A NOVEL AND FAST TECHNIQUE FOR THE DIFFERENTIATION OF CARBON AND CARBON COMPOUNDS IN COAL

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Introduction:

The different types of coal are normally classified with the help of thermal methods. One of the main aims of such methods is to determine the amount of carbon not bound to any other elements in the coal, called "fixed" carbon here[2] which is probably equivalent to the term "free" or even "elemental" carbon in other investigations. A short tentative method was for it suggested by Swain[1] using Differential Thermal Analyses requiring standards with known amounts of chemically determined carbon in which the carbon has to be a very similar form to that of the sample. This is very inconvenient considering the many different forms of carbon alone in one coal. The standard test for the classification of coal is published by the Bureau of Mines[2]. It does not need any Standards and the precision of the carbon determination is very high. But this method needs specially built equipment, is time consuming and needs several samples of the same coal.

Recent improvements in the design and reliability of automatic Thermoanalyses instrumentation makes it desirable to reinvestigate this technique for the determination of "fixed" carbon in coal to see if it would be possible to adapt the Bureau of Mines carbon test to one of the automatic Thermoanalyses techniques with the smallest amount of change.

The Bureau of Mines test is made in the following way. The first sample of the coal is used to determine the moisture in coal by the weight difference of bedfresh coal and air dried and heated (105°C) coal. The ash content of the coal is measured in a second sample by heating it in an aerated oven for 1 1/2 hrs. at 750°C and weighing the remaining ash. The volatile matter is determined by heating a third sample to 950°C in an enclosed container for 7 minutes and measuring the weight difference occurred on the sample during the heating. The fixed carbon content is derived by deducting the weight of water, ash and volatile matter from the original weight of the coal.

From the several Thermoanalysis techniques Thermogravimetry seems to be especially suited to use for the fixed carbon test as it can measure the weight change of the sample in different atmospheres as function of the temperature as required by the Bureau of Mines test.

The fixed carbon test could be made with the help of Thermogravimetry in the following way. First the sample is heated in an inert gas atmosphere (nitrogen, helium) to 950°C linearly with temperature. Then the sample is automatically cooled to about 350°C and reheated up with the same heating rate in an oxidizing atmosphere (air or helium oxygen mixture) to about 800°C. The weight loss of the coal recorded in the oxidizing atmosphere is the amount of fixed carbon in the sample. Water and all volatile matter were removed in the run in the inert atmosphere, and as only ash is left after the run in the oxydizing atmosphere, the weightloss in this atmosphere indicates the amount of fixed carbon.

If one assumes a heating rate of 15°C/min., which is usually used in thermogravimetry the test will take about two and a half hours. Increase in the heating rate to about 25°C/min. should have little effect on the reproducibility (1 - 3%) of Thermobalances. The advantage of measuring fixed carbon with the help of thermogravimetry is that the test can be done in a very similar way as the manual test but a shorter time, on a single sample, fully automatically on standard instrumentation and the fixed amount of carbon is recorded permanently on a graph paper or a print out. At the same time a record is made of the amount of water, of the volatile matter and the ash.

The disadvantage of thermographic equipment against other thermoanalysis instrumentation is that it is delicate to handle, vibration sensitive, relatively expensive and any off-coming gases are difficult to measure.

If one is more interested in measuring the amount of fixed carbon and would like to do this on a more rugged, smaller and less expensive instrument which might be hand portable, Evolved Gas Analysis seems to be the better choice. In Evolved Gas Analysis instead of weight changes the gases evolving from the sample are measured. Therefore, instead of a delicate and expensive balance mechanism, a sturdy, small and sensitive all gas detector like the Thermoconductivity detector can be used. For special gases even higher sensitivity gas detectors can be used, for hydrocarbons, f.e. flame ionsation detectors capable of detecting 10^{-9} grams. And as a weight change can only occur when gases evolve, Evolved Gas Analysis gives principally the same information as Thermogravimetry.

