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Guidelines for Sample Collecting and Analytical Methods Used in the U.S. Geological Survey for Determining Chemical Composition of Coal

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METRIC-ENGLISH EQUIVALENTS

Metric unit	English equivalent	Metric unit	English equivalent
Length			
millimetre (mm)	= 0.03937 inch (in)	litre per second (l/s)	= .0353 cubic foot per second
metre (m)	= 3.28 feet (ft)	cubic metre per second per square kilometre [(m ³ /s)/km ²]	= 91.47 cubic feet per second per square mile [(ft ³ /s)/mi ²]
kilometre (km)	= .62 mile (mi)	metre per day (m/d)	= 3.28 feet per day (hydraulic conductivity) (ft/d)
Area			
square metre (m ²)	= 10.76 square feet (ft ²)	metre per kilometre (m/km)	= 5.28 feet per mile (ft/ml)
square kilometre (km ²)	= .386 square mile (mi ²)	kilometre per hour (km/h)	= .9113 foot per second (ft/s)
hectare (ha)	= 2.47 acres	metre per second (m/s)	= 3.28 feet per second
Volume			
cubic centimetre (cm ³)	= 0.061 cubic inch (in ³)	metre squared per day (m ² /d)	= 10.764 feet squared per day (ft ² /d)
litre (l)	= 61.03 cubic inches	cubic metre per second (m ³ /s)	= 22.826 million gallons per day (Mgal/d)
cubic metre (m ³)	= 35.31 cubic feet (ft ³)	cubic metre per minute (m ³ /min)	= 264.2 gallons per minute (gal/min)
cubic hectometre (hm ³)	= 810.7 acre-foot (acre-ft)	litre per second (l/s)	= 15.85 gallons per minute
litre	= 2.113 pints (pt)	litre per second per metre [(l/s)/m]	= 4.83 gallons per minute per foot [(gal/min)/ft]
litre	= 1.06 quarts (qt)	kilometre per hour (km/h)	= .62 mile per hour (mi/h)
litre	= .26 gallon (gal)	metre per second (m/s)	= 2.237 miles per hour
cubic metre	= .00026 million gallons (Mgal or 10 ⁶ gal)	gram per cubic centimetre (g/cm ³)	= 62.43 pounds per cubic foot (lb/ft ³)
cubic metre	= 6.290 barrels (bbl) (1 bbl=42 gal)	gram per square centimetre (g/cm ²)	= 2.048 pounds per square foot (lb/ft ²)
Weight			
gram (g)	= 0.035 ounce, avoirdupois (oz avdp)	centimetre	= .0142 pound per square inch (lb/in ²)
gram	= .0022 pound, avoirdupois (lb avdp)	Temperature	
tonne (t)	= 1.1 tons, short (2,000 lb)	degree Celsius (°C)	= 1.8 degrees Fahrenheit (°F)
tonne	= .98 ton, long (2,240 lb)	degrees Celsius (temperature)	= [(1.8 × °C) + 32] degrees Fahrenheit
Specific combinations			
kilogram per square centimetre (kg/cm ²)	= 0.96 atmosphere (atm)		
kilogram per square centimetre	= .98 bar (0.9869 atm)		
cubic metre per second (m ³ /s)	= 35.3 cubic feet per second (ft ³ /s)		

Guidelines for Sample Collecting and Analytical Methods Used in the U.S. Geological Survey for Determining Chemical Composition of Coal

By Vernon E. Swanson and Claude Huffman, Jr.

ABSTRACT

This report is intended to meet the many requests for information on current U.S. Geological Survey procedures in handling coal samples.

In general, the exact type and number of samples of coal and associated rock to be collected are left to the best judgement of the geologist. Samples should be of unweathered coal or rock and representative of the bed or beds sampled; it is recommended that two channel samples, separated by 10 to 100 yards (10 to 100 metres) and weighing 4 to 5 pounds (1.8 to 2.3 kilograms) each, be collected of each 5 feet (1.5 metres) of vertical section. Care must be taken to avoid any sample contamination, and to record the exact locality, thickness, and stratigraphic information for each sample.

Analytical methods are described for the determination of major, minor, and trace elements in coal. Hg, As, Sb, F, Se, U, and Th are determined in the raw coal, and the following 34 elements are determined after ashing the coal: Si, Al, Ca, Mg, Na, K, Fe (total), Cl, Ti, Mn, P, S (total), Cd, Li, Cu, Zn, Pb, B, Ba, Be, Co, Cr, Ga, La, Mo, Nb, Ni, Sc, Sr, Ti, V, Y, Yb, and Zr. The methods used to determine these elements include atomic absorption spectroscopy, X-ray fluorescence spectroscopy, optical emission spectroscopy, spectrophotometry, selective-ion electrode, and neutron activation analysis. A split of representative coal samples is submitted to the U.S. Bureau of Mines for proximate, ultimate, forms of sulfur, and Btu determinations.

