

Analytical Chemistry of Liquid Fuel Sources

**Tar Sands, Oil Shale,
Coal, and Petroleum**

**Peter C. Uden, Sidney Siggia,
and Howard B. Jensen**

ADVANCES IN CHEMISTRY SERIES

170

Analytical Chemistry of Liquid Fuel Sources

Tar Sands, Oil Shale, Coal, and Petroleum

**Peter C. Uden and
Sidney Siggia, EDITORS**

University of Massachusetts

Howard B. Jensen, EDITOR

Laramie Energy Research Center

Based on a symposium cosponsored
by the Divisions of Petroleum Chemistry
and Analytical Chemistry at the 173rd

Meeting of the American Chemical

Society, New Orleans, Louisiana

March 21-25, 1977.

ADVANCES IN CHEMISTRY SERIES

170

AMERICAN CHEMICAL SOCIETY

WASHINGTON, D. C. 1978



Library of Congress CIP Data

Analytical chemistry of liquid fuel sources.

(ACS advances in chemistry series; 170 ISSN 0065-2393)

Papers presented at a symposium held in Mar. 1977 at New Orleans, sponsored by the Division of Petroleum Chemistry and the Division of Analytical Chemistry of the American Chemical Society.

Includes bibliographies and index.

1. Liquid fuels—Congresses.

I. Uden, Peter C., 1939— II. Jensen, Howard Barnett, 1921— III. Siggia, Sidney. IV. American Chemical Society. Division of Petroleum Chemistry. V. American Chemical Society. Division of Analytical Chemistry. VI. Series: Advances in chemistry series; 170.

QD1.A355 no. 170 [TP343] 540'.8s [662'.6]
78-10399

ISBN 0-8412-0395-4 ADCSAJ 170 1-342 1978

Copyright © 1978

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each article in this volume indicates the copyright owner's consent that reprographic copies of the article may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc. for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating new collective works, for resale, or for information storage and retrieval systems.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission, to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto.

PRINTED IN THE UNITED STATES OF AMERICA

Advances in Chemistry Series

Robert F. Gould, *Editor*

Advisory Board

Kenneth B. Bischoff	Nina I. McClelland
Donald G. Crosby	John B. Pfeiffer
Jeremiah P. Freeman	Joseph V. Rodricks
E. Desmond Goddard	F. Sherwood Rowland
Jack Halpern	Alan C. Sartorelli
Robert A. Hofstadter	Raymond B. Seymour
James P. Lodge	Roy L. Whistler
John L. Margrave	Aaron Wold

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers, distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Volumes in the ADVANCES IN CHEMISTRY SERIES maintain the integrity of the symposia on which they are based; however, verbatim reproductions of previously published papers are not accepted. Papers may include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

The role of analytical chemistry in the broadening field of liquid fuel technology increasingly exemplifies the latest advances in technique and instrumentation. Indeed, so complex is the area that the whole range of presently available methods for quantitation and characterization are needed in its study.

Over the past few years, established analytical chemical methodology for crude oil and refined petroleum derivatives has been extended to the rapidly expanding field of coal liquefaction products and has assisted in the substantive reappraisal of such potential liquid fuel sources as oil shale, tar sands, and similar bitumenous deposits. While many of the analytical problems of separation, identification, and characterization are common to all of these fields, each area exhibits distinct requirements calling for specific development of appropriate methodology. Indeed, the added chemical complexity of the nonpetroleum-based liquid fuel sources presents many novel challenges to the chemical investigator.

In order to bring together present expertise in the various areas of liquid fuel analysis and characterization, the ACS Divisions of Petroleum Chemistry and Analytical Chemistry cosponsored a symposium wherein papers presented both reviewed general and specific analytical methodology of particular liquid fuel sources and also introduced applications of many currently developing techniques. Methods ranged from high-resolution gas and liquid chromatography to electron microprobe, carbon-13 NMR, EPR, and computer modeling. Efforts were made to indicate where techniques developed in one fuel liquids area could be applied usefully in others.

