

The Determination of Mercury in Coal by Flameless Atomic Absorption

G. William Kalb

TraDet Inc., Columbus, Ohio

Recently there has been considerable interest in the potential release of volatile mercury to the atmosphere from power plants. The mercury, naturally occurring in coal at very low levels, is volatilized during combustion of the coal in fossil fuel fired steam generating plants. The present consumption of coal (in excess of 300 million tons per year) could result in the release of a significant quantity of mercury to the atmosphere. This potential problem has resulted in the need for the development of analytical procedures for determining the mercury concentrations in coal.

The United States Bureau of Mines instigated a round-robin analytical program for mercury in coal with 12 independent laboratories in the Spring of 1971. Eleven coal samples, representing a cross-section of coals in this country, were furnished to each participant. Each participating laboratory developed its' own analytical method and submitted its' data to the Bureau of Mines at the completion of analyses. The methods and results presented in this paper represent our participation in this program.

Analytical procedures presently being utilized for mercury in coal determinations may be divided into four general categories: (1) neutron activation, (2) amalgamation-flameless atomic absorption, (3) wet digestion-flameless atomic absorption, and (4) oxygen bomb combustion-flameless atomic absorption. All of these methods can produce accurate results although some are considerably more difficult than others. This paper presents an amalgamation-flameless atomic absorption procedure.

The cold vapor flameless atomic absorption procedure for mercury was developed for the analyses of water and other digestible materials such as fish, tissue, etc.¹ The material is digested in a strong acidic oxidizing media. This solution is then reduced and aerated, volatilizing the mercury which is carried by an air stream through a quartz cell located in the optical path of an atomic absorption spectrophotometer. Gold and silver amalgamation was added as an intermediate step to (1) increase sensitivity (preconcentrate the mercury after aeration) and (2) eliminate interferences from aromatic organic compounds, sulfide, and water vapor that also absorb at the 2536 Å mercury line.² Coal, which is extremely difficult to wet digest, was not directly amenable to the above procedure. The method is adapted to mercury in coal analysis by firing the coal sample in a closed system, volatilizing the mercury which is separated from the other gaseous by-products and then analyzed by flameless atomic absorption. The mercury is isolated from the interferences by bubbling the volatiles through an acidic oxidizing solution in which the mercury is oxidized and subsequently absorbed into the solution. After the solution is reduced and aerated, an air stream carries the mercury through a silver or gold amalgamator which quantitatively adsorbs the mercury. The amalgam is then fired in an induction furnace, instantaneously revolatilizing the mercury which is carried through a quartz tube in the optical path of the spectrophotometer. The mercury absorption is recorded on a strip chart recorder as a very sharp peak with a sensitivity of 0.01 µg of mercury.

A schematic of the apparatus is shown in Figure 1. A Deco single or double induction furnace is used in conjunction with a Perkin-Elmer Model 303 atomic absorption spectrophotometer. An air flow rate of 1.5 to 2.0 liters per minute is maintained through the system during the analysis. The combustion chamber (A) is constructed of quartz and is designed to hold a quartz enclosed graphite crucible. A picture of the oxidation chamber (B) is shown in Figure 2. A drying tube (E) is filled with magnesium perchlorate. The amalgamator (F) is constructed of $\frac{1}{2}$ inch diameter quartz tubing and contains a porous plate that supports 6 - 8 grams of 0.007 inch thick gold or silver foil cut into approximately 1/16 inch square sections. The absorption cell is constructed of pyrex with quartz endplates.

A 500 mg coal sample is weighed in a quartz graphite crucible and positioned in the induction furnace (A). The air flow rate is adjusted and the sample is fired for $1\frac{1}{2}$ minutes at the variac control setting of 60% and then fired an additional 30 seconds at a 75% setting. Initial firing of the sample at 75% will result in 'flashing' of the sample and a resultant plugging of the combustion chamber. Volatilized mercury and the other gaseous by-products are bubbled through the acidic oxidizing solution in the aeration chamber (E). The three-way stopcock (D) is opened to vent the non-absorbed combustion products. After the two minute firing period and collection of the mercury in the oxidizing solution, the excess oxidant and mercury are reduced by the addition of a reducing agent with a syringe through the septum cover (C). The solution is then aerated for two minutes collecting the revolatilized mercury on the gold or silver amalgamator (F). The induction furnace (F) is then fired, instantaneously releasing the mercury which is carried by the air stream through the quartz cell. The detachable tube containing the reduced oxidizing agent is replaced with fresh solution and the procedure is repeated for another coal sample. Approximately 5 minutes is required for each determination. Blank determinations must be routinely performed. Standards are obtained by replacing the oxidizing solution with known mercury in water samples and repeating the above procedure deleting the combustion step.

Preliminary investigations included studying ICl_3 , $\text{KMnO}_4\text{-H}_2\text{SO}_4$, and $\text{KMnO}_4\text{-HNO}_3$ as possible oxidizing solutions. Mercury would not amalgamate when aerated from ICl_3 solutions, possibly due to some interference from I_2 which is also released. Some stability and equilibrium problems were observed with $\text{KMnO}_4\text{-H}_2\text{SO}_4$ solutions. $\text{KMnO}_4\text{-HNO}_3$ provided a stable oxidizing solution and was used to obtain the reported data. The solution is prepared by adding 5 ml of concentrated HNO_3 to 25 ml of a filtered 6% KMnO_4 solution which is then diluted to 50 ml with distilled water for each analysis. The blank determinations are made on these solutions. A considerable excess of permanganate must be present in the tubes since the SO_2 released from the coal in the combustion process will also reduce the permanganate. These solutions are prepared in mass and are stored immediately prior to the beginning of a series of analyses. After the volatilized mercury is collected in the oxidizing solution the excess permanganate is reduced with 5 ml of a 10% hydroxylamine hydrochloride solution and the mercury is then reduced with 1 ml of 20% SnCl_2 in 50% HCl . Both of these reducing agents are added by syringe through the septum cover.

The 1.5 to 2.0 liter per minute air flow rate is a compromise between the optimum flow rates for greatest sensitivity, quickest cooling of the quartz-graphite crucible after firing, and fastest aeration (revolatilization of all the mercury) of the reduced oxidizing solution. Compressed air was found to be adequate, eliminating the necessity of using oxygen. Gold and silver foil both worked very well in the amalgamator but the silver foil did require daily cleaning.

The coal samples were air dried. The samples furnished by the United States Bureau of Mines were received crushed to minus 60 mesh, the Illinois Geological Survey samples were crushed to minus 20 mesh and the Tennessee Valley Authority samples were run as sampled from the Muscle Shoals' Colbert Steam Generating Plant. The TVA samples include three fly ash samples. The results of the analyses are presented in Table 1. The total sulfur and pyritic sulfur values were furnished by the Bureau of Mines and the Illinois Geological Survey. The sulfur concentrations were determined from moisture free samples. This data is included because of the suggested concentration of the mercury in the pyritic fraction of the coal.³

Table 1. Results of analyses of mercury in coal.

Sample No.	DRB-A	DRB-B	DRB-C	DRB-D	DRB-E
State	Ohio	Ohio	Ohio	W. Va.	Pa.
Seam	#9	#6-A	Pgh. #8	Hernshaw	Pgh.
County	Belmont	Harrison	Jefferson	Kanawha	Washington
Type Mining	strip	deep	strip	deep	deep
Preparation	raw	raw	washed	washed	washed
Total Sulfur %	4.34	3.28	4.24	1.02	1.42
Pyritic Sulfur %	2.11	2.25	2.85	0.17	0.55
Determinations	0.23	0.34	0.22	0.070	0.13
(ppm)	0.15	0.36	0.24	0.06	0.15
	0.15	0.33	0.17	0.15	0.077
	0.18	0.67	0.32	0.094	0.085
	0.19	0.43	0.22	0.080	0.13
	0.14	0.37	0.20	0.12	0.075
	0.15	0.41	0.28	0.028	0.082
	0.22	0.63	0.22	0.031	0.14
Average (ppm)	0.18	0.44	0.23	0.079	0.11
Standard Deviation	0.035	0.13	0.047	0.042	0.023

Table 1. Cont.

Sample No.	G-1	P-1	P-2	P-3	P-4	P-5
State	Indiana	Ky./W.Va.	Mont.	Mont.	Colo.	Ariz.
Seam	Ind. #3	#9	Rosebud	Tebo/Weir	Nucla	Red
County	Clay	Muhlenberg	Rosebud	Henry	Montrose	Navajo
Mining Type						
Preparation	washed	raw	raw	wash/raw	raw	raw
Total Sulfur %	4.37	4.46	0.85	9.37	0.80	0.44
Pyritic Sulfur %	1.67	2.43	0.26	5.81	0.23	0.11
Determinations (ppm)	0.043	0.20	0.056	0.17	0.040	0.046
	0.036	0.20	0.054	0.20	0.034	0.041
	0.060	0.36	0.080	0.21	0.041	0.066
	0.060	0.26	0.073	0.22	0.043	0.035
	0.054	0.24	0.048	0.22	0.033	0.071
Average (ppm)	0.051	0.25	0.062	0.20	0.038	0.052
Standard Deviation	0.010	0.066	0.014	0.021	0.004	0.016

Sample No.	C16987	C16891	TVA1013	TVA1014	TVA1013	TVA1014	TVA1015
State	Ill.	Ill.	Ky.	Ky.	---	---	---
Seam	Herrin #6	Herrin #6					
Sample Type					fly ash	fly ash	fly ash
Preparation	raw	raw					
Total Sulfur %	3.46	4.45					
Pyritic Sulfur %	2.07	2.36					
Determinations (ppm)	0.071	0.13	0.20	0.17	0.20	0.21	0.16
	0.096	0.11	0.21	0.14	0.14	0.17	0.15
	0.21	0.14	0.17	0.20	0.15	0.25	0.17
	0.13	0.12	0.27	0.14	0.20	0.11	0.14
	0.17	0.10	0.17	0.13	0.14	0.14	0.13
Average (ppm)	0.13	0.12	0.20	0.16	0.17	0.17	0.15
Standard Deviation	0.056	0.016	0.041	0.029	0.031	0.051	0.016

With 500 mg samples the procedure has a sensitivity of approximately 0.02 ppm. Precision was undetermined due to the apparent lack of homogeneity of some samples. This is illustrated with the values obtained for sample DRB-B. This coal represents the highest mercury concentration of those coals investigated. Although it represents the finest mesh group (minus 60 mesh) specific analyses resulted in extremely high mercury concentrations. The large variation between determinations of this sample suggests a non-homogeneous distribution of the mercury in the coal.

A modification of this procedure utilizes a double amalgamation reaction and eliminates the liquid oxidizing solution. A schematic of the apparatus is shown in Figure 3. The procedure is a modification of the double amalgamation method developed by Suhr.⁴ The horizontal resistance wound tube furnace containing separate furnaces for the coal combustion and both amalgams used by Suhr is replaced with a vertical quartz tube containing the quartz graphite crucible and both amalgams. An air or oxygen stream is maintained through the system during the whole procedure. During the subsequent steps requiring the firing of the coal, amalgam 1, and amalgam 2 the quartz tube is lowered stepwise positioning the single induction furnace at the desired location.

The method consists of firing the coal sample in the quartz graphite crucible and then lowering the quartz tube firing each successive amalgam respectively. The system is vented, bypassing the quartz absorption cell, until the last amalgam is fired. After firing the final amalgam the mercury is carried by the air stream through the quartz absorption cell located in the optical path of the spectrophotometer. The double amalgamation is used to ensure the complete removal of any interferences. When silver foil is used a sulfide coating forms on the silver resulting in a constantly decreasing sensitivity with each successive analysis. Gold foil works very well in the amalgamators. This system has the advantage that there is no blank determination required.

SUMMARY

A method was presented for the analysis of coal for mercury at naturally occurring levels. The procedure consists of firing the coal in an induction furnace, separating the mercury from other interfering gaseous by-products by collection in a strongly acidic oxidizing solution and on a silver or gold amalgamator, and then determining the mercury concentration by a cold vapor flameless atomic absorption method. A modification of this procedure to perform a direct double amalgamation is briefly described.

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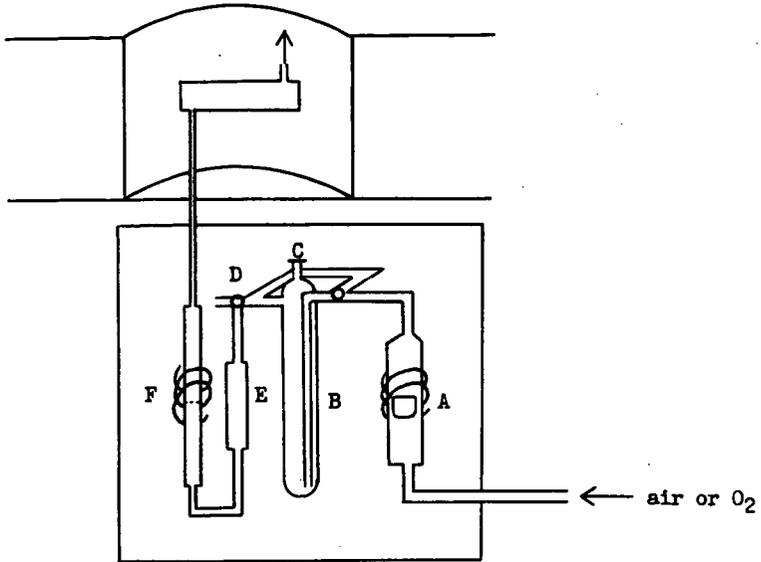


Figure 1. Schematic of mercury in coal apparatus.

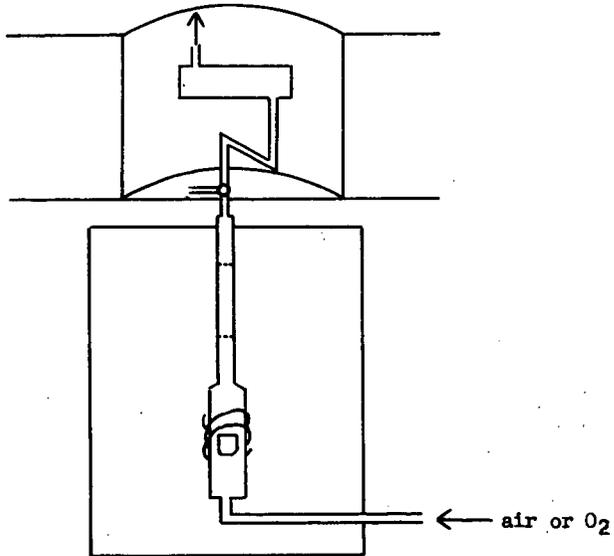


Figure 3. Schematic of modification for mercury in coal determinations by double amalgamation.

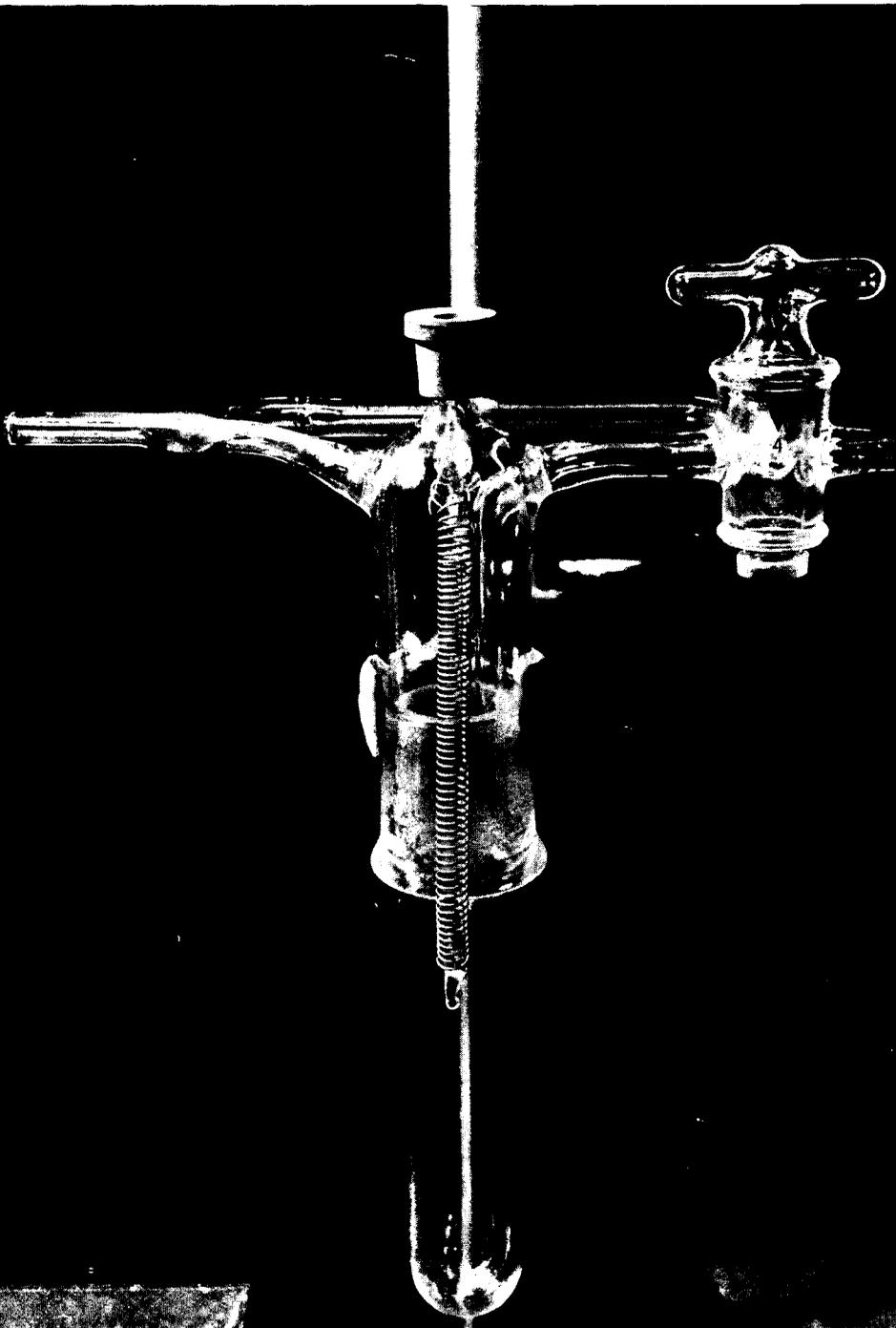


Figure 2.

A COMBUSTION BOMB METHOD FOR THE
DETERMINATION OF MERCURY IN COAL

Robert C. Streeter

Bituminous Coal Research, Inc.
350 Hochberg Road
Monroeville, Pennsylvania

INTRODUCTION

Earlier workers have described the use of an oxygen combustion bomb in conjunction with procedures for determining trace amounts of mercury in a variety of organic substances. In 1958, Borchardt and Browning reported a procedure for the analysis of microgram quantities of mercury in paper. (1) One-gram samples of paper were rolled into a cylinder, placed inside a platinum coil, and ignited under 25 to 30 atm of oxygen in a Parr combustion bomb containing 15 ml of 0.1 N potassium permanganate solution and 10 ml of 10 percent sulfuric acid solution. The contents of the bomb were subsequently transferred to a separatory funnel, treated with hydroxylamine sulfate solution to reduce the permanganate, and extracted with a dithizone solution in chloroform. Mercury was determined colorimetrically on the dithizone-chloroform extract. The method was found to be suitable for the determination of mercury in the range of 1 to 10 micrograms per gram (ppm).

Various modifications of the procedure of Borchardt and Browning have been reported by several workers at the University of Tokyo. Thus, Fujita et al. described a similar technique in which combustion was carried out in the presence of 1.0 N nitric acid previously added to the bomb. (2) The oxidation products were subsequently reduced by the addition of hydroxylamine hydrochloride and urea solutions, and mercury was extracted with a solution of dithizone in carbon tetrachloride. The procedure was developed primarily for the determination of mercury in rice which had been treated with mercurial fungicides, although various other materials including vegetable oils, human hair, and tissue samples from mercury-poisoned rats were analyzed with apparent success. Values as low as 0.17 ppm were reported for the combustion of 4 grams of unpolished rice grain (the maximum amount that could be burned completely in the bomb).

Fujiwara and Narasaki have discussed the relative merits of using the oxygen combustion bomb for trace element determinations in a variety of samples. (3) They suggested that the interior of the bomb should be platinum-coated to reduce contamination of the sample or interactions of the combustion products with the bomb walls.

Ukita et al. also reported the determination of mercury in rice, wheat, and various biological materials by a combination of the bomb combustion method and atomic absorption spectrophotometry. (4) The combustion procedure was similar to that of Borchardt and Browning in that a potassium permanganate solution, acidified with sulfuric acid, was used in the bomb to trap combustion products. After combustion, the liquid from the bomb was

treated with hydroxylamine hydrochloride, rinsed into a 100 ml volumetric flask, and diluted with 1 N sulfuric acid. Aliquots of this solution were treated with 10 percent stannous chloride solution to reduce mercury, which was then determined by a flameless atomic absorption technique. Ukita et al. advocate the use of a platinum-coated stainless steel bomb to avoid dissolution of trace amounts of iron, nickel, and other metals from the bomb walls during combustion. However, it was also reported that these extraneous metals did not interfere with the determination of mercury by the stannous chloride reduction method. Detection limits as low as 0.05 μg for samples of 0.5 to 1.0 g were reported.

This paper describes a procedure for the determination of nanogram quantities of mercury in whole coal. The method involves decomposition of the coal in a combustion bomb under 24 atm of oxygen in the presence of a nitric acid solution containing hydroxylamine hydrochloride. Following combustion, the contents of the bomb are diluted to a known volume and mercury is determined by a flameless atomic absorption technique involving stannous chloride reduction. The procedure has given repeatable results for the analysis of trace amounts of mercury in coal, and it can be carried out with standard equipment accessible to most coal analysis laboratories.

EXPERIMENTAL

Apparatus

Combustions were carried out in a standard 360 ml stainless steel combustion bomb (Parr Instrument Co., Model No. 1102) using No. 34 B. & S. gauge nichrome fuse wire and a quartz combustion crucible. The crucible, originally of 10 ml capacity, had to be cut down with a diamond saw to about 6 ml capacity to allow proper placement of the fuse wire in the bomb. Other components of the Parr Series 1200 adiabatic calorimeter, including the Series 2900 ignition unit, were used routinely in these tests.

An Instrumentation Laboratory Model 153 atomic absorption spectrophotometer, incorporating a Varian Techtron hollow cathode mercury lamp and a 100 millivolt Honeywell Electronik 194 strip chart recorder, was used for the spectrophotometric determination of mercury. The instrument conditions were maintained as follows: slit width, 320 μm ; wavelength, 253.7 nm; scale, 0.25; photomultiplier tube (R 372) voltage, 620 v; hollow cathode lamp current, 4 ma; mode, high damp; gas flow, 1 liter He/min; chart speed, 1 inch/min. The absorption cell, shown in Figure 1, consisted of a Plexiglas tube 125 mm long and 22 mm I.D.; the tube was fitted with removable quartz windows by means of modified polyethylene snap caps. The cell was mounted directly on top of the nitrous oxide burner head, and its position could be adjusted using the standard controls on the instrument. A cylindrical, flat-bottom cold test jar (Fisher No. 13-415) of approximately 100 ml capacity and incorporating a Teflon-covered micro stirring bar was employed as the reaction vessel for stannous chloride reductions. Helium purge gas was admitted to the reaction vessel through a fritted gas dispersion tube. Connections to the absorption cell were made with Tygon tubing.