To detect the amount of fixed carbon in coal the sample can be run very similarly as in Thermogravimetry by heating it up first in an inert carriergas stream (helium, nitrogen) to 950°C; then cooled down to about 350°C and reheated to about 800°C in an oxydizing atmosphere. The fixed carbon which was left over from the inert gas run is converted to carbon dioxide in the oxidizing atmosphere and indicated by the thermoconductivity detector. The area under the carbon dioxide peak is measured and with the help of a calibration run of ultrapure carbon converted to milligrams

of carbon. If a calibration is made for water and the remaining ash in the crucible is weighted, then also Evolved Gas Analysis, short EGA, can measure the content of water, volatile matter (by difference), fixed carbon and ash in coal. The advantage of the EGA method over the other methods lies mainly in its ruggedness, smaller size and low cost. The precision of the fixed carbon determination should be similar to the Thermogravimetric method. If it can be verified that for all existing coal the carbon peak can be recognized in the oxidizing atmosphere without removing the volatile gases as it could be done in the samples which were run in this investigation, then the EGA test for the fixed carbon would be much simpler than any of the other mentioned tests.

EGA systems have been designed by the author in the past and applied among other fields with another investigator to the determination of carbon in the airborne particulate.[5] The question arose how well this method is suited for determination of fixed carbon in coal. In the following the feasibility of such an approach is being studied and reported results seem to encourage further investigation of this approach.

Method:

In the following an improved EGA system is described based on earlier work of the author[3].

Figure 1 shows the basic EGA design used in this investigation. The weighted sample is filled into a quartz cuvette, which is held in place by a sample holder. A thermocouple measures in the middle of an average size sample the temperature. A platinum shield protects and enhances the output of the thermocouple. Through a small hole at the tip of the thermocouple passes prewarmed carriergas into sample taking with it any evolving gases to the detector. The shown portion of the EGA head is heated by a surrounding oven linearly with temperature.

To achieve high sensitivity and reproducibility by creating a very similar chemical and physical environment for each sample and to be adaptable to many different samples, the EGA design has the following characteristics:

(1) Uniformity of temperature at the sample (1°C)

(2) The free space in the sample chamber and the connecting tubing to the detector area as small as possible to allow least dilution, highest sensitivity and fastest response.

(3) The carrier gas is preheated to the sample temperature.

(4) The carrier gas flows through the sample powder.

(5) The sample temperature is measured in the sample.

(6) Any cold spots are avoided.

(7) The pressure can be changed from 10^{-6} mm Hg to 500 psi.

(8) The temperature range is from -100°C to 1200°C.

(9) Differential Thermal Analysis set up is also available in the EGA head.

(10) The unit is made from chemically inert Inconel 600.

The complete schematic of the EGA system is shown in Figure 2.

The carrier gas is supplied by high purity gas tanks (impurities 2 ppm) and is pressure regulated and if necessary, mixed in a special tee with oxygen, before it enters the reference side of the thermoconductivity cell, from where it flows into the EGA head, where it is first prewarmed in the forechamber to the sample temperature. From there, the carrier gas flows through the sample, where it takes any offcoming gas from the sample through a small annular space between the forechamber and the sealing tube to the sample side of the thermoconductivity detector, where any unbalance in the sensing bridge created by the evolved gases is indicated by a recorder, which also indicates with a second pen the sample temperature and with the help of a disc integrator the area under the gas peak.

As the thermoconductivity detector does not alter in any way the offcoming gases, they can be injected for further study with a gas sample valve into a gas chromatograph, where the offcoming peaks can be separated and identified. Further identification can be made by mass spectrometry or other detectors for specific gases.

The EGA-head is located in a furnace which is heated linearly with temperature by a temperature programmer. The thermoconductivity detector is located on the top of the furnace next to the EGA head to avoid cold spots and allow immediate detection of offcoming gases.

In order to calibrate the system, first baselines in different atmospheres and heating rates with no sample in the EGA head were obtained. No significant deviation could be observed (2%) in the ranges used for the coal samples. The bimetallic temperature controller for the Thermoconductivity cell creates a small just visible sinuous deviation of the baseline. Over 800°C the very hot offcoming carriergas is in the heat exchanger coil not more properly cooled down to the T/C temperature range and creates a downward imbalance in the thermoconductivity cell. A

longer and better temperature stabilized coal would extend considerably the useful range of the temperature.

To measure the amount of carbon in the coal samples 2 mgr of ultrapure spectrographic grade carbon (0.0001%) was filled into the quartz cuvette of the EGA head and the area under the peak determined as figure #3 shows. This run was as the following runs obtained under the following conditions: Heating rate 10°C/min., paper advance 6"/hour, helium gas flow 20cc/min., oxygen gas flow 10cc/min., Thermoconductivity detector 140 mA, 150°C, sensitivity 4, fullscale on recorder 2 mV. The blue line across the diagram indicates the sample temperature, the red line the offcoming gas and the disc integrator trace the area under the peak. One can see that the CO_2 comes off around 760°C and that the area underneath the peak corresponds to 94 squares per milligram carbon.