Many of the papers presented at that symposium have been revised and updated for the present volume and we thank all the contributors for their cooperation in this project. We are also grateful to the ACS Divisions of Petroleum Chemistry and Analytical Chemistry for their support.

HOWARD B. JENSEN
United States Department of Energy
Laramie Energy Research Center
Laramie, WY
June 30, 1978

SIDNEY SIGGIA and
PETER C. UDEN
Department of Chemistry
University of Massachusetts
Amherst, MA

Analytical Chemistry of Liquid Fuel Sources

ADVANCES IN CHEMISTRY SERIES 170

ERRATUM

Page 213

The correct address for Uden, Carpenter, DiSanzo, Hackett, and Sigga is:

Department of Chemistry
GRC Tower I
University of Massachusetts
Amherst, MA 01003

CONTENTS

Preface	ix
1. Spontaneous Combustion Liability of Subbituminous Coals: Development of a Simplified Test Method for Field Lab/Mine Applications	1
William A. Schmeling, Jeannette King, and Josef J. Schmidt-Collerus	
2. Analysis of Five U.S. Coals: Pyrolysis Gas Chromatography-Mass Spectrometry-Computer and Thermal Gravimetry-Mass Spectrometry-Computer Methods	13
E. J. Gallegos	
3. A ^1H and ^{13}C NMR Study of the Organic Constituents in Different Solvent-Refined Coals as a Function of the Feed Coal ...	37
D. L. Wootton, W. M. Coleman, T. E. Glass, H. C. Dorn, and L. T. Taylor	
4. Analysis of Solvent-Refined Coal, Recycle Solvents, and Coal Liquefaction Products	54
Joseph E. Schiller	
5. Structural Characterization of Solvent Fractions from Five Major Coal Liquids by Proton Nuclear Magnetic Resonance	66
I. Schwager, P. A. Farmanian, and T. F. Yen	
6. New Techniques for Measuring PNA in the Workplace	78
R. B. Gammage, T. Vo-Dinh, A. R. Hawthorne, J. H. Thorngate, and W. W. Parkinson	
7. Characterization of Mixtures of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography and Matrix Isolation Spectroscopy ...	99
G. Mamantou, E. L. Wehry, R. R. Kemmerer, R. C. Stroupe, and E. R. Hinton	
8. Chromatographic Studies on Oil Sand Bitumens	117
M. Selucky, T. Ruo, Y. Chu, and O. P. Strausz	
9. Petroleum Asphaltenes: Chemistry and Composition	128
J. F. McKay, P. J. Amend, T. E. Cogswell, P. M. Harnsberger, R. B. Erickson, and D. R. Latham	
10. Organometallic Complexes in Domestic Tar Sands	143
J. F. Branthaver and S. M. Dorrence	
11. Analyses of Oil Produced during in Situ Reverse Combustion of a Utah Tar Sand	150
S. M. Dorrence, K. P. Thomas, J. F. Branthaver, and R. V. Barbour	
12. Mass and Electron Paramagnetic Resonance Spectrometric Analyses of Selected Organic Components of Cretaceous Shales of Marine Origin	159
E. W. Baker, W. Y. Huang, and J. G. Rankin	

13. A Preliminary Electron Microprobe Study of Green River and Devonian Oil Shales	181
E. A. Hakkila, N. E. Elliott, J. M. Williams, and E. M. Wewerka	
14. Analysis of Oil Shale Materials for Element Balance Studies	195
Thomas R. Wildeman and Robert R. Meglen	
15. Aspects of Chromatographic Analysis of Oil Shale and Shale Oil ..	213
P. C. Uden, A. Carpenter, Jr., F. P. DiSanzo, H. F. Hackett, S. Siggia, and D. E. Henderson	
16. Olefin Analysis in Shale Oils	232
L. P. Jackson, C. S. Allbright, and R. E. Poulson	
17. Comparative Characterization and Hydro-Treating Response of Coal, Shale, and Petroleum Liquids	243
Carlton H. Jewitt and George D. Wilson	
18. High-Precision Trace Element and Organic Constituent Analysis of Oil Shale and Solvent-Refined Coal Materials	255
J. S. Fruchter, J. C. Laul, M. R. Petersen, P. W. Ryan, and M. E. Turner	
19. Chemical Class Fractionation of Fossil-Derived Materials for Biological Testing	282
Bruce R. Clark, C. H. Ho, and A. Russell Jones	
20. HPLC Techniques for Analysis of Residual Fractions	295
Harry V. Drushel	
21. Analytical Characterization of Solvent-Refined Coals Comparison with Petroleum Residua	307
R. B. Callen, C. A. Simpson, and J. G. Bendoraitis	
Index	323

