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Analytical Methods for Coal and Coal Products

Edited by CLARENCE KARR, JR.
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Volume III



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Preface

The world reserves of coal are larger than those of petroleum and natural gas, and the production capacity for coal currently exceeds that for oil shale, tar sands, peat, and the other less developed fossil energy reserves. As a result, coal is the projected resource alternative for energy and materials well into the next century. With this increasing importance of coal there is also an increasing need to meet improved environmental standards and to supply economic uses for by-products. This is seen in the current work on modifications of combustion and ancillary technologies for the generation of electric power without deterioration of the environment, and the carbonization of unfamiliar as well as traditional coals for the manufacture of metallurgical coke with controlled emissions. In addition, there are the emerging technologies for commercial production of synthetic liquid and gaseous fuels from coal that present special problems in their development, as well as the need to meet restrictions in air and water pollution and to utilize wastes.

A major key for solving these problems in the use of unfamiliar coals, the development of new coal conversion processes, the marketing of new solid, liquid, and gaseous fuels, the utilization of by-products, and the control of emissions is the use of appropriate analytical methods. The goal of these three volumes is to supply, insofar as feasible, a detailed presentation of what constitutes the first comprehensive reference work devoted exclusively to the subject of analytical methodology for coal and coal products. I have divided these volumes into a total of twelve parts, each part containing several chapters devoted to a particular subject. Some parts are based on major processes or products, such as liquefaction (Volume I), carbonization (coke, pitch) and combustion (Volume II), and gases (Volume III). However, the complex analytical problems involved are generally not limited to any specific process, and there are many problems that are held in common. Thus Volume III also includes discussion of waste products, by-products, environmental problems, and miscellaneous analytical problems, as well as special instrumental techniques for solving various problems.

Because different aspects of a particular subject are frequently scattered through various chapters in the volumes, cross-references between chapters have been entered. In addition, the subject indexes have been made as detailed as was practical, and the reader will benefit from examination of pertinent subjects in the indexes of all three volumes. Many individual subjects are located in the indexes of two or three volumes. The multiauthorship of the chapters has permitted a diversity of viewpoints and opinions on various analytical problems. A careful reading of these volumes will show that definitive solutions are not yet available in a number of instances. This is not an unexpected situation because coal and some of its products may well comprise the most difficult materials to analyze of all the world's major resources. There is therefore a clear need for continued research on the fundamentals of analysis of coal and coal products, and the development of reliable and accurate analytical instrumentation, including on-stream applications.

I am deeply indebted to all the many experts, both in the United States and abroad, who have made the publication of this multivolume reference work possible, and to the organizations involved for their generous cooperation. The interested reader can find more about the circumstances and details of the preparation of this work in the Prefaces to Volumes I and II.

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*Chapter 38***Coke Oven Gas Analysis***Dan P. Manka*

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I. INTRODUCTION

Major volumes of coke oven gas are generated by the carbonization of coal for the production of blast furnace coke. Typically, 80 million ft³ of gas is produced daily as a result of the coking of 7500 tons of coal. Approximately 11,000 ft³ of dry gas is generated per ton of typical coking coal. The volume of gas is dependent on the volatile matter of the coal mixture charged to the coke ovens. An additional volume is present from the volatilization of the moisture present in the charged

3

coal. Although a major portion of this moisture is condensed, coke oven gas is saturated with water at the gas temperature prevailing throughout the chemical products recovery system.

The gas is treated for the removal of tar, ammonia, naphthalene, and aromatics in the recovery system. A portion of the treated gas flows to the coke batteries for underfiring of the coke ovens to supply heat for the carbonization of the coal in the ovens. The major portion of the treated gas flows to the steel producing mills where it serves as fuel for heating many furnaces.

Methods of analysis for the major chemical products in the coke oven gas† are described in this chapter, beginning with the analysis of fixed gases flowing from the top of the coke oven to the analysis of sulfur compounds and hydrogen cyanide in the treated gas. The latter is important in the desulfurization of coke oven gas in order to meet EPA regulations for concentrations of inorganic and organic sulfur compounds in the treated gas prior to its use as a fuel.