INTRODUCTION

Frequent requests for information from industry, university, and government groups for our coal geochemical methods have prompted the preparation of this report. The demand for high-quality complete chemical data on coal can only become greater with increased coal use; in order to establish reliability and comparability of analytical data, some standards and guidelines are required. The data are fundamental in determining the economic value of the coal, in evaluating environmental effects of coal mining and of coal use, and in determining potential byproduct recovery and the adaptability of the coal to beneficiation, gasification, liquefaction, and

other technologic processes of coal treatment. The data also can be used to correlate coal beds, to indicate the bog, marsh, or lagoonal environments of peat accumulation, and to determine postdepositional processes of preservation and alteration of the coal.

Most of the guidelines and methods described here were adopted during the comprehensive Southwest Energy Study conducted by the U.S. Department of the Interior in late 1971. The resulting report (Swanson, 1972), which included analyses of 71 coal samples and 16 powerplant ash samples, marked the beginning of a new period of modern coal analyses. Since then, more than 3,000 samples of coal and associated rock have been analyzed by the U.S. Geological Survey; most of the analyses have been made publically available in several reports (Swanson, 1972; U.S. Geological Survey and Montana Bureau of Mines and Geology, 1973, 1974; Swanson, Huffman, and Hamilton, 1974; Swanson and others, 1976). Major segments of the data have also been summarized in a series of papers presented at national scientific meetings (Medlin and others, 1975a, b; Coleman and others, 1975; Millard and Swanson, 1975; Hatch and Swanson, 1976), and prepared by the State Geological Surveys (Glass (Wyo.), 1975; Conwell (Alaska), 1976). Pertinent data have also been incorporated into several environmental impact statements and in many published reports on local areas by geologists of the U.S. Geological Survey.

GUIDELINES ON COLLECTING COAL SAMPLES

Specific instructions on the exact type, number, and distribution of samples to be collected cannot

be given, but some general guidelines should be followed:

1. The judgment of the geologist must be applied toward obtaining samples which will be most representative of the coal bed.
2. Only samples of fresh or unweathered coal should be submitted for analysis, preferably collected from a newly exposed mine face or from a drill core. The samples should be shipped to the laboratory within a few days after collection to minimize the effect of oxidation and exposure to air on the moisture content and on the forms of sulfur.
3. The objective should be to obtain a complete channel sample or core of the minable bed; if the coal bed is more than 5 feet (1.5 m) thick, a good rule-of-thumb is to collect one sample of each 5-foot (1.5-m) interval of coal (for example, four samples of a bed 20 ft, or 6 m, thick). Special-type samples (prominent fusain band or pyrite lens, for example) will also be analyzed at the discretion of the geologist.
4. Generally, 4 to 5 pounds (1.8 to 2.3 kg) of coal should be included in each sample; for rock samples, 2 pounds (0.9 kg) is sufficient.
5. A satisfactory channel sample, for example, can be obtained from a coal bed in a mine by first exposing a new, fresh face of the coal, then chipping an approximately 3-inch by 3-inch (7.5 cm by 7.5 cm) channel downward from the top of the bed with a chisel or pick-point hammer, producing coal fragments 2 inches (5 cm) or less across. Positioning a horizontal plastic sheet below the level of channel cutting is sometimes helpful, particularly if coal accumulates in excess of the desired sample size, and cone-and-quartering separation of the coal is needed to obtain the representative sample.
6. Plastic bags (10 x 15 in., or 25.4 x 38 cm, or larger; thickness 0.006 in. or 0.15 mm) should be used for the sample, and care should be taken to avoid contact of the coal with metal during and after collecting sample (the use of a geologic hammer, of course, cannot be avoided); sample number, date of collection, and key description should be written with a felt-tipped marker pen (permanent ink) on each bag, *and* on a label attached to the tie on the bag.
7. A rule-of-thumb should be never to collect just a single sample from one locality—always collect two samples, or, if a mine face is several hundred yards (metres) long, collect three channel samples. The main reasons for collecting two or three samples are that short-distance compositional changes can be assessed and that possible analytical errors can be spotted.
8. Core samples of coal are better than samples of weathered coal, but contamination by drilling fluids generally makes trace-element analysis unreliable. Name and composition of drilling fluids used should accompany list of core samples submitted for analysis.
9. Shale splits, siltstone partings, or bone coal less than a few inches (5–10 cm) thick generally should be included in a channel sample if it is probable that this material will be included in mined coal. Special samples of these non-coal materials should also be collected, based on the judgment of the geologist, to determine their possible contribution to abnormal element concentrations.
10. If project objectives include the obtaining of knowledge of coal shipped or of plant feed, extra care should be taken to collect at least two representative raw coal, cleaned coal, blend-pile, and conveyor-belt samples. Such sample sets should include, where possible, representative samples of the sink-fraction of washed coal, and of furnace-bottom ash and fly ash from precipitator and scrubber units.
11. Where geochemical data on seatrock or underclay and overburden rock are desired, representative samples should be collected, according to the preceding guidelines. In collecting overburden samples, one of two methods may be preferable, depending on local conditions: (a) Channel samples of 5- or 10-foot (1.5- or 3-m) intervals; or (b) two samples of each lithology, which can be related to measured sections and assigned weighted values.
12. If permission to sample is obtained from a company, the offer should be made, and the promise kept, to provide the company with a copy of the analytical results as soon as they are completed; where possible, obtain available analytical data from the company for comparison with your analyses. It should be made clear to the company or landowner that the analyses of your samples will be part of

the public record; the collection of samples which requires a promise to withhold analyses on a "company confidential" basis should be done only for compelling scientific purposes.

