A Summary of Oil and Gas Production and Reserve Histories of the Appalachian Basin, 1859–1972

GEOLOGICAL SURVEY BULLETIN 1409

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

A Summary of Oil and Gas Production and Reserve Histories of the Appalachian Basin, 1859–1972

By BETTY M. MILLER

GEOLOGICAL SURVEY BULLETIN 1409

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1975

UNITED STATES DEPARTMENT OF THE INTERIOR

ROGERS C. B. MORTON, *Secretary*

GEOLOGICAL SURVEY

V. E. McKelvey, *Director*

Library of Congress Cataloging in Publication Data
Miller, Betty M.
A summary of oil and gas production and reserve histories of the Appalachian basin
1859-1972.
(Geological Survey Bulletin 1409)
Bibliography: p.
Supt. of Docs. no.: I 19.3:1409
1. Petroleum—Appalachian region. 2. Gas, Natural—Appalachian region.
I. Title: A summary of oil and gas production II. Series: United States Geological
Survey Bulletin 1409.
QE75.B9 no. 1409 [TN872.A5] 557.3'08s [338.2'7'280974] 75-619101

For sale by the Superintendent of Documents, U. S. Government Printing Office
Washington, D. C. 20402
Stock Number 024-001-02670-8

CONTENTS

ILLUSTRATIONS

TABLES

CONVERSION TO METRIC SYSTEM

In this report the main units of measurement are barrels (petroleum), miles, feet, and cubic feet. These and other units may be converted to the metric system by multiplying by the following factors:

English unit *To convert*	*Multiply by*	*Metric unit* *To obtain*
Acres	0.4047	Hectares
Barrels (petroleum)	0.16	Cubic metres
Btu	0.252	Kilogram calories
Cubic feet[1]	0.0283	Cubic metres
Feet	0.3048	Metres
Miles	1.609	Kilometres
Square feet	0.09	Square metres

---

[1] Barrel equivalents for cubic feet of natural gas are based on the Btu equivalent of methane gas, 5,426 cubic feet per barrel.

A SUMMARY OF OIL AND GAS PRODUCTION AND RESERVE HISTORIES OF THE APPALACHIAN BASIN, 1859-1972

By BETTY M. MILLER

ABSTRACT

The Appalachian basin extends over 100 million surface acres from the Adirondack Mountains in New York southward into northern Alabama. This Paleozoic sedimentary basin was the birthplace of the modern petroleum industry in the United States, and its oil and gas fields have the longest production history of any on the North American Continent. The Appalachian basin's commercial development dates from the discovery of oil in a stray sand of Late Devonian age in the Drake well in Pennsylvania, August 1859; the first commercial gas production was recorded in 1882.

This report presents a comprehensive compilation of the oil and gas production and reserve histories of the Appalachian basin from 1859 through 1972, based chiefly upon published information from State and Federal agencies, private agencies, and petroleum companies. A detailed bibliography accompanies the report.

Beginning in 1859, with 2,000 barrels, the annual oil production in the basin increased to a peak of 36.3 million barrels in 1900. After 1900 the annual oil production declined irregularly over the years until in 1972 it was 21.3 million barrels. Total cumulative oil production for the Appalachian basin through 1972 was approximately 2.7 billion barrels.

Annual production of natural gas in the Appalachian basin was recorded as 1.3 billion cubic feet in 1882. Gas production reached a peak in 1917 with more than 522 billion cubic feet, and then declined to approximately 460.4 billion cubic feet in 1972. Total cumulative natural gas production for the basin through 1972 is approximately 31.2 trillion cubic feet.

The known cumulative oil and natural gas production from 1859 through 1972 is categorized by geologic age for each State within the basin and for the total basin. The major oil and gas reservoirs are of Devonian age, and have produced 70.6 percent of the oil and 45.4 percent of the natural gas. The Mississippian is the second most important section, and accounts for 14.7 percent of the oil and 32.4 percent of the natural gas production. Silurian reservoirs are third in importance, having yielded 10.2 percent of the oil and 15.1 percent of the gas produced. The three major oil-producing States in the basin are Pennsylvania, with a cumulative total of 1.3 billion barrels, West Virginia, with 507.7 million barrels, and Ohio, with 317.9 million barrels. The major gas-producing States are West Virginia, with a total production of 14.2 trillion cubic feet, Pennsylvania, with 8.7 trillion cubic feet, Ohio, with 4.9 trillion cubic feet, and eastern Kentucky, with 2.8 trillion cubic feet

Summary compilations categorized by State and geologic age are reported for the distribution of the estimated total proved recoverable hydrocarbons (oil, natural gas, and natural gas liquids) in the Appalachian basin. The four most potentially productive States are West Virginia, 3.853 billion barrels equivalent; Pennsylvania, 3.258 billion barrels equivalent; Ohio, 1.494 billion barrels equivalent; and eastern Kentucky, 1.008 billion barrels equivalent. Total proved recoverable hydrocarbons for the basin are estimated at 10 billion barrels equivalent. Of this total, approximately 8 percent of the recoverable oil reserves and 27 percent of the recoverable gas reserves have not yet been produced. Categorized by geologic age, the sources of these recoverable reserves are as follows: Devonian, approximately 52.2 percent; Mississippian, 27.7 percent; and Silurian, 13.8 percent of the total.

Original oil-in-place data were also used in separate studies of distribution by geologic age in determining the estimated recovery factor for the basin. The average percentage of ultimate hydrocarbon recovery in the Appalachian basin, based upon past and present technology, is approximately 20 percent, as compared with 31.4 percent for the entire United States.

Estimates of wastage of oil and natural gas in the Appalachian basin, based upon old published accounts, may be as high as 100 million barrels of crude oil and natural gas liquids (approximately 3 percent or more of the total proved reserves for 1859–1972); and nearly 10 trillion cubic feet of natural gas (more than 25 percent of the total proved gas reserves for 1882–1972).

Drilling reports for each State are summarized for deepest drilling records, production depth records, and annual average footage per well drilled. The deepest drilling in the basin through 1972 was in Pennsylvania, where a well was drilled to 18,834 feet. Since 1972 several deeper wells have been drilled in West Virginia, reaching depths greater than 20,000 feet. The deepest known production was from a hole drilled in 1964 in Pennsylvania at 11,458 feet in the Silurian Tuscarora Sandstone. The average footage per well drilled within the Appalachian basin during the period 1947–68 was approximately 2,662 feet.

Stripper well production surveys are summarized for each State. Records show that 100 percent of the production from Pennsylvania and West Virginia, the leading hydrocarbon-producing States, is from stripper wells. Ohio has 82 percent of its production from stripper wells, Kentucky, 94 percent, and New York, 100 percent.

All production, reserve, and estimated oil-in-place data are based upon known reservoirs. Projections or extrapolations into unexplored or currently nonproductive formations within the Appalachian basin are outside the scope of this report.

INTRODUCTION

PURPOSE AND SCOPE OF REPORT

This report is a comprehensive summary of the oil and gas production and reserve histories of the Appalachian basin from 1859 through 1972. These histories were used in making a regional synthesis of Appalachian basin data to evaluate the basin's petroleum potential and to delineate potentially productive areas within selected stratigraphic intervals in the basin.

The Appalachian basin, as the term is used by the petroleum industry in the United States, comprises those Paleozoic sedimentary rocks lying between the west face of the Blue Ridge Mountains on the east and the crests of the Cincinnati and Findlay arches and of the

Nashville dome on the west, and stretching from the Canadian border on the north to the northern border of the overlapping Cretaceous rocks in Alabama on the south. This report on the Appalachian basin encompasses production and reserve data from all of West Virginia and parts of New York, Pennsylvania, Ohio, Maryland, Virginia, Kentucky, and Tennessee. Because no significant production occurred in those parts of the Appalachian basin that fall within the States of North Carolina, Georgia, Alabama, and New Jersey, these States are not included in the data compilations. The production in Ontario, Canada, is not included in this report. It should be noted that all production and reserve data pertaining to the Lima-Findlay (Trenton) fields on the Findlay-Cincinnati arch in Ohio and all data for the western side of the Nashville dome in Kentucky and Tennessee are excluded here from the Appalachian basin records because these areas lie outside the basin. This will account for differences between data reported here and production and reserve data for the Appalachian basin published in other sources in which these two areas were included in the totals for the Ohio and Kentucky records.

This report presents information on the oil and gas developments in the Appalachian basin from 1859 through 1972 for all the States included within the basin and also for geologic age categories. The report includes data on oil and gas production, proved reserves, original oil-in-place, number of wells drilled, deepest drilling records, average footage drilled, and percent stripper-well production.

PREVIOUS INVESTIGATIONS

A detailed compilation of the oil and gas production and reserve histories for the entire Appalachian basin from 1859 through 1972 has not been previously published. Although many individual State agencies and U. S. Bureau of Mines reports (U. S. Bureau of Mines, 1924-1931, 1932-1971) provide piecemeal information, there are no comprehensive summary reports for the entire basin.

METHODS OF INVESTIGATION

This report is based chiefly upon published information from State and Federal agencies, the American Gas Association (AGA), the American Petroleum Institute (API), the American Association of Petroleum Geologists (AAPG), the Independent Petroleum Association of America (IPAA), the Interstate Oil Compact Commission (COMPACT), and on many other published reports from miscellaneous sources. Additional information was provided by correspondence with some industrial companies and other private organizations and through communications with various officials of State geological surveys. A detailed list of published references and other sources of information is included at the end of this report.