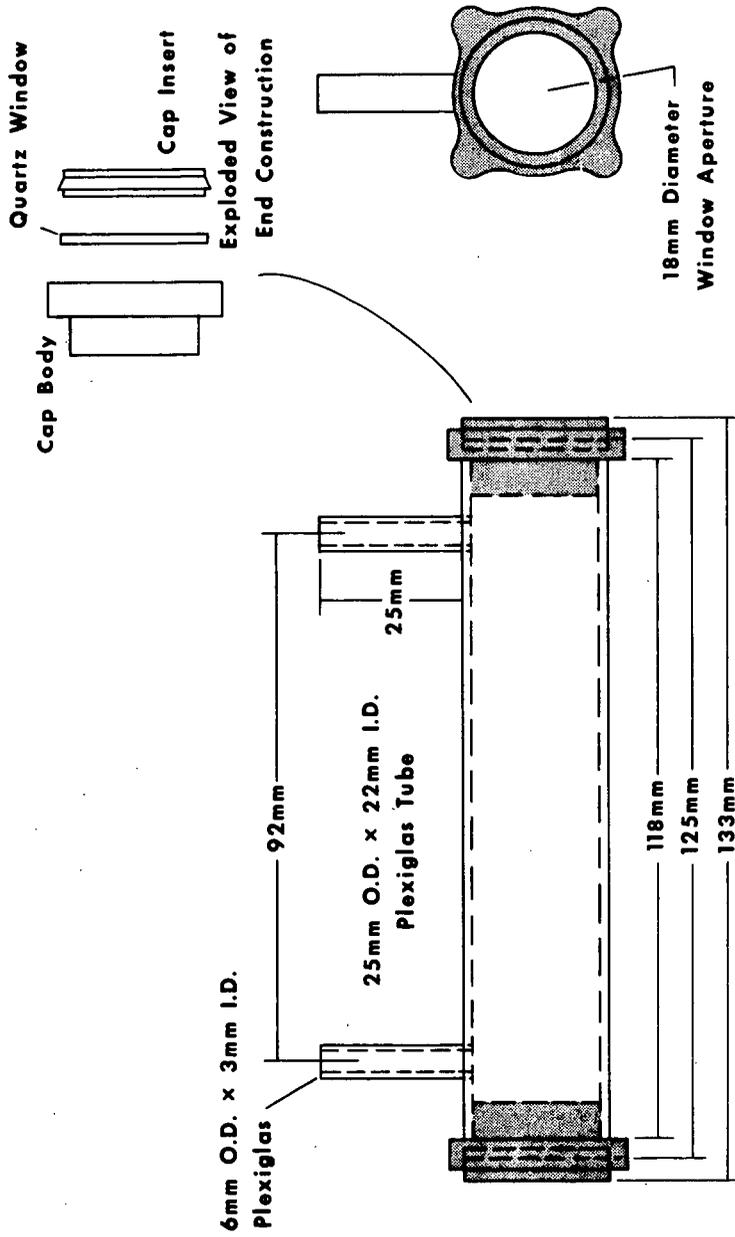


Figure 1. Mercury Absorption Cell

Procedure

A 0.500 gram sample of minus 60 mesh coal was weighed in a tared quartz combustion crucible. The crucible was placed in the electrode support of a stainless steel bomb containing 20 ml each of 1 N nitric acid and 10 percent hydroxylamine hydrochloride solution. The level of the liquid in the bomb should be below the bottom of the combustion crucible to avoid incomplete combustions. The fuse wire was attached, the bomb was assembled, and oxygen gas was added to a pressure of 24 atm (gauge). The bomb was then placed in the calorimeter (a cold water bath in a large stainless steel beaker is also satisfactory) and the sample was ignited using appropriate safety precautions ordinarily employed in bomb calorimetry work. After combustion and a temperature equilibration period of about five minutes, the bomb was rolled on its side several times to rinse down the inner walls and the combustion gases were slowly released. The bomb was then opened and its contents were emptied into a 100 ml volumetric flask. The interior surfaces of the bomb and the quartz crucible were rinsed well with 1 N nitric acid and the volumetric flask was filled to the mark with 1 N nitric acid.

Ordinarily, a 10 ml aliquot of the sample solution was pipetted into the reaction vessel containing the micro magnetic stirring bar. However, the size of the aliquot could be varied between 1 and 15 ml depending on the mercury concentration. Approximately 2 ml of a 1 percent stannous chloride solution was added using a Pasteur pipet, and the sample was diluted to a total volume of 20 ml with deionized water. The reaction vessel was then stoppered and the helium inlet tube was adjusted so that the frit was just above the stirring bar. The solution was stirred for one minute, after which the helium purge gas flow was initiated at a rate of one liter per minute. The gas was not recirculated as in some procedures, but was passed directly through the absorption cell and into an exhaust system. The absorption peak height was recorded on the strip chart and was converted to nanograms of mercury by comparison with standards run under the same conditions. All results were corrected for reagent blanks.

RESULTS AND DISCUSSION

A sample of Lower Kittanning seam coal was analyzed by the procedure described above. Results from 21 separate combustion tests over a 6-month period were used in evaluating the precision of the method. In each test, duplicate 10-ml aliquots of the sample solution were taken for atomic absorption analysis. These data showed a mean mercury concentration of 0.319 μg per gram of coal (as-received basis) with a standard deviation of 0.015 μg , corresponding to a relative standard deviation of 4.8 percent.

This same coal has also been analyzed for mercury elsewhere by other techniques, including neutron activation and the dithizone colorimetric method. Based on a statistical analysis of these independent results, the calculated "best value" for the Lower Kittanning coal has been reported as $0.31 \pm 0.03 \mu\text{g/g}$. (5) This result is considered to be in good agreement with that obtained by the oxygen combustion bomb method.

Mercury present in the 10 ml aliquot taken after the combustion of 0.500 g of the Lower Kittanning coal generally produced a peak height of about 20 chart divisions on the strip chart recorder. After subtraction of the reagent blank, which was normally about 4 chart divisions, the remainder of 16 chart divisions corresponded to the 16 ng of mercury actually present in the 10 ml aliquot. The most widely used definition of detection limit is that concentration of an element necessary to displace the average absorbance reading by an amount equivalent to the peak-to-peak noise of the base line. (6) At the instrument settings employed in these measurements, the background noise was ordinarily ± 1 chart division. Thus, the detection limit of the method was on the order of $0.040 \mu\text{g/g}$. This detection limit can be improved, of course, by the use of larger coal samples for combustion (up to 1.0 g) and/or larger aliquots of the solution taken for stannous chloride reduction.

It was found necessary to check for background levels of mercury in the combustion bomb at frequent intervals, particularly after a comparatively large amount of mercury had been introduced to the bomb via unknowns or standards. This was accomplished by repeated firings of 0.5 g benzoic acid pellets until a stable, consistently low blank was obtained. In addition, the condition of the bomb itself is believed to be quite critical to the success of the procedure. Thus, at one point in the development of the method, it was observed that mercury recoveries from both standards and previously analyzed coal samples were unexplainably low. An inspection of the bomb revealed numerous small cracks and fissures on the inner walls of the bomb. The bomb was sent to the manufacturer for reboring, polishing, and pressure testing, and after it was returned normal results were once again obtained.

The presence of chloride ion in the trapping solution is apparently necessary to stabilize the mercury released from the coal during combustion, presumably through the formation of complex ions. In the absence of a chloride ion source, the results were erratic and mercury recoveries were usually low. In addition to hydroxylamine hydrochloride, both ammonium chloride and sodium chloride were used with comparable results, although the latter has the disadvantage of introducing extraneous metal cations to the system. Hydrochloric acid would probably be the preferred reagent for this purpose, although all samples of reagent grade HCl employed in these studies were found to contain significant trace levels of mercury, leading to unacceptably high reagent blanks.

The effects of several variables involved in the cold vapor atomic absorption step of the procedure were investigated. The first of these was the flow rate of helium gas used to entrain the mercury vapor subsequent to stannous chloride reduction. The results of these tests for standard solutions containing 100 ng of mercury are shown in Table 1. The data indicate that sensitivity can be increased by decreasing the helium flow rate. However, above 1.0 liter/min the increases are marginal and are offset by impractically long peak recording times. For these reasons, a flow rate of 1.0 liter/min was considered to be the optimum setting.

TABLE 1. EFFECT OF HELIUM FLOW RATE ON PEAK HEIGHT AND PEAK RECORDING TIME.

<u>Flow Rate,</u> <u>liters/min</u>	<u>Peak Height,</u> <u>chart divisions</u>	<u>Peak Recording</u> <u>time, min</u>
3.5	31.0	0.50
2.5	33.4	0.50
1.6	41.5	0.50
1.0	48.3	0.75
0.4	52.5	2.00
0.1	54.5	6.00

A second variable involves the unoccupied or dead space volume above the solution in the reaction vessel, which is dependent on the volume of the reaction vessel as well as the volume of solution contained therein. Although the results of these tests were not sufficiently consistent to afford a good correlation, there was a definite indication that the sensitivity was increased as the dead space volume decreased. This relationship was particularly evident as the size of the reaction vessel was decreased. The results suggested that the reaction vessel should be as small as possible, yet sufficiently large to avoid carry-over of appreciable amounts of moisture into the absorption cell due to frothing of the sample (this problem was observed frequently during the course of these studies).

A third variable considered was the reaction time (with stirring) between the addition of the reducing agent and the beginning of the helium gas purge. The results with standard solutions containing 100 ng of mercury were essentially identical over a range of reaction times between 10 seconds and 4 minutes. Consequently, a reaction period of one minute was judged to be adequate for the procedure.

The combustion bomb method for the determination of mercury in coal has given reproducible results for several coals analyzed in this laboratory. However, there are several parameters involved in the overall procedure which have not been quantified, and further work would be helpful in defining their effects. These include the following:

1. Both the concentrations and volumes of the nitric acid and hydroxylamine hydrochloride solutions used in the bomb to trap mercury.
2. The length of time the solution remains in the bomb after firing the sample. Preliminary data have indicated that waiting periods on the order of one hour resulted in significant losses of mercury.

3. Handling of the bomb after combustion. Although some amount of mixing of the contents would seem desirable, vigorous agitation is precluded by the presence of the silica combustion capsule in the bomb, as well as the possibility that some of the liquid will enter the valve mechanism and be subsequently expelled when pressure is released from the bomb.

4. Loss of mercury due to adsorption on the walls of the bomb. Although this effect is known to exist, it seems to occur in an erratic fashion and can only be compensated for by firing blanks of benzoic acid until a stable background level of mercury is obtained. This effect is particularly troublesome, as the mercury adsorbed during combustion of one sample may be later desorbed to contaminate a subsequent sample.

5. The timing of various steps in the procedure involving transfer and dilution of the sample solution prior to atomic absorption analysis. Each of these operations involves possible loss of or contamination from adsorbed mercury. Although attempts were generally made in these studies to carry out the atomic absorption analysis as soon as possible after combusting the sample, the chronology of operations in this phase of the procedure was not entirely consistent.

In summary, the oxygen combustion bomb procedure as described herein is considered reliable for the analysis of trace amounts of mercury in coal. It is sufficiently simple and rapid, and can be carried out with equipment available in most modern coal analysis laboratories.

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"AN EVALUATION OF THREE NEUTRON ACTIVATION
ANALYSIS METHODS FOR MERCURY IN COAL"

Jack N. Weaver, Nuclear Engineering Department, N.C. State University, Raleigh, N.C.
Darryl J. von Lehmden, Environmental Protection Agency, Division of Atmospheric
Surveillance, Source Sample and Fuels Analysis Branch, Research Triangle Park, N.C.

INTRODUCTION

Due to the rapid growth in heavy industry in the United States, man has displaced many chemical elements from their natural environment and has poured them back into his daily environment. In order to determine the extent chemical elements in process raw materials and fuels contribute to the environment, the Environmental Protection Agency has initiated a program of analysis for a variety of elements including mercury, beryllium, cadmium, arsenic, vanadium, manganese, nickel, antimony, chromium, zinc, copper, lead, selenium, boron, fluorine, lithium, silver and tin. To conduct this analysis program on raw materials and fuels has required the evaluation of analytical techniques available for chemical elements in trace quantities, especially for mercury.

In just such an endeavor, the Environmental Protection Agency (EPA) in conjunction with the Nuclear Engineering Department of North Carolina State University (NCSU) evaluated neutron activation analysis (NAA) of mercury in a round-robin series of coal samples from the U.S. Bureau of Mines. This round-robin series was selected for two reasons. These were (1) extensive and careful efforts had gone into selecting and preparing the coal samples; and (2) the many laboratories (both atomic absorption and neutron activation analysis) participating in the series provided an excellent check on the accuracy of the results.

To completely cover the ranges of mercury expected in the coal samples, three types or variations of NAA were tried. These were:

1. Instrumental NAA using a 3×10^{13} n/cm²-sec irradiation and counting on a large (Lithium drifted germanium) Ge(Li) co-axial detector.
2. A 3×10^{13} n/cm²-sec irradiation followed by radiochemistry and counting on a 3" x 3" NaI detector.
3. A 3×10^{13} n/cm²-sec irradiation and counting on a newly developed 10 mm Ge(Li) Low Energy Photon Detector.

TABLE #1
 Geological Background of Coal Samples

<u>Sample #</u>	<u>Geological Location</u>	<u>Mining Process</u>
DRB-A	Belmont Co., Ohio	Strip - raw
DRB-B	Harrison Co., Ohio	Deep - raw
DRB-C	Jefferson Co., Ohio	Strip - washed
DRB-D	Kanawha Co., W. Va.	Deep - washed
DRB-E	Washington Co., Pa.	Deep - washed
G-1	Clay Co., Indiana	Deep - washed
P-1	Muhlenberg Co., Ky.	Raw
P-2	Rosebud Co., Mont.	Raw
P-3	Henry Co., Mo.	Washed - raw
P-4	Montrose Co., Colo.	Raw
P-5	Navajo Co., Ariz.	Raw

EXPERIMENTALSampling and Preparation for Irradiation

Fresh samples of coal representative of the mines listed in Table I were obtained and sample preparation was as follows:

1. Each plastic bottle was washed with a 2-1 mixture of concentrated nitric acid and hydrochloric acids, rinsed first with distilled water and then with acetone. The bottles were air dried and capped.
2. Coals were sampled, crushed to minus 60 mesh, divided equally and placed in the cleaned sample bottles.

From these coal samples, three sets of samples of each were carefully transferred to pre-cleaned low mercury content poly-irradiation vials. After weighing, these were heat sealed along with sets of carefully calibrated 1 and 5 microgram mercury standards. These samples provided the necessary number to perform duplicate analyses with each of the three techniques.

Nuclear Parameters

Weight of coal: 0.25 to 0.50 grams

Reactor neutron flux: 3×10^{13} n/cm²-sec

Irradiation time: 4 hours

Decay times: Approximately 4 days for Technique 1 and 3 and approximately 7 days for Technique 2.

Technique #1

Radiochemistry and Counting on a 3" x 3" NaI (Well-Type) Detector

1. Approximately 24 hours after irradiation, the poly vial containing approximately 0.5 gram of coal dust was opened and the contents were completely transferred to a clean distillation flask.
2. Using 100 ug of mercuric oxide as a carrier and 8 to 9 ml of fuming H₂SO₄ for digestion, the solution was mixed, then heated.
3. Next, fuming nitric acid was added. The addition of HNO₃ was repeated until charring was complete.
4. A small amount of water and potassium bisulfate was added to drive off the nitric acid and nitric fumes.
5. After appropriate cooling and transfer of the contents to a 300 ml calibrated beaker, the normality was adjusted to approximately 0.2 N and a standard dithiozone extraction procedure was used to remove the mercury.

6. The final extraction (approx. 50 ml) containing the mercury was poured into a 150 cc wide bottom plastic bottle for counting on a 3" x 3" (well-type) NaI detector.
7. The 0.07 MeV photopeak of Hg-197 was utilized for the classic method of data reduction and statistical evaluation.
8. Figures #1 and 2 illustrate the typical gamma spectrum of this extraction and the mercury standard respectively.

Technique #2
Instrumental NAA Using a 36 cc Ge(Li) Detector Coupled to a
4096 Nuclear Data Multichannel Analyzer

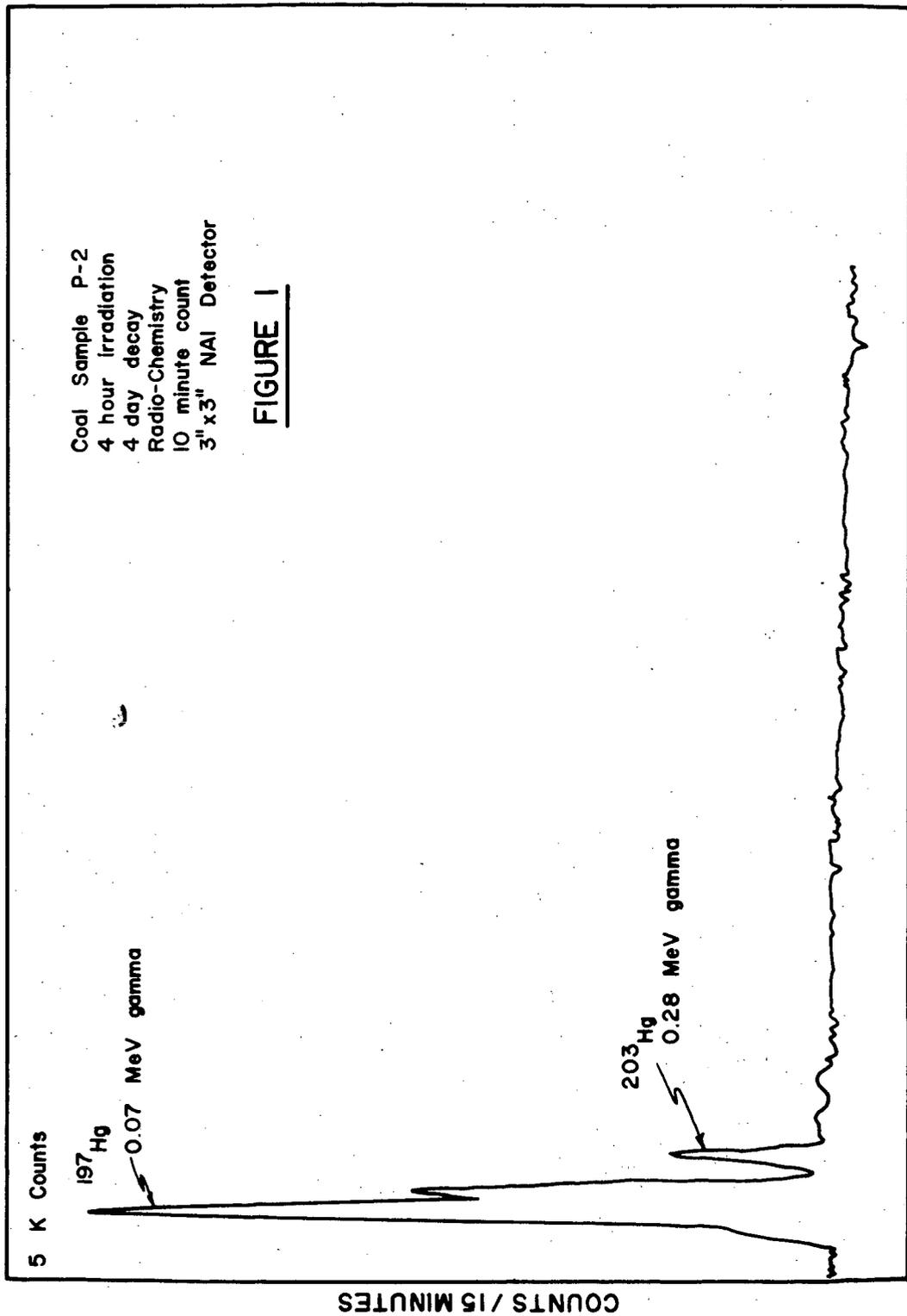
1. After a 7-day decay, the poly irradiation container was opened and the coal powder was transferred to a flat bottom plastic 100 ml bottle for counting. The bottle was tapped to provide a uniform spread of the powder over the bottle bottom.
2. Each sample was counted for 30 minutes on a 36 cc co-axial Ge(Li) detector coupled to a 4096 Nuclear Data Multichannel Analyzer.
3. Data reduction was performed using the classic method and the 0.07 MeV x-ray of Hg-197.
4. Figures #3 and 4 illustrate the spectra obtained with this counting system for unknown and standard respectively.

Technique #3
Instrumental NAA Using a 10 mm Ortec Low Energy Photon Detector
Coupled to a RIDL 400 Channel Analyzer

1. After a 4-day decay, the poly irradiation container was opened and the coal powder was transferred to a flat bottom plastic 15 ml bottle for counting. The bottle was tapped gently to provide a uniform spread of the powder over the bottle bottom, thus insuring the geometry over the 10 mm surface of the detector window.
2. Each sample was counted for 30 minutes on a 10 mm Ge(Li) Ortec Low Energy Photon Detector coupled to a 400 channel RIDL analyzer.
3. Data reduction was performed using the classic method and the 77.97 KeV x-ray of Hg-197.
4. Figures #5 and 6 illustrate the spectra obtained with this counting system for unknown and standard respectively.

RESULTS

The results of all three NAA techniques plus the average results of the same samples analyzed by 8 other laboratories participating in the coal round-robin analysis are shown in Table 2. The other laboratory techniques were flameless atomic absorption and neutron activation analysis with radio-chemistry.