In another investigation[4] it was found that the temperature of the carbon peak depends strongly on the presence of certain catalysts, some of which occur like iron, in its many forms, in relative large concentrations in coal. These catalysts may cause downward shifts of the carbon peak in the order 300 to 400°C. Therefore, the carbon peak in coal may be expected in the temperature range of 450 and 600°C.

The next three figures show typical EGA diagrams of coal powder. In figure 4, 5 milligrams of coal powder from the Mary Lee seam in Alabama was run in a helium oxygen atmosphere from room temperature to 900°C. First a negative peak occurs at 270°C followed by a shoulder at 400°C and a sharp peak at 470°C, which seems to be located on a lower broader peak as indicated by the dashed line. This peak can be identified as coming from the carbon of the coal by the following method which also allows to measure the area under the peak. First the volatile matter of the coal sample (broad peak) is removed by heating the sample in a pure helium atmosphere as seen in the next Figure 5. The evolved gas trace shows a shoulder at 200°C a peak around 500°C a shoulder at 725 and a peak at 770°C without returning to zero at the end of the run (900°). The peak around 500°C is most probably due to carbon with the oxygen derived from decomposing material. The area of this peak indicates a smaller amount of carbon than a similar area in the last figure as the carrier gas flow is reduced in this run by the amount of oxygen present in the earlier run and all evolved gases appear therefore in higher concentration (66%).

In Figure #6 the remaining sample from the run shown in Figure #5 is reheated in a helium-oxygen atmosphere. The diagram shows a declining baseline between 300°C and 600°C and a single peak at 490°C. As the offcoming gas for this peak and all the other peaks around 500°C is CO_2 they are due to the carbon in the coal. If one compares the areas of the carbon peaks in these three

runs one finds that the area of the carbon peak in this run (Figure #6) and the corrected area of the carbon peak in the run before result in the area of the carbon peak in the first run (Figure #4). Using the calibration run with ultrapure carbon (Figure #3) one can now find the weight of the fixed carbon in the coal sample and calculate the percentage of carbon in coal.

To check the above calculations each sample was before and after each run weighted in a Cahn Micro balance. In this way according to the standard method, the amount of fixed carbon could be determined by subtracting the weight of the volatile matter (including the water) and the weight of the ash from the original weight of coal.

The results from four different samples are shown in the last Figure (#7).

In this table the amount of fixed carbon in the four samples is shown first as determined by the EGA method and then by the standard method using weight difference. One can see that the results of these two methods are very close in spite of quite varying fixed carbon content in the coal. Also, on the diagram is the amount of volatile matter and ash indicated. One can see here on the other hand that the areas determined by EGA corresponding to the volatile matter do not compare well to their measured weight loss. This is easy to understand because the thermoconductivity of each of the offcoming gases is different and causes wide variations in the weight of the volatile area calculated from the area.

The capital letters H_e, 0, H_e+0, indicate that the run was made correspondingly in Helium alone, in Helium Oxygen after the Helium run, in Helium Oxygen with a fresh sample.

In summary the present investigation indicates that the EGA method(as measured on four actual samples) compares favorably with the standard manual weight difference method as published by the Bureau of Mines in measuring the amount of fixed carbon in coal. As the EGA method is much faster, requires only one very small sample (larger samples can be easily handled) is fully full automatic (no attendance), the whole instrument probably can be made hand portable and the strong possibility exists that only one run is necessary; therefore, further study of this approach on a much larger scale is suggested.

Acknowledgement:

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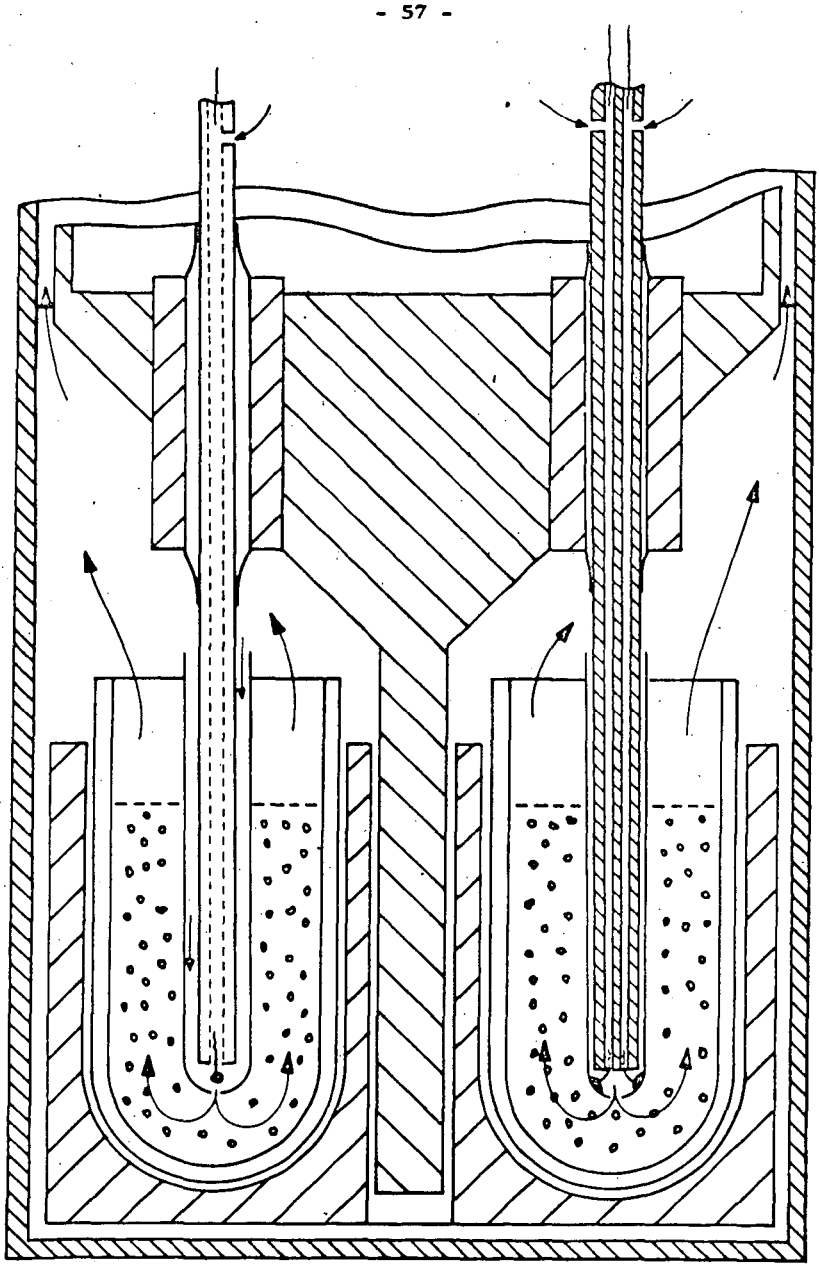
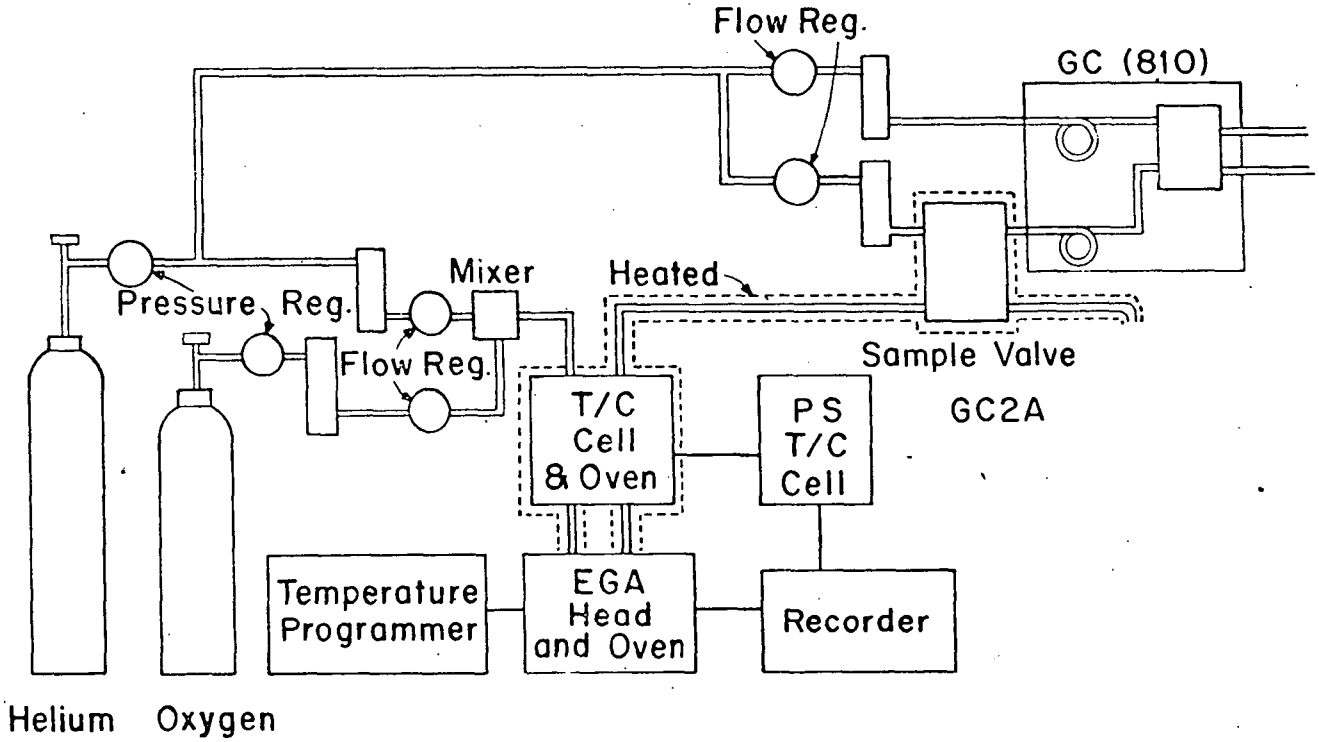