GENERAL GEOLOGY

STRUCTURE

The Appalachian basin is a large spoon-shaped geologic feature extending southwestward from approximately the Adirondack Mountains in New York into northern Alabama (see fig. 1). The basin is bounded on the west by the Cincinnati arch in western Ohio and on the east by the Blue Ridge Mountains of Virginia. Structurally, the Appalachian basin extends to the Blue Ridge on the east; however, there is evidence to indicate that Paleozoic strata lie below the thrust plates of metamorphic rocks of the Blue Ridge and that the eastern boundary of the Appalachian basin in southwestern Virginia and North Carolina may lie as much as 50 miles east of the west edge of the Blue Ridge anticlinorium. The boundaries of the Appalachian basin coincide roughly with the boundaries of the Appalachian Plateau and the Valley and Ridge physiographic provinces, although along its northwestern, western, and southwestern margins, the basin extends beyond the Plateau. The greatest length of the basin is approximately 900 miles. Its greatest width is about 300 miles; however, in most places it is much narrower. The entire area as reported by Roth (1968, p. 1707) comprises at least 100 million surface acres.

The Appalachian basin originated as a sedimentary trough or depression on the Precambrian surface which was covered by Cambrian seas. Large quantities of marine and continental sediments were deposited in the basin throughout most of the Paleozoic Era. The sediments were derived primarily from landmasses to the east, although some detritus was derived from sources to the north and west of the basin. During the Paleozoic there was a sequence of depositional settling, subsidence, and elevation in the basin. During the Paleozoic, the seas encroached westward and then receded as epeirogenic movements occurred. The Cincinnati arch was an important influence in the formation of the Appalachian basin, acting as a barrier to the westward migration of the seas and the clastic materials which they carried and functioning as a fulcrum during the orogenies occurring during the basin's formation (Roth, 1968, p. 1707).

STRATIGRAPHY

All systems of the Paleozoic Era are represented in the Appalachian basin. The youngest beds in the central part of the basin are of Permian age, surrounded by outcrops of Pennsylvanian rocks. The Pennsylvanian caps the major part of the Appalachian Plateau south of the New York-Pennsylvania border. Mississippian, Devonian, Silurian, and older strata crop out in sequence along the western, northern, and southeastern margins (Fettke, 1953, p. 71). At the southwestern end of

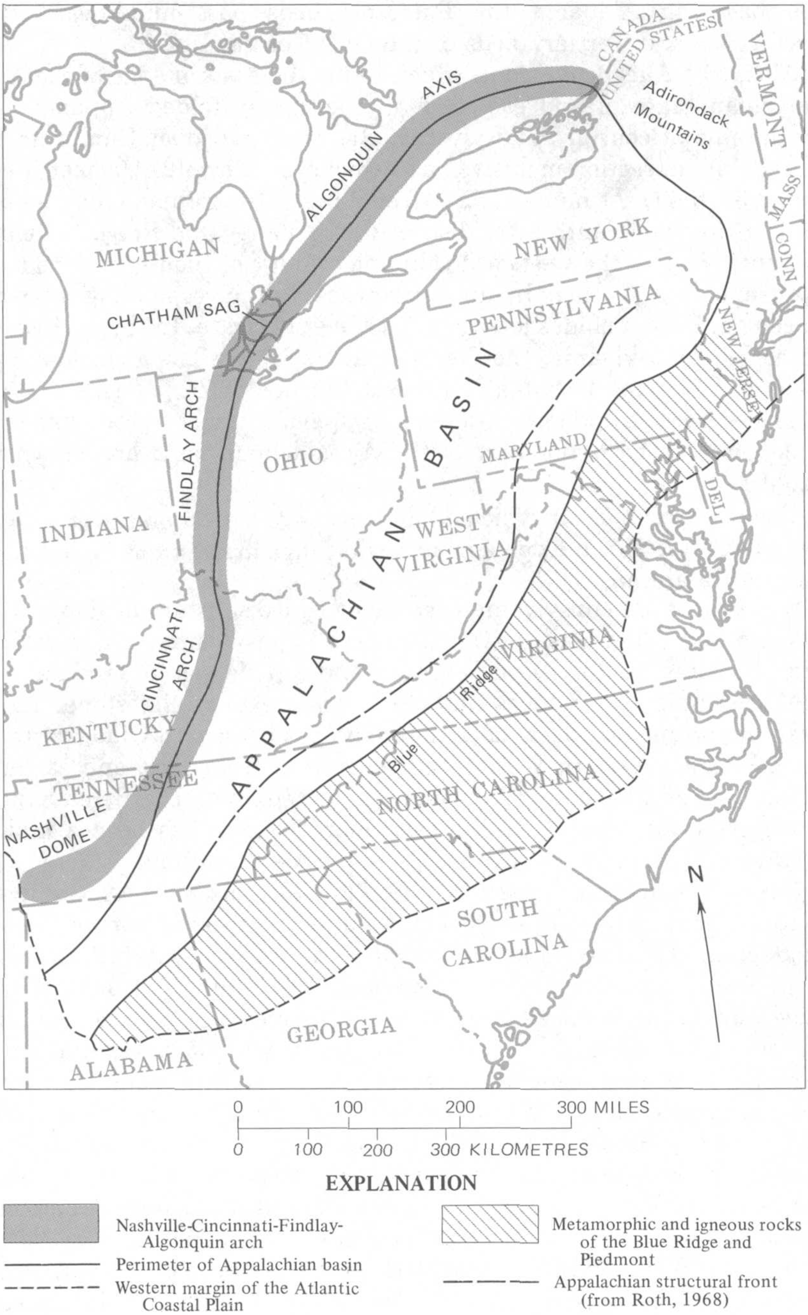

FIGURE 1. — Map of the Appalachian basin (modified from Colton, 1961, and Roth, 1968).

the basin in Alabama the Paleozoic beds pass underneath the Cretaceous and Tertiary beds of the Gulf Coastal Plain.

Along the Allegheny Front, which forms the eastern edge of the Appalachian Plateau, and east of it in the closely folded Appalachian Mountains of central Pennsylvania, the exposed Upper Cambrian to Mississippian section inclusive has a thickness of over 21,000 feet (Fettke, 1953, p. 71). As much as 5,000 feet of post-Mississippian rock is present in the folded anthracite district in the Valley and Ridge of Pennsylvania. Due to the westward thinning of most of the formations and the truncating of others by unconformities, the corresponding interval in central Ohio includes less than 5,000 feet of strata. In the southwest corner of Pennsylvania, the Pennsylvanian System has a thickness of 1,500 feet and the Permian, 1,100 feet (Fettke, 1953, p. 71).

The succession and nature of the principal oil- and gas-producing pay zones within the major part of the Appalachian basin are shown in table 1.

The reservoir rocks in which oil and gas have been found in commercial quantities in the Appalachian basin range in age from Pennsylvanian to Cambrian.

Sandstones of Pennsylvanian age have yielded substantial volumes of gas and oil in southeastern Ohio, western Pennsylvania, northwestern West Virginia, and eastern Kentucky and a little gas in Virginia.

Mississippian sandstones and, to a lesser extent, limestones have been important producers of both oil and gas in eastern Ohio, western Pennsylvania, western West Virginia, eastern Kentucky, and eastern Tennessee, and have produced some gas in Virginia. The Berea Sandstone, near the base of the Mississippian System, has been a major producer of oil in Pennsylvania, Ohio and West Virginia.

Major oil and natural gas production in New York has been confined to sandstones in the Upper Devonian Series. The major part of the oil production in Pennsylvania and much of that in West Virginia has also come from Upper Devonian sandstones; large volumes of natural gas have also been produced from these sandstones. Upper and Middle Devonian black shales in eastern Kentucky and southwestern West Virginia have been a major source of gas. Substantial volumes of gas have been encountered in fractured Huntersville Chert (of Price, 1929) and Oriskany Sandstone of Middle and Early Devonian age, respectively, in southwestern Pennsylvania, western Maryland, and northeastern West Virginia. The Lower Devonian Oriskany Sandstone has been the source of large volumes of gas in south-central New York, north-central Pennsylvania, and western West Virginia. Gas and some oil have also been produced from the Oriskany Sandstone in eastern Ohio.

The Newburg sand, a porous zone correlated with rocks in the Middle Silurian Lockport Dolomite of New York, produces considerable gas and some oil in northern Ohio. The so-called Corniferous limestone of eastern Kentucky consists of two dolomites, the Peebles and the Lilley (of Foerste, 1917) of the Middle Silurian Lockport Group, and is a major producer of petroleum. The Big Six sand, which is thought to correlate with the Keefer Sandstone of the Middle Silurian, is a source of gas in eastern Kentucky. The "Red", "White", and "Gray Medina" sands of the Albion Group of the Lower Silurian have been an outstanding source of gas in western New York and in central and eastern Ohio. In Ohio, where these sands are commonly called Stray, Red, and White Clinton sands by drillers, some oil has also been produced (Calvert, 1964a, b).

To date, rocks older than the Silurian have contributed relatively small amounts (less than 2 percent) of oil and gas to the total production of the Appalachian basin. A little gas has been produced from the Trentor Limestone of the Middle Ordovician on the southwest flank of the Adirondack Mountains in New York.

Limestones of Trenton, Black River, and Stones River ages (Middle Ordovician) have produced a little oil and gas in south-central Kentucky and north-central Tennessee. Gas in commercial volumes has been discovered in eastern Kentucky in a sand that occurs a short distance above the unconformity at the top of the Lower Ordovician Knox Dolomite. A small oil field in Virginia produces from fractured Trenton Limestone. A little oil and gas have been obtained from the Knox Group of Early Ordovician and Late Cambrian age in central Tennessee and shows of oil occur in this dolomite in eastern Kentucky (Fettke, 1953, p. 72).

To date, the most encouraging production in rocks older than Silurian are the recent discoveries and good yields from the Trempealeau Dolomite in central Ohio in the uppermost unit of the Cambrian sequence.