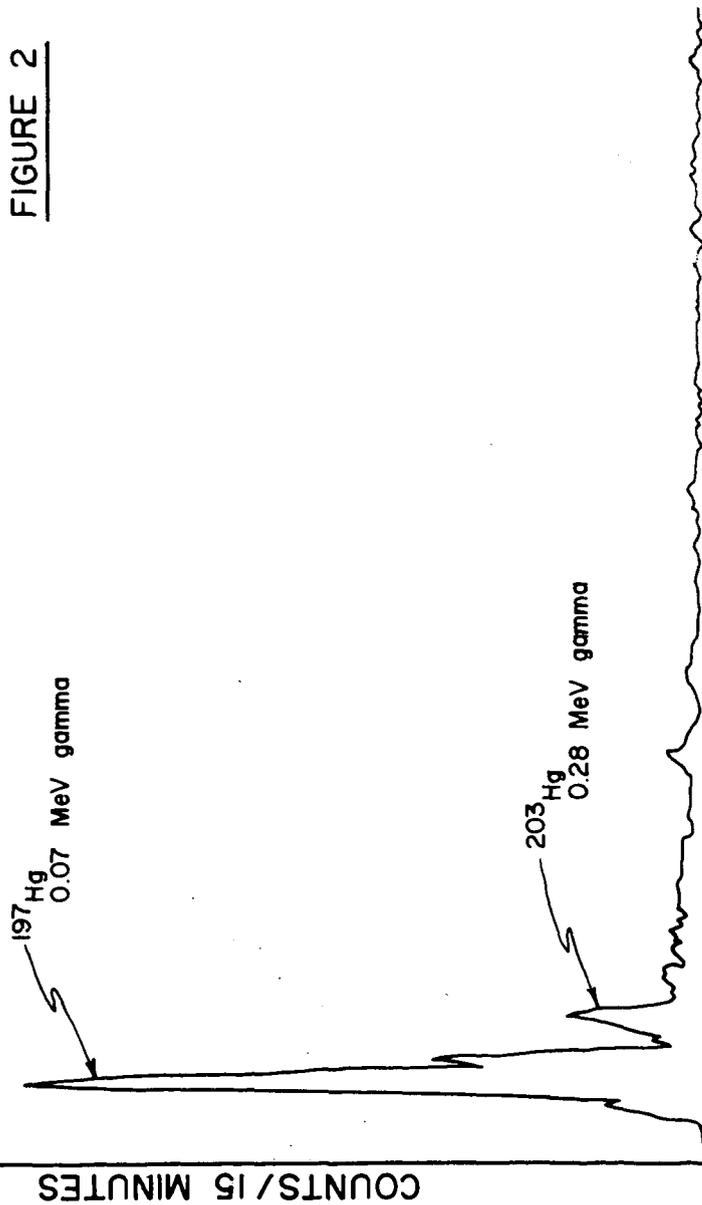


Coal Sample P-2
4 hour irradiation
4 day decay
Radio-Chemistry
10 minute count
3" x 3" NAI Detector

FIGURE 1

MERCURY STANDARD
1 ugram
4 hour irradiation
4 day decay
10 minute count
3" x 3" NaI Detector

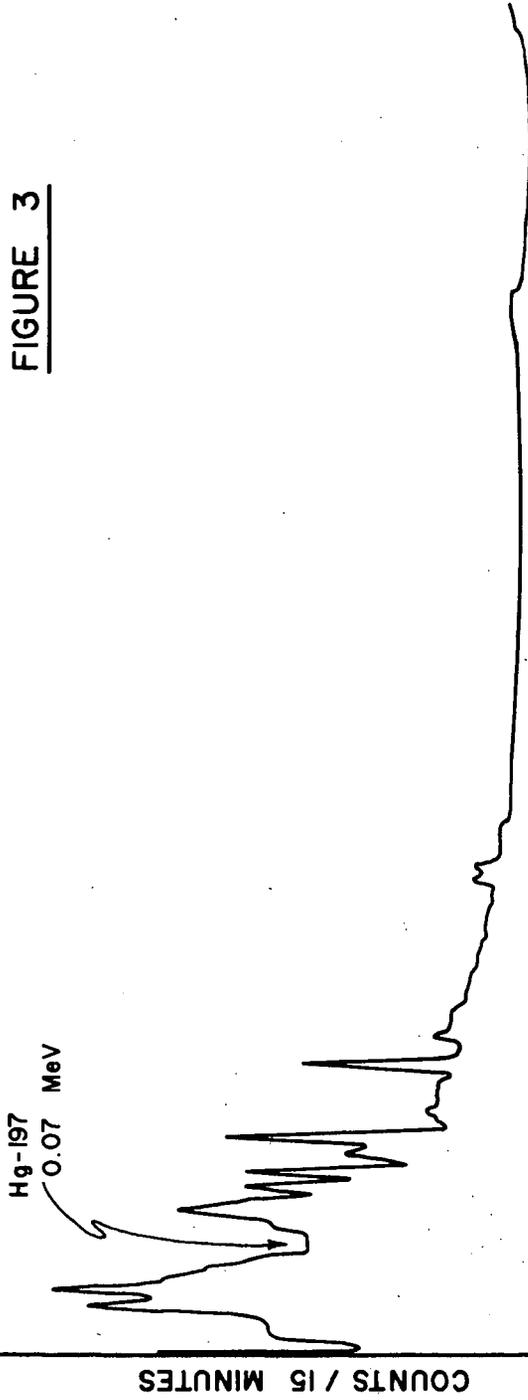
FIGURE 2



GAMMA ENERGY

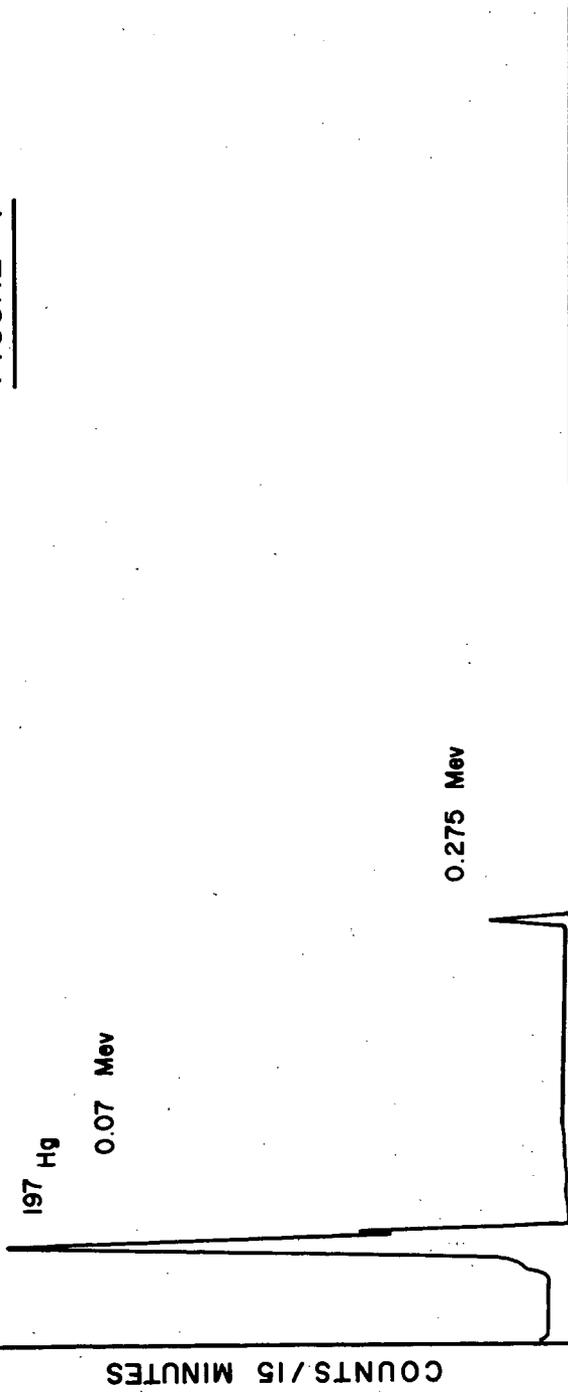
Coal Sample P-2
4 hour irradiation 10^{13} flux
7 day decay
15 minute count on a lithium drifted
germanium detector

FIGURE 3



5 ugrams MERCURY STANDARD
4 hour irradiation 10^{13} flux
15 minute count on a lithium drifted
germanium detector
7 day decay

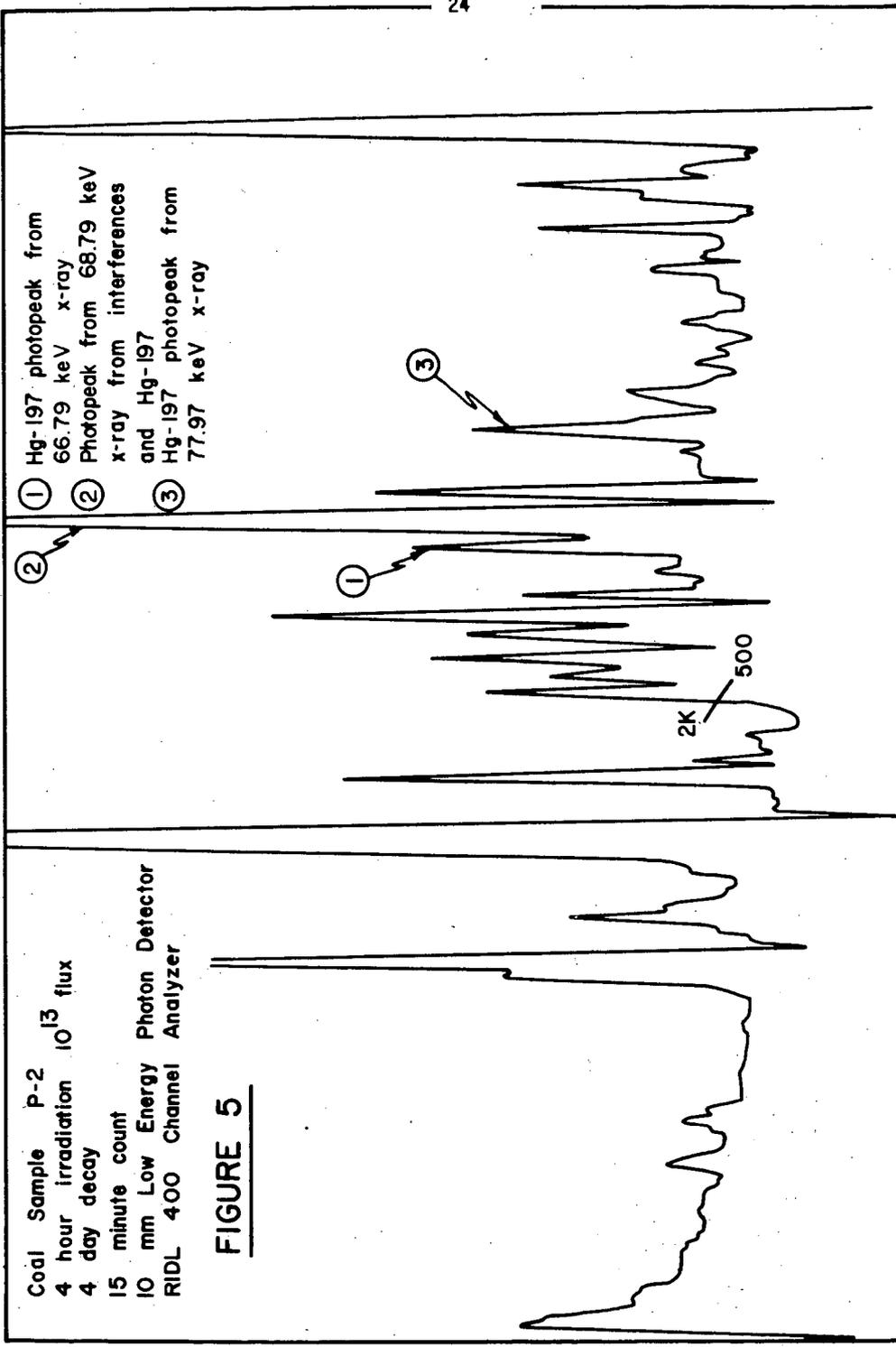
FIGURE 4



GAMMA ENERGY in MeV

Coal Sample P-2
 4 hour irradiation 10^{13} flux
 4 day decay
 15 minute count
 10 mm Low Energy Photon Detector
 RIDL 400 Channel Analyzer

FIGURE 5

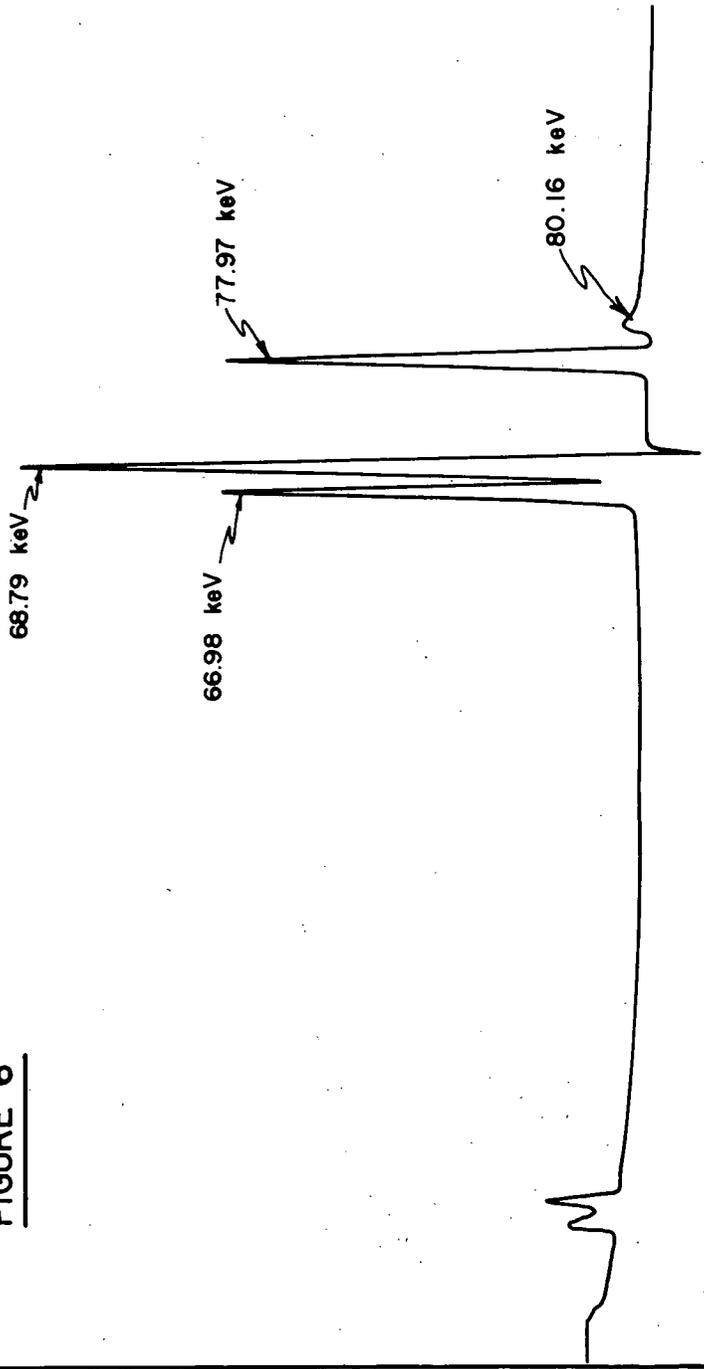


MERCURY STANDARD

5 ugrams Hg
4 hour irradiation 10^{13} flux
15 minute count
10 mm Low Energy Photon Detector
RIDL 400 Channel Analyzer

Hg - 197
65 hour half-life

FIGURE 6



GAMMA ENERGY IN keV

COUNTS / 15 MINUTES

TABLE #2

Total Mercury Levels in Coal

(ppm)

Sample Description	Radio Chemistry and NaI	Instrumental and 36 cc Ge(Li)	Instrumental & Low Energy Photon	Average of Laboratories Using NAA and AAA
DRB-A	0.130	< 0.37	0.16	0.14
DRB-B	0.380	0.17	0.43	0.44
DRB-C	0.230	0.54	0.27	0.24
DRB-D	0.069	0.19	0.09	0.07
DRB-E	0.100	0.16	0.12	0.13
G-1	0.086	0.15	0.10	0.07
P-1	0.170	0.55	0.17	0.17
P-2	0.057	< 0.42	0.07	0.06
P-3	0.150	0.48	0.17	0.15
P-4	0.035	0.43	0.07	0.05
P-5	0.058	< 0.34	0.08	0.06

DISCUSSION OF RESULTS

As can be seen from the description of each technique, the three methods were kept as simple to perform as possible since we were striving to achieve a rapid, accurate procedure for routine coal analysis. This simplicity was developed in conjunction with thorough efforts to maintain duplicate conditions for both standards and unknowns. In evaluating the three NAA techniques for mercury analysis in coal, the following conclusions were reached:

Technique #1 involving NAA and radiochemistry proved to be a very reliable method of analysis with close agreement of results to other laboratory results. However, the total number of samples that can be analyzed is limited by the restriction of having to dissolve the coal and perform time-consuming radiochemistry. A great deal of technician contact is required in the chemical separation, and the visual interpretation of the different steps of the separation could lead to recovery errors if on a routine basis. A significant amount of glassware is required plus the obvious limitation of hood space versus number of separation units that can occupy that space. Hence, the main drawbacks to radio-chemical separation are the tie-up of equipment and manpower with a limited analysis rate, plus possible recovery errors.

Technique #2 using a large coaxial Ge(Li) detector for instrumental NAA proves to be inadequate as the results in Table 2 illustrate. In this matrix and at these sub-microgram levels, interferences from other elements prevent an accurate analysis using the 0.07 MeV gamma ray of Hg-197. Similar work by McLain and Leddicotte ¹ at Georgia Tech confirm these results in that large volume Ge(Li) detectors do not possess the required resolution in the x-ray region of the energy spectrum. Note the poor energy curve for mercury in Figure #3.

Technique #3 using the Low Energy Photon Ge(Li) detector (LEPD) for instrumental NAA by far appears to offer the most promise for future analysis of environmental matrices such as coal, fuel oils, air particulates, etc. The fact that all that is required is a 4-10 hour irradiation at a flux of 10^{13} neutrons/cm²-sec, plus a 24-72 hour decay, and a 20 minute count on a 16 mm LEPD (this work was performed using a 10 mm detector width, but the 16 mm is preferred due to the increase in sensitivity versus cost) means that highly accurate, inexpensive, and instrumental NAA can be performed at a rapid analysis rate.

The main factor behind the LEPD's usefulness is that of its extremely fine resolution (220 eV at 55 KeV which in this case clearly defines Hg-197's 66.98, 68.79, 80.16 KeV x-rays and 77.97 KeV gamma ray. Hence, even with possible interferences, the choice of 1 of 3 or 4 photopeaks allows one to accurately perform the quantitative analysis. When photopeak count rate ratios do not compare those of the Hg-197 standard, a half-life determination based on a second count can be used to choose the photopeak for quantitative analysis.

SUMMARY

An evaluation of three NAA techniques for mercury analysis in coal has been presented with special emphasis given to the use of a 16 mm Low Energy Photon Ge(Li) Detector for rapid instrumental NAA.

Preliminary results show the possibility that many other elements with nuclides having low energy x-rays can easily be analyzed in coal using the LEPD gamma detector.

1/ D. M. Walker, M. E. McLain, and G. W. Leddicotte, "Semiconductor Detector Optimization for Trace Mercury Analysis in Environmental Samples", Georgia Institute of Technology, Atlanta, Georgia

GAS ANALYSIS WITH CARBON MOLECULAR SIEVE

Daniel M. Ottenstein and Walter R. Supina and Patrick W. Byrnes

Supelco, Inc.
 Supelco Park
 Bellefonte, Pennsylvania 16823

Fisher Scientific Co.
 711 Forbes Avenue
 Pittsburgh, Pa. 15219

INTRODUCTION

Carbosieve B is a unique adsorbent for gas solid chromatography which can be used for the separation of:

- (1) Permanent gases
- (2) Sulfur and nitrogen oxides
- (3) Light hydrocarbons C₁ to C₄
- (4) Certain lower molecular weight compounds such as formaldehyde, methanol and water
- (5) Water from most organics

Because of its inertness it can be used for the determination in the parts per million and parts per billion concentration level. Due to its unique structure, it will elute compounds in an order different from that obtained with other adsorbents or packings.

Carbosieve B is manufactured by SUPELCO, INC. Kaiser¹ described its use for the determination of trace quantities of water and as a general purpose GSC packing². Zlatkis et al. have also described its chromatographic properties for light gas analysis³.

Carbosieve B is a highly pure carbon with a surface area of approximately 1000m²/g and pore radius in the range of 10-12 Angstroms, making it essentially a carbon molecular sieve. Its high purity eliminates the adsorption problems that are normally encountered with conventional carbon and other adsorbents; this is an important feature. Its unique surface and structure cause separations which, in many instances, are considerably different from that obtained with other adsorbents.

This adsorbent is highly nonpolar; Rohrschneider Constants show this very well and are as follows:

Benzene (x)	Ethanol (y)	MEK (z)	Nitromethane (u)	Pyridine (s)
-1.03	-0.84	-0.62	-1.93	-1.51

All values are negative indicating that Carbosieve B is even more nonpolar than squalane. Because of its nonpolar character, water is eluted before all organic compounds, even before methane.

APPLICATIONS

PERMANENT GAS SEPARATIONS

Permanent gases such as H₂, O₂, N₂, CO, CH₄ and CO₂ can be separated with Carbosieve B. To do this it is necessary to temperature program the column from room temperature to 175°C. O₂ and N₂ are not easily separated so that a 9 ft. x 1/8" stainless steel column is needed, packed with 120/140 mesh Carbosieve B. The column is held isothermally for four minutes, then programmed at the rate of 30°C/min.

to 175°C. The components are eluted in the order of H_2 , O_2 , N_2 , CO , CH_4 and CO_2 . Under these conditions, oxygen and argon are not separated from each other. Figure 3 shows a chromatogram of CO , CH_4 and CO_2 in air.

SEPARATION OF HYDROCARBONS

Carbosieve B can be used to separate hydrocarbons in the $C_1 - C_4$ range. To do this, the column must be operated above ambient temperature. The C_5 and higher molecular weight hydrocarbons are not eluted from the columns. They appear to be permanently adsorbed by the Carbosieve B. Conceivably they could be eluted if the column temperature were raised sufficiently, but this would result in pyrolysis of the sample. In the $C_1 - C_3$ range, the compounds are eluted by the degree of unsaturation, with saturated compounds eluted last. This is in contrast to conventional polar columns where the order would be (a) paraffinic (b) olefinic (c) acetylenic. The polar columns would be useful for traces of paraffins in olefins or olefins in acetylenic compounds, but for traces of acetylene in olefins, or olefins in paraffins, Carbosieve B is unique.

C_2 Hydrocarbons

The C_2 's are separated in the order acetylene, ethylene and ethane. These components along with methane are shown separated in Figure 4 at 150°C with a 3 ft. x 2mm glass column.

C_3 Hydrocarbons

The C_3 's are also separated by the degree of saturation. They are eluted in the order of methylacetylene, allene, propylene, and propane. Cyclopropane and allene are not separated from each other and are eluted together. The separation of the C_3 's along with methane and the C_2 's is shown in Figure 5 with a 3 ft. column at 200°C.

C_4 Hydrocarbons

In preliminary work with the C_4 's, it has been possible to elute iso and n-butane, but not the unsaturated C_4 's. The iso and n-butane peaks are relatively broad and are not resolved with a 3 ft. x 2mm column at 275°C. Separation of $C_1 - C_4$ is shown in Figure 6 at 275°C.

Acetylene in Ethylene

Zlatkis³ has shown that traces of acetylene can be determined in ethylene. The principal advantage of Carbosieve B for this analysis is that acetylene is eluted before ethylene. This allows a large sample to be used without swamping the acetylene peak, as is the case where ethylene is eluted first.

The separation shown in Figure 2 was carried out with a 3 ft. x 2mm column, Carbosieve B, 45/60 mesh at 140°C, flow 40ml/min. N_2 and a flame ionization detector was used here. Sample size 1.5ml, sensitivity 2×10^{-10} A.F.S., lmv recorder.

SEPARATION OF PERMANENT GASES AND METHANE, ETHYLENE AND ACETYLENE

If it is not necessary to separate O_2 and N_2 but only air, CO , CH_4 , CO_2 , acetylene, ethylene and ethane, the separation can be carried out with a 4 ft. x 1/8" column with Carbosieve B, 60/80 mesh programmed from 30 to 170°C as shown in Figure 7. If O_2 and N_2 are also to be separated along with CO , CO_2 , methane, ethane, ethylene and acetylene, the 9 ft. x 1/8" column used in Figure 3 can be used with the C_2 's eluted in order of acetylene, ethylene and ethane.

SEPARATION OF WATER, FORMALDEHYDE AND METHANOL

Kaiser² first reported this difficult separation; it can be readily made with Carbosieve B as shown in Figure 1. The separation was made of a formaldehyde solution containing 36-38% formaldehyde, 10% methanol and the remainder water. The conditions used are as follows: Column, 4 ft. x 3mm I.D. glass packed with 60/80 mesh Carbosieve B; Column Temp., 200°C; Flow rate, 75ml/min. Helium: Sample size, 0.5 microliters.

A thermal conductivity detector is used here because it responds to all three components. A flame detector is less suitable since water is not seen at all and formaldehyde only poorly. Note that the order of elution for the three components differs from that obtained with porous polymers.