EGA Samplechamber 1970

FIGURE 1



Schematic for EGA Determinations 1970

FIGURE 2

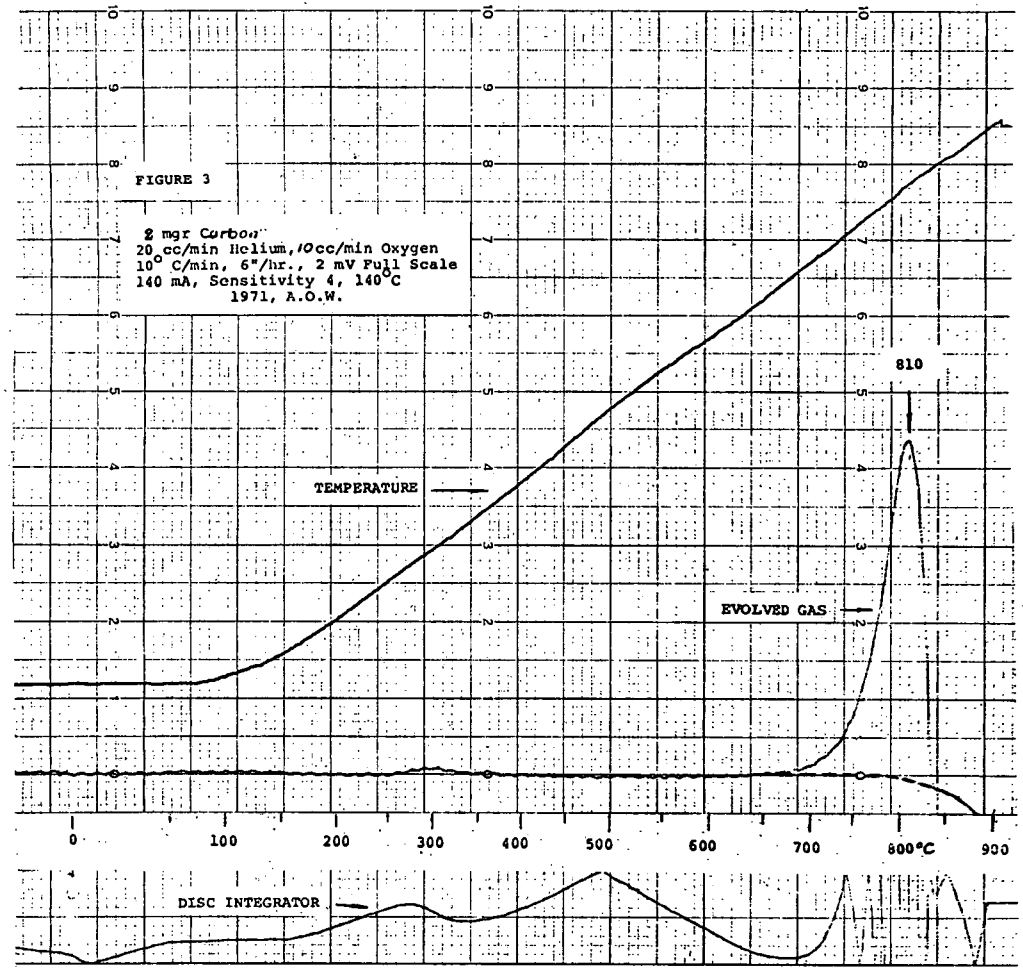


FIGURE 3
2 mgr Carbon
20 cc/min Helium, 10 cc/min Oxygen
10° C/min, 6"/hr., 2 mV Full Scale
140 mA, Sensitivity 4, 140°C
1971, A.O.W.
810
TEMPERATURE
EVOLVED GAS
DISC INTEGRATOR
0
100