OIL AND GAS PRODUCTION AND RESERVES

HISTORICAL COMMENT

The modern petroleum industry in the United States began in the Appalachian basin and the oil and gas fields of this basin have the longest production history of any on the North American Continent. Although the basin's commercial development dates from the discovery of oil in a stray sand of Late Devonian age at a depth of 69 feet in the Drake well along Oil Creek south of Titusville in northwestern Pennsylvania in August 1859, the first recorded reference to petroleum in this area was reported in 1627. Joseph Delaroche Daillon, a French missionary, having penetrated into the Lake Erie Wilderness, now a part of New York State, wrote in a letter dated July 18, 1627, that he had seen "a good kind of oil which the Indians called Antonontons" coming from

TABLE 1. — *Principal oil- and gas-producing*

[Correlation between units for each State not implied. Maryland omitted as it has only limited production from two horizons in the Lower Devonian. Table modified from Meyer and Edgerton (1968, table 51). Data from Calvert (1961, 1964b), Cardwell and others (1970), Cram (1971), Hunter (1955, 1964), Kreidler (1953), Landes (1970), Lytle (1950), McGuire and Howell (1963), Milhous (1960), Sitler and Wehmeyer (1962), Thomas and Nosow (1960),

System	Series	Southern New York	Pennsylvania	Southeastern Ohio
PERMIAN		(No production)		
PENNSYLVANIAN	Upper		Murphy sd Little Dunkard sd Big Dunkard sd	Carroll sd Goose Run sd Mitchell sd Wolf Creek sd Peeker sd First Cow Run sd Buell Run sd Macksburg 300-foot sd
	Middle		Freeport sd Kittanning sd Clarion sd "First Salt" sd "Second Salt" sd	Second Cow Run sd Macksburg 500-foot sd Macksburg 700-foot sd Germantown sd Schram sd "First Salt" sd "Second Salt" sd Brill sd
	Lower		"Maxton" sd	"Maxton" sd
MISSISSIPPIAN	Upper		"Big Lime" (Greenbrier Ls)	"Big Lime" Lime sd
	Lower		Lime sd Big Injun sd Squaw sd Second sd Berea Ss Murrysville-Thirty Foot sd	Keener sd Big Injun sd Squaw sd Hamden sd Weir sd Berea Ss "Second Berea" ss Cussewago Ss
DEVONIAN (PART)	Upper	Bradford First sd Sugar Run sd Chipmunk sd Bradford Second sd Harrisburg Run sd Richburg sd	Gantz sd Hundred foot-First Venango sd Nineveh sds Red Valley sd Thirty foot-Second Venango sd Snee sd Knox Third sd Knox Fourth sd Knox Fifth sd Gordon Stray sd Gordon-Third Venango sd McDonald Fourth sd McDonald Fifth sd Bayard sd Elizabeth sd Warren First sd Warren Second sd Bradford First-Glade-Queen-Eighty Ft sds Clarendon sd Speechley sd Balltown sd Tiona sds Bradford Second sd Cooper sd Bradford Third sd Kane sds Haskill sds	Ohio Sh

pay zones in the Appalachian basin

Wilson (1968), Weaver (1962), and Wallace Dewitt, Jr. (written commun., 1974). Abbreviations are as follows: Fm, formation; Mbr, member; Ls, limestone; Ss or ss, sandstone; Dol or dol, dolomite; Gp, group; Sh or sh, shale; sd(s), sand(s). Quotation marks (") mean local or driller's name].

West Virginia	Virginia	Central and eastern Kentucky	Tennessee
Carroll sd Sewickley coal Pittsburgh coal Minshall sd Murphy sd Moundsville sd First Cow Run sd Big Dunkard sd			
Burning Springs sd "Peeker" sd- Second Cow Run sd Horseneck sd "First Salt" sd "Second Salt" sd	Salt sd	Beaver sd Horton sd Pike sd "First Salt" sd "Second Salt" sd "Third Salt" sd Lee Fm (part)	
"Maxton" sd			
Princeton sd Ravencliff sd Maxton sd "Big Lime"	Ravencliff sd Maxton sd Greenbrier Ls ("Big Lime") Little Valley Ls (sds)	Maxton or "Maxon" sd Girkin ("Gasper") Fm Ste. Genevieve Ls St. Louis Ls Warsaw Ls	Unnamed sds Glen Dean Ls "Gasper" Fm St. Louis Ls Warsaw Ls
Keener sd Big Injun sd Squaw sd Weir sd Berea Ss Murrysville sd	Berea Ss	Keener sd- Fort Payne Chert Red Injun sd Big Injun sd Weir sd Sunbury Sh Berea Ss Beaver sd-Beaver Creek sd Borden sd	Fort Payne Chert Borden sd
Gantz sd (now gas storage) Fifty foot sd Thirty foot sd Gordon Stray sd Gordon sd McDonald Fourth sd McDonald Fifth sd Sixth-Bayard sd Seventh-Elizabeth sd Warren First sd Burnside sd Warren Second sd Clarendon sd Speechley (Tiona) sd Balltown-Cherry Grove sd Riley sd Benson sd Elk-Porter sd "Kane" sd "Childress zone" sd		Brown sh (Black sh)	Chattanooga Sh

TABLE 1. — *Principal oil- and gas-producing*

System	Series	Southern New York	Pennsylvania	Southeastern Ohio
DEVONIAN (PART)	Middle	Hamilton Fm Onondaga Ls	Onondaga Ls	
	Lower	Oriskany Ss	Huntersville Chert Oriskany Ss	Oriskany Ss
SILURIAN	Upper	Salina Gp	Salina Fm	Salina Gp Newburg Dol
	Middle	Lockport Dol	"Lockport" Dol	"Lockport" Dol "Packer Shell-Little Lime"
	Lower	"Gray Medina" sd "Red Medina" sd "White Medina" sd	"Red Medina" sd "White Medina" sd	Stray Clinton sd Red Clinton sd (Albion Sd) White Clinton sd Medina sd
ORDOVICIAN	Upper			
	Middle	Ls of Trenton Gp		Trenton Dol Black River Ls Glenwood Fm St. Peter Ss
	Lower	Beekmantown Dol	Beekmantown Dol	Beekmantown Dol
CAMBRIAN	Upper	Potsdam Ss	Gatesburg Fm	Copper Ridge Dol (Trempealeau Dol) Mount Simon Ss
	Middle	(No production)		
	Lower			

a spring near the present town of Cuba in Allegany County, N. Y. (Carll, 1887, p. 575).

Prior to the Drake well, the presence of oil and gas had been observed at a number of scattered localities in the basin and had been utilized on a small scale for illuminating, lubricating, and medicinal purposes. The literature relating to the early history of the salt industry in the Appalachian basin cites many instances of both natural gas and oil having been found during drilling for brine. According to the U. S. Geological Survey (1885), the salt industry made the first commercial use of gas at Malden, W. Va., where brine was evaporated by use of natural gas from wells drilled in 1807 and 1808. Because crude oil was considered a nuisance which greatly hampered the extraction of salt from the brine, the salt well drillers attempted to avoid finding oil in their drilling. Many of their tools, however, which were developed for drilling brine wells, were used to drill the early oil wells.

Although the salt industry used the natural gas byproducts from brine wells, historians generally agree that the first well drilled for the express purpose of finding natural gas was near the town of Fredonia, Chautauqua County, N. Y., in 1821 (Roth, 1968, p. 1702). In spite of these early uses it was not until about 1882, when gas was transported *pay zones in the Appalachain basin* — Continued

West Virginia	Virginia	Central and eastern Kentucky		Tennessee
"Brown" sh Hamilton Fm				
Huntersville Chert Oriskany Ss Healing Springs Ss Mbr of New Scotland Ls	Oriskany Ss	"Onondaga" Ls (Irvine sd)	"Corniferous" ls	
Unnamed dol Williamsport sd Newburg sd		Salina Fm Peebles sd		
"Lockport" Dol Big Six sd (Keefer Ss)		"Lockport" Dol Big Six sd		"Lockport" Dol
Clinton sd (Tuscarora Ss)		Clinton sd Brassfield Ls		
Juniata Fm		Leipers Ls		
Trenton Dol Black River Ls	Trenton Ls "Black River" (Witten) Ls Moccasin Ls	Sunnybrook sd-Granville sd "Black River" Ls "St. Peter" Ss		Trenton Ls "Black River" Ls Stones River Ls
		"Beekmantown" Dol (Knox Dol)		Knox Gp
Rome Fm		Rome Fm "Basal" sd		

to Pittsburgh, Pa., from a gas well about 15 miles east of the city, that the natural gas industry began. By 1885 the natural gas industry was well established in the Appalachian area.

ANNUAL PRODUCTION OF OIL AND GAS

For the purposes of this report, the first recorded oil production in the Appalachian basin began in 1859, and the first recorded gas production in 1882. Any production or wastage figures prior to these dates are highly speculative for reasons which will be commented on later in this report.

Beginning in 1859 with 2,000 barrels, the annual oil production in the Appalachian basin rose until it reached a peak of 36.3 million barrels in 1900. This represented 57 percent of the total oil production of the United States in that year. By the end of 1900, or during the first 40 years of the petroleum industry's history, 73.5 percent of the total cumulative oil production in the United States had come from this basin.

After 1900, oil production declined until, in 1915, it had dropped to a low of 24.8 million barrels. An upward trend followed the introduction of secondary recovery methods, particularly waterflooding, which was used in the Bradford field of Pennsylvania, and in 1937 production was 37.6 million barrels. Production again declined until 1960, when it was approximately 19.3 million barrels. An upward surge in 1964 to 31.9 million barrels reflected the new discoveries in the Cambrian of Ohio. Since then the trend has again been gradually downward.

The annual oil production for 1972 was approximately 21.3 million barrels, representing only 0.65 percent of the total U. S. oil production that year. At the end of 1972, the cumulative production of the Appalachian basin accounted for only 2.75 percent of the total cumulative production of the United States, in contrast to 73.5 percent at the end of 1900. This change in the relative importance of Appalachian basin oil fields emphasizes the rapidity with which the American oil industry has grown and the magnitude it has attained since the beginning of the present century.