TRACE ANALYSIS

Trace Gases

Kaiser² has shown that trace analysis is possible with Carbosieve B, and that it is possible to detect parts per billion of hydrocarbons using reversion gas chromatography. This technique consists of pulling a large, known volume of the sample through the column, allowing the impurities to collect. Then carrier gas is turned on and the column is heated, by a moving oven, which causes the sample to move through the column. This technique allows for the sample to be highly concentrated in the column.

Since Carbosieve B does not bleed, it can be used with ultra high sensitivity detectors such as helium ionization.

TRACE WATER ANALYSIS

Kaiser¹ has shown that trace quantities of water can be determined using a Carbosieve B column. Because of the low affinity for water of its carbon surface, water is quickly eluted from a Carbosieve B column without tailing even before methane. To carry out trace water analysis, care must be taken to prevent water from being adsorbed on the wall of the column tube. Kaiser has shown that quartz is less adsorptive than glass or stainless steel tubing

SULFUR GASES

Sulfur dioxide is readily eluted from Carbosieve B columns without indication of tailing as shown in Figure 8. Kaiser⁴ has found that SO₂ can be determined down to 30 ppm. Below that level the SO₂ is lost on the column.² Consequently, Carbosieve B can be recommended only for higher concentrations of SO₂. Hydrogen sulfide tails badly at relatively high concentration so Carbosieve B cannot be recommended for H₂S analysis at this time.

OXIDES OF NITROGEN

Both nitrous oxide (N₂O) and nitric oxide (NO) can be separated from each other as well as other gases with Carbosieve B. No information of nitrogen dioxide (NO₂) is available as yet.

Nitrous oxide is readily separated from other compounds and is eluted after CO₂ and before acetylene. Figure 9 shows N₂O separated from air, methane and CO₂. This separation was carried out at 100°C with a 3 ft. x 1/8" stainless steel column with 60/80 mesh Carbosieve B.

Nitric oxide is eluted from Carbosieve more rapidly than N_2O . At room temperature it is quickly eluted after N_2 and before CO . This is shown in Figure 10 with a 6 ft. x 1/8" stainless steel column with 60/80 mesh Carbosieve B.

Special precautions must be observed when NO is to be separated. The column must be conditioned with hydrogen to prevent the NO peak from tailing. This can be done with either pure hydrogen or a mixed gas such as nitrogen or helium and hydrogen. We have tried a 94% N_2 -6% H_2 mixture and found this comparable to pure hydrogen for conditioning. Conditioning for one hour at 200, 300 and 400°C seemed to give essentially the same results. It should be noted that none of the work with NO dealt with trace quantities.

If the column is to be operated at room temperature for NO and then temperature programmed to higher temperatures, the carrier gas should contain hydrogen. If the column is heated without hydrogen in the carrier gas, then the NO peak will tail. This was found with helium as the carrier gas. We found the column gradually deteriorated for NO when the column was repeatedly temperature programmed to 200°C to elute other components. Our work with NO and the hydrogen deactivation has been exploratory, and at this point we are not certain that it can be reproduced.

Both NO and N_2O can be separated from O_2 , N_2 , CO , CO_2 and methane with a 6 ft. x 1/8" column. The column is operated at room temperature till CO is eluted, then the column is programmed quickly to 150°C to elute methane, CO_2 and N_2O . When the column is programmed, the carrier gas must be dry.

MISCELLANEOUS RETENTION DATA

Data prepared by Kaiser in Table 1 compares Carbosieve B, Porapak Q and Molecular Sieve 5A. Note that the values are retention volumes, not retention times. Water is shown to elute before methane and CO_2 on the Carbosieve B but it is evident that it takes quite some time for butane to be eluted, even at 250°C.

The data in Table 2 were obtained in our laboratory using a 3 ft. x 1/8" O.D. stainless steel column packed with 60/80 Carbosieve B and operated at 40ml/min. and are absolute retention times.

HANDLING OF CARBOSIEVE B

Carbosieve B is supplied in fifteen cc evacuated, sealed vials. When the vial is opened, unused material should be transferred to a glass bottle and tightly closed. To avoid contamination, Carbosieve B should not be exposed to the atmosphere for prolonged periods of time. Because of its high surface area, it tends to readily pick up contaminants from the air; these can be removed but it requires extensive conditioning of the column. To avoid oxidation and damage to its surface, do not heat Carbosieve to over 200°C in air; do not heat columns above this temperature if the carrier gas is not free of oxygen. Columns that are to be temperature programmed should be conditioned for a number of hours at or slightly above the highest temperature anticipated.

Carbosieve B should be used with a carrier gas that is free of oxygen to avoid oxidation of its surface. If oxidation should occur, the peak will show tailing. Oxygen can be removed catalytically by means of specially designed traps which are installed in the carrier gas line.

If temperature programming is used, it is imperative that the carrier gas also be dry. Use of a device such as a molecular sieve trap to remove water is recommended. If the carrier gas is not dry, an irregular base line will be obtained when the column is programmed with a broad peak for water seen in the vicinity of the CO_2

peak. This is a problem with a thermal conductivity detector, but not a flame which does not respond to water.

A drying cartridge should be used to remove water from the carrier gas. One must assume that all carrier gases have some moisture in them. We also find it necessary to install a small drying trap after the flow controller in the instrument. We have seen in several instances where it is the flow controller bleeding moisture that causes the base line problem even though the carrier gas was being dried. One can also heat the carrier gas tubing from the cylinder to the chromatograph to remove moisture from the walls of the tubing, but this is unnecessary if the trap is placed after the controller. A short section of tubing filled with Molecular Sieve 5A is adequate for this. Once this is done, heat the column to the maximum temperature which you expect to reach and hold the column at that temperature for several hours to condition it.

The problem of moisture in the carrier gas is illustrated in Figure 11 which shows the peak for water after CO_2 . The size and position of the water peak will depend on the amount of water present.

REFERENCES

- (1) Kaiser, R., *Chromatographia* 2, 453 (1969)
- (2) Kaiser, R., *Chromatographia* 3, 38 (1970)
- (3) Zlatkis, A., Kaufman, H. R. and Durbin, D. E., *J. Chromatog. Sci.* 8, 416 (1970)
- (4) Kaiser, R., Private Communication

TABLE 1

	Carbosieve B		Porapak Q 150°C	Molecular Sieve 5A	
	150°C	250°C		150°C	250°C
O ₂	1.22	-	0.28	0.32	-
N ₂	1.22	-	0.28	0.56	-
CO	1.75	-	0.28	1.34	-
CO ₂	9.09	1.80	0.78	43.0	-
CH ₄	4.71	1.03	0.40	1.01	-
C ₂ H ₂	21.6	4.08	1.11	-	14.2
C ₂ H ₄	40.5	6.59	1.04	63.9	-
C ₂ H ₆	64.1	9.42	1.23	7.36	-
C ₃ H ₈	-	54.9	3.09	-	47.8
C ₄ H ₁₀	-	126.0	7.83	-	-
C ₅ H ₁₂	-	-	16.72	-	-
CHOH	27.1	3.96	3.78	-	-
CH ₃ OH	65.7	8.35	5.59	-	-
C ₂ H ₅ OH	-	38.3	12.35	-	-
H ₂ O	4.59	0.51	2.61	-	-

Specific Retention Volume V_g at 150°C

Methane	3.0ml/gm
Ethane	47.4ml/gm
Propane	506.1ml/gm

In the table above (prepared by Kaiser) retention volumes for a number of compounds are compared for several types of columns. In all cases column length was one meter.

TABLE 2

RETENTION TIMES (ABSOLUTE)

	Column Temperature		
	100°C	150°C	200°C
	Time in Minutes		
H ₂	0.23	0.2	0.15
Argon	0.23	0.2	0.15
O ₂	0.23	0.2	0.15
N ₂	0.23	0.2	0.15
NO	0.23	0.2	0.15
CO	0.23	0.2	0.15
CH ₄	0.5	0.3	0.15
CO ₂	0.92	0.4	0.27
N ₂ O	1.45	0.6	0.3
Acetylene	2.4	0.85	0.4
H ₂ S	4.7	0.450	0.3
Ethylene	5.4	1.6	0.7
Ethane	9.8	2.6	1.0
SO ₂	-	5.0	1.6
Methyl Acetylene	-	-	3.7
Cyclopropane	-	12.8	4.2
Allene	-	15.7	4.5
Propylene	-	-	6.0
Propane	-	-	8.6
Water	-	0.15	0.15
Formaldehyde	-	0.35	0.2
Methanol	-	1.0	0.45

Column: 3 ft. x 1/8" S.S., 60/80 mesh Carbosieve B Flow: 40ml/min.

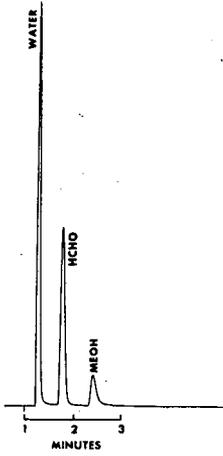


FIGURE 1 - Water-Formaldehyde-Methanol Separation

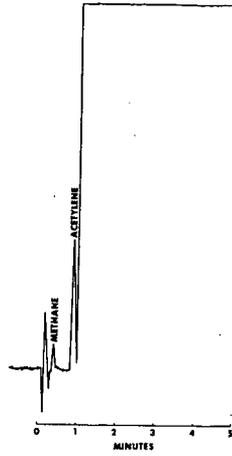


FIGURE 2 - Trace Acetylene in Ethylene

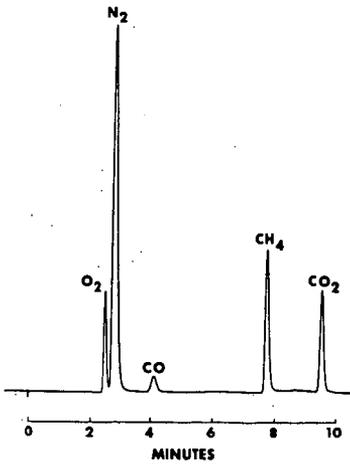


FIGURE 3 - Separation of O_2 , N_2 , CO , CH_4 and CO_2

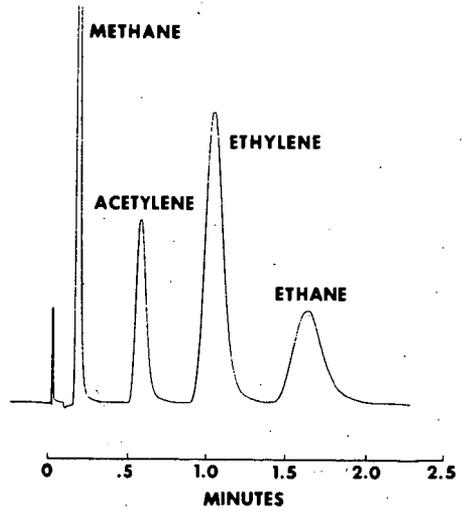


FIGURE 4 - Separation of Methane and C_2 's

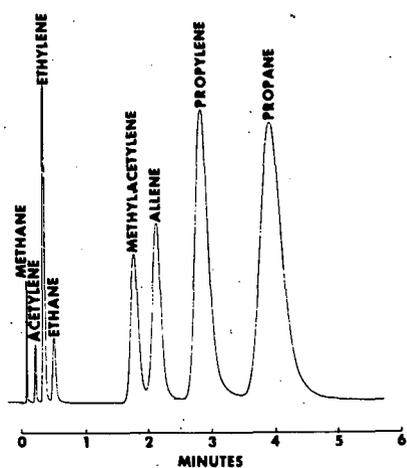


FIGURE 5 - Separation of C_1 's, C_2 's and C_3 's

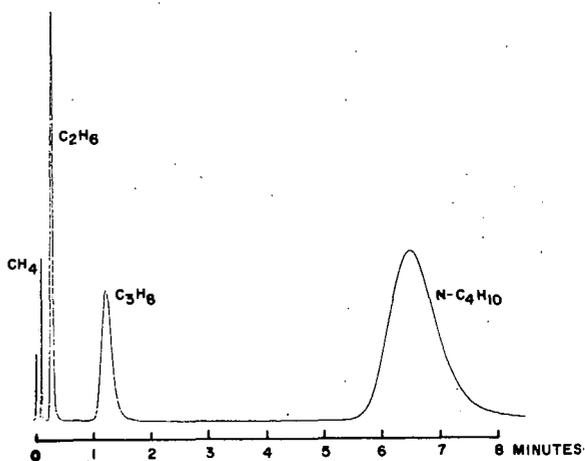


FIGURE 6 - Separation of n-Paraffins - C_1 - C_4

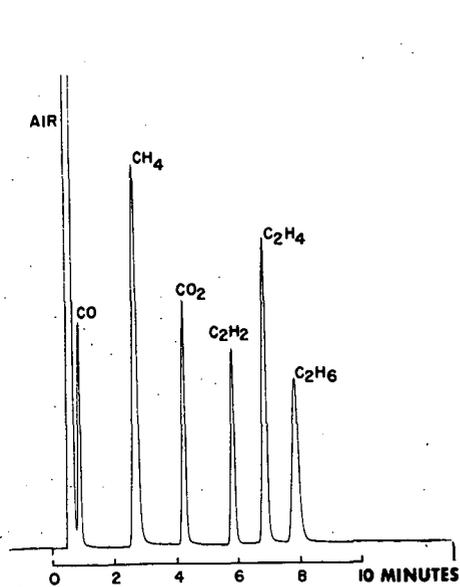


FIGURE 7 - Separation of Air, CO, CH_4 , CO_2 , C_2H_2 , C_2H_4 , and C_2H_6

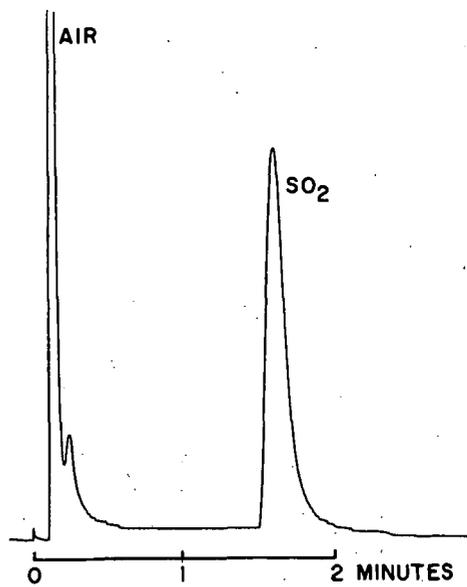


FIGURE 8 - Separation of Air and SO_2

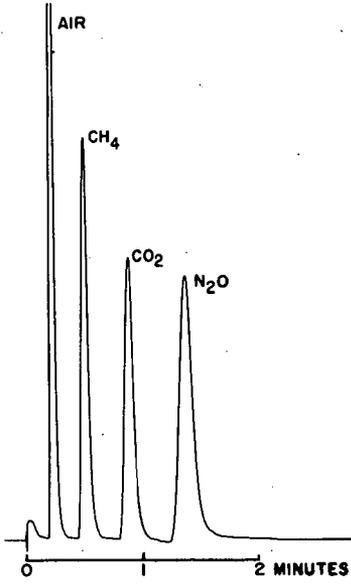


FIGURE 9 - Separation of Air, CH₄, CO₂ and N₂O.

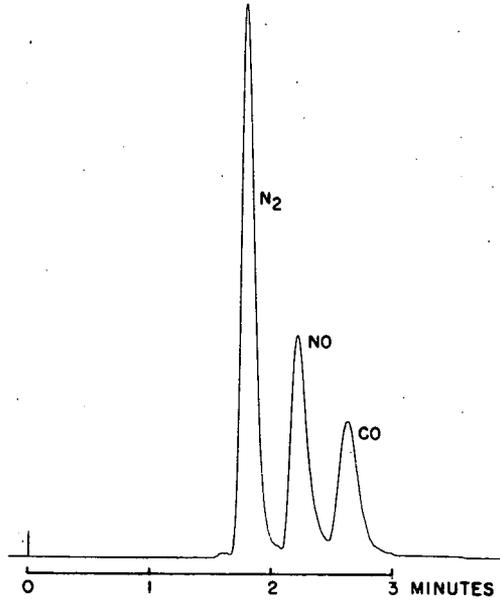


FIGURE 10 - Separation of N₂, NO and CO

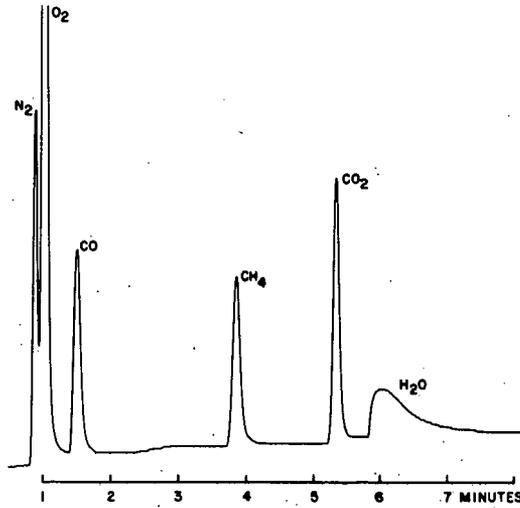


FIGURE 11 - Separation of O₂, N₂, CO, CH₄, CO₂ and H₂O.

THE ISOLATION AND DETERMINATION OF AROMATICS IN GASOLINE BY GAS CHROMATOGRAPHY

L. L. Stavinoha and F. M. Newman

U.S. Army Fuels and Lubricants Research Laboratory
Southwest Research Institute
San Antonio, Texas 78284

INTRODUCTION

Evaluation and control of the aromatic hydrocarbon content of motor gasolines used in engine deposition and exhaust emission tests have necessitated the development of quantitative methods of analysis for the determination of aromatics. Gas liquid chromatographic analyses involving selective separation of saturates and olefins from aromatics through the use of polar liquid phases offer advantages in specificity when compared to other approaches, such as open tubular column GLC techniques⁽¹⁾, due to the large variety of hydrocarbons present in broad boiling-point range fuels. However, the existing standard method using selective separation has an upper temperature limit of 300°F⁽²⁾, which excludes the analysis of motor gasolines. This upper temperature has been extended by the method described in this paper. This method combines selective isolation with a highly repeatable sampling technique and a quantitative analytical separation method. Benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, isopropylbenzene, and C₉+ aromatics containing components with boiling points as high as 486°F are quantitatively determined. An extended method provides for the analysis of fuels having boiling points as high as 550°F.

EXPERIMENTAL

Apparatus. A high-pressure, high-temperature liquid sampling valve, obtained from Valco, Inc., Houston, Texas, was interfaced to an oven constructed in this laboratory. The oven was equipped with columns and switching valves as illustrated schematically in Figure 1. Isothermal heat control was obtained using a fan, heating coils, and a powerstat. This oven was interfaced to a Hewlett-Packard Model 7621 gas chromatograph equipped with a dual hydrogen-flame ionization detector (HFID), multilevel-oven temperature programmer, electrometer, and a 1-mV, 1/2-sec recorder. The electrometer output, coupled to a Vidar Autolab Model 6230 digital integrator equipped with an ASR-33 Teletype, provided retention times and peak areas as hard copy printout and punched paper tape records. Experiments to establish the separating characteristics of CEF columns were conducted in the Hewlett-Packard Model 7621 gas chromatograph. The detector inlet was modified to use flow restrictors made of 5-in. lengths of 0.010-in.-I.D. stainless steel tubing crimped to effect increased back pressure.

Reagents. Hydrocarbons used in calibration standards for composition and retention time determinations were 99+ mole percent pure and were obtained from the following sources:

- benzene, toluene, 3,5-di-isopropylbenzene—J. T. Baker Chemical Co., Phillipsburg, New York.
- ethylbenzene—Phillips Petroleum Company, Bartlesville, Oklahoma.
- o-xylene—Matheson Coleman & Bell, Norwood, Ohio.
- n-propylbenzene, 1,2,4-trimethylbenzene, n-pentylbenzene—Eastman Kodak Company, Rochester, New York.

The N,N-bis(2-cyanoethyl) formamide (CEF) used as the liquid phase in the separating column (C₁ in Figure 1) was obtained from Applied Science Laboratories, Inc., State College, Pennsylvania. The Dexsil 300 liquid phase used in the analytical column (C₃ in Figure 1) was obtained from Analabs, Inc., North Haven, Connecticut. The SE-30 liquid phase used in the restrictor column (C₂ in Figure 1) was obtained from Varian Aerograph, Walnut Creek, California, and the Chromosorb solid supports were also obtained from Varian Aerograph.

Column Preparation. All column packings were prepared by mixing dissolved liquid phase, using the solvents recommended by the manufacturer, with the column solid support on a weight-percent basis, and removing the solvent in a vacuum rotary evaporator at 115°F. After the columns were packed, they were conditioned at the maximum operating temperatures and carrier gas flows for 24 hr, except for the high-load CEF columns which were conditioned for a minimum of 3 days.

Chromatographic Procedure. The chromatographic system, schematically illustrated in Figure 1, was designed to analyze both the aromatic and the saturate-olefin fractions of gasoline. The chromatographic operating conditions common

to both of these analyses are given in Table I. For the aromatic fraction analysis, Valves V_2 and V_3 are initially in position A as in Figure 1; at 5 min, V_2 is turned 90 deg CW to position B; at 7 min, V_3 is turned 90 deg CW to position B. For the saturate-olefin fraction analysis, V_2 and V_3 are initially in positions A and B, respectively; at 4.5 min, V_2 is turned to position B; at 6.5 min, V_3 is turned to position A.

At the end of each test, the valves were returned to their initial positions for the next test and carrier gas flow allowed to stabilize for a minimum of 3 min.

Quantitation of Aromatics. Because of the many aromatic hydrocarbons present in gasolines, a direct or absolute calibration technique (as opposed to internal standardization) was employed using the calibration standard described in Table II.

Sampling Procedure. All gasoline samples were stored at 0°F in sealed metal containers or room temperature in 75-ml, nitrogen-pressurized stainless steel cylinders, double-ended with stainless steel valves. The cylinders were used to pressure introduce the sample into the GLC system via a 1- μ l heated liquid sampling valve. The sample was passed through a 7- μ m stainless steel filter before entering the liquid sampling valve, and other hydrocarbon samples were also introduced into the GLC system through the use of the liquid sampling valve, unless otherwise indicated. The cylinders were filled with 50 to 55 ml of test fluid after evacuation of the cylinder. Approximately 5 ml of the sample was used to purge the liquid sampling system during filling. The liquid sampling valve was held at 175°C, and the nitrogen driving pressure was 450 psig.

RESULTS AND DISCUSSION

Establishing the Separating Characteristics of N,N-bis(2-cyanoethyl) formamide. The effects of N,N-bis(2-cyanoethyl) formamide (CEF) liquid phase loading and column length have been investigated at a column oven temperature of 120°C which is 5°C lower than the manufacturer's recommended maximum operating temperature. An n-heptane mixture containing 3% v tetradecane and 10% v benzene was injected by syringe into various columns both with and without a flow restrictor between the column and detector. The tetradecane could not be completely resolved from the benzene using 15, 25, and 35% wt CEF in columns varying in length up to 5 ft. Separation was effected using 35% wt CEF in columns at least 3 ft long when flow restrictors were employed between the column and detector. The data presented graphically in Figure 2 demonstrate the increased separating ability at a measured pressure of 37 psig between the restrictor and the column which was supplied carrier gas through a flow controller at a pressure of 70 psig. Also demonstrated in Figure 2 is the effect of CEF loading. At a loading of 15% wt CEF, benzene elutes before tetradecane; at a loading of 25% CEF, no separation is effected; and at 35% CEF, the desired separation was obtained with tetradecane being eluted before benzene. Under the latter condition, pentadecane was eluted before benzene but was not fully resolved. A 3-ft column containing 35% wt CEF was chosen for the GLC system in Figure 1 to allow ample time to effect column switching and assure quantitative isolation of benzene and higher boiling-point aromatics from tetradecane and lower boiling-point hydrocarbons. Most of the gasolines which were analyzed contained less than 0.25% v material having boiling points above that of tetradecane.

