

EXPERIENCE WITH THE ANALYSIS OF COAL

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Abstract - Current requirements for analytical support for coal research have created the need for new, highly efficient analytical methods. The traditional proximate, ultimate and ash fusion analysis have had to be updated or replaced and improved methods had to be developed for the determination of trace elements in coal and coal-related products (including ash, slag, effluent waters and product gas (from gasification)). A few examples of such developments which have been implemented in our laboratory during the last few years will be discussed. To obtain reliable analytical results proper sampling procedures and sample pretreatment are of paramount importance.

INTRODUCTION

During the development phase of coal conversion processes, a large amount of analytical information has to be supplied and rapid analytical procedures giving as much information as possible are required. The standard procedures used in the coal trade are not very suitable for this purpose because they are too time-consuming and they generally examine no more than one property of the sample per analysis. While there are many ways of speeding up and updating the coal analytical techniques, we will limit ourselves here to the experience we have obtained in our laboratory.

DETERMINATION OF MAIN ELEMENTS

Earlier (Ref. 1) we reported that reducing the intakes for element determinations in coal from several hundreds milligrams to a few milligrams can lead to much more rapid analytical methods with precisions and accuracies which are practically equal to those of the established standard methods. In Table 1 a comparison is given of elemental analysis results

TABLE 1. Results of (semi-)microanalyses for coal compared with results of a round robin series of tests following standard procedures

Element	Av. concentration found in round robin series, %w	Concentration found by rapid method, %w
C	72.97	73.36
H	4.16	4.20
S	0.63	0.61
Cl	0.004	0.008
N	1.64	1.76
Si	3.12	3.11
Al	2.32	2.27
Fe	0.29	0.26
Ca	0.13	0.13
Mg	0.022	0.019

obtained with rapid micro or semi-micro methods and those from a round robin series of tests carried out by eight laboratories using standard methods. In our work, carbon and hydrogen

were determined by means of the Perkin-Elmer 240 CHN Analyzer, sulphur (Ref. 2), chlorine (Ref. 3) and nitrogen (Ref. 4) by microcoulometric procedures.

Analysis of the main coal ash elements was carried out by means of inductively coupled plasma emission spectrometry according to the procedure of Botto (Ref. 5). To do this the coal ash is first fused with lithium tetraborate in an automatic flux preparation apparatus*. After the fusion is finished the salt melt is automatically transferred into a beaker containing dilute nitric acid. After dissolution of the melt the element composition is determined. The flux apparatus can handle six samples at a time, the acid solutions are obtained with 20 to 30 minutes.

Oxygen in coal and coal ashes were determined by fast neutron analysis. Though the total oxygen content is, in most cases not so important for process development, the knowledge of its concentration can be of great help in establishing the correctness of the other element concentrations. A correct element balance is a good yardstick for the exactness of the other main element determinations. Furthermore, we have found that the oxygen content of coal ashes as calculated from the oxides of the main elements is approximately 3 % low.

DETERMINATION OF TRACE ELEMENTS

Mainly because of concern for environmental repercussions, we have investigated the behaviour of approximately 30 elements in a coal gasification unit. (A simplified flow scheme of this unit is given in Fig. 1.) In order to be able to check the correctness of the results

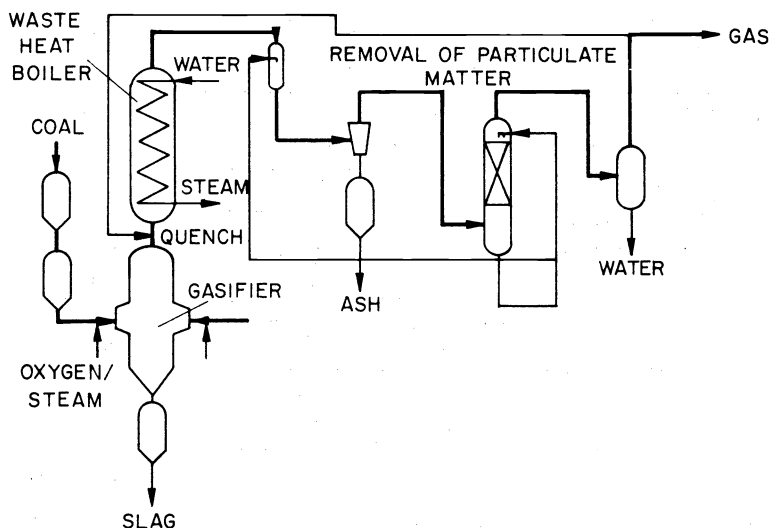


FIG. 1. Simplified flow scheme of the coal gasification plant at the Shell Harburg refinery

we have compared the amounts of the elements in the ingoing and outgoing product streams. Hence, we had to analyse the coal feed, the slag and ash streams, water and product gas.