TABLE 2. — *Estimated annual crude oil production in the Appalachian basin, 1859–1972*

[Reported in thousands of barrels]

Year	Production	Year	Production	Year	Production
1859	2	1897	35,230	1935	33,303
1860	520	1898	31,717	1936	35,080
1861	2,133	1899	33,069	1937	37,585
1862	3,076	1900	36,295	1938	35,314
1863	2,631	1901	33,618	1939	34,842
1864	2,136	1902	32,883	1940	34,167
1865	2,517	1903	32,472	1941	30,652
1866	3,617	1904	31,882	1942	30,110
1867	3,367	1905	30,800	1943	29,249
1868	3,666	1906	28,834	1944	26,434
1869	4,235	1907	27,628	1945	24,639
1870	5,280	1908	27,435	1946	26,479
1871	5,225	1909	28,468	1947	25,719
1872	6,313	1910	29,069	1948	25,832
1873	9,913	1911	25,969	1949	24,002
1874	10,946	1912	27,825	1950	23,826
1875	8,807	1913	27,457	1951	23,202
1876	9,128	1914	25,791	1952	23,223
1877	13,344	1915	24,753	1953	22,931
1878	15,389	1916	25,087	1954	21,365
1879	19,901	1917	27,643	1955	21,368
1880	26,253	1918	27,745	1956	22,028
1881	27,568	1919	34,344	1957	22,545
1882	30,227	1920	32,745	1958	22,585
1883	23,307	1921	32,588	1959	21,486
1884	23,956	1922	31,210	1960	19,294
1885	21,534	1923	30,379	1961	21,739
1886	26,624	1924	29,074	1962	21,510
1887	22,878	1925	29,550	1963	21,473
1888	16,942	1926	30,452	1964	31,916
1889	22,356	1927	32,163	1965	28,208
1890	30,066	1928	32,640	1966	25,540
1891	35,849	1929	35,308	1967	23,722
1892	33,432	1930	35,417	1968	24,424
1893	31,366	1931	31,516	1969	23,525
1894	30,783	1932	30,732	1970	22,444
1895	30,960	1933	28,513	1971	20,339
1896	33,971	1934	31,509	1972	21,300
				Total	2,738,000

---

[1] Annual crude oil production data for the Appalachian basin States were compiled from many sources (see, for example, U.S. Bureau of Mines references) and exclude the greater part of the Lima-Trenton production in Ohio and the production in western Kentucky after oil was discovered there in 1943. However, it was impossible to trace all of the Lima-Trenton production on an annual basis in the data for Ohio's total annual production. This difficulty and the many sources of data account for the minor differences between total cumulative production figures given here and those given in table 4.

Table 2 shows the estimated annual crude oil production for the Appalachian basin from 1859 through 1972. The estimated total production for each year consists of a summation of the oil production data for each respective State within the basin compiled from many different sources of reference. These annual production figures were adjusted to eliminate the major part of the Lima-Trenton production in Ohio and the oil production from the western side of the Nashville dome in Tennessee and Kentucky — areas which are not considered as a part of the Appalachian basin in this report. The data in table 2 were used to plot the oil-production curve for the Appalachian basin for the years 1859–1972 as shown in figure 2.

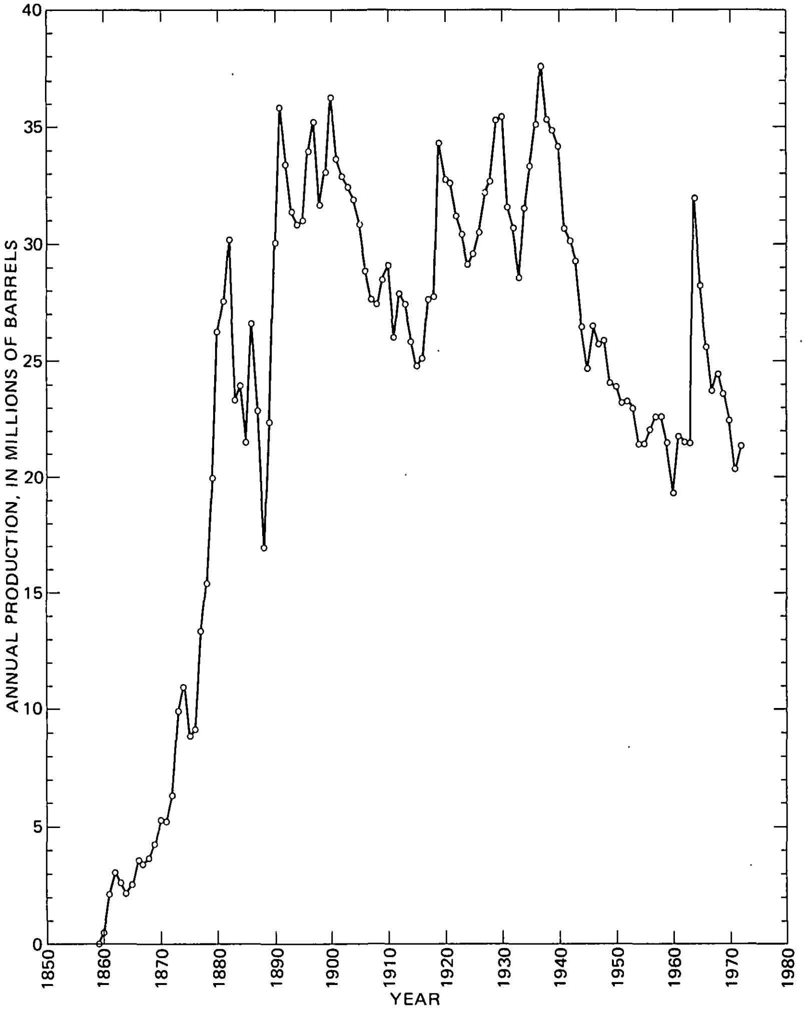

FIGURE 2. — Annual oil production for the Appalachian basin, 1859–1972.

Beginning in 1882, with a reported annual production of natural gas of 1.3 billion cubic feet, the Appalachian basin reached its peak natural gas production in 1917 with more than 522 billion cubic feet reported. Production declined to approximately 460.4 billion cubic feet produced in 1972, a figure which represents approximately 2 percent of the total natural gas production for the United States for that year. At the end of 1972 the cumulative natural gas production of the entire Appalachian basin accounted for about 7 percent of the total cumulative gas production of the United States, in contrast to approximately 63 percent of the total at the end of 1917.

Table 3 shows the estimated annual natural gas production for the Appalachian basin from 1882 through 1972. The estimated total production figure for each year is derived from natural gas production data compiled from a variety of sources for each respective State within the basin. The data in table 3 were used to plot the natural gas production curve for the Appalachian basin for the years 1882–1972 as shown in figure 3.

TABLE 3. — *Estimated annual natural gas production in the Appalachain basin, 1882–1972*

[Reported in millions of cubic feet]

Year	Production	Year	Production	Year	Production
1882	1,282	1913	425,266	1943	514,388
1883	3,419	1914	425,863	1944	471,062
1884	21,154	1915	446,852	1945	430,250
1885	120,232	1916	509,835	1946	440,124
1886	224,176	1917	522,116	1947	465,566
1887	313,562	1918	461,737	1948	443,512
1888	400,601	1919	420,995	1949	379,078
1889	261,185	1920	436,223	1950	411,179
1890	242,743	1921	319,891	1951	449,580
		1922	360,867	1952	404,911
1891[2]	Total production: 2,844,922 Estimated annual average: 203,209				
1892		1923	388,695	1953	412,391
1893		1924	354,616	1954	449,894
1894		1925	342,201	1955	429,808
1895		1926	352,124	1956	413,892
1896		1927	335,589	1957	421,677
1897					
1898		1928	341,432	1958	426,158
1899[3]		1929	335,660	1959	435,517
1900		1930	333,951	1960	455,910
1901		1931	291,658	1961	437,683
1902		1932	251,435	1962	420,203
1903					
1904		1933	247,822	1963	426,280
		1934	285,131	1964	405,630
1905	204,543	1935	328,288	1965	418,900
1906	306,337	1936	351,850	1966	429,360
1907	314,837	1937	419,325	1967	441,428
1908	295,375				
		1938	365,902	1968	465,588
1909	354,150	1939	401,722	1969	450,727
1910	373,173	1940	428,187	1970	478,811
1911	371,726	1941	465,856	1971	471,165
1912	419,945	1942	487,318	1972	460,413
				Total	31,672,854

---

[1] Annual natural gas production data for the Appalachian basin States were compiled from many sources (see, for example, U.S. Bureau of Mines references). This method accounts for differences between total cumulative production figures given here and those given in table 5.

[2] Annual production figures for the years 1891 through 1901 were not available on a yearly basis. However, total production for this 14-year span is available and is reported accordingly.

[3] Unpublished data on gas production for Ohio and West Virginia for the years 1899–1905 were obtained through written communications with J. R. Ebright (East Ohio Gas Company, Cleveland, Ohio, January 1974) and G. C. Grow, Jr. (Transcontinental Gas Pipe Line Corporation, Newark, N. J., September 1973).

PROCEDURES

PREPARATION OF SAMPLE SOLUTION

REAGENTS

Hydrochloric acid, concentrated, A.C.S.

Hydrochloric acid, 6 *M*.

Magnesium oxide-magnesium nitrate slurry. Suspend 37.5 g magnesium oxide and 52.5 g magnesium nitrate hexahydrate in enough water to make 500 ml. Shake vigorously immediately before using.

Nitric acid, concentrated, A.C.S.

Oxalic acid, reagent grade, 5 percent. Dissolve 5 g of dihydrate in 100 ml water.

Perchloric acid, 70–72 percent.

Potassium iodide. Prepare by dissolving 15 g of salt in 100 ml water. Store in dark bottle.

