New and Refined Methods of Trace Analysis Useful in Geochemical Exploration
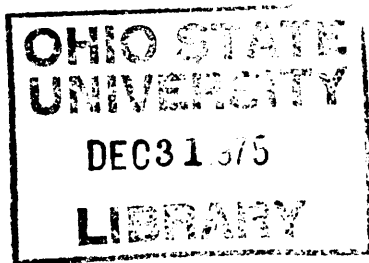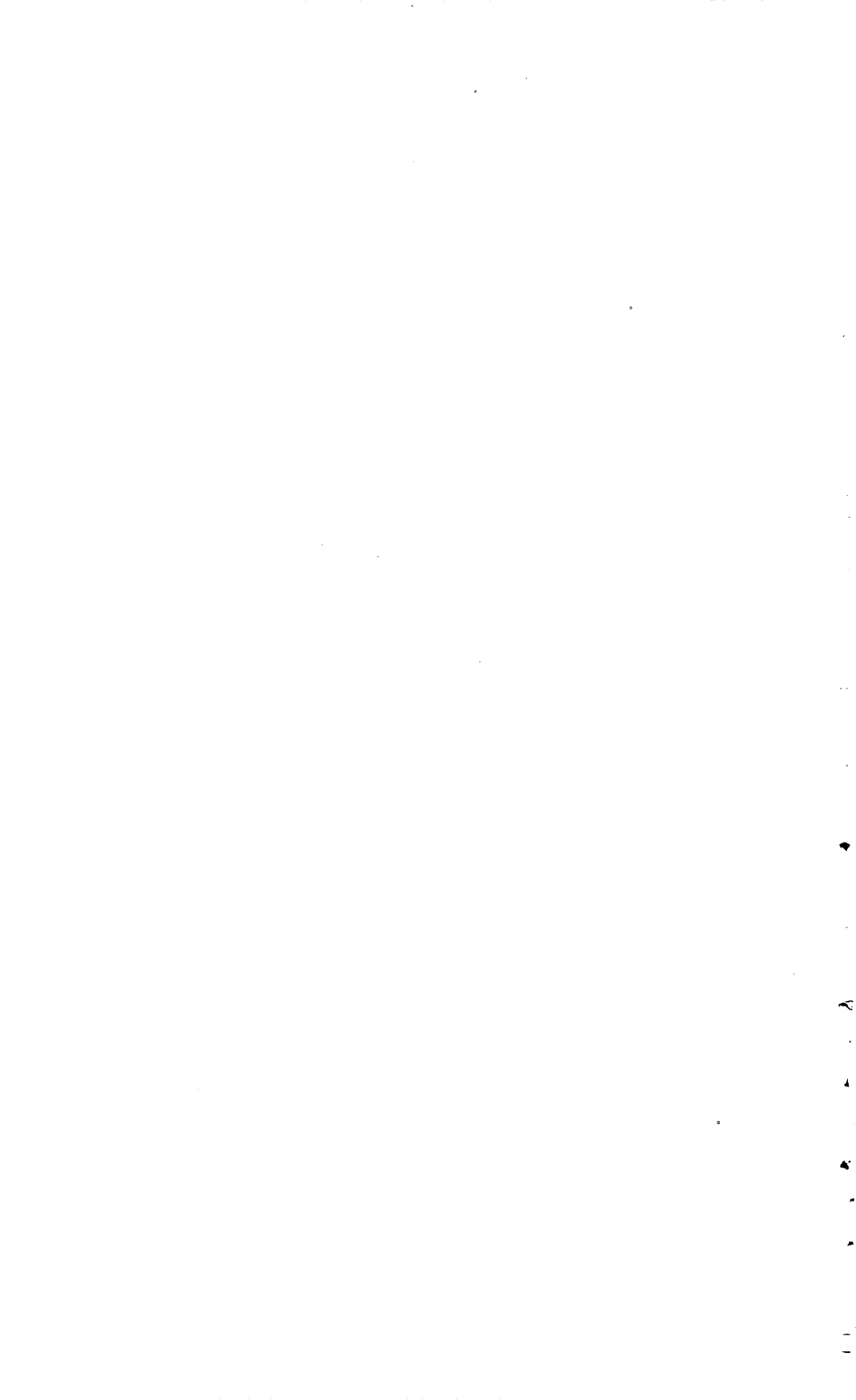
GEOLOGICAL SURVEY BULLETIN 1408

New and Refined Methods

of Trace Analysis Useful in

Geochemical Exploration

F. N. Ward, *Editor*

A collection of methods additional to
those presented earlier in U.S. Geological
Survey Bulletins 1152 and 1289

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

V. E. McKelvey, *Director*

CONTENTS

ABBREVIATIONS

A	ampere (A is closed up to its value, such as 2,176A).
A	angstrom (A is separated by a space from its value, such as 372 A).
A/min..........	angstroms per minute.
a.c.	alternating current.
A.C.S.	American Chemical Society—A measure of purity of reagent; purity equals or exceeds that specified by a Committee of the American Chemical Society.
APDC..........	ammonium 1-pyrrolidine dithiocarbamate.
APDC/MIBK	ammonium 1-pyrrolidine dithiocarbamate–methyl isobutyl ketone.
γ	activity coefficient.
B.O.D.	Biochemical Oxygen Demand.
°C.................	degree Celsius.
cm...............	centimetre.
cm^3..............	cubic centimetre.
cm^3/min	cubic centimetres per minute.
DAB.............	diaminobenzidine.
DADC..........	diethylammonium diethyldithiocarbamic acid.

DADC/MIBK diethylammonium diethyldithiocarbamic acid–methyl isobutyl ketone.
DAN .... diaminonaphthalene.
d.c. .... direct current.
g.................... gram.
> .... greater than.
HC............... hollow cathode lamp.
< .... less than.
l.................... litre.
l/min .... litres per minute.
lb/in^{2}g .... pounds per square inch, gage.
pH .... measure of hydrogen ion activity.
μg............... microgram.
μg/g .... micrograms per gram.
μg/l .... micrograms per litre.
μg/ml......... micrograms per millilitre.
μm............... micrometre.
mA............... milliampere.
mg .... milligram.
MIBK........... methyl isobutyl ketone, the common name for 4-methyl-2-pentanone.
ml .... millilitre.
mm .... millimetre.
mv................ millivolt.
M .... molar; a molar solution contains one gram mole of solute in 1,000 ml of solution. Except for common acids and bases, the units of concentration are expressed as weight/volume in which a given weight of the reagent is dissolved in a specified volume of water or other solvent.
ng .... nanogram $= 1 \times 10^{-9}$ gram.
ng/ml .... nanograms per millilitre.
nm .... nanometre $= 1 \times 10^{-9}$ metre.
N.................. normal; a normal solution contains one equivalent weight of solute in 1 litre of solution. One equivalent weight is that number of grams that react with 1.008 grams of hydrogen.
IX .... one times—refers to scale expansion in atomic absorption procedures.
O.D.............. outside diameter.
ppb.............. parts per billion = 1 part in 10^9 parts.
ppm............. parts per million = 1 part in 10^6 parts = micrograms per gram or micrograms per millilitre for most aqueous solutions.
r/min........... revolutions per minute.
$\bar{\$}$ .... standard taper.
TISAB .... total ionic strength adjustment buffer.
v.................... volt.

NEW AND REFINED METHODS OF TRACE ANALYSIS USEFUL IN GEOCHEMICAL EXPLORATION

INTRODUCTION

By F. N. WARD

This bulletin is composed of 11 short papers which describe one or more methods developed during the last 5 years and found useful by the U.S. Geological Survey for determining trace amounts of 14 elements in geologic materials, including soils, rocks, brines, and vegetation. The elements are antimony, arsenic, bismuth, cadmium, cobalt, copper, fluorine, lead, mercury, molybdenum, nickel, selenium, silver, and zinc. As with methods given in previous publications in this series (Ward and others, 1963; Ward and others, 1969), these methods either have been adapted from existing procedures or have been developed in the U.S. Geological Survey laboratories to increase the analytical capacity of the Survey in its continuing effort to develop means of identifying both large and small exploration targets composed of different minerals that have economic potential and that are commonly concealed or buried beneath the present surface.

Some of the methods have been modified for specific applications; for example, the method described by Nakagawa was developed to measure trace amounts of eight elements in a single solution of magnetite or of a plant ash. Other methods illustrate applications of existing methods to different sample media—for example, the analysis of vegetation by atomic absorption techniques. A few of the methods are the products of original research—for example, the atomic absorption determination of bismuth, cadmium, and lead in vegetation after oxygen flask combustion. None of the methods should be considered as final; all are subject to improvement to obtain better sensitivity, to achieve a greater degree of freedom from interferences, and to permit application to different types of geologic materials.

With the exception of the spectrographic method described by Mosier, all these methods feature a sample breakup—partial in some procedures—by hot acid digestion, oxygen flask combustion, or fusion with appropriate fluxes, followed by solvent extraction, complexation, or distillation to achieve separation and enrichment of the desired element

in a uniform matrix amenable to atomic absorption or other techniques of measurement.

A few of the methods terminate with a colorimetric measurement, which may appear to relegate the procedures to some form of alchemy, especially in view of the pronounced trend toward instrumental analysis since about 1960. The justification for these procedures, if such is required, is simply that, despite the fast communication and rapid transportation of the day, many exploration groups do not have sophisticated instruments nor do they wish to buy the skill needed to maintain such instruments. On the other hand, several methods described in this bulletin terminate with an atomic absorption measurement. They are obviously useful only to groups having such instruments. Of the methods based on atomic absorption spectrometry, both flame and flameless procedures are described. The two flameless methods given for mercury illustrate the advantage of allowing two different research groups to attack the same problem concomitantly.

Methods of chemical analysis for trace elements based on fluorescence generally have not been well received by geochemists. Perhaps the lack of popularity arises from a combination of the peculiar skill needed by the analyst for successful application of fluorescence to geochemical exploration, the cost of instrumentation usually considered to be necessary, and the lengthy preparations involved in making fluorescence measurements. Despite these limitations, the advantages of greater sensitivity and selectivity often predominate, as is true for the selenium method described by Harms and Ward. In fact, that method for determining selenium has no peer, except for the procedures requiring activation or possibly spark-source mass spectrography facilities.

The use of selective-ion electrodes to measure trace amounts of ions in solution is relatively new, and the simplicity of the procedure is deceiving with respect to the complex phenomena represented. The measurement is made by immersing the selective-ion electrode in a solution and reading the potential developed against a reference electrode. In short, the detection of a given ion is as simple as a pH measurement. Explanation of the complex phenomena, as well as the technology involved in the development of sensors in the ion-selective electrodes, is beyond the scope of this bulletin, but it will be enough to say that the electrode senses the activity of a particular ion in a selective manner—similar to the way a thin glass membrane senses the activity of hydrogen ions. Pure, or properly "doped" crystals of rare earths are one class of sensors, and they act the same as the glass membrane by selectively allowing certain ions to behave as if they were passing through the crystal and developing a potential. The kind of crystal and doping govern the selectivity. Of more than a dozen selective-ion electrodes available today, the fluoride electrode is perhaps the most widely used. It consists of a crystal of pure lanthanum fluoride sealed in an inert epoxy tube and

connected through an internal solution to a lead wire terminating in a suitable plug (Ross, 1969). Crenshaw and Ward describe a method for determining fluorine in soils and rocks, using such an electrode to sense the change in potential caused by a known-increment addition step.

The papers in this report were selected by the editor on the basis of improvements made in a given procedure, hints and helps to promote the usefulness of a method, and demand for, and interest in, an analytical procedure by the exploration geochemist. Each paper includes a description of the method, a list of reagents and apparatus necessary for the procedure, analytical data, and appropriate documentation. The information presented in this bulletin reflects the thrust of recent research in new methodology by the U.S. Geological Survey in the field of geochemical and biogeochemical exploration.

REFERENCES CITED

Ross, J. W., Jr., 1969, Solid-state and liquid membrane ion-selective electrodes, *in* Ion-selective electrodes: [U.S.] Natl. Bur. Standards Spec. Pub. 314, p. 57–88.

Ward, F. N., Lakin, H. W., Canney, F. C., and others, 1963, Analytical methods used in geochemical exploration by the U.S. Geological Survey: U.S. Geol. Survey Bull. 1152, 100 p.

Ward, F. N., Nakagawa, H. M., Harms, T. F., and VanSickle, G. H., 1969, Atomic-absorption methods of analysis useful in geochemical exploration: U.S. Geol. Survey Bull. 1289, 45 p.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

ATOMIC ABSORPTION DETERMINATION OF ANTIMONY IN GEOLOGIC MATERIALS

By JOHN B. McHUGH and ERIC P. WELSCH

CONTENTS

TABLES

ABSTRACT

Antimony in soils and rocks is solubilized by fusing the sample with potassium pyrosulfate and digesting the melt from the fusion with $8 N$ hydrochloric acid. The antimony is then extracted into MIBK (methyl isobutyl ketone, which is the common name for 4-methyl-2-pentanone) and determined by atomic absorption spectrophotometry. As little as 1 ppm antimony can be detected in the sample, with a precision and accuracy comparable to that of the rhodamine B colorimetric method.

5

INTRODUCTION

Trace amounts of antimony along with other volatile elements commonly occur as halos around base-metal deposits, and the determination of these trace amounts of antimony can be a useful tool in the search for such deposits, especially where they are hidden by residual or transported materials. For example, Erickson and others (1966) showed that antimony is present in the suite of elements associated with the Carlintype gold deposits of Nevada. The determination of small amounts of antimony in overlying soils elsewhere may provide a clue to the presence of similar deposits.

The rhodamine B colorimetric method (Ward and others, 1963) is now used by the U.S. Geological Survey to determine antimony. However, because atomic absorption spectrophotometry is widely used and measurements with this equipment are generally fast, simple, relatively accurate, and free of interferences, it seemed reasonable to apply atomic absorption measurement to antimony. The Perkin-Elmer analytical methods manual (1968) described an atomic absorption procedure for determining as little as 0.1 μg/ml antimony in aqueous solution. By combining the colorimetric sample preparation procedure with atomic absorption, a procedure was developed for analyzing 100 samples per day as compared with 40 samples by the older colorimetric method.

Briefly, the method consists of sample decomposition by fusion with potassium pyrosulfate, digestion in 8 N hydrochloric acid, oxidation of the dissolved antimony to the pentavalent state with ceric sulfate, extraction of the antimony with MIBK, and atomization of the extract in the flame of an atomic absorption spectrophotometer.

LABORATORY REAGENTS AND APPARATUS

REAGENTS

Standard antimony solution (0.1 percent): Dissolve exactly 1.370 g of potassium antimony tartrate in 6 N hydrochloric acid, dilute to 500 ml with 6 N hydrochloric acid.

Dilute standard antimony solution (0.01 percent): Dilute 10.0 ml of 0.1 percent standard antimony solution to 100 ml with 6 N hydrochloric acid.

Dilute standard antimony solution (0.001 percent): Dilute 10.0 ml of 0.01 percent standard antimony solution to 100 ml with 6 N hydrochloric acid.

Ceric sulfate solution: Dissolve 52 g ceric sulfate ($H_4Ce(SO_4)_4$) in 1litre of demineralized water containing 30 ml of concentrated sulfuric acid.

Hydrochloric acid, concentrated, reagent grade.

Hydrochloric acid, 6 N: Dilute 500 ml concentrated hydrochloric acid to 1 litre with demineralized water.

Hydrochloric acid, 8 *N:* Dilute 660 ml concentrated hydrochloric acid to 1 litre with demineralized water.

MIBK, reagent grade.

Potassium pyrosulfate, powder, reagent grade.

APPARATUS

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

Centrifuge, International, Size 2, model K, or other centrifuge of similar performance capable of 1,200 to 8,500 r/min and centrifugal force of 380 to 4,400 times gravity.

Culture tube, screwcap, 16 by 150 mm.

Culture tube, screwcap, 25 by 150 mm.

Fusion rack (Marranzino and Wood, 1956), consisting of a rotating disk to which as many as 11 tubes can be clipped and their contents fused as they pass over a group of Bunsen burners.

PROCEDURE

SAMPLE PREPARATION

Weigh 0.25 g of < 80-mesh sample of rock or soil and place in a 16–by 150–mm screwcap culture tube. Add about 1.0 g of potassium pyrosulfate and mix thoroughly. A 1-g scoop can be devised to expedite this addition. Fuse by hand over a Bunsen burner or on a specially designed fusion rack (Marranzino and Wood, 1956) until the sample is completely attacked by the flux. Remove the tube from the heat and rotate it so that the melt will cool in a thin film on the walls of the tube. Add 6 ml of 8 *N* hydrochloric acid to the sample tube and place the tube in a boiling water bath until the melt is dissolved. Do not boil the sample solution. Remove the tube from the water bath and allow to cool. Add 0.5 ml ceric sulfate solution and mix. Add 2 ml MIBK, cap the tube, and shake vigorously for 1 minute. Centrifuge the sample for 5 minutes at 1,500 r/min to facilitate MIBK recovery and to insure a clean organic layer. Determine the antimony content by aspirating the MIBK layer in the flame of an atomic absorption spectrophotometer. Samples must be aspirated within 1 day after extraction.

STANDARD PREPARATION AND INSTRUMENT CALIBRATION

Prepare the standards in the same manner as the samples but in sufficient volume for instrument calibration. The potassium pyrosulfate fusion is deleted from the standards for the sake of expediency. No difference has been noticed in the resulting standards due to this deletion.

---

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

Add 30 ml 8 *N* hydrochloric acid to each of four 25- by 150-mm screw-cap culture tubes. Add 0.2 ml and 1.0 ml of the 0.001 percent antimony standard to the first two tubes. Add 0.5 ml and 1.0 ml of the 0.01 percent antimony standard to the last two tubes. Add 0.5 ml of the ceric sulfate solution to each of the four tubes and mix. Add 10.0 ml of MIBK and shake standards vigorously for 1 minute. Centrifuge the standards for 5 minutes at 1,500 r/min to facilitate phase separation. These standards contain 0.2, 1, 5, and 10   g antimony per millilitre, respectively, and are stable for 1 day.

Preparation of the blank requires less adherence to the sample preparation procedure. MIBK washed with a small amount of 8 *N* hydrochloric acid provides an adequate blank once the reagent purity has been established. The acid phase may be discarded upon completion of the wash.

The Perkin-Elmer model 403 spectrophotometer was operated under the following parameters:

Wavelength: 2,176A.

Slit: 3 (0.3 mm).

Lamp: Antimony hollow cathode run at 20 mA.

Air pressure: 50 lb/in²g on incoming line, 30 lb/in²g on control box, flowmeter setting 46.

Fuel pressure: Acetylene pressure 12 lb/in²g on gage, 8 lb/in²g on control box, flowmeter setting 18.

Burner: Three-slot (Boling).

Aspiration of the MIBK standard solutions under the preceding parameters produced the following values:

Micrograms Sb/ml MIBK	*Absorbance*
0.2	0.010
1.0	.038
5.0	.166
10.0	.340

DISCUSSION

Selecting the proper agent for adequate decomposition of the sample was the first problem in developing a suitable method. Fusion with sodium carbonate or digestion with hydrofluoric acid is unduly vigorous for all but a few rare antimony minerals. Sulfuric and nitric acids oxidize the MIBK; boiling in hydrochloric acid and aqua regia results in volatilization of antimony chloride. Potassium pyrosulfate was chosen as an agent for sample decomposition because of its ability to break down sulfides and oxides readily without the above problems. Most antimony minerals will decompose and go into solution when fused with potassium pyrosulfate and taken up with 8 *N* hydrochloric acid (Dolezal and others, 1968; Rankama and Sahama, 1950).

MIBK extracts about 50 percent of antimony (III) from 8 N hydrochloric acid but extracts 95–100 percent of antimony (V). For this reason Ce(IV) is added to oxidize all antimony to the higher valence. From 1 N acid only 25 percent of antimony(V) is extracted, whereas from 8 N acid, virtually all of antimony(V) is extracted.

The method of complexing with ammonium pyrrolidine dithiocarbamate (at ph 3) and extraction with MIBK was also used with good results but was found to be more time consuming than the 8 N hydrochloric acid-ceric sulfate-MIBK method.

Approximately 70 percent of the MIBK is recovered when the following three conditions are met:

Acid temperature of about 25°C.

Ratio of MIBK to acid between 1:2 and 1:3.

Acid concentration of 8 N.

The recovery of MIBK increases with higher temperatures, lower MIBK-to-acid ratio, and lower acid concentrations. Because 100 percent of the antimony is extracted into the recovered MIBK, it is essential that the preceding conditions are constant for samples and standards.

The MIBK layer should not be allowed to stand over the acid for more than a day because 8 N hydrochloric acid will eventually react with, and become miscible with, the MIBK.

The presence of any aqueous phase in the atomic absorption spectrophotometer system will yield erroneously high values. To prevent this error, centrifuge the samples and standards prior to aspiration. At the same time, rinse the burner assembly and drain line with MIBK and aspirate MIBK for 5 minutes before aspirating the samples.

INTERFERENCES

Mostyn and Cunningham (1967) found no significant interference from 16 common metals on antimony absorption.

PRECISION AND ACCURACY

The precision, or repeatability, of the atomic absorption and colorimetric procedures was established by determining the antimony contents of five replicates of seven samples (table 1). The precision of the atomic absorption method is within acceptable limits for geochemical exploration studies. Two to eight percent relative standard deviation was obtained, except for one low sample in which the values ranged from 3.2 to 2.4 ppm, giving a relative standard deviation of 16 percent.

The accuracy of the atomic absorption procedure was investigated by comparing the antimony content of 27 samples (table 2) determined by the colorimetric and atomic absorption methods. The accuracy of the atomic absorption method is good, with agreement on all but 3 of the 27 samples compared.

TABLE 1.—*Precision of antimony determinations by atomic absorption procedure and by colorimetric procedure*

[Leaders (....) indicate that values are too low for significance]

Sample No. [1]	Values of 5 replicates (ppm)		Standard deviation (ppm)	Relative standard deviation (percent)
	Range	Mean		
Atomic absorption procedure				
Sb–1	21.6–27.2	24.3	2.09	8.6
Sb–2	12.0–12.6	12.1	.27	2.2
Sb–3	4.8– 5.6	5.4	.31	5.8
Sb–4	4.8– 5.6	5.4	.31	5.8
BCI–436	< 1.0– 1.0	< 1.0	...	...
BCI–438	2.4– 3.2	2.7	.44	16.3
Universal standard-I..........	37.6–42.4	39.9	2.20	5.5
Colorimetric procedure				
Sb–1	15.0–20.0	18.0	1.94	10.7
Sb–2	9.0–10.0	9.5	.50	5.3
Sb–3	2.0– 2.5	2.4	.22	9.3
Sb–4	4.5– 5.0	4.8	.28	5.7
BCI–436	< 1.0– 1.0	< 1.0	...	...
BCI–438	< 1.0– 1.0	< 1.0	...	...
Universal standard–I.........	44.0–47.0	45.4	1.15	2.5

[1] *Material and location*
Sb–1 through Sb–4: Rock from Nevada.
BCI–436, BCI–438: Stream sediment from Maine.
Universal standard–I: Gossan from Colorado.

TABLE 2.—*Antimony content of rock samples from Humboldt County, Nev.*

[Samples supplied by R. L. Erickson, U.S. Geological Survey]

Sample No. (BBG–)	Antimony content (ppm)		Sample No. (BBG–)	Antimony content (ppm)	
	Colorimetric method[1]	Atomic absorption method		Colorimetric method[1]	Atomic absorption method
001	12	6	027	19	16
002	1	2	028	5	6
003	< 1	2	034	3	6
004	< 1	3	039	4	6
005	1	2	048	3	4
009	5	16	049	1	1
018	1	2	050	< 1	1
019	2	4	084	9	6
020	2	3	086	18	13
021	2	5	148	11	12

[1] Analyst, James H. Turner, U.S. Geological Survey, Denver, Colo.

REFERENCES CITED

Dolezal, J., Povondra, P., and Sulcek, Z., 1968, Decomposition techniques in inorganic analysis: New York, Am. Elsevier Publishing Co., 224 p.

Erickson, R. L., VanSickle, G. H., Nakagawa, H. M., McCarthy, J. H., Jr., and Leong, K. W., 1966, Gold geochemical anomaly in the Cortez district, Nevada: U.S. Geol. Survey Circ. 534, 9 p.

Marranzino, A. P., and Wood, W. H., 1956, Multiple-unit fusion rack: Anal. Chemistry, v. 28, No. 2, p. 273-274.

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

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

Rankama, Kalervo, and Sahama, T. G., 1950, Geochemistry: Chicago, Univ. Chicago Press, 912 p.

Ward, F. N., Lakin, H. W., Canney, F. C., and others, 1963, Analytical methods used in geochemical exploration by the U.S. Geological Survey: U.S. Geol. Survey Bull. 1152, p. 38-39.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

DETERMINATION OF ARSENIC
IN VEGETATION

By T. F. HARMS and F. N. WARD

CONTENTS

TABLES

ABSTRACT

Arsenic in vegetation is determined by either of two reactions after either a wet diges-
tion of the sample under reflux with a hot mineral acid mixture or a dry ignition
of the sample with added fixative to minimize loss of arsenic by volatilization. After
sample preparation by one of the procedures, arsenic is separated by distillation, and
the evolved arsine is collected in an iodine solution and subsequently reacted with molyb-
date to form a heteropoly compound, which on reduction forms a blue compound,
or is alternatively reacted with silver diethyldithiocarbamate to form a red-violet com-

pound. Sensitivities of about 0.5–1 part per million are achieved by either method of measurement, and the relative standard deviation is on the order of 10–20 percent.

INTRODUCTION

The usefulness of arsenic as a pathfinder element in the search for concealed ore deposits has long been recognized (Delavault and Manson, 1971). Pathfinder elements are defined as those elements associated with, but more easily determined or identified than, the principal element. The association of arsenic with gold is a good example, and arsenic levels, which are more easily measured than those of gold, can be used to delineate areas of possible gold occurrence.

Using sampling media other than soils and rocks, Warren, Delavault and Barakso (1964) described the pathfinder role of arsenic in biogeochemical prospecting and noted that first-year growth, and twigs considered as second-year growth, of Douglas-fir established in mineralized ground contained more than 2 ppm arsenic in the ash. Later, Warren, Delavault, and Cross (1967) observed even greater enrichment. The ash of Douglas-fir established in a soil over gold-arsenopyrite mineralized ground contained 560 ppm arsenic in contrast to 8 other species whose ash contained less than 4 ppm arsenic. Such enrichment suggests that the tips and twigs of Douglas-fir are useful as a sampling medium to locate exploration targets for arsenic and associated elements, such as gold and, possibly, others.

A slight variation of the pathfinder concept is shown in work by Burbank, Luedke, and Ward (1972), who use arsenic as an indicator element of mineralized volcanic pipes in the western San Juan Mountains, Colo.

In this chapter two methods are given for determining trace amounts of arsenic in air-dried vegetation. After sample preparation by dry ignition or by wet ignition and the distillation of the arsine from the bulk of the sample, the arsenic content is estimated by either one of the following methods:

1. Arsine is collected in an iodine solution which oxidizes the arsenic (III) to arsenic (V) which in turn reacts with ammonium molybdate in acid medium to form the heteropoly molybdiarsenate, which, on subsequent reduction with hydrazine, forms a blue compound of unknown composition.
2. Arsine is reacted with silver diethyldithiocarbamate in pyridine to form a red- to red-violet compound.

The sensitivities achieved by both methods are roughly the same, and the choice of which to use has to be governed by other considerations, such as facilities available and possible interferences. Both methods are adequate to determine anomalous amounts (> 1 ppm) of arsenic in the leaves and twigs of deciduous and evergreen trees, as well as in shrubs, grasses, and other vegetal matter.

DISTRIBUTION OF KNOWN OIL AND GAS
PRODUCTION BY GEOLOGIC AGE

The known cumulative oil production through 1972 in the Appalachian basin, as categorized by geologic age for each respective State and for the total basin, is shown in table 4. The recorded cumulative production for the basin from 1859 through 1972 is approximately 2.523 billion barrels of oil and 362 million barrels of natural gas liquids (a total of 2.885 billion barrels).

Table 5 shows the known cumulative natural gas production through 1972 in the Appalachian basin, categorized by geologic age for each State and for the total basin. The recorded cumulative gas production for the basin from 1882 through 1972 is approximately 31.2 trillion cubic feet.

Three major sources were used for data in these two tables: the American Petroleum Institute (API), the American Association of Petroleum Geologists (AAPG), and the Independent Petroleum Association of America (IPAA).

DISTRIBUTION OF KNOWN RECOVERABLE
RESERVES BY GEOLOGIC AGE

The recoverable oil reserves for the Appalachian basin are based upon estimates from known producing horizons. The recoverable reserves consist of the cumulative oil production through 1972 plus the remaining recoverable reserves (as of January 1973) that are expected
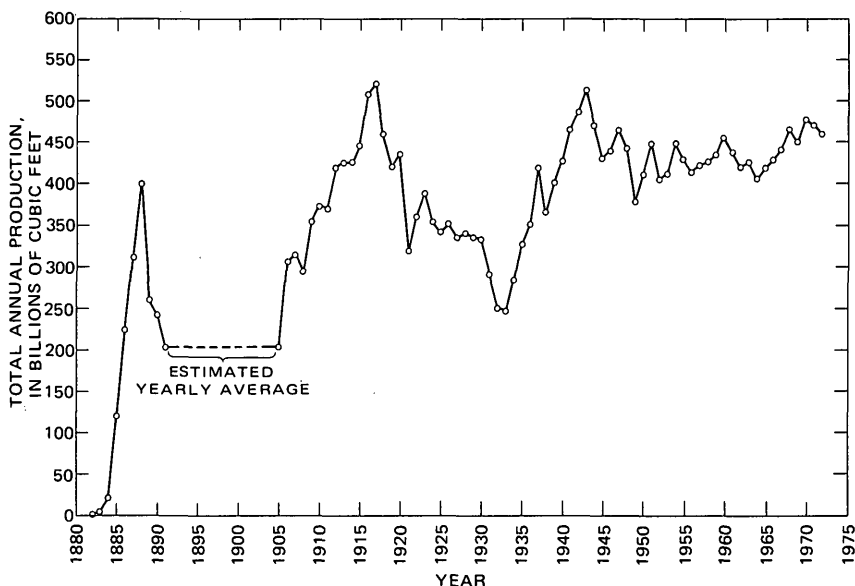

FIGURE 3. — Annual natural gas production for the Appalachian basin, 1882–1972.