Because space is limited in this chapter for a complete description of the analytical methods, it is assumed that the analyst is familiar with standard methods of analysis and with the operation of a gas chromatograph. It is of interest that all of the coke oven gas components discussed in this chapter are also included in the analysis of stack gas for environmental assessment (Volume II, Chapter 36).

II. COKE OVEN GAS FLOW DIAGRAM

The flow diagram of gas is practically the same in all coke plants. As more desulfurization processes are installed, these will vary in location depending on the type of system being installed.

In the flow diagram in Fig. 1, coke oven gas rises from the coke oven a, through standpipe b, to gooseneck c, where it is contacted with flushing liquor (ammonia liquor). Tar and moisture are condensed. Ammonia chloride, and a portion of the ammonia, fixed gases, hydrogen cyanide, and hydrogen sulfide are dissolved by the liquor. The gas, liquor, and tar enter the gas collecting main d, which is connected to all the ovens of a battery. In some cases there may be two gas collecting mains to a battery. The gas, liquor, and tar are separated in tar decanters. The tar f, separated from the liquor e, flows to tar storage g. A portion of the liquor e is pumped to the gooseneck c on the top of each oven. The remainder of the liquor is pumped to the ammonia liquor still h, where it is contacted with live steam to drive off free

† Analyses of coke oven effluents for polynuclear aromatics are given in Chapter 43.

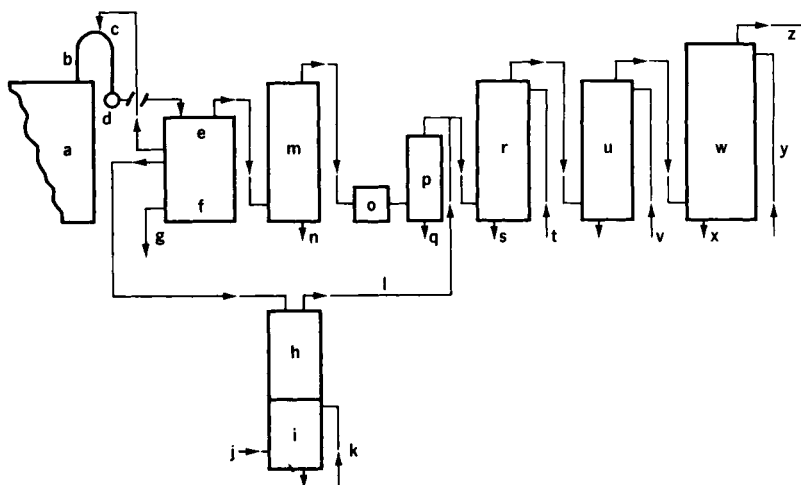


Fig. 1. Flow diagram of coke oven gas. The lettered items are identified in the text.

ammonia, fixed gases, hydrogen cyanide, and hydrogen sulfide. As the liquor flows from the free still *h* to the fixed still *i*, it is contacted with lime or sodium hydroxide *k* to liberate free ammonia from ammonium chloride. Live steam, admitted at *j* flows up through the fixed and free stills, and the ammonia, fixed gases, hydrogen cyanide, and hydrogen sulfide are added through *l* to the main coke oven gas stream ahead of the ammonia saturator *r*.

The coke oven gas, separated from liquor and tar in *e*, is cooled indirectly with water in the primary coolers *m*. The fine tar that separates from the gas is pumped through *n* to the tar storage tank. The cooled gas is pumped by exhausters *o* to the electrostatic precipitators *p*, where additional fine tar is condensed and pumped through *q* to the tar storage tanks. The gas is contacted with a dilute solution of sulfuric acid in the ammonia saturator *r* to remove free ammonia. The ammonium sulfate-laden acid flows through *s* to the ammonia crystallizer (not shown) where crystals of ammonium sulfate are separated and the remaining sulfuric acid is pumped back to the ammonia saturator through *t*.

The ammonia-free gas flows to the final coolers *u*, where it is further cooled by direct water contact. The water plus condensed naphthalene flows from the cooler through tar which absorbs the naphthalene. The water is cooled and recirculated into the final cooler through *v*.