Prior to the determination of the trace elements, the solid samples have to be dissolved in order to obtain aqueous solutions. We have found so far, that the lithium tetraborate melting procedure is not so suitable because of interfering effects from the walls of the platinum crucibles used for the fusion. Ashing of the coal or the slags and ashes to remove residual carbon may lead to losses of the volatile compounds of some elements. The best results are obtained if the samples are mineralized in closed systems or under complete reflux. We have successfully used a quartz reflux apparatus as described by Koch (Ref. 6), and a Buchi 445 Digester. In the latter apparatus six samples can be treated simultaneously. Gas samples can be collected using suitable adsorbents which can be mineralized.

The determination of the elements in the aqueous solutions is carried out by inductively coupled plasma emission spectrometry or, in those cases where lower detection limits are required, by carbon furnace atomic absorption spectrometry.

* Claisse fluxer, manufactured by Corporation Scientifique Claisse, Inc. 7-1104 Place de Mirici, Quebec Canada G1S4N8.

In Table 2 some results are given of concentrations and balances found in this investigation; the distribution of the elements over the various streams is illustrated in Fig. 2. The reactor bottom and cyclone bottom waters refer to water in which the slag and ash streams have been sluiced off.

TABLE 2. Recovery of elements/ash in coal gasification process

Element/ash	Concentration in the coal feed	Recovery in product streams, %
Ash	6.11 %w	99.7
Silicon	1.26 %w	103
Sulphur	1.12 %w	90
Fluorine	93 mg/kg	86
Boron	19 mg/kg	117
Beryllium	2.3 mg/kg	109
Selenium	0.94 mg/kg	107
Uranium	1.75 mg/kg	92

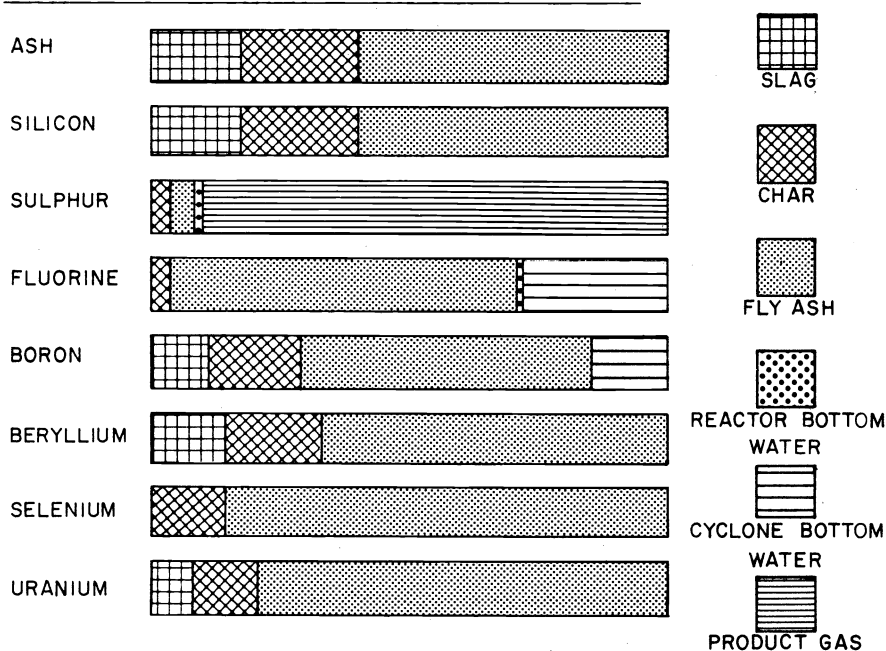


FIG. 2. Mass distribution of ash and elements during coal gasification

The success of an element review as described above depends highly on the sampling procedure. Sampling has to be done by analytical staff in close co-operation with the operators of the plant. All the samples have to be taken at the same time intervals to ensure as much as possible a constant ash throughput. Mass flows have to be known in order to allow balance calculations to be made as a check on the correctness of the results. The solids samples have to be well ground to provide a representative sample for analysis. Aqueous samples have to be carefully preserved in order to avoid wall adsorption or contamination.