TABLE 4. — *Known cumulative oil and natural gas liquids production in the Appalachian basin, 1859–1972, categorized by State and geologic age.*

[Reported in thousands of barrels. Leaders (_ _ _) indicate no record of production]

	Oil production						Total oil production	Total cumulative natural gas liquids production	Total cumulative production of oil and natural gas liquids
	Pennsylvanian	Mississippian	Devonian	Silurian	Ordovician	Cambrian			
Pennsylvania _ _ _ _	1,864	18,967	1,255,472	326	1	_ _	1,276,630	84,770	1,361,400
West Virginia _ _ _	54,829	282,778	170,073	0	_ _	_ _	[2][5]507,680	[1][3]190,285	697,965
Virginia _ _ _ _ _ _	0	0	0	0	281	_ _	[2]281	0	281
New York _ _ _ _ _	0	0	223,842	0	275	[6]80	[1]223,842	0	223,842
Eastern Tennessee _	0	1,527	0	62	275	[6]80	[3][1]1,944	0	1,944
Eastern Kentucky _	4,595	41,629	123,309	18,225	6,932	19	[1]194,709	[1]79,500	274,209
Ohio[4] _ _ _ _ _ _	19,572	25,429	9,536	238,393	6,357	18,570	[3]317,857	[1]7,530	325,387
Total[5]	80,860	370,330	1,782,232	257,006	13,846	18,699	2,522,943	362,085	2,885,028
Percentage of total oil production _ _	3.2050	14.6785	70.6410	10.1868	0.5487	0.7400	100	_ _	_ _

[1] See API references.
[2] See AAPG references.
[3] See IPAA references.
[4] Lima-Trenton production excluded.
[5] No conversions were made from barrels to metric tons in this report due to the variations in the API gravities of the crude oils produced. For example, gravities ranging from 20° to 45° API give a range in conversion from 6.7 barrels per metric ton to 7.85 barrels per metric ton (Zaba and Doherty,1956, p. 685).
[6] Includes some Ordovician.

TABLE 5. — *Known cumulative gas production in the Appalachian basin, 1882–1972, categorized by State and geologic age.*

[Reported in millions of cubic feet].

Geologic age	Pennsylvania	West Virginia	Virginia	New York	Eastern Tennessee	Eastern Kentucky	Ohio[1]	Maryland	Total	Percent of total production
Pennsylvanian _ _ _	173,534	1,416,730	1,150	0	0	100,726	295,390	0	1,987,530	6.3753
Mississippian _ _ _	977,562	7,792,015	53,300	0	2,129	945,077	344,621	0	10,114,704	32.4445
Devonian _ _ _ _ _	7,502,580	4,675,209	2,875	190,630	0	1,540,683	196,927	48,865	14,157,769	45.4132
Early Devonian and Late Silurian _ _ _	0	0	0	0	0	46,038	0	0	46,038	.1477
Silurian _ _ _ _ _	23,690	283,346	172	324,464	164	138,115	3,938,531	0	4,708,318	15.1026
Ordovician _ _ _ _	0	0	0	2,726	0	8,343	61,540	0	72,773	.2334
Cambrian _ _ _ _ _	200	0	0	16	0	1,947	86,155	0	88,318	.2833
Total _ _ _ _ _	[2]8,677,566	[2][3]14,167,300	[2][3]57,497	[2][3]517,836	[4]2,293	[3]2,780,929	[2][3][4]4,923,164	48,865	31,175,450	100.0000

[1] Findlay gas field not included.
[2] See AAPG references.
[3] See API references.
[4] See IPAA references.

to be produced in the future if there are no substantial changes in present economic relationships and known production technology. Table 6 shows the estimated recoverable oil reserves in the Appalachian basin categorized by geologic age for each respective State and for the total basin. The estimated total recoverable oil reserves for the basin are approximately 2.747 billion barrels. Considering the cumulative production of 2.523 billion barrels, only 8 percent of the total known recoverable oil reserves remain to be produced.

Table 7 shows the distribution by State and geologic age of the estimated original oil-in-place in the Appalachian basin. The original oil-in-place figures are taken from API (1973) and are defined (AGA and others, 1973) as follows:

The estimated number of stock tank barrels of crude oil in *known* reservoirs prior to any production is defined as "original oil-in-place." Known reservoirs include (1) those that are currently productive; (2) those to which proved reserves have been credited but from which there has been no production; and (3) those that have been depleted.

The estimation of original oil-in-place is based on calculations using volumetric or material balance methods when sufficient factual data are available concerning reservoir rock, fluid properties, reservoir limits, and production performance. Where such data are not available, or are seriously incomplete, the estimation procedure utilizes information and performance characteristics from reservoirs believed to be comparable.

The estimated total original oil-in-place for the Appalachian basin is approximately 14.249 billion barrels. With an estimated ultimate recovery of 2.747 billion barrels for the basin, this presently constitutes only a 19.3 percent recovery factor for the basin.

The estimated proved natural gas reserves consist of the cumulative natural gas production through 1972 plus the remaining proved reserves as of January 1973. Table 8 shows the estimated proved natural gas reserves for the Appalachian basin, categorized by geologic age for each State and for the total basin. Devonian reservoirs have by far the best gas, as well as oil, reserves known in the basin. With a cumulative gas production of 31.2 trillion cubic feet (table 5) and an estimated proved gas reserve of 36.7 trillion cubic feet, approximately 15 percent of the total known natural gas reserves remain to be produced.

Table 9 shows the estimated recoverable reserves of natural gas liquids for the Appalachian basin for four of the eight States and categorized by geologic age (data from IPAA, 1973). The total reported recoverable reserves of natural gas liquids are 494 million barrels. With a cumulative production of natural gas liquids reported to be 362 million barrels (table 4), 27 percent of the recoverable reserves remain.

DISTRIBUTION OF TOTAL HYDROCARBONS BY GEOLOGIC AGE

One of the methods of evaluating the total hydrocarbons found per cubic mile of sediment within a specific basin is to convert the number of cubic feet of the natural gas reserves to an equivalent in barrels, and to add this equivalent to the total barrels of crude oil reserves plus

TABLE 6. — *Estimated ultimate recoverable oil reserves in the Appalachian basin, categorized by State and geologic age.*

[Reported in thousands of barrels. All values are based upon proved reserves from known reservoirs only]

Geologic age	Pennsylvania	West Virginia	Virginia	New York	Eastern Tennessee	Eastern Kentucky	Ohio[1]	Total	Percent of total reserves
Pennsylvanian	1,918	58,506	0	0	0	4,959	26,728	92,111	3.3533
Mississippian	19,522	301,738	0	0	1,923	44,926	35,619	403,728	14.6976
Devonian	1,292,199	181,476	0	233,088	0	133,076	13,357	1,853,196	67.4649
Silurian	335	0	0	0	77	19,668	333,931	354,011	12.8877
Ordovician	>2	0	299	0	347	7,481	8,905	17,034	.6201
Cambrian	0	0	0	0	[2]100	21	26,702	26,823	.9764
Total	1,313,976	541,720	299	233,088	2,447	210,131	445,242	[3]2,746,903	100.0000

[1]Lima-Trenton production not included.
[2]Includes some Ordovician.
[3]Includes 2,522,943 thousand barrels produced through 1972.

TABLE 7. — *Estimated original oil-in-place in the Appalachian basin, categorized by State and geologic age*

[Reported in thousands of barrels. All values are based upon API figures (1973) and are for proved producing horizons in known reservoirs only]

Geologic age	Pennsylvania	West Virginia	Virginia	New York	Eastern Tennessee	Eastern Kentucky	Ohio[1]	Total	Percent of total oil-in-place
Pennsylvanian	9,646	244,090	0	0	0	15,303	197,888	466,927	3.2791
Mississippian	98,163	1,297,530	0	0	6,409	138,636	263,836	1,804,574	12.6643
Devonian	6,497,666	1,027,746	0	1,116,739	0	410,655	98,939	9,151,745	64.2262
Silurian	1,685	0	0	0	259	60,694	2,473,464	2,536,102	17.7981
Ordovician	7	0	1,424	0	1,156	23,084	65,959	91,630	.6430
Cambrian	0	0	0	0	[2]334	65	197,866	198,285	1.3893
Total	6,607,167	2,569,366	1,424	1,116,739	8,158	648,437	3,297,952	14,249,243	100.0000

[1]Lima-Trenton field not included.
[2]Includes some Ordovician.

TABLE 8. — *Estimated ultimate natural gas reserves in the Appalachian basin, categorized by State and geologic age.*

[Reported in millions of cubic feet. All values are based upon known reservoirs only]

Geologic age	Pennsylvania	West Virginia	Virginia	Maryland	New York	Eastern Tennessee	Eastern Kentucky	Ohio[1]	Total	Percent of total reserves
Pennsylvanian	201,670	1,648,654	1,867	0	0	0	109,375	338,299	2,299,865	6.2621
Mississippian	1,136,061	9,067,597	86,554	0	0	7,329	1,080,263	394,682	11,772,486	32.0542
Devonian	8,719,019	5,440,558	4,669	113,365	241,868	0	2,223,963	225,533	16,968,975	46.2032
Early Devonian and Late Silurian	0	0	0	0	0	0	54,688	0	54,688	.1489
Silurian	27,531	329,731	280	0	411,673	0	164,063	4,510,652	5,443,930	14.8227
Ordovician	0	0	0	0	3,459	564	10,937	70,479	85,439	.2326
Cambrian	232	0	0	0	20	0	2,552	98,670	101,474	.2763
Total	10,084,513	16,486,540	93,370	113,365	657,020	7,893	3,645,841	5,638,315	[2]36,726,857	100.0000

[1]Findlay gas field not included.
[2]Includes 31,175,450 million cubic feet produced through 1972.

TABLE 9. — *Estimated ultimate recoverable reserves of natural gas liquids in the Appalachian basin, categorized by State and geologic age.*

[Reported in thousands of barrels. All values are based upon known reservoirs only. No reserves have been reported for eastern Tennessee or New York]

Geologic age	Pennsylvania	West Virginia	Eastern Kentucky	Ohio	Total	Percent of total reserves
Pennsylvanian	1,710	27,237	3,789	605	33,341	6.7458
Mississippian	9,633	149,803	37,417	706	197,559	39.9725
Devonian	73,927	89,882	77,032	403	241,244	48.8116
Early Devonian and Late Silurian	0	0	1,894	0	1,894	.3833
Silurian	233	5,447	5,683	8,063	19,426	3.9307
Ordovician	0	0	379	126	505	.1021
Cambrian	2	0	88	176	266	.0540
Total	85,505	272,369	126,282	10,079	[1]494,235	100.0000

[1]Includes 362,085 thousand barrels produced through 1972.

reserves in barrels of natural gas liquids. This will give a rough estimate of the total recoverable hydrocarbons in the basin.

Table 10 shows the total recoverable reserves of hydrocarbons (oil, gas, and natural gas liquids) for the Appalachian basin (10 billion barrels total), categorized by geologic age.

Table 11 is similar to table 10, with one important exception: the estimated values for original oil-in-place have been substituted for the recoverable reserve figures for crude oil. The reader should be cautioned that although oil-in-place figures may be useful in evaluating producing formations or, possibly, source beds, they can be very misleading if they are mistakenly considered as representing recoverable reserves. Based upon present technology, the average percentage of ultimate hydrocarbon recovery in the Appalachian basin is approximately 20 percent, as compared to an average of 31.4 percent for the entire United States (API data, *in* AGA and others, 1973). The average recovery percentages for each State reported on in the Appalachian basin range from 13.5 percent for Ohio to 32.4 percent for Kentucky (API, 1973).

By finding the sum of all the known estimated hydrocarbons (oil-in-place, natural gas liquids, and natural gas) within the explored portions of the Appalachian basin, the grand total can be estimated at approximately 21.5 billion barrels (equivalent).

All data (production, reserves, and estimated original oil-in-place) are based upon known reservoirs. No projections, extrapolations, or extensions into undrilled formations or unexplored portions of the Appalachian basin have been considered in this report.

SPECULATIONS ON WASTAGE

It is impossible to assign any substantiated figures to the total amounts of oil and gas wasted[1] during the early history of the petroleum industry in the Appalachian basin. Reviews of the early literature from State surveys, early published histories of petroleum developments, and early reports from the U. S. Bureau of Mines convince the reader that significant amounts of crude oil were wasted and the tremendous wastage of natural gas was on an even greater scale.

Much of the wastage can be attributed to lack of knowledge concerning production techniques, transportation, and usage. However, a greater part of the wastage appears to have been due to excessive drilling of oil and gas wells when there were no uses or markets for the products, no means of storage or facilities for transportation and poor prices. Unnecessary wells were punched into the ground and the gas allowed to escape into the air and the oil to run down the creeks and fill the swamps. Fires, explosions, and deaths were common and are

---

[1] "Waste" is defined here as meaning to use up or spend without real need, gain, or purpose; not put to full or proper use; produced in excess of what is or can be used; a useless or profitless spending, or consuming; destroyed uselessly or dissipated.

TABLE 10. — Estimated total recoverable hydrocarbons in the Appalachian basin, categorized by geologic age.

[All values are based upon known reservoirs only]

Geologic age	Total recoverable reserves of crude oil[1] and natural gas liquids[2] (thousands of barrels)	Total natural gas recoverable reserves[3] (millions of ft[4])	Equivalent barrels[4] of natural gas reserves (thousands of barrels)	Total recoverable reserves of hydrocarbons (thousands of barrels)	Percent of total recoverable hydrocarbons for basin
Pennsylvanian	125,451	2,299,865	423,860	549,311	5.4877
Mississippian	601,286	11,772,486	2,169,643	2,770,929	27.6821
Devonian	2,094,440	16,968,975	3,127,345	5,221,785	52.1666
Early Devonian and Late Silurian	1,894	54,688	10,079	11,973	.1196
Silurian	373,439	5,443,930	1,003,305	1,376,744	13.7539
Ordovician	17,537	85,439	15,746	33,283	.3325
Cambrian	[5]27,089	101,474	18,702	45,791	.4576
Total	3,241,136	36,726,857	6,768,680	10,009,816	100.0000

[1]From table 6.
[2]From table 9.
[3]From table 8.
[4]The conversion factor is based upon the BTU equivalent of methane, 5,426 cubic feet per barrel.
[5]Includes some Ordovician.

TABLE 11. — Estimated total hydrocarbons in the Appalachian basin, calculated using original oil-in-place and categorized by geologic age.

[Reported in thousands of barrels. All values are based upon known reservoirs only]

Geologic age	Total estimated oil-in-place[1] plus natural gas liquid reserves[2]	Equivalent barrels[3] of natural gas reserves	Total hydrocarbons	Percent of total hydrocarbons
Pennsylvanian	500,267	423,860	924,127	4.2958
Mississippian	2,002,132	2,169,643	4,171,775	19.3926
Devonian	9,392,990	3,127,345	12,520,335	58.2012
Early Devonian and Late Silurian	1,894	10,079	11,973	.0556
Silurian	2,555,528	1,003,305	3,558,833	16.5434
Ordovician	92,134	15,746	107,880	.5015
Cambrian	[4]198,532	18,702	217,234	1.0099
Total	14,743,477	6,768,680	21,512,157	100.0000

[1]From table 7.
[2]From table 9.
[3]From table 8.
[4]Includes some Ordovician.

documented in every State within the Appalachian basin (Derrick's Handbook of Petroleum, 1898; 1900).

Wastage in the early history of the Appalachian basin is well documented, as the following examples show.

It is simply impossible to ascertain the total production in cubic feet of natural gas in the United States. The data do not exist for such a statement. Nor is it essential to ascertain this total production of all wells. The only production that has any commercial importance is that which is utilized. The amount that is wasted has no commercial value, at least that can be observed. Only that gas which has been consumed in doing useful work will be taken into consideration in this statement of total consumption. The waste cannot be considered.[Joseph D. Weeks, *in* U.S. Geological Survey, 1885, p. 155.]

The first laws pertaining to the conservation of oil and gas were not enacted until 1878 [in Pennsylvania], nearly 20 years after the first rush to the fields, late in 1859. The early development was attendant with appalling waste and dissipation. [Arnold and Kemnitzer, 1931, p. 96.]

Not withstanding the law upon the statute books requiring the several gas and oil companies operating in the State [West Virginia] to shut in all gas wells and prevent the waste of this precious fuel, there is yet an enormous waste going on in several counties of the State. * * * In one county alone (Wetzel) it is estimated that the waste of gas, counting that which escapes with the oil production, and which the present statute does not therefore prohibit, amounts to much more than 100 million cubic feet daily. [White, 1899, p. 25.]

White later reported (1904, p. 29) that "* * * 200–250 million cubic feet is daily wasted through unplugged wells, leaking joints, and from producing oil wells," and he estimated that the "* * * State [of West Virginia] has lost more than $150,000,000 worth * * *" of natural gas in the decade from 1894 to 1904. At the 1904 price of 10 cents per 1,000 cubic feet this would have been an estimated 1.5 trillion cubic feet in one decade.

In 1873 J. T. Henry wrote,

Though Western Pennsylvania has produced numerous flowing wells of wonderful capacity, there is no quarter of the world where the production attained such prodigious dimensions, as in 1862, on Black Creek, in the township of Enniskillen (Ontario). The first flowing well was struck there on January 11, 1862, and before October not less than thirty-five wells had commenced to drain a store-house, which provident nature had occupied untold thousands of years in filling for the uses — not for the amusement — of man. There was no use for the oil at that time. The price had fallen to ten cents per barrel. The unsophisticated settlers of that wild and wooded region seemed inspired by an infatuation. Without an object save the gratification of their curiosity at the unwonted sight of a combustible fluid pouring out of the bosom of the earth, they seemed to vie with each other in plying their hastily and rudely erected "spring poles" to work the drill, that was almost sure to burst at a depth of a hundred feet, into a prison of petroleum. Some of these wells flowed three hundred, and six hundred barrels per day. Others flowed a thousand, two thousand, and three thousand barrels per day. Three flowed, severally, six thousand barrels per day; and the "Black and Matthewson" well flowed seven thousand five hundred barrels per day. Three years later that oil would have brought ten dollars per barrel in gold. Now, its escape was the mere pastime of fullgrown boys. It floated on the waters of Black Creek to the depth of six inches, and formed a film on the surface of Lake Erie. At length the stream of oil became ignited, and the column of flame raged down the winding of the creek in a style of such fearful grandeur as to admonish the Canadian Squatter of the danger, no less than the inutility of his oleaginous pastimes. From detailed deter-

minations, Professor Winchell says, "I have ascertained that, during the spring and summer of 1862, not less that five million barrels of oil floated off on the water of Black Creek — a national fortune totally wasted."

During the period from 1883 to the close of 1889, natural gas "* * * was used in the most extravagant and reckless manner, and it was paid for at rates that were in many instances less than one-half the price of equivalent coal. Large quantities were allowed to escape and burn from the mouths of hundreds of stand pipes from Saturday afternoon until Monday morning. It is highly probable that in these 6 years of reckless consumption four times the present production was consumed annually." (F. H. Oliphant, *in* U.S. Geological Survey, 1901, p. 614.)

The annual production of natural gas for the year 1901, the date of F. H. Oliphant's statement, was approximately 203 billion cubic feet. If four times this amount were consumed annually during the 6 years (1883 through 1889), or 812 billion cubic feet, then in 6 years 4.877 trillion cubic feet would have been consumed, according to Oliphant's estimates. That is 13.3 percent of the total estimated proved natural gas reserves (36.727 trillion ft^3) (see table 8) for the entire Appalachian basin through 1972. Another 1.5 trillion cubic feet for one decade from West Virginia, as cited earlier, added to the above 4.877 trillion cubic feet means that more than 6.3 trillion cubic feet, or 17.1 percent of the total estimated proved natural gas reserves for the entire basin were wasted in these early years.

The U.S. Geological Survey, in 1921, in reporting on the wastage problem, cited some of the difficulties encountered in obtaining accurate information. "The Geological Survey has attempted from time to time to get figures on the quantity of gas wasted, but the returns made to it have been wholly inadequate for this purpose, because the operators generally have no idea as to the quantities of gas that are being lost or needlessly consumed." (U.S. Geological Survey, 1921).

The above report was able to give wastage figures for 3 years, 1919–1921, on the basis of information gathered from the gas-producing States. For States reported on within the Appalachian basin these figures are as follows (U.S. Geological Survey, 1921, p. 349, 352):

State	Percent of production wasted		
	1919	1920	1921
Kentucky	28	28	27
New York	.1	1	2
Ohio	12	18	19
Pennsylvania	4	2	2
West Virginia	1	2	2
Average for all gas-producing States	7	7	9

A very rough estimate of the total wastage of oil and gas during the history of their production in the Appalachian basin, based upon old

published reports and very incomplete and fragmentary data, might be as great as 100 million barrels of crude oil and natural gas liquids (approximately 3 percent or more of the known total proved reserves), and nearly 10 trillion cubic feet of natural gas (more than 25 percent of the total proved natural gas reserves).

DRILLING AND PRODUCTION INFORMATION

The total number of recorded exploration, development, and service wells drilled in the Appalachian basin from 1859 through 1972 is reported by API and AAPG (1973) to be 608,401. Excluding service wells, the total number of wells drilled for oil and gas for the entire Appalachian basin has been reported by the IPAA (1973) as 592,523.

The deepest drilling depths and deepest producing depths for oil and gas recorded for each State in the Appalachian basin through 1973 are shown in table 12.

TABLE 12. — *Deepest drilling and production depth for oil or gas in States of the Appalachian basin, through 1973*

[Data from API (1971) for all States except West Virginia (AAPG, 1973)]

State	Deepest drilling			Deepest production		
	Feet	Year	Horizon	Feet	Year	Horizon
Kentucky _____	13,170	1959	Granite basement	9,665	1970	Second St. Peter sand
Maryland _____	8,700	1966	Helderberg Formation	8,658	1966	Oriskany Sandstone
New York _____	13,500	1958	Potsdam Sandstone	5,013	1941	Do.
Ohio _____	11,442	1967	Cambrian	8,114	1968	Cambrian-Ordovician
Pennsylvania _____	18,834	1966	_ _ do _ _	11,458	1964	Tuscarora Sandstone
Tennessee _____	10,748	1967	_ _ do _ _	3,107	1954	Chattanooga Shale
Virginia _____	14,176	1965	_ _ do _ _	6,158	1954	Silurian
West Virginia _____	18,554+	1973	(¹)	8,552	1970	Oriskany Sandstone

¹Still drilling.

The average footage of wells drilled in each State in the basin was recorded for the 22-year period of 1947 through 1968 and is shown on the following table (API, 1971):

State	Average footage	Total number of years in which wells were drilled
Kentucky _____	1,541	22
Maryland _____	5,395	10
New York _____	1,499	22
Ohio _____	1,898	22
Pennsylvania _____	2,359	22
Tennessee _____	1,169	17
Virginia _____	4,735	10
West Virginia _____	2,700	22

According to the Interstate Oil Compact Commission, the major part of the present production in the Appalachian basin is from stripper wells, which they define as a well "capable of producing only 10 barrels of oil per day or less during the year under consideration" (COMPACT, 1973). The percentages of total production from stripper wells in the

Appalachian basin States in 1972, as reported by two sources, were as follows:

State	Percent (COMPACT, 1973)	Percent (IPAA, 1973)
Kentucky _____	94.08	98.5
New York _____	100	97.4
Ohio _____	82.22	70.0
Pennsylvania _____	100	100
Tennessee _____	6.70	7.5
Virginia _____	100	100
West Virginia _____	100	100
Maryland _____	0	0

According to these surveys all the major oil production within the Appalachian basin is from stripper wells capable of producing 10 barrels or less of oil per day. Within the States of Kentucky, New York, Pennsylvania, Tennessee, and Virginia, the entire remaining proved reserves are classified as stripper-well reserves. In West Virginia and Ohio the stripper-well reserves make up 53 percent and 70 percent respectively of the remaining proved reserves (COMPACT, 1973; API, 1973). In addition, over a third of these stripper-well reserves are being recovered by secondary methods of operation.

In light of the energy shortage in the United States, development of known reserves is a necessity. It is doubtful that additional significant resources will be found in the parts of the Appalachian basin that have already been adequately explored; however, through 1974 only 42 wells had been drilled in the basin below 10,000 feet, and some hope of deeper prospects still encourages additional exploration (Bee, 1974).

REFERENCES CITED

American Association of Petroleum Geologists, 1938–1970, 1971, 1972, 1973 [Developments of North America — Annual reports on production and reserves]: Am. Assoc. Petroleum Geologists Bull., v. 22-54, no. 6, 1938–1970; v. 55, 56, no. 7, 1971, 1972; v. 57, no. 8, 1973.

American Gas Association, American Petroleum Institute, and Canadian Petroleum Association, 1973, Reserves of crude oil, natural gas liquids, and natural gas in the United States and Canada and United States productive capacity as of December 31, 1972: Washington, D.C., Am. Petroleum Inst., v. 27, 251 p.

American Petroleum Institute, 1971, Petroleum facts and figures: Washington, D.C., Am. Petroleum Inst., 604 p.

Arnold, Ralph, and Kemnitzer, W. J., 1931, Petroleum in the United States and possessions: New York and London, Harper & Brothers Publishers, 1052 p.

Bee, D. A., 1974, Recent developments in deep drilling in the Appalachian basin: Soc. Petroleum Engineers A.I.M.E. Deep Drilling and Production Symposium, Amarillo 1974, Soc. Petroleum Engineers Preprint SPE-5183, p. 169–174.

Calvert, W. L., 1961, Summary of oil and gas activity in Ohio during 1960: Ohio Div. Geol. Survey Rept. Inv. 40, 96 p.

_____1964a, Summary of oil and gas activity in Ohio during 1963: Ohio Div. Geol. Survey Rept. Inv. 50, 99 p.

_____1964b, Oil and gas fields of Ohio (including underground storage areas) [revised]: Ohio Div. Geol. Survey, scale 1 in.:6 mi.

Cardwell, D. H., Patchen, D. G., and Woodfork, L. D., and others, 1970, Oil and gas fields in West Virginia [revised]: West Virginia Geol. and Econ. Survey, map with 31 p. text [April]; 17 p. supp. [May].

Carll, J. F., 1887, Report on the oil and gas regions: Pennsylvania Geol. Survey Ann. Rept. 1886, pt. 2, p. 575–786.

Colton, G. W., 1961, Geologic summary of the Appalachian basin, with reference to the subsurface disposal of radioactive waste solutions: U.S. Geol. Survey TEI-791, 121 p.

Cram, I. H., ed., 1971, Future petroleum provinces of the United States — Their geology and potential: Am. Assoc. Petroleum Geologists Mem. 15, v. 1, p. 1-803; v. 2, p. 805–1496.

Derrick Publishing Company, 1898, 1900, The Derrick's hand-book of petroleum — A complete chronological and statistical review of petroleum developments from 1859 to 1898; 1898 and 1899: Oil City, Pa., Derrick Publishing Co. [v. 1] (pub. 1898) 1859-1898, 1062 p.; v. 2 (pub. 1900) 1898-1899, 533 p.

Fettke, C. R., 1953, Oil and gas developments in the Appalachian Basin, past and present: Pennsylvania Geol. Survey, 4th ser., Bull. M37, p. 69–83 [repr. from Mines Mag., v. 42, no. 11, p. 69-83, 1952].

Foerste, A. F., 1917, Notes on Silurian fossils from Ohio and other central States: Ohio Jour. Sci., v. 17, p. 187-204, 233–267.

Henry, J. T., 1873, The early and later history of petroleum, with authentic facts in regard to its development in western Pennsylvania: Philadelphia, J. B. Rodgers Co., 607 p.

Hunter, C. D., 1955, Development of natural gas fields of eastern Kentucky: Kentucky Geol. Survey, ser. 9, Repr. 11 [repr. from Petroleum Engineer, v. 27, no. 5, p. B47, B49-B50, B52, 1955], unpaged.

————1964, Gas development, production, and estimated ultimate recovery of Devonian shale in eastern Kentucky: Kentucky Geol. Survey, ser. 10, Spec. Pub. 8, p. 21–29.

Independent Petroleum Association of America, 1973, The oil producing industry in your State [1973 ed.]: Independent Petroleum Assoc. America, 106 p.

Interstate Oil Compact Commission, and National Stripper Well Association, 1973, National stripper well survey, January 1, 1973 [United States]: Oklahoma City, Okla., Interstate Oil Compact Comm., 10 p.

Kreidler, W. L., 1953, History, geology and future possibilities of gas and oil in New York State: New York State Mus. Circ. 33, 58 p.

Landes, K. K., 1970, Petroleum geology of the United States: New York, Wiley-Interscience, 571 p.

Lytle, W. S., 1950, Crude oil reserves of Pennsylvania: Pennsylvania Geol. Survey, 4th ser., Bull. M32, 256 p.

McGuire, W. H., and Howell, Paul, 1963, Oil and gas possibilities of the Cambrian and Lower Ordovician in Kentucky: Lexington, Ky., Spindletop Research Center, [216] p.

Meyer, R. F., and Edgerton, C. D., Jr., 1968, Petroleum and natural gas, in Mineral resources of the Appalachian Region: U. S. Geol. Survey Prof. Paper 580, p. 145-163 and table 51.

Milhous, H. C., 1960, Key development years just ahead: World Oil, v. 150, no. 7, p. 92–95.

Price, P. H., 1929, Pocahontas County: Virginia Geol. Survey County Repts., 531 p.

Roth, E. E., 1968, Natural gases of Appalachian basin, in Natural gases in rocks of Paleozoic age, Pt. 3, V. 2 of Natural gases of North America, Symposium: Am. Assoc. Petroleum Geologists Mem. 9, p. 1702-1715.