The cooled gas enters the wash oil scrubbers *w*, also known as benzole scrubbers, where it contacts wash oil, a petroleum oil, pumped

into the scrubbers through y. The aliphatic and aromatic compounds are extracted from the gas by the wash oil. The principal components are benzene, toluene, xylenes, indene, and solvent, also known collectively as light oil. The benzolized wash oil is pumped through x to the wash oil still (not shown) where live steam strips out the light oil compounds. The debenzolized wash oil is cooled and returned to the wash oil scrubber. In some plants the light oil is further processed and fractionated into benzene, toluene, and xylenes and into a high-boiling solvent fraction. Naphthalene is also present in the light oil. Plants with low volumes of light oil do not have facilities for refining, therefore, the oil is sold to large refineries.

The gas from the wash oil scrubbers flows through z to a gas holder which tends to equalize the pressure. Booster pumps distribute a portion of the gas for underfiring of the coke ovens, but the major portion flows to the steel plant where it is used as a fuel in the many furnaces.

III. DETERMINING END OF COKING CYCLE BY GAS ANALYSIS

The length of a coking cycle for carbonizing of coal in an oven is determined from experience and the range of the flue temperature. Most coke plants also have experimental coke ovens to determine coking cycles for variable coal mixes and at different flue temperatures. Another method to determine the end of this cycle is by analysis of the gas flowing from the oven into the standpipe. This section will describe this approach.

A. Sampling System

The gas sample from the standpipe must be cooled, separated from tar and water, and filtered before it is analyzed for H_2 , O_2 , N_2 , CH_4 , CO , CO_2 , and illuminants.

The sampling train in Fig. 2 has been used successfully for the continuous pumping of gas to a sample bottle or to a gas chromatograph. It is designed to operate for several hours so that many samples can be analyzed before there is an accumulation of tar in probe c or in the separators d.

Standpipe b is located on the gas discharge end on top of coke oven a. Normally, there is an opening on the side of the standpipe where live steam is admitted to remove accumulated tar in the pipe. This opening is ideally located for gas sampling since it is generally about 2-3 ft above the oven.

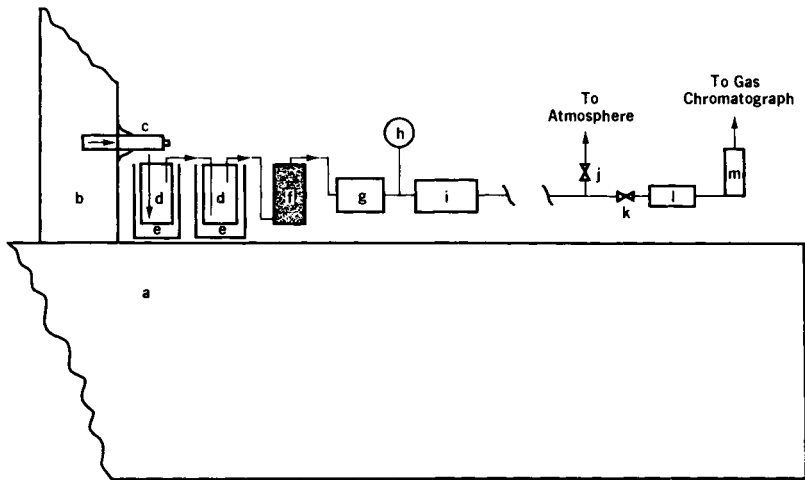


Fig. 2. Sampling gas from top of coke oven. The lettered items are identified in the text.

The probe *c*, extending to approximately the center of the standpipe, is a $\frac{3}{4}$ - or 1-in. heavy wall stainless steel pipe. The end of the pipe in the gas stream is sealed, and the other end has a plug for removing accumulated tar. A $\frac{1}{4}$ in. by approximately 3 in. slot is cut along the length of the pipe in the gas stream extending from the closed end. When the probe is inserted into the standpipe, *it is important* that the slot face the direction of gas flow. This position decreases the amount of tar pumped in with the sample gas. The probe is inserted into a plug similar to the one used for the steam line and is pushed through the opening in the standpipe until the plug seals the opening. This insertion should be done rapidly to prevent excessive flow of coke oven gas through the opening. The probe extending outside of the pipe and the $\frac{1}{4}$ in. pipe from the probe to the first separator *d* should be insulated.