200
300
400
500
600
700
800°C
900

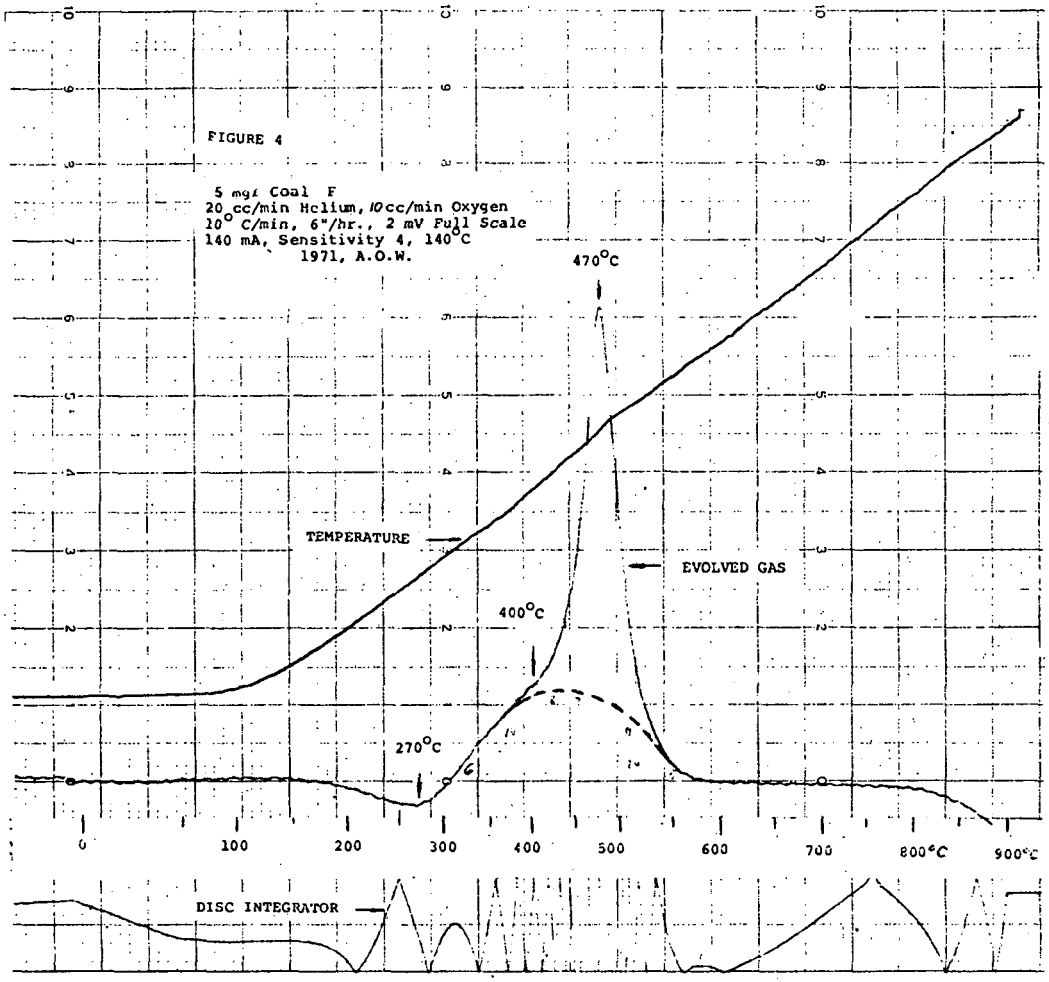


FIGURE 4
5 mg. Coal F
20 cc/min Helium, 10 cc/min Oxygen
10° C/min, 6"/hr., 2 mV Full Scale
140 mA, Sensitivity 4, 140°C
1971, A.O.W.
470°C
TEMPERATURE
EVOLVED GAS
400°C
270°C
0
100
200
300
400
500
600
700
800°C
900°C
DISC INTEGRATOR