Sitler, G. F., Jr., and Wehmeyer, K. L., Jr., 1962. Ohio offering potential from the bottom of the column: Oil and Gas Jour., v. 60, no. 2, p. 108–114.

Thomas, G. R., and Nosow, Edmund, 1960, Drilling outlook remains good: World Oil, v. 150, no. 7, p. 95-100.

U.S. Bureau of Mines, 1924-1931, Mineral resources of the United States [annual volumes for the years indicated]: Washington, U.S. Govt. Printing Office.

———1932-1971, Minerals yearbook [annual volumes for the years indicated]: Washington, U. S. Govt.Printing Office.

U.S. Geological Survey, 1882-1923, Mineral resources of the United States [annual volumes for the years indicated]: Washington, U.S. Govt. Printing Office.

Weaver, O. D., 1962, Revival of the Appalachians: Oil and Gas Jour., v. 60, no. 8, p. 88-97.

White, I. C., 1899, Petroleum and natural gas, Pt. 4 *of* West Virginia Geological Survey: West Virginia Geol. and Econ. Survey [Rept.], v. 1, p. 123-378.

———1904, Petroleum and natural gas, Pt. 1 *of* West Virginia Geological Survey: West Virginia Geol. and Econ. Survey [Rept.], v. 1A, p. 1-512.

Wilson, E. N., 1968, Some aspects of drilling activities in eastern Kentucky in 1965-1966: Kentucky Geol. Survey, Ser. 10, Spec. Pub. 15, p. 56-63.

Zaba, Joseph, and Doherty, W. T., 1956, Production, Chap. 6, *in* Practical petroleum engineers handbook [4th ed.]: Houston, Tex., Gulf Publishing Co., p. 461-751.

SELECTED REFERENCES

[Page numbers shown in brackets at end of references are those that pertain specifically to oil and gas]

Alkire, R. L., 1952, Oil and gas in Perry County [Ohio]: Ohio Div. Geol. Survey Rept. Inv. 10, Petroleum and Nat. Gas Ser. 2, 64 p.

Alkire, R. L., compiler, 1953, Oil and gas well drilling statistics, 1952: Ohio Div. Geol. Survey Rept. Inv. 19, Petroleum and Nat. Gas Ser. 4, 67 p. [p. 35-59].

———1954, Oil and gas well drilling statistics, 1953: Ohio Div. Geol. Survey Rept. Inv. 20, Petroleum and Nat. Gas Ser. 5, 53 p. [p. 11-39, 48-53].

———1955, Drilling and production statistics, Pt. 1, *in* Oil and gas in Ohio, 1954: Ohio Div. Geol. Survey Rept. Inv. 24, Petroleum and Nat. Gas Ser. 7, p. 1-38, [p. 11-38].

American Association of Petroleum Geologists, 1938-1970, 1971, 1972, 1973 [Developments of North America — Annual reports on production and reserves]: Am. Assoc. Petroleum Geologists Bull., v. 22-54, no. 6, 1938-1970; v. 55, 56, no. 7, 1971, 1972; v. 57, no. 8, 1973.

American Gas Association, American Petroleum Institute, and Canadian Petroleum Association, 1973, Reserves of crude oil, natural gas liquids, and natural gas in the United States and Canada and United States productive capacity as of December 31, 1972: Washington, D.C., Am. Petroleum Inst., v. 27, 251 p.

American Petroleum Institute, 1971, Petroleum facts and figures: Washington, D.C., Am. Petroleum Inst., 604 p.

Arnold, Ralph, and Kemnitzer, W. J., 1931, Petroleum in the United States and possessions: New York and London, Harper & Brothers Publishers, 1052 p. [p. 61-226].

Ashley, G. H., 1910, Outline introduction to the mineral resources of Tennessee: Tennessee Geol. Survey Bull. 2-A, 65 p. [p. 56-59].

Ashley, G. H., and Robinson, J. F., 1922, The oil and gas fields of Pennsylvania — V. 1, Introduction: Pennsylvania Geol. Survey, 4th ser., Bull. M1, 79 p. [p. 22-45].

Bailey, W. F., 1930, Petroleum possibilities in Tennessee: Oil and Gas Jour., v. 28, no. 46, p. 42, 148, 150.

———1930, Geologic structure map of Smithland gas field, Lincoln County, Tennessee: Tennessee Div. Geology.

———1931, Natural gas producing areas in eight Tennessee Counties: Oil and Gas Jour., v. 29, no. 51, p. 90, 173, 174.

———1935, Natural gas from Paleozoic horizons in southern Cincinnati arch region, *in* Ley, H. A., ed., Geology of natural gas: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 853-879.

Beebe, B. W., and Curtis, B. F., eds., 1968, Natural gases in rocks of Cenozoic age, Pt. 1, V. 1; Natural gases in rocks of Mesozoic age, Pt. 2, V. 1; *and* Natural gases in rocks of Paleozoic age, Pt. 3, V. 2; Papers of general scope, Pt. 4, V. 2, *of* Natural gases of North America — a symposium in two volumes: Am. Assoc. Petroleum Geologists Mem. 9, v. 1, p. 1–1226; v. 2, p. 1227–2493.

Belden, Henry, 1952, The Canton gas pool: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 59–70.

Born, K. E., 1943, Oil and gas in Middle Tennessee, with map of pools, columnar section, table of data, and history of developments [map]: Tennessee Div. Geology, 1 sheet.

Born, K. E., and Burwell, H. B., 1939, Geology and petroleum resources of Clay County, Tennessee: Tennessee Div. Geology Bull. 47, 188 p. [p. 79–82, 150–157].

Bostick, N. H., and Damberger, H. H., 1971, The carbon ratio rule and petroleum potential in NPC region 9, *in* Future petroleum potential of NPC region 9 (Illinois Basin, Cincinnati arch, and northern part of Mississippi Embayment), Symposium, Champaign, Ill., 1971, Proc.: Illinois Geol. Survey Illinois Petroleum 95, p. 142–151.

Bownocker, J. A., 1903, The occurrence and exploitation of petroleum and natural gas in Ohio: Ohio Div. Geol. Survey, 4th ser., Bull. 1, 325 p.

_____1910, The Bremen oil field [Ohio]: Ohio Div. Geol. Survey, 4th ser., Bull. 12, 68 p. [p. 7–16].

Brewer, Charles, Jr., 1933, Oil and gas geology of the Allegany State Park, 1931: New York State Mus. Circ. 10, 22 p. [p. 1–9].

Burgess, R. J., 1963, New strikes spark Cambrian play in Ohio, south Ontario, Pt. 1: Oil and Gas Jour., v. 61, no. 9, p. 180–183.

_____1963, Ohio, southern Ontario areas on threshold of big Cambrian play, Pt. 2: Oil and Gas Jour., v. 61, no. 10, p. 128–131.

Burwell, H. B., and Milhous, H. C., 1967, Oil and gas map, Scott County, Tennessee: Tennessee Div. Geology.

_____1967, Oil and gas map, Morgan County, Tennessee: Tennessee Div. Geology.

Calvert, W. L., 1961, Summary of oil and gas activity in Ohio during 1960: Ohio Div. Geol. Survey Rept. Inv. 40, 96 p. [p. 5–29].

_____1962, Summary of oil and gas activity in Ohio during 1961: Ohio Div. Geol. Survey Rept. Inv. 43, 108 p. [p. 5–35].

_____1963, Summary of oil and gas activity in Ohio during 1962: Ohio Div. Geol. Survey Rept. Inv. 47, 125 p. [p. 5–122].

_____1964, Summary of oil and gas activity in Ohio during 1963: Ohio Div. Geol. Survey Rept. Inv. 50, 99 p. [p. 3–99].

_____1964, Oil and gas fields of Ohio (including underground storage areas) [revised]: Ohio Div. Geol. Survey, Scale 1 in.:6 mi.

Cardwell, D. H., 1971, The Newburg of West Virginia: West Virginia Geol. and Econ. Survey Bull. 35, 54 p. [p. 4–19].

Cardwell, D. H., Patchen, D. G., and Woodfork, L. D., and others, 1970, Oil and gas fields in West Virginia [revised]: West Virginia Geol. and Econ. Survey, map with 31 p. text [April]; 17 p. supp. [May].

Carll, J. F., 1887, Report on the oil and gas regions: Pennsylvania Geol. Survey Ann. Rept. 1886, pt. 2, p. 575–786 [p. 575–635].

Cathcart, S. H., 1952, Recent developments in exploration in northern and central Pennsylvania [abs.]: Am. Petroleum Inst. Drilling and Production Practice, 1951, p. 394.

Colton, G. W., 1961, Geologic summary of the Appalachian basin, with reference to the subsurface disposal of radioactive waste solutions: U.S. Geol. Survey TEI-791, 121 p.

Connor, W. T., DeBrosse, T. A., Bendler, E. P., Buschman, W. J., and Johnson, A. W., 1970, Ohio, *in* Oil and gas developments in Maryland, Ohio, Pennsylvania, Virginia, and West Virginia: Am. Assoc. Petroleum Geologists Bull., v. 54, no. 6, p. 947–950.

Cooper, F. D., 1972, The mineral industry of Pennsylvania in 1970: Pennsylvania Geol. Survey Inf. Circ. 73, 35 p. [p. 1–19]; preprint from U.S. Bur. Mines Minerals Yearbook, 1970.

Cram, I. H., ed., 1971, Future petroleum provinces of the United States — Their geology and potential: Am. Assoc. Petroleum Geologists Mem. 15, v. 1, p. 1–803; v. 2, p. 805–1496.

Crawford, T. J., 1958, Compilation of coal and petroleum production data for Kentucky: Kentucky Geol. Survey, ser. 10, Rept. Inv. 1, 43 p. [p. 13, 32–42].

DeBrosse, T. A., 1972, Ohio oil and gas: Ohio Div. Mines [Ann.] Rept. 1971, p. 27–32.

DeGolyer and MacNaughton, 1958, Twentieth century petroleum statistics, 1958: Dallas, Tex., DeGolyer and MacNaughton, 87 p. [p. 15–87].

Derrick Publishing Company, 1898, 1900, The Derrick's hand-book of petroleum — A complete chronological and statistical review of petroleum developments from 1859 to 1898; 1898 and 1899: Oil City, Pa., Derrick Publishing Co. [v. 1] (pub. 1898) 1859–1898, 1062 p.; v. 2 (pub. 1900) 1898–1899, 533 p.

_____1916, 1920, The Derrick's hand-book of petroleum — Statistical abstract of the petroleum industry from 1900 to 1915; 1916 to 1919: Oil City, Pa., Derrick Publishing Co., v. 3 (pub. 1916) 1900–1915, 86 p.; v. 4 (pub. 1920) 1916–1919, 61 p.

_____1920, 1921, The Derrick's annual review of oil fields for 1920; 1921: Oil City, Pa., Derrick Publishing Co., 1920, 10 p.; 1921, 40 p.

_____1922, 1923, 1924, The Derrick's annual review of oil fields of United States, Mexico, and Canada for 1922; 1923; 1924: Oil City, Pa., Derrick Publishing Co., 1922, 51 p.; 1923, 20 p.; 1924, 20 p.

Edwards, Jonathan, Jr., 1970, Deep wells of Maryland: Maryland Geol. Survey Basic Data Rept. 5, 8 p. [p. 3–4].

Fenstermaker, C. D., 1969, Résumé of current activity of the oil industry northeast of the Mississippi River — geographic, geologic — and magnitude of recent years' discoveries: Kentucky Geol. Survey, ser. 10, Spec. Pub. 17, p. 50–77 [p. 50–75].

Fettke, C. R., 1948, Subsurface Trenton and sub-Trenton rocks in Ohio, New York, Pennsylvania, and West Virginia: Am. Assoc. Petroleum Geologists Bull., v. 32, no. 8, p. 1457–1492.

_____1953, Oil and gas developments in the Appalachian Basin, past and present: Pennsylvania Geol. Survey, 4th ser., Bull. M37, p. 69–83 [repr. from Mines Mag., v. 42, no. 11, p. 69–83, 1952].

Finn, F. H., 1949, Geology and occurrence of natural gas in Oriskany sandstone in Pennsylvania and New York: Am. Assoc. Petroleum Geologists Bull., v. 33, no. 3, p. 303–335.

Floto, B. A., 1955, The possible presence of buried Niagaran reefs in Ohio and their relationship to the Newburg oil and gas zone, Pt. 2, in Oil and gas in Ohio, 1954: Ohio Div. Geol. Survey Rept. Inv. 24, Petroleum and Nat. Gas Ser. 7, p. 39–58 [p. 39–51].

Floyd, R. J., 1965, Tennessee rock and mineral resources: Tennessee Div. Geology Bull. 66, 119 p. [p. 88–94].

Garrett, S. G., 1931, Oriskany gas field of Pennsylvania and New York: Am. Assoc. Petroleum Geologists Bull., v. 15, no. 7, p. 837–839.

Glenn, L. C., 1915, Recent oil developments near Oneida, Scott County, Tennessee: Resources of Tennessee [Tennessee Geol. Survey], v. 5, no. 4, p. 174–194 [p. 190–194].

_____1921, Oil fields of Kentucky and Tennessee: Am. Inst. Mining Metall. Engineers Trans., v. 65, p. 122–139.

Hall, J. F., 1952, Oriskany sand study: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 39–58.

Haney, Gene, 1968, Newburg gas development, Kanawha and Jackson Counties, West Virginia: Kentucky Geol. Survey, ser. 10, Spec. Pub. 15, p. 111–117.

Hartenstein, W. G., 1967, Hydrocarbon whys and wherefores: Oil and Gas Jour., v. 65, no. 52, p. 200–213 [p. 200–207].

Hartnagel, C. A., 1925, The oil fields of New York State: Am. Assoc. Petroleum Geologists Bull., v. 9, no. 4, p. 798–802.

Hartnagel, C. A., and Broughton, J. G., 1951, The mining and quarry industries of New York State, 1937 to 1948: New York State Mus. Bull. 343, 130 p. [p. 66–83].

Hartnagel, C. A., and Russell, W. L., 1929, New York oil fields, *in* V 2. *of* Structure of typical American oil fields; Relation of oil accumulation to structure, Symposium, 12th Ann. Convention, Tulsa, Okla., 1927: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 269–289.

Haught, O. L., 1959, Oil and gas in southern West Virginia: West Virginia Geol. and Econ. Survey Bull. 17, 34 p. [p. 9–34].

_____1959, Oil and gas report and map of Doddridge and Harrison Counties, West Virginia: West Virginia Geol. and Econ. Survey Bull. 16, 39 p. [p. 12–19].

_____1960, Oil and gas report on Lewis and Gilmer Counties, West Virginia: West Virginia Geol. and Econ. Survey Bull. 18, 14 p. [p. 7–24]. `

_____1964, West Virginia's oil and gas — Lubricants and fuels: West Virginia Geol. and Econ. Survey Bull. 26, 39 p.

_____1964, Oil and gas report on Braxton and Clay Counties, West Virginia: West Virginia Geol. and Econ. Survey Bull. 29, 19 p. [p. 8–19].

_____1965, Oil and gas report on Barbour and Upshur Counties, West Virginia: West Virginia Geol. and Econ. Survey Bull. 31, 15 p. [p. 8–15].

_____1965, Geology of oil and gas: West Virginia Geol. and Econ. Survey Circ. 3, 31 p. [p. 31].

_____1968, Oil and gas report on Ohio, Brooke and Hancock Counties, West Virginia: West Virginia Geol. and Econ. Survey Bull. 33, 14 p. [p. 6–14].

_____1972, Sissonville (Elk-Poca) gas field, West Virginia, *in* King, R. E., ed., Stratigraphic oil and gas fields — Classification, exploration methods, and case histories: Am. Assoc. Petroleum Geologists Mem. 16, and Soc. Exploration Geophysicists, SEG Spec. Pub. 10, p. 313–317.

Haught, O. L., and McCord, W. R., 1960, Oriskany gas development and structural map, Onondaga-Huntersville, West Virginia: West Virginia Geol. and Econ. Survey Rept. Inv. 20, 28 p. [p. 20–28].

Headlee, A. J. W., 1949, The composition and properties of natural gas in the Appalachian fields: Appalachian Geol. Soc. Bull., v. 1, p. 24–33.

_____1960, Deep tests reflect near-peak gas yield: World Oil, v. 150, no. 7, p. 100–104.

Henry, J. T., 1873, The early and later history of petroleum, with authentic facts in regard to its development in western Pennsylvania: Philadelphia, J. B. Rodgers Co., 607 p. [p. 129–139].

Heyman, Louis, 1969, Geology of the Elk Run gas pool, Jefferson County, Pennsylvania: Pennsylvania Geol. Survey, 4th ser., Bull. M59, 18 p.

Hice, R. R., 1912, The mineral production of Pennsylvania, App. G: Pennsylvania Topog. and Geol. Survey Rept., 1910-12, p. 156-177 [p. 158-173].

_____1915, The mineral production of Pennsylvania for the year 1913: Pennsylvania Geol. Survey Rept. 11, 108 p. [p. 42–51].

Hoeing, J. B., 1905, The oil and gas sands of Kentucky: Kentucky Geol. Survey Bull. 1, 233 p. [p. 9–15].

Hunter, C. D., 1935, Natural gas in eastern Kentucky, *in* Ley, H. A., ed., Geology of natural gas: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 915–947.

_____1955, Development of natural gas fields of eastern Kentucky: Kentucky Geol. Survey, ser. 9, Repr. 11 [repr. from Petroleum Engineer, v. 27, no. 5, p. B47, B49–B50, B52, 1955], unpaged.

_____1964, Gas development, production, and estimated ultimate recovery of Devonian shale in eastern Kentucky: Kentucky Geol. Survey, ser. 10, Spec. Pub. 8, p. 21–29.

Independent Petroleum Association of America, 1973, The oil producing industry in your State [1973 ed.]: Independent Petroleum Assoc. America, 106 p.

Interstate Oil Compact Commission, and National Stripper Well Association, 1973, National stripper well survey, January 1, 1973 [United States]: Oklahoma City, Okla., Interstate Oil Compact Comm., 10 p.

Jenkins, E. B., 1965, Resume of drilling activity in Eastern Kentucky in 1963: Kentucky Geol. Survey, ser. 10, Spec. Pub. 10, p. 110-112.

Jillson, W. R., 1920, The oil and gas resources of Kentucky [2d ed.]: Kentucky Geol. Survey, ser. 5, Bull. 1, 630 p. [p. 18-27, 38-43, 93-95, 102-114].

———1922, Oil field stratigraphy of Kentucky: Kentucky Geol. Survey, ser. 6, v. 3, 738 p. [p. 1-20].

———1926, New oil pools of Kentucky: Kentucky Geol. Survey, ser. 6, v. 12, 394 p. [p. 76-88, 93, 118-126, 213-215, 221-222, 257-259, 282-288, 291-298, 321-346].

———1929, Administrative report for the (Sixth) Kentucky Geological Survey, years 1928 and 1929: Kentucky Geol. Survey, ser. 6, Pamph. 22, 108 p. [p. 57-63].

———1937, Natural gas in eastern Kentucky: Louisville, Ky., Standard Printing Co., 237 p. [p. 1-14].

Kelley, D. R., Lytle, W. S., Wagner, W. R., and Heyman, Louis, 1969, Oil and gas developments in Pennsylvania in 1968: Pennsylvania Geol. Survey, 4th ser., Prog. Rept. 177, 48 p. [p. 1-36].

———1970, The petroleum industry and the future petroleum province in Pennsylvania, 1970: Pennsylvania Geol. Survey, 4th ser., Bull. M65, 39 p.

———1970, Oil and gas developments in Pennsylvania in 1969 with ten year review and forecast: Pennsylvania Geol. Survey, 4th ser., Prog. Rept. 181, 65 p. [p. 1-63].

Kelley, D. R., and McGlade, W. G., 1969, Medina and Oriskany production along the shore of Lake Erie, Pierce field, Erie County, Pennsylvania: Pennsylvania Geol. Survey, 4th ser., Bull. M60, 38 p.

Kentucky Geological Survey, 1959, Oil production in Kentucky for year 1958: Kentucky Geol. Survey, ser. 10, Spec. Pub. 2, p. 82.

———1961, Oil production in Kentucky for year 1960: Kentucky Geol. Survey, ser. 10, Spec. Pub. 4, p. 83.

———1965, Oil production in Kentucky for year 1963: Kentucky Geol. Survey, ser. 10, Spec. Pub. 10, p. 113.

———1968, Oil production in Kentucky for 1964-1966: Kentucky Geol. Survey, ser. 10, Spec. Pub. 15, p. 118-119.

———1969, Oil production in Kentucky for 1967 and 1968: Kentucky Geol. Suvey, ser. 10, Spec. Pub. 17, p. 83-84.

Knight, W. V., 1969, Historical and economic geology of Lower Silurian Clinton sandstone of northeastern Ohio: Am. Assoc. Petroleum Geologists Bull., v. 53, no. 7, p. 1421-1452.

Knodell, J. D., Jr., 1960, The Kentucky oil and gas conservation act of 1960: Kentucky Geol. Survey, ser. 10, Spec. Pub. 3, p. 38-47 [p. 38-39].

Kreidler, W. L., 1953, History, geology and future possibilities of gas and oil in New York State: New York State Mus. Circ. 33, 58 p. [p. 5-58].

———1958, Oriskany and deeper gas and oil possibilities in New York State [abs.]: Am. Petroleum Inst. Drilling and Production Practice, 1957, p. 295.

———1959, Selected deep wells and areas of gas production in eastern and central New York: New York State Mus. and Sci. Service Bull. 373, 243 p.

———1963, Selected deep wells and areas of gas production in western New York: New York State Mus. and Sci. Service Bull. 390, p 1-19.

Kreidler, W. L., Van Tyne, A. M., and Jorgensen, K. M., 1972, Deep wells in New York State: New York State Mus. and Sci. Service Bull. 418A, 319 p.

Landes, K. K., 1970, Petroleum geology of the United States: New York, Wiley-Interscience, 571 p. [p. 3-51].

Le Van, D. C., 1962, Wells drilled for oil and gas in Virginia prior to 1962: Virginia Div. Mineral Resources, Mineral Resources Rept. 4, 47 p.

Linn, E. H., 1954, Devonian oil and gas possibilities in central Pennsylvania [abs.]: Am. Petroleum Inst. Drilling and Production Practice, 1953, p. 364.

Lockett, Robert, 1968, Production of gas in northern Cincinnati arch province, *in* Natural gases in rocks of Paleozoic age, Pt. 3, V. 2 *of* Natural gases of North America — symposium in two volumes: Am. Assoc. Petroleum Geologists Mem. 9, p. 1716-1745.

Lusk, R. G., 1927, The significance of structure in the accumulation of oil in Tennessee: Am. Assoc. Petroleum Geologists Bull., v. 11, no. 9, p. 905-917.

Lytle, W. S., 1950, Crude oil reserves of Pensylvania: Pennsylvania Geol. Survey, 4th ser., Bull. M32, 256 p.

Lytle, W. S., and Fairall, Virginia, compilers, 1964, Oil and gas fields of Pennsylvania: Pennsylvania Geol. Survey, 4th ser., Map 3.

Lytle, W. S., and Heyman, Louis, 1972, Oil and gas developments in Pennsylvania in 1971: Pennsylvania Geol. Survey, 4th ser., Prog. Rept. 184, 39 p. [p. 1-27].

Lytle, W. S., Heyman, Louis, and Kelley, D. R., 1971, Oil and gas developments in Pennsylvania in 1970: Pennsylvania Geol. Survey, 4th ser., Prog. Rept. 183, 50 p. [p., 1-31].

Lytle, W. S., Heyman, Louis, and Wagner, W. R., 1968, Oil and gas developments in Pennsylvania in 1967: Pennsylvania Geol. Survey, 4th ser., Prog. Rept. 175, 38 p. [p. 1-29].

McCaslin, J. C., 1973, Deep Ohio section needs closer look: Oil and Gas Jour., v. 71, no. 49, p. 85.

———1974, "Considerable" Ohio oil and gas yet untrapped: Oil and Gas Jour., v. 72, no. 4, p. 169.

MacFarlane, R. M., and Ault, R. K., 1960, Nuclear logging in the Appalachian Basin: World Oil, v. 150, no. 7, p. 153-154, 160, 164.

McGuire, W. H., 1965, Porosity zones in the Knox Dolomite of northeastern Kentucky: Kentucky Geol. Survey, ser. 10, Spec. Pub. 10, p. 94-96.

McGuire, W. H., and Howell, Paul, 1963, Oil and gas possibilities of the Cambrian and Lower Ordovician in Kentucky: Lexington, Ky., Spindletop Research Center, [216] p.

———1964, Geology of the St. Peter sandstone in Clark and Estill Counties, Kentucky: Kentucky Geol. Survey, ser. 10, Spec. Pub. 8, p. 68-82.

Magbee, B. D., and Alkire, R. L., 1954, Oil and gas in Morgan County [Ohio]: Ohio Div. Geol. Survey Rept. Inv. 22, Petroleum and Nat. Gas Ser. 6, 69 p. [p. 8-69].

Merrill, F. J. H., 1895, Mineral resources of New York State: New York State Mus. Bull. 15, v. 3, p. 361-595 [p. 557-560].

Meyer, R. F., and Edgerton, C. D., Jr., 1968, Petroleum and natural gas, *in* Mineral resources of the Appalachian Region: U.S. Geol. Survey Prof. Paper 580, p. 145-163 and table 51.

Milhous, H. C., 1958, General geology and history of oil and gas development in northern Tennessee: Kentucky Geol. Survey, ser. 10, Spec. Pub. 1, p. 53-62.

———1960, Key development years just ahead: World Oil, v. 150, no. 7, p. 92-95.

Miller, R. L., and Fuller, J. O., 1954, Geology and oil resources of the Rose Hill district — the Fenster area of the Cumberland overthrust block — Lee County, Virginia: Virginia, Geol. Survey Bull. 71, 383 p.

Moore, W., S., 1957, A resume of fracturing in the eastern Kentucky: Kentucky Geol. Survey, ser. 9, Spec. Pub. 11, p. 70-75.

Multer, H. G., 1963, Geology of the Silurian producing zones in the Moreland oil pool, Wayne County, northeastern Ohio: Ohio Div. Geol. Survey Rept. Inv. 46, 45 p.

National Petroleum Council, 1970, U.S. crude oil data, 1860-1944 [compiled by the [U.S.] Petroleum Administration for War in 1945]: National Petroleum Council, v. 2, 142 p. [p. 3-50].

———1972, An initial appraisal by the Oil Supply Task Group 1971-1985 — U.S. Energy Outlook, An Interim Rept.: [Washington, D.C.], National Petroleum Council, 107 p. [p. 16-50].

Nelson, W. A., 1921, Description of oil and gas areas in Tennessee and conditions affecting new areas: Tennessee Geol. Survey Bull. 25, p. 49–66.

Newby, J. B., Torrey, P. D., Fettke, C. R., and Panyity, L. S., 1929, Bradford oil field, McKean County, Pennsylvania, and Cattaraugus County, New York, *in* V. 2 *of* Structure of typical American oil fields; Relation of oil accumulation to structure, Symposium, 12th Ann. Convention, Tulsa, Okla., 1927: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 407–442.

Newland, D. H., and Hartnagel, C. A., 1932, Recent natural gas developments in south-central New York: New York State Mus. Circ. 7, 58 p. [p. 1–18].

_____1939, The mining and quarry industries of New York State for 1934 to 1936; [and] Natural gas developments in New York State for the period 1935 to 1938: New York State Mus. Bull. 319, 158 p. [p. 73–156].

Norling, D. L., DeBrosse, T. A., and Buschman, W. J., Jr., 1965, Summary of oil and gas activity in Ohio during 1964: Ohio Div. Geol. Survey Rept. Inv. 56, 139 p.

Ohio Division of Geological Survey, 1952, Wells drilled in Ohio, 1888–1951 [revised]: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 82–84 [data from U.S. Bur. Mines Minerals Yearbooks, The Derrick's Handbooks of Petroleum and the A.I.M.E. Ann. Rev.].

_____1952, Natural gas production and consumption in Ohio: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 85 [data from U.S. Bur. Mines Minerals Yearbooks].

_____1952, Petroleum production in Ohio, 1876–1951: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 86 [data from U.S. Bur. Minerals Yearbooks and A.P.I.].

_____1958, The story of Ohio's mineral resources [revised]: Ohio Div. Geol. Survey Inf. Circ. 9, 14 p. [p. 4–14].

Oil and Gas Journal, 1973, Drilling spree hits Pennsylvania: Oil and Gas Jour., v. 71, no. 48, p. 90–91.

Orton, Edward, 1899, Petroleum and natural gas in New York: New York State Mus. Bull. 30, v. 6, p. 395-526.

_____1952, The Berea grit as a source of oil and gas in Ohio: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 76–78 [repr. from Ohio Geol. Survey Rept., v. 6, chap. 4, p. 340–343, 1888].

_____1952, The Mecca oil field: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 78–80 [repr. from Ohio Geol. Survey Rept., v. 6, chap. 4, p. 328–332, 1888].

_____1952, The Belden or Grafton oil field: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 80–81 [repr. from Ohio Geol. Survey Rept., v. 6, chap. 4, p. 332–333, 1888].

Overbey, W. K., Jr., 1961, Oil and gas report on Jackson, Mason, and Putman Counties, West Virginia: West Virginia Geol. and Econ. Survey Bull. 23, 25 p. [p. 19–25].

_____1963, Oil and gas research, Chap. 5, *in* The West Virginia geological and economic survey — Its accomplishments and outlook: West Virginia Geol. and Econ. Survey [Rept.], v. 23, p. 81–102.

Patchen, D. G., 1968, Oriskany Sandstone-Huntersville Chert gas production in the eastern half of West Virginia: West Virginia Geol. and Econ. Survey Circ. 9, 27 p.

_____1968, A summary of Tuscarora Sandstone ("Clinton Sand") and pre-Silurian test wells in West Virginia: West Virginia Geol. and Econ. Survey Circ. 8, 29 p. [p. 1–18].

_____1968, Keefer Sandstone gas development and potential in West Virginia: West Virginia Geol. and Econ. Survey Circ. 7, p. 1–6.