The two separators *d* for cooling the gas and for separation of tar and water are identical. These are made from 4 in. pipe, 10- to 12-in. long, one end sealed, and a flange with a gasket on the top end. The inlet pipe extends approximately half-way into the separator. Both separators are kept in a bucket of water *e*. The separators should be pressure tested before they are used. The remaining piping is $\frac{1}{4}$ in. copper tubing with Swaglock fittings. Although most of the tar is condensed in the separators, the gas is drawn through glass wool in a glass tube *f* to remove the lighter tar oil. This glass tube can be a glass bottle normally used in the laboratory to dry gases with Drierite. It has an inlet con-

nection on the bottom, an outlet connection near the top, and a metal screw cap with a seal on the top. Tygon tubing is used for the metal tube to glass connection. The gas flows through a final filter g that removes submicron particles, such as the Pall Trinity "Junior Size" Epocel cartridge. The gas is drawn from the standpipe by a peristaltic pump i. Good results are obtained with this type of pump using a $\frac{1}{2}$ - or $\frac{3}{8}$ -in.-diameter plastic tube for conveying the gas. The tubing is easily replaced if it becomes broken or contaminated. A vacuum gauge h ahead of the pump is valuable to detect plugging of lines or separators. When vacuum reaches 20 in., it is most probable that tar is accumulating in the probe. A rod inserted into the probe through the plug opening of the probe will generally be sufficient to reopen the pipe.

Gas from the pump passes through valve k and is dried in tube l containing Drierite. The flow to the sample loop of the chromatograph is maintained at 50 cm³/min as indicated by rotometer m. Excess sample gas is vented to atmosphere through valve j.

B. Orsat Analysis

If a portable gas chromatograph is not available, a gas sampling bottle can be filled with the dried gas after rotometer m. Analysis of hydrogen, oxygen, carbon dioxide, carbon monoxide, methane, and illuminants concentrations in the gas can be determined on an Orsat equipped with combustion apparatus to determine hydrogen and methane. However, the analysis time is lengthy so that the number of analyses made near the end of the coking cycle are too limited to obtain a true picture of the coking cycle end point.

C. Gas Chromatographic Analysis

The use of a portable gas chromatograph located in a sheltered area near the sampling system is the best method to follow the course of the coking cycle.

The curves in Fig. 3 are based on the analytical results obtained on a gas chromatograph with a thermal conductivity detector. The separation column is a $\frac{1}{8}$ in. \times 10 ft stainless steel tube containing No. 5A Molecular Sieve, and the reference column is a $\frac{1}{8}$ in. \times 67 in. stainless steel tube containing Porapak Q. The operating conditions are argon flow 12 cm³/min to each column, 100 mA cell current, column and cell temperature is 40°C. The chromatograph is standardized with a gas containing 50% H₂, 30% CH₄, 10% CO, 5% CO₂, and N₂ the balance.

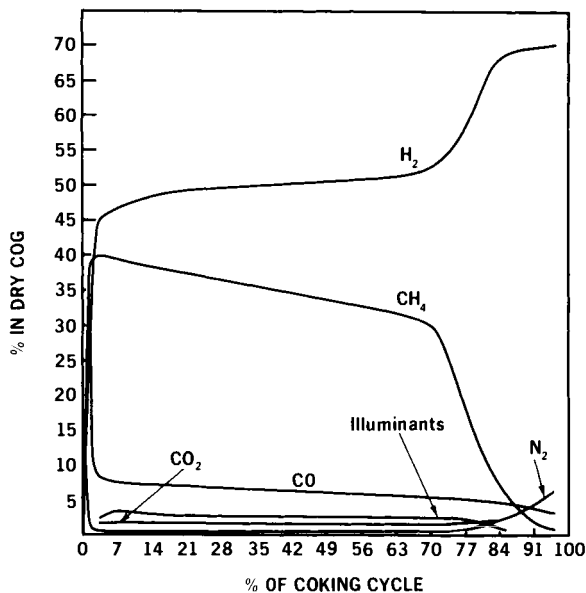


Fig. 3. Composition of coke oven gas during coking cycle.

