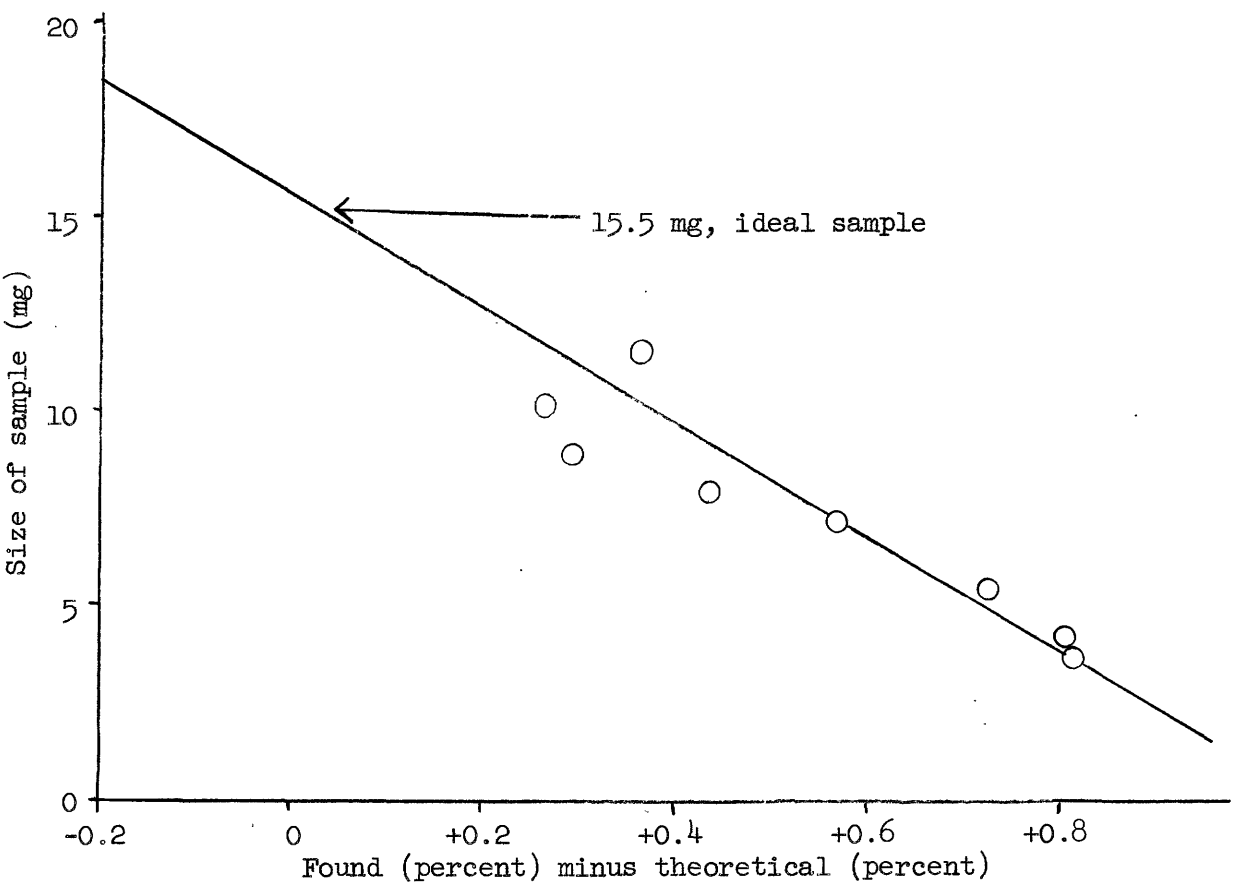


Figure 19.--Dependence of hydrogen analyses upon sample size

Table 10.--Analyses of a standard sample of benzoic acid

(Nat. Bur. Standards no. 140)

Sample size (mg)	Percent carbon found	Percent hydrogen found
10.058	69.25	5.21
3.810	69.60	5.76
5.790	68.76	4.98
7.989	68.96	5.38
4.151	68.44	5.75
5.549	69.18	5.67
7.220	68.96	5.51
11.471	68.91	5.31
8.864	68.73	5.24
8.644	69.06	5.48

analysis for inorganic and mineralogic analysis also indicate the desirability of having this tool available in the Trace Elements Section Washington Laboratory. Following discussions with F. S. Grimaldi, T. Botinelly, and A. W. Helz, it has been decided that a justification for purchase of a suitable instrument should be presented as soon as possible. To date conferences have been held with representatives of three of the manufacturers of infrared equipment. It is hoped that a justification including a thorough bibliography of pertinent literature will be prepared before January 1, 1953.