_____1969, Geology and drilling history of the Newburg sand in West Virginia: Kentucky Geol. Survey, ser. 10, Spec. Pub. 17, p. 26-41.

Perkins, Hunt, 1968, Subsurface geology of the Sulphur Lick–Tompkinsville area, Monroe County, Kentucky: Kentucky Geol. Survey, ser. 10, Spec. Pub. 15, p. 46-55.

Potential Gas Committee, 1973, Potential supply of natural gas in the United States (as of December 31, 1972): Golden, Colorado School Mines Found., Inc., Mineral Resources Inst., Potential Gas Agency, 48 p.

Price, P. H., Tucker, R. C., and Haught, O. L., 1938, Geology and natural resources of West Virginia: West Virginia Geol. and Econ. Survey [Rept.], v. 10, 462 p. [p. 348–373].

Ray, E. O., 1959, Resume of drilling activities in Eastern Kentucky in 1958: Kentucky Geol. Survey, ser. 10, Spec. Pub. 2, p. 48–50.

———1961, Resume of drilling activities in Eastern Kentucky in 1960: Kentucky Geol. Survey, ser. 10, Spec. Pub. 4, p. 60–63.

Read, M. C., 1952, The Neff gas wells: Ohio Div. Geol. Survey Rept. Inv. 13, Petroleum and Nat. Gas Ser. 3, p. 71–76 [repr. from Ohio Geol. Survey Rept., v. 3, chap. 67, p. 340–347, 1878].

Reeves, Frank, and Price, P. H., 1950, Early Devonian gas in northern West Virginia and pre-Devonian oil prospects: Am. Assoc. Petroleum Geologists Bull., v. 34, no. 11, p. 2095–2132.

Ridge, J. D., and DeYoung, J. H., Jr., 1972, Historical statistics of Pennsylvania's mineral industries, 1966-1970: Pennsylvania State Univ. Coll. Earth and Mineral Sci. Expt. Sta. Bull. 87, 76 p. [p. 33–40].

Roth, E. E., 1939, Natural-gas reserves, Appalachian natural-gas province [abs.]: Am. Petroleum Inst. Drilling and Production Practice, 1938, p. 455.

———1968, Natural gases of the Appalachian basin, in Natural gases in rocks of Paleozoic age, Pt. 3, V. 2 of Natural gases of North America — a symposium in two volumes: Am. Assoc. Petroleum Geologists Mem. 9, p. 1702-1715.

Roth, E. E., and others, 1948, [Appalachian district natural gas reserve estimates] [table], in U.S. Federal Power Commission, Natural gas investigations (Docket G-580) — Report of Commissioners Nelson Lee Smith and Harrington Wimberly: Washington, U.S. Govt. Printing Office, p. 34.

Rothrock, H. E., 1949, Mayfield pool, Cuyahoga County, Ohio: Am. Assoc. Petroleum Geologists Bull., v. 33, no. 10, p. 1731-1746.

Schanz, J. J., Jr., 1957, Historical statistics of Pennsylvania's mineral industries, 1759-1955: Pennsylvania State Univ. Coll. Mineral Industries Expt. Sta. Bull. 69, 94 p.

———1963, Historical statistics of Pennsylvania's mineral industries, 1956-1960: Pennsylvania State Univ. Coll. Mineral Industries Expt. Sta. Bull. 79, 80 p.

———1967, Historical statistics of Pennsylvania's mineral industries, 1961-1965: Pennsylvania State Univ. Coll. Earth and Mineral Sci. Expt. Sta. Bull. 84, 76 p. [p. 36–44].

Schmidt, J. J., and Cottingham, K. C., 1954, The development of underground storage in Ohio, Pt. 2, in Alkire, R. L., compiler, Oil and gas well drilling statistics, 1953: Ohio Div. Geol. Survey Rept. Inv. 20, Petroleum and Nat. Gas Ser. 5, p. 40–47.

Shaw, E. W., and Mather, K. F., 1919, The oil fields of Allen County, Kentucky, with notes on the oil geology of adjoining counties: U.S. Geol. Survey Bull. 688, 126 p.

Shearrow, G. G., 1957, Oil and gas developments in Ohio, 1956: Ohio Div. Geol. Survey Rept. Inv. 32, 29 p. [p. 8–26].

———1958, Oil and gas developments in Ohio, 1957: Ohio Div. Geol. Survey Rept. Inv. 35, 27 p. [p. 1–24].

Shearrow, G. G., 1968, The story of Ohio's southeastern sleeper: Oil and Gas Jour., v. 66, no. 14, p. 210-212.

Shearrow, G. G., and DeBrosse, T. A., 1959, Oil and gas developments in Ohio, 1958: Ohio Div. Geol. Survey Rept. Inv. 37, 29 p., [p. 1–26].

———1960, Oil and gas developments in Ohio, 1959: Ohio Div. Geol. Survey Rept. Inv. 39, 30 p. [p. 1–25].

Simmons, A. C., 1956, Waterflood development of the Weir sand of eastern Kentucky: Kentucky Geol. Survey, ser. 9, Spec. Pub. 9, p. 24–39 [p. 24–30].

Singewald, J. T., Jr., 1954, Gas fields, in Geology and water resources of Garrett County [Maryland]: Maryland Geol. Survey Bull. 13, p. 95–116.

——1960, Oil and gas potential a question mark: World Oil, v. 150, no. 7, p. 112–113.

Sisler, J. D., and Tucker, R. C., 1935, Natural gas in West Virginia, in Ley, H. A. ed., Geology of natural gas: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 989–995.

Sitler, G. F., Jr., and Wehmeyer, K. L., Jr., 1962, Ohio offering potential from the bottom of the column: Oil and Gas Jour., v. 60, no. 2, p. 108–114.

Stack, Wayne, 1965, Some aspects of waterflooding in the Big Sinking field, Lee County, Kentucky: Kentucky Geol. Survey, ser. 10, Spec. Pub. 10, p. 70–93.

Statler, A. T., 1971, Fort Payne production in the Oneida West area, Scott County, Tennessee, in Future petroleum potential of NPC region 9 (Illinois Basin, Cincinnati arch, and northern part of Mississippi Embayment), Symposium, Champaign, Ill., 1971, Proc.: Illinois Geol. Survey Illinois Petroleum 95, p. 94–110.

Stearns, R. G., and Mitchum, R. M., Jr., 1962, Pennsylvania rocks of southern Appalachians: Tennessee Div. Geology Rept. Inv. 14, p. 74–96.

Stout, Wilber, 1916, Geology of southern Ohio, including Jackson and Laurence Counties and parts of Pike, Scioto, and Gallia: Ohio Geol. Survey, 4th ser., Bull. 20, 723 p. [p. 658–670].

Stout, W., Lamborn, R. E., Ring, D. T., Gillespie, J. S., and Lockett, J. R., 1935, Natural gas in central and eastern Ohio, in Ley, H. A. ed., Geology of natural gas: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 897–914.

Sutton, D. G., 1971, Exploration potential of the Rough Creek fault system, in Future petroleum potential of NPC region 9 (Illinois Basin, Cincinnati arch, and northern part of Mississippi Embayment), Symposium, Champaign, Ill., 1971, Proc.: Illinois Geol. Survey Illinois Petroleum 95, p. 69–78.

Sutton, Emmett, 1965, Trempealeau reservoir performance, Morrow County field, Ohio: Jour. Petroleum Technology, v. 17, p. 1391–1395.

Swain, J. F., 1950, Geology and occurrence of oil in Medina sand of Blue Rock-Salt Creek pool, Ohio: Am. Assoc. Petroleum Geologists Bull., v. 34, no. 9, p. 1874–1886.

Thomas, G. R., and Nosow, Edmund, 1960, Drilling outlook remains good: World Oil, v. 150, no. 7, p. 95–100.

Torrey, P. D., 1935, Summary of geology of natural gas fields of New York and Pennsylvania, in Ley, H. A. ed., Geology of natural gas: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 949–987.

U.S. Bureau of Mines, 1924–1931, Mineral resources of the United States [annual volumes for the years indicated]: Washington, U.S. Govt. Printing Office.

——1932–1971, Minerals yearbook [annual volumes for the years indicated]: Washington, U.S. Govt. Printing Office.

[U.S.] Federal Power Commission, 1948, Natural gas investigation (Docket G-580) — Report of Commissioners N. L. Smith and Harrington Wimberly: Washington, U.S. Govt. Printing Office, 498 p. [p. 31–63].

U.S. Geological Survey, 1882–1923, Mineral resources of the United States [annual volumes for the years indicated]: Washington, U.S. Govt. Printing Office.

Wagner, W. R., 1966, Stratigraphy of the Cambrian to Middle Ordovician rocks of central and western Pennsylvania: Pennsylvania Geol. Survey, 4th ser., Bull. G49, 156 p. [p. 5–30].

Wagner, W. R., and Lytle, W. S., 1968, Geology of Pennsylvania's oil and gas: Pennsylvania Geol. Survey Educ. Ser. 8, 28 p.

Walker, F. H., 1955, Oil and gas developments in Kentucky in 1954: Kentucky Geol. Survey, ser. 9, Spec. Pub. 8, p. 28–34.

Walker, F. H., 1955, Exploration extensive in east Kentucky: Kentucky Geol. Survey, ser. 9, Repr. 11 [repr. from Petroleum Engineer, v. 27, no. 9, p. B34, B36, B38, B40, 1955], unpaged.

———1957, Oil and gas developments in Kentucky in 1956: Kentucky Geol. Survey, ser. 9, Spec. Pub. 11, p. 7-15.

———1965, Oil and gas conservation activities: Kentucky Geol. Survey, ser. 10, Spec. Pub. 10, p. 97-101.

Weaver, O. D., 1962, Revival of the Appalachians: Oil and Gas Jour., v. 60, no. 8, p. 88-97.

Webb, E. J., 1969, Geologic history of the Cambrian system in the Appalachian basin: Kentucky Geol. Survey, ser. 10, Spec. Pub. 18, p. 7-15.

———1969, Cambrian exploration in Appalachia: Oil and Gas Jour., pt. 1, v. 67, no. 44, p. 100-101; pt. 2, v. 67, no. 45, p. 266-267.

Whieldon, C. E., and Eckard, W. E., 1963, West Virginia oil fields discovered before 1940: U.S. Bur. Mines Bull. 607, 187 p.

White, I. C., 1899, Petroleum and natural gas, Pt. 4, V. 1, of West Virginia Geological Survey: West Virginia Geol. and Econ. Survey [Rept.], p. 123-378 [p. 125-155].

———1904, Petroleum and natural gas, Pt. 1, V. 1A of West Virginia Geological Survey: West Virginia Geol. and Econ. Survey [Rept.], p. 1-512, 615-625 [p. 25-44].

Wilpolt, R. H., and Marden, D. W.,1959, Geology and oil and gas possibilities of Upper Mississippian rocks of southwestern Virginia, southern West Virginia, and eastern Kentucky: U.S. Geol. Survey Bull. 1072-K, p. 587-656 [p. 593-596] [1960].

Wilson, E. N., 1968, Some aspects of drilling activities in eastern Kentucky in 1965-1966: Kentucky Geol. Survey, ser. 10, Spec. Pub. 15, p. 56-63.

———1971, Fort Payne production in the Cumberland Saddle area of Kentucky and Tennessee, in Future petroleum potential of NPC region 9 (Illinois Basin, Cincinnati arch and northern part of Mississippi Embayment), Symposium, Champaign, Ill., 1971, Proc.: Illinois Geol. Survey Illinois Petroleum 95, p. 79-93.

Woodward, H. P., 1954, A review of the deep Appalachian structural basin: New York Acad. Sci. Trans., ser. 2, v. 17, p. 83-98.

———1955, Some properties of the deep Appalachian basin [abs.]: Am. Petroleum Inst. Drilling and Production Practice, 1954, p. 308.

———1956, The Appalachian region, in Guzman, E. J., ed., Symposium sobre yacimientos de Petroleo y Gas: Internat. Geol. Cong., 20th, Mexico 1956, v. 3, p. 327-349.

———1957, Structural elements of northeastern Appalachians: Am. Assoc. Petroleum Geologists Bull., v. 41, no. 7, p. 1429-1440.

———1957, Chronology of Appalachian folding: Am. Assoc. Petroleum Geologists Bull., v. 41, no. 10, p. 2312-2327.

———1958, Emplacement of oil and gas in Appalachian basin, in Weeks, L. G., ed., Habitat of oil: Tulsa, Okla., Am. Assoc. Petroleum Geologists, p. 494-510.

World Oil, 1960, Offshore areas are main hope: World Oil, v. 150, no. 7, p. 108-110.

Young, D. M., 1953, Natural gas development in southwestern Virginia: Kentucky Geol. Survey, ser. 9, Spec. Pub. 3, p. 27-33.

———1955, Natural gas production in southwestern Virginia: Petroleum Engineer, v. 27, no. 6, p. B29-B32.

———1960, Appalachian Rim is likely area: World Oil, v. 150, no. 7, p. 104-105.

———1971, Oil and gas development in Virginia during 1970: Virginia Minerals, v. 17, no. 2, p. 22-23.

Youse, A. C., 1964, Gas producing zones of Greenbrier (Mississippian) limestone, southern West Virginia and eastern Kentucky: Am. Assoc. Petroleum Geologists Bull., v. 48, no. 4, p. 465-486.

Zaba, Joseph, and Doherty, W. T., 1956, Production, Chap. 6, in Practical petroleum engineers handbook [4th ed.]: Houston, Tex., Gulf Publishing Co., p. 461-751 [p. 685-725].

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

DETERMINATION OF SELENIUM
IN VEGETATION

By T. F. HARMS and F. N. WARD

CONTENTS

TABLES

ABSTRACT

Selenium in vegetation is determined, after wet ignition under reflux with a hot mineral-acid mixture, by the reaction of selenium with 2, 3-diaminonaphthalene to form 4, 5-benzopiazselenol, whose fluorescence is proportional to the selenium concentration. The reaction is sensitive to about 0.02 microgram of selenium and, accordingly, the lower limit of the method is 0.02 parts per million. Recoveries of added selenium are about 90 percent, and the relative standard deviation is on the order of 10–15 percent.

INTRODUCTION

The amount of selenium concentrated in vegetation can be a useful indicator of concealed ore bodies in the soils or rocks supporting the

37

vegetation and can provide a basis for studying the effect of the natural environment on man and animals. For example, when the selenium content of forage crops is below 0.04 ppm, animals suffer from a selenium deficiency, and, when the selenium content exceeds 4 ppm, animals suffer from selenium toxicity (Lakin, 1973; Allaway, 1968). These limits indicate a range for which any method of determining selenium in vegetation has to be useful, but the upper limit is not restrictive.

The main thrust of our work was to develop a short, simple analytical method for determining selenium in vegetation, but the full objectives are broader and include setting base levels of selenium in a wide variety of vegetation in order to locate areas of enrichment or rejection of selenium by a plant.

Previous analytical methods for determining selenium in vegetation have traditionally been long and tedious. Such methods require (1) either wet ignition or digestion of the vegetation under reflux, or ignition in the presence of so-called fixatives (Robinson and others, 1934) to avoid losses, and (2) subsequent distillation to separate the volatile bromide of selenium.

Under reducing conditions, elemental selenium forms in the bromide distillate and colors it light pink to orange. Small amounts of elemental selenium remain in solution, but larger amounts, 0.5 mg or more, precipitate and can be filtered. The selenium content was measured by visually comparing the color of the solution or the precipitate obtained from a sample with that obtained under similar conditions from a known material.

The sensitivities of earlier procedures ranged from 1 to 10 ppm of selenium. Although this range was considered adequate at the time, the recognition that smaller amounts of selenium—less than 0.1 ppm—in animal feed stuff were significant (Schwarz and Foltz, 1957; Muth and others, 1958) triggered new research in methodology and improvements in reagents and equipment. For example, Cheng (1956) developed a colorimetric method based on the reaction of selenium with 3,3'-DAB with a sensitivity of 50 ppb using a 1-cm absorption cell. Later, Parker and Harvey (1962) suggested that 2,3-DAN was a more effective reagent. Several methods based on the reaction of selenium with these reagents have been reported. Dye, Bretthauer, Seim, and Blincoe (1963) developed a spectrophotometric and fluorometric procedure using DAB. Recently, in an effort to establish a standard procedure for evaluation purposes, Olsen (1969) selected the fluorometric method using DAN. Wilkie and Young (1970) have improved the existing DAN procedure by devising a technique for stabilizing DAN.

The fluorometric procedure, based on the reaction of selenium with DAN, is sensitive to about 0.02 μg of selenium. Such sensitivity seems adequate to measure the small amounts in vegetation that are indicative of the average composition of solutions percolating through the Earth's

crust as well as those concentrations required to evaluate the role of selenium in vegetation and its effect on the natural environment of man and animals.

REAGENTS

Ammonium hydroxide (1+4). Add 20 ml of concentrated annomium hydroxide to 80 ml of water.

2,3-DAN. Prepare reagent in partly darkened room by adding 0.1 g of the powder to 10 ml concentrated hydrochloric acid. Allow to stand for about 10 minutes and then dilute to 100 ml with water. Extract the solution with 10-ml portions of hexane by shaking the mixture of solution and hexane vigorously 3 times only, and then by allowing the mixture to separate 3–4 minutes only. Examine each hexane extract with low-intensity ultraviolet light, and when the fluorescence of the extract is negligble, store the aqueous reagent (DAN) in a brown bottle under a one-half-cm layer of hexane. Keep refrigerated and use in partly darkened area.

Ethylenediamine tetraacetic acid–hydroxylamine hydrochloride (EDTA–$NH^2OH \cdot HCl$). Dissolve 9.3 g of disodium salt of ethylene-diamine tetraacetic acid and 25 g of hydroxylamine hydrochloride in 1 l of water.

Formic acid (1+1). Dilute concentrated acid with equal volume of water.

Hexane, reagent grade.

Hydrochloric acid (1+4). Add 20 ml concentrated acid to 80 ml of water.

Nitric acid, reagent grade, redistilled.

Perchloric acid, 70 percent.

Quinine sulfate, 1,000 μg/ml. In a 100-ml volumetric flask dissolve 0.1 g quinine (alkaloid base) in mixture of 1 ml sulfuric acid and 2 ml water. When dissolved, dilute to 100-ml mark with water.

Quinine sulfate, 100 μg/ml. Dilute 10 ml of the 1,000-μg/ml standard to 100 ml with sulfuric acid (1+99), for example, 1 ml concentrated sulfuric acid plus 99 ml water.

Quinine sulfate, 2 μg/ml. Dilute 20 ml of 100-μg/ml standard to 100 ml with sulfuric acid (1+99).

Selenium standard solution, 1,000 μg/ml. In a 50-ml volumetric flask dissolve 0.05 g pure selenium in 5 ml of warm perchloric acid. Dilute to 50-ml mark with water.

APPARATUS

Fluorometer. Galvanek-Morrisson Mark V or similar instrument.[1]

Burner, Fisher type.

Centrifuge, International, size 2, model K or other centrifuge or similar performance capable of 1,200 to 8,500 r/min and centrifugal force of 380 to 4,400 times gravity.

---

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

Oven—Cenco Catalog No. 95106A or similar oven.
pH meter—Any one of several laboratory types is suitable.

PROCEDURE

1. Weigh 1.0 g dry pulverized sample into a 30-ml Kjeldahl flask and add 10 ml of redistilled nitric acid and 1 glass boiling bead.
2. Let stand at room temperature for 4 hours or longer.
3. Heat flask for 15 minutes with low heat, and then gradually increase the heat until the nitric acid is refluxing in the neck of the flask.
4. Allow the nitric acid to reflux for 15 minutes, remove heat, and allow flask to cool for 5 minutes.
5. Add 2 ml perchloric acid, washing down neck of flask with the acid.
6. Heat the flask slowly until the acids reflux, and allow the refluxing to continue for 15 minutes.
7. Increase the heat and boil until the white fumes of perchloric acid appear. Continue fuming for 15 minutes.
8. Remove the flask from heat and allow to cool. Add 2 ml water and 2 ml of (1+4) hydrochloric acid, using both water and acid to wash down the neck and sides of the flask. Mix.
9. Heat the flask in a boiling water bath for 30 minutes and transfer the contents to a 50-ml beaker, rinsing the flask with three or four 2-ml portions of water, and add the rinse water to the 50-ml beaker.
10. Add 2.5 ml of (1+1) formic acid and (1+4) NH_4OH or (1+1) HCl to adjust pH of sample solution to 2. (Use pH meter.)
11. Adjust the volume of the solution to 30 ml with water, add 2 ml of EDTA–$NH_2OH \cdot HCl$ reagent, and mix.
12. Perform steps 13 through 17 in a partly darkened room.
13. Add 2 ml DAN reagent, mix, and place samples in 80°C oven for 20 minutes.
14. Remove samples from oven and allow to cool for 30–40 minutes, then decant sample solution into a 60-ml separatory funnel. Do not rinse beaker.
15. Add 3.0 ml hexane and shake funnel vigorously 3 times only. Allow phases to separate (3–4 min. Drain, discard the aqueous layer, and transfer the hexane layer (upper) to a cuvette.
16. Centrifuge tube for 2 minutes and read the fluorescence of the sample solution, using 4 ml of a 2 $\mu g/ml$ solution of quinine to calibrate the fluorometer.
17. Calculate the amount of selenium by comparing fluorescence of unknowns with that of standard solutions, observing the specific instructions unique to the particular fluorometer used.

DISCUSSION OF STANDARD CURVES

Standard curves, ranging from 0.02 to 0.5 ppm selenium in original

samples, were prepared in two ways. In the first procedure, the standard solutions, which were prepared by dilution of 1,000 μg/ml selenium standard solution, were taken through the entire determination, including digesting with nitric and perchloric acids. In the second procedure, the calculated amounts of selenium were pipetted from dilutions of the 1,000 μg/ml standard solution into 50-ml beakers followed by addition of 1+1 formic acid and pH adjustment, as directed in step 10. Complete steps 11 through 17 for the second procedure.

Fluorescence values obtained by the first procedure are more precise than those obtained by the second procedure. Values obtained by the second procedure tend to be erratic, especially at higher levels, although, in fact, either procedure can be used if the differences are not the deciding factor.

RECOVERY OF ADDED SELENIUM

Increasing amounts of soluble selenium were added to 1-g portions of a sample of alfalfa collected near Delta, Utah, and each portion, including that of the digestion step, was analyzed for selenium (table 13). In general, the recoveries are above 80–90 percent, which is adequate for most applications.

TABLE 13.—*Recovery of added selenium*

[Leaders (...) indicate measurement not made]

Run No.	Selenium		
	Added (μg)	Found (μg)	Recovered (percent)
1...................................	None...............	0.06	...
2...................................	0.02	.07	88
3...................................	.05	.10	91
4...................................:.....	.1	.15	94
5...................................	.2	.23	88
6...................................	.5	.59	105

REPEATABILITY

· The repeatability of the procedure was tested by making repeat determinations on samples of *Atriplex* collected in San Juan County, N. Mex. These determinations were repeated 4 times on 5 samples and 3 times on 4 samples. The number of times of repetition were chosen randomly, and the range of the repeat runs, as well as certain derived data, are shown in table 14. In general the relative standard deviations are about 10 percent, although a few are 20 percent or more.

Another test of precision was provided by a geologist who submitted for analysis 950 plant samples representing 10 species of trees and shrubs from Missouri (J. A. Erdman, oral commun., 1972). Into this group of samples he inserted 40 randomly selected samples in duplicate and randomly interspersed them without knowledge of the analyst. The

TABLE 14.—*Repeatability of selenium determinations*

| Sample No. | Selenium (ppm) | | | | | | Relative standard deviation (percent) |
	1	2	3	4	Mean	Standard deviation	
1.................	0.12	0.13	0.14	...	0.13	0.02	15
2.................	.64	.66	.68	0.78	.69	.06	9
3.................	.67	.68	.72	...	.69	.03	4
4.................	.60	.64	.90	...	.71	.16	23
5.................	1.1	1.4	1.6	1.8	1.5	.3	20
6.................	1.5	1.5	1.5	1.8	1.6	.15	9
7.................	1.5	1.5	1.7	...	1.6	.11	7
8.................	4.5	4.6	4.8	5.2	4.8	.31	6
9.................	4.5	4.5	6.0	6.0	5.2	.87	17

logarithmic variance of the analytical method is 0.00738 which means that the analyses are reproducible within a factor of 1.22 at the 68-percent level of confidence, or within a factor of 1.49 at the 95-percent level of confidence.

The lack of analyzed samples to test the method is an obvious drawback, but the recovery and repeatability data are good enough to suggest the potential application of our procedure to the measurement of small amounts of selenium in vegetation. These amounts may provide clues to concealed ore bodies and information for the assessment of the effect of selenium in the natural environment on man and animals.

REFERENCES CITED

Allaway, W. H., 1968, Control of the environmental levels of selenium, *in* Missouri Univ. Ann. Conf. on Trace Substances in Environmental Health, 2d, Proc.: p. 181–206.

Cheng, K. L., 1956, Determination of traces of selenium-3, 3-diaminobenzidine as selenium (IV) organic reagent: Anal. Chemistry, v. 28, no. 11, p. 1738–1743.

Dye, W. B., Bretthauer, Erich, Seim, H. J., and Blincoe, Clifton, 1963, Fluorometric determination of selenium in plants and animals with 3,3′-diaminobenzidine: Anal. Chemistry, v. 35, no. 11, p. 1687–1693.

Lakin, H. W., 1973, Selenium in our environment, *in* Kothny, E. L., ed., Trace elements in the environment: Am. Chem. Soc., Advances in Chemistry Ser. 123, p. 96–111.

Muth, O. H., Oldfield, J. E., Remmert, L. F., and Schubert, J. R., 1958, Effects of selenium and vitamin E on white muscle disease: Science, v. 128, p. 1090.

Olsen, O. E., 1969, Fluorometric analysis of selenium in plants: Jour. Assoc. Official Agr. Chemists, 52, p. 627–634.

Parker, C. A., and Harvey, L. G., 1962, Luminescence of some piazselenols—A new fluorimetric reagent for selenium: Analyst, v. 87, p. 558–565.

Robinson, W. O., Dudley, H. C., Williams, K. T., and Byers, H. G., 1934, Determination of selenium and arsenic by distillation, in pyrites, shales, soils and agricultural products: Indus. and Eng. Chemistry Anal. Ed., v. 6, no. 4, p. 274–276.

Schwarz, Klaus, and Foltz, C. M., 1957, Selenium as an integral part of Factor 3 against dietary necrotic liver degeneration: Am. Chem. Soc. Jour., v. 79, p. 3292–3293.

Wilkie, J. B., and Young, Mamie, 1970, Improvement in the 2,3-diaminonaphthalene reagent for microfluorescent determination of selenium in biological materials: Jour. Agr. and Food Chemistry, v. 18, no. 5, p. 944–945.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

ATOMIC ABSORPTION DETERMINATION OF BISMUTH, CADMIUM, AND LEAD IN VEGETATION AFTER OXYGEN FLASK COMBUSTION

By T. F. HARMS and F. N. WARD

CONTENTS

TABLES

ABSTRACT

Samples of vegetation and other organic-rich materials are burned in a closed oxygen-containing flask and the combustion products are collected in dilute nitric acid. After pH adjustment, chelates of these elements are formed with ammonium-1-pyrrolidine dithiocarbamate and extracted into MIBK (4-methyl-2-pentanone). The organic solvent is analyzed for bismuth, cadmium, and lead by atomic absorption spectrometry.

INTRODUCTION

The evaluation of different ways of sample breakdown is essential for the development of useful analytical methods for determining trace constituents of vegetation because of the influence of that step on the type

43

of measurement contemplated. Wet digestion of dried vegetative material with hot oxidizing acids under reflux is especially useful to retain volatile elements, such as arsenic, antimony, and mercury, and is also useful for multiple analysis, that is, analyzing for more than one element; however, wet digestions are usually long, tedious, and inappropriate for a large number of samples. Ignition of the dried vegetative material is more easily automated than wet digestions and usually leaves a residue easily solubilized with dilute acids. Without special precaution and care, however, volatile elements are lost, thus limiting the applicability. In the mid-1950's Schöniger (1955) devised a technique of sample breakdown consisting of burning the vegetative matter or other organic material in an atmosphere of pure oxygen contained in a closed flask, and dissolving the combustion products in a suitable acid or base. The ignition technique, called variously oxygen-flask or Schöniger oxidation, is rapid and complete, and, in its use, no volatile products are lost. The acidic or basic collector of the evolved products can be used for multiple analysis, within the limits of the measuring procedure.

The oxygen-flask technique has been modified to meet specific needs, and Gutenmann and Lisk (1960) and Gutenmann and others (1961) provide examples of such modifications. These workers analyzed a variety of vegetative material, including apples, potatoes, cherries, and cabbage, for arsenic, bromine, chlorine, manganese, mercury, and nickel. Belcher, MacDonald, and West (1958) burned metallo-organic compounds containing one or more of several elements in the oxygen flask and achieved total recovery of boron, cadmium, magnesium, and zinc. Recovery of lead and bismuth was incomplete, and arsenic appeared to be lost completely. However, other volatile elements, such as selenium, are recovered satisfactorily after such an oxidation step (Allaway and Cary, 1964). Thus, less volatile elements, such as copper, lead, and perhaps bismuth, would likely be retained, depending partly on the treatment after the ignition.

The sample size of dried vegetative matter is limited to 1 g or less when oxygen flask ignitions are used. This limitation emphasizes a need for as much sensitivity as possible for the final measurement of the element. If atomic absorption measurements are used, a severalfold increase in sensitivity can be achieved by extracting the metal with a suitable organic solvent and aspirating the solvent in the flame of a laminar-flow burner. Mulford (1966) found that the formation of metal chelates which are preferentially soluble in suitable organic solvents offers a means of increasing the sensitivity. He studied several chelating agents and suitable organic solvents and concluded that the APDC had the greatest potential. Previously, Malissa and Schöffmann (1955) had studied this reagent as well as several other carbamates. They showed that several carbamates, including the ammonium salt, will chelate a

large number of elements over a wide range in pH values. Among the elements that are not thus chelated are the alkalis and alkaline earths.