SUBMITTING SAMPLES

After the samples have been collected and are ready to be shipped, a simple list of sample-description information should be prepared. The samples should be listed by number, each sample number followed by the name and thickness of the coal bed (or thickness of unit sampled, related to top of bed), the name and age of the formation and member which include the coal bed, the precise location of the sampled locality (preferably by latitude and longitude to the nearest second, or by quarter section, township and range), the name of mine and company owner, the date the sample was collected, and the name of the collector. (Use of the metric system for units of measurement is encouraged.) For example:

<i>Sample No.</i>	<i>Sample description</i>
HC-21-72....	Channel sample of Waynesburg coal bed, 1.24 m thick, lower member of Waynesburg Formation, Upper Pennsylvanian; 40°13'20", 80°11'10" [1.6 km ENE. of McGovern], Washington County, Pa.; Zonk mine, Southwest Consolidated Co.; coll. by John Smith, Oct. 16, 1976.

Any additional information considered useful concerning the unit sampled can be included in the sample description; for example, the distribution and thickness of visible pyrite or partings, the degree of weathering, or even a sketch showing relations of stratigraphic units and lithologies.

A copy of the list of sample descriptions should be enclosed with the samples and, to assure this information arrives, another copy should also be sent by mail in another envelope.

Samples to be shipped should be sent by the commercial carrier most conveniently available to the geologist. In most places, packing the samples in small cartons and sending by mail is the easiest procedure. Because the coal and, especially, rock samples can cut through the plastic bag while jostled during mail handling, care should be taken to cushion the sample bags in the cartons with wadded newspapers or other packing material.

We recognize that the sampling procedures outlined above do not adhere to the details of the much more extensive and time-consuming procedures proposed and used by others (for example Burrows,

1907; Holmes, 1911; Fieldner and Selvig, 1938; Schopf, 1960). Rather, the individual geologist must use good judgement in selecting representative and quality samples. So many variable factors are involved—such as time available to collect a large number of samples, natural coal-bed alteration, time of sample exposure during laboratory preparation, and continued improvement of analytical techniques—that rather loose, general guidelines seem the most appropriate to encourage the collection of many samples of the different kinds of coal from the different areas of the United States.

ANALYTICAL METHODS FOR DETERMINATION OF MAJOR, MINOR, AND TRACE ELEMENTS IN COAL

The analytical work performed on coal samples received in the U.S. Geological Survey laboratories is outlined in figure 1. An undried 600 g (about 1 qt) split of samples representative of the set collected is sent to the U.S. Bureau of Mines at Pittsburgh, Pa., for the routine coal analysis. This analysis sequence includes (1) proximate analysis (percent ash, moisture, fixed carbon, and volatile matter), (2) ultimate analysis (percent carbon, hydrogen, oxygen, nitrogen, and sulfur), (3) Btu determination, and (4) sulfur analysis (percent organic sulfur, pyrite sulfur, and sulfate sulfur). The analytical methods used by the Bureau of Mines have been described in U.S. Bureau of Mines Bulletin 638 (Staff Office of the Director of Coal Research 1967) and will not be described in this report. The remainder of all analytical work and sample preparation shown in the analysis sequence flow diagram (fig. 1) is performed by the U.S. Geological Survey laboratories.

The Geological Survey laboratories routinely provide the following analytical determinations on coal samples:

1. Percent ash.
2. Major composition of the coal ash: SiO₂, Al₂O₃, Na₂O, K₂O, CaO, MgO, total Fe as Fe₂O₃, P₂O₅, MnO, TiO₂, Cl and total S as SO₃.
3. Trace element composition of the coal ash:
 - (a) Individual quantitative determinations—Cd, Cu, Li, Pb, and Zn.
 - (b) Semiquantitative spectrographic analysis—15 to 30 elements detected by this method.

4. Trace element composition of raw coal—quantitative determinations for As, F, Hg, Sb, Se, U, and Th.
5. In addition, individual quantitative chemical determinations may be made if abnormal amounts of certain elements are indicated by semiquantitative spectrographic analysis, or on a spot-check basis—Ag, Au, Be, Ge, Mo, Ni, and V.

Except for the specialized analyses run by the U.S. Bureau of Mines, all the analyses indicated for coal (fig. 1) are those routinely run on rock and soil samples. The forms of sulfur in rocks and soils are determined in our laboratory, and the organic carbon, carbonate, and total carbon contents are also determined.

SAMPLE PREPARATION

Each coal sample is poured, as received, into a cone-shaped pile on kraft paper, flattened, and portions separated and collected with a scoop or spatula from random locations in the sample. A 600-g (about 1 qt) sample of each coal sample is thus collected in a plastic bag, placed in a 1-quart ice cream container, and transmitted to the U.S. Bureau of Mines, Pittsburgh, Pa., for ultimate and proximate analysis, and for Btu and forms of sulfur determinations. The remainder of the sample is placed in disposable aluminum pie pans and dried at 25° to 32°C and at about 30 percent relative humidity in an air-circulating oven. Some coal samples take as long as 82 hours to dry thoroughly.