As a bibliographic aid and for use in following current research, a Keysort card has been designed and 25,000 cards with the necessary files and equipment have been ordered. The card that has been designed is approximately 6 x 6 1/2 inches in size and is surrounded by a double row of holes spaced five to the inch. The card will be printed for use in recording spectrographic, analytical chemical, mineralogic, or organic chemical information. It is anticipated that separate codes will be devised to cover interests of the various groups in the laboratory.

CONFERENCES

With the organization in July 1952 of a complete program on the mineralogy and organic geochemistry of lignites the need to review current and past work on the subject became pressing. Investigators who are already working on this subject or who had indicated the intention of studying in their laboratories certain phases of the problem are: Farrington Daniels, University of Wisconsin; James M. Schopf, U. S. Geological Survey, Columbus, Ohio; Donald Peppard, Argonne National Laboratory, Chicago; and Keith Brown, Oak Ridge National Laboratory. Early in July Deul and Breger spent three days in Columbus discussing mutual problems with Schopf. In October a trip was made to the Survey laboratories in Denver where lengthy discussions were held with N. M. Denson, project chief for all field investigations on the uraniferous lignites. These conferences were followed by a field trip to Wyoming where work of the past two seasons on the uraniferous coals of the Red Desert was discussed by Harold Masursky, party chief, and George Piperingos. Besides Deul and Breger, the field conference included Harry A. Tourtelot,

James D. Vine, and George Moore, all from the Survey's Fuels Branch, and Theodore Botinelly of the Geochemistry and Petrology Branch.

En route to Washington side trips were made by Deul and Breger to the Universities of Wisconsin and Illinois. Dr. Peppard had indicated that he has to date carried out no research on the uraniferous lignites.

At the University of Wisconsin discussions were held with Professor Farrington Daniels and his group which is investigating aspects of the extraction of uranium from ashed lignites. Agreement was reached to provide Professor Daniels with a split of the coal collected in the Red Desert so that work at the University of Wisconsin can be directly correlated with that of the Survey in Washington.

At the University of Illinois numerous discussions were held with members of the Illinois State Geological Survey who are working on various aspects of the structure of coal. In particular, a great deal of time was spent with Howard Clark, an organic microchemical analyst, who has spent many years working with coals.

In recognition of the fact that the uraniferous coals probably represent only a relatively small and perhaps unimportant part of the general problem involving uranium and organic sediments, conferences were held while in Denver on the organic geochemistry of various substances such as crude oils, black shales, asphalts, tar sands, and coals. Taking part in one or more of these discussions were the following Survey members: Breger, Myers, and Horr of the Geochemistry and Petrology Branch; Tourtelot of the Fuels Branch; and Gott, Erickson, Mytton, and Page of the Mineral Deposits Branch.

Gott and Erickson have collected a considerable amount of preliminary information on the association of uranium and other minor elements with a variety of naturally occurring organic substances. Some laboratory work has also been carried out, especially on the extraction of organic sediments by benzene. Following a thorough discussion of their data the following two suggestions were made:

First, the depositional environment in which organic material has collected may be a governing factor in determining whether an association between the organic substances and uranium may be anticipated. It was pointed out that most coals (fresh-water deposits) are not appreciably radioactive, whereas most marine black shales seem to be uranium bearing. In the absence of absolute geologic evidence, we must have some criterion by which to determine whether a substance is of fresh-water or marine origin, in order to consider proper depositional environment as a factor for the concentration of uranium in organic sediments. In this respect it is felt that the minor and trace elements in the ash of an organic sediment may be very helpful in interpreting the origin of the substance. Accordingly, it was suggested that more organic sediments of various types be collected and spectrochemically analyzed, presumably in Denver under the direction of A. T. Myers, so that we will have sufficient statistical data upon which to base our conclusions.