Allan (1961) determined the content of copper in vegetation and soils by atomic absorption spectroscopy using APDC and ethyl acetate or MIBK to extract the chelated copper. Willis (1962) determined the content of lead, bismuth, mercury, and nickel in urine with an extraction step using APDC and methyl n-amyl ketone. These examples serve to illustrate the widespread use of the carbamate-ketone combinations to eliminate possible interferences and to increase the sensitivity of the measurements of the elements. The predominant use of MIBK probably reflects a fact of economy and availability, rather than a demonstrated superiority.

Accordingly, our procedure includes a Schöniger oxidation and collection of the combustion products in dilute nitric acid followed by pH adjustment, addition of APDC, extraction of chelated metals into MIBK, and finally aspiration of the solvent in an atomic absorption instrument.

REAGENTS AND APPARATUS

Ammonium hydroxide, 5 M. Dilute 340 ml concentrated ammonium hydroxide to 1,000 ml with metal-free water.

Ammonium 1-pyrrolidine dithiocarbamate (APDC), 1 percent. Dissolve 1 g of APDC in 100 ml water. Prepare fresh daily.

Bismuth, 1,000 μg/ml. Dissolve 0.5 g metal in 500 ml concentrated nitric acid. Prepare 100- μg/ml standard solution by tenfold dilution of concentrated standard solution with water. Prepare less concentrated standard solutions by tenfold dilution with 1 M nitric acid.

Cadmium standard solution, 1,000 μg/ml. Dissolve 0.114 g cadmium oxide in 10 ml 8 M nitric acid. Dilute to 100 ml with water. Prepare 100- μg/ml and 10- μg/ml solutions by tenfold dilutions with 1 M nitric acid.

Lead standard solution, 1,000 μg/ml. Dissolve 0.16 g lead nitrate in small amount of water. Add 5 ml concentrated nitric acid and dilute to 100 ml with metal-free water. Prepare 10- μg/ml solution by tenfold dilution, keeping nitric acid concentration the same as for the more concentrated standard solution.

4-methyl–2-pentanone (MIBK).

Oxygen, gaseous.

Magnetic stirrer and Teflon-coated spin bars.

Combustion flasks, oxygen, 2-l capacity. Thomas-Lisk type with ignition basket, safety outlet, and balloon.

Die—0.5-in. diameter.

pH meter.

Press, hydraulic—Range up to 20,000 lb/in^{2}g.

Perkin-Elmer model 303 or equivalent.

PROCEDURE

1. Weigh 0.5 g of dried vegetation into the 0.5-in. die, and press into a pellet with the hydraulic press.
2. Remove pellet from die, wrap in small filter paper cut with 1-in. tail, and place in basket attached to stopper of a 2-1 combustion flask.
3. Place a magnet in the flask and add 60 ml 0.5 M nitric acid.
4. Flush the flask with oxygen for approximately 30 seconds, ignite tail of paper enclosing vegetation pellet and quickly insert the paper with the pellet into flask.
5. After combustion is complete, place flask on a magnetic stirrer and stir vigorously for 30 minutes so that the ash remaining in the ignition basket is dissolved in the acid.
6. Transfer the solution to a 150-ml beaker and rinse basket and flask 3 times with distilled water, adding these portions of rinse water to the solution in the beaker.
7. Adjust the pH to 2.2 using 5 M ammonium hydroxide.
8. Transfer the solution to a 125-ml separatory funnel, add 2.5 ml of 1 percent APDC solution and mix well.
9. Add 10 ml of MIBK and shake vigorously for 2 minutes.
10. Allow the phases to separate, transfer the organic layer to a stoppered test tube, aspirate in atomic absorption instrument, and record the absorbance reading.

PREPARATION OF STANDARDS

To series of 150-ml beakers each containing 60 ml of 0.5 M nitric acid add individually 0.0, 0.1, 0.2, 0.6, and 1.0 ml of 0.001 percent standard cadmium solution. In the same order, add individually 2.0, 1.4, 0.8, 0.2, and 0.0 ml of 0.01 percent standard lead solution. Adjust pH of each solution to 2.2 with 5 M ammonium hydroxide and add 2 ml APDC. Extract aqueous solutions with 20 ml of MIBK. These standard solutions will contain 0.0, 0.05, 0.1, 0.3, and 0.5 μg/ml of cadmium and 10, 7, 4, 1, and 0 μg/ml of lead in the organic layer. Aspirate the ketone (organic layer) as in step 10 of procedure.

EXPERIMENTS AND RESULTS

Recoveries of added amounts of bismuth, cadmium, and lead were tested first by adding increasing amounts of these elements to filter papers and burning these papers in an oxygen flask and absorbing the combustion products in 0.5 M nitric acid. Then, these solutions were atomized directly in an atomic absorption instrument, and the meter readings were compared with those obtained from dilute nitric acid solutions to which similar amounts of standard solutions had been added

TABLE 15.—*Recovery of added element after ignition (aqueous)*
[Leaders (...) indicate that data are missing]

| Element added | Concentration of element in final volume (ppm) | Meter reading | |
		After direct addition	After ignition
Bismuth......................	5	10	10
	10	20	20
Cadmium	0.5	...	22
	1.0	50	47
	1.5	...	71
	2.0	100	96
Lead...........................	1 .	...	3
	2	5	6
	5	.....	14
	10	30	28
	30	90	...

directly (table 15). The meter readings in the right-hand column show recoveries of 96–100 percent, and one can conclude that bismuth, cadmium, and lead are recovered after combustion.

Similar experiments were made to test the recovery when solvent extraction is used to enrich the analyte and thereby achieve greater sensitivity. Enrichment may be as great as tenfold with bismuth and lead; fivefold with cadmium. Accordingly, increasing amounts of bismuth, cadmium, and lead were pipetted from standard solutions onto filter paper, allowed to dry, and combusted in an oxygen flask. After ignition, the acidic solution of the combustion products was shaken with an MIBK solution of APDC, and the carbamates of bismuth, cadmium, and lead were extracted into the organic solvent. The MIBK solutions were aspirated in an atomic absorption instrument, and the meter readings were compared with those obtained from MIBK solutions of the metal carbamates extracted directly from nitric acid solutions containing similar amounts of standard solutions as added to filter papers (table 16).

Similar meter readings after ignition and after direct addition show that the losses of bismuth, cadmium, and lead during combustion are insignificant, and one can conclude that sample solution of vegetation can be prepared in this manner. The recovery data in tables 15 and 16 show also that insignificant losses of bismuth, cadmium, and lead occur during combustion of organic materials in an oxygen flask. Other elements tested, such as cobalt, nickel, and zinc, were not recovered uniformly and, hence, are not included in this paper.

Determinations of bismuth, cadmium, and lead in various organic-rich materials after oxygen flask combustion were compared with those obtained after hot-acid digestion. The bismuth values were below the limit of detection, but the cadmium and lead were measurable, and the comparison is given in table 17.

TABLE 16.—*Recovery of added element after ignition (organic solvent)*

[Leaders (...) indicate that reading is missing]

		Meter reading	
Element added	Concentration of element in final volume (ppm)	After direct addition	After ingition
Bismuth......................	0.5	11	9
	1.0	24	18
	2.0	45	34
	4.0	78	73
Cadmium	.1	20	23
	.2	42	46
	.5	98	101
Lead...........................	.1	...	3
	.5	5	5
	1	10	10
	2	21	19
	5	50	50
	10	100	98

TABLE 17.—*Determination of lead and cadmium after sample digestion*

Sample No.	Material	Lead (ppm)		Cadmium (ppm)	
		Hot acid	Oxygen flask[1]	Hot acid	Oxygen flask[1]
1	Cedar wood........................	< 2.5	<5	<1	<1
2	Cedar bark	2.5	< 5	2	2
3	Oak leaves.........................	< 2.5	< 5	2.6	3
4	Cedar leaves......................	5	5	<1	<1
5	Asparagus..........................	5	5	5.4	6
6	Oak leaves.........................	2.5	5	<1	1
7	Onions..............................	5	8	6.8	5
8	Chestnut oak leaves..........	7.5	8	<1	1.4
9	Poplar leaves	10	10	38	40
10..............	...do................................	15	10	40	38
11..............	Elm leaves.........................	10	11	5.6	5
12..............	...do................................	10	12	5.8	6
13..............	Poplar leaves	12	15	44	46
14..............	Onions..............................	18	18	12	12
15..............	Oak bark...........................	20	20	1.1	0.8
16..............	Yellow birch leaves	38	32	17	15
17..............	Poplar bark.......................	30	35	61	64
18..............	Poplar twigs.....................	50	52	40	42
19..............	Yellow birch roots...........	55	54	13	12
20..............	Yellow birch wood...........	95	94	22	22
21..............	Yellow birch twigs...........	160	160	13	12

[1]Our procedure.

The wet digestion of dry material is with a perchloric-nitric acid mixture (Ward and McHugh, 1964). Cadmium was measured in the acidic sample solution by atomic absorption spectrometry; lead was measured either by atomic absorption spectrometry or by colorimetry (Ward and others, 1963) depending on the lead level.

Data in tables 15–17 indicate that multiple analyses can be made on a single small sample of organic-rich material, using our procedure.

REFERENCES CITED

Allan, J. E., 1961, The determination of copper by atomic absorption spectrophotometry: Spectrochim. Acta, v. 17, p. 459–466.

Allaway, W. H., and Cary, E. E., 1964, Determination of submicrogram amounts of selenium in biological materials: Anal. Chemistry, v. 36, no. 7, p. 1359–1362.

Belcher, Ronald, MacDonald, A. M. G., and West, T. S., 1958, The determination of metals in organic compounds by the closed flask method: Talanta, v. 1, p. 408–410.

Gutenmann, W. H., and Lisk, D. J., 1960, Rapid determination of mercury in apples by modified Schöniger combustion: Jour. Agr. Food Chemistry, v. 8, no. 4, p. 306–308.

Gutenmann, W. H., Saint John, L. E., Barry, D. L., Jones, E. D., and Lisk, D. J., 1961, Modified Schöniger combustion for determination of residues of arsenic, bromide, chloride, manganese, and nickel in pesticide-treated plant material: Jour. Agr. Food Chemistry, v. 9, no. 1, p. 50–51.

Malissa, H., and Schöffmann, E., 1955, Über die Verwendung von substituierten Dithiocarbamaten in der Mikroanalyse. III: Mikrochim. Acta, 1, p. 187–202.

Mulford, C. E., 1966, Solvent extraction techniques for atomic absorption spectroscopy: Atomic Absorption Newsletter, v. 5, p. 88–90.

Schöniger, W., 1955, Eine mikroanalytische Schnellbestimmung von Halogen in organischen Substanzen: Mikrochim. Acta, 1, p. 123–129.

Ward, F. N., Lakin, H. W., Canney, F. C., and others, 1963, Analytical methods used in geochemical exploration by the U.S. Geological Survey: U.S. Geol. Survey Bull. 1152, 100 p.

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.

Willis, J. B., 1962, Determination of lead and other heavy metals in urine by atomic absorption spectroscopy: Anal. Chemistry, v. 34, no. 6, p. 614–617.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

DETERMINATION OF MERCURY IN NATURAL WATERS, PLANTS, AND SOILS BY A COLD-VAPOR PROCEDURE

By MARGARET E. HINKLE and GEORGE L. CRENSHAW

CONTENTS

ILLUSTRATION

TABLES

ABSTRACT

The recent interest in mercury and its behavior in the natural environment has triggered the development of new, rapid, and sensitive analytical procedures for mercury. In our method, the elemental and ionic mercury fractions of natural waters and acid digestates of plants and soils can be determined. After ionic mercury is reduced to the elemental form with stannous chloride, a stream of nitrogen flushes the mercury vapor from the reaction flask into the mercury-vapor absorption detector. From 10 to 400 nanograms of mercury can be detected in the sample solution. Mercury amounts determined by this method were as little as 0.05 micrograms per litre in water samples and as much as 49,000 parts per billion in mud samples.

INTRODUCTION

During the last few years, interest has increased rapidly in the associations and behavior of mercury in the natural environment. Mercury has been used in geochemical exploration as a pathfinder element in the search for concealed ore deposits (Hawkes and Webb, 1962, p. 73; McCarthy, Gott, and Vaughn, 1969). Studies of the geochemical associations of mercury are leading to the understanding of mercury transport and deposition (White, 1967; Dickson and Tunell, 1968). Recently, mercury lost from industrial processes has spurred the study of mercury in the environment (U.S. Geological Survey, 1970).

Several analytical procedures are now in use for determination of mercury in various kinds of samples. The most sensitive methods involve measurement of mercury vapor by a mercury-vapor absorption detector utilizing the 2,537-angstrom line of mercury. The mercury in samples of water is often concentrated in some way prior to measurement, either by amalgamation on silver (Hinkle and Learned, 1969; Fishman, 1970) or by extraction with dithizone (Chau and Saitoh, 1970). Omang (1971) treated water samples with $KMnO_4$ and H_2SO_4 to decompose organic interferences and, then, reduced the mercury to elemental form and measured it directly from the solution by flameless atomic absorption spectrophotometry. The most convenient method of soil analysis is by direct heating of the sample in an induction furnace and subsequent measurement of evolved mercury (Vaughn and McCarthy, 1964). Extensions of this method, useful for organic-containing soils, include acid digestions of the sample, followed by reduction with stannous ion (Hatch and Ott, 1968), and dithizone extraction of the acid digestate (Pyrih and Bisque, 1969) prior to measurement of the mercury by atomic absorption spectrophotometry. The most thorough method of sample dissolution for analysis of mercury in plants is digestion of 0.5–1 g

ground air-dried plant material under reflux with a mixture of nitric, sulfuric, and perchloric acids (Ward and McHugh, 1964); the mercury is then determined colorimetrically with dithizone.

In our procedure, mercury is measured in a variety of samples—waters, soils, and plants—by one generalized method. A special feature of our method is the use of a bulbous-shaped reaction flask, which permits more efficient mixing of sample solution and reagents than conventional reaction bottles. This feature is especially useful for plants and for soils and sediments containing organic materials. Our procedure eliminates the tedious dithizone color development of acid-digested plants and soils.

Elemental and ionic mercury species in natural waters are separated and measured by this procedure. Mercury-containing solutions disproportionate into mercuric, mercurous, and elemental mercury forms, depending on such conditions as availability of complexing agents and temperature. The concentrations of different species occurring in a natural water may indicate the mode of transport of the mercury.

Elemental mercury is measured by flushing mercury vapor from an acidified water sample into the mercury-vapor absorption chamber in a stream of nitrogen. The ionic mercury is reduced to the elemental form with stannous chloride, and the elemental mercury thus produced is swept into the detection unit with nitrogen. Acid digestates of soil and plant samples are also treated with stannous chloride and the reduced mercury flushed into the vapor absorption detector for measurement.

From 10 to 400ng can be measured in a 50-ml sample solution.

EQUIPMENT

Reaction flask train (fig. 1):

> *Reaction bubbler flask.*—Pyrex, commercially available from Ace Glass, Inc.,[1] Vineland, N.J.: The reaction flask is 8 in. high and has a 3½-in.-long neck with ℥29/42 fitting. The body of the flask expands to a 2¼-in. diameter, and will hold 50 ml when half filled. Below the body, the flask narrows to a ¾-in. diameter for the remaining 3½-in. of total length.

> *Reaction bubbler flask head.*—Pyrex, commercially available from Ace Glass, Inc., Vineland, N.J.: The reaction bubbler flask head holds both the gas inlet and outlet tubes and fits into the ℥29/42 fitting of the reaction bubbler flask. The 9-in.-long gas inlet tube extends down nearly to the bottom of the narrow part of the reaction flask and ends in a fritted glass dispersion plug. The gas outlet tube is fitted with a ball-joint connection.

> *Outlet to dryer and mercury detector.*—Ball-joint connection

[1] Use of a specific brand name does not necessarily constitute endorsement of the product by the U.S. Geological Survey.
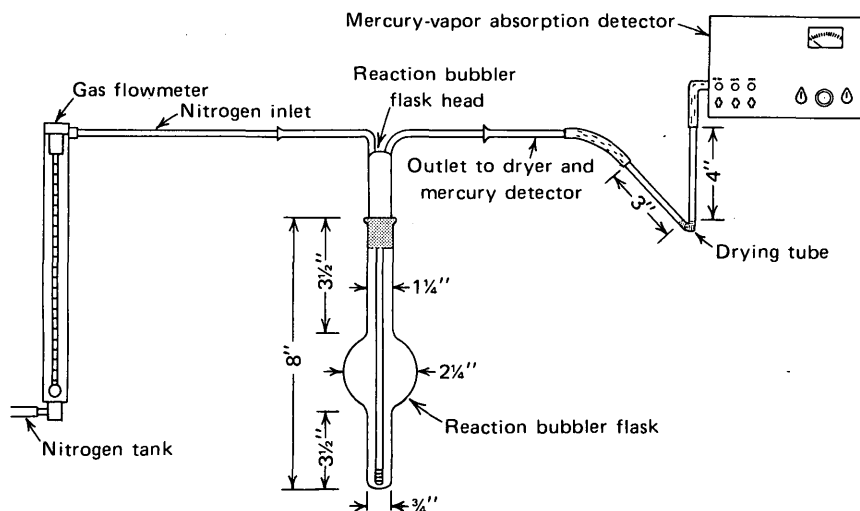
FIGURE 1.—Diagram of mercury detector. Not to scale.

Reaction flask train (fig. 1)—Continued

Outlet—Continued

attached to Tygon tubing. The ball joint is connected to the gas outlet of the reaction bubbler flask head, and the Tygon tubing is connected to the drying tube. Wash with sulfuric acid, water, and acetone and dry thoroughly under a heat lamp between determinations.

Drying tube.—Bend an approximately 7-in. length of Pyrex glass tubing (O.D. 18 mm standard wall) into a V shape. Make at least six of these drying tubes. Place a 0.5-g scoop of $Mg(ClO_4)_2$ drying agent in each bent tube. Attach one end of a drying tube to the reaction flask with the outlet connector and attach the other end of the drying tube to the mercury detector with Tygon tubing. The glass drying tube should be washed, rinsed with acetone, and dried under a heat lamp between determinations.

Mercury-vapor absorption detector.—An atomic-absorption instrument utilizing the 2537-angstrom line of mercury (described by Vaughn and McCarthy, 1964) was used. A chamber with quartz windows can be placed in beam of a hollow cathode lamp, mercury passed into the chamber and measured as in flame spectroscopy.

Nitrogen inlet (from gas flowmeter to reaction flask).—Tygon tubing with ball-joint connection.

Gas flowmeter.—Nitrogen should be delivered to the sample solution in the reaction flask at a reproducible rate of about 1,000 cm^3/min. Attachments are Tygon tubing and a ball-joint connection.

Heat lamp, or drying oven.

Syringe, 10-cm³ capacity.

Special equipment for solution of plants:

    250-ml round-bottom flasks.

    Heating mantles for flasks.

    Variable rheostats.

    Water-cooled condensers for the round-bottom flasks.

    Glass boiling beads.

Special equipment for solution of rocks, soils, and sediments:

    Alcohol lamp or hotplate

    Pyrex test tubes or flasks with ℥ necks

    ℥ – Standard taper. 12-in. air condensers to fit test tubes or flasks.

REAGENTS

All reagents should be prepared with demineralized water.

Hydrochloric acid, reagent grade.

Sulfuric acid, reagent grade.

Stannous chloride solution: Dissolve 10 g of $SnCl_2$ in 100 ml 6 N HCl.

Magnesium perchlorate, anhydrous.

Nitrogen, dry.

Mercury standard solution: Dissolve 0.1354 g of reagent-grade mercuric chloride in 100 ml of 1 N sulfuric acid. This standard contains 1,000 μg/ml mercury. By dilution with water, prepare fresh a 1-μg/ml (1,000-ng/ml) standard as needed.

Mercury-saturated air: Place a few grams of mercury in a Dewar flask Stopper the flask with a 2-hole rubber stopper. Through one hole insert a thermometer, and through the other hole insert a glass tube fitted with a rubber membrane stopper through which the syringe can be inserted to withdraw mercury-saturated air.

Additional reagents for waters containing H_2S:

    Sodium chlorate: Dissolve 10.6 g of $NaClO_3$ in 1,000 ml water.

    Hydroxylamine hydrochloride: Dissolve 50 g $NH_2OH \cdot HCl$ in 100 ml water.

Additional reagents for solution of plants:

    Nitric acid, reagent grade.

    Perchloric acid, reagent grade.

    Hydrogen peroxide, 30 percent.

    Antifoaming agent, Dow-Corning Antifoam B; solution of 25 ml diluted to 100 ml with water.

Additional reagents for solution of rocks, soils, and sediments:

    Potassium bromide, reagent grade.

    Potassium persulfate, reagent grade, saturated aqueous solution.

    Phenol solutions: Dissolve 1 g of reagent in 100 ml water.

    Sulfuric acid, 18 N: Mix equal volumes of acid and water.

PROCEDURE FOR DETERMINATIONS

ELEMENTAL AND IONIC MERCURY IN WATER

[Limited to maximum volume of 50 ml water]

Place 5 ml of hydrochloric acid in the reaction flask. Bubble N_2 through it for 1–2 minutes to remove mercury contamination and undissolved gases. Add 50 ml of water sample or a suitable smaller aliquot of sample diluted to 50 ml with mercury-free water. Attach the outlet and drying tubes, connecting the reaction flask to the mercury detector. Bubble N_2 through the system and record the meter reading. This reading represents the elemental Hg content.

To determine ionic Hg in the same sample aliquot, turn off the nitrogen flow, replace the outlet and drying tubes in the delivery train, remove the reaction flask head and add 2 ml of $SnCl_2$ reagent to the sample. Reassemble the train and again bubble N_2 through the apparatus. Record the meter reading.

Run a blank on the $SnCl_2$ solution after each determination.

MERCURY IN WATER SAMPLES HAVING AN H_2S ODOR

H_2S (Hydrogen sulfide), if present, must first be oxidized because it causes a false reading on the meter. Place 5 ml of hydrochloric acid in the reaction flask and bubble N_2 through it for 1–2 minutes. Remove reaction flask head and add 5 ml $NaClO_3$ solution. Add the sample solution and mix well. Add 5 ml hydroxylamine hydrochloride solution and mix well. Attach the delivery train connecting the reaction flask to the mercury meter. Raise the reaction flask head and add 4 ml $SnCl_2$ solution. Replace the reaction flask head, bubble N_2 through the system, and record the meter reading.

Run blanks on the solutions of $SnCl_2$, $NaClO_3$, and $NH_2OH \cdot HCl$.

MERCURY IN PLANTS

Place 1 g of ground air-dried plant material in a round-bottom flask. Add 5 ml each of nitric, sulfuric, and perchloric acids. Digest under reflux for 4 hours. Cool slightly, add 2 ml of 30 percent hydrogen peroxide, cool to room temperature, and dilute with water to 100 ml.

Place 5 ml hydrochloric acid in the reaction flask and bubble N_2 through it for 1–2 minutes. Remove reaction flask head, and place sample aliquot in the reaction flask. Hydrochloric acid is not necessary for aliquots of acid digestates 20 ml and over. Add water to 50 ml volume. Add 1–2 drops of antifoaming agent, if necessary. Add 2 ml $SnCl_2$ solution for sample aliquots 25 ml and under; add 4 ml $SnCl_2$ for aliquots greater than 25 ml. Attach outlet and drying tubes, connecting the reaction flask and mercury meter. Bubble N_2 through the system. Record meter reading.

Run blanks on $SnCl_2$ solution, acid digestion mixture, and anti-foaming agent.

MERCURY IN WATER SAMPLES OF HIGH ORGANIC CONTENT OR WHICH CONTAIN AMMONIA GAS

Use 25-ml aliquots of water samples. Follow the same procedure as that for the determination of mercury in plants.

MERCURY IN SOILS, ROCKS, AND SEDIMENTS

The sample is attacked as described by Ward and Bailey (1960).

Place 0.1–0.2 g of -80-mesh sample in flask or tube. Add 0.05 g KBr. Add 3 ml (1+1) H_2SO_4. Attach 12-in. air condenser. Heat over alcohol flame or on hotplate to incipient boil. Add 0.5 ml saturated $K_2S_2O_8$ solution through the top of the air condenser. Alternately, heat to incipient boil and remove the flask from the heat so that Br_2 fumes do not escape out the top of the condenser for 1 minute, keeping the flask as hot as possible without losing fumes. Add another 0.5 ml saturated $K_2S_2O_8$ solution and heat for 1 more minute. Cool the flask. When cool, wash down the air condenser with water. Add 0.5 ml aqueous phenol solution to remove excess bromine.

To measure mercury, pour entire sample solution and solid materials into the reaction flask. Rinse out test tube with water and add rinsings to the reaction flask. Add water to about 50 ml. For samples containing more than 400 ng of mercury, the sample solution in the test tube should be diluted with water to a specific volume, and aliquots taken of this dilution. Add 2 ml $SnCl_2$ solution. Attach outlet and drying tubes, connecting the reaction flask to the mercury detector. Bubble N_2 through the system. Record the meter reading.

Run blanks of $SnCl_2$ solution and digestion reagents.

STANDARDS

IONIC MERCURY

To a series of reaction bubbler flasks each containing a mixture of 5 ml hydrochloric acid, 2 ml stannous chloride solution, and about 40 ml water which has been previously degassed with nitrogen, add individually 10, 20, 40, 80, 100, 200, and 400 ng of Hg^{+2}. Successively, connect each flask to the nitrogen inlet and to the outlet to dryer, and bubble nitrogen through the flask. Record meter readings for the different amounts of mercury.

ELEMENTAL MERCURY

Place about 50 ml water in the reaction flask. With a syringe, inject a given volume of mercury vapor into the outlet tube. At any given tem-

perature, mercury-saturated air contains a definite concentration of mercury. The concentration of mercury in 1 cm³ of mercury-saturated air can be calculated from knowledge of the vapor pressure of mercury at different temperatures (Weast, 1968, p. D111) and use of the ideal gas law $PV=nRT$: 1 cm³ of mercury-saturated air contains 13 ng of Hg at 20°C, 18 ng of Hg at 24°C, and 25 ng of Hg at 28°C.

Attach the outlet tube of the reaction flask and bubble N_2 through the system to sweep the mercury into the detector unit. Record the meter reading, and repeat for different volumes of mercury-saturated air. Plot meter readings versus amounts of mercury on log-log paper.

Calculation

For soils, sediments, plants:

$$\frac{\mu g}{1} Hg = \frac{\text{Total volume (ml)}}{\text{aliquot (ml)}} \times \frac{\text{nanograms measured}}{\text{sample weight (grams)}}$$
$$\times \frac{10^{-3} \mu g}{ng} \times \frac{10^3 ml}{1}.$$

For water:

$$\frac{\mu g}{1} Hg = \frac{ng \text{ measured}}{ml \text{ of sample}} \times \frac{10^{-3} \mu g}{ng} \times \frac{10^3 ml}{1}.$$

DISCUSSION

Elemental mercury standards must be prepared by injecting Hg vapor directly into the inlet to the drying tube and detector part of the reaction train. The standards cannot be prepared by injecting Hg vapor into aqueous solutions, because some of the elemental mercury dissociates and is not swept out of solution by the nitrogen flow. The dissociated Hg can be recovered by adding $SnCl_2$ and be reduced to the elemental form, but this reduced mercury is then considered to be ionic. About 25–35 percent of elemental Hg was lost by dissociation in attempts to prepare standards by injecting Hg vapor by syringe through a rubber membrane stopper into water and 1 N HCl solutions. In contrast, all the Hg vapor injected into solutions can be recovered by amalgamation on silver screens (Hinkle and Learned, 1969).

The special shape of the reaction flask is beneficial for good mixing when nitrogen is bubbled through the solution. Thorough but rapid mixing of $SnCl_2$ with the sample solution is needed to quickly reduce ionic Hg to elemental Hg, so that the Hg vapor will be pushed through the detector in a plug. A flow rate of 1,000 cm³/min N_2 will sweep a plug of elemental Hg vapor from this flask and, thus, give a sharp response from the detector. Mercury standards measured by reaction in the bulbous-shaped flask gave approximately twice the scale deflection on the mercury detector as did the same standards measured in a reagent bottle-type reaction flask.

Nitrogen is used in this procedure because it is free of mercury, and no special filters are necessary as would be needed with an air stream. A tank of N_2 is also convenient to transport to the field, and the slow flow rate of 1,000 cm^3/min makes N_2 economical to use. The flow rate of N_2 should be kept constant because the standard curve changes for different flow rates.

The tube through which the plug of Hg vapor is pushed into the detector must be kept dry. Small amounts of moisture along the interior walls of the tubing will absorb Hg vapor and cause analytical results to be low. Even when no moisture is visible in the tubing, the $Mg(ClO_4)_2$ dehydrating agent will become warm due to water absorption. About 0.5 g of $Mg(ClO_4)_2$ absorbs moisture adequately for each analysis; smaller amounts are inadequate; larger amounts, such as 1 g, tend to absorb Hg vapor as well as the moisture.

Hydrochloric acid is commonly contaminated by mercury. In addition to the mercury contamination, HCl and Cl_2 fumes from the acid often cause high blank values. Both of these problems are overcome by degassing the hydrochloric acid with nitrogen for 1–2 minutes prior to adding the sample to the reaction flask; the acid should give a zero instrument reading. Usually, the 2–4 ml of $SnCl_2$ will have a negligible blank value, but sometimes the $SnCl_2$ solution absorbs mercury from the air; hence, a blank should always be run. Also, blanks should be run on other reagents used in any particular analysis. Hydrochloric acid is preferred over sulfuric or nitric acid in this procedure, to help avoid oxidation of elemental Hg to ionic Hg.

Ammonia gas in a water sample will cause a high mercury reading on the mercury detector. Conversely, dissolved organic substances, such as petroleum, will prevent any Hg present from leaving the water sample and, thus, will cause low mercury values. Both ammonia and organic interferences can be eliminated by an acid reflux of the water sample. When organic interference in a sample is suspected, aqueous Hg standards cannot be recovered, then the sample should be refluxed with nitric, sulfuric, and perchloric acids.