FURTHER AUTOMATIZATION

The determination of carbon, hydrogen, sulphur, nitrogen and chlorine and of the combustion residue has been simplified and speeded up by the introduction of the combustion mass spectrometric element analysis technique (CME) as described by van Leuven (Ref. 7). A diagram of the apparatus is given in Fig. 3. The principle of the method is the combustion of a few milligrams of a sample in a quartz tube followed by on-line monitoring of the combustion gases (CO_2 , H_2O , SO_2 , HCl , NO , etc.) by means of a quadrupole mass spectrometer. After about 90 seconds the analysis is finished and a print-out of the element composition is obtained.

In this flash combustion system some of the sulphur and chlorine can be left behind in the residue in the form of stable salts. This can be prevented by adding some tungsten trioxide to the sample to decompose these salts (Ref. 2,3). Table 3 compares some results of CME analysis with results obtained by ISO methods.

More information about coal samples can be obtained with the mass spectrometric detection system, by replacing the flash combustion with a programmed heating procedure in an inert atmosphere. Results obtained with this procedure, the pyrolysis/combustion mass spectrometric element (PCME) analysis compare very well with results of the proximate coal analysis where moisture, volatile material, fixed carbon and ash are determined.

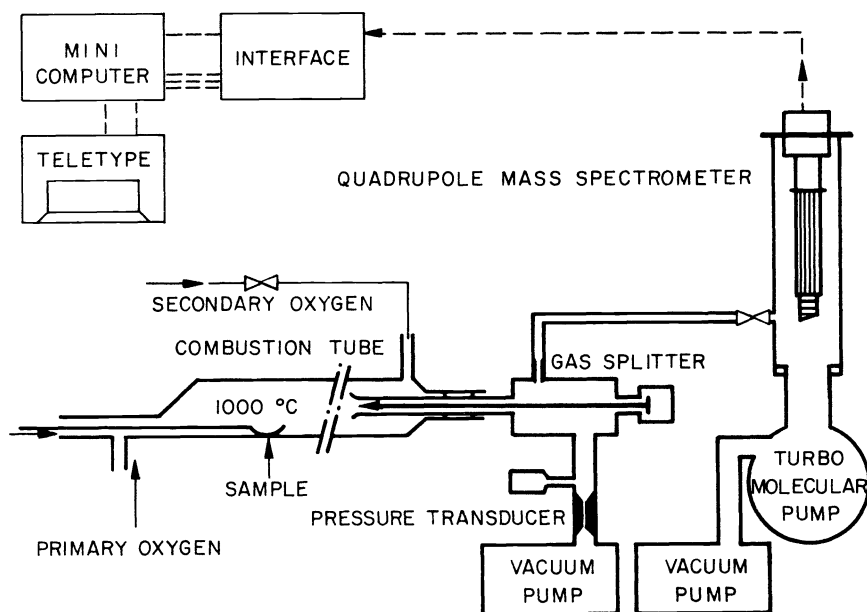


FIG. 3. Diagram of combustion mass spectrometric element analysis apparatus

TABLE 3. Results of coal analyses by ISO and CME

Element	Method	Coal samples		
		1	2	3
C	ISO 625	58.97	68.90	78.58
	CME	58.63	68.18	78.48
H	ISO 625	3.68	5.58	4.98
	CME	3.70	5.60	4.98
N	ISO 332	1.26	0.91	1.54
	CME	1.3	0.9	1.7
S	ISO 334	2.89	0.28	1.07
	CME	2.62	0.28	0.98
Cl	ISO 475	0.255	0.042	0
	CME	<0.3	<0.3	<0.3
Ash	ISO 1171	28.0	8.7	7.3
	CME	25.2	7.3	6.6

Fig. 4 illustrates the modifications to the system. The entry to the combustion tube is filled with helium and in this helium atmosphere the coal sample is heated at such a rate that a temperature of 1000 °C is reached in approximately 400 seconds. The volatile material enters the second part of the quartz tube where oxygen is introduced and combustion takes place. The combustion gases are continuously monitored by the mass spectrometer. The sample residue containing the non-volatiles, including the fixed carbon, which has so far remained in the sample boat, is finally passed into the oxygen-containing part of the combustion tube and burned. The ash content is measured by weighing the residue. The inert gas heating part of the analysis cycle is split into the determination of the moisture content, i.e. the water coming off up to 110 °C, and of the volatile material obtained during the rest of the pyrolysis. A general view of the apparatus is given in Fig. 5.