Spontaneous Combustion Liability of Subbituminous Coals: Development of a Simplified Test Method for Field Lab/Mine Applications

WILLIAM A. SCHMELING, JEANNETTE KING,
and JOSEF J. SCHMIDT-COLLERUS

Denver Research Institute, University of Denver, Denver, CO 80208

Eighteen subbituminous coal samples were tested for their liability to spontaneous combustion using a combination of temperature-programmed air oxidation and gas-liquid chromatography, the latter being used in lieu of the conventional Orsat apparatus. Various column and switching arrangements as well as operational parameters were investigated with emphasis on simplicity and the ultimate objective to develop a portable instrument which can be used effectively for on-site testing or in field laboratories. Such an instrument could be utilized with fresh samples, thus preventing the usual sample degradation. Correlations of gas concentrations as a function of temperature and the S-index (which reflects the liability of the coal to spontaneous combustion) were determined by this method. The values obtained and the evaluation of the effectiveness of the tested analytical method are discussed.

The conservation of our fossil fuel resources is of great concern in these times of energy shortages. This is true for coal, especially in view of the eminent development of large-scale synfuel production from this resource. The danger of spontaneous oxidation and heating is a constant threat during mining, within large raw material storage bins for gasification or liquefaction operations, and/or in mine tailings. In order to minimize losses of coals, machinery, and even personnel, it is expedient

to detect spontaneous self-heating liabilities in coals as early as possible so that timely remedial action may be taken.

Since coals release gaseous products, it was thought that this property might be used as an indicator of a coal's susceptibility to spontaneous oxidation. Probably the most systematic research in this area was carried out by Winmill and Graham (1) in a special laboratory for the study of spontaneous coal combustion operated by the Doncaster Coal Owners Association. These investigations were published in a series of papers in the "Transactions of the Institution of Mining Engineers" between 1913 and 1935. The tangible results of this work were the development of a method using the evolution of carbon monoxide, in combination with the determination of oxygen deficiency, for the evaluation of the spontaneous heating liability of coals. This method has now been in general use for about forty years. However, more recent developments of sophisticated gas analysis equipment has all but replaced the classical Orsat method (2, 3). In particular, gas chromatography is capable of analyzing all constituents associated with coal oxidation to a high degree of accuracy. Furthermore, some GC models are portable and can be used in the field operated by personnel without extensive training.

Besides measuring gaseous effluents directly at the mine site, laboratory tests have been designed for evaluating a coal's liability to spontaneous heating. Finely ground samples are heated either adiabatically or nonadiabatically while being exposed to a flow of moist air. The effluent gas concentrations, particularly carbon monoxide, carbon dioxide, and oxygen are indicative of a coal's liability to spontaneous combustion. Using this method, coal samples may be classified according to an S-index (susceptibility) (4) which categorizes them as either very dangerous, not very dangerous, or not dangerous with respect to spontaneous heating.

This paper describes a nonadiabatic method for the evaluation of eighteen subbituminous coal samples using the S-index values. Laboratory methods for conducting the coal oxidation as well as the analysis of the effluent gases by gas chromatography are discussed. The objective of these experiments was to develop a methodology which ultimately might be amenable to the construction of a portable instrument usable in the field or in a mine lab. This could reduce sample handling and produce fairly accurate results in a considerably shorter period of time.

Experimental

Coal samples originating from a Wyoming subbituminous coal field varied in size from fines to 1 cm³ in diameter and were received in air-tight plastic containers. The samples, as received, were ground to 0.3–0.5-mm size in a glove box under a slightly pressurized nitrogen atmosphere. To accomplish this, the coal was ground initially with a

mortar and pestle. Final size reduction was carried out with a Waring blender run for short periods to minimize the production of fines. Then 100-g portions were stored in plastic bags in a nitrogen atmosphere.