H_2S in a water sample will also cause a high Hg reading on the detector. In addition, mercury in a water sample may be in the form of an HgS^{-1} complex which breaks down to elemental sulfur on acidification; mercury may adsorb on the sulfur and not be swept out by the nitrogen. Strong oxidizing agents, such as Br_2, rapidly oxidize S^{-2} to SO_4^{-2} (Latimer, 1952, p. 71). Addition of 10 ml of freshly prepared chlorine-water solution immediately removes all evidence of H_2S or elemental sulfur in a sample; excess Cl_2 is reduced by addition of hydroxylamine hydrochloride, and also by doubling the usual volume of $SnCl_2$. Sodium chlorate solutions stronger than 0.1 M cannot be used in preparation of the chlorine water, because the mercury recovery drops,

either from chlorine-mercury complex formation or from oxidizing conditions too strong to be reduced by the hydroxylamine hydrochloride and stannous chloride.

Halides generally do not interfere with mercury determinations on natural water samples. As much as 1 M (35,000 μg/ml) chloride ion, in addition to the chloride from the hydrochloric acid and chlorine water, can be tolerated before mercury recovery is affected. All added mercury can be recovered from solutions containing 1,000 μg/ml bromide, much more bromide than is found in natural brines. In unpolluted natural waters, iodide ion is the only halide which may occur in sufficient concentrations to interfere with mercury recovery. As much as 30 μg/ml iodide ion (concentration of a brine) in a water sample can be tolerated; however, 40-50 μg/ml iodide ion causes a 50-percent drop in mercury recovery. Any natural water sample with a concentration of 40-50 μg/ml iodide must be diluted with iodide-free water before analysis.

To check out possible interferences from other elements, aliquots of various dissolved metals were added to a solution of 100 ng Hg standard in 50 ml 1 N HCl and carried through the reduction procedure. No interferences were seen from 2,000 μg Cd or from 5,000 μg As, Sb, or Pb in the 50-ml sample solution. These concentrations are unlikely in natural water samples and in diluted acid digestions of most plant materials and soils. Metals easily reduced to their elemental form by $SnCl_2$ were found to lower mercury recovery by adsorbing the elemental Hg; a few other metals also cause low mercury recovery (table 18).

TABLE 18.—*Concentrations of elements causing loss in mercury recovery*

[μg in 50-ml sample solution]

Pd	0.02	Tl	100
Te	.05	Cu(II)	200
Se	.5	In	300
Pt	2	Ag	[1]1,000
Au	5	Zn	2,000

[1]AgCl precipitate.

The presence or absence of undigested soil, sediment, and rock materials in the reaction flask has no effect on mercury recovery when the sample is freshly digested. If the acid digestate has been standing for 1 or 2 days before analysis, some mercury might adsorb onto the undigested solid material and cause low mercury recovery if the solid material is not placed in the reaction flask along with the sample solution. Analysis of the sample soon after digestion is the best procedure.

RESULTS

The precision of our method was checked for both elemental and ionic mercury. To check the precision for elemental Hg, different volumes

of mercury vapor were repeatedly injected into the detector, following the procedure for preparation of the standard curve. The relative standard deviation was 10 percent or less for approximately 6.5 ng of injected elemental Hg (table 19). The precision of ionic Hg was checked by running aqueous mercury standards through the procedure. The relative standard deviation ranged from 40 percent at the threshold value to 4 percent at the midrange value (table 20), showing acceptable precision for the quantities of ionic Hg measured. Total mercury includes both elemental and ionic mercury and replicate analyses of total mercury content of waters, soils, and plants also yielded acceptable data (table 21).

To check the accuracy of our procedure, various kinds of samples were analyzed by our method as well as by the following methods: (1) Water samples were analyzed by the silver screen method (Hinkle and Learned, 1969); (2) sediment samples were run by direct heating in an induction furnace and measurement of evolved Hg vapor in a mercury detector (Vaughn and McCarthy, 1964); and (3) plant samples were run by the complete acid digestion—dithizone colorimetric method (Ward and McHugh, 1964). The mercury content of samples analyzed by our procedure compares favorably with that of samples analyzed by other procedures (table 21).

Our procedure has proved useful for the determination of mercury in a variety of samples, such as water and aqueous solutions of plants,

TABLE 19.—*Precision of elemental mercury measurement*

| Hg vapor added (ng) | Number of determinations | Mercury recovered (ng) | | | Relative standard deviation (percent) |
		High	Low	Mean and standard deviation	
6.5	5	7	6.5	6.7±0.3	4.5
13	11	14	11	13.8±1.4	10.1
26	9	29	23	26±2	7.7
65	3	66	62	64±2	3.1

TABLE 20.—*Precision of ionic mercury measurement*

| Hg^{+2} added (ng) | Number of determinations | Mercury recovered (ng) | | | Relative standard deviation (percent) |
		Low	High	Mean and standard deviation	
5	7	2	9	5±2	40
10	5	8	12	10±2	20
20	5	19	24	20±2	10
50	5	45	54	50±4	8
100	9	84	115	100±10	10
200	5	180	200	195±8	4
400	6	360	420	400±19	4.8

TABLE 21.—*Results of mercury analyses, in parts per billion*

[Leaders (...) indicate sample not analyzed; Nd, not detected]

Sample No.	Sample type	Cold vapor method (this paper)				Induction furnace and direct vapor absorption detection[1]		Acid digestion and dithizone detection[2]		Silver screen method[3]	
		Number of determinations	Low	High	Mean and standard deviations	Number of determinations	Mean	Number of determinations	Mean	Number of determinations	Mean
		Total mercury found									
FRS-6.........	Stream sediment, high organic............	2	300	500	400±100	3	300	...	...	...	...
MRS-4.........	Stream sediment............	2	640	1,025	830±140	6	700	...	...	...	...
PBD-3.........	..do............	3	950	1,450	1,210±205	6	1,210	...	...	...	...
FPP-5.........	Mud pot in Yellowstone National Park............	3	48,000	50,000	49,000±1,000	6	46,500	...	...	...	...
NA-5.........	Plant............	2	400	470	435±35	...	...	4	<200	...	...
NA-2.........	..do............	7	1,000	2,500	1,700±720	...	...	12	1,700	...	...
NA-3.........	..do............	2	2,900	3,100	3,000±1,000	...	...	12	4,000	...	...
H-17............	Water, high H_2S content.	6	0.05	0.16	0.1±0.04	...	...	...	...	3	0.1
H-2............	Water, high NH_3 content	3	.2	.4	0.3±0.08	...	...	...	...	3	.8
H-5............	Water, high H_2S content.	6	.8	1.7	1.2±0.3	...	...	...	...	3	.2
71-2207.........	Water............	4	.3	.6	0.5±0.1	...	...	...	...	3	.6
H-11............	..do............	4	.7	1.2	1.0±0.2	...	...	...	...	3	1.6
		Ionic mercury									
71-2207.........	Water............	2	0.5	0.6	0.55±0.05	...	...	...	...	...	...
H-11............	..do............	3	.2	.4	0.3±0.1	...	...	...	...	...	...
		Elemental mercury									
71-2207.........	Water............	2	Nd	0.06	<0.05	...	...	...	...	...	...
H-11............	..do............	3	0.3	.6	0.5±0.2	...	...	...	...	...	...

[1]Vaughn and McCarthy (1964). [2]Ward and McHugh (1964). [3]Hinkle and Learned (1969).

soils, and sediments. Measurement of mercury is quick, and the data obtained by our method are comparable to data obtained by older methods.

REFERENCES CITED

Chau, Yiu-Kee, and Saitoh, H., 1970, Determination of submicrogram quantities of mercury in lake waters: Environmental Sci. and Technology, v. 4, no. 10, p. 839–841.

Dickson, F. W., and Tunnell, G., 1968, Mercury and antimony deposits associated with active hot springs in the western United States, in Ore deposits of the United States, 1933–1967, v. II: Am. Inst. Mining, Metall., and Petroleum Engineers (Graton-Sales Volume), p. 1673–1701.

Fishman, M. J., 1970, Determination of mercury in water: Anal. Chemistry, v. 42, no. 12, p. 1462–1463.

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

Hawkes, H. E., and Webb, J. S., 1962, Geochemistry in mineral exploration: New York, Harper and Row, 415 p.

Hinkle, M. E., and Learned, R. E., 1969, Determination of mercury in natural waters by collection on silver screens, in Geological Survey research 1969: U.S. Geol. Survey Prof. Paper 650-D, p. D251–D254 [1970].

Latimer, W. M., 1952, The oxidation states of the elements and their potentials in aqueous solutions [2d ed.]: New York, Prentice-Hall, 392 p.

McCarthy, J. H., Jr., Gott, G. B., and Vaughn, W. W., 1969, Distribution and abundance of mercury and other trace elements in several base- and precious-metal mining districts, in Exploration for mineral resources—Idea Conf., 4th Ann. 1968: New Mexico Bur. Mines and Mineral Resources Circ. 101, p. 99–108.

Omang, S. H., 1971, Determination of mercury in natural waters and effluents by flameless atomic absorption spectrophotometry: Anal. Chim. Acta, v. 53, no. 2, p. 415–420.

Pyrih, R. Z., and Bisque, R. E., 1969, Determination of trace mercury in soil and rock media: Econ. Geology, v. 64, no. 7, p. 825–828.

U.S. Geological Survey, 1970, Mercury in the environment: U.S. Geol. Survey Prof. Paper 713, 67 p.

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 [1965].

Ward, F. N., and Bailey, E. H., 1960, Camp and sample-site determination of traces of mercury in soils and rocks: Am. Inst. Mining, Metall., and Petroleum Engineers Trans., v. 217, p. 343–350.

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 [1965].

Weast, R. C., ed., 1968, Handbook of chemistry and physics, 49th ed.: Cleveland, Ohio, Chemical Rubber Co. 2,092 p.

White, D. E., 1967, Mercury and base-metal deposits with associated thermal and mineral waters, in Geochemistry of hydrothermal ore deposits: New York, Holt, Rinehart and Winston, p. 575–631.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

DETERMINATION OF MOLYBDENUM IN NATURAL WATERS AND BRINES AFTER SEPARATION USING A CHELATING RESIN

By H. M. NAKAGAWA and F. N. WARD

CONTENTS

ILLUSTRATION

TABLES

ABSTRACT

The use of the molybdenum content in streams, other natural waters, and brines as a guide to mineralization requires a rapid field method for determining 1 microgram per litre or less of molybdenum in the water. After a preliminary collection on the

65

chelating resin A–1, and subsequent elution with dilute alkali, the molybdenum is measured by a field-applicable colorimetric procedure based on the formation of the thiocyanate complex of molybdenum(V). Experiments show that a resin column 5 centimetres long and 1.2 centimetres in diameter is adequate for collection of as much as 300 micrograms of molybdenum from a sample adjusted to a pH of about 1 and that the flow rate through the column should not be greater than 20 millilitres per minute. The alkaline elution removes the collected metal and regenerates the resin simultaneously. The method provides for the direct determination of molybdenum in the field and eliminates the need for transporting bulky water samples to the laboratory.

INTRODUCTION

Inasmuch as molybdenum in the form of molybdenite is a minor constituent of many base-metal deposits, one promising method of geochemical prospecting for such deposits is based on the detection of traces of molybdenum in the dispersion products of a base-metal deposit. Under mild alkaline conditions molybdenum is relatively mobile, and small amounts ultimately reach the natural-water systems. The measurement of the small amounts of molybdenum in natural waters and brines thus provides a means of searching out molybdenum-rich ore bodies, and such measurements require a rapid and moderately accurate method for determining small amounts of the element.

The kind of analytical method needed has a direct relation to the concentration of molybdenum in natural waters, and the range in concentration can only be tentatively established because of the scarcity of published data. In a study limited to surface waters of Colorado, Voegeli and King (1969) detected molybdenum in 89 percent of samples collected. The amount detected ranged from 1 to 3,800 μg/l. On the basis of these data and other meager data available, the lower limit of a really useful method should be near 1 μg/l. The achievement of such a limit demands a sensitive method, and the ultimate field application limits the type of method.

Molybdenum reacts with a number of reagents to form colored complexes which are necessary for the simple colorimetric determinations widely used in the field (Hawkes, 1957). The reaction with thiocyanate is extremely sensitive, and the amber-colored molybdenum thiocyanate is readily extracted into an immiscible solvent, such as isopropyl ether. In the laboratory, the absorbance of as little as 5×10^{-9} g of molybdenum extracted into isopropyl ether as the thiocyanate complex is readily measured. Thus, with a favorable partition coefficient, 5 ml of a water or brine containing 1 μg/l of the molybdenum is enough for easy measurement in the laboratory. Using visual comparisons of absorption, we established that 20 times more of the sample is required for positive measurement in the field. For example, a volume of at least 100 ml is needed for the field measurement of molybdenum, but only 5 ml is needed for the laboratory measurement. Solvent extraction of a large volume with

only 1 ml of solvent is impracticable; hence, some other means of concentration of the molybdenum is needed. Moreover, solvent extraction of natural waters is often undesirable because of the color imparted to the solvent by small amounts of dissolved organic matter and certain inorganic salts.

Ion-exchange resins offer a better means of concentrating and separating the molybdenum than does the direct application of solvent extraction. Such resins (Morachevskii and Gordeeva, 1957; Canney and Hawkins, 1960) have been used to collect traces of metals from natural waters, but these resins often failed with brines and other waters containing large amounts of dissolved solids. In our method, the chelating resin we used (A-1, also known as Chelex 100)[1] differs primarily from more familiar resins, such as Dowex 1 or Dowex 50, by the kinds of active groups attached to the styrene divinyl-benzene copolymer matrix. Chelating resin A-1 contains active iminodiacetate groups, and the arrangement of these groups results in a resin showing a marked affinity for heavier elements, such as copper, lead, or zinc. The resin is particularly suited to removing traces of heavy metals from sea water (Riley and Taylor, 1968) and from solutions of concentrated salts (Forberg and Lundgren, 1960), as well as from industrial waste (Biechler, 1965). These applications suggest the use of the chelating resin A-1 for collecting small amounts of molybdenum from natural waters in which the salt content may range from that of fresh waters from a mountain spring to that of saline waters from a desert environment.

REAGENTS AND APPARATUS

Chelating resin A-1, 50–100 mesh. Available as Chelex 100 from Bio-Rad Laboratories, Richmond, Calif.

Ferrous ammonium sulfate, reagent grade, 1 percent. Dissolve 1 g of salt in 100 ml of 0.1 M sulfuric acid.

Hydrochloric acid, reagent grade, concentrated.

Isopropyl ether, practical grade, is suitable if it is free of peroxides. To test for peroxides, shake 5 ml of the ether with 5 ml of an acidified aqueous solution of potassium iodide. If the aqueous solution shows more than a faint tinge of the yellow color, which is due to the free iodine produced by the reaction of peroxides with iodide, the ether contains appreciable quantities of peroxides and is unsatisfactory for use. Immediately before use of isopropyl ether, shake 25 ml ether with 2 ml each of potassium thiocyanate and stannous chloride reagents.

Phenolphthalein indicator. Dissolve 0.05 g reagent in 50 ml alcohol and add 50 ml water.

Potassium thiocyanate, 10 percent aqueous. Dissolve 10 g salt in 100

---

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

ml water. Prepare fresh daily.

Sodium hydroxide, 3 M. Dissolve 120 g reagent in 1 litre water.

Standard molybdenum solution, 100 μg/ml. Dissolve 0.075 g pure molybdic anhydride in dilute sodium hydroxide, dilute with water to about 50 ml, add hydrochloric acid until solution is just acid, and make up to 500 ml with water. Less concentrated standard solutions are prepared as needed by a tenfold dilution of the concentrated standard solution with water.

Stannous chloride solution, 10 percent. Dissolve 10 g dihydrate in 17.2 ml concentrated hydrochloric acid and dilute to 100 ml with water.

Water, rendered metal free by passing it through any of several commercially available resins.

Columns, glass. Approximate dimensions, length 30 cm; inside diameter, 1.3 cm. The columns drain through a Teflon valve attached by an aluminum coupling. Several columns available commercially from SGA Scientific, Inc., are satisfactory.

Glass wool.

pH meter or other device to measure pH; pH papers are unsatisfactory.

Separatory funnels, 125 ml, Squibb type.

Borosilicate glass evaporating dish.

Hotplate.

PROCEDURE

Pretreatment of resin and separation of molybdenum: May be done in the laboratory or in the field at temporary quarters, such as trailer camps.

Pretreatment of resin: Prepare a slurry by soaking the chelating resin A-1 overnight in about 1½ times its volume of 3 M sodium hydroxide. Pack glass wool into the bottom of the resin column until the thickness is about 2 cm, then pour a sufficient amount of the resin slurry into the column to produce a resin column 5 cm in length. Wash resin with 125 ml water, and drain all but about 2 ml of the wash water.

Separation of molybdenum: Adjust pH of the sample solution—usually 100 ml—to 1.1±0.5 with dilute hydrochloric acid, and percolate sample solution downward through the resin column at a flow rate not exceeding 20 ml per minute. Wash resin with 25 ml water, and discard wash water.

Elute the resin column with 10-20 ml of 3 M sodium hydroxide and wash resin with water—10-20 ml—until the column length is 5 cm. Neutralize the combined eluant and wash water—the volume should not exceed 40 ml—with concentrated hydrochloric acid, using a drop of phenolphthalein as an indicator, and, finally, make the volume up to 50 ml with water.

Estimation of molybdenum: Transfer the 50-ml sample solution to a 125-ml separatory funnel and add the following reagents, shaking after each addition:

     1 ml ferrous ammonium sulfate solution,

     5.5 ml concentrated hydrochloric acid,

     3 ml potassium thiocyanate solution, and

     3 ml stannous chloride solution.

In laboratory:

Cool mixture to about 25°C, add 4 ml isopropyl ether, and shake funnel for 30 seconds. Allow phases to separate, then drain aqueous phase into a 150-ml beaker. Transfer ether to 5-ml volumetric flask and return the contents of the beaker to the funnel. Add 2.5 ml isopropyl ether and repeat the extraction procedure. Allow phases to separate; drain and discard aqueous phase and combine ether extracts. Make up to mark on volumetric flask with fresh ether.

Mix contents of volumetric flask and determine molybdenum content by measurement of absorbance at 470 nm and subsequent reference to a previously established standard curve.

In field:

Cool mixture to about 25°C, add 1 ml isopropyl ether and shake funnel for 1 minute. When phases separate, hold funnel vertically and view the shallow layer of the organic solvent at right angles to the funnel. Compare color of sample solution with that of standard solutions, prepared as follows:

To a series of 125 ml separatory funnels each containing 50 ml water add individually 0.1, 0.2, 0.5, 1.0 and 10.0 μg molybdenum from standard molybdenum solution. To each funnel add ferrous ammonium sulfate solution, hydrochloric acid, thiocyanate, and stannous chloride as directed under estimation. Cool mixtures in each funnel to about 25°C, add 1 ml isopropyl ether to each, and shake each funnel for 1 minute.

EXPERIMENTAL WORK AND RESULTS

Collection of molybdenum on resin: In order to maintain uniform conditions, the pH of each water sample is adjusted to 1.1±0.5 and the resin column is washed with a definite volume of water before percolation of the sample through the resin. Either nitric acid or hydrochloric acid can be used to adjust the pH of each water sample, but with the nitric acid the optimum pH range for best recovery of molybdenum is small, as measured by our procedure. A difference of as little as 0.1 of a pH unit often resulted in losses of as much as 2 μg of the added molybdenum. In contrast to the pH adjustment of the sample with nitric acid, the hydrochloric acid adjustment is less critical. Aliquots of water sample containing 10 μg molybdenum were ad-

justed to different pH values, and the aliquots were passed down
through a resin column. Satisfactory recoveries were obtained with
the initial pH values, ranging from 0.7 to 1.5, as shown in figure 2.
The optimum initial pH range is wide; hence, the close adjustment
of the pH is less critical when hydrochloric acid is used in place of
nitric acid.
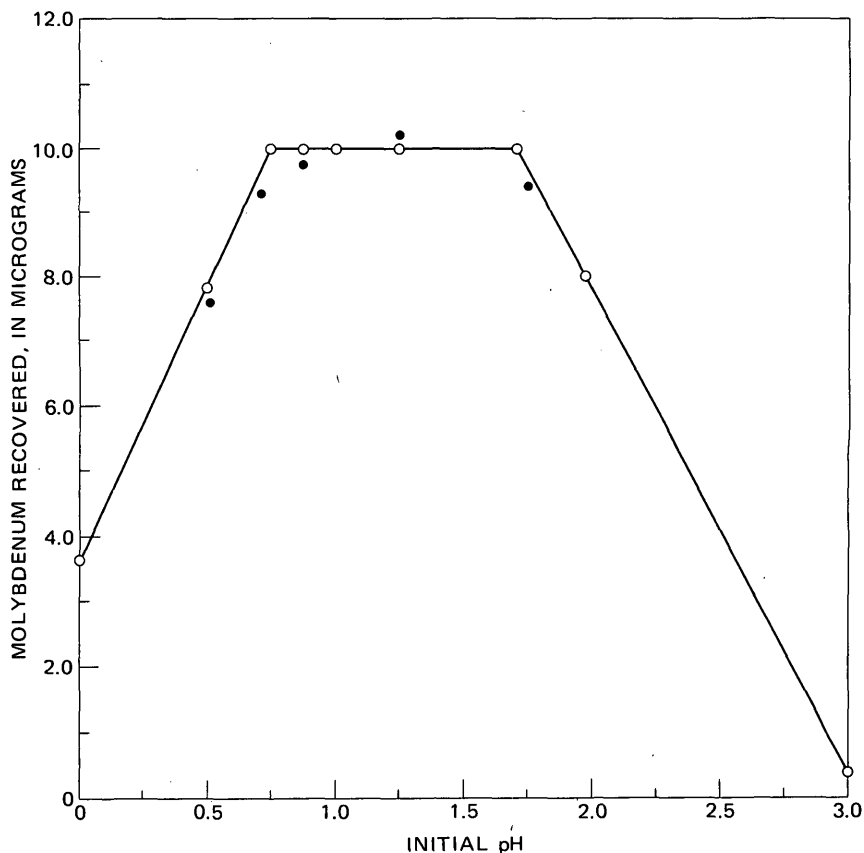
FIGURE 2.—Recovery of molybdenum after different initial pH adjustments with hydro-
chloric acid (circle) and nitric acid (dot).

Elution of molybdenum: Nitric acid and hydrochloric acid are both
    useful for eluting the collected molybdenum, but each has certain dis-
    advantages. When nitric acid is used, excellent recoveries are made
    from new batches of resin, but with successive use and regeneration
    of a given batch of resin, the recoveries of added molybdenum vary
    erratically. Nitric acid appears to have a degenerative effect on the
    resin.

Hydrochloric acid is satisfactory except for the fact that molybdenum is subsequently determined by its reaction with thiocyanate, and this reaction proceeds maximally in a narrow concentration range of hydrochloric acid. Start, preferably, with a neutral solution and add the requisite amount of acid to produce the optimum acid concentration. The acid concentration of the eluent could conceivably differ from time to time, and such differences would require a careful adjustment for maximum reaction between the molybdenum and the thiocyanate.

Because the resin is easily converted to the sodium form upon contact with dilute sodium hydroxide, we assumed that the sodium ion would displace any molybdenum or other metal ions on the resin. Indeed, this reaction does proceed rapidly and has the further advantage of eluting the collected molybdenum and regenerating the resin in the same step. The alkaline effluent poses no problem in the subsequent analysis.

Elution time: The alkaline elution causes the resin to swell, which, in turn, affects the flow rate of the elutriant. The swelling occurs rapidly enough to be the chief factor in controlling the flow of the effluent, and other factors, such as hydrostatic head, are insignificant. In fact, the flow increases slightly with swelling.

Interferences: Of the elements which Sandell (1959, p. 646) listed as possible interferences in the thiocyanate method—chromium, cobalt, copper, uranium, vanadium, niobium, rhenium, and tungsten—only the last three could cause appreciable interference in our procedure. The tungsten interference can be eliminated by the addition of sodium citrate or tartrate. The rhenium interference can be removed by a modification introduced by Hoffman and Lundell (1939) in which molybdenum and rhenium are separated by a preferential reduction of the molybdenum with mercury and extraction of the molybdenum(V) thiocyanate into an immiscible solvent. Rhenium is not reduced and, consequently, does not form an extractable species. Mercurous nitrate has also been proposed for the preferential molybdenum reduction (Tarayan and Musheggan, 1958).

Niobium may possibly interfere in our method. The recovery of 5 μg of added molybdenum in the presence of 25, 50, or 100 μg of niobium is approximately 80 percent. However, the occurrence of niobium in natural water is so infrequent that this element can probably be ignored.

Flow rate of sample solution: In order to measure the optimum flow rate for complete recovery of the molybdenum in a water sample, 10 μg of the element was added to each of several 100-ml portions of water; then the portions were passed through a 6-in. column at different rates. Data in table 22 show the molybdenum recovery at

different flow rates of feed. Complete recoveries are observed at flow rates of 20 ml per minute or less; thus, 1 litre of sample passes through the resin column in less than 1 hour.

Volume of sample: If one stipulates 0.1 μg as the minimum amount of molybdenum definitely perceptible under the conditions of our procedure, theoretically, he could analyze waters containing 1 ppb of molybdenum with only a 100-ml sample. He could analyze waters containing 0.1 ppb of molybdenum using a 1-litre sample. In a field trial of the procedure, we analyzed natural waters containing as little as 0.2 ppb.

Length of resin bed: Sample solutions containing 10 μg of molybdenum were adjusted to a pH of 1.1 with hydrochloric acid, and each solution was passed through resin columns of different length, as shown in table 23. A 2.5-cm column shows poor recovery and a 5-cm column shows satisfactory recovery; columns of greater length are unnecessary except when testing samples containing relatively large amounts of molybdenum. Such amounts can be determined directly without separation on a resin.

TABLE 22.—*Molybdenum recovery at different flow rates of feed*

Sample No.	Molybdenum added (μg)	Flow rate of feed (ml/min)	Molybdenum recovered (μg)
1......................	10	33	8.7
2......................	10	25	9.5
3......................	10	20	10
4......................	10	10	10

TABLE 23.—*Molybdenum recovery from different column lengths*

Sample No.	Molybdenum added (μg)	Length of column (cm)	Molybdenum recovered (μg)
1......................	10	2.5	8.8
2......................	10	5	9.8
3......................	10	7.5	10
4......................	10	10	10
5......................	10	15	10

Preliminary experiments show that a 15-cm column collects as much as 10,000 μg of molybdenum from a water sample before permitting a breakthrough—for example, failure to react with the metal. At the 10-μg level, a 5-cm column is adequate, and it is of interest to determine the maximum amount of molybdenum that may be collected on that column. Such data are shown in table 24, and one may readily conclude

that in the range from 10 to 1,000 μg of added molybdenum, about 90 percent is collected on the 5-cm column. Long before the quantity of molybdenum in a 50- to 100-ml water sample exceeds 1,000 μg, the determination can be made directly (L. C. Huff, oral commun., 1966). To date, no brines have contained more than 1,000 μg of molybdenum in a 100-ml sample. Thus, the 5-cm column is entirely satisfactory in practice.

TABLE 24.—*Molybdenum retention on column*

Sample No.	Molybdenum added (μg)	Molybdenum recovered from column, (μg)	Sample No.	Molybdenum added (μg)	Molybdenum recovered from column, (μg)
1	10	10	6	300	310
2	20	19	7	400	370
3	50	52	8	500	450
4	100	100	9	1,000	870
5	200	194			

Precision and accuracy: In order to measure the overall precision of the separation and estimation, standard solutions—one containing 2 μg, another 5 μg, and another 10 μg of molybdenum—were prepared and passed through the column. The data for several repeat determinations are given in table 25.

TABLE 25.—*Repeatability of molybdenum determinations*

Sample No.	Molybdenum added (μg)	Number of determinations	Molybdenum found (μg)			
			Low	High	Mean and confidence limits at 95-percent level	Relative standard deviation (percent)
1	2	5	1.6	2.	1.8±0.2	11.1
2	5	9	4.3	5.3	4.9±0.3	8.2
3	10	38	8.8	10.7	10.0±0.2	5.0

The overall accuracy of the method was tested in the following manner: Appropriate volumes of different samples of natural water were evaporated to dryness in a borosilicate glass evaporating dish placed on a hotplate. Spectrophotometric (Ward and others, 1963) and spectrographic determinations were made on these residues and compared with spectrophotometric determinations made after resin collection (table 26). Except for sample SM–1, the data obtained by all three methods are comparable, and the agreement is good enough to suggest that the spectrophotometric method after resin collection is

TABLE 26.—*Determination of molybdenum in water and water residues*

[Leaders (...) indicate data not available]

Sample no	Location	pH	Molybdenum in material analyzed (μg/l water)		
			Residue analyzed		Water (resin collection)
			Spectrographic	Spectrophotometric	Spectrophotometric
TB–3...........	Arizona...........	8.8	5	5	8
SM–12.........	...do................	8.6	7	6	6
SM–10.........	...do................	7.9	9	8	...
SM–8...........	...do................	8.0	...	12	10
SM–1...........	...do................	8.2	8	20	15
SM–5...........	...do................	7.8	12	18	16
SM–3...........	...do................	8.0	23	30	31
3420	Wyoming........	8.4	27	...	32
SM–11.........	Arizona...........	8.3	39	44	46
TB–1...........	...do................	7.9	40	55	60
3415	Wyoming........	8.2	73	...	85

applicable to waters containing different amounts of total dissolved solids, varying fourfold or fivefold.

Molybdenum bound in an uncharged organic complex would not be collected on the ion-exchange resin; hence, one might expect the quantities collected on the resin. All the data obtained to date are on waters from the Western States, and significant differences are not observed, possibly because of the small amount of organic matter present in these samples.

The method is relatively short and has already proved to be useful in defining the distribution of molybdenum in several areas of the Southwestern States.

REFERENCES CITED

Biechler, D. G., 1965, Determination of trace copper, lead, zinc, cadmium, nickel, and iron in industrial waste waters by atomic absorption spectrometry after ion exchange concentration on Dowex A-1: Anal. Chemistry, v. 37, no. 8, p. 1054–1055.