The dried coal sample is crushed, and a 300-g (about 1-pint) reserve is split out for storage to be used for future petrographic, mineralogic, or chemical studies. The balance of crushed coal is ground in a vertical Braun¹ pulverizer equipped with ceramic plates set to pass about 80 mesh, and mixed. The ground coal sample (analytical split) is distributed to the analytical laboratories.

INDIVIDUAL ANALYTICAL METHODS

ANALYSIS OF COAL ASH

Atomic absorption spectrometry methods are used for the determination of Mg, Na, Cd, Cu, Li, Mn, Pb, and Zn in the ash of coal, and X-ray fluorescence spectroscopy methods are employed for Al, Ca, total Fe, K, P, Si, total S, Ti, and Cl. In addition, 63 elements are looked for by a semiquantitative six-step

emission spectrographic method. Of these, 17 are generally found to be of interest in the coal ash: B, Ba, Be, Co, Cr, Ga, Ge, La, Mo, Nb, Ni, Sc, Sr, V, Yb, Y, and Zr. The other 46 elements are also reported when detected by the spectrographic method (table 1), even though 18 of these elements are quantitatively determined by other methods.

ASHING

A portion of the ground raw coal (25 to 75 g) is weighed and transferred to a 100-ml fused silica dish. The dish is placed in a cold muffle furnace and, with the furnace door partly open, the temperature is gradually elevated over a 4-hour period to 450°C. The temperature is then increased to 525°C and maintained until the sample is completely ashed. An occasional stirring or mixing of the sample during ashing is desirable. The ash is weighed, and the percentage of ash calculated. The ash is mixed thoroughly with a spatula and transferred to a suitable container. About 3 g of coal ash is required for the analyses by six-step spectrographic, X-ray fluorescence, and atomic absorption methods.

ATOMIC ABSORPTION SPECTROSCOPY

A short description of the atomic absorption methods for the determination of MgO, Na₂O, Cu, Li, Mn, and Zn follows: 0.500 g of coal ash is weighed into a 100-ml platinum dish. Ten millilitres of demineralized water, 10 ml HNO₃, and 10 ml of HF are added to the dish. The dish is covered and allowed to stand overnight. Seven millilitres of HClO₄ is added to the dish. The dish is placed on a steam bath for 1 hour and then placed on a hot plate to fume off the acids to near dryness. The dish is removed from the hot plate and the sides of the dish are washed down with water. Five millilitres of HClO₄ is added and the dish is returned to the hot plate. The dish is heated until all acids are evaporated. Twenty-five millilitres of water and 5 ml of HCl are added to the dish. The dish is covered, placed on a steam bath, and digested for 30 minutes. The solution is transferred to a 100-ml volumetric flask and diluted to volume with water. Aliquots or dilutions of this sample are then aspirated into the air-acetylene flame of an atomic absorption spectrometer to determine the elements listed. The sample aliquot used for the determination of Mg was made to contain 1 percent La. The instrumental parameters used for the listed elements are those recommended by the Perkin-Elmer Corp.

Cd and Pb are also determined by atomic absorption spectroscopy on a separate split. In this method 1.000 g of coal ash is weighed and transferred to a