The oxygen absorption apparatus was of a nonadiabatic type as described by Chamberlain, et al. (5). A schematic of the apparatus is shown in Figure 1.

Provision was made to either run air or nitrogen through the system. The latter was used for purging purposes prior to an experimental run. Air (60 mL/min) from a compressed tank was filtered to remove impurities and bubbled through water to attain 90–95% relative humidity. It was heated then in an oil bath by passing through a glass coil in order to heat it to the temperature of the coal. After reacting with the coal, the air and effluent gases passed through a moisture trap before entering the gas chromatograph. Flow rates were monitored on either side of the coal reaction chamber. A programmed temperature controller (Model West), in conjunction with a 5-W immersion heater, supplied heat to the oil bath at a rate of 25°C per hr. The temperatures of the coal and oil bath were measured with chrome–alumel thermocouples connected to a potentiometer. The 100-g coal samples were heated to 200°C or higher over approximately an 8-hr period. Oil bath and coal temperatures were recorded every 30 min and an effluent gas analysis was run on a Beckman GC-4 gas-chromatograph.

In this method, gas chromatography was used for analyzing the effluent gases because it is rapid and sensitive to low concentrations of the constituent gases. Suitable adsorption column configurations and operational parameters (adsorbent chemicals, temperatures, and carrier-gas flow rate) had to be developed. Since the objective was to use a relatively simple system that might be adaptable to field methods, it meant a reasonable carrier-gas flow rate (20–60 mL/min) and relatively low temperatures of operation (isothermal if possible). Many methods for separating mixtures containing oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, and ethane have been described in the literature (6, 7, 8, 9). These involve connecting adsorption columns for light components (O_2 , N_2 , CH_4 , CO) with partition columns for the remaining gases. The gases of concern in the coal self-oxidation experiments are O_2 , CH_4 , CO , and CO_2 . Reported methods for separation of these gases use (with some variations) two columns in series. The first column consists of 1/4-in. tubing, 4–10 ft long, and is filled with an adsorbent to remove CO_2 and separate it from the remainder of the constituents. The adsorbents generally used are silica gel, Chromosorb 102, or Poropak Q. The second column (of more or less the same size tubing) is capable of separating the permanent gases and light hydrocarbons. Molecular sieve adsorbents such as 13X or 5A are usually used for this purpose. The objective is to allow all but the CO_2 to pass into the second column, then switch to a bypass position and allow the CO_2 to elute directly to the detector while the remainder of the gases are held in the second column. After the CO_2 is eluted completely, the system is switched back to the series position and the remaining gases (O_2 , CH_4 , and CO) are separated and passed to the detector. Reported temperatures (isothermal or programmed) and carrier-gas flow rates vary to some extent but otherwise the methods are similar.