A number of results obtained by PCME analysis are compared with results obtained by the corresponding ISO methods in Table 4. A good correlation is obtained.

The mass spectrometric procedure has the advantage over the commercially available systems for proximate analysis that intermediate cooling and weighing of the sample is not necessary because the weight losses are calculated from the quantity of combustion gases formed. Furthermore, the way in which the volatile compounds came off during pyrolysis and combustion can be determined and plotted as is illustrated in Fig. 6.

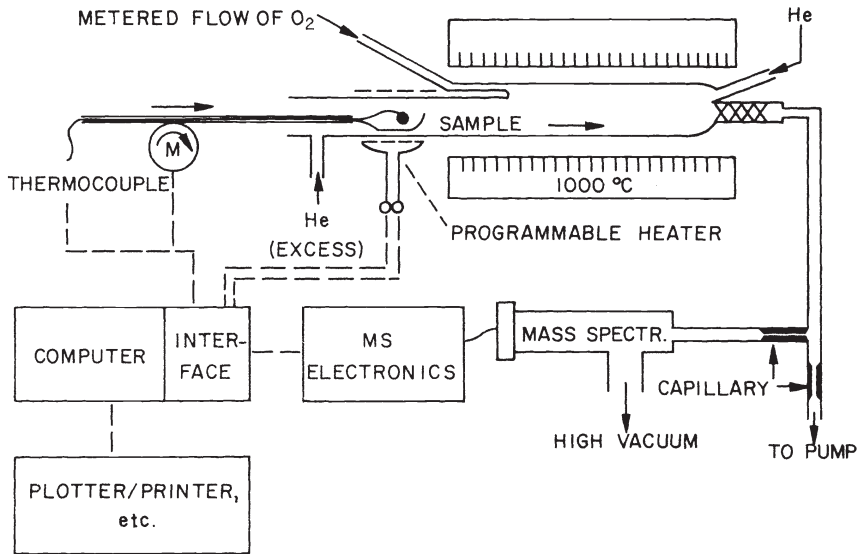


FIG. 4. Pyrolysis/combustion/mass spectrometric element analysis



FIG. 5. View of PCME apparatus

TABLE 4. Comparison of proximate analysis of coal samples by ISO and PCME methods

Coal sample	Results, %w							
	ISO				PCME			
	Moisture	Volatile matter	Fixed carbon	Ash	Moisture	Volatile matter	Fixed carbon	Ash
1	0.6	5.7	91.6	2.7	0.3	4.8	92.3	2.9
2	0.6	11.0	83.2	5.8	0.5	11.0	83.0	6.0
3	0.9	34.4	61.8	3.8	1.0	34.5	61.8	3.8
4	18.2	49.3	43.9	6.9	19.2	47.8	46.8	5.4
5	14.6	39.7	48.8	11.5	15.6	37.6	51.4	11.0
6	16.3	49.0	47.7	3.4	16.2	47.8	48.9	3.3