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

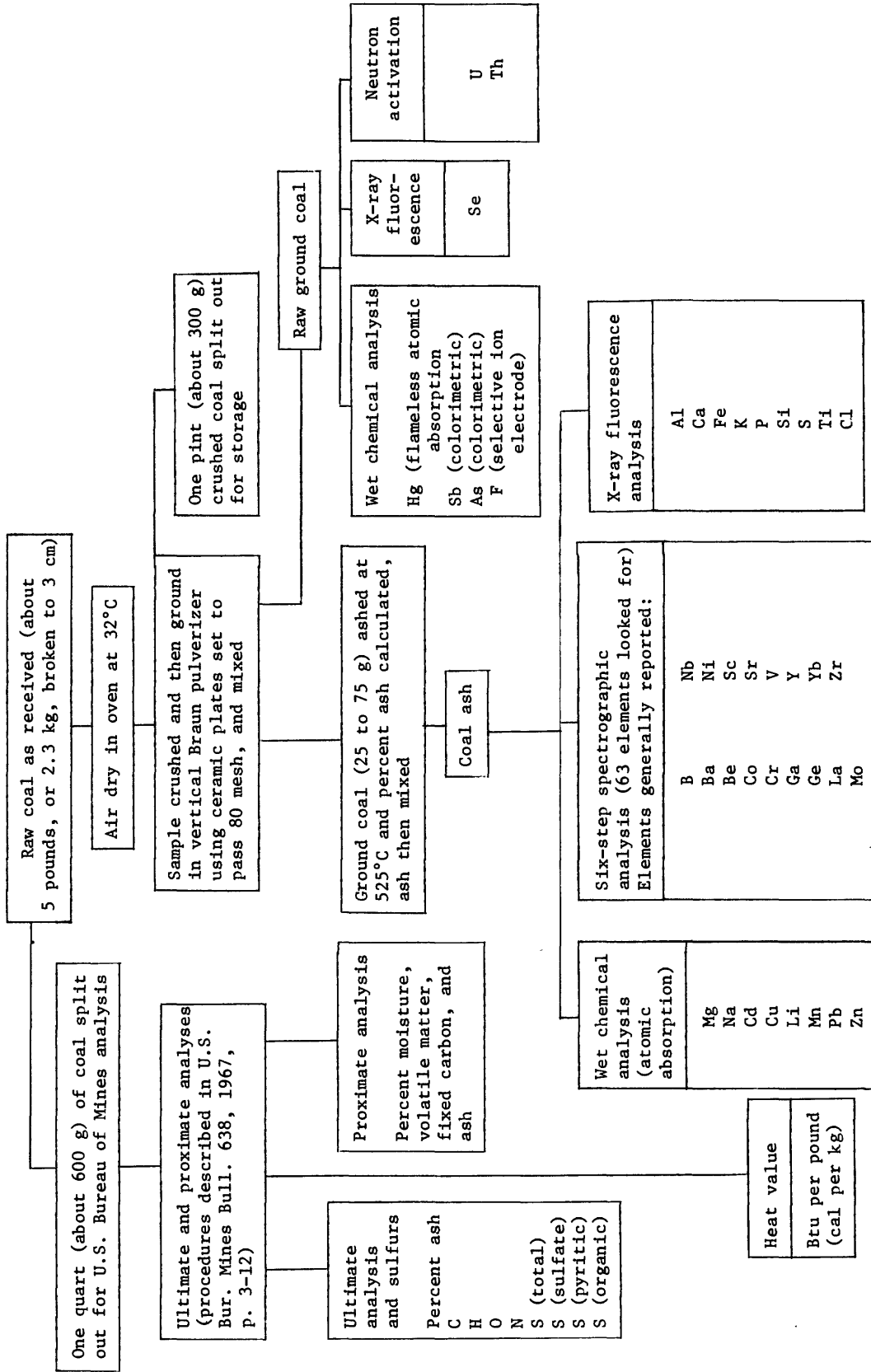


FIGURE 1.—Flow chart showing sequence of sample preparation and chemical analysis.

150-ml beaker. Ten millilitres of water and 10 ml HNO₃ are added to the beaker. The beaker is covered with a watch glass, placed on a shaking hot plate, and boiled until the volume of the solution is reduced to about 5 ml. The beaker is removed from the hot plate and the sides of the beaker and lid are washed down with about 20 ml water. The beaker is placed on a steam bath and the contents digested for 1 hour. The contents of the beaker are transferred to a 50-ml volumetric flask, cooled, and diluted to volume with water. The solids are allowed to settle overnight. A portion of the clear sample solution is aspirated into the air-acetylene flame of the atomic absorption instrument using deuterium background correction to determine both Cd and Pb. The instrumental parameters used are those recommended by the Perkin-Elmer Corp.

The sample weights and the lower limits of determination by atomic absorption methods for each of the elements in coal ash are as follows:

Element	Sample wt. (g)	Lower limit
Mg.....	0.5	0.01 percent
Na.....	.5	.01 percent
Cd.....	1.0	1 ppm
Cu.....	.5	10 ppm
Li.....	.5	5 ppm
Mn.....	.5	25 ppm
Pb.....	1.0	25 ppm
Zn.....	.5	10 ppm

The concentration of each element determined in the coal ash is normally converted to the whole-coal basis using the percent ash value in this calculation. A coal that contains 10 percent ash would lower the above limits of determination by a factor of 10 for the converted values.

X-RAY FLUORESCENCE SPECTROSCOPY

X-ray fluorescence methods developed in our laboratory by James S. Wahlberg are employed for the determination of Al, Ca, total Fe, K, P, Si, total S, Ti, and Cl in the coal ash. In this method 0.800 g of coal ash is fused with 6 g of flux (mixture of 43 percent Li₂B₄O₇, 55 percent Na₂B₄O₇, and 2 percent NaBr) in a 20-ml platinum crucible. The NaBr is added to the fusion mixture to facilitate easy removal of the solidified button from the platinum crucible. This fused button is X-rayed and counted to determine the listed elements.

An Automated General Electric¹ vacuum spectrometer is used to determine the listed elements. The

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instrument parameters used are given in the following tabular form:

Element	Crystal ¹	MA ² on X-ray tube	X-ray tube target	2θ angle (degrees)
Al.....	PET.....	60	Cr	144.67
Ca.....	LiF.....	20	Cr	113.08
Total Fe.....	LiF.....	20	W	57.52
K.....	PET.....	60	Cr	50.64
P.....	PET.....	60	Cr	89.40
Si.....	PET.....	60	Cr	109.06
Total S.....	NaCl.....	60	Cr	144.53
Ti.....	LiF.....	60	Cr	86.13
Cl.....	NaCl.....	60	Cr	113.91

¹PET, pentaerythritol. ²MA, megaamperes.