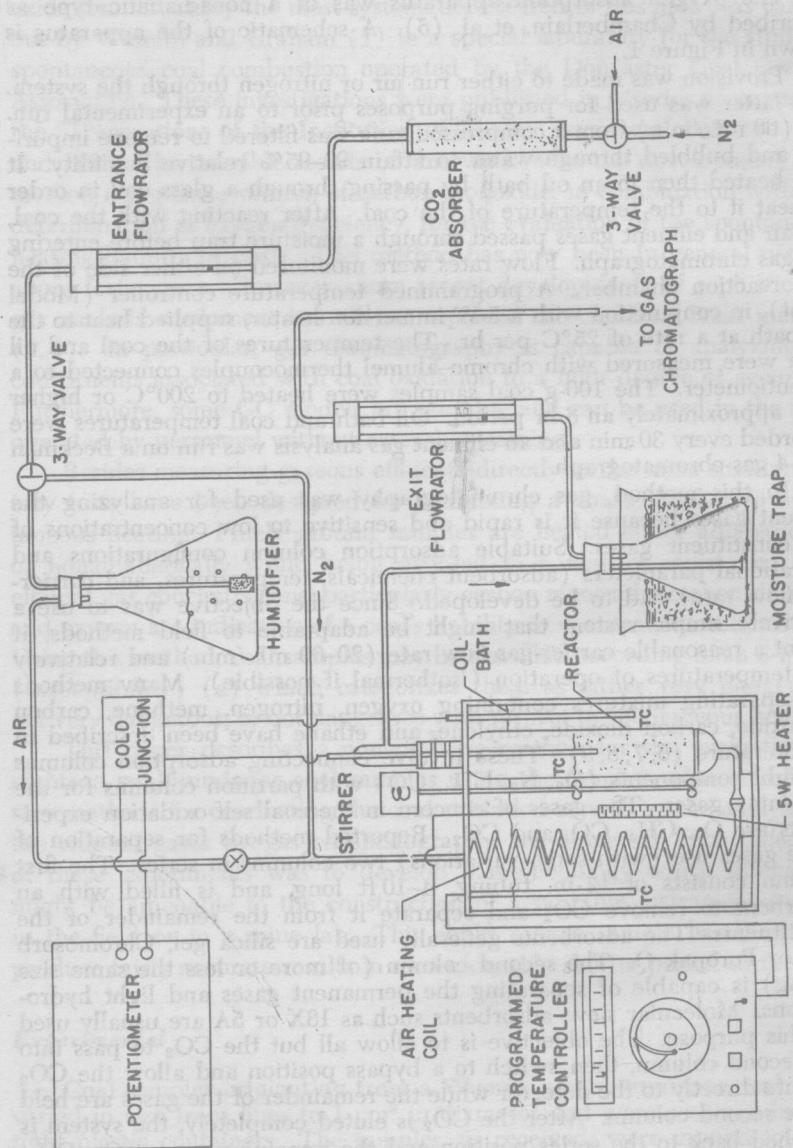


Figure 1. Nonadiabatic apparatus for determining spontaneous combustion liability of coal

Initial experiments utilized low carrier-gas flow rates and temperatures in order to ensure a sufficient retention of CO_2 in the first column (Chromosorb 102). This was accomplished to some extent; however, there was also some adsorption of CH_4 , and it was difficult to switch to the bypass position without partial or total loss of either CO_2 or CH_4 . On the other hand, if sufficient time was allowed for CH_4 to elute from Column 1 before switching to the bypass position, part of the CO_2 was also eluted, yielding only a partial detection as shown in Figure 2a. The

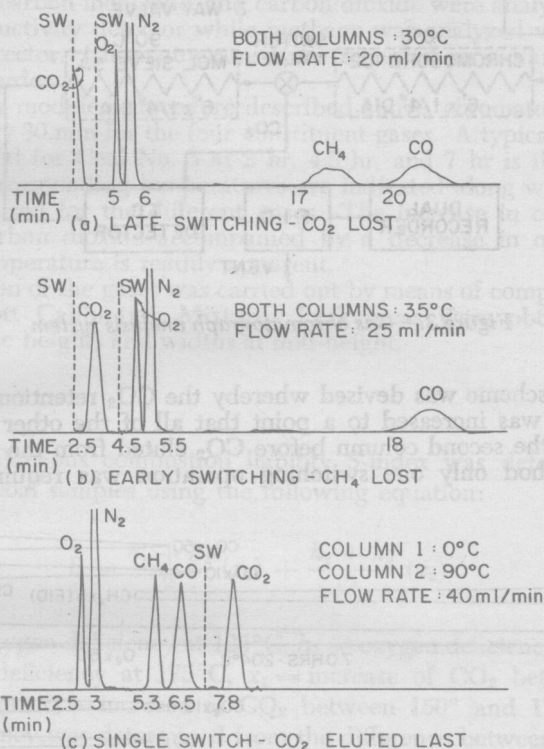


Figure 2. Chromatograms from various column-switching configurations.