Canney, F. C., and Hawkins, D. B., 1960, Field application of ion-exchange resins in hydrogeochemical prospecting, *in* short papers in the geological sciences: U.S. Geol. Survey Prof. Paper 400-B, p. B89–B90.

Forberg, Sevald, and Lundgren, Svante, 1960, Activation analysis of trace metals in sodium triphosphate: Anal. Chemistry, v. 32, no. 9, p. 1202–1203.

Hawkes, H. E., 1957, Principles of geochemical prospecting: U.S. Geol. Survey Bull. 1000-F, 355 p.

Hoffman, J. I., and Lundell, G. E. F., 1939, Separation and colorimetric determination of rhenium and molybdenum: U.S. Natl. Bur. Standards Jour. Research, v. 23, p. 497–508.

Morachevskii, Yu. V., and Gordeeva, M. N., 1957, Separation of molybdenum from iron, aluminum, and calcium by means of ion-exchange anionates: Zavodskaya Lab., v. 23, p. 1066–1067.

Riley, J. P., and Taylor, D., 1968, Chelating resins for the concentration of trace elements from sea water and their analytical use in conjunction with atomic absorption spectrophotometry: Anal. Chim. Acta, v. 40, p. 479–485.

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

Tarayan, V. M., and Musheggan, L. G., 1958, New method of separation of rhenium from molybdenum: Akad. Nauk Armyan. SSR Doklady, v. 27, p. 157–160.

Voegeli, P. T., and King, R. U., 1969, Occurrence and distribution of molybdenum in the surface water of Colorado: U.S. Geol. Survey Water-Supply Paper 1535-N, 32 p.

Ward, F. N., Lakin, H. W., Canney, F. C., and others, 1963, Analytical methods used in geochemical exploration by the U.S. Geological Survey: U.S. Geol. Survey Bull. 1152, 100 p.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

DETERMINATION OF FLUORINE IN SOILS AND ROCKS BY KNOWN-INCREMENT ADDITION AND SELECTIVE-ION ELECTRODE DETECTION

By George L. Crenshaw and F. N. Ward

CONTENTS

TABLE

ABSTRACT

In the determination of fluorine in soils and rocks by known-increment addition and selective-ion electrode detection, the sample is sintered with a sodium carbonate-potassium nitrate flux, and the sinter is leached with water. The leachate is treated with a citric acid–sodium citrate buffer, and fluorine is measured in the buffered solution by a selective-ion electrode connected to an expanded scale meter equipped with a known-increment scale for direct addition of known amounts of fluoride.

INTRODUCTION

In the early 1900's Hillebrand (1919) determined fluorine in silicate and carbonate rocks by fusing the powdered sample with alkali carbon-

ate to render fluorine water-soluble, separating alumina and other inter-
ferences by ammonium carbonate precipitation, and measuring the solu-
bilized fluorine either by weighing precipitated calcium fluoride or by
noting its bleaching effect on a yellow color produced by the action of
hydrogen peroxide on titanate solution. In the early 1930's Willard and
Winter (1933) reported a method in which they separated the fluorine
from the acid digestate of the sample by steam distillation. The distilled
fluorine was measured by titration with thorium nitrate in the presence
of alizarin as an indicator. The impact of their work was so great that
the Willard and Winter procedure became the method of choice, and
subsequent variations or improvements attest to its caliber. Reynolds
and Hill (1939) incorporated many of these improvements in a method
for determining fluorine in natural phosphates and phosphatic fertil-
izers. Later, Peck and Smith (1964) offered an improved fluorine mea-
surement based on the stable colored complex formed between fluorine
and a zirconium-SPADNS (sodium salt of 2- (4-sulfophenylazo)-1,8-di-
hydroxynaphthalene-3,6-disulfonic acid) reagent. Their method retained
the steam distillation step, especially for silicate rocks in which the
fluorine contents are in the range of a few hundred parts per million.

Trace amounts of fluorine have also been separated by gaseous dif-
fusion of hydrogen fluoride and collected on an alkali-impregnated
support (Singer and Armstrong, 1954; Hall, 1963; and Stuart, 1970). Mea-
surements of the separated fluorine involved titration and colorimetry,
except in the method of Stuart which made use of the selective-ion elec-
trode that had been introduced previously by Frant and Ross (1966) for
sensing fluoride ion activity. Singer and Armstrong (1968) also utilized
the capability of the fluoride electrode for measuring the fluorine con-
tent of bone.

Measurement of the fluoride activity by the fluoride electrode grew
in popularity because of the high degree of selectivity and the ease of
making the measurements by immersing the electrode into an aqueous
solution and reading the developed potential on a sensitive voltmeter.
Because of the good selectivity of the electrode, separation of fluorine
from the bulk of the sample appeared unnecessary, and once again atten-
tion focused on fusions to effect sample solution. Typical examples of
such application to silicate rocks and other geologic materials are those
described by Ficklin (1970) and Ingram (1970).

Selective-ion electrodes sense activity. Except in dilute solutions, the
activity and concentration are seldom equivalent. They are related to
each other in the following way:

$$A = \gamma C_f,$$

where
   A is the activity of fluoride ion,
   C_f is concentration of free fluoride ion, and
   γ is the activity coefficient.

The activity coefficient varies with total ionic strength, approaching unity in dilute solutions and decreasing with increased ionic strength. From an analytical perspective one is interested in concentration, and, ideally, measurements with a selective-ion electrode should be made on dilute solutions. Measurements on concentrated solutions require some means of estimating the ionic strength so as to relate activity and concentration. Again, ideally, selective-ion electrode measurements on dilute solutions are not always feasible because of the innate sensitivity of the sensing element of the electrode, and measurement on concentrated solutions is hindered by the difficulty of estimating ionic strength because of the possible assortment of ions present in solutions of geologic materials. At low pH values, 3-4, fluorine appears to form a complex species not sensed by the electrode (Srinivasan and Rechnitz, 1968), and at high pH values hydroxyl ion interferes, especially with fluoride levels less than about 1×10^{-5} M. Thus, a practicable method requires pH control and knowledge of, or ability to repeat, ionic strength levels. Achieving the latter by dilution is not so practical as the addition of a high ionic strength solution, called swamping, so as to nullify relatively small variations due to different kinds of geologic materials.

The pH requirement and the need to achieve similar ionic strength levels suggest the use of appropriate swamping agents and buffers, such as a mixture of acetic acid and its salts, which provide a great buffer capacity. In order to meet these conditions, Frant and Ross (1968) devised an acetate buffer, a mixture of acetic acid, sodium chloride, and sodium citrate, which—when properly balanced for acidity and mixed with the sample solution in equal volumes—not only automatically adjusted the pH to the optimum value but also swamped the ionic potential so that variations from sample to sample exerted no appreciable effect on the response of the electrode. The buffer is known by the acronym TISAB, which stands for total ionic strength adjustment buffer. This buffer not only maintained an optimum pH but also contained a small amount of sodium citrate or disodium salt of cyclohexylene dinitrilotetra-acetic acid to inhibit the formation of aluminum fluoride not sensed by the electrode. The buffer also contained a relatively large amount of sodium chloride to maintain a large ionic potential so that variations in the ionic potential of the different sample solutions have no significant effect on the total ionic potential.

The composition of the TISAB used in our procedure is listed under "Reagents." We modified this by increasing the citrate content, but it did not prove to be advantageous.

The sample is sintered with an alkali carbonate-nitrate flux, and the water-soluble fluorine is mixed with the acetate buffer to accomplish the pH adjustment and to provide a nearly constant ionic strength in the analyte solution. The potential due to fluoride-ion activity is measured by adding a known amount of fluoride standard solution and observing the change caused by the addition.

REAGENTS AND APPARATUS

Citric acid–sodium citrate reagent. Dissolve 193 g of citric acid in 1 litre of solution. Mix with an equal volume of sodium citrate solution, which is prepared by dissolving 294 g of the salt in 1 litre of solution. Adjust the pH of the mixture to 3 with 6 M hydrochloric acid.

Flux. Mix two parts by weight of sodium carbonate with one part of potassium nitrate.

Hydrochloric acid, 6 M. Mix equal volumes of concentrated acid and fluorine-free water.

Sodium fluoride standard solution. 1,000 μg/ml. Dissolve 2.21 g of reagent grade salt in 1 litre of fluorine-free water. Prepare appropriate dilute standard solutions by dilution of stock solution.

Sodium hydroxide, 5 M. Dissolve 200 g of sodium hydroxide in 1 litre of water.

TISAB (Frant and Ross, 1968). Prepare by dissolving 171 ml glacial acetic acid in 1,500 ml water and adding 174 g sodium chloride. Add 0.9 g sodium citrate and adjust the pH to 5.5 with 5 M sodium hydroxide solution. Dilute to 3 l with water.

Expanded-scale pH meter with known-increment scale. Orion model 407 was used.[1]

Selective-ion electrode for fluoride. Orion model 94–09 was used with Orion model 90–01 single-junction reference electrode.

Beakers, polypropylene, 100 ml.

Burner.

Crucibles, nickel.

PROCEDURE

1. Weigh 0.25 g finely ground sample into nickel crucible and mix with 1.25 g flux.
2. Sinter mixture over burner until bubbling subsides. Cool.
3. Add 10 ml water to the crucible and let stand overnight.
4. Stir contents of crucible with small stirring rod and transfer to a 100-ml volumetric flask.
5. Rinse crucible twice with 10-ml portions of water and add to flask. Rinse once with 10 ml citric acid–sodium citrate reagent and add to the flask.
6. Swirl flask to liberate the carbon dioxide formed by reaction of acid with carbonate and dilute to volume with water.
7. Transfer contents of flask to a polypropylene beaker immediately and let stand at least one-half hour, or until carbon dioxide ceases evolving.
8. Transfer a 50-ml aliquot to a clean polypropylene beaker and mix with 50 ml TISAB.

---

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

9. Immerse the electrodes into the solution and stir slowly for 1 minute. Adjust meter to midscale.
10. Add 1 ml 100- μg/ml fluorine standard solution and continue stirring for 3 minutes.
11. Read parts per million fluorine from known-increment scale and convert to parts per million in sample as follows:

$$\text{F, ppm in sample} = \frac{\text{scale reading} \times 10^4}{\text{sample weight} \times \text{aliquot}}.$$

EXPERIMENTS AND RESULTS

Although this procedure is usable with any expanded-scale ion meter, it is designed around the Orion meter model 407, which has a special scale to facilitate known-increment addition and subtraction techniques. The useful range of this scale is from about 0.2 to 2 ppm fluoride in the analyte solution and, in the 100-ml volume suggested, the molarity of the fluoride ion is, respectively, 10^{-5} to 10^{-4}. At such molarities, the response of the fluoride electrode is essentially constant over a pH range of 5 to 8 (Frant and Ross, 1966). Ficklin (1970) recommended a pH range of 5.5 to 6.5 and, fortuitously with the materials he tested, a 0.5-M citric acid solution was effective in maintaining the suggested pH range. Geologic materials vary widely in composition, and, conceivable, the citric acid may fail to adjust the resulting pH to the optimum range primarily because of the relatively low buffer capacity of citric acid and its salts.

Citrate is, however, advantageous for complexing aluminum and preventing complex formation between aluminum and fluoride. The fluorine in such a complex is not sensed by the electrode; hence, the formation of that complex would lead to low results for fluorine. Edmond (1969) and Ingram (1970) have been notably successful in complexing aluminum with citrate so that the fluoride activity can be measured without a lengthy distillation to separate fluorine from the bulk of the sample. Increasing the amount of citrate to complex even larger amounts of aluminum than had been complexed in the past seemed to provide a logical way to promote repeatability, as well as to provide greater flexibility.

In one of the experiments, we increased the citrate by substituting the citric acid–sodium citrate reagent for TISAB and adding it to the sample solution in equal proportions. The results are given in table 27.

With some of the samples we used no buffer at all, and with other samples we used TISAB and the citric acid–sodium citrate reagent to adjust the pH. The results using the excessive amount of citrate seemed to be greater, and we modified the TISAB by increasing the citrate about tenfold. Illustrative results on U.S. Geological Survey standard rocks by TISAB alone, citric acid–sodium citrate alone, and modified TISAB

TABLE 27.—*Fluorine content in U.S. Geological Survey standard rocks, in samples reported by other workers, and in rocks and soils analyzed by the methods described in present report*

[Leaders (...) indicate data not available; numbers have been rounded to two significant figures. Each number in parentheses is the number of determinations averaged]

Sample No.	Material	Fluorine content (ppm)							
		U.S. Geological Survey rocks, recommended values[1]	Ficklin (1970)[2]	Peck and Smith (1964)[3]	W. D. Goss (oral commun., 1969)	Present report			
						TISAB	With citrate	Modified TISAB	With no buffer
AGV-1	Andesite	435	360 (5)	400	...	500 (10)	540 (5)	...	...
BCR-1	Basalt	470	510 (5)	500	...	550 (5)	...	...	...
G-2	Granite	1,290	1,120 (5)	1,300–1,400	...	1,600 (5)	...	1,500 (5)	...
GSP-1	Granodiorite	3,200	3,500 (5)	3,800–3,900	...	3,800 (15)	4,300 (5)	4,000 (5)	...
CC-272	Breccia	...	1,573 (5)	...	2,400	2,300 (10)	2,400 (15)	...	...
HC-2-67	Soil	...	742 (5)	...	1,000	1,400 (10)	1,600 (15)	...	...
BCT-128	..do	...	...	...	...	1,400 (5)	1,500 (5)	...	1,800 (5)
BCT-146	..do	...	...	...	...	900 (5)	900 (5)	...	1,200 (5)

[1] 1972 values for international geochemical reference samples, Flanagan (1973).
[2] Selective ion electrode.
[3] Distillation and titration.

(increased citrate content) are compared in table 27 with those obtained by Ficklin's procedure. The modified TISAB proved to be detrimental and was subsequently abandoned. The substitution of citric acid–sodium citrate reagent did not provide any remarkable advantage and was likewise abandoned in favor of the original formulation of TISAB. The final procedure includes the addition of enough citric acid–sodium citrate reagent to provide a citrate concentration in the final volume of about 10,000 μg/ml and sufficient TISAB to adjust the pH of the sample solution to the optimum range and to provide a high ionic strength medium.

A comparison of the fluorine contents of several U.S. Geological Survey standard rocks and of other rocks and soils, as determined by the known-increment addition method with the amounts as determined by several other methods, is also given in the table. Fluorine was seprated by distillation prior to measurement on all of the values reported by Peck and Smith (1964) and W. D. Goss (oral commun., 1969).

The favorable comparison is adequate to recommend the known-increment addition method, and the ease of making the addition along with the few operations required combine to validate the recommendation.

REFERENCES CITED

Edmond, C. R., 1969, Direct determination of fluoride in phosphate rock samples, using the specific ion electrode: Anal. Chemistry, v. 41, no. 10, p. 1327–1328.

Ficklin, W. H., 1970, A rapid method for the determination of fluoride in rocks and soils, using an ion-selective electrode, in Geological Survey research 1970: U.S. Geol. Survey Prof. Paper 700-C, p. C186–C188.

Flanagan, F. J., 1973, 1972 values for international geochemical reference samples: Geochim. et Cosmochim. Acta, v. 37, p. 1189–1200.

Frant, M. S., and Ross, J. W., Jr., 1966, Electrode for sensing fluoride ion activity in solution: Science, v. 154, p. 1553–1554.

———1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Anal. Chemistry, v. 40, no. 7, p. 1169–1171.

Hall, R. J., 1963, The spectrophotometric determination of sub-microgram amounts of fluorine in biological specimens: Analyst, v. 88, no. 1043, p. 76–83.

Hillebrand, W. F., 1919, The analysis of silicate and carbonate rocks [a revised and enlarged edition of Bulletin 422]: U.S. Geol. Survey Bull. 700, 285 p.

Ingram, B. L., 1970, Determination of fluoride in silicate rocks without separation of aluminum using a specific ion electrode: Anal. Chemistry, v. 42, no. 14, p. 1825–1827.

Peck, L. C., and Smith, V. C., 1964, Spectrophotometric determination of fluorine in silicate rocks: Talanta, v. 11, p. 1343–1347.

Reynolds, D. S., and Hill, W. L., 1939, Determination of fluorine, with special reference to analysis of natural phosphates and phosphatic fertilizers: Indus. and Eng. Chemistry, Anal. Ed., v. 11, no. 1, p. 21–27.

Singer, Leon, and Armstrong, W. D., 1954, Determination of fluoride: Anal. Chemistry, v. 26, no. 5, p. 904–906.

———1968, Determination of fluoride in bone with the fluoride electrode: Anal. Chemistry, v. 40, no. 3, p. 613–614.

Srinivasan, K., and Rechnitz, G. A., 1968, Activity measurements with a fluoride-selective membrane electrode: Anal. Chemistry, v. 40, no. 3, p. 509–512.

Stuart, J. L., 1970, A simple diffusion method for the determination of fluoride: Analyst, v. 95, no. 1137, p. 1032–1038.

Willard, H. H., and Winter, O. B., 1933, Volumetric method for determination of fluorine: Indus. and Eng. Chemistry, Anal. Ed., v. 5, no. 1, p. 7–10.

NEW AND REFINED METHODS OF TRACE ANALYSIS
USEFUL IN GEOCHEMICAL EXPLORATION

ATOMIC ABSORPTION DETERMINATION OF SILVER, BISMUTH, CADMIUM, COBALT, COPPER, NICKEL, LEAD, AND ZINC IN CALCIUM- AND IRON-RICH GEOLOGIC MATERIALS

By H. M. NAKAGAWA

CONTENTS

TABLES

ABSTRACT

An atomic absorption method is presented for the determination of as little as 1–2 parts per million silver, bismuth, cadmium, cobalt, copper, nickel, lead, and zinc in

85

ferruginous and calcareous materials. In other procedures the presence of different amounts of iron and calcium causes erroneous results, but in the atomic absorption procedure these interfering elements are removed prior to the analysis of the trace elements. Iron is removed by extraction of ferric bromide with methyl isobutyl ketone; calcium is removed by extraction of the carbamates of the elements of interest into methyl isobutyl ketone. The trace elements are then measured by atomic absorption spectrometry.

INTRODUCTION

Speed, brevity, simplicity, and versatility are factors largely responsible for the overwhelming application of atomic absorption methods to the analysis of trace elements in geologic materials. Formerly, methods based on molecular absorption (colorimetry) were widely used, but such methods required a high degree of skill on the part of the analyst as compared with that required by atomic absorption methods. In the application of atomic absorption methods to geochemical exploration, the trace elements are determined directly by atomizing a dilute acid solution of sample of soil, rock, or plant ash into an acetylene-air flame of a conventional atomic absorption instrument (Ward and others, 1969).

The present report is concerned with the simultaneous determination by atomic absorption of silver, bismuth, cadmium, cobalt, copper, nickel, lead, and zinc from a single sample solution. Large-size (1–5 g) samples from material, such as gossan, laterite, magnetite, calcareous rocks, or plant ash, are needed to furnish threshold amounts of the elements, particularly for bismuth and lead which are the least sensitive.

Analytical results from iron- or calcium-rich sample media are subject to error (either positive or negative). Several methods were considered, either to minimize the error caused by large amounts (>1 percent) of iron and (or) calcium or to remove them from the sample solution. Some of these methods included the addition to the sample solution of complexing agents (such as fluoride for iron), reducing agents to reduce iron(III) to iron(II), and the use of ion-exchange resins. Other methods tried were the precipitation of the iron or calcium from the sample solution, the use of nonabsorbing lines, and the addition of overwhelming amounts of iron and calcium to the standard solutions in order to simulate the chemical composition of the unknown material. None of these methods were adequate because of the large amounts of extraneous salts formed during complexation or reduction and because of the danger of loss of analyte by coprecipitation with calcium, iron, or other major components of the sample solution.

Obviously some other means of removing the iron and calcium or means of minimizing the effect of the iron and calcium had to be devised. Solvent extraction is the technique of choice, and the manner of application is given below.

In previous work with gold and tellurium, large amounts of iron had to be separated (Thompson and others, 1968; Nakagawa and Thompson,

1968) and this separation was accomplished by extraction. Ferric bromide extracts into MIBK, and using this extraction Denaro and Occleshaw (1955) successfully separated iron(III) from manganese, aluminum, cobalt, and nickel contained in a hydrobromic acid–ammonium bromide solution. In addition, they observed that zinc and copper extracted only slightly, and at low concentrations of hydrobromic acid the iron(III) bromide extracted more efficiently than the zinc. Also, Menis and Rains (1960) observed that even microgram quantities of iron could be quantitatively extracted with MIBK. Moreover, Scott, Roberts, and Cain (1967) found that other solvents, such as isobutyl acetate, were efficient in separating iron(III) from minor constituents of ore samples. Isobutyl acetate is considerably more expensive than MIBK, and sheer economics precludes its use except in special applications. In the method described in this paper, hydrobromic acid is added after sample attack, and iron(III) bromide is removed by extraction into MIBK.

Iron is conveniently removed as the bromide by extraction into MIBK and the elements of interest are removed from calcium by chelation and extraction into MIBK containing 1 percent DADC. The MIBK is atomized into a flame of an atomic absorption instrument.

REAGENTS

Standard silver solution, 1,000 ppm: Dissolve exactly 0.158 g silver nitrate in 100 ml 1+1 HCl.

Standard bismuth solution, 1,000 ppm: Dissolve 0.1 g bismuth metal in 50 ml concentrated nitric acid and dilute to 100 ml with demineralized water.

Standard cadmium solution, 1,000 ppm: Dissolve 0.1142 g cadmium oxide in 100 ml 1+1 HCl.

Standard cobalt solution, 1,000 ppm: Dissolve 0.394 g cobalt chloride ($CoCl_2 \cdot 6H_2O$) in 100 ml of 1+1 HCl.

Standard copper solution, 1,000 ppm: Dissolve 0.0393 g of clear uneffloresced crystals of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 100 ml of 1+1 HCl.

Standard nickel solution, 1,000 ppm: Dissolve 0.496 g nickel nitrate [Ni $(NO_3)_2 \cdot 6H_2O$] in 100 ml 1+1 hydrochloric acid.

Standard lead solution, 1,000 ppm: Dissolve 0.16 g lead nitrate in 100 ml of 1+1 HCl.

Standard zinc solution, 1,000 ppm: Dissolve 0.1 g zinc metal in 100 ml of 1+1 HCl.

Combined dilute standard solution, 10 ppm: Dilute 1 ml of 0.1 percent standard solution of each element to 100 ml with 1+1 HCl.

Ammonium hydroxide, concentrated reagent grade.

Hydrobromic acid, concentrated reagent grade.

Hydrochloric acid, concentrated reagent grade.

Hydrofluoric acid, 48 percent, reagent grade.

Nitric acid, concentrated reagent grade.

DADC, 1 percent in MIBK: Dissolve 1 g DADC in 100 ml MIBK.

MIBK, reagent grade.

Cresol red indicator: Dissolve 0.1 g in 26 ml of 0.01 M NaOH and dilute to 250 ml with demineralized water.

Tartrate buffer: Dissolve 18.6 g tartaric acid and 23 g sodium tartrate in 1 litre demineralized water.

APPARATUS

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

Teflon beakers.

Hotplate.

pH meter.

PROCEDURE

SAMPLE SOLUTION

Silicate rocks:

Place the weighed sample (up to 1.0 g) in a Teflon beaker having a capacity of at least 50 ml. Moisten the sample with 2 ml demineralized water. Add 2 ml of concentrated nitric acid and 25 ml of hydrofluoric acid. Let stand at least 2 hours, or overnight preferably, and evaporate the contents over moderate heat to dryness. Repeat the addition of nitric and hydrofluoric acids, let stand for 2 hours, and again evaporate to dryness. Add 1 ml of concentrated nitric acid, 15 ml of 6 M hydrochloric acid and warm the beaker and contents to dissolve the residue. Generally, this treatment is adequate for most siliceous-type materials. Transfer the contents of the beaker to a 25-ml volumetric flask; wash the beaker 3 times with 2-ml portions of 6 M hydrochloric acid and add each wash to the volumetric flask. Adjust the volume to 25 ml with 6 M hydrochloric acid. The acidity of the sample solution is 6.5 M.

Magnetite:

Place the weighed sample (up to 1.0 g) in a suitable beaker having a capacity of at least 50 ml. Moisten the sample with 2 ml demineralized water, add 10 ml concentrated hydrochloric acid, and evaporate to dryness using moderate heat. Add 2 ml concentrated nitric acid and again evaporate to dryness. Add 1 ml concentrated nitric acid, 15 ml 6 M hydrochloric acid and warm the beaker and contents to dissolve the residue. Transfer the contents of the beaker to a 25-ml volumetric flask, wash the beaker three times with 2-ml portions of 6 M hydrochloric acid and add each wash to the volumetric flask. Adjust the volume to 25 ml with 6 M hydrochloric acid. The acidity of a magnetite solution is 7 M.

Plant ash:
Follow the same directions as given for magnetite. The final acidity of a plant ash solution is 6.5 M.

IRON REMOVAL

Transfer the entire sample solution to a 125-ml separatory funnel, add 0.5 ml concentrated hydrobromic acid, 10 ml MIBK, and shake for 5 seconds. Drain the aqueous phase into a second 125-ml separatory funnel and discard the spent MIBK phase. Repeat the MIBK extractions until the organic layer remains colorless. Generally, three extractions are sufficient to remove as much as 1,000 mg of iron. If it is necessary to use three MIBK extractions for complete removal of iron, then all the samples and standard solutions in a given job lot must be treated in a similar manner.

For sample solutions of magnetite only, add 2 ml demineralized water before adding other reagents necessary for iron removal. The addition of 2 ml demineralized water lowers the acidity of the magnetite solution from 7 to 6.5 M, which would make its acidity identical to the acidity of solutions of other materials and of standard solutions.

If iron is not present in the original sample solution (calcites, plant ash, and so forth), the preceding step may be omitted.

EXTRACTION

To the iron-free aqueous solution in the separatory funnel add 5 ml tartrate buffer, 3 drops cresol red indicator solution, and enough concentrated ammonium hydroxide to cause the solution to become pale yellow or colorless. Let the solution cool to ambient temperature and adjust the final pH to a meter reading of 2 using either 1 M hydrochloric acid or 1 M ammonium hydroxide. Add 10 ml of 1 percent DADC/MIBK solution and shake for 1 minute. The pH (2.8) of the sample solution at this point will be at the optimum. Discard most of the aqueous phase and transfer the remaining aqueous and organic solutions to a clean test tube.

ESTIMATION

Atomize the organic extract out of the sample solution and convert reading to parts per million using a standard curve which was calculated from tracings obtained by using an automatic null recorder readout accessory and a 10-mv strip-chart recorder. The burner used was a narrow-slot air-acetylene premix burner. For each element the analyst should use the recommended settings as supplied by the manufacturer of the instrument.

PREPARATION OF STANDARDS

Aliquots of 0.0, 0.1, 0.2, 0.5, 1.0, 2.0 and 3.0 ml of the combined standard solution are diluted to 25 ml with 6 M hydrochloric acid in volumetric

flasks each containing 1 ml of concentrated nitric acid. Transfer to 125-ml separatory funnels, add 0.5 ml concentrated hydrobromic acid and 10 ml MIBK to each funnel and shake for 5 seconds. Drain the aqueous phase from each funnel into clean separatory funnels and repeat the MIBK extractions the same number of times as the samples. Discard the organic phase after each extraction. To the aqueous solution add 5 ml of tartrate buffer, 3 drops of cresol red indicator solution and adjust the pH to 2. Let cool and extract the metals with 10 ml DADC/MIBK. The organic layer in each separatory funnel contains respectively, 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, and 3.0 ppm each of the following elements: Bismuth, cadmium, cobalt, copper, lead, nickel, silver, and zinc. Atomize each standard in the atomic absorption instrument and prepare a standard curve from the absorbance measurements.

EXPERIMENTS
EFFECT OF IRON AND CALCIUM ON ATOMIC ABSORPTION MEASUREMENTS

The determination of trace constituents of geologic materials is hampered by large ratios of macroconstituents, such as iron and (or) calcium to the trace constituents. Iron-rich materials, such as magnetite, contain up to 70 percent elemental iron, and the ratio of iron to a trace constituent at the 0.001 percent level (10 ppm) is 70,000. The determination of the trace constituent in such materials is difficult. Similar relations hold in other geologic materials, expecially in plant ash in which the calcium content can be as much as 40 percent. Accordingly, the effect of such ratios is of importance and the following experiments were made to evaluate the effect.

In the procedures for silicate rocks, magnetite, and plant ash, sample weights up to 1 g are suggested. With a 1-g sample, a conversion factor of 10 changes the concentration of the analyte measured in the organic solvent to the concentration in the original sample. In the absence of all elements of interest, increasing amounts of iron were added to control sample solutions so that the amounts of iron present in the organic extract corresponded to 1–100 percent. Each solution was atomized into an air-acetylene flame, and the absorption was measured for each element of interest in the control sample solution. The iron concentration in the original sample at which the interference—enhancement or depression—equaled or exceeded the sensitivity of the element of interest is given in table 28.

A similar experiment was made with increasing amounts of iron in the presence of a fixed amount of each element of interest corresponding to 10 ppm in a control sample. The iron concentration in the control sample at which the interference—enhancement or depression—equaled or exceeded the sensitivity of the element of interest is shown in table 28.

TABLE 28.—*Amounts of iron causing interference in the absence or presence of analyte elements*

Element	Sensitivity, this report (μg/g of sample)	Iron in sample causing interference (percent)	
		Analyte absent	Analyte present
Silver	1	10	10
Bismuth.........................	5	5	10
Cadmium	1	10	5
Cobalt............................	1	5	5
Copper...........................	1	10	50
Nickel	1	5	1
Lead...............................	5	5	10
Zinc................................	1	5	1

Relatively small amounts of iron (1–5 percent) interfere in the measurement of cadmium, cobalt, nickel, and zinc. As little as 10 percent iron causes interference in the measurement of silver, bismuth, and lead. The measurement of copper is relatively free of interference from iron.