Most of these elements are conventionally reported as oxides. The lower limits of determination in the ash are:

Element ¹	Sample Weight (g)	Lower limit (percent)
Al ₂ O ₃	0.8	0.2
CaO.....	.8	.02
Total Fe (as Fe ₂ O ₃).....	.8	.02
K ₂ O.....	.8	.02
P ₂ O ₅8	.1
SiO ₂8	.2
Total S (as SO ₃).....	.8	.04
TiO ₂8	.02
Cl.....	.8	.1

¹MgO, Na₂O, and MnO, as determined by atomic absorption method, are also included in tables showing major-oxide composition of ash.

EMISSION SPECTROSCOPY

A six-step semiquantitative optical emission spectrographic method developed in our laboratory by Myers, Havens, and Dunton (1961) and Myers and Havens (1970) is used to look for 63 elements; the trace elements generally found to be of interest are B, Ba, Be, Co, Cr, Ga, Ge, La, Mo, Nb, Ni, Sc, Sr, V, Y, Yb, and Zr. In this method, 1 part coal ash is mixed with 1.15 parts of a mixture of 9 parts quartz (SiO₂) and 1 part Na₂CO₃. Ten milligrams of the resulting mixture is in turn mixed with 20 mg of pure graphite powder, and this final mixture is burned in a d-c arc for 120 seconds, collecting the spectra on photographic plates. The resulting spectra are visually compared with reference standards. The element determinations are identified with geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, and so forth, but are reported as midpoints of these brackets, 1., 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, and so forth; there are thus 6 brackets to the decade. The precision of a reported value is approximately plus-or-minus one bracket at the 68-percent confidence level, or two brackets at the 95-percent confidence level.

The approximate lower limits of determination for the elements analyzed by the six-step spectrographic method in the ash of coal samples are shown in table 1.

TABLE 1.—Approximate visual lower limits of determination in ash for the elements in coals analyzed by the six-step spectrographic method

[Si and Na not reported because quartz and sodium carbonate are added as part of method. Some combinations of elements raise or lower the limits of determination]

Element	Percent	Element	Percent
Fe.....	0.002	Si.....
Mg.....	.005	Al.....	0.02
Ca.....	.005	Na.....
Ti.....	.0005	K.....	1.5
		P.....	.5
Element	ppm	Element	ppm
Mn.....	2	Ce.....	500
Ag.....	1	Ga.....	10
As.....	2,000	Ge.....	20
Au.....	50	Hf.....	200
B.....	50	In.....	20
Ba.....	5	Li.....	200
Be.....	3	Re.....	100
Bi.....	20	Ta.....	1,000
Cd.....	100	Th.....	500
Co.....	10	Tl.....	100
Cr.....	2	Yb.....	2
Cu.....	2	Pr.....	200
La.....	100	Nd.....	150
Mo.....	7	Sm.....	200
Nb.....	20	Eu.....	200
Ni.....	10	Gd.....	100
Pb.....	20	Tb.....	700
Pd.....	5	Dy.....	100
Pt.....	100	Ho.....	50
Sb.....	500	Er.....	100
Sc.....	10	Tm.....	50
Sn.....	20	Lu.....	70
Sr.....	10	Ir.....	100
Te.....	5,000	Os.....	100
U.....	1,000	Rh.....	5
V.....	15	Ru.....	20
W.....	200		
Y.....	20		
Zn.....	700		
Zr.....	20		

ANALYSIS OF RAW COAL

The more volatile elements As, F, Hg, Sb, and Se are determined in the ground raw coal sample. U and Th are also determined on the raw coal sample.

MERCURY

The flameless atomic absorption spectroscopy method (Huffman and others, 1972) is used to determine mercury. In this method, 0.200 g of ground coal is digested under oxidizing conditions using the

HNO₃-H₂SO₄-HClO₄ digestion procedure developed by V. E. Shaw (oral commun., 1973). Mercury in the sample solution is reduced to its elemental state with stannous chloride and then aerated from solution onto a silver screen placed in the vapor train. This silver screen is subsequently heated, and the mercury vapor is carried by an airstream to an absorption cell, where its concentration is determined by atomic absorption spectrometry. The lower limit of the determination is 0.01 ppm.

ANTIMONY

The Rhodamine-B spectrophotometric method of Ward and Lakin (1954) is used to determine antimony. D. R. Norton (oral commun., 1973) of our laboratory has modified this method for coal samples to obtain a lower limit of determination. In this method 1.0 g of raw coal is mixed with a slurry of magnesium oxide and magnesium nitrate. The slurry is dried at 110°C and then ashed in a muffle furnace gradually raising the temperature to 550°C. This ashing technique takes 4 to 5 hours. The ashed sample and magnesium salts are fused with 3.0 g potassium pyrosulfate and leached with 6 N HCl containing glycerol. Sodium sulfate is added to reduce antimony to Sb⁺³. The solution is filtered into a 125-ml extraction flask and the residue washed. After cooling to 15°C, the antimony is oxidized to Sb⁺⁵ with ceric sulfate and the excess oxidant reduced with hydroxylamine hydrochloride. After dilution with water to an acid concentration of 1.5 N, the solution is cooled to 15°C and the antimony chloride complex is extracted with isopropyl ether. The extract is washed and then reacted with an acidic solution of Rhodamine-B to form a red-violet dispersion whose absorption at 560 mμ is measured with a spectrophotometer. The limit of determination of this method is 0.1 ppm Sb.