best results which could be determined under these operating conditions involved unreasonably long residence times for CH_4 and CO , and produced flat, wide peaks. If the bypass switching was carried out in time to yield a well-defined CO_2 peak; CH_4 could be missed entirely (see Figure 2b). Using shorter columns and higher flow rates, oxygen had begun eluting from Column 2 after switching back to series position following CO_2 elution from Column 1. Juggling of temperatures, flow rates, and column lengths and adsorption materials produced all of the peaks; however, switching had to be very precise. In view of these

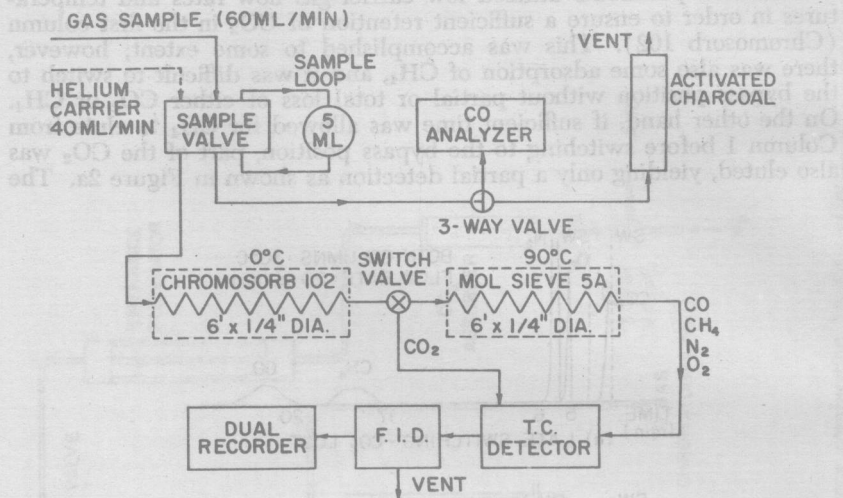


Figure 3. Gas chromatograph analysis system

problems, a scheme was devised whereby the CO₂ retention time in the first column was increased to a point that all of the other constituents eluted from the second column before CO₂ eluted from the first column. By this method only one switching operation was required, and by

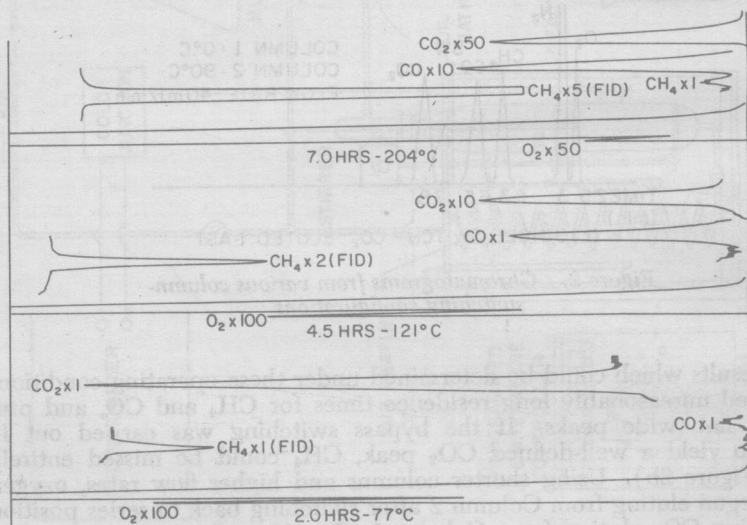


Figure 4. Chromatograms produced from the oxygen absorption of Coal No. 5

adjusting temperatures and flow rate, a reasonably short analysis time could be attained (*see* Figure 2c). Column temperatures were maintained at 0°C and 90°C, respectively, with a helium-gas flow rate of 40 mL/min.

A schematic of the gas chromatographic analysis system is shown in Figure 3. A 5-mL sampling loop was used in conjunction with the sampling valve shown. During the first stages of oxidation, carbon monoxide was monitored with an Ecolyzer CO analyzer. The residual gases were adsorbed ultimately on to an activated charcoal filter.

Oxygen, carbon monoxide, and carbon dioxide were analyzed using a thermal conductivity detector while methane was analyzed with a flame ionization detector. Chromatograms were recorded on a Varian G-2000 dual pen recorder.