Establishing Operating Procedure. Because of CEF's upper temperature limit of 125°C and the need to hold the CEF column's temperature constant during separation of the aromatics, versatility in the analysis of the aromatics was not provided with the use of CEF alone. Through the use of appropriate valving, the CEF column can be used to isolate the aromatic fraction on another column which can then be temperature programmed to provide the desired separation of the aromatics present. The simplest system would involve the valving described in Figure 3, with the valve switching time determined and an appropriate temperature program chosen for the analytical column to effect the desired aromatics separation. A somewhat more complicated system, described schematically in Figure 1, was chosen for use in this laboratory. In this system, a packed column having SE-30 liquid phase was placed in the same oven as the CEF column to provide the required back pressure in the CEF column to obtain the desired separating efficiency. A needle valve or small bore tube could be used to provide the back pressure if no subsequent analysis of the effluent were made. The SE-30 column at 120°C provided long-term back pressure stability and a fair separation of hydrocarbons in the gasoline boiling-point range when the effluent was detected rather than vented. During the isolation process on the CEF column, it was important that the back pressure remained constant. The Dexsil 300 column in Figure 1 was used to analyze the CEF column effluent. Dexsil 300 has a lower bleed level than materials such as SE-30.

This system allowed for the analysis of both the aromatic and the saturate-olefin fractions, depending upon the valve switching sequence chosen. Preliminary separations had to be made to optimize the operating parameters involving both oven temperature programming and valve switching times. A calibration standard was specifically formulated to provide the following:

- (1) Checks of the system's isolating efficiency by comparing the analytical ratios of benzene (10% v) to toluene (10% v) with the ideal ratio (1:1) and by determining the presence or absence of tetradecane, which should be

absent; the same criteria were used to establish the time at which the backflush valve, V_2 in Figure 1, and the column switching valve, V_3 , were turned. The column switching valve was turned 1 to 2 min after the turning of the backflush valve.

- (2) A calibration of the system in terms of aromatic concentration vs digital integrator area over a nominal concentration range of 1 to 10% v through the use of response factors.
- (3) A calibration of the system in terms of boiling-point temperature vs retention time.

By varying the time before backflushing the CEF column, it was possible to separate higher boiling-point saturates from the aromatics, as the data in Figure 4 illustrate. Figure 4a shows the relative recovery with no valve switching. All of the saturate and aromatic components of the sample were recovered, and, except in Figure 4a, the effluent from the CEF column was switched to the Dexsil 300 column 2 min after the backflush time. As the backflush time was varied from 5 to a maximum of 9 min, increasing amounts of saturates as well as aromatics were vented, and, as a result, they were not a part of the analyzed effluent from the CEF column. In order to raise the applicable boiling point (548°F at a backflush time of 9 min), analysis of the lower boiling-point aromatics had to be sacrificed. This higher boiling-point procedure had to be used in addition to the standard procedure in order to analyze fuels for the lower boiling aromatics as well as for aromatics boiling above 486°F.

In order to analyze the saturate-olefin fraction of the fuel, the aromatics were vented through the SE-30 column and the saturate-olefin fraction passed into the Dexsil 300 column. The valve switching schedule for this analysis was not the same as that for the aromatics' analysis. The Dexsil 300 column at 0°C did not create as much back pressure on the CEF column as did the SE-30 column at 120°C. The result of the lower back pressure was twofold and predictable from Figure 2. The lower back pressure resulted in shorter retention time and lower isolation efficiency, but the effects were slight.

A 1- μ l liquid sampling valve was used to eliminate sample injection errors due to the wide volatility ranges of gasolines. Neither peak areas from calibration standards nor premium or regular grade gasolines varied outside of the repeatability established for triplicate analyses, when the valve temperature or nitrogen pressure on the sample cylinder was varied over the ranges of 160° to 190°C and 400 to 500 psig, respectively. Without having been disassembled, the valve was operated at 175°C and 450 psig nitrogen in the analysis of several hundred samples over the past year.

Analyses of Full-Range Motor Gasolines. Analytical results for two motor gasolines, one a premium grade and the other a regular grade, were chosen to demonstrate the type of results routinely obtainable through the use of this GLC system. Figure 5 contains reproductions of chromatograms obtained from these two gasolines and the calibration standard described in Table II. A chromatogram was obtained for both the aromatic fraction and the saturate-olefin fraction of each of the three samples. The calibration standard provided a linear volumetric relationship based on integrated peak area and a linear boiling-point relationship based on peak retention time for the aromatics. The aromatic volumetric data in Tables III and IV were computed on the basis of the summed weighted areas for the aromatics contained in the calibration standard and were not rounded off so as to reflect precision for the triplicate analyses of each of the gasolines. Only the areas for benzene, toluene, and ethylbenzene were weighted by multiplying by the response factors, 0.904, 0.939, and 0.973, respectively. These response factors were experimentally determined during detector optimization which also included evaluation of o-xylene, n-propylbenzene, 1,2,4-trimethylbenzene, and n-pentylbenzene for linear concentration response. These response factors also compare favorably with values of 0.893, 0.935, and 0.971, respectively, which are the reciprocals of published response factors.⁽³⁾ Response factors for other aromatics vary ± 3 percent from unity, which is a deviation directly translatable as a relative error for many of the unresolved aromatics. The use of carrier gas, makeup carrier gas, hydrogen, and purge airflow rates for optimized detector response and sensitivity in this system revealed negligible deviations from linearity for the aromatics investigated except for benzene and toluene. Relative deviations of approximately ± 2 percent of the concentration in the range 3 to 15 percent by volume were found for both benzene and toluene.

The repeatability for triplicate analyses was found to be particularly good as indicated by the data contained in Tables III and IV for the two gasolines. Similarly, good repeatability was obtained for the calibration standard. For an externally calibrated system, reproducibility within these repeatability limits was therefore a function of the repeatability with which the calibration standards could be prepared and analyzed.

The interpretation of variations in aromatic concentrations between gasoline samples or batches of reference fuels is directly dependent upon the accuracy with which they are determined. The approach used to establish relative errors was to evaluate the accuracy of analyses of blends prepared from pure hydrocarbons. By use of a single batch of the calibration standard described in Table II as an absolute calibrant, an analysis was made of blends of benzene, toluene, ethylbenzene, o-xylene, 1,2,4-trimethylbenzene, n-propylbenzene, n-pentylbenzene, and 3,5-di-isopropyltoluene in n-heptane. The highest relative errors observed for benzene, toluene, and ethylbenzene at concentrations of 15, 10, 5, 2.5, 1.25, and 0.625 percent

by volume were +4, +4, +2, +4, +4, and +8 percent, respectively. Essentially, the same maximum values were observed for the other aromatics except that concentrations above 5% v were not evaluated. Since additional errors could exist in the analysis of a gasoline sample, as opposed to these blends, the relative errors observed were increased for the concentration ranges of 5 to 20, 2 to 5, and 0.5 to 2 percent by volume to ± 4 , ± 6 , and ± 10 percent, respectively. These were the more liberal values used as guides in evaluating data obtained by the aromatics procedure in this laboratory. Obviously, much more accurate analyses were possible for the resolved aromatics through the use of multiple standards and repetitive analyses. For the purposes for which these data are presently used, accuracy achievable without the use of multiple standards and repetitive analyses has been adequate, since new batches of calibration standards are analyzed to maintain reproducibility. In this way, fuels were analyzed with better month-to-month reproducibility than would be indicated from the relative error.

The boiling points reported for the aromatics in Tables III and IV were obtained through a linear best fit of boiling point versus retention time data given in Figure 6 for the aromatic fraction analysis. Retention time repeatability for the peaks was found to vary no more than ± 3 sec from the mean retention times over the entire range for triplicate analyses. Some of the C_9+ aromatic peaks given in Tables III and IV have boiling points near the 486°F upper temperature limit and are therefore not considered to be definitely aromatic.

Generally, the saturate-olefin fractions of fuels were not analyzed in detail except for determining their boiling-point distributions, data which have been found useful in the evaluation of other analytical methods both in use and under development. The boiling-point data in Figure 7 for the boiling-point distribution of the saturate-olefin fractions of the two gasolines were obtained through a fourth order polynomial best fit of the boiling point vs retention time data in Figure 6. Areas for the individual peaks in the chromatograms shown in Figure 5 for the saturate-olefin fractions were divided by the total of the peak areas and normalized to obtain a distribution in terms of weight percent.

While the ability of CEF to isolate the aromatics from the saturates plus olefins in gasolines has been demonstrated and taken advantage of in the analytical procedures discussed in this paper, these procedures do not provide for the specific determination of the aromatic hydrocarbons which have been identified simply as C_9+ . Methods for greatly improving resolution of the C_9+ aromatics are being considered for future evaluation.

CREDIT

This work was conducted under a contract with the U.S. Army Coating and Chemical Laboratory, Aberdeen Proving Ground, Maryland.

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TABLE I. CHROMATOGRAPHIC OPERATING CONDITIONS FOR THE ISOLATION AND DETERMINATION OF AROMATIC AND SATURATE-OLEFIN FRACTIONS OF MOTOR GASOLINES

Instrument	Hewlett-Packard Model 7621 GC
Detector	Hydrogen-Flame Ionization
Liquid Sampling Valve:	
Temperature	175°C
Pressure	450 psig N ₂
Volume	1 µl
Detector Temperature	250°C
CEF Column	35% wt N,N-bis(2-cyanoethyl) formamide on 60/80 Chromosorb P, AW-DMCS, 3' X 0.19" I.D. X 0.25"-O.D. aluminum
SE-30 Column	5% wt SE-30 on 100/120 Chromosorb G, AW-DMCS, 15' X 0.09" I.D. X 0.13"-O.D. stainless steel (316)
Dexsil 300 Column	4% wt Dexsil 300 on 80/100 Chromosorb G, AW-DMCS, 15' X 0.09" I.D. X 0.13"-O.D. stainless steel (316)
CEF Column Oven Temperature	120°C
Dexsil 300 Column Oven	12 min at 0°C, linear program of 8°C/min. to 225°C, 10 min at 225°C, recover to 0°C
Carrier Gas Flow	25 ml helium/min
Auxiliary Carrier Gas Flow	60 ml helium/min
Hydrogen Flow	35 ml/min
Airflow	375 ml/min
Recorder Attenuation	32

TABLE II. CALIBRATION STANDARD

Component Identification Number*	Component	Concentration, % v
1	Benzene	10.0
2	Toluene	10.0
3	Ethylbenzene	8.0
4	m+p-Xylene	0.0
5	o-Xylene	0.0
6	Isopropylbenzene	0.0
7	n-Propylbenzene	4.0
8	1,2,4-Trimethylbenzene	2.0
9	n-Pentylbenzene	1.0
10	n-Butane	0.5
11	n-Pentane	0.8
12	n-Hexane	28.2
13	n-Heptane	28.2
14	n-Octane	0.8
15	n-Nonane	0.8
16	n-Decane	0.8
17	n-Undecane	0.8
18	n-Dodecane	0.8
19	n-Tridecane	0.8
20	n-Tetradecane	0.8
21	n-Pentadecane	0.8
22	n-Hexadecane	0.8

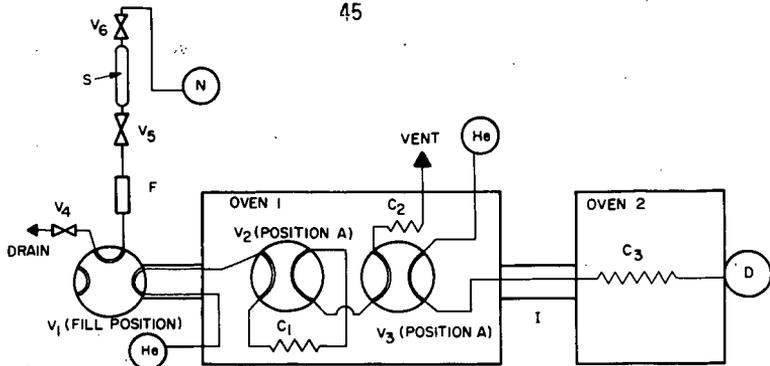
*Same component identification numbers used throughout this paper.

TABLE III. THE AROMATIC COMPOSITION OF A PREMIUM GRADE GASOLINE

Component	Average Retention Time, sec	B.P., °F	Volumetric Concentration, %		
			Run 1	Run 2	Run 3
Benzene	1255	176	0.770	0.765	0.759
Toluene	1451	231	16.990	16.952	16.987
Ethylbenzene	1593	277	3.134	3.129	3.122
m+p-Xylene	1617	285	11.201	11.187	11.229
o-Xylene	1651	296	3.566	3.553	3.563
Isopropylbenzene	1682	306	0.133	0.136	0.136
C ₉ +	1725	319	0.535	0.531	0.528
C ₉ +	1743	325	2.626	2.617	2.620
C ₉ +	1765	332	1.517	1.517	1.516
C ₉ +	1800	342	3.147	3.144	3.143
C ₉ +	1839	355	0.616	0.611	0.612
C ₉ +	1873	366	1.384	1.381	1.379
C ₉ +	1913	378	0.966	0.962	0.957
C ₉ +	1945	388	0.093	0.091	0.089
C ₉ +	1972	396	0.599	0.599	0.595
C ₉ +	1994	403	0.109	0.107	0.104
C ₉ +	2013	410	0.302	0.304	0.300
C ₉ +	2066	426	0.441	0.446	0.452
C ₉ +	2110	440	0.015	0.016	0.012
C ₉ +	2137	448	0.014	0.024	0.012
C ₉ +	2203	468	0.032	0.037	0.033
C ₉ +	2224	475	0.006	0.010	0.006
Total			48.190	48.119	48.154

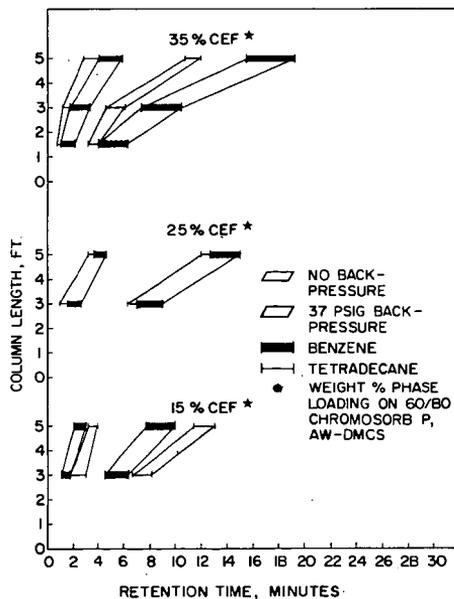
TABLE IV. THE AROMATIC COMPOSITION OF A REGULAR GRADE GASOLINE

Component	Average Retention Time, sec	B.P., °F	Volumetric Concentration, %		
			Run 1	Run 2	Run 3
Benzene	1257	176	0.419	0.403	0.405
Toluene	1447	231	2.713	2.651	2.682
Ethylbenzene	1595	277	1.965	1.911	1.933
m+p-Xylene	1617	284	7.798	7.726	7.774
o-Xylene	1652	295	2.880	2.846	2.875
Isopropylbenzene	1684	305	0.149	0.146	0.148
C ₉ +	1728	319	0.657	0.619	0.634
C ₉ +	1746	325	3.365	3.323	3.351
C ₉ +	1768	332	1.958	1.934	1.953
C ₉ +	1802	343	4.346	4.305	4.333
C ₉ +	1842	355	0.911	0.907	0.908
C ₉ +	1875	365	2.079	2.056	2.068
C ₉ +	1916	379	1.463	1.440	1.451
C ₉ +	1947	388	0.143	0.138	0.142
C ₉ +	1974	397	0.915	0.903	0.909
C ₉ +	1996	404	0.198	0.180	0.185
C ₉ +	2015	409	0.497	0.494	0.498
C ₉ +	2068	426	0.724	0.714	0.722
C ₉ +	2110	440	0.030	0.026	0.028
C ₉ +	2139	448	0.026	0.024	0.024
C ₉ +	2156	454	0.015	0.013	0.014
C ₉ +	2205	468	0.064	0.061	0.061
C ₉ +	2225	475	0.012	0.011	0.011
Total			33.327	32.831	33.109



- OVEN 1 ISOTHERMAL CEF COLUMN OVEN
 OVEN 2 TEMPERATURE PROGRAMMED DEXSIL 300 COLUMN OVEN
 V₁ HEATED SAMPLING VALVE IN FILL POSITION; TURN 90° CW TO INJECT POSITION.
 V₂ BACKFLUSH VALVE IN POSITION A; TURN 90° CW TO POSITION B.
 V₃ COLUMN SWITCHING VALVE IN POSITION A; TURN 90° CW TO POSITION B.
 V₄, V₅, V₆ SHUT-OFF VALVES
 F 7 MICROINCH IN LINE SAMPLE FILTER
 C₁ CEF COLUMN
 C₂ SE-30 COLUMN
 C₃ DEXSIL 300 COLUMN
 N NITROGEN PRESSURE REGULATOR
 S HIGH PRESSURE CYLINDER CONTAINING SAMPLE
 He HELIUM CARRIER GAS
 D FLAME IONIZATION DETECTOR
 I HEATED INTERFACE, SAME TEMPERATURE AS OVEN 1

FIGURE 1. SCHEMATIC DIAGRAM OF GAS CHROMATOGRAPHIC SYSTEM FOR THE ISOLATION AND DETERMINATION OF AROMATICS IN GASOLINE



Note: Conditions—All columns were 0.19 in. I.D. aluminum; oven temperature was 120°C; helium carrier gas flow rate was 25 ml/min.

FIGURE 2. EFFECT OF COLUMN PARAMETERS ON THE SEPARATION OF TETRADECANE FROM BENZENE

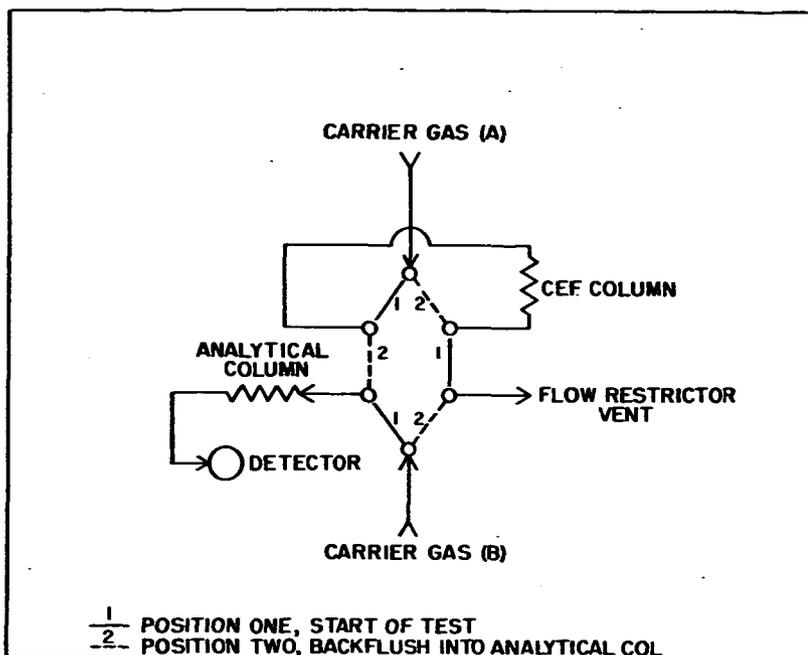


FIGURE 3. SIMPLIFIED SYSTEM FOR AROMATICS ANALYSIS USING TWO-POSITION VALVE

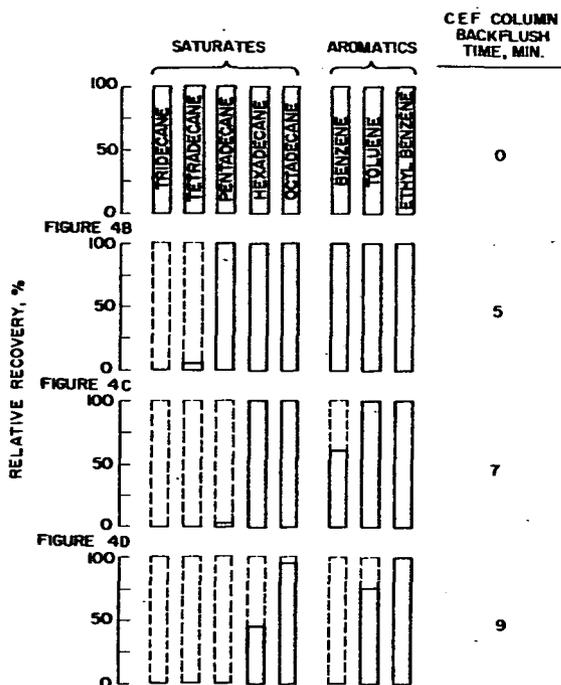
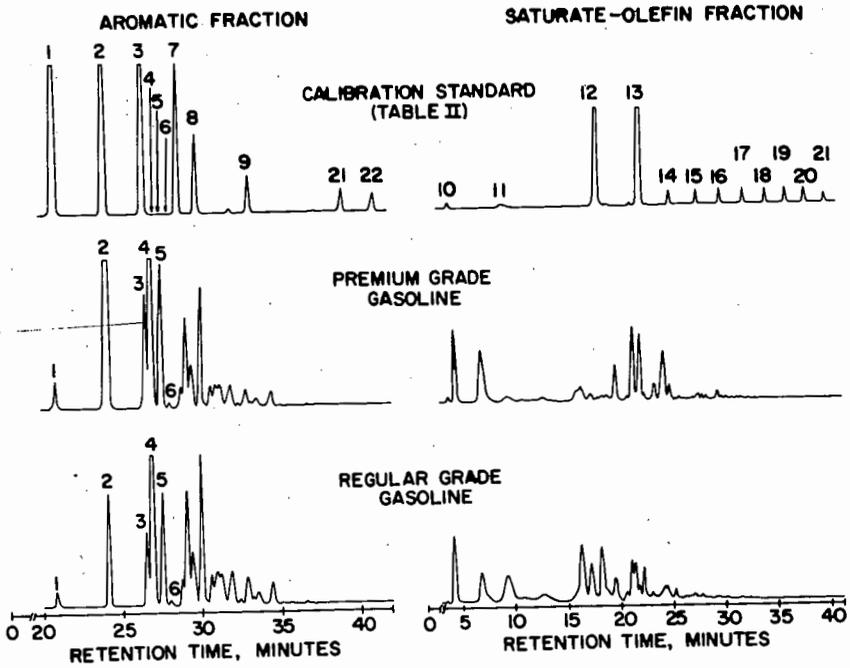


FIGURE 4. EFFECT OF CEF COLUMN BACKFLUSH TIME ON ANALYTICAL RECOVERY



Note: Component identification numbers are given in Table II.