ARSENIC

The heteropoly blue spectrophotometric method described by Rader and Grimaldi (1961) is used to determine arsenic. Sample decomposition (1 to 2 g) and sample solution is made with HNO₃, HClO₄, and H₂SO₄ acids. In this method, As is distilled as arsenious chloride after reduction with bromide and hydrazine sulfate and is determined spectrophotometrically. The limit of determination on raw coal is 1.0 ppm.

FLUORINE

A fluoride specific-ion electrode is used to determine fluorine. In this procedure 0.250 g of ground

coal is mixed in a zirconium crucible with a slurry of MgO and MgNO₃. The mixture is dried at 110°C, then ashed in a muffle furnace which is gradually raised to 525°C. The ashed mixture is fused with 1.0 g NaOH over an open burner with the zirconium crucible covered. The crucible and lid are placed in a plastic beaker, water is added to dissolve the fused mass, and then filtered into a 100-ml volumetric flask. The residue is washed with about 5 ml of a 1 percent w/v solution of NaOH, diluted to volume with water, and mixed. A 50-ml aliquot of the sample solution is transferred to a 100-ml volumetric flask, diluted to volume with 1 M ammonium citrate solution, and mixed. Fifty millilitres of this solution is poured into a plastic beaker and the potential is measured by the fluoride-ion electrode. In some cases, about 10 minutes is required for equilibrium to be reached. The lower limit of determination of the method is about 20 ppm.

SELENIUM

An X-ray fluorescence method developed by J. S. Wahlberg (written communication, 1972) is followed in the determination of selenium. In this method 2.000 g of raw coal is decomposed with a sodium peroxide fusion. Selenium is then reduced and precipitated with hydrazine sulfate, potassium iodide, and sodium sulfite, with Te added as carrier. The precipitate is collected on a millipore filter for X-ray determination. The lower limit of determination is 0.1 ppm Se.

URANIUM AND THORIUM

A delayed neutron activation method described by Amiel (1962) is used to determine these two elements. The raw coal sample of 5.000 g is irradiated in a neutron flux of 2×10^{12} n/cm²/s (neutrons per square centimetre per second) for 1 minute, and within seconds after irradiation is counted for 2 minutes with a ring of 6 boron trifluoride detectors. The lower limit of the determination is 0.1 ppm U and 2.0 ppm Th.

ACCURACY OF ANALYTICAL METHODS

The accuracy of analytical methods as applied to coal samples is rather difficult to evaluate because of the lack of standard samples of coal. Only two National Bureau of Standards standard coal samples are available, NBS Standard Reference Material 1632 and NBS Standard Reference Material 1630. Of these, the NBS-1630 coal has been certified only for its mercury content. The EPA-NBS coal sample (NBS-1632) has been analyzed for selected trace elements by the National Bureau of Standards and also by an interlaboratory roundrobin comparison initiated by the U.S. Environmental Protection Agency. Elements determined in the roundrobin included: As, Be, Cd, Cr, Cu, F, Fe, Hg, Mn, Ni, Pb, S, Se, Tl, Th, U, V, and Zn. The U.S. Geological Survey laboratory was one of the many participating laboratories. Table 2 compares our results with those obtained by the National Bureau of Standards and

TABLE 2.—Comparative results for EPA-NBS interlaboratory trace element study
[All values in parts per million in moisture-free coal (NBS-1632), except sulfur, in percent. Values in parentheses given for information only. Leaders (...) indicate no data available]

Element	NBS certified value	All labs, grand mean	U.S. Geological Survey	
			Quantitative methods described	Six-step emission spectrographic method
As	5.9 ± 0.6	6.24	5.3
Cd	0.19 ± 0.03	.9	<1
Cr	20.2 ± 0.5	22.7		15
Cu	18.0 ± 2	17	15
Hg	0.12 ± 0.02	0.22	.13	
Mn	40 ± 3	41.3	42	30
Ni	15 ± 1	19.0	15	10
Pb	30 ± 9	30.4	28.3	20
Se	2.9 ± 0.3	4.6	2.9	
Th	(3)	4.7	
U	1.4 ± 0.1	1.7	1.43	
V	35 ± 3	34.9	20
Zn	37 ± 4	129.5	38	
Be	(1.5)	1.75	1
S	1.28	1.19	
F	183.5	85	

¹Questionable mean; wide scatter or limited data.