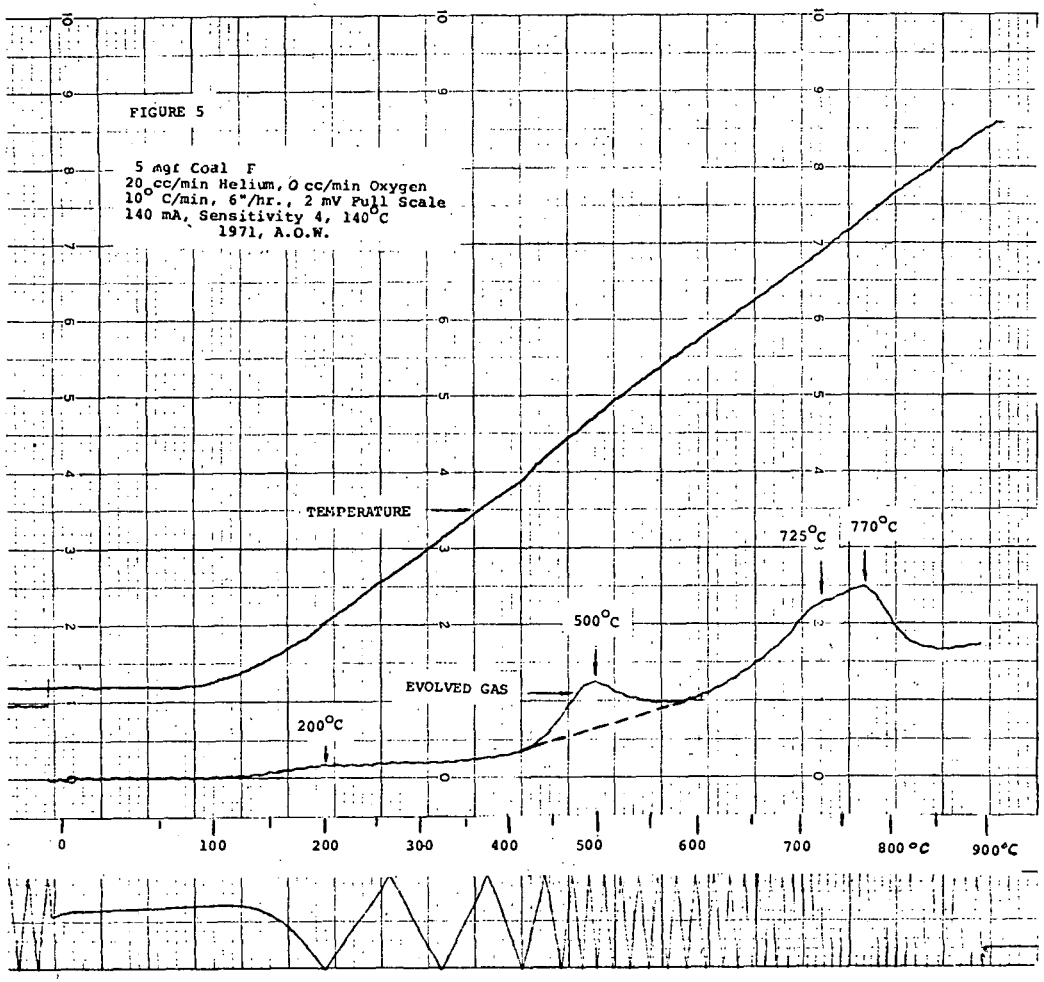


FIGURE 5
5 mgr Coal F
20 cc/min Helium, 0 cc/min Oxygen
10° C/min, 6"/hr., 2 mV Full Scale
140 mA, Sensitivity 4, 140°C
1971, A.O.W.
TEMPERATURE
EVOLVED GAS
200°C
500°C
725°C
770°C
0
100
200
300
400
500
600
700
800 °C
900°C