Using the modified procedure described above, chromatograms were obtained every 30 min for the four constituent gases. A typical chromatogram produced for Coal No. 5 at 2 hr, 4.5 hr, and 7 hr is illustrated in Figure 4. Corresponding temperatures are indicated along with recorder attenuations used for the different gases. The increase in carbon monoxide and carbon dioxide accompanied by a decrease in oxygen with increasing temperature is readily apparent.

Calibration of the gases was carried out by means of comparison with a special Scott Calibration Mixture. Peak areas were obtained from products of the heights and widths at mid-height.

Results

The spontaneous combustion liability S-index was determined for the eighteen coal samples using the following equation:

$$S = \frac{h_1 + h_2}{2} (x_1) + \frac{h_2 + h_3}{2} (x_2) \quad (1)$$

where h_1 = oxygen deficiency at 125°C, h_2 = oxygen deficiency at 150°C, h_3 = oxygen deficiency at 175°C, x_1 = increase of CO₂ between 125° and 150°C, and x_2 = increase of CO₂ between 150° and 175°C. The oxygen deficiency was determined from the difference between the initial and final oxygen concentration. All values were reported as volume percentages.

S-Indices for various coal samples are tabulated (together with the exhaust gas analysis at 150° and 175°C) in Tables I and II. As can be observed, the S-index values range from ca. 13–47. These values represent a rather broad liability range. Values greater than 30 are considered to be in the dangerous category. The increase in carbon monoxide and carbon dioxide along with a decrease in oxygen with an increase in S-index is also obvious; however, it is much more pronounced at 175°C. Maximum gas concentrations for carbon monoxide and carbon dioxide in the effluent gases obtained at temperatures in the vicinity of 200°C were

Table I. Summary of S-Indices and Exhaust Gas Analyses at 150°C

Exhaust Gas Analysis (Vol %)

S-Index	Coal No.	O ₂	CO ₂	CO	CH ₄
2.42 ^a	6	12.25	0.74	.26	^b
12.81	10	14.00	0.98	.43	.0005
13.31	7	11.50	1.61	.69	.0046
15.82	5	13.25	2.50	.57	.0032
16.75	3	12.85	1.51	.51	.0036
18.75	12	15.00	1.42	.28	^b
20.66	2	12.90	1.95	.59	.0032
22.19	16	10.85	1.64	.94	^b
22.85	11	11.25	1.68	.52	^b
24.35	4	9.50	2.00	.73	.0042
25.84	14	10.75	1.91	.73	.0044
27.93	15	13.50	1.72	.56	.0025
28.34	13	11.40	1.67	.63	.0052
28.66	18	11.25	2.18	.70	.0037
33.93	17	12.25	2.50	.71	^b
34.51	1	9.50	1.92	.67	.0002
41.00	9	10.75	1.81	.67	.0053
47.32	8	10.24	2.32	.65	.0042

^a Low sample weight.^b No measurement obtained.

Table II. Summary of S-Indices and Exhaust Gas Analyses at 175°C

Exhaust Gas Analysis (Vol %)

S-Index	Coal No.	O ₂	CO ₂	CO	CH ₄
2.42	6	8.90	0.89	0.27	^b
12.81	10	9.75	2.12	0.93	.0023
13.31	7	6.75	2.35	1.25	.0099
15.82	5	9.60	3.58	1.09	.0061
16.75	3	8.75	2.73	1.07	.0080
18.75	12	7.00	2.92	1.15	^b
20.66	2	8.25	3.39	1.01	.0077
22.19	16	5.25	2.87	1.56	^b
22.85	11	6.00	3.08	0.95	.0017
24.35	4	2.73	3.16	1.77	.0143
25.84	14	5.00	3.44	1.55	.0095
27.93	15	6.50	3.65	1.06	.0053
28.34	13	5.50	3.50	1.75	.0178
28.66	18	5.58	3.85	1.65	.0084
33.93	17	5.50	4.75	1.42	.0015
34.51	1	3.00	3.72	2.04	.0025
41.00	9	3.00	4.18	1.85	.0130
47.32	8	3.25	5.02	1.72	.0133

^a Low sample weight.^b No measurement obtained.