Stannous chloride. Prepare by dissolving 4 g of dihydrate in 10 ml concentrated hydrochloric acid.

Sulfuric acid, concentrated, A.C.S.

DRY IGNITION

1. Weigh 1 to 2 g of ground air-dried vegetation in an evaporating dish and wet with small amount of water.
2. Add 10 ml of magnesium oxide-magnesium nitrate slurry and mix well.
3. Place dish on hot steam bath and dry.
4. Transfer dish to preheated muffle furnace and ignite the vegetation at 550°–600°C for 2 to 4 hours.
5. Remove dish from muffle furnace, cool, moisten ash with minimum amount of water, and cover dish with cover glass. Add about 15 ml 6 *M* hydrochloric acid.
6. Heat dish and contents on steam bath until sample dissolves.
7. Filter hot acid solution through Whatman No. 41 filter paper into a 125-ml Erlenmeyer flask. Rinse dish and filter with several portions of hot water and continue until filtrate has a volume of about 60 ml.
8. To the filtrate, add 8 ml concentrated hydrochloric acid, 2 ml of potassium iodide, and 0.5 ml stannous chloride. Mix and heat in boiling water bath about 5 minutes. Cool flask and contents.
9. Distill arsine as described under the headings entitled "Molybdenum Blue Reaction" and "Silver Diethyldithiocarbamate Reaction."

WET IGNITION

1. Weigh 1 to 2 g of air-dried vegetation into a 250-ml Erlenmeyer flask.
2. Add 15 ml concentrated nitric acid, mix, and add 25 ml of 1+1 mixture

of concentrated sulfuric acid and concentrated (70–72 percent) perchloric acid.

3. Heat flask and contents on hotplate until white fumes evolve. If, during heating, brown fumes cease evolving and sample turns brown, discard and start over, using a larger volume (20–25 ml) of concentrated nitric acid.
4. After about one-half hour and while white fumes are still evolving, remove flask from hotplate. Cool, add 10 ml oxalic acid solution and return flask to hotplate.
5. Heat flask and contents until white fumes evolve freely.
6. Remove flask from hotplate, cool, and add 2- by 50-ml portions of water twice and mix well.
7. Add 2 ml potassium iodide and 0.5 ml stannous chloride, mix and allow mixture to stand 15 minutes.
8. Distill arsine as described under the headings entitled "Molybdenum Blue Reaction" and "Silver Diethyldithiocarbamate Reaction."

DISTILLATION AND ESTIMATION

MOLYBDENUM BLUE REACTION

REAGENTS

Acetic acid, glacial

Ammonium molybdate. Dissolve 1.5 g of the reagent in 100 ml of 1+9 sulfuric acid. Prepare fresh daily.

Arsenic standard solution, 1,000 μg/ml. Dissolve 0.132 g of arsenious oxide in 2 ml of 1 *M* sodium hydroxide. Dilute with 5–10 ml water, add 3 ml concentrated hydrochloric acid, and make up to 100 ml with water. From this stock solution, prepare less concentrated standard solutions as needed by dilution of appropriate volumes with water.

Hydrochloric acid, 1 *M*. Prepare by diluting 8.3 ml of concentrated acid with water to 100 ml.

Hydrazine sulfate. Prepare by dissolving 1 g of reagent-grade salt in 100 ml of water.

Lead acetate. Prepare by dissolving 17.5 g of salt in 100 ml of water containing 5 ml glacial acetic acid.

Potassium iodide-iodine reagent, stock solution, 0.02 *N*. Prepare by dissolving 8 g potassium iodide and 2.54 g iodine in 25 ml water. Dilute to 1 l with water and store in the dark.

Potassium iodide-iodine reagent, 0.002 *N*. Prepare by diluting 10 ml of stock solution to 100 ml with water. Store in the dark.

Sodium meta-bisulfite. Prepare daily by dissolving 0.5 g of the reagent in 10 ml water.

Zinc, mossy, arsenic-free.

APPARATUS

The distillation apparatus used was described by Kingsley and Schaffert (1951) and is commercially available from Corning Glass Works,[1] Corning, N.Y. Catalog No. 33680.

1. Assemble the distillation apparatus of Kingsley and Schaffert, using a 250-ml Erlenmeyer flask containing sample solution prepared by either wet or dry ignition. Place lead acetate-saturated glass wool in the trap and 15 ml of 0.0002 *N* potassium iodide-iodine reagent in collecting test tube.
2. Separate sample flask from apparatus and add 4–6 g arsenic-free zinc and quickly connect flask to trap.
3. Allow the evolved arsine and hydrogen to bubble through the iodine solution for 45 minutes.
4. After about 45 minutes, remove test tube receiver from apparatus and add the following:
    - 2 ml 1 *M* hydrochloric acid
    - 2 ml ammonium molybdate reagent
    - 2 drops hydrazine sulfate reagent
5. Mix reagents of step 4 and add 1–2 drops of sodium meta-bisulfite reagent.
6. Make volume up to 25 ml with water, mix, and place test tube in boiling water bath for 10 minutes.
7. Cool and read absorbance at 835 nm.
8. Compare the absorbance of an unknown with that obtained from standard solutions, prepared as follows:

    To a series of 125-ml flasks each containing 8 ml concentrated hydrochloric acid add individually 0.0, 1, 2, 4, 8, and 16 μg of arsenic. Make each up to 60 ml with water and continue with step 8 under dry ignition to prepare a series of standard solutions. Plot absorbance values versus concentration and use resulting curve for comparison in step 7.

SILVER DIETHYLDITHIOCARBAMATE REACTION

REAGENTS

Arsenic standard solution, 1,000 μg/ml. See "Reagents" under "Molybdenum Blue Reaction."

Lead acetate. See "Reagents" under "Molybdenum Blue Reaction."

Pyridine, reagent grade.

Silver diethyldithiocarbamate absorbing solution. Prepare by dissolving 250 mg of the carbamate in 50 ml reagent-grade pyridine.

Zinc, granular, 20-mesh, arsenic-free.

---

[1] Use of a specific company name does not necessarily constitute endorsement of the company by the U.S. Geological Survey.

APPARATUS

Arsine generator. The distillation apparatus is described in the Fisher Scientific Co. catalog (1974).

1. Assemble distillation apparatus, marketed by Fisher Scientific Co., with sample solution in 125-ml generating flask, a piece of lead acetate-saturated glass wool in scrubber (trap) and 3 ml of carbamate reagent in the absorber. Lubricate standard taper joints with water to assure a tight seal.
2. Disconnect generating flask from scrubber, add 6 g of zinc to flask and quickly connect flask to scrubber and pass the evolved arsine through the trap and the absorbing solution.
3. After 30 minutes, disconnect generating flask from scrubber and transfer the absorbing solution to a 1-cm cuvette and measure absorbance at 540 nm using absorbing solution in null cell.
4. Obtain arsenic concentration by referring the measured absorbance of sample solution to a standard curve prepared as follows:

   To a series of 125-ml Erlenmeyer flasks, each containing 60 ml water, 8 ml concentrated hydrochloric acid, 2 ml potassium iodide, and 0.5 ml stannous chloride, add individually 0.5, 1.0, 2.0, 3.0, 6.0, 8.0, and 10.0 μg of arsenic. Mix and heat in boiling water bath about 5 minutes. Cool flask and contents. Distill contents of each flask as in steps 1, 2, and 3, collecting the evolved arsine in the pyridine solution of silver diethyldithiocarbamate. Plot absorbance values versus concentration to prepare standard curve.

DISCUSSION

In the presence of relatively large amounts of hydrochloric acid, such elements as antimony and germanium form volatile chlorides and may possibly distill with the arsine. Phosphine may distill also, and all these elements interfere with the molybdenum blue reaction. On the other hand, phosphine does not interfere with the reaction of arsine with silver diethyldithiocarbamate, and antimony forms a compound having a different color and, thus, is not a serious interference. Bhargava, Donovan, and Hines (1972) found that up to 0.1 percent antimony did not interfere when the sample solution was accomplished with acid mixtures containing sulfuric acid as one component.

EXPERIMENTS

The effect of different amounts of sulfuric acid is significant at the wavelength used to measure the absorbance of the blue compound. Sandell (1959) suggested 0.25 *N* as the optimum concentration, but, under the conditions of our method, we observed a range in sulfuric acid concentration from 0.1 to 0.4 N over which the absorbance was constant. Such a range was observed at 10- and 20-μg levels of arsenic, and this range suggests more flexibility in the molybdenum blue reaction than heretofore observed.

RESULTS

A scarcity of analyzed samples of vegetation precludes adequate comparison of results of our procedure with those obtained by other procedures. Arsenic values reported by Bowen (1967) on a standard kale sample are inconsistent, varying from about 0.1 to nearly 2 ppm. The Standard Reference Orchard Leaves of the National Bureau of Standards (Meinke, 1971) was unavailable at the time our procedures were being tested.

Repeatability of the proposed procedures was tested by repeat determinations on limited amounts of samples from the southwestern United States. The data given in table 3 were obtained using the wet ignition procedure of, and subsequent measurement by, the molybdenum blue reaction.

TABLE 3—*Repeatability of arsenic determinations (molybdenum blue)*

Sample No.	Material	Arsenic Number of determinations	Low (ppm)	High (ppm)	Average (ppm)	Standard deviation (ppm)	Relative standard deviation (percent)
399	Aspen leaves	8	2	3	2.1	0.4	19
435	Rabbitbrush	6	6	9	7.0	1.1	16
433	...do	13	5	12	7.8	2.2	28
432	...do	7	10	13	11.9	.9	8
438	Sage	7	10	17	12.5	2.6	21
440	...do	8	12	18	15.5	2.2	14
446	...do	10	23	30	25.8	2.7	10

The standard deviation of sample Nos. 433 and 432 appears to be out of line for undetermined reasons; otherwise, the relative standard deviation seems to be in the range of 10 to 20 percent. This range is in better accord with our experience using the kinds of methods presented in this bulletin.