The spectrochemical analyses of organic sediments present a problem because certain elements may be lost during the preliminary ashing procedure. Whereas it is felt that these losses will probably be insignificant, it was nevertheless suggested that a number of "spiked" samples be run to determine

any serious errors which may not have been noted thus far. It was also suggested that a copy of the Ph. D. thesis by Stanley Southwick (M.I.T., 1951) be obtained. Southwick studied ashing losses in working with crude oils.

The vanadium-nickel ratio may be a criterion for the identification of sediments as being fresh water or marine in origin. This was suggested by an examination of Erickson's data, where it was apparent, among some 20 or more analyses, that there were only two glaring exceptions to the rather constant vanadium-nickel ratio. The Green River shale, which is known to be fresh water in origin and is not appreciably uraniferous, has a vanadium-nickel ratio which differs by several orders of magnitude from that of most other substances analyzed. The other exception was the Athabaska tar sand, a sediment the origin of which has never been fully explained. The Athabaska deposit has been considered by some geologists to be a petroleum residue, which would suggest a marine origin. This has never been proved, however, and in recent years there has even been discussion of a fresh-water origin for the tar sands, a possibility which may be indicated by its vanadium-nickel ratio.

To summarize, further analyses should be carried out on as wide a variety of organic sediments as possible. If possible, a criterion should be established for the environment in which the tar, asphalt, shale, or other organic sediment was deposited. On the basis of chemical and geological considerations and uranium analyses, it may be possible to derive considerable information as to the organic geochemistry of uranium. In a

practical way, this may considerably narrow down the search for uranium-bearing organic sediments.

Second, the manner in which uranium is held in organic sediments is not well understood. It has been suggested that porphyrin complexes may be important, but this has never been demonstrated.

There is some evidence, based on the work which has been done in Denver, that the uranium in certain sediments may be present in the form of organo-uranium complexes. According to Horr, the Soxhlet extraction of naturally occurring organic material with hot benzene for a period of about 6 hours has led to the recovery of most of the uranium in the extract. It is unlikely that a uranium salt would be soluble in benzene and it is, therefore, reasonable to expect that an organo-uranium complex may have been peptized by the benzene and that the uranium was carried into the extract in colloidal solution. It has been pointed out that although U_3O_8 should be extremely insoluble in benzene, if it is sufficiently finely divided it may enter into a colloidal solution just as would an organo-uranium complex. This may be checked by examination of the extract after evaporation of the benzene.

If an organo-uranium complex does exist, then there may be a relationship between uranium and oxygen, nitrogen, or sulfur in the extract. It is to determine such relationships that an organic microanalytical laboratory is now being set up. The need for carbon-hydrogen ratios in the study of organic substances of geological importance is pressing because the carbon-hydrogen ratio provides some indication of the nature of the organic material under consideration. It was proposed that carbon-hydrogen

ratios, together with other analyses and ultraviolet and infrared absorption spectra should provide some indication as to the nature and structure of organic substances and their uranium complexes.

One difficulty in the rapid evaluation of data on the uranium content of organic substances was pointed out. To date it has been customary to report all uranium values in percentages without reference to a fixed base for comparison. In this respect it has been very useful to employ material balances wherever the material being studied has been fractionated. A case in point arose during a discussion of the uranium content of crude oils. Although the ash of crude oils may contain 0.0X to 0.00X percent of uranium, the ash itself only amounts to perhaps 0.01 percent of the total oil. Thus a rapid examination of the data did not immediately suggest that the percentage of uranium in most crude oils is extremely low.