FIGURE 5. REPRODUCTION OF CHROMATOGRAMS FOR A CALIBRATION STANDARD, A PREMIUM GRADE GASOLINE, AND A REGULAR GRADE GASOLINE

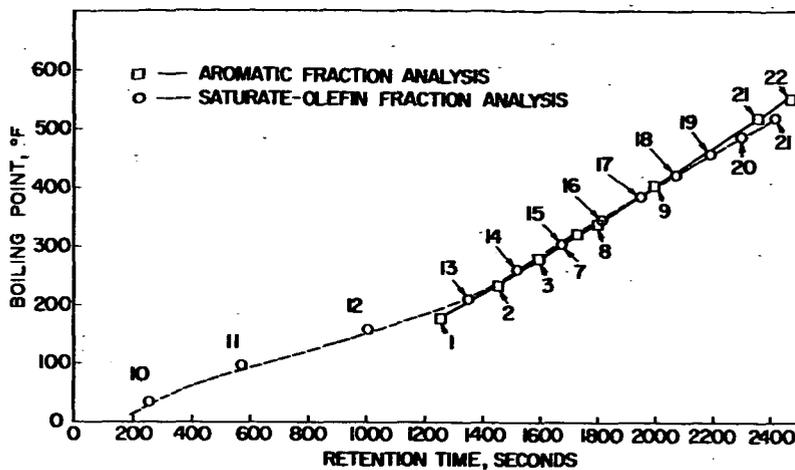


FIGURE 6. CALIBRATION CURVES FOR BOILING POINT VERSUS CHROMATOGRAPHIC PEAK RETENTION TIME

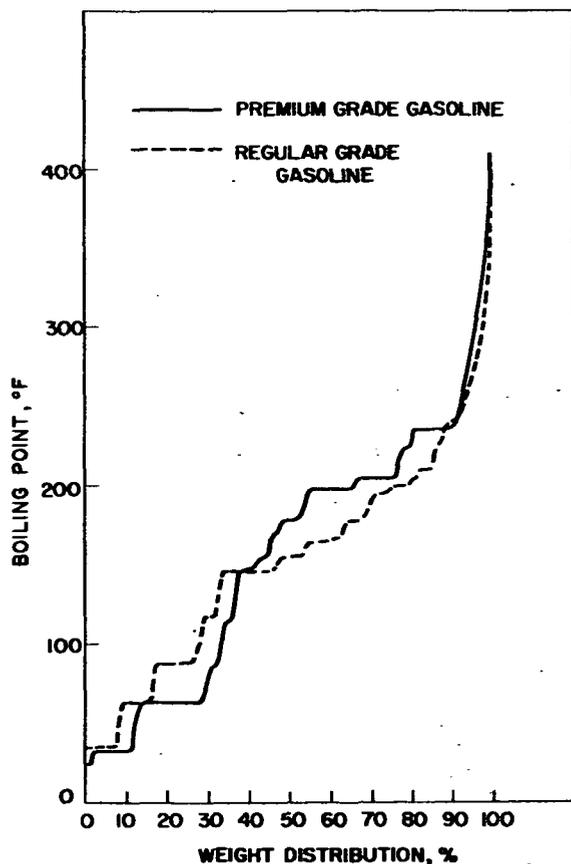


FIGURE 7. BOILING-POINT DISTRIBUTION OF THE SATURATE-OLEFIN FRACTIONS OF TWO GASOLINES

Analysis of Water Extracts of Hydrocarbon Mixtures

S. Wasik and Robert L. Brown

Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

INTRODUCTION

Concern over the pollution of water systems by oil has generated a desire for improved methods of analyzing water for dissolved hydrocarbons (1). The complexity of crude oil and oil products makes the analysis of their water extracts difficult. It can be simplified by physically or chemically separating the components of the extract into hydrocarbon groups such as saturated hydrocarbons, olefins, aromatics, and polar hydrocarbons. One approach to this separation problem involves the analysis of hydrocarbons in a gas which has passed through the extract. Elution times for the various hydrocarbons will depend on their partition coefficients; e.g., the slightly soluble aliphatic compounds will be removed far more rapidly than the more soluble aromatic hydrocarbons. Group separations can thus be based on group elution times.

In the present work, helium was used as the stripping gas and its hydrocarbon content was determined by gas chromatography. For group separation it is not essential to achieve an equilibrium distribution of the hydrocarbons between the two phases, although this gives the highest sensitivity. If equilibrium can be approximated, however, the method yields a direct determination of the partition coefficients from the elution times. In practice, it is not difficult to approach equilibrium closely. Under such conditions, plots of the log of the chromatographic peak area against the volume of helium passed through the extract will be linear, and the slopes of the plots will depend only on the volume of the extract and the partition coefficients of the solutes. Partition coefficients for members of a group, and thus the slopes of the log plots can be drastically changed by the addition of complexing agents. This greatly facilitates group identification. The method is similar to the multiple phase-equilibrium scheme described by McAullife (2). It differs, however, in that it is a continuous process and that it utilizes group complexing agents.

EXPERIMENTAL

Apparatus

The extract was contained in a vertically-mounted glass tube 50 cm long and 1 cm in diameter. Bubbles of helium were injected into the bottom of this cell from a very small opening in the end of a 1/16-inch stainless steel tube. This orifice was made by pinching off the end of the tube and reopening it slightly with a file. A pressure head of 80 psig across this hole produced a helium flow of 1 ml/min in the form of small bubbles averaging approximately 0.1 mm in diameter. The outlet of the cell was connected to a gas sampling valve with 1/16-inch stainless steel tubing. The extract was introduced into the cell from a pipette, with the amount chosen to bring the liquid level almost to the top of the cell thereby minimizing the dead volume in the gas phase. A dye experiment showed that the rising bubbles kept the liquid phase well stirred. The cell was immersed in a water bath whose temperature was controlled to $\pm 0.1^\circ\text{C}$.

The chromatographic column was a 1/4-inch by 12-foot length of stainless steel tubing packed with 60-80 mesh glass beads that had been coated with 1.0% w/w of an aqueous solution of 6.0 M silver nitrate. The column was used at room temperature. An electronic integrator was used to measure peak areas.

Analysis of Data

Assume that the concentration of a particular hydrocarbon in the helium leaving the cell is proportional to its concentration in the extract at that moment. One then has the relation $C = C_s/K$, where C is the hydrocarbon concentration in the helium, C_s is its concentration in the water extract, and $1/K$ is the proportionality factor. If there were equilibrium, K would be equal to the partition coefficient. If V is the volume of helium which has been passed through the extract, one can show that the ratio of C to its value, C_0 , at zero helium volume is given by the expression

$$-\log_e(C/C_0) = K^{-1}(V/V_s), \quad (1)$$

where V is the volume of the extract. A plot of \log_e of this ratio or $\log C$ versus V/V_s or V should be linear if K is constant, and the slope will give its value. Having determined K , one can calculate C_s provided C is known. In particular, the initial amount of hydrocarbon in the extract can be determined from C_s and K .

A series of experiments with benzene, for which extensive solubility data are available (3), gave linear log plots and a value of K close to the equilibrium value. This technique should thus provide a convenient means for determining partition coefficients even though more work is necessary to learn how to discover and correct for non-equilibrium effects.

The log plots can be used to identify chromatographic peaks as to hydrocarbon group. For example, saturated hydrocarbons may be identified by the low K values they have in aqueous solution. The concentration of saturated hydrocarbons will diminish to approximately 97% of their original concentration when V is equal to V_s . This very sharp decrease in peak area with helium volume is the same for all saturated hydrocarbons and can be used to identify this group. This also provides a way of quickly eliminating the saturated hydrocarbons from the analysis thereby simplifying the identification of other types of hydrocarbons. The polar hydrocarbons have a much larger value of K and can easily be identified by means of the log plots.

Peaks may also be identified as to hydrocarbon group by the addition of reagents to the extract, thus changing the value of K in equation 1 (4). Mercuric ions complex very strongly with olefins ($K = 10,000$) but not with the aromatics. Addition of mercuric ions lowers the partial pressure of the olefins so much that their peak area is reduced practically to zero. The olefins may thus be identified as those peaks that disappear after the addition of mercuric ions to the extract. The same procedure may be used for the identification of aromatic compounds by the addition of silver ions to the extract. Although the silver-aromatic complex is not as strong as the mercuric-olefin complex the effect is sufficient for identification purposes.

A water extract containing a normal paraffin (decane), an olefin (octene-1), and aromatic (ethylbenzene), and a polar compound (ethylacetate) was used to illustrate the identification of peaks as to hydrocarbon group. The procedure is shown graphically in Fig. 1 as semi-log plots of the peak area versus helium volume for each component in the water extract. The large difference in K values of the saturated hydrocarbons compared to the polar hydrocarbons is illustrated by the difference in slopes of the two compounds. The plots also show the large effects that mercuric and silver ions have on the olefinic and aromatic compounds, respectively. In the olefinic case the peak area went to zero whereas in the aromatic case the peak area was reduced to a much lower value followed by a linear plot with a reduced slope. For this latter case, the lowering of the peak area and the value of the resulting slope depends upon the concentration of the silver ion, the stability constant of the silver-aromatic complex, and the volume of the water extract.

There are solutes whose peaks overlap for the particular chromatographic column being used but which happen to belong to different hydrocarbon groups. The use of the log plots and mercuric and silver ion additions can be very helpful both in recognition of the overlap condition and in the identification of the peak

components. For example, consider the case of a saturated hydrocarbon peak overlapping a peak from any other group. Passage through the cell of a volume of helium equal to that of the extract would so reduce the concentration of the saturated hydrocarbon in the helium stream, that essentially only one peak would remain.

Analysis Time

In order for the analytical scheme presented in this paper to be practical, it is essential that the chromatography be capable of quick analyses. Columns packed with glass beads coated with aqueous silver nitrate were found to be ideal for this work. We achieved a complete separation of meta- from para-xylene in less than two minutes and an almost complete separation of sec-butylbenzene from iso-butylbenzene in six minutes. These two separations have been achieved (5) on a 100,000 plate capillary column in 60 and 120 minutes, respectively.

CONCLUSIONS

The method of analysis presented in this paper is restricted to systems in which the solute molecules are fairly insoluble in the solvent. Water extracts of crude and processed oils are ideal because at equilibrium, from 75 to 98% of the hydrocarbons are in the vapor phase. There is little loss in sensitivity because the vapor is injected directly into the analytical column. The big advantage is the ease with which the analysis can be divided into hydrocarbon groups. For instance, if only the aromatic fraction of the water extract were of interest, the saturated hydrocarbons could be blown out with the helium and the olefins taken out by complexing with mercuric ions, leaving only the aromatics and the polar hydrocarbons. The aromatic "fingerprint" could then be obtained by comparing the chromatograms before and after silver ions were added to the cell. This analysis by groups could be important in toxicity studies or oil identification.

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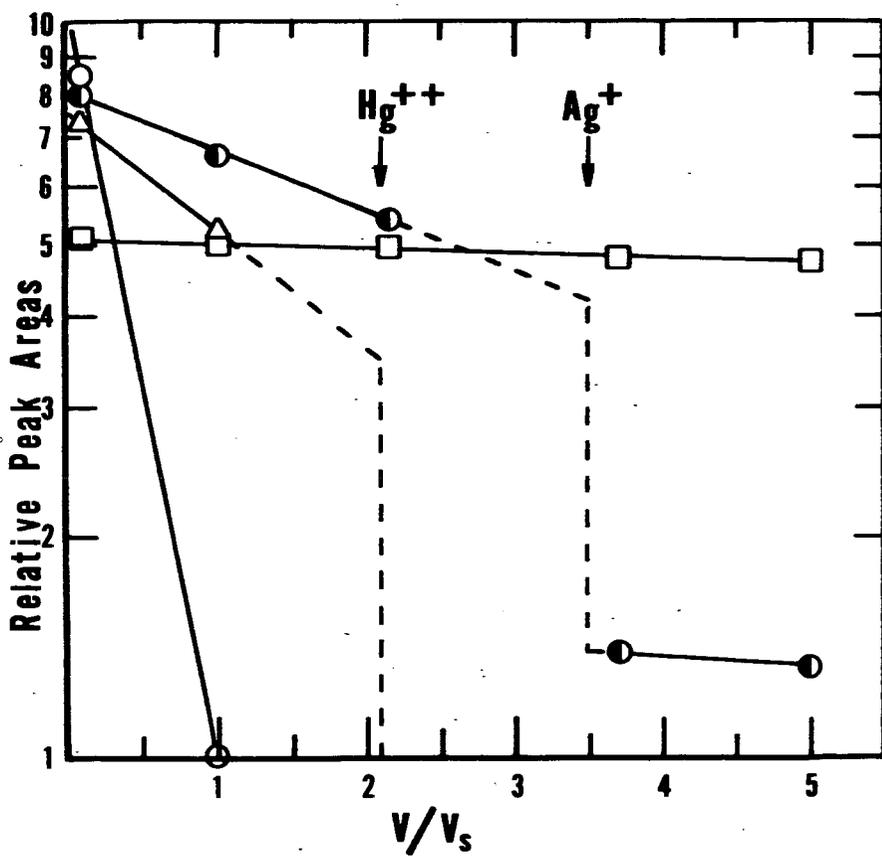


FIGURE CAPTION

Hydrocarbon group-identification scheme. Open circles indicate peak areas for n-decane; half-filled circles, ethylbenzene; triangles; octene-1; and squares, ethylacetate. V is the volume of helium passed through the cell and V_g is the volume of the aqueous extract. The arrows indicate the values of V/V_g at which H_g^{++} and A_g^+ ions were added to the extract.

INTERPRETATION OF GAS CHROMATOGRAPHIC SPECTRA IN
ROUTINE ANALYSIS OF GASOLINE EXHAUST HYDROCARBONS

B. Dimitriades, C. J. Raible, C. A. Wilson, and S. I. Mayo*

Bartlesville Energy Research Center
Bureau of Mines, U. S. Department of the Interior
P. O. Box 1398, Bartlesville, Okla. 74003

INTRODUCTION

In studies of atmospheric pollution from automobile emissions a practical method is required to routinely analyze the emission samples for hydrocarbon components, and that method must be sensitive and capable of discriminating hydrocarbons of different molecular size and different photochemical reactivity.² To meet this need the Bureau is developing a gas chromatographic (GLC) method as a part of its studies of environmental contamination from motor gasoline combustion.

Earlier work resulted in a chromatographic method with adequate sensitivity and acceptably short analysis time^{2/}. Interpretation of the chromatographic spectra was questionable, however, because it was based on a single set of peak-identity assignments obtained from only a few exhaust samples. For more accuracy, spectra interpretation should be based on peak-identity assignments obtained separately for each exhaust sample -- a tedious and time-consuming practice. When numerous exhaust samples must be analyzed daily, a common requirement, a rapid and accurate method of chromatographic spectra interpretation, is needed. The study undertaken to develop such a method and the results of that study are described in this report.

EXPERIMENTAL PROCEDURES

The objective of this study was to explore the use of chromatographic-column retention times for identifying component peaks. With adequate retention time repeatability^{2/}, the success of this peak-identification method depends only on the degree to which the composition of the material represented by each peak is constant. Preliminary evidence suggested that composition within each of most of the peaks on a chromatogram of exhaust emissions is indeed constant, at least among exhaust samples obtained from different engines using the same fuel. Additional data were needed to confirm or refute that evidence.

The ideal experimental procedure would have called for tests to determine peak identities in chromatograms of exhaust samples obtained from a variety of engines and fuels. To simplify the procedure, one engine was operated with varied air-fuel ratios and ignition-timing conditions because, in our opinion, differences in the composition of combustion products from different engines, using the same fuel, result primarily from differences in air-fuel ratio and ignition timing. For verification, data obtained from tests with one fuel and four engines operated at two ambient temperatures were included in this study.

* Present address, Post Office Box 374, Decatur, Miss., 39327; formerly with the Bartlesville Energy Research Center.

A 1968 Valiant, equipped with a 6-cylinder, 225-CID engine, was operated following the 7-mode California cycle on a chassis dynamometer under four sets of engine conditions: Rich, with vacuum spark advance (VSA); rich, without VSA; lean, with VSA; and lean, without VSA. Compositions of the three experimental fuels were as follows:

Fuel No.	Component level, volume %		
	Saturates	Olefins	Aromatics
1	66.0	15.1	18.9
2	60.7	10.2	29.1
3	53.1	1.9	45.0

Four automobiles, a 1968 Delta 88 (455 CID), a 1968 Fury I (318 CID), a 1968 Impala (307 CID), and a 1968 Galaxie (302 CID), were operated identically as described for the Valiant automobile. All four cars were operated with the fuel No. 4, at ambient temperatures of 70° and 95° F. The composition of fuel No. 4 was: Saturates, 41.8%; olefins, 12.4%; aromatics, 45.8%.

All fuel and exhaust samples were collected and analyzed by the routine methods of this laboratory^{2/}. Peaks in the resultant chromatographic spectra were identified by a subtractive column technique^{3/}, and from retention time and component stability data. Subtractive agents used were mercuric sulfate, sensitive to unsaturated aliphatics, and palladium sulfate, sensitive to aromatics. Exhaust was analyzed chromatographically before and after passing through the subtractive columns. Thus, each peak in the chromatogram from the untreated exhaust was identified as a hydrocarbon type (paraffin, aliphatic unsaturate, aromatic) or, if a mixture of hydrocarbons, the composition of that mixture was described. Also, exhaust samples were allowed to stand in the dark and under solar irradiation, and component losses were measured. From these component-loss data, peaks representing components that are thermally and photochemically reactive were identified.

Because the identification of peaks was based mainly on the subtractive column data and because the performance of the subtractive agents was questionable, synthetic mixtures of paraffins, olefins, and aromatics of varying structure and molecular size were prepared and used to evaluate the performance of the subtractive columns.

RESULTS AND DISCUSSION

Results from measurements of efficiency of the subtractive columns showed two anomalies in the function of the mercuric sulfate column. First, contrary to expectations, certain olefins were not removed quantitatively by the column. Second, new peaks appeared in the chromatograms of column-treated samples. Further investigation of these new peaks by mass spectrometry revealed that they represented 3-methyl-2-butanone and 3-methyl-2-pentanone, formed from reaction of the subtractive agent with 2-methyl-2-butene and 3-methyl-trans-2-pentene, respectively. Mercury sulfate, therefore, is inadequate as a subtractive agent for certain hydrocarbons, but current data do not permit linking this inadequacy to a specific class or classes of exhaust components. The problem was considered in subsequent work in peak identification, and data were analyzed carefully to obtain peak identities least affected by the deficiencies of the subtractive column.

Results from the peak-identification study generally verified the earlier observation that composition of material represented by each peak in exhaust chromatograms is nearly constant among all the chromatograms of exhaust from different engines but the same fuel. Results were as follows:

In the tests with three fuels and one engine operated under varied conditions, each exhaust chromatogram contained about 165 peaks of which 135 to 145 represented either individual components or mixtures of components of similar type. The remain 20 to 30 peaks represented mixtures of different type components, such as paraffins with olefins or with aromatics. When the chromatographed exhaust samples originate from different fuels, the composition of the material represented by each peak varies significantly from chromatogram to chromatogram. When the exhaust samples were obtained under varied engine conditions but with the same fuel, variation in within peak composition was much smaller and comparable to the variation caused by experimental error. The magnitude of this variation in within-peak composition is best evaluated from its effect upon the chromatographic analysis, as illustrated next.

In emission studies, chromatographic analyses are commonly used to compute the reactivity or pollution potential of exhaust hydrocarbon emissions. This computation follows Jackson's equation^{4/}

$$R = \sum X_i r_i$$

where R designates reactivity of the exhaust hydrocarbon mixture, and X_i and r_i are mole fractions and specific reactivities, respectively, of i th component. By use of mole fraction values for a typical exhaust and published values for specific rate-of- NO_2 -formation reactivities^{4/}, the variation in within-peak composition observed in these tests was calculated to cause maximum variation in exhaust reactivity value equivalent to $\pm 2.3\%$, $\pm 1.8\%$, and $\pm 1.7\%$ for fuels 1, 2, and 3, respectively.

Similar results were obtained from the tests using four engines and fuel No. 4. Variation in within-peak composition among the exhaust chromatograms was equivalent to a $\pm 2.0\%$ variation in exhaust reactivity value.

Part of any observed variation in within-peak composition is caused by experimental error. Thus, for any two chromatograms from replicate tests, the range of within-peak compositions was as much as about one-half of that observed among chromatograms from all tests. Therefore, true variation in within-peak composition should affect calculated reactivity values by no more than about $\pm 1\%$, which is considered unimportant.

These results indicate that in chromatograms of exhaust from different engines but the same fuel, each peak represents nearly the same component or component mixture. This simplifies spectra interpretation because exhaust peaks must be identified only once for each parent fuel. These peak identities, consequently, can be used to interpret chromatographic spectra of all exhaust samples from that fuel. This method of interpreting chromatographic spectra is now used routinely by the Bureau of Mines^{2/}.

ACKNOWLEDGMENT

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CLASS COMPOSITION OF LIQUID FUELS
BY LIQUID CHROMATOGRAPHY

W. A. Dark

Waters Associates Inc., Framingham, Massachusetts

Liquid fuels are complex mixtures of hydrocarbons, obtained from the distillation of petroleum products.

A simple, rapid estimation of combustion character of a fuel can be made if the amount of aliphatic, aromatic, and di aromatic hydrocarbons can be determined.

Most saturated aliphatics in the heptane-decane range have heats of combustion of 1200-1300 k cal/mole and require about 45 cubic feet of air per cubic foot of organic vapor for complete combustion. The unsaturated aliphatics have heats of combustion about 10% less than the corresponding saturate member and require about 40 cubic feet of air per cubic foot of organic vapor for complete combustion. Mono aromatic compounds have heats of combustion of 750 k cal/mole and require about 35 cubic feet of air per cubic foot of organic vapor for complete combustion. The naphthanic compounds have heats of combustion of 1500 k cal/mole and require some 60 cubic feet of air per cubic foot of organic vapor for complete combustion. Bi phenyl compounds have heats of combustion of 1800-1900 k cal/mole and require some 75 feet of air per cubic foot of organic vapor for complete combustion.

Thus, if the amount of saturated aliphatic, aromatic, and di aromatic hydrocarbons are known, estimation of the heat of combustion and air requirements of a fuel can be made. It must be remembered, however, that in most combustion processes the amount of air is fixed because of draft. Knowing the availability of air for the combustion, and that required by the fuel, allow estimates to be made as to whether the combustion will be complete or not.

The information on the class composition of a liquid fuel can be obtained in less than 12 minutes using Waters' technology.

SCOPE

This method describes a procedure for the determination of the aliphatic, aromatic, naphthanic, and bi phenyl compounds in petroleum fractions that distill below 600°F. Samples should be depentanized if they contain any of the following -- C₃ or lighter hydrocarbons; more than 5% C₄ hydrocarbons; more than 10% C₄ and C₅ hydrocarbons.

OUTLINE OF METHOD

The sample, 2λ , is introduced by means of a microliter syringe into a high pressure, high speed liquid chromatograph.

The hydrocarbons are retained according to their sorption affinities into aliphatic, aromatic, naphthanic, and bi phenyl compounds.

The detector is a low volume differential refractometer that displays the mass of material eluting from the end of the column. The response of the detector is dependent upon the index of refraction difference between the solute and the solvent.

With this method a semi skilled technician can perform a separation in twelve minutes.

The recorder gives a permanent display of the separation. No additions have to be made to the sample and colored or fluorescing compounds will not interfere.

The separation can be done in the laboratory without any special precautions.

Once equilibrium has been established during initial start up, the equipment is ready for use at any time.

APPARATUS

The separation has been achieved on a Waters' ALC model 201 under the following conditions:

Column: PORASIL T - 4 ft. x 2.3 mm I.D.

Solvent: n-heptane - J. T. Baker - Baker Grade M 955
boiling range 98-99°C

Flow rate: 1.0 ml/min.