The data in table 4 show that both the molybdenum blue reaction and the silver diethyldithiocarbamate reaction give essentially the same results. A casual examination of these data suggests that small amounts of arsenic are lost on dry ignition; however, the differences are small and one may not draw any such conclusion with certainty.

TABLE 4.—*Determination of arsenic by molybdenum blue and carbamate*

Sample No. (ADD-)	Arsenic (ppm)	
	Molybdenum blue wet ignition	Silver diethyldithiocarbamate dry ignition
407	1	<1
399	2	1
439	4	4
441	4	2
437	5	4
445	5	3
430	6	7
436	6	4
442	6	8
431	7	5
435	7	7
433	8	9
429	9	10
434	10	9
432	12	10
444	15	16
438	16	12
440	18	18
446	28	24

REFERENCES CITED

Bhargava, O. P., Donovan, J. F., and Hines, W. G., 1972, Rapid spectrometric determination of arsenic in iron and steel: Anal. Chemistry, v. 44, no. 14, p. 2402–2404.

Bowen, H. J. M., 1967, The determination of antimony, cadmium, cerium, iridium, and silver in biological material by radioactivation: Analyst, v. 92, no. 1091, p. 118–123.

Burbank, W. S., Luedke, R. G., and Ward, F. N., 1972, Arsenic as an indicator element for mineralized volcanic pipes in the Red Mountains area, western San Juan Mountains, Colorado: U.S. Geol. Survey Bull. 1364, 31 p.

Delavault, R. E., and Manson, R. J., 1971, Spectroscopic determination of arsenic in geochemical samples, *in* Geochemical exploration (International Geochemical Exploration Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. v. 11, no. 11, p. 552–553.

Kingsley, G. R., and Schaffert, R. R., 1951, Microdetermination of arsenic and its application to biological material: Anal. Chemistry, v. 23, no. 6, p. 914–919.

Meinke, W. W., 1971, Standard reference materials for clinical measurements: Anal. Chemistry, v. 43, no. 6, p. 28A–47A.

Sandell, E. B., 1959, Colorimetric determination of traces of metals [3d ed.]: New York, Interscience Publishers, 1032 p.

Warren, H. V., Delavault, R. E., and Barakso, J., 1964, The role of arsenic as a pathfinder in biogeochemical prospecting: Econ. Geology, v. 59, p. 1381–1385.

Warren, H. V., Delavault, R. E., and Cross, C. H., 1967, Some problems in applied geochemistry, *in* Cameron, E. M., ed., Symposium on geochemical prospecting, Ottawa, 1966, Proc. (sponsored by Natl. Advisory Comm. on Research in the Geological Sciences): Canada Geol. Survey Paper 66-54, p. 253–264.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

FLAMELESS ATOMIC ABSORPTION METHOD FOR DETERMINATION OF TRACE AMOUNTS OF MERCURY IN VEGETATION

By JOHN B. MCHUGH and ROBERT L. TURNER

CONTENTS

TABLES

ABSTRACT

Mercury is determined by a flameless atomic absorption procedure on solutions of vegetation which were obtained through digestion with sulfuric acid and hydrogen peroxide under controlled temperature conditions. Mercury is reduced to the elemental state, vaporized, passed through an absorption cell at a controlled rate, and vented.

A detection limit of 25 parts per billion is achieved with good accuracy, and a precision of about 30 percent relative standard deviation. This method can be used to analyze as many as 25 samples per day.

INTRODUCTION

The analysis of vegetation and other organic-rich materials for mercury is useful in biogeochemical exploration, and exploitation of this use demands an analytical method with greater sensitivity than is now available. The length of the method is also a factor—shorter methods usually prove to be more useful. Flameless atomic absorption methods are generally short and provide the needed sensitivity for mercury.

Although plants do not appear to be efficient in concentrating mercury from soils of medium mercury content (50–300 ppb), these same plants do accumulate high concentrations of mercury if their root systems are in contact with cinnabar or soils having a relatively high mercury content. Under these conditions, mineralized areas can be detected by measuring the mercury content of the vegetation (Shacklette, 1970).

A single-extraction colorimetric method for determining mercury in vegetation was devised by Ward and McHugh (1964) and has proven useful in geochemical exploration. About 10 samples could be prepared and analyzed per day with a sensitivity of about 400 ppb. At that time, the speed and sensitivity were adequate, but recent demands for greater speed and sensitivity emphasized the need for a new method. Such demands are met in the atomic absorption methods and especially in those utilizing the flameless measurements; for example, those in which ground-state atoms of the sample are introduced as a vapor and not as a fine dispersion of sample solution. Using the flameless approach, Hatch and Ott (1968) devised the first of several methods which are capable of more than 5 times greater output at increased sensitivities of about 25 ppb. The procedure proposed here differs from that by Hatch and Ott primarily in the aeration of mercury vapor during absorption measurement. Our procedure is a single pass method, whereas the procedure of Hatch and Ott circulates the evolved mercury vapor through a closed system.

A method devised by Vaughn and McCarthy (1964), especially for determining mercury in soils and rocks, is capable of greater output and with increased sensitivity, 10 ppb, but organic material interferes; hence, the method is limited to materials with low organic content and cannot be used for vegetation.

LABORATORY REAGENTS AND APPARATUS

REAGENTS

Standard mercury solution (1,000 μg/ml): Dissolve 0.1354 g of mercuric chloride in 100 ml of 1 *N* sulfuric acid.

Standard mercury solution (100 μg/ml): Dilute 10.0 ml of 0.1 percent mercury solution to 100 ml with 1 *N* sulfuric acid. Prepare fresh monthly.

Standard mercury solution (1 μg/ml): Dilute 1.0 ml of 0.01 percent mercury solution to 100 ml with 1 *N* sulfuric acid. Prepare fresh weekly.

Hydrochloric acid, concentrated, reagent grade.

Hydrogen peroxide, 50 percent, reagent grade.

Hydroxylamine sulfate, reagent grade.

Potassium permanganate solution: Dissolve 5 g of potassium permanganate in 100 ml of demineralized water.

Sodium chloride-hydroxylamine sulfate solution: Dissolve 30 g each of sodium chloride and hydroxylamine sulfate in demineralized water and dilute to 1 litre.

Stannous chloride solution (10 percent): Dissolve 100 g of stannous chloride in 170 ml concentrated hydrochloric acid, dilute to 1 litre with demineralized water.

Sulfuric acid, concentrated, reagent grade.

Sulfuric acid, 1 *N*: Dilute 28 ml of concentrated sulfuric acid to 1 litre with demineralized water.

APPARATUS

Atomic absorption spectrophotometer, Perkin-Elmer, model 403 or equivalent.[1]

Absorption cell, cylindrical cell, 100-mm length, 22-mm O.D., quartz window, inlet and outlet ports to fit Ŧ 7/15 ground-glass joint.

Reaction bottle, B.O.D. bottle, 300-ml capacity, with Coleman model MAS-50 bubbler.

Water bath, Blue M Electric Co., model MW 1110A, 115 v, 50/60 cycle A.C., ambient to 100°C temperature range.

The Perkin-Elmer model 403 atomic absorption spectrophotometer was operated under the following parameters, as suggested for flame atomic absorption method (Perkin-Elmer Corp., 1968):

Wavelength: 2,537A

Slit: 3 (0.3 mm)

Lamp: Mercury hollow cathode run at 10 mA

Air pressure and flow: 20 lb/in^{2}g on incoming line. Air is obtained by disconnecting the nebulizer oxidant tube from the atomic absorption unit and connecting this tube to the reaction bottle. Air flow is set at 1.8 litres/min by adjusting air pressure and flowmeter on the control box.

Absorption cell: The cell is secured to the 4-inch flat-top burner head with two rubber bands. The inlet port is attached to the reaction

---

[1] Use of a specific brand name does not necessarily constitute endorsement of the product by the U.S. Geological Survey.

bottle with Tygon tubing and the exit port vented to the exhaust hood with Tygon tubing.

PROCEDURE

SAMPLE PREPARATION

The freshly collected plants are dried 1 to 2 days at 35°C and ground in a Wiley mill to approximately 2 mm size.

SAMPLE DIGESTION

To a 150-ml beaker containing 2 g of dried and ground vegetation, add 25 ml concentrated sulfuric acid. After the sample is well coated by the acid, add about 30 ml of hydrogen peroxide in small increments, maintaining the temperature below 95°C during the addition. Upon completion of the peroxide addition, place sample in a constant-temperature water bath, set for 95°C, and allow sample to cook for about 6 hours or until elimination of excess peroxide. Remove the sample from the water bath, cool slightly, and test for peroxide elimination by adding 1 drop of potassium permanganate. Brown coloration, possibly accompanied by precipitation of manganese dioxide, indicates incomplete elimination of peroxide; if such occurs, return sample to water bath and continue heating until test shows complete elimination of peroxide. Finally, remove the sample from the water bath, cool slightly, and slowly add 75 ml demineralized water. Cool sample solution to room temperature.

STANDARDS PREPARATION

From the 1-μg/ml mercury standard, pipet 0, 0.1, 0.5, 1.0, and 3.0 ml into a series of 150-ml beakers, each containing 25 ml concentrated sulfuric acid. To each beaker add one drop of hydrogen peroxide. Place the standards in the constant-temperature water bath for 30 minutes at 95°C. Remove the standards from the water bath, cool slightly, and slowly add 74 ml of demineralized water. Proceed with estimation of mercury.

ESTIMATION OF MERCURY

Estimation of mercury is the same for standards and samples.