In the study of crude oils a separation, by means of pentane, into soluble oil and asphaltenes was suggested. The distribution of uranium between these two major fractions could then be determined. The uranium will probably be found in the asphaltene fraction; if so it may be possible to attempt a correlation of organic nitrogen and uranium in the asphaltenes and thus to investigate the possible existence of uranium-porphyrin complexes.

The term "hydrocarbons" as used by most geologists for asphaltic and bituminous sediments is incorrect and misleading to the chemists. It was therefore urged that the term "hydrocarbons" be dropped in favor of asphalt, bitumen, crude oil, black shale, etc. Unfortunately, there is no clear distinction between these substances at present and the nomenclature is, at best, very poor. It was suggested, therefore, that Breger consider organizing

and amplifying the pertinent literature with a view to publishing a report on organic sediments. This report would be designed to clarify the nature, origin, structure, and nomenclature of these materials for interested geologists and chemists.

CONCLUSIONS AND PROPOSED WORK

A. Heavy-liquid separation of minerals from lignite from the Mendenhall strip mine, Harding County, S. Dak., has shown that 93 percent of the uranium in the coal is associated with the organic material rather than with the mineral separates. As the mineral-free coal still contains 13.8 percent of ash, the Himus-Basak fine-grinding process will be used to determine whether this ash represents unseparated mineral matter or inorganic constituents of the organic material. No uranium minerals have to date been isolated from the lignite. The jarosite, quartz, calcite, gypsum, and "allophane" which have been isolated from the coal contain less uranium than does the coal itself. Application of the Basak procedure, in which the mineral-free coal is ground in a ball mill with kerosene, should lead to the concentration of any minerals still present in the coal.

B. Uranium can easily be leached from the Mendenhall coal by dilute acid which also extracts a number of trace elements of possible economic interest. Leaching of the coal following beneficiation to remove acid-consuming minerals should be even more satisfactory in that it would result in a concentrate of uranium and also a low-ash coal for fuel or possible chemical use.

C. Uranium is not held in the coal by ion exchange. The uranium seems to be present in the form of organo-uranium complexes or ionic organo-uranium compounds which are soluble at a pH less than 2.18.

It is well known that under certain conditions uranium forms insoluble complexes or compounds with such complex substances as tannins and albumins. Porphyrins may also react with uranium to produce insoluble products. In view of the evidence that in the Mendenhall lignite uranium exists in association with organic substances, it is now necessary to characterize the organic material which has been extracted from the coal by 1 N or 6 N hydrochloric acid.

Several analytical schemes have been proposed for the isolation of organic substances from the coal in order to prove or disprove possible associations with uranium. If arrangements can be made for infrared absorption analysis, this should be very helpful, and it may be possible to carry out other characterizations, especially for porphyrins, by ultraviolet absorption analysis. Because porphyrins contain nitrogen, uranium-nitrogen ratios may provide information on the existence of uranium-porphyrin complexes.

If tannins play an important role in the retention of uranium by the coal, then it may be possible to degrade the tannins to gallic acid for identification of a uranium-tannin complex. Several uranium-tannin complexes have already been prepared as blanks for this work.

Chemical studies on organo-uranium compounds or complexes are particularly difficult because, first, it is necessary to dissolve or break up the complex in order to isolate the organic material; second, the treatment of the organic substances with strong alkali or acid may change its chemical

structure; third, besides the chemical problems, the organic substances are also colloidal in structure and can be expected to undergo physical and chemical changes during isolation and characterization; and, fourth, more than one organic substance may be and probably is responsible for the retention of uranium.

Preliminary studies have already begun and it is felt that many of the problems outlined above will be solved with further and more intense investigation.

D. There is no obvious correlation of uranium with any trace elements in the coal except, perhaps, molybdenum. Comparison of uranium and molybdenum contents in individual samples does not always indicate a correlation between the two elements. Sample-to-sample comparisons will be carried out in detail by application of punched-card sorting techniques so that any relationships which may exist between uranium and any other trace elements, especially molybdenum, can be observed.