Pressure drop: 550 psig

Attenuator setting: 8X

Sample volume: 2.0λ

Chart speed: 12 in/hr

Septum material: Buna-N

Retention volumes:	saturated aliphatic	}	4.92 mls
	unsaturated aliphatic		
	cyclo aliphatic		
	aromatics		6.59 mls
	naphthanic		8.17 mls
	bi phenyls		9.15 mls

APPLICATIONS

Chromatograms are attached displaying the separation of a standard mixture and four different liquid fuels. The standard is a mixture of n-octane, benzene, 2-methyl naphthalene and p-methyl biphenyl. The samples are a jet fuel, #2 fuel oil, two #6 fuel oil, and bunker C fuel.

Note the difference of composition between the two #6 fuel oils from the different refineries.

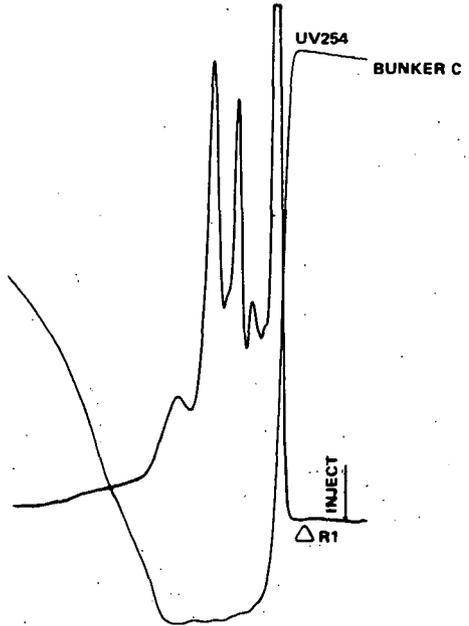
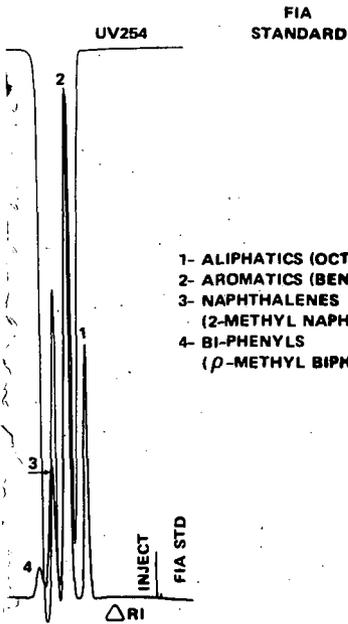
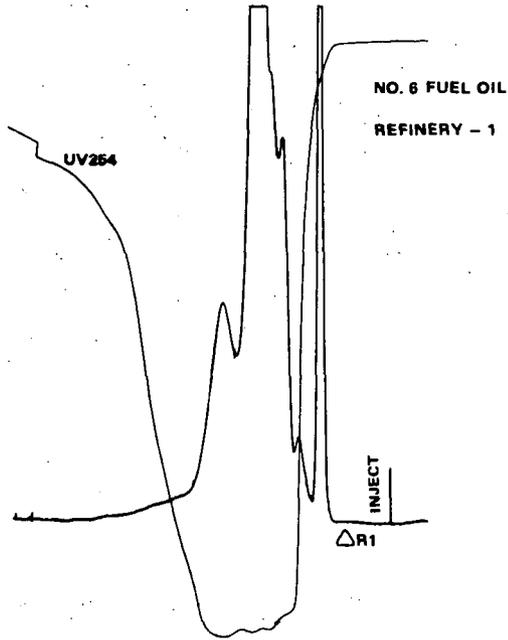
The chromatographic evidence confirms what is known about these fuels, as you go from the jet fuel through #2-#6 fuel oil to the bunker C the amount of condensed aromatics increase.

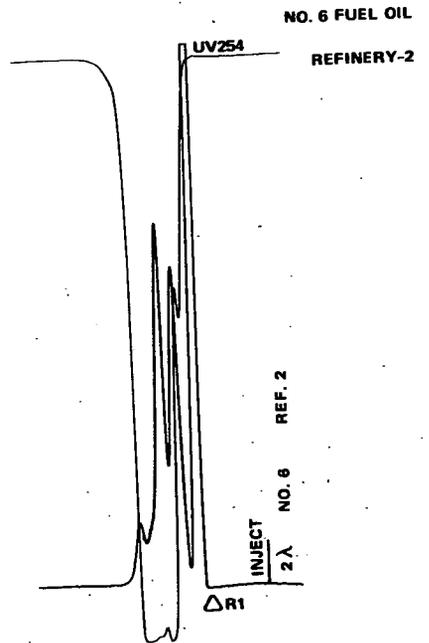
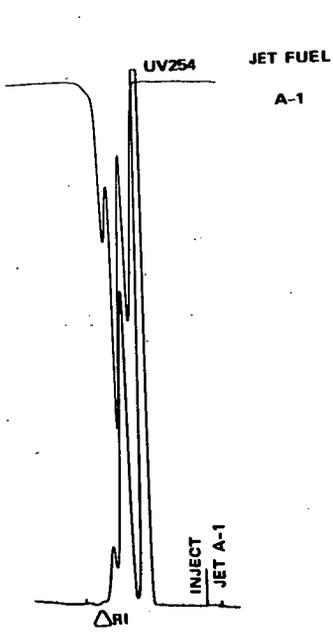
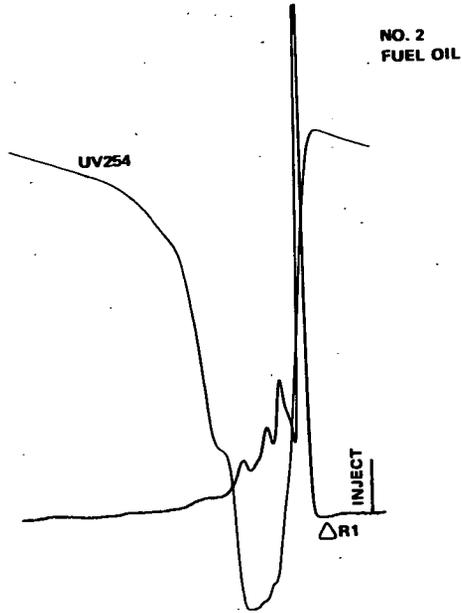
Thus, by determining composition of a fuel and knowing the air required for complete combustion, the draft requirement of a combustion process could be adjusted.

Reproducibility of the method, as determined from ten runs of the #2 fuel oil, is -

aliphatics	±0.80%
aromatics	±1.40%
naphthalenic	±1.18%
bi phenyl	±1.80%

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FLUORESCENCE SPECTROSCOPY IN THE CHARACTERIZATION OF HIGH-BOILING PETROLEUM DISTILLATES

J. F. McKay and D. R. Latham

Laramie Energy Research Center, Bureau of Mines, U.S. Dept. of the Interior, Laramie, Wyo.

INTRODUCTION

Although many workers have attempted to use fluorescence spectroscopy in the characterization of crude oils (1-5), the technique has found limited application in the characterization of crude oil fractions. This is a result of several factors. First, separation schemes have not been developed for obtaining simplified petroleum fractions that are suitable for fluorescence analysis. Second, commercial instrumentation that enables many spectra to be recorded in a small amount of time has not been available. Third, the lack of success in characterization of total crude oils has probably dampened the enthusiasm of some workers as to the potential of the fluorescence technique. Drushel and Sommers (6) successfully employed a combination of GLC and fluorescence and phosphorescence spectroscopy to identify pyridines, quinolines, indoles, and carbazoles in a light catalytic cycle oil. Their work showed that fluorescence and phosphorescence, when used under proper experimental conditions, can supplement other spectroscopic methods in the characterization of petroleum distillates. The separation scheme used here, like that of Drushel and Sommers, separates distillates into fractions that are simple enough to be analyzed by fluorescence spectroscopy. The separation scheme was designed to isolate concentrates of compound types, not individual compounds.

This paper demonstrates that fluorescence spectroscopy is an analytical technique which can be useful in the characterization of high-boiling distillates. Acid concentrates isolated from a Wilmington, Calif., 400-500°C distillate and a Wesson, Tex., 400-500°C distillate were examined. Carbazoles, 11H-benzo[a]carbazoles, 1,2,7,8-dibenzphenanthrenes (picenes), 7H-benzo[c]carbazoles, chrysenes, benzo[a]pyrenes, and perylenes were identified in the acid contents by fluorescence spectroscopy. Examination of other 400-500°C concentrates resulted in the identification of coronenes, benzo[ghi]perylens, and benz[a]anthracenes.

EXPERIMENTAL

Apparatus

Anion Exchange Chromatography. - The preparation of ion exchange resins used for obtaining acid concentrates from high-boiling petroleum distillates has been described (7).

Gel Permeation Chromatography. - The details of the gel permeation chromatographic separation of a Wilmington, Calif., 400-500°C acid concentrate have been published (8). A water-jacketed glass column, 1.3 cm i.d. by 150 cm, packed with 80 g of cross-linked styrene gel was used with methylene chloride as solvent.

Thin-Layer Chromatography. - Thin-layer chromatographic plates 20 cm by 20 cm were prepared using a slurry of silica gel G and water. The layers were approximately 250 microns thick. The plates were conditioned at 100°C for several hours and were developed using cyclohexane 85%, diethyl ether 12%, and glacial acetic acid 3%. Visualization was effected by means of long (350 nm) and short (254 nm) wavelength ultraviolet light.

Infrared Spectroscopy. - Infrared analyses were performed using a Perkin-Elmer Model 521* infrared spectrometer. Methylene chloride was used as the solvent for all infrared analyses.

*Reference to specific brand names or models of equipment is made for information only and does not imply endorsement by the Bureau of Mines.

Fluorescence Spectroscopy. - A Perkin-Elmer MPF-2A spectrofluorimeter was used for recording all fluorescence emission and excitation spectra. Continuously variable slits enabled spectra to be rapidly obtained. Fluorescence-free cells having a 1 cm path were used in this work.

Materials

Model Compounds. - The model compounds were obtained commercially. Approximately half of the compounds were found by fluorescence analysis to be contaminated with impurities that fluoresced. The desired model compounds were separated from the impurities using thin-layer chromatography on silica gel G or aluminum oxide G.

Solvents. - The methylene chloride used for the gel permeation chromatographic separation and subsequent infrared analysis was Baker and Adamson Co. reagent grade which had been flash distilled. Fluorescence analysis of this material did not detect aromatic hydrocarbons or other fluorescing impurities.

The cyclohexane used for thin-layer chromatography and fluorescence analyses was Phillips Petroleum Co. research grade which had been passed over silica gel. Fluorescence analysis of this material did not detect aromatic hydrocarbons or other fluorescing impurities.

Fluorescence Emission and Fluorescence Excitation Spectra of Model Compounds

Cyclohexane was used as the solvent for obtaining all spectra. Fluorescence emission and fluorescence excitation spectra of model compounds were recorded at room temperature in very dilute solutions (10^{-3} to 10^{-5} molar). Typical spectra were recorded at one concentration, the sample diluted tenfold, and the spectra again recorded. This process was repeated until the relative intensities of the bands within each spectrum remained constant. In only a few cases did the band intensities change when the spectra were recorded in extremely dilute solutions. Using this procedure, spectra distorted by concentration phenomena, such as excimer formation, were avoided.

Each sample was irradiated at several different wavelengths to reduce the possibility that impurities were contributing to the emission spectrum of the model compound. Similarly, excitation spectra were recorded with the emission monochromator set at different wavelengths to reduce the possibility that impurities were contributing to the excitation spectra of the model compound.

Separation Procedure

A diagram of the separation procedure is shown in Figure 1. Samples of a Wilmington, Calif., crude oil and a Wason, Tex., crude oil were vacuum distilled (7), and the nominal 400-500°C distillates were collected. The distillates were passed over an anion exchange resin, and the materials which were retained on the resin were defined as the acid concentrates (7). The acid concentrates (100-200 mg) were separated by gel permeation chromatography (8). The gel permeation chromatographic fractions were analyzed by infrared spectroscopy to determine the separation obtained by the GPC treatment. The GPC fractions that contained predominantly phenols and nitrogen compounds, fractions 35 through 47, were further separated by thin-layer chromatography. The individual TLC fractions were removed from the plate, and the samples were extracted from the silica gel with cyclohexane. Traces of silica gel were filtered from the cyclohexane solution. The fluorescence emission and fluorescence excitation spectra were then recorded. Blank extraction runs were periodically made on the silica gel (using TLC plates which had been developed) to demonstrate that fluorescent impurities were not being extracted from the silica gel. In addition, a solvent blank was analyzed by fluorescence spectroscopy before the emission spectrum of each TLC fraction was recorded to show that traces of fluorescing compounds were not present in the solvent or in the sample cell.

RESULTS AND DISCUSSION

Fluorescence Emission and Fluorescence Excitation Spectra of Model Compounds

Identification by fluorescence spectroscopy of aromatic ring systems present in complex mixtures such as petroleum distillates requires a comparison of the oil sample spectra with those of model ring systems. Fluorescence emission spectra and tables of spectra of many heterocyclic and polyaromatic compounds have appeared in the literature (9-15); but these spectra were recorded in a variety of solvents, at different temperatures, making them difficult to use in our study. These problems have been overcome by obtaining samples of heterocyclic and polyaromatic compounds and recording the emission and excitation spectra using a uniform solvent, temperature, and recording procedure. Peak maxima of both fluorescence emission and fluorescence excitation spectra of heterocyclic and polyaromatic compounds which may be used to identify aromatic ring systems are presented in Table 1. The most intense peak in each spectrum is underlined, and the compounds are listed according to the wavelength of the most intense fluorescent band. These spectra have not been corrected for variances of spectral source and phototube response with wavelength.

Application of Fluorescence Spectroscopy to the Characterization of a Wilmington 400-500°C Acid Concentrate

Figure 2 shows the TLC chromatogram of the Wilmington gel permeation chromatographic fractions. Examination of Figure 2 shows that the silica gel G thin-layer treatment did not completely separate some aromatic ring systems. Because of this incomplete separation, ultraviolet analyses were of limited value in the characterization of these fractions. Fluorescence analysis, however, was useful in characterizing these fractions because emission spectra and excitation spectra of each component ring system could be instrumentally isolated and recorded. Each sample was irradiated at several different wavelengths to obtain an optimum emission spectrum. Similarly, excitation spectra were obtained by recording the excitation spectra with the emission monochromator set at several different wavelengths.

11H-Benzo[a]carbazoles were identified in GPC fractions 35 through 43. Figure 3 shows the fluorescence emission and fluorescence excitation spectra of 11H-benzo[a]carbazoles found in the Wilmington 400-500°C acid concentrate together with the corresponding spectra of the model compound 11H-benzo[a]carbazole. Visual examination of the thin-layer chromatographic plate indicated that 11H-benzo[a]carbazoles represented a large percentage of the material found in these fractions. Snyder and Buell (16) have previously identified and made quantitative estimates of 11H-benzo[a]carbazoles and 7H-benzo[a]carbazoles in cracked gas oils using ultraviolet spectroscopy. In the work described here a quantitative estimation of the benzcarbazoles in the acid concentrate is precluded by the use of thin-layer chromatography as well as by problems inherent in the fluorescence method.

The appearance of the 11H-benzo[a]carbazole aromatic ring system in a rather large number of GPC fractions is presumably due to the presence of a homologous series. Mass spectral analysis of a GPC fraction from a Wason 400-500°C acid concentrate containing 11H-benzo[a]carbazoles indicated that a homologous series was indeed present.

Although a complex mixture of alkyl-substituted 11H-benzo[a]carbazoles appears to be present in a single TLC fraction, the fine structure of the fluorescent emission spectrum of the mixture is the same as that of the parent model compound, within the detection limits of the spectrometer. This behavior was expected, based on the work of Monkman and Porro (12) concerning the effects of methyl substitution on the fluorescence of benz[a]anthracenes and of Schoental and Scott (11) concerning the effects of methyl substitution on the fluorescence of naphtho(2':1':2)-fluorene. The effects of methyl substitution on these systems were not large. Our data suggest that alkyl substitution or multiple alkyl substitution does not significantly alter the vibrational

Table 1. - Fluorescence excitation and fluorescence emission spectra of model compounds*

Compound	Fluorescence excitation spectra		Fluorescence emission spectra	
	Wavelength, nm		Wavelength, nm	
Fluorene	<u>268</u>	<u>275(s)</u>	<u>293</u>	<u>303</u>
Naphthalene	<u>269</u>	<u>278</u>	<u>288</u>	<u>324</u>
9-Methylcarbazole	<u>249</u>	<u>293</u>	<u>322</u>	<u>334</u>
(N-Methylcarbazole)				<u>349</u>
Carbazole	<u>249</u>	<u>293</u>	<u>320</u>	<u>335</u>
2-Methylcarbazole	<u>250</u>	<u>297</u>	<u>319</u>	<u>335</u>
3-Methylcarbazole	<u>252</u>	<u>296</u>	<u>325</u>	<u>350</u>
11H-Benzo[b]fluorene	<u>270</u>	<u>288</u>	<u>319</u>	<u>342</u>
(2,3-Benzofluorene)			<u>326</u>	<u>342</u>
11H-Benzo[a]fluorene	<u>255</u>	<u>265</u>	<u>296</u>	<u>347</u>
(1,2-Benzofluorene)			<u>306</u>	<u>365</u>
Triphenylene	<u>262</u>	<u>277</u>	<u>288</u>	<u>354</u>
11H-Benzo[a]carbazole	<u>255</u>	<u>279</u>	<u>306</u>	<u>364</u>
(1,2-Benzocarbazole)				<u>373</u>
7H-Benzo[c]carbazole	<u>263</u>	<u>286</u>	<u>324</u>	<u>381</u>
(3,4-Benzocarbazole)				<u>381</u>
Chrysene	<u>261</u>	<u>271</u>	<u>297</u>	<u>363</u>
			<u>308</u>	<u>375</u>
Phenanthrene	<u>261</u>	<u>278</u>	<u>285</u>	<u>383</u>
			<u>296</u>	<u>404</u>
7H-Dibenzo[c,g]carbazole	<u>278</u>	<u>303</u>	<u>350</u>	<u>348</u>
(3,4,5,6-Dibenzocarbazole)			<u>363</u>	<u>357</u>
Dibenz[a,c]anthracene	<u>269(s)</u>	<u>279</u>	<u>289</u>	<u>367</u>
(1,2,3,4-Dibenzanthracene)				<u>386</u>
Picene	<u>287</u>	<u>304</u>	<u>328</u>	<u>377</u>
(1,2,7,8-Dibenzphenanthrene)				<u>388</u>
				<u>398</u>
				<u>421</u>
				<u>449</u>

Table 1. - cont'd

Compound	Fluorescence excitation spectra		Fluorescence emission spectra	
	Wavelength, nm		Wavelength, nm	
Anthracene	260 312 325 341 358 377		380 401 424 451	
Pyrene	308 322 337		374 379 384 389 395	
Benz[a]anthracene (1,2-Benzanthracene)	255 271 280 290 317 329 344 360		387 408 435 462	
1,3H-Dibenz[<i>a</i> , <i>i</i>]carbazole (1,2,7,8-Dibenzocarbazole)	297 324 338 355 373 394		394 405 417 428 443	
Benz[<i>b</i>]chrysene (2,3,7,8-Dibenzphenanthrene)	255 289 305		394 418 444 470(s)	
Benz[<i>k</i>]fluoranthene (1,2,7,8-Dibenz[<i>g</i> , <i>p</i>]chrysene)	280 292 303 340 353		395 409	
Benz[<i>ghi</i>]perylene (1,2,3,6,7,8-Dibenzchrysene)	301 324 335 351		396 407 418 446 473	
Dibenzo[<i>def</i> , <i>p</i>]chrysene (1,2,3,4-Dibenzopyrene)	292 297 319 334 373 394		396 407 418 445	
Naphtho[1,2,3,4- <i>def</i>]chrysene (1,2,4,5-Dibenzopyrene)	276 293 305 330 342 358 376		397 408 420 446	
Benz[<i>e</i>]acephenanthrylene (3,4-Benzofluoranthene)	255 299 310		403 413 429 459 489(s)	
Benzo[<i>a</i>]pyrene (1,2-Benzopyrene)	256 269 286 300 333 349 365 385		405 410 429 457	
Dibenzo[<i>c</i> , <i>g</i>]phenanthrene (3,4,5,6-Dibenzophenanthrene)	239 272 312 332		405 424 446(s)	
Benzo[<i>ghi</i>]perylene (1,12-Benzopyerylene)	291 302 331 348 364 385		399 408 420 446	

Table 1. - cont'd

Compound	Fluorescence excitation spectra		Fluorescence emission spectra	
	Wavelength, nm		Wavelength, nm	
Dibenzo[def,mno]chrysene (Anthanthrene)	260	<u>296</u> 308 <u>384</u> 401 407 422 430	<u>432</u>	<u>459</u> 494
Benzo[nt]pentaphene (3,4,9,10-Dibenzopyrene)	247	274 285 <u>297</u> 316 332 355 373 395	<u>434</u> 450	<u>462</u> 480 494
Perylene	<u>255</u> 370 388 410 438		<u>440</u> 466 500 540(s)	
Coronene	<u>292</u> 303 <u>324</u> 340		411 <u>422</u> 428 <u>435</u> <u>446</u> <u>455</u> <u>475</u> <u>485</u> 508	
Dibenzo[<u>b</u> ,def]chrysene (3,4,8,9-Dibenzopyrene)	<u>272</u> 300 <u>312</u> 399 422 448		<u>451</u> 480 518	
Fluoranthene	241 256 266 280 <u>290</u> 311 <u>326</u> 344 360		409(s) <u>418</u> (s) <u>436</u> <u>463</u>	
Ovalene	314 <u>328</u> 342 <u>399</u> 422 448		450 <u>462</u> 475 <u>482</u> 490 <u>503</u> <u>509</u> <u>514</u> 539	

*The most intense peak in each spectrum is underlined. Shoulders are indicated by (s).

energy levels of the ground and excited states. Spectra of substituted ring systems in the oil are superimposable on those of the unsubstituted model compounds. This negligible effect of alkyl substitution is important because it allows mixtures of compounds having the same aromatic nucleus—compound types—to be identified by fluorescence spectroscopy.

Substitution effects would be predicted to be smaller for large polyaromatic molecules than for small molecules. Thus, as higher boiling distillates are studied, the fluorescence fine structure of the aromatic systems should not be affected by substitution, enhancing the use of fluorescence spectroscopy in the characterization of these materials.

Chrysenes and carbazoles were observed in the Wilmington acid concentrate GPC fractions 39 through 41. The emission and excitation spectra of a TLC spot from GPC fraction 41 together with corresponding model compound spectra are shown in Figure 4. These two compound types appear to represent a relatively small percentage of the material being examined. The distribution of these ring systems in only a few GPC fractions suggests that these compound types are not as extensively substituted as the 11H-benzo[a]carbazoles.

7H-Benzo[a]carbazoles, benzo[a]pyrenes, and perylenes were observed in Wilmington acid concentrate GPC fractions 43 through 45. The emission and excitation spectra of 7H-benzo[c]-carbazoles and perylenes obtained from GPC fractions 43-45 together with the corresponding model compound spectra are shown in Figure 5. 7H-Benzo[c]carbazoles and perylenes appeared to be more predominant in these GPC fractions than benzo[a]pyrenes, yet neither of these ring systems represented a large percentage of the total material being investigated. Perylene has been identified by ultraviolet absorption spectroscopy in high-boiling distillates by Carruthers and Cook (17) and also in marine sediments off southern California by Orr and Grady (18). Again, the GPC distribution of these compound types suggests that the polyaromatic ring systems are not extensively substituted.