To the cooled solutions, add potassium permanganate solution, stirring until a pink coloration persists. Add 20 ml sodium chloride-hydroxylamine sulfate solution to each. Pour the solution into the reaction bottle, add 10 ml stannous chloride solution, mix well, and attach the aerator. Begin the aeration of the solution using the air-pressure tube from the atomic absorption instrument. Maximum absorption values are recorded for both standards and samples. The preparation and estimation of standards and samples should be done on the same day.

DISCUSSION OF PROCEDURE

The rate of air flow through the reaction system must be known and calibrated on a particular unit and must be maintained at a constant rate for all standards and samples. The air-flow rate for the system in this experiment which produced a maximum absorbance is 1.8 l/min. A faster air-flow rate produces a lower absorbance because the mercury vapor passed through the absorption cell too fast for the meter to respond properly. A slower air-flow rate produces a dilution of the mercury vapor by pushing smaller portions of vapor per unit of time through the absorption cell. The slower rate produces a lower maximum reading. Note that the data in table 5 are unique for this particular system and will vary due to the total free air volume of the system.

TABLE 5.—*Absorbance obtained with known amounts of mercury*

Mercury (μg)	*Absorbance*
0.0	0.006
.1	.023
.2	.044
.5	.097
1.0	.183
2.0	.350
3.0	.500

The temperature of standard and sample solutions must be maintained at 95°C during digestion. Experiments were run with standard solutions digested at temperatures ranging from 80° to 145°C. At 145°C, 70 percent of the mercury was lost. At 125°C, 50 percent of the mercury was lost. At 95° and 80°C there was no detectable mercury loss. Digestion of the samples was slower at 80°C than at 95°C; therefore, the latter temperature was found to be the most advantageous. The samples are heated to 95°C in the water bath after the plant material has been destroyed and are maintained at this temperature for 30 minutes, or until the excess hydrogen peroxide has been broken down.

RESULTS

RECOVERY OF ADDED MERCURY

To test our procedure, a given amount of mercury was added to three different portions of three plant samples, and the portions were analyzed. The results are shown in table 6.

TABLE 6.—*Recovery of added mercury*

[Three determinations on each sample]

Plant Sample No.	Mercury found in plant sample (μg)	Total amount of mercury standard added to plant sample (μg)	Mercury found in plant sample after standard addition (μg)
X-5	0.025	0.10	0.15
NA-5	.55	1.0	1.58
NA-2	1.60	1.0	2.60

PRECISION

The precision of our procedure was found by analyzing 6 samples 5 times each. The results are given in table 7. In the table the data under the column head "absorbance" are given in terms of absorbance units in order to include the less-than values on the last two samples of mesquite and cottonwood. The range in concentration, expressed in parts per million, corresponding to these absorbance values is included in table 4 under the column head "Atomic Absorption Method."

The relative standard deviations ranged from 5.4 to 33.9 percent, and such precision compares favorably with that of an earlier dithizone procedure (Ward and McHugh, 1964).

TABLE 7.—*Precision of determinations*

Sample No	Plant name and location	Absorbance		Relative standard deviation (percent)	Mean (ppm)
		Range	Mean		
NA-1	Chamise, Calif.	0.246-0.317	0.283	9.6	1.4
NA-2	Baccharis, Calif.	.243-0.290	.261	7.8	1.2
NA-3	...do	.474-0.544	.511	5.4	2.9
NA-5	...do	.046-0.086	.065	24.8	.4
X-5	Mesquite, Lebanon Hot Springs Ariz.	.006-0.012	.010	25.0	.025
X-6	Cottonwood, Lebanon Hot Springs, Ariz.	.006-0.017	.014	33.9	.025

ACCURACY

The accuracy of the proposed procedure was tested by comparing the results obtained on four samples with those obtained earlier by the dithizone procedure. The results are given in table 8.

TABLE 8.—*Accuracy comparison*

[Five determinations on each sample]

Sample No.	Plant name	Dithizone method (ppm)		Atomic absorption method (ppm)	
		Range of values	Mean	Range of values	Mean
NA-1	Chamise	1.6-2.2	1.8	1.2-1.6	1.4
NA-2	Baccharis	1.2-1.3	1.2	1.1-1.4	1.2
NA-3	...do	2.3-2.7	2.5	2.7-3.1	2.9
NA-5	...do	.4-0.7	.6	.3-0.5	.4

A range of values obtained on each sample by both procedures is considered to be more meaningful than a single number simply because of the small amounts of mercury present in these materials. Despite the handicap of working with nearly mercury-free samples, the recovery data, the precision data, and the comparison data attest to applicability and usefulness of our procedure.

Although the procedure and equipment described have proved useful in acquiring the sort of data given in this paper, other commercially available equipment, such as the Perkin-Elmer mercury analyzer, is equally useful and, indeed, preferable if available.

REFERENCES CITED

Hatch, R. W., and Ott, W. L., 1968, Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry: Anal. Chemistry, v. 40, no. 14, p. 2085-2087.

Perkin-Elmer Corp., 1968, Analytical methods for atomic absorption spectrophotometry: Norwalk, Conn., Perkin-Elmer Corp., 522 p.

Shacklette, H. T., 1970, Mercury content of plants, *in* Mercury in the environment: U.S. Geol. Survey Prof. Paper 713, p. 35-36.

Vaughn, W. W., and McCarthy, J. H., Jr., 1964, An instrumental technique for the determination of submicrogram concentrations of mercury in soils, rocks, and gas, *in* Geological Survey research 1964: U.S. Geol. Survey Prof. Paper 501-D, p. D123-D127.

Ward, F. N., and McHugh, J. B., 1964, Determination of mercury in vegetation with dithizone—A single extraction procedure, *in* Geological Survey research 1964: U.S. Geol. Survey Prof. Paper 501-D, p. D128-D130.

NEW AND REFINED METHODS OF TRACE ANALYSIS USEFUL IN GEOCHEMICAL EXPLORATION

ATOMIC ABSORPTION DETERMINATION OF MOLYBDENUM IN PLANT ASH

By H. M. NAKAGAWA, J. R. WATTERSON, and F. N. WARD

CONTENTS

TABLES

ABSTRACT

Trace amounts of molybdenum in plant ash are determined by atomic absorption spectrometry after sample breakdown with hot hydrochloric acid. The molybdenum is extracted into MIBK (4-methyl-2-pentanone) and atomized into a nitrous oxide-acetylene flame. With a threefold scale expansion and a limited volume of extractant, as little as 0.1 part per million of molybdenum in the ash can be measured with relative standard deviations of 5–10 percent. Such sensitivity is comparable to that of existing colorimetric procedures, and this feature plus the attainable speed and simplicity of the method commends the atomic absorption method to widespread application in biogeochemical prospecting.

INTRODUCTION

During the last decade or two Warren and Delavault (1965) in Canada, and Kovalevskii (1969) and Malyuga (1958) in the U.S.S.R., and perhaps others, have established the usefulness of the molybdenum content of vegetation as a diagnostic parameter in biogeochemical exploration. Trees and smaller plants take up varying amounts of molybdenum depending on several factors which include species, soil conditions, and availability of molybdenum to plant roots, for example, from molybdenum-bearing bedrock and outcrops.

Because the molybdenum content of trees and plants is small, it is moderately difficult to measure. Initially, such amounts were measured in the plant ash by optical emission spectrographic methods requiring precision instruments and skilled analysts, which, in turn, limited the analytical output and hindered widespread application to biogeochemical prospecting. In time, colorimetric procedures, simpler methods of analysis based on the reaction of molybdenum with a color-forming reagent—both inorganic and organic—were developed to supplement the optical emission methods (Reichen and Ward, 1951; Stanton and Harwick, 1967).

The availability and dependability of both types of determinations of molybdenum in plant ash provided a choice for the prospector who depended chiefly on knowledge gained by experience. For example, the optical emission methods were used by Brooks and Lyon (1966) to determine molybdenum in plant ash, and these methods seem to be preferred by most Soviet workers; a colorimetric procedure, however, was used by Griffitts and Ward (1970) when the analyses had to be made in the field.

Colorimetric and optical emission methods of determination of molybdenum in plant ash have generally proved adequate for the problems at hand. Gradually, these procedures are being replaced with atomic absorption methods in geochemical and biogeochemical exploration for elements, such as copper, zinc, and manganese. This trend has not been so pronounced for molybdenum, partly because of the relatively poor sensitivity of molybdenum in an air-acetylene flame. David (1961) achieved a sensitivity of 3 μg/ml of molybdenum for 1 percent absorption using a fuel-rich air-acetylene flame. Later, Mostyn and Cunningham (1967) attained a sensitivity of slightly more than 1 ppm for 1 percent absorption.

The luminosity of the fuel-rich flame produces a high background radiation that affects the responsive surface of the photomultiplier cathode and causes operator fatigue (Kirkbright, Peters, and West, 1966; Kirkbright, Smith and West, 1966). The latter workers adopted a suggestion of Willis (1965) and used a nitrous oxide-acetylene flame that not only provided better sensitivity but exhibited fewer interferences—notably the depressive effect of phosphate on calcium.

Initially, nitrous oxide-acetylene flames showed a tendency to frequent flashbacks. Most instrument manufacturers have now developed means to minimize the danger of flashbacks. Because of this improvement in technology, chemists are less reluctant to use nitrous oxide-acetylene flames for refractory elements, such as molybdenum. The nitrous oxide-acetylene flame has the advantage of a higher temperature than air-acetylene without the greater flame velocity of oxyacetylene flames.

Our atomic absorption procedure is potentially a good replacement for the existing colorimetric method because of its suitability to larger batch-type operations and because of the achievable sensitivities.

Analysts in our laboratory use a nitrous oxide-acetylene flame and a threefold scale expansion. They routinely achieve a sensitivity of about 0.05 μg of molybdenum for 1 percent absorption, with minimum effort to optimize the atomic absorption measurement. With a 1-g sample of plant ash and 5 ml of MIBK as suggested in our procedure, the conversion factor is 5, and as little as 0.25 ppm molybdenum in plant ash can be determined. If the molybdenum is extracted into 2 ml of MIBK, which is about the minimum volume needed for measurement, as little as 0.1 ppm molybdenum in the ash can be determined.