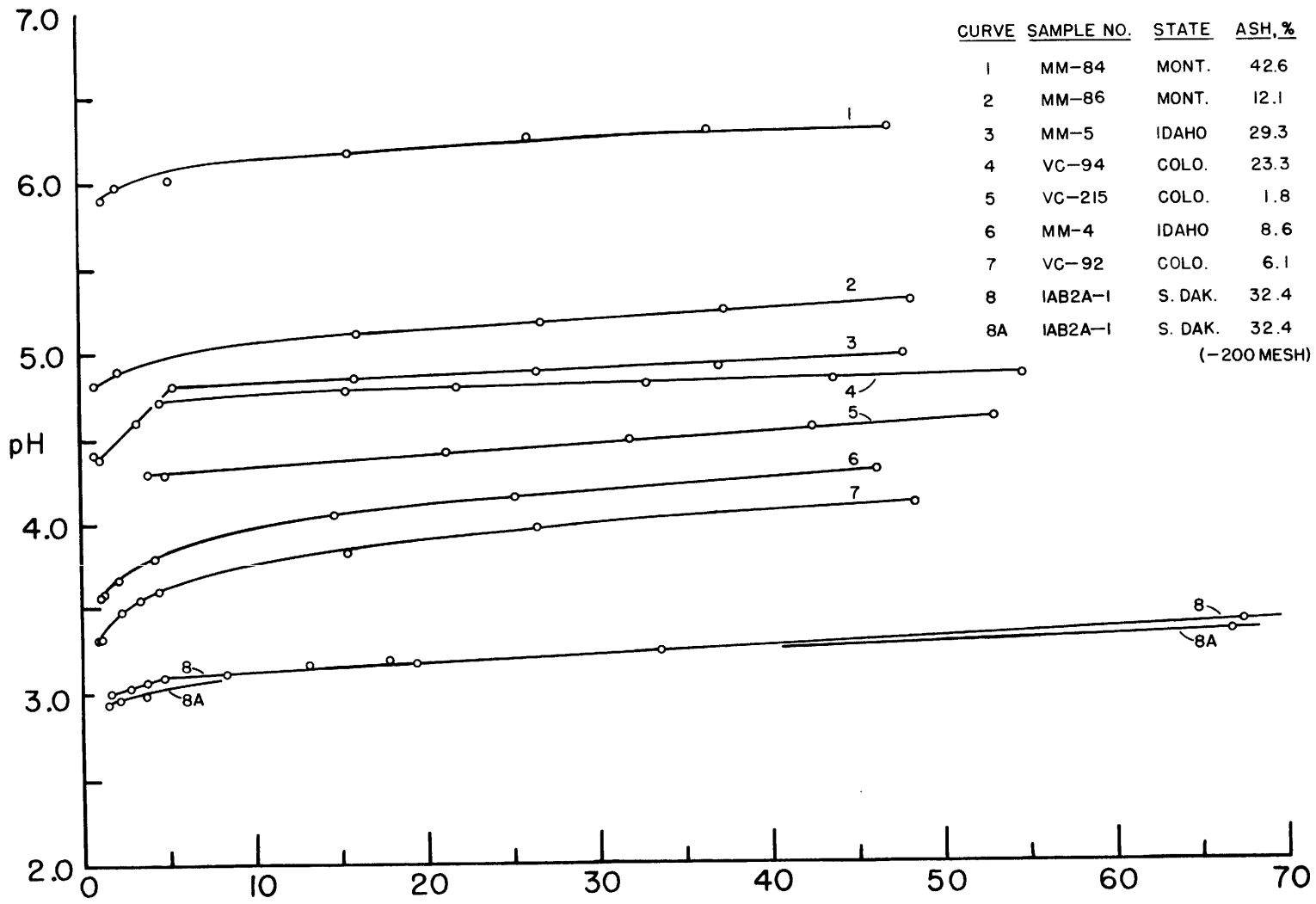
E. Attempts to pass water through a column of -50 mesh coal, even under a pressure of 15 psi of nitrogen, have met with failure unless diatomaceous earth was mixed with the coal to increase its porosity. The fact that the coal gels and becomes impervious to water should be considered in evaluating any hypothesis concerned with the syngenetic or epigenetic origin of uraniferous coals.