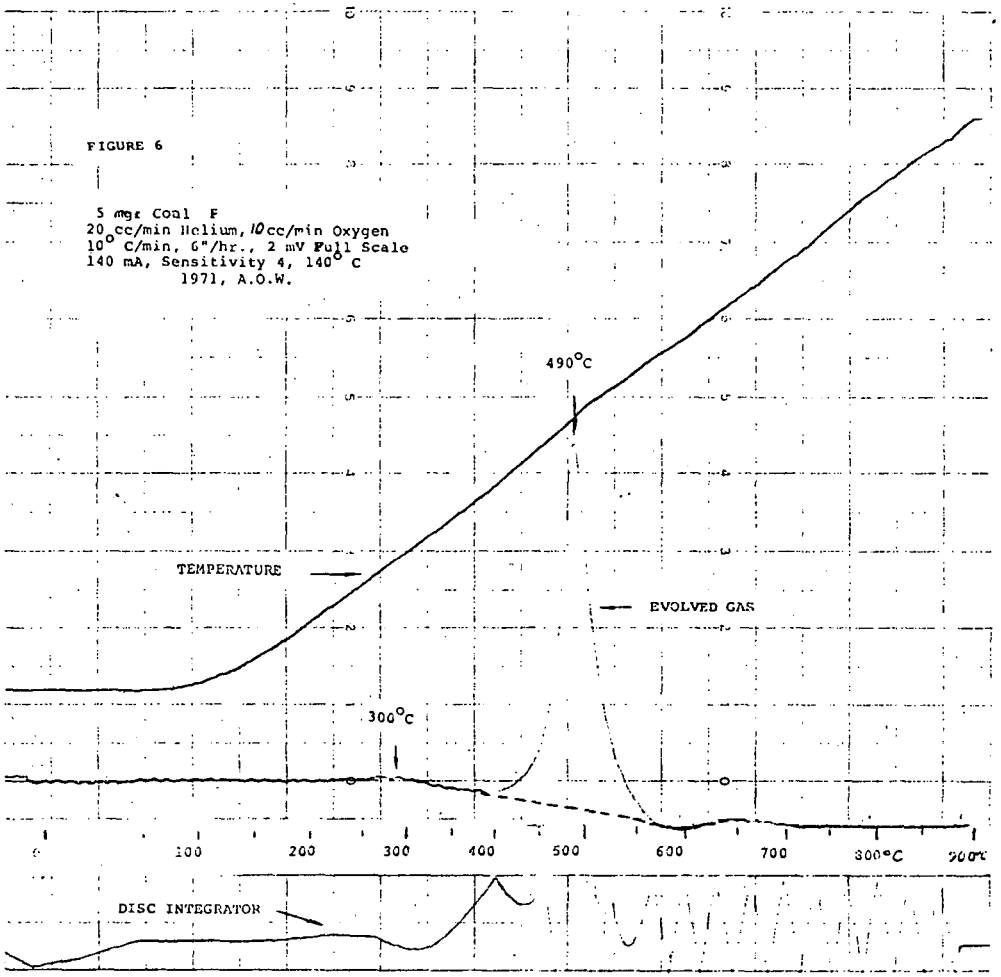


FIGURE 6
5 mg. Coal F
20 cc/min Helium, 10 cc/min Oxygen
10° C/min, 6"/hr., 2 mV Full Scale
140 mA, Sensitivity 4, 140° C
1971, A.O.W.
490°C
TEMPERATURE
EVOLVED GAS
300°C
100
200
300
400
500
600
700
800°C
900°C
DISC INTEGRATOR

COAL	Sample Weight		FIXED CARBON					VOLATILE MATTER			ASH	
			EGA			WEIGHT		EGA	WEIGHT			
			Area Sqs.	Wt. mgr.	%	Wt. mgr.	%	Area Sqs.	Wt. mgr.	%	mgr.	%
A		He	33	0.35	7			696				
Mathies Pa. (Pittsburgh)	5 mgr.	0	206	2.2	44	2.49	50.0				0.65	12.5
		H + O	228	2.42	48.5			232	1.85	37		
B		He	40	0.42	8.5			677				
Rubena, Pa. (Pittsburgh)	5 mgr.	0	226	2.40	48.0						0.35	7
		H + 0	251	2.67	53.5	2.65	53	236	2.00	40		
E		He	15	0.16	3.2			664				
Olga, W.Va. (Pocahontas #4)	5 mgr.	0	335	3.49	70.0	3.66	73.2				0.277	5.5
		H + 0	351	3.66	73.4			186	1.063	21.3		
F		H	25	0.26	5.3			752				
Segco #1, Ala. (Mary Lee)	5 mgr.	0	202	2.15	43	2.375	47.5				0.75	15
		H + 0	226	2.4	48			218	1.875	37.5		

FIGURE 7

Comparison of EGA Versus Weight Method