TABLE 3.—Comparison of USGS analyses with Illinois State Geological Survey analyses

[Col. 1, USGS values (As, Cu, Mn, Pb, Cd, F, Sb, and Zn by wet chemical methods, all others by six-step spectrographic method); col. 2, Illinois values]

Sample	Ca		Fe		K		Mg		Na		Ti	
	1	2	1	2	1	2	1	2	1	2	1	2
Major elements (percent)												
15278.....	0.68	0.82	1.11	1.65	0.18	0.17	0.06	0.05	0.031	0.048	0.05	0.06
16264.....	.73	.56	2.31	2.05	.17	.15	.05	.04	.040	.051	.04	.05
16408.....	.10	.23	3.71	3.51	.14	.13	.04	.03	.014	.007	.03	.05
16317.....	.90	.73	1.35	1.57	.15	.17	.05	.05	.017	.017	.04	.06
15263.....	.04	.10	2.25	2.65	.11	.14	.04	.04	.013	.014	.05	.05
Sample	As		B		Be		Cd		Co		Cr	
	1	2	1	2	1	2	1	2	1	2	1	2
Trace elements (ppm)												
15278.....	3.6	5.6	150	1.5	1.5	0.4	0.3	2	5	10	9
16264.....	9.5	9.6	150	139	2	3.0	7.0	2.7	1	2	10	16
16408.....	55	57	30	49	.7	.9	<.3	<.4	7	17	10	7
16317.....	25	24	100	85	2	2.8	21	28	5	9	20	26
15263.....	79	73	150	2	3.0	4.4	3.8	5	11	7	7
Sample	Cu		F		Ga		Ge		Hg		Mn	
	1	2	1	2	1	2	1	2	1	2	1	2
Trace elements (ppm)—continued												
15278.....	6	8	60	60	3	2.4	15	9	0.80	0.39	100	78
16264.....	9	10	64	69	3	4.3	20	15	.32	.24	70	81
16408.....	13	16	91	83	2	2.7	<3	2	.29	.30	15	13
16317.....	14	20	53	52	3	4.7	20	12	.18	.10	150	67
15263.....	32	44	55	41	5	3.5	20	22	.28	.22	7	12
Sample	Mo		Ni		Pb		Sb		V		Zn	
	1	2	1	2	1	2	1	2	1	2	1	2
Trace elements (ppm)—continued												
15278.....	1	5	5	8	5	9	0.4	0.2	15	27	162	137
16264.....	<1	5	7	22	57	51	.7	.8	10	22	305	159
16408.....	1	6	10	26	44	40	.5	2.0	15	31	24	26
16317.....	5	9	20	30	66	72	2.9	4.3	30	32	2,420	2,668
15263.....	1	2	50	40	76	96	5.4	5.7	20	23	340	425

with the grand mean of all participating laboratories. Our quantitative values for As, Cu, Hg, Mn, Ni, Pb, Se, Th, and U agreed well with the NBS values. Our F and S values agreed with the grand mean of the few laboratories reporting. Our six-step spectrographic values for Be, Cr, Cu, Mn, Ni, Pb, and V are acceptable but appear to be somewhat low.

Five previously analyzed coal samples obtained from Dr. Harold J. Gluskoter of the Illinois Geological Survey were analyzed in our laboratory for selected major and trace elements. All values are reported on a whole-coal basis, even though many determinations were made on ash. The results obtained in our laboratory are compared with those obtained by the Illinois Survey laboratories in table

3. Our results for the major elements Ca, Fe, K, Mg, Na, and Ti agreed well with theirs. The agreement between laboratories is generally good for the trace elements As, B, Be, Cd, Cr, Cu, F, Ga, Ge, Hg, Mn, Pb, Sb, V, and Zn. The agreement for Co, Mo and Ni is poor enough to suggest need for further study. The analytical methods used by the Illinois Geological Survey on these samples have been described by Ruch, Gluskoter, and Shimp (1974).

National Bureau of Standards coal sample 1630 has been certified to contain 0.13 ppm Hg. This sample has been analyzed in this laboratory many times and our values range from 0.12 ppm to 0.15 ppm Hg, with a standard deviation of about 0.01 ppm.

COMMENTS AND RECOMMENDATIONS

The guidelines for collecting coal samples and the analytical methods described here are those currently used by the U.S. Geological Survey. The analytical methods are periodically modified to improve efficiency and accuracy, and, as new and better methods and instruments become available, they are adopted and used. For example, new polarographic methods are now being tested for analysis of Cd and Pb in coal ash; and research continues in the application of neutron activation analysis (Millard and Swanson, 1975) and X-ray fluorescence analysis for a suite of other elements.

Similarly, the need and emphasis for data on different elements change. Thus, Cl analysis has been added to, and Te and Tl analyses have been dropped from, the list of elements included in the coal analyses routinely reported by the U.S. Geological Survey.

Copies of all analyses of coal samples are sent to the geologist who collected the samples; extra copies of the analyses are, if requested, also sent to the geologist to give to, for example, owners of property from which samples were collected.

All analyses are reported by the laboratory either as percent or as parts per million (ppm). Further, it is recommended that all analytical data, when included in the geologist's written report, should be reported as percent or parts per million:

1. Proximate and ultimate analyses and forms of sulfur analyses, in percent, on an as-received, moisture-free, and moisture- and ash-free basis.
2. Major-oxide composition of ash, in percent of ash.
3. Trace-element composition, in parts per million, as analyzed on ash of coal, or raw coal, and, when desirable, all trace elements on ash of coal may be converted to "whole coal" on an air-dried basis.
4. Btu values (British thermal units per pound of coal) are, of course, not shown in percent or parts per million, simply as Btu/lb or Btu.

All of the locality, stratigraphic, and analytical data are stored in and are retrievable from the U.S. Geological Survey's computer system.

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