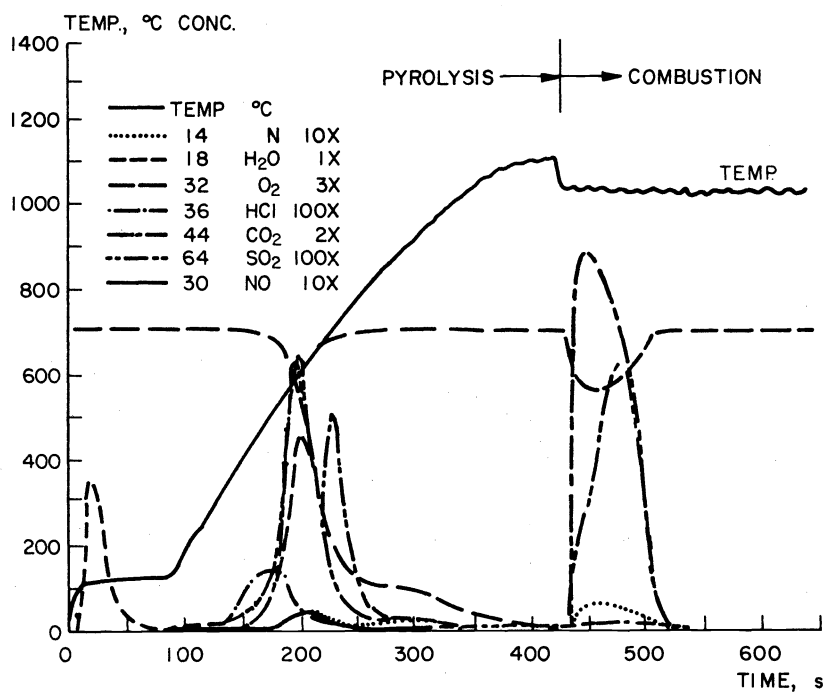


FIG. 6. Analysis of a coal sample (14 mg)

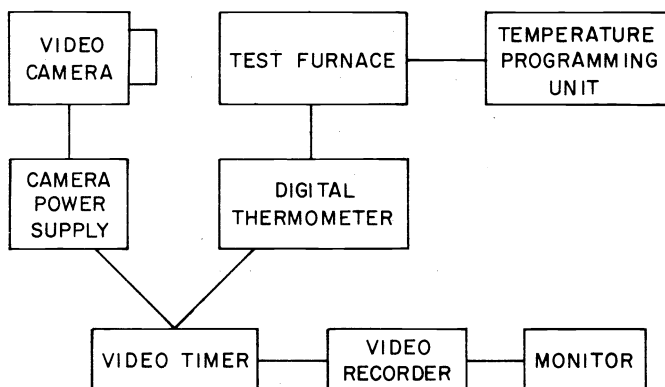
This figure shows that at 110 °C only water is obtained. At approximately 600 °C hydrocarbons appear (simultaneous signals of H₂O and CO₂) and parts of the sulphur compounds decompose (presumably organic sulphur compounds and pyritic sulphur. At 800 °C mainly hydrogen is found, indicating that at this temperature the coal has started to pyrolyse.

In the combustion part of the curves (1000 °C), the fixed carbon is burnt. During this process hydrogen and the rest of the sulphur and nitrogen compounds are found.

The oxygen consumption is measured and from the difference between the oxygen present in the combustion products and the oxygen consumption, estimates can be made of the amount of oxygen which was present in the "organic" part of the sample.

The determination of coal ash fusibility is often required in process development work. The method, for example, as described in ISO 540 is rather time-consuming, it requires 6 hours for a duplicate analysis. Most of this time is needed to record the behaviour of a pre-made ash cone in an oven. We have speeded up the inspection procedure by extending the original set-up with a video camera and a recorder. The video camera has been provided with distance rings and a grey filter while the front of the lens system is cooled by a stream of air. The temperature in the furnace is measured with a digital thermometer. The signals from the camera and thermometer are mixed together in a video timer, thus we obtain the temperature

and the shape of the ash cone on the video tape. When the tape is displayed on a monitor, with the monitor speeded up, the final results can be easily and quickly read. A scheme of the set-up is given in Fig. 7.



PARTS OF THE REGISTRATION APPARATUS:

VIDEO CAMERA	: SONY CH-1400 CE
POWER UNIT	: SONY PU-1401 CE
DIGITAL THERMOMETER	: CRL TYPE 204, Pt. 10% Rh/Pt, RANGE 0-1799 °C, WITH BCD OUTPUT
VIDEO TIMER	: FOR-A VTG-88
VIDEO RECORDER	: VHS SYSTEM
MONITOR	: SONY PVM-90 CE

FIG. 7. Schematic diagram of apparatus for ash fusibility determinations

CONCLUSIONS

The described methods are in full use in our laboratory. It is obvious that considerable time-savings can be achieved with these methods. For example, the microcoulometric determination of sulphur, nitrogen and chlorine can be carried out in 10 to 15 minutes. A combustion mass spectrometric ultimate analysis requires approximately 2 minutes, while the PCME analysis can be carried out in 10 minutes. The introduction of a video camera in the ash fusion determination reduces the manipulative time from 6 to 1.5 hours for a duplicate analysis.

Much attention has to be paid to the sampling procedures. When plant samples have to be analysed, close co-operation between the plant operators and the analytical chemists is essential.

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