REAGENTS AND APPARATUS

Molybdenum standard solution, 100 ppm. Prepare by dissolving 0.075 g pure molybdic anhydride in 10 ml of 1 *M* sodium hydroxide, dilute with water, add 1 *M* hydrochloric acid drop by drop until solution is slightly acid, then dilute to 500 ml with 6 *M* hydrochloric acid.

Molybdenum standard solution, 10 ppm. Prepare by diluting 10 ml of the 100-ppm standard to 100 ml with 6 *M* hydrochloric acid.

Molybdenum standard solution, 1 ppm. Prepare by diluting 10 ml of the 10-ppm standard to 100 ml with 6 *M* hydrochloric acid.

Hydrochloric acid, concentrated.

Hydrochloric acid, 6 *M*. Mix equal volumes of concentrated acid and demineralized water.

Sodium hydroxide, 1 *M*. Prepare by dissolving 4 g of reagent in 100 ml of demineralized water.

MIBK, reagent grade.

Test tubes, screwcap, 16 by 150 mm.

Hotplate.

Beakers, 50-ml capacity.

Pipets, 5 ml.

Centrifuge—useful but not essential.

Atomic absorption instrument, Perkin-Elmer model 303 or equivalent.

WORKING STANDARD SOLUTIONS

1. Using 100-ppm molybdenum solution, pipet 0.5-, 0.25-, and 0.1-ml aliquots into 16- by 150-mm screwcap tubes each containing 10

ml of 6 *M* hydrochloric acid. Add 5 ml MIBK, cap and shake tube for 1 minute. Allow phases to separate and atomize upper layers of each tube to calibrate instrument. Upper layer in each tube contains, respectively, 10, 5, and 2 ppm molybdenum.

2. Using 10-ppm molybdenum solution, pipet 0.5-, 0.25-, and 0.1-ml aliquots into 16- by 150-mm screwcap tubes each containing 10 ml 6 *M* hydrochloric acid and proceed as in solution 1. Upper layers contain respectively 1, 0.5, and 0.2 ppm molybdenum.
3. Using 1-ppm molybdenum solution, pipet 0.5-, 0.25-, and 0.1- ml aliquots into 16- by 150-mm screwcap tubes each containing 10 ml 6 *M* hydrochloric acid and proceed as in solution 1. Upper layers contain, respectively, 0.1, 0.05, and 0.02 ppm molybdenum.

OPTIMUM WORKING RANGE

1×—0.2–10 ppm.
3×—0.02–1 ppm.

OPERATING CONDITIONS

Wavelength: 313. 3 nm.
Source: HC.
Lamp Current: 30 mA.
Slit: 4 (0.7 nm).
Flame: Nitrous oxide-acetylene, reducing (rich red).

PROCEDURE

1. Place a weighed sample up to 1.0 g in a 50-ml beaker and add 3 ml concentrated hydrochloric acid. Place beaker on hotplate and at moderate heat evaporate concentrated acid to dryness.
2. Remove beaker from hotplate, cool, and add 5 ml of 6 *M* hydrochloric acid. Return beaker to hotplate and warm for few minutes.
3. Transfer contents of beaker to a 16- by 150-mm screwcap tube and wash beaker with 5 ml of 6 *M* hydrochloric acid. Add wash acid to the tube.
4. Add 5 ml MIBK to tube, cap, and shake tube for 1 minute.
5. Let tube stand or centrifuge to separate the phases. Aspirate the clear upper layer into a nitrous oxide-acetylene flame of an atomic absorption instrument.
6. Measure the molybdenum concentration after calibration of the instrument with working standard solutions and observing the recommended operating parameters.

RESULTS

Under the conditions in our laboratory we measured absorbances, as shown in table 9. These values are indicative of the sensitivity achieved

TABLE 9.—*Absorbance of standard molybdenum solutions*
[Leaders (...) indicate measurement not made]

Molybdenum content (μg/ml)	Scale expansion	
	None	Threefold
0.02	...	0.0015
.05	...	.0029
.1	0.0044	.0058
.2	.0088	.0107
.5	.0223	.0252
1.	.0419	.0480
2.	.0851	...
5.	.2048	...
10.	.3979	...

in a routine situation, but under different conditions the actual sensitivities achieved will differ slightly.

The precision of our procedure was established by repeat determinations of molybdenum in the ash of fir, alfalfa, and desertholly (table 10). Generally, the relative standard deviations are in the order of 5–10 percent. The value on sample CR-9 probably results from fortuitous circumstances and does not seem to signify a trend to lower relative standard deviations with higher levels of molybdenum.

TABLE 10.—*Repeatability of molybdenum determinations in ash of trees and plants*

Sample No.	Name	Molybdenum (ppm)				
		Low	High	Mean	Standard deviation	Relative standard deviation, (percent)
CRT-48	Fir	0.50	0.65	0.60	0.05	8.3
A-4	Alfalfa	3.6	5.0	4.2	.4	9.5
A-2	...do	19	23	20.7	1.4	6.8
A-3	...do	23	26	24.5	1.2	4.9
A-1	...do	35	39	36.2	1.5	4.1
A-5	...do	45	51	48.2	2.8	5.8
CR-9	Fir	125	130	128	2.7	2.1
P-26	Desertholly	250	300	270	19.2	7.1

The accuracy and validity of this atomic absorption method were established by comparing the results with those obtained earlier by colorimetric and spectrographic methods, as shown in tables 11 and 12. The colorimetric procedures differ primarily in the method of sample attack (methods are described in the footnotes of the tables). The validity, sensitivity, and production potential of this procedure are characteristics that suggest its use in a service function, where results are the chief objective and methods development is of secondary consideration.

TABLE 11.—*Molybdenum in plant ash, Death Valley, Calif.*

Sample No	Name	Molybdenum (ppm)		
		Emission spectrographic method[1]	Colorimetric method[2]	Atomic absorption (this paper)
P-1	Desertholly	5	6	5
P-3	Rush	5	4	2
P-7	Pickleweed	5	6	4
P-9	Desertholly	7	8	6
P-12	Saccatone grass	7	16	10
P-17	Pygmy cedar	10	12	8
P-6	Salt grass	20	16	18
P-11	Arrowweed	20	24	26
P-5	...do	50	32	25
P-4	Mesquite	50	48	32

[1] Analyses made in 1961 by Uteana Oda.

[2] Analyses made by colorimetric method in 1961 by H. M. Nakagawa using a lithium nitrate fusion of plant ash, followed by solution in hot dilute hydrochloric acid.

TABLE 12.—*Molybdenum in plant ash, Catheart Mountain, Maine*

Sample No.	Molybdenum (ppm)		
	Colorimetric method[1]	Colorimetric method[2]	Atomic absorption (this paper)
	Fir		
CRT-47	...	3	< 0.4
CR-12	4	5	4
CR-11	8	8	4
CR-10	60	60	58
CRT-28	...	120	113
CR-9	140	150	130
CRT-39	...	150	175
CR-8	200	230	200
CR-7	240	230	240
	Spruce		
CR-6	20	10	6
CRT-29	...	15	15
CR-5	20	20	20
CRT-31	...	40	48
CRT-37	...	150	160
CR-19	4	5	2.2

[1] Hot hydrochloric acid digestion of samples; analyses made in 1968 by C. S. E. Papp.

[2] Bisulfate fusion of samples; analyses made in 1970 by G. A. Nowlan.

REFERENCES CITED

Brooks, R. R., and Lyon, G. L., 1966, Biogeochemical prospecting for molybdenum in New Zealand: New Zealand Jour. Sci., v. 9, no. 3, p. 706–718.

David, D. J., 1961, The determination of molybdenum by atomic-absorption spectrophotometry: Analyst, v. 86, p. 730–740.

Griffitts, W. R., and Ward, F. N., 1970, Observations on the geochemistry of molybdenum at Eagle Mountain, Guyana, *in* Geochemical prospecting methods and techniques seminar, 2d, 1970, Proc., Mineral Resources Development Ser. 38, Economic Commission for Asia and the Far East: United Nations [N.Y.], p. 166–169.

Kirkbright, G. F., Peters, M. K., and West, T. S., 1966, Determination of small amounts of molybdenum in niobium and tantalum by atomic-absorption spectroscopy in a nitrous oxide-acetylene flame: Analyst, v. 91, p. 705–708.

Kirkbright, G. F., Smith, A. M., and West, T. S., 1966, Rapid determination of molybdenum in alloy steels by atomic-absorption spectroscopy in a nitrous oxide-acetylene flame: Analyst, v. 91, p. 700–704.

Kovalevskii, A. L., 1969, Biogeochemical prospecting for molybdenum [in Russian]: Geol. Geofiz., no. 9, p. 124–126.

Malyuga, D. P., 1958, An experiment in biogeochemical prospecting for molybdenum in Armenia: Geochemistry, no. 3, p. 314–337.

Mostyn, R. A., and Cunningham, A. F., 1967, Determination of antimony by atomic-absorption spectrometry: Anal. Chemistry, v. 39, no. 4, p. 433–435.

Reichen, L. E., and Ward, F. N., 1951, Field method for the determination of molybdenum in plants: U.S. Geol. Survey Circ. 124, 4 p.

Stanton, R. E., and Harwick, A. J., 1967, Colorimetric determination of molybdenum in soils and sediments by zinc dithiol: Analyst, v. 92, p. 387–390.

Warren, H. V., and Delavault, R. E., 1965, Further studies of the biogeochemistry of molybdenum: Western Miner, v. 38, no. 10, p. 64–72.

Willis, J. B., 1965, Nitrous oxide-acetylene flame in atomic-absorption spectroscopy: Nature, v. 207, p. 715–716.