The standard gas is admitted into the sample line ahead of the Drierite in 1 and the flow rate maintained through the sample loop the same as for coke oven gas. The sample loop capacity is 0.5 cm^3 and is dependent on the sensitivity of the detector using argon as carrier gas.

If the detector has insufficient sensitivity for CO and CH₄, a carrier gas containing 8% hydrogen and 92% helium may be used at a cell current of 150 mA.

Concentrations of CO₂ and illuminants, as ethylene, can be obtained on the Porapak column. The chromatograph must also be equipped with a sample valve for this column and a polarity switch so that the peaks are positive on the chart paper of the recorder. However, CO₂ and illuminants are not necessary to determine the end point; therefore, these can be ignored or periodically determined by the Orsat method. A chromatogram of these same gas components, but in much different proportions from underground gasification of coal, is shown in Chapter 41, Fig. 3.

D. Results

The plot of the analytical results in Fig. 3 are those for coking dry coal for 14 hr at a flue temperature of 2300°F. Concentration of hydrogen

approaches a maximum of over 70%, and the methane approaches the minimum of less than 1% near the end of the coking cycle. Generally, coking is continued for an additional 30 min after these analytical values are reached, and then the coke is pushed from the oven.

Similar curves are reported (Beckmann *et al.*, 1962) for the coking of wet coals. However, the coking cycle is 18–19 hr because a large amount of water must be evaporated from the wet coal charged to the ovens.

IV. AMMONIA

Ammonia is recovered from coke oven gas because it is marketable and it is deleterious to the heating system if it remains in the gas used as fuel in the steel plant.

This section describes analysis of ammonia in coke oven gas entering the ammonia saturators by wet chemical methods and by gas chromatography.†

In the flow diagram in Fig. 1, coke oven gas containing ammonia enters the saturator *r*, where it is contacted with a dilute solution of sulfuric acid which recovers the ammonia as ammonium sulfate.

A. Wet Chemical Methods

Most wet chemical methods are similar; therefore, one method will be described in more detail.

1. Sampling System

The $\frac{1}{4}$ in. sampling line, preferably stainless steel, in Fig. 4 is extended horizontally to the center of the gas main which carries the gas to the ammonia saturator. Either the end of the probe in the gas main is bent to a 90° angle, or an elbow is attached to the end. The probe should be inserted so that the bent end, or the elbow, faces in the direction of gas flow. This method reduces the amount of naphthalene included with the gas sample. A $\frac{1}{4}$ in. valve *b* is attached to the end of the probe located outside of the gas main.

The pipe is extended from the valve to two traps, *c* and *d* in series, to collect entrained and condensed water. The traps are glass bottles about 10-in. long which have neck openings large enough for a neoprene rubber stopper fitted with two $\frac{1}{4}$ in. glass tubes. Two glass bottles

† Analysis of coke plant ammonia still effluent and waste liquor is given in Chapter 44, Table VII.

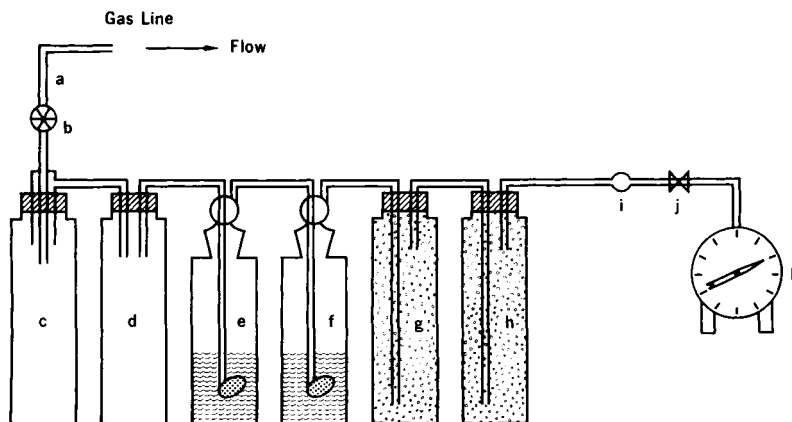


Fig. 4. Absorption apparatus for ammonia in coke oven gas. The lettered items are identified in the text.

with ground-glass heads also serve well as traps. Short connections between glass tubing and pipe can be made with Tygon tubing.