F. Radioactive disequilibrium in the gypsum and jarosite separated from the Mendenhall lignite indicates that these minerals were probably formed by the weathering of the coal during the past 10,000 years. Individual grains of jarosite and gypsum will be studied by means of nuclear emul-

sions sensitive to alpha particles in an attempt to determine if earlier weathering took place.

G. To account for the manner in which uranium may have been introduced into uraniferous lignites it was necessary to have some information regarding the pH of the coal. Referring to figure 20, a total of eight lignites from Colorado, Idaho, Montana, and South Dakota were chosen for a series of simple studies. Taking 5 g of each sample (-50 mesh, except as noted) the material was mixed with the minimum amount of water necessary to form a thick paste. The pH of this paste was measured and then more water in known amounts was added and the pH was measured after each addition. In several cases it was difficult to wet the lignite and the addition of a drop or two of wetting agent (Aerosol, pH 7.2) was necessary. Figure 20 shows that all the lignites tested had pH's lower than 6.5, even after dilution in the ratio of about 50 parts by weight of water per part of coal. Although the accurate measurement of pH in colloidal solutions or suspensions is difficult, it is obvious that suspension in water of any of the lignites tested results in the formation of a "buffered" solution. The acidity of each of these coals is undoubtedly dependent upon its rank, the nature and quantity of its minerals, and its history of weathering. The lignite from the Mendenhall strip mine is the most acid of the lignites tested. Use of -200 or -50 mesh material made little difference in the results of these tests.

It is known that certain alkaline uranyl carbonates and alkaline-earth carbonates are extremely soluble in water (Bachelet, 1952a and b). These compounds are sensitive to acids and break up with the release of carbon



CURVE	SAMPLE NO.	STATE	ASH, %
1	MM-84	MONT.	42.6
2	MM-86	MONT.	12.1
3	MM-5	IDAHO	29.3
4	VC-94	COLO.	23.3
5	VC-215	COLO.	1.8
6	MM-4	IDAHO	8.6
7	VC-92	COLO.	6.1
8	IAB2A-1	S. DAK.	32.4
8A	IAB2A-1	S. DAK.	32.4 (-200 MESH)

pH CURVES FOR SELECTED LIGNITES

FIGURE 20

dioxide. It is considered possible, therefore, that a uranium-bearing solution came into contact with the lignite, a zone of low pH, with the subsequent decomposition of complex soluble salts, such as:

$$Na_4(UO_2)(CO_3)_3$$

$$Na_6(UO_2)_2(CO_3)_5$$

$$Mg_2(UO_2)(CO_3)_3$$

In the presence of the acid (HA), the following reaction would be expected:

$$Na_4(UO_2)(CO_3)_3 + 6\ HA \longrightarrow 4\ NaA + UO_2A_2 + 3CO_2 + 3\ H_2O$$

In the case of lignite the acid, represented by HA, is unknown in structure and, for the sake of balancing the above equation, is assumed to be monobasic. If this acid were an organic acid, then it is quite conceivable that a compound such as UO_2A_2 might be insoluble above pH 2.18. This process might, therefore, account for the introduction of the uranium and its retention in coal.

H. Further experiments are now under way to determine if there is relationship between the pH of lignite and its uranium content. Five core samples from Hole 4 in the Slim Buttes area, Harding County, S. Dak., have been chosen for this work. The possibility must not be neglected that if the uranium content of a lignite is dependent upon its acidity, then measurement of pH may serve as a useful field method for uranium assay within a restricted area.

I. The absence of pyrite, an almost universal mineral constituent of coal, and the abundance of authigenic gypsum and jarosite indicate the extreme weathering to which the lignite from the Mendenhall strip mine has been exposed. The absence of detrital mineral grains with a specific gravity

greater than 3.2 indicates that the lignite was deposited in a peculiar depositional environment. Because this lignite has such unusual characteristics, any general conclusions with regard to uraniferous lignites will have to await examination of other coals. Although it is desirable to investigate an unweathered uraniferous coal, such material has not as yet been found.

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