In the absence of any of the elements of interest, increasing amounts of calcium were added to solutions corresponding to calcium concentrations in a control sample ranging from 1 to 100 percent. Each solution was atomized into an air-acetylene flame and the absorption measured for each element of interest. The observations are shown in table 29.

TABLE 29.—*Amounts of calcium causing interference in the absence or presence of analyte elements*

[Leaders (...) indicate entry not available]

Element	Sensitivity, this report (μg/g of sample)	Calcium in sample causing interference (percent)	
		Analyte absent	Analyte present
Silver	1	5	50
Bismuth.........................	5	5	5
Cadmium	1	5	1
Cobalt............................	1	5	10
Copper...........................	1	50	10
Nickel	1	5	1
Lead...............................	5	...	1
Zinc................................	1	5	1

Small amounts of calcium (1–5 percent) interfere with the measurement of bismuth, cadmium, nickel, lead, and zinc. Cobalt and copper measurements are affected by 10 percent calcium, and only the silver measurement is relatively free from calcium interference.

Thus far, no attempt has been made to describe the nature of the iron or calcium interference. In some samples, the interference is one of enhancement and in others one of depression. In a few examples, both occur and so the effect can be graphically described as concave or convex,

depending on which—enhancement or depressions—occurs at lower concentrations of the interferent.

EFFECT OF HYDROCHLORIC ACID ON
EXTRACTION OF IRON BROMIDE INTO MIBK

The extraction of iron, silver, and cadmium with MIBK is critically dependent on the hydrochloric acid concentration of the solution, but the extraction of such elements as bismuth, cobalt, copper, nickel, lead, and zinc is slight and not appreciably affected by different acid concentrations. Large amounts of iron are extracted by MIBK from a strong acid concentration, such as 8 M hydrochloric acid, but MIBK is appreciably soluble in the acid, and at slightly greater acid concentrations than 8 M, the ketone is mutually soluble. The resulting single phase defeats the objective, and higher acid concentrations have to be avoided. From 8 M hydrochloric acid, about half of the cadmium extracts along with iron; however, at this acid concentration the retention of silver in the aqueous phase is maximum. At the other extreme—for example, 1 M hydrochloric acid—approximately 75 percent of the silver extracts with iron into the ketone, but most of the cadmium remains behind in the aqueous phase. The use of 6.5 M hydrochloric acid seems to be a satisfactory compromise; the extraction of iron is appreciable, and the extraction of silver and cadmium is minimized. Compensation for the small losses of cadmium is made by treating samples and standards similarly. Small losses of the other elements occur also, especially with repeated MIBK extractions, but generally three extractions are sufficient to separate iron from the analyte elements. Under the conditions just described, three such extractions remove as much as 1,000 mg of iron, and that amount is more than adequate for any conceivable iron-rich geologic samples.

EXTRACTION OF ANALYTE FROM
LARGE AMOUNTS OF CALCIUM

Many investigators, including Sprague and Slavin (1964), Mansell (1965), and Mulford (1966), have successfully used the APDC/MIBK system to remove trace amounts of several elements such as copper, bismuth, lead, cadmium, cobalt, nickel, iron, and manganese from various media, such as concentrated potassium chloride solution and other brines. The extraction is somewhat pH dependent; and, although the APDC/MIBK system is applicable over a fairly wide range, Mansell (1965) experienced difficulties in preparation of aqueous solutions of APDC even at a 1-percent level. Another system, DADC/MIBK has a wider range, especially for the elements of interest. Moreover, DADC is completely soluble in MIBK and is less sensitive to strong acids (Stary, 1964).

Accordingly, the pH of the iron-free sample solution is adjusted to optimum (2.8) and shaken with a relatively immiscible solution of DADC/MIBK. The phases are separated, and the ketone is atomized in an atomic absorption instrument. The efficiency of this extraction is shown by the data in table 30.

TABLE 30.—*Recovery of 1 ppm of each element in the presence of varying amounts of iron and calcium*

Milligrams	Parts per million							
	Ag	Bi	Cd	Co	Cu	Ni	Pb	Zn
Iron (III) 3.5	0.9	1	0.90	0.9	1.0	0.9	1.1	1.0
10	.9	1	.90	.9	1.1	.9	1.0	.8
100	1.0	1.0	1.0	.9	1.0	.9	1.1	1.0
500	1.0	1	1.1	.9	1.0	.9	.9	1.1
1,000	1.1	1.0	1.2	.8	1.0	1.1	1.0	1.1
Calcium (II) 5	.9	1.0	1.0	1.0	1.1	1.1	1.0	1.1
10	.9	1.0	1.0	1.0	1.1	1.0	1.0	1.1
100	.9	1.0	1.0	.9	1.1	1.1	1.0	1.1
500	1.1	.9	1.1	1.0	1.1	1.1	1.0	1.1
1,000	1.0	1.0	1.0	.9	1.0	.9	1.0	1.2

Recoveries of analyte are satisfactory in the presence of overwhelming quantities of iron and (or) calcium. Moreover, because no perceptible enhancement or depression occurs when analyte metals were added, the iron and calcium solutions used in this study appear to be free of such metals. Data shown in tables 28 and 29 result from the interference of iron and calcium.

It was found by experimenting with different commercially available atomic absorption instruments that the iron or calcium levels causing significant interference in the absence or presence of analyte differ, depending on the particular instrument.

Foster (1971) observed that the effects of calcium on lead, zinc, nickel, copper, and manganese determinations by atomic absorption spectrometry became more noticeable with shorter wavelengths, except for zinc. He also observed that the use of a continuum lamp largely eliminated the background interference.

RESULTS

Table 31 compares the results of the determinations of several elements obtained by the atomic absorption procedure, described in this report, and by semiquantitative spectrographic analysis. In general, the agreement between the two methods is good. Special effort was made to achieve high sensitivity for bismuth in magnetite only. This was accomplished

TABLE 31.—*Comparison of two methods for determination of several elements in diverse materials*

[AA, atomic absorption; spec, semiquantitative spectrographic; M, major constituent; Nd, not detected at limit of detection; <, less than; >, greater than; ≥, greater than or equal to; leaders (...) indicate data not available; results are in parts per million, except as indicated]

Sample No.	Material	Ag		Bi		Cd		Co		Cu		Ni		Pb		Zn	
		AA	Spec	AA	Spec	AA	Spec	AA	Spec	AA	Spec	AA	Spec	AA	Spec	AA	Spec
E-590	Limestone	17	20	<2	>1,000	130	70	1.5	<5	225	100	17	15	5,800	[1]≥10M	2,200	2,000
E-243	Limonite	550	500	3,300		35	70	<1	<5	5,400	5,000	<1	<5	4,000	7,000	...	[1]>2
PC-859	Gossan	3	1	<2	<5	65	70	400	100	30	20	250	100	90	70	...	[1]>1
E-276	Caliche	23	20	525	300	35	50	<1	<5	550	1,500	5	5	5,000	[1]≥10M	11,000	[1]>1
E-94	Quartz monzonite	25	35	<2	<5	145	200	6	20	325	300	35	50	1,900	1,000	...	[1]>2
M-238	Magnetite	.12	ND	.70	<5	.45	Nd	65	50	28	15	145	100	48	50	800	1,000
VC-3	Plant ash	2	3	<2	<5	5	<20	3	5	140	150	30	50	270	700	...	5,000

[1]Results in percent.

TABLE 32.—*Precision data for eight elements in magnetite and limestone*

[Leaders (...) indicate data not calculable; results are in parts per million, except for RSD, relative standard deviation, given in percent]

Material	Values	Ag	Bi	Cd	Co	Cu	Ni	Pb	Zn
Magnetite	High	0.17	1.0	0.51	75	33	165	60	1,000
	Low	.10	.60	.26	40	23	125	45	700
	Mean[1]	.13±0.03	.76±0.20	.41±0.11	65±18	28±4	145±18	48±9	830±45
	RSD	22	23	23	22	13	10	15	4
Limestone	High	18	<2	130	1.7	230	19	5,800	2,320
	Low	16	<2	105	1.1	200	17	5,250	1,850
	Mean[1]	17±0.9	...	120±13	1.4±0.3	221±15	18±1	5,470±270	2,120±190
	RSD	4	...	9	18	6	5	4	4

[1]Confidence limits at 95-percent level.

by reducing the volume of the extractant DADC/MIBK from 10 ml to 3 ml. As little as 0.6 ppm bismuth in a 1-g sample can be detected by this special treatment.

All samples in this study, with the exception of the magnetite and plant ash samples, were treated with hydrofluoric and nitric acids before being solubilized in hydrochloric acid. The magnetite and plant ash samples were treated with nitric and hydrochloric acids, as described on pages 88 and 89. Materials such as limestone, limonite, gossan, caliche and quartz monzonite were subjected to the same treatment as magnetite, but low results were obtained in many samples. The low results are probably attributable to those metals being encompassed in the crystal lattice of the minerals and not completely solubilized without the use of hydrofluoric acid.

Precision was obtained by analyzing iron- and calcium-rich samples five times at different intervals, and the results are shown in table 32. The relative standard deviation and the confidence limits at the 95-percent level were calculated by the method given by Youden (1951, p. 20). The relative standard deviation of the magnetite sample is higher than that of the limestone; however, a pure magnetite sample is difficult to obtain.

A method of analysis has been developed for the determination of several trace elements in iron and (or) calcium-rich materials. Iron interference is removed by a simple MIBK extraction and the trace elements chelated with DADC. Calcium does not form a chelate with DADC and is eliminated from interfering. Although the method is designed primarily for use with sample media, such as magnetite, calcite and plant ash, it can be used, in part or in its entirety, for nearly all types of geologic materials.

REFERENCES CITED

Denaro, A. R., and Occleshaw, V. J., 1955, The extraction of some metallic bromides from aqueous solutions with methy ethyl ketone and methyl iso-butyl ketone: Anal. Chim. Acta, v. 13, p. 239–247.

Foster, J. R., 1971, The reduction of matrix effects in atomic absorption analysis and the efficiency of selected extractions on rock-forming minerals, in Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 554–560.

Mansell, R. E., 1965, Notes on the extraction of manganese with chelating agents and MIBK: Atomic Absorption Newsletter, v. 4, no. 5, p. 276.

Menis, O., and Rains, T. C., 1960, Extraction and flame photometric determination of iron: Anal. Chemistry, v. 32, no. 13, p. 1837–1841.

Mulford, C. E., 1966, Solvent extraction techniques for atomic absorption spectroscopy: Atomic Absorption Newsletter, v. 5, no. 4, p. 88.

Nakagawa, H. M., and Thompson, C. E., 1968, Atomic absorption determination of tellurium, in Geological Survey research 1968: U.S. Geol. Survey Prof. Paper 600-B, p. B123–B125.

Scott, T. C., Roberts, E. D., and Cain, C. A., 1967, Determination of minor constituents in ferrous materials by atomic absorption spectrophotometry: Atomic Absorption Newsletter, v. 6, no. 1, p. 1.

Sprague, S., and Slavin, W., 1964, Determination of very small amounts of copper and lead in KCl by organic extraction and atomic absorption spectrophotometry: Atomic Absorption Newsletter, no. 20, p. 11.

Stary, J., 1964, The solvent extraction of metal chelates: New York, The Macmillan Co., p. 164.

Thompson, C. E., Nakagawa, H. M., and VanSickle, G. H., 1968, Rapid analysis for gold in geologic materials, *in* Geological Survey research 1968: U.S. Geol. Survey Prof. Paper 600-B, p. B130-B132.

Ward, F. N., Nakagawa, H. M., Harms, T. F., and VanSickle, G. H., 1969, Atomic-absorption methods useful in geochemical exploration: U.S. Geol. Survey Bull. 1289, 45 p.

Youden, W. J., 1951, Statistical methods for chemists: New York, John Wiley & Sons, 126 p.

NEW AND REFINED METHODS OF TRACE ANALYSIS USEFUL IN GEOCHEMICAL EXPLORATION

USE OF EMISSION SPECTROSCOPY FOR THE SEMIQUANTITATIVE ANALYSIS OF TRACE ELEMENTS AND SILVER IN NATIVE GOLD

By Elwin L. Mosier

CONTENTS

TABLES

ABSTRACT

A spectrographic method for the semiquantitative determination of trace elements and silver in native gold has been developed. Silver, because it is commonly found alloyed with native gold as a major constituent, is determined in percent. Other elements (As, B, Ba, Be, Bi, Ca, Cd, Co., Cr, Cu, Fe, Ga, Ge, Hg, In, La, Mg, Mn, Mo, Nb, Ni, Pb, Pd, Pt, Sb, Sc, Si, Sn, Sr, Ta, Te, Ti, V, W, Y, Zn, and Zr) are determined as trace impurities and reported in parts per million. Direct-current arcanode excitation was chosen because of its simplicity and sensitivity. Five-milligram samples are arced

in an aluminum oxide–graphite mixture at 15 amperes current. The resulting spectra are recorded on Spectrum Analysis No. 1, 35-millimetre film and visually compared with standard films prepared by arcing mixtures of spectrographically pure powders in a graphite base, pure gold, and aluminum oxide. By analyzing the gold in its native state, this method avoids the necessity of complicated sample preparation.

INTRODUCTION

Semiquantitative determination of trace elements in gold by emission spectrography is hindered by the difficulty of preparing adequate standards. Much of the previous work on the trace-element analysis of native gold has been qualitative (Crook, 1939; Warren and Thompson, 1944), but Mertie (1940) discussed quantitative determinations made on native gold by R. E. Stevens and E. T. Erickson of the U.S. Geological Survey. Antweiler and Sutton (1970) described a semiquantitative spectro-chemical method in which they dissolved native gold in aqua regia, evaporated the solution to dryness, and analyzed the dried residue. However, they were unable to analyze for the highly volatile elements, such as arsenic, mercury, tellurium, and zinc, because these elements were lost during sample preparation. The method also lacked adequate sensitivity for many elements. The desirability for increased sensitivity and the importance of obtaining data on volatile elements closely associated with gold emphasize the need for a new semiquantitative procedure.

Selection of a method suitable for the analysis of trace elements in native gold was made after considering the following criteria: (1) Samples of native gold are generally small; therefore, the method should provide for the analysis of a large number of elements from a single electrode charge; (2) the detection limits of all elements should be as low as possible; (3) sample preparation should cause minimal change in the natural chemical composition of native gold; (4) standards should be prepared to encompass wide ranges of concentrations; and (5) for the purpose of identifying the genetic origin of gold, the precision and accuracy should be such that one would be able to assign a signature to native gold based on its trace-element composition.

The following procedure meets these criteria.

METHOD OF ANALYSIS

The instrumentation employed and operating parameters are listed below:

APPARATUS AND SPECTROGRAPHIC OPERATING CONDITION

Spectrograph: Jarrell-Ash 1.5-m Wadsworth-mounted, having a dispersion of 5.45 A/mm over a spectral range from 2,100 A to 4,800 A in the second order.
Source: Jarrell-Ash Spectro Varisource (Model 43650).

Discharge: 15 amps d.c. arc.

Sample Electrode: Ultra Carbon 101L anode.

Counter Electrode: Ultra Carbon 5001.

Analytical Gap: 5 mm held constant.

Exposure Time: 96 seconds—no preburn.

Slit Width: 10 microns.

Filter: 100 percent transmission over 36 percent transmission 0.8 cm aperture mask on grating.

Film: 35-mm Kodak Spectrum Analysis No. 1, processed with D–19 developer for 2 minutes 15 seconds at 20°C, stopped in cold running water (30 sec), fixed for 3 minutes, rinsed in cold water, and air dried.

Comparator: Jarrell-Ash console microphotometer (Model 21–000).

Campbell, Mosier, and Antweiler (1973) reported that laboratory treatments of native gold with various acid washes, roasting, or amalgamation may affect the chemical composition of the gold. To prevent altering the chemical composition of the gold, and to achieve the maximum amount of data possible, the gold is arced in its metallic state. Therefore, after retrieval from its source, no sample preparation is required other than handpicking under a binocular microscope and, if desired, cleaning in an acid wash to remove surface coating. Direct-current arc-anode excitation was chosen because of its simplicity and the sensitivity it provided for a wide range of elements.

Experience showed that a total energy burn was required to obtain reliable data on many of the elements. For this reason, an electrode with a small crater size and undercut design (Ultra Carbon 101L)[1] was selected to create greater heat intensity in the electrode cavity. Thus, a total energy burn and a fast volatilization of the sample are achieved without burning excessive graphite from the electrode.

A means of buffering the sample was found to be necessary. When gold is arced alone it has a tendency to "jump out" of the electrode cavity. Arcing gold in graphite results in an erratic burn of the arc and high background radiation. Also, the time required for total volatilization is greater than 2 minutes. Several codistillation agents were tried; of these, a mixture of aluminum oxide and graphite gave the best results. The addition of aluminum oxide resulted in a smooth even burn throughout the exposure period, whereas graphite prevented the aluminum oxide from forming a bead.

Time-burn studies showed that volatile elements (As, Bi, Cd, Ga, Hg, In, Pb, Sb, Te, and Zn) are completely volatilized in 30 seconds, whereas aluminum, gold, and less volatile elements are codistilled and volatilized in 90 seconds. Therefore, to insure a total energy burn, the exposure time was set at 96 seconds. The electrode charge was empirically determined to be 5 mg gold, 5 mg graphite, and 2.5 mg aluminum oxide.

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

To achieve the sensitivity desired and to maintain a high contrast between line intensity and background radiation, a technique developed for the analysis of plant ash proved successful (Mosier, 1972). The technique utilizes a Hartmann diaphragm and step-filter (100 percent over 36 percent) assemblage which enables the simultaneous recording of volatile elements from a 30-second burn at 100-percent transmission and of less volatile elements from a total energy burn (96 seconds) at 36-percent transmission. Thus, from the same electrode charge used for a total energy burn, volatile elements are detected at low concentration levels. In essence a dual analysis is achieved from one electrode charge.

PROCEDURE

Five milligrams gold, 5 mg graphite (grade SP–1), and 2.5 mg aluminum oxide are weighed and manually mixed in a weighing pan. The mixture is transferred into the cavity of a Ultra Carbon 101L electrode (or equivalent) with the aid of a Teflon funnel and packed tightly with a venting tool. Eleven test samples and one standard sample are weighed for each film.

The arcing sequence is as follows: (1) Set the fishtail aperture on the slit for a 2-mm-high spectrum and the automatic timer at 30 seconds; (2) initiate an arc at 3A and immediately increase to 15A; (3) when the arc stops after the 30-second burn, position the Hartmann diaphragm to block out the top half (100-percent portion) of the spectrum, reset the timer for 66 seconds and reignite the arc at 3A, increasing immediately to 15A; (4) on completion of the burn, rack the camera 2 mm and repeat the sequence for the next sample. This technique produces a 2-mm-high spectrum with the top half representing a 30-second burn at 100-percent transmission and the bottom half representing a total energy burn (96 seconds) at 36-percent transmission. It should be noted that the optics of a Wadsworth-mount spectrograph produces an inverse spectrum, and, when projected in the suggested comparator, the bottom half is the 100-percent portion.

The film is processed and the results are obtained by visual comparison with master films made by exactly the same technique as that described, except that synthetic standards are substituted for unknowns. The analytical lines used and the detection limits obtained are given in table 33 (Meggers and others, 1961). When possible, the total energy portion of the spectrum is used for making comparisons. The short-burn portion of the spectrum is used only for volatile elements whose concentrations are below the detection limits of the total energy burn.

STANDARDS

Because it would be virtually impossible to achieve adequate standards in a metallic gold matrix, two sets of standards were prepared in a graph-

TABLE 33.—*Analytical lines[1] and detection limits*

Element	Wavelength (A)	Detection limit (ppm)	Element	Wavelength (A)	Detection limit (ppm)
Ag	2,721.8	0.5	Mo	3,170.4	5
As	2,780.2	20	Nb	3,163.4	10
B	2,497.7	1	Ni	3,101.6	10
Ba	4,554.0	10	Pb	2,833.1	1
Be	3,131.1	1	Pd	3,242.7	5
Bi	3,067.7	1	Pt	3,064.7	10
Ca	4,226.7	5	Sb	2,598.1	10
Cd	3,261.1	10	Sc	3,353.7	2
Co	3,044.0	10	Si	2,881.6	5
Cr	2,843.3	5	Sn	2,840.0	5
Cu	3,274.0	1	Sr	3,464.5	100
Fe	2,599.6	5	Ta	2,653.3	50
Ga	2,943.6	1	Te	2,385.8	20
Ge	3,039.1	5	Ti	3,242.0	5
Hg	2,536.5	10	V	3,102.3	5
In	3,039.4	5	W	2,947.4	20
La	3,337.5	20	Y	3,242.3	5
Mg	2,795.5	5	Zn	3,302.6	50
Mn	2,798.3	1	Zr	3,392.0	10

[1]Meggers, Corliss, and Scribner (1961).

TABLE 34.—*Concentration range of elements in standards*

[Results are rounded to reporting values and are in parts per million except where noted. Leaders (...) indicate the element is not present in the standard]

	Standard No. 1				Standard No. 2	
Ag (percent)	Hg	Cu,Pb,Si	Bi,La,W, Y,Zr	As,Cu,Fe,Pb, Te,Ti,Zn	Be,La,Mn,Pd, Pt,Sb,Si,Ta	B,Ba,Bi,Ca,Cd, Ce,Cr,Ga,Ge,In, Mg,Mo,Nb,Ni,Sc, Sn,Sr,V,W,Y,Zr
50	50,000	...	...	5,000	...	...
20	20,000	...	...	2,000	...	...
10	10,000	...	...	1,000	...	...
5	5,000	...	...	500	500	...
2	2,000	...	...	200	200	200
1	1,000	...	...	100	100	100
.5	500	20,000	10,000	50	50	50
.2	200	10,000	5,000	20	20	20
.1	100	5,000	2,000	10	10	10
.05	50	2,000	1,000	5	5	5
.02	20	1,000	500	2	2	2
.01	10	500	200	1	1	1

ite matrix. Spectrographically pure compounds were added in specified amounts to the graphite to obtain the desired concentration of each element. Table 34 gives the concentration range of the standards for the 38 elements sought.

To obtain standards in a geometric progression desirable for semi-quantitative analysis, the reciprocal of the cube root of 10 (0.464) was

used as the dilution factor (Myers and others, 1961; Grimes and Marranzino, 1968). By use of the 0.464 dilution factor, the succeeding standards prepared contain concentrations in order of magnitudes of 100, 46.4, 21.5, 10, and so forth. For semiquantitative use these numbers are rounded to 100, 50, 20, 10, and so forth, when comparisons are made with sample films. Those lines which are estimated to fall between the above values are arbitrarily given values of 70, 30, 15, 7, and so forth (Ward and others, 1963).

To obtain uniformity between the standard and sample electrode charge, 5 mg of 99.999 percent purity gold, 5 mg of graphite base standard, and 2.5 mg of aluminum oxide are weighed, mixed, and packed into the electrode cavity. The first four standards of standard set No. 1 are an exception to this. These standards contain less than 5 mg gold to compensate for their high silver content. Pure graphite is added to bring the weight to 15 mg. Table 35 illustrates the amounts to be weighed for these four standards.

TABLE 35.—*Electrode charge for the first four standards of standard No. 1*
[Values are reported in milligrams]

Gold wire	Pure graphite	Aluminum oxide	Standard
2.7	2.3	2.5	5
3.9	1.1	2.5	5
4.5	.5	2.5	5
4.8	.2	2.5	5

PRECISION AND ACCURACY

The nature of gold, which varies greatly from grain to grain as well as from deposit to deposit (Gay, 1963), creates a problem in determining the analytical precision on a natural gold sample. To obtain a homogeneous sample for the purpose of determining the precision of the method, a nugget of native gold was cleaned in hydrofluoric acid to remove the surface coating and then heated at 1,300°C for 30 minutes. Ten splits of the homogenized sample and ten splits of a natural occurring sample from the same source area were then analyzed; the results are shown in table 36. Assuming that the procedure was successful in homogenizing the sample, the results show the analytical variance is generally within a factor of 2, whereas the natural variance can be as great as a factor of 20. The differences in the two sets of data are probably due to the influence of the acid wash and heating during the homogenizing process.

Accuracy proved to be more difficult to determine than precision, because there was no homogeneous gold sample available with known amounts of several trace impurities. However, a gold standard was obtained that had been annealed with 1-percent copper. To obtain a

TABLE 36.—*Results of homogenized and natural-occurring gold samples from the same source area*

[Except for silver, concentrations are in parts per million. Leaders (...) indicate the element was not detected]

Ag (percent)	Bi	Ca	Cu	Fe	Hg	Mg	Mn	Pb	Si	Ti
Homogenized sample										
10	1.5	20	500	500	...	10	5	1,000	30	...
10	2	5	500	500	...	10	7	1,000	15	...
10	2	30	500	500	...	20	7	1,500	20	...
10	2	10	500	500	...	15	7	1,000	15	...
10	2	10	500	500	...	10	7	1,000	15	...
10	1.5	10	500	500	...	10	5	1,000	15	...
10	2	30	500	500	...	20	5	2,000	20	...
10	2	30	500	500	...	20	7	2,000	30	...
10	1	200	500	500	...	20	7	1,000	20	...
10	1.5	10	500	500	...	10	5	1,000	15	...
Natural sample										
10	15	70	200	500	2,000	200	10	700	2,000	50
15	10	200	200	1,000	2,000	200	15	500	2,000	70
10	2	50	150	700	1,500	200	10	200	2,000	100
10	10	50	200	300	1,000	150	7	500	1,500	50
15	10	100	200	700	1,500	200	10	500	5,000	100
15	3	50	150	500	2,000	200	10	100	7,000	70
10	3	50	500	500	100	50	5	1,000	500	5
10	2	15	200	200	2,000	100	5	150	1,000	20
10	1.5	30	200	500	1,500	150	7	30	1,500	70
10	2	20	150	150	1,000	100	5	100	1,500	20

standard with 2,000 ppm copper in gold for the purpose of establishing some understanding of the accuracy, each of five electrodes was charged with 1 mg of the 1-percent copper standard and 4 mg pure gold. The five replicate samples were then analyzed and comparisons made with a standard film. The comparisons gave 2,000-ppm copper reading for all five samples, proving the method accurate, at least for copper. The same accuracy cannot be assumed for all elements sought; however, experience has shown that the combined accuracy and precision is sufficient to distinguish differences in the chemical composition of native gold originating from various source areas.

CONCLUSION

The study of trace element and silver content of native gold for the purpose of establishing the genetic origin of the gold requires the analysis of a wide range of elements from samples that may be extremely small. Preparation of samples for analysis must not result in the alteration of the natural chemical composition of gold by loss of certain volatile elements. A fast effective semiquantitative spectrographic method has been developed to meet these requirements. To eliminate

the necessity of complicated sample-preparation techniques which may result in loss of volatile elements or otherwise alter the natural chemical composition of gold, the gold is analyzed in its metallic state by use of direct-current arc anode excitation. Thus, after the gold is retrieved from its source, no further preparation is required other than hand-picking under a binocular microscope and, if desired, cleaning in an acid wash to remove the surface coating. A split-slit technique utilizing a Hartmann diaphragm and step filter assemblage enables a dual analysis from one electrode charge by simultaneously recording volatile elements from a short burn at 100-percent transmission and less volatile elements from a total energy burn at 36-percent transmission on separate portions of the spectrum.

A major difficulty in analyzing native gold is the acquisition of adequate standards with which to make comparisons. In this procedure standards are effected by the admixture of spectrographically pure compounds in a graphite base and volatilized in the presence of pure gold. Aluminum oxide is added to both sample and standard electrode charges as a codistillation agent to produce a smooth even-burning arc throughout the exposure period.

The analysis of several hundred gold samples from various source areas has shown the method to be effective in the determination of distinguishing chemical characteristics of gold. Therefore, the method is of value in aiding the understanding of the geologic principles involved during the deposition of gold deposits (J. C. Antweiler and W. L. Campbell, oral commun., 1971).

ACKNOWLEDGMENT

REFERENCES CITED

Antweiler, J. C., and Sutton, A. L., Jr., 1970, Spectrochemical analyses of native gold samples: U.S. Geol. Survey Rept. USGS–GD–70–003, 28 p.: available only from U.S. Dept. Commerce Natl. Tech. Inf. Service, Springfield, Va. 22161, as Rept. PB1–94899.

Campbell, W. L., Mosier, E. L., and Antweiler, J. C., 1973, Effects of laboratory treatments on silver and other elements in native gold: U.S. Geol. Survey Jour. Research, v. 1, no. 2, p. 211–220.

Crook, W., 1939, Spectrographic and metallographic study of native gold: Metals Technology, Tech. Pub. 998, 14 p.

Gay, N. C., 1963, A review of the geochemical characteristics of gold in ore deposits: Witwatersrand Univ. Econ. Geology Research Unit Inf. Circ. 12, 70 p.

Grimes, D. J., and Marranzino, A. P., 1968, Direct-current arc and alternating-current spark emission spectrographic field methods for the semiquantitative analysis of geologic materials: U.S. Geol. Survey Circ. 591, 6 p.

Meggers, W. J., Corliss, C. H., and Scribner, B. F., 1961, Tables of spectral-line intensities; U.S. Natl. Bur. Standards Mon. 32, pts. 1 (arranged by element) and 2 (arranged by wavelength).

Mertie, J. B., Jr., 1940, Placer gold in Alaska: Washington Acad. Sci. Jour., v. 30, no. 3, p. 93–124.

Mosier, E. L., 1972, A method for semiquantitative spectrographic analysis of plant ash for use in biogeochemical and environmental studies: Appl. Spectroscopy, v. 26, no. 6, p. 636–641.

Myers, A. T., Havens, R. G., and Dunton, P. J., 1961, A spectrochemical method for the semiquantitative analysis of rocks, minerals, and ores: U.S. Geol. Survey Bull. 1084–I, p. 207–229.

Ward, F. N., Lakin, H. W., Canney, F. C., and others, 1963, Analytical methods used in geochemical exploration by the U.S. Geological Survey: U.S. Geol. Survey Bull. 1152, 100 p.

Warren, H. V., and Thompson, R. M., 1944, Minor elements in gold: Econ. Geology, v. 39, no. 7, p. 457–471.