The traps are connected by means of glass tubing and short Tygon tubing to two gas washing bottles in series, e and f (Ace Glass No. 7162, 500 mliter capacity, porosity A) containing sulfuric acid solution. They connect to empty trap g for collecting any entrained sulfuric acid solution. Finally, they connect to trap h filled with iron oxide shavings to remove hydrogen sulfide. The inlet tube in this trap extends to within 2 in. of the bottom of the bottle. The outlet tube is connected to a tube i, loosely filled with glass wool, then to a needle valve j (Fisher No. 14-630-8A). The end of the valve is connected to a wet gas meter k with Tygon tubing.

2. Procedure

Add 140 mliter of 10% sulfuric acid and a drop of methyl orange to each of the two gas washing bottles. Assemble the apparatus, except the probe, according to the description. Open the valve on the probe to blow out accumulated water. Then connect the probe end to the first trap. The valve should be fully open. Make certain that the meter is level and that the indicating dials are set to zero.

Pass gas through the apparatus at the rate of 3-6 ft³/hr. Record the time, temperature of the meter thermometer, meter reading, and barometric pressure each hour. Pass 15 ft³ of gas through the apparatus depending on the expected ammonia content of the gas. Use the needle valve to control gas flow.

Combine the contents of the two gas washing bottles and the trap g into a 1 liter Florence flask. Rinse each bottle three times and add the washings to the flask. Neutralize the contents with about 125 mliter of 50% sodium hydroxide solution. Distill through a Kjeldahl trap and bubble the vapors into 50 mliter of *N/1* sulfuric acid solution in a 500 mliter Erlenmeyer flask in a water-cooled trough. Distill until there are about 400 mliter of liquid condensate. Transfer the liquid into a 600 mliter beaker, rinse the flask three times with distilled water, and add the washings to the beaker.

Back titrate the acid in the beaker with *N/1* sodium hydroxide using methyl orange indicator.

Measure the amount of condensate in the first two traps, c and d. Wash out the traps several times with distilled water and add the washings to the condensate. Add 18% sodium hydroxide solution and determine the ammonia content as above.

3. Calculations

Calculate the average meter temperature and barometric pressure during the absorption test. Correct the meter reading to standard conditions of 60°F and 30 in. Hg pressure.

a. NH_3 Calculations for Absorption Train

(1) Milliliters of $\text{H}_2\text{SO}_4 \times$ normality – milliliters of $\text{NaOH} \times$ normality = net milliliters of *N/1* H_2SO_4 combined with NH_3 .

(2) Net milliliters of $\text{H}_2\text{SO}_4 \times 0.017 =$ grams of NH_3 .

(3)
$$\frac{\text{grams of NH}_3}{\text{corrected number of cubic feet used in test}} = \text{grams of NH}_3/\text{cubic foot.}$$

(4)
$$\frac{\text{grams of NH}_3/\text{cubic foot} \times 1,000,000}{453.6} = \text{pounds of NH}_3/1,000,000 \text{ ft}^3.$$

b. NH_3 Calculations for Condensate

(1) Net milliliters of 1*N* H_2SO_4 combined with $\text{NH}_3 \times 0.017 =$ grams of ammonia in condensate.

(2)
$$\frac{\text{grams NH}_3 \text{ in condensate} \times 1,000,000}{\text{corrected cubic feet of gas in test} \times 453.6} = \text{pounds of NH}_3/1,000,000 \text{ ft}^3.$$

If only the total ammonia content is desired, the condensates in the