The presence of aromatic ring systems such as chrysene and benzo[a]pyrene in the acid concentrates has not been explained. Fluorescence analysis permitted the identification of the aromatic ring systems present in the acid concentrates but yielded no information concerning substitution with OH or NH functional groups or whether small amounts of hydrocarbons have been retained in the acid concentrates by entrainment or by some bonding mechanism, such as hydrogen bonding.

Application of Fluorescence Spectroscopy to the Characterization of a Wason 400-500° Acid Concentrate

A survey of the fluorescing aromatic compound types in a Wason 400-500°C acid concentrate indicated that compound types similar to those found in the Wilmington oil were present in the Wason oil. 11H-Benzo[a]carbazoles, carbazoles, and 7H-benzo[c]carbazoles were identified in various TLC fractions as shown in Figure 6. These compound types were eluted from the GPC column in GPC fractions similar to those of the corresponding compound types of the Wilmington 400-500°C acid concentrate. Chrysenes, perylenes, and benzo[a]pyrenes were not found in the Wason acid concentrate; however, 1,2,7,8-dibenzphenanthrenes (picenes) were identified in the Wason acid concentrate.

Application of Fluorescence Spectroscopy to the Characterization of Other 400-500°C Concentrates

Figure 7 shows the fluorescence emission and fluorescence excitation spectra of ring systems which have been identified in other 400-500°C concentrates. The emission and excitation spectra of compound types isolated from these concentrates are shown here to demonstrate the general applicability of the fluorescence method for the characterization of high-boiling distillates.

CONCLUSIONS

Fluorescence spectroscopy is a powerful analytical technique for characterizing high-boiling petroleum fractions, when used under proper experimental conditions. Data which are useful for identification of compound types can only be obtained from relatively simple fractions, not from complex mixtures. Ion exchange chromatography and gel permeation chromatography together with thin-layer chromatography appear to be satisfactory methods for obtaining oil samples which are suitable for fluorescence analysis. In addition, spectra should be recorded using very dilute solutions in order to avoid problems such as concentration quenching and excimer formation.

For qualitative applications, such as the identification of compound types in high-boiling distillates, the fluorescence technique has proven useful for the following reasons: (1) Emission and excitation spectra of an individual ring system may often be instrumentally resolved even though the sample contains a mixture of aromatic ring systems. (2) The two spectra which are obtained aid in the identification of the sample. An emission spectrum alone may not permit the unambiguous identification of a ring system. When this occurs, the excitation spectrum may be used to identify the sample. (3) Due to the high sensitivity of the instrumentation, very small samples, micrograms or nanograms, may be used.

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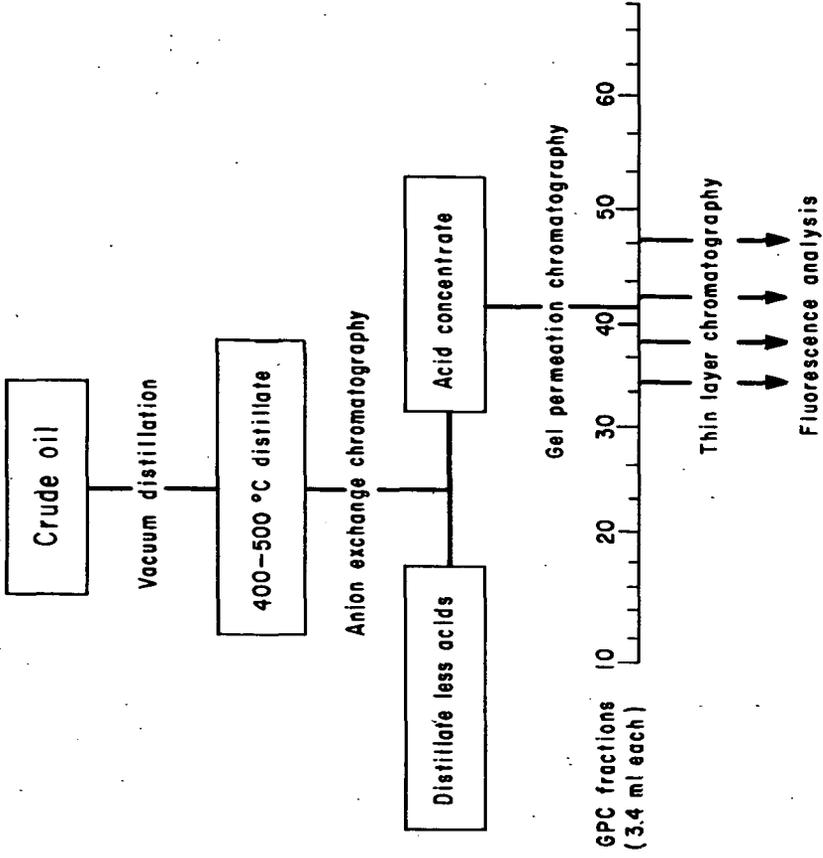
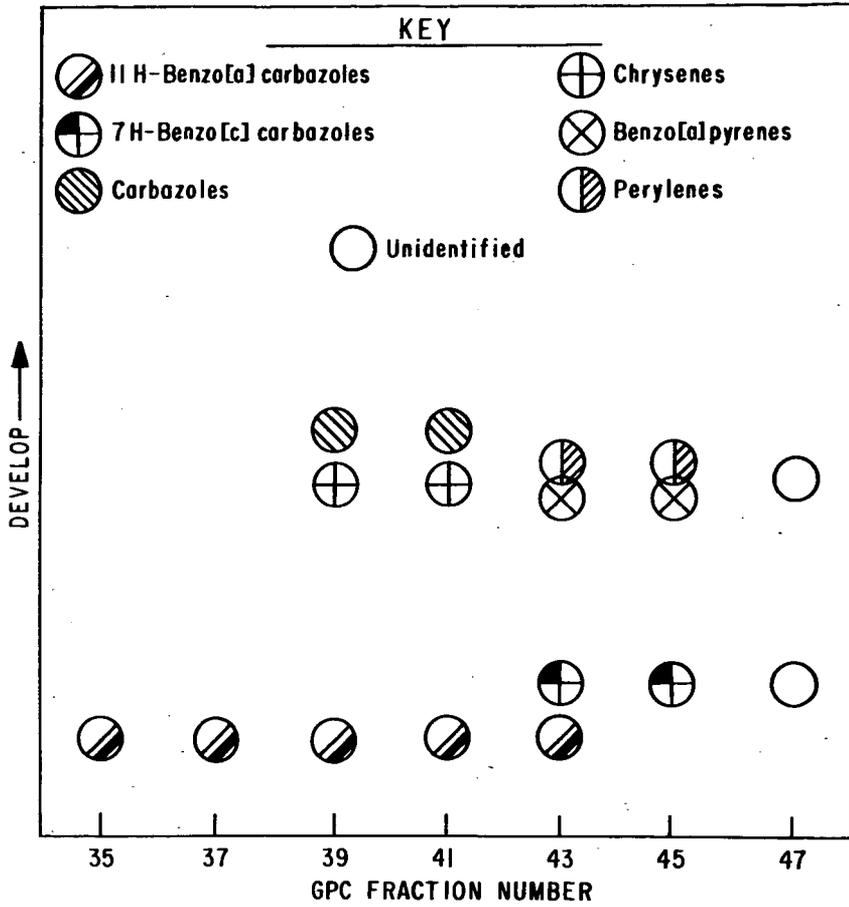


FIGURE 1.-Separation Scheme.



**FIGURE 2.-Thin-Layer Chromatogram of Wilmington Acid
GPC Fractions.**

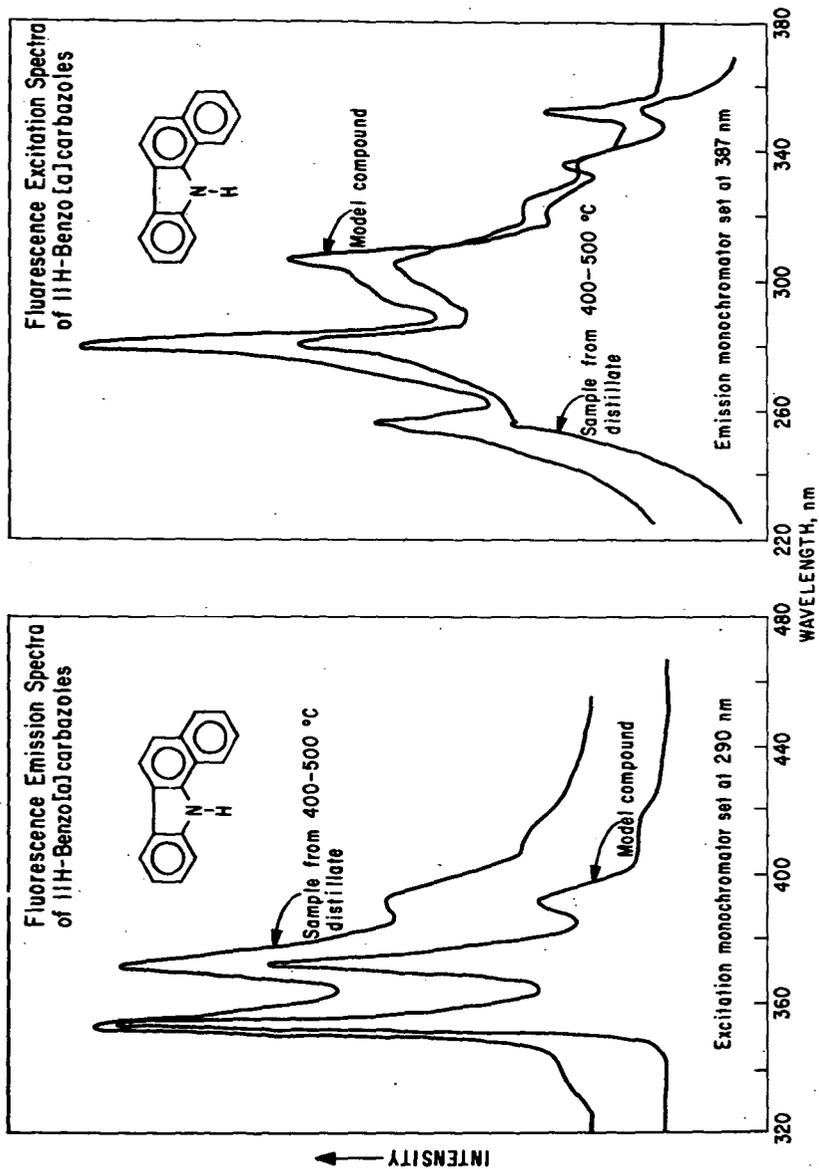


FIGURE 3.- Fluorescence Emission and Excitation Spectra.

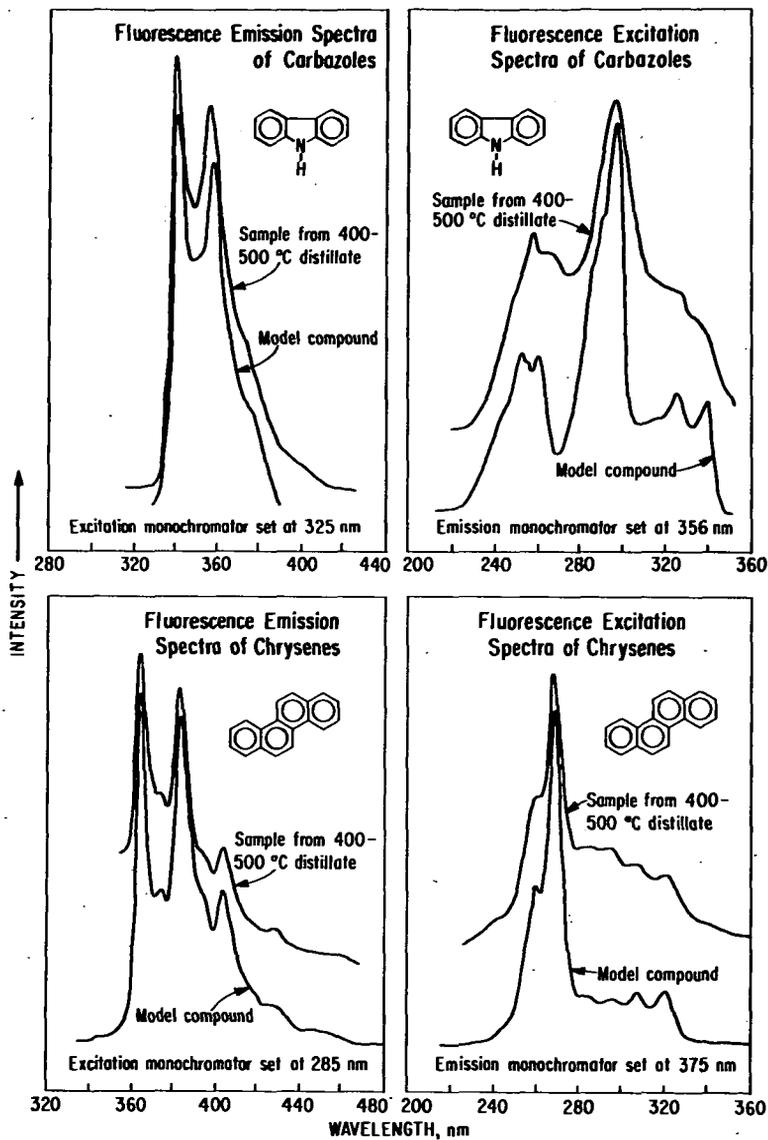


FIGURE 4-Fluorescence Emission and Excitation Spectra.

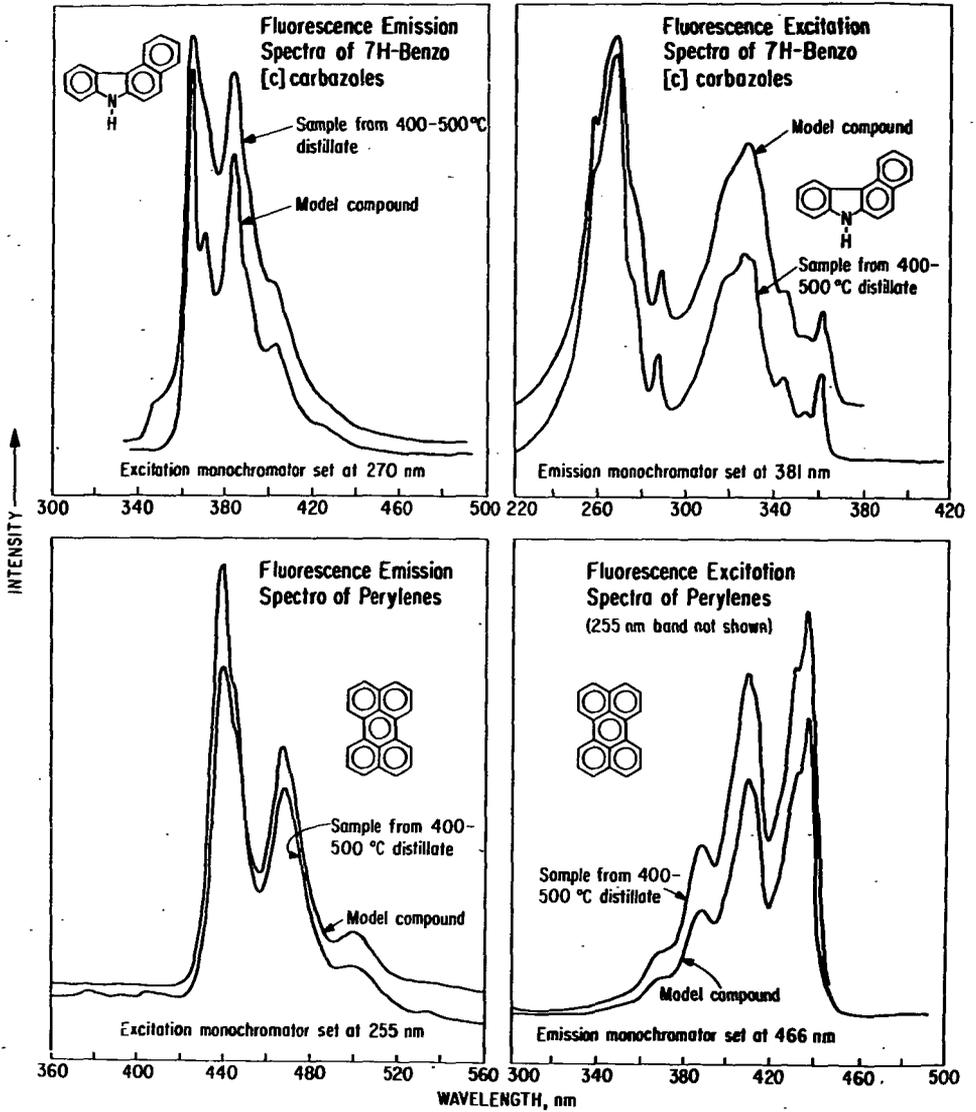


FIGURE 5-Fluorescence Emission and Excitation Spectra.

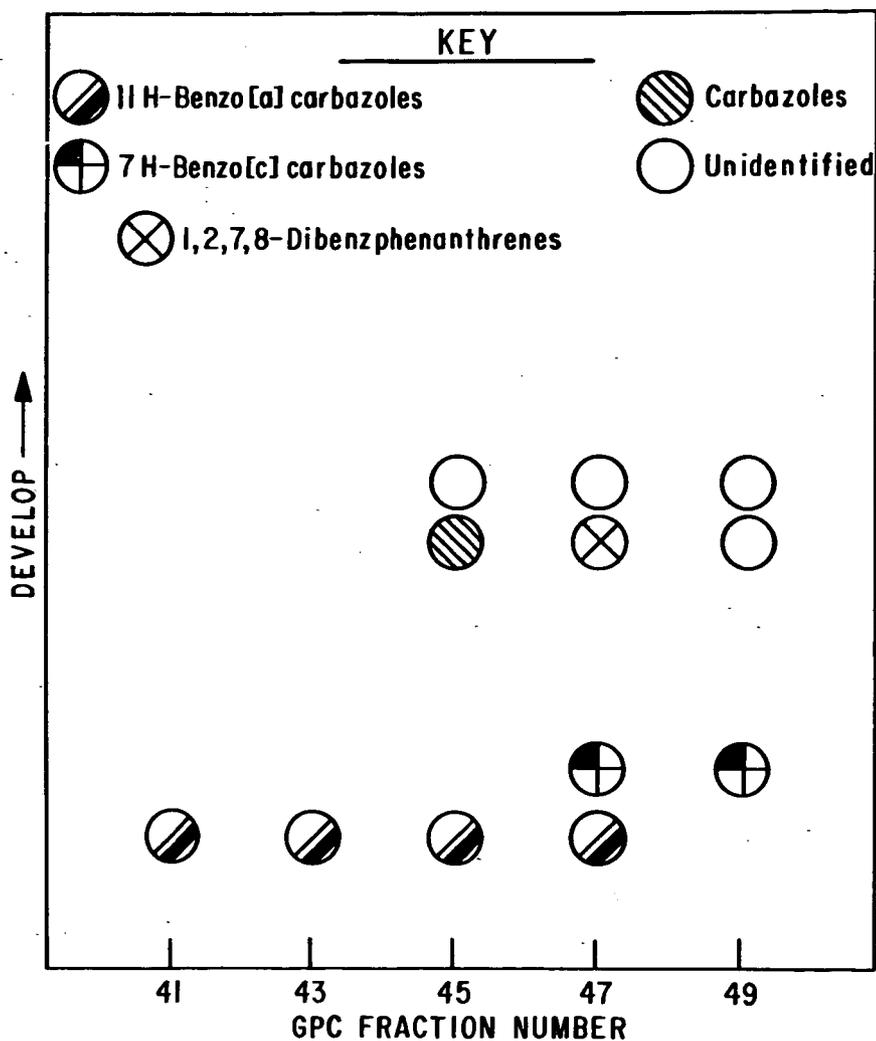


FIGURE 6.-Thin-Layer Chromatogram of Wasson Acid GPC FRACTIONS.

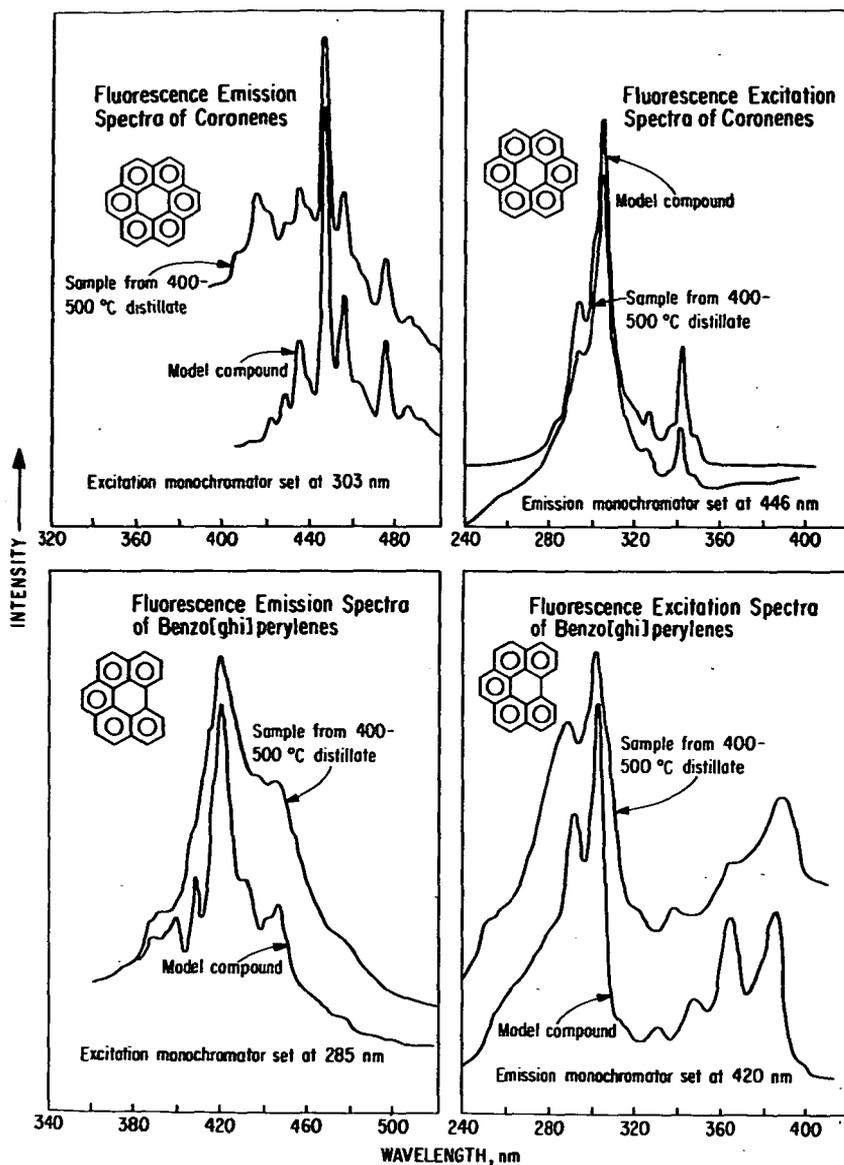


FIGURE 7-Fluorescence Emission and Excitation Spectra.

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Dr. Harold L. Lovell
Secretary-Treasurer
ACS Division of Fuel Chemistry
Pennsylvania State University
109 Mineral Industries Building
University Park, Pennsylvania 16802
Telephone: Area 814 - 865-2372

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