

EVOLUTION OF VOLATILE SULFUR COMPOUNDS DURING TEMPERATURE-PROGRAMMED
PYROLYSIS-COMBUSTION WITH A QUADRUPOLE GAS ANALYZER

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The evolution of sulfur species during combustion of pyrolysis volatiles from coal IBC-109 (1.13% sulfur, 0.42% chlorine) of the Illinois Basin Coal Sample Program has been studied using a pyrolysis-combustion apparatus in conjunction with a quadrupole gas analyzer (QGA). This work is part of an on-going project which investigates the role of sulfur and chlorine in coal in boiler corrosion. A better understanding of the behavior of these elements in coal during combustion may help elucidate the mechanism of boiler corrosion. The experimental conditions are designed to simulate the formation of sulfur compounds during coal combustion.

The pyrolysis-combustion apparatus used with the QGA to study the release of gases from coal is capable of heating the coal sample from the ambient to about 850°C at different heating rates. Major components include a quartz tube reactor, a gas flow controller, two split-tube furnaces, a programmable temperature controller, 50- μ m capillary tubing connecting a Dycor QGA to the pyrolysis system, and a microcomputer (Fig. 1). Approximately 0.5 gram of coal is heated nonisothermally under a controlled atmosphere (air, nitrogen, oxygen, or other gases) in the quartz-tube reactor which consists of two consecutive chambers. The coal is pyrolyzed in the first chamber under a nitrogen atmosphere and the volatile products are carried to the second chamber where they are combusted at 850°C under a constant flow of oxygen. The gaseous products are sampled through the capillary tube and monitored with a quadrupole gas analyzer. The different gaseous species are determined in the QGA by monitoring the atomic mass associated with different species, such as mass 64 for SO₂ and 44 for CO₂. The data from the QGA and temperature controller are transmitted to a microcomputer and stored as ASCII files on the hard disk.

The release of sulfur compounds from the coal was monitored as the temperature was increased from the ambient to 850°C at a heating rate of 50°C/min. Sulfur dioxide (SO₂) was released from coal IBC-109 primarily between 250° and 650°C (Fig. 2). The SO₂ profile showed a small initial release of sulfur between 250° and 400°C followed by a main peak between 400° and 550°C with a maximum at 510°C, and then by a small peak close to 625°C. The main SO₂ peak is associated with the release of volatile matter from the coal. The smaller higher temperature peak is probably associated with the release of pyritic sulfur^{1,2}. The initial small broad peak of SO₂ is unusual relative to other SO₂ profiles from Illinois coals² but may be characteristic of this sample. Perhaps there is a significant amount of weakly bonded organic sulfur compounds which are released in the initial volatilization of IBC-109.

When the combustion atmosphere was changed to a reducing condition, gaseous COS and H₂S were detected. Figure 3 compares the profiles for SO₂ and COS under an oxidizing condition where the excess oxygen concentration in the combustion chamber never fell below 5 percent (Run 3) to where a reducing condition occurred in the combustion chamber during the major release of volatiles (Run 4). An

obvious peak was obtained for COS in Run 4. The H₂S profile is more difficult to comprehend because of the presence of oxygen isotope ¹⁸O in the oxygen flow. The combination of ¹⁸O and ¹⁶O gives a mass of 34 for oxygen (¹⁶O¹⁸O), the same as H₂S. Thus the profile of mass-34 will mimic that of O₂ (mass 32). When O₂ is consumed, the oxygen (mass 32) will drop to background levels as will the ¹⁶O¹⁸O profile (mass 34). Figure 4 shows this effect for masses 32 and 34 of a blank run where the oxygen flow was shut off between 400° and 625°C. If H₂S is present under a reducing condition, a peak should occur in the mass-34 profile during the period of O₂ depletion. Figure 5 shows typical profiles of sulfur species, including mass 34, obtained when the O₂ was consumed during the experiment. The H₂S peak is observed in the trough of the mass-34 profile. As the rate of volatile gases released from the coal sample decreases, the O₂ concentration is no longer completely consumed and the reduced gas species disappear.

For this high-chlorine coal, we also attempted to monitor the evolution of HCl gas (mass 36) with QGA. Only a very weak peak was obtained for mass 36 during complete combustion with sufficient oxygen however, when the combustion atmosphere was under a reducing condition, a better gas release profile was obtained for the species of mass 36. This improved profile of mass-36 is probably not due to HCl. With the occurrence of H₂S under the reducing condition, the enlarged peak of mass-36 (Fig. 5) is most probably a result of the presence of the naturally occurring heavy sulfur isotope ³⁴S in the hydrogen sulfide (H₂³⁴S, total mass = 36).

Thus, the sulfur species formed in the combustion gas are controlled by the oxidizing condition in the combustion chamber. The experiments indicate that sulfur dioxide (SO₂) is the predominant sulfur species observed during combustion of pyrolysis volatiles. In some of the experiments, during the major release of volatiles, between 450° and 550°C, all oxygen in the pyrolysis system was consumed and a reducing condition occurred which resulted in the detection of additional sulfur species (COS and H₂S).

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References

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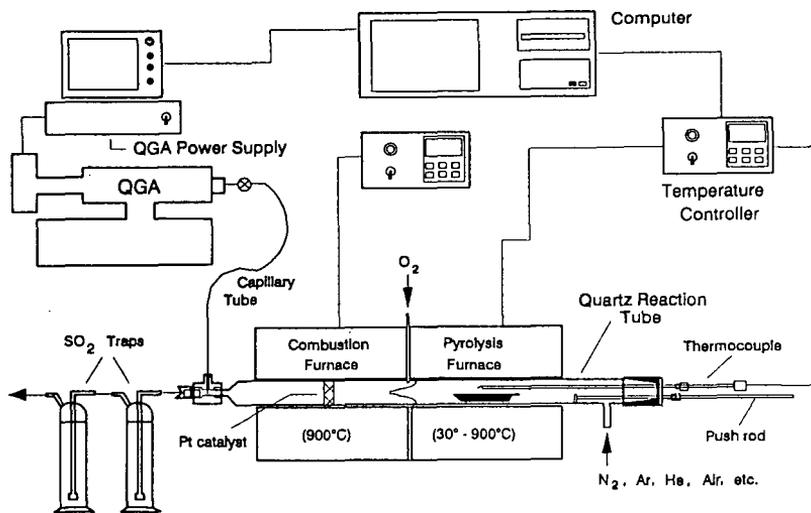


Figure 1. The experimental setup of a temperature-programmed pyrolysis-combustion system in conjunction with a quadrupole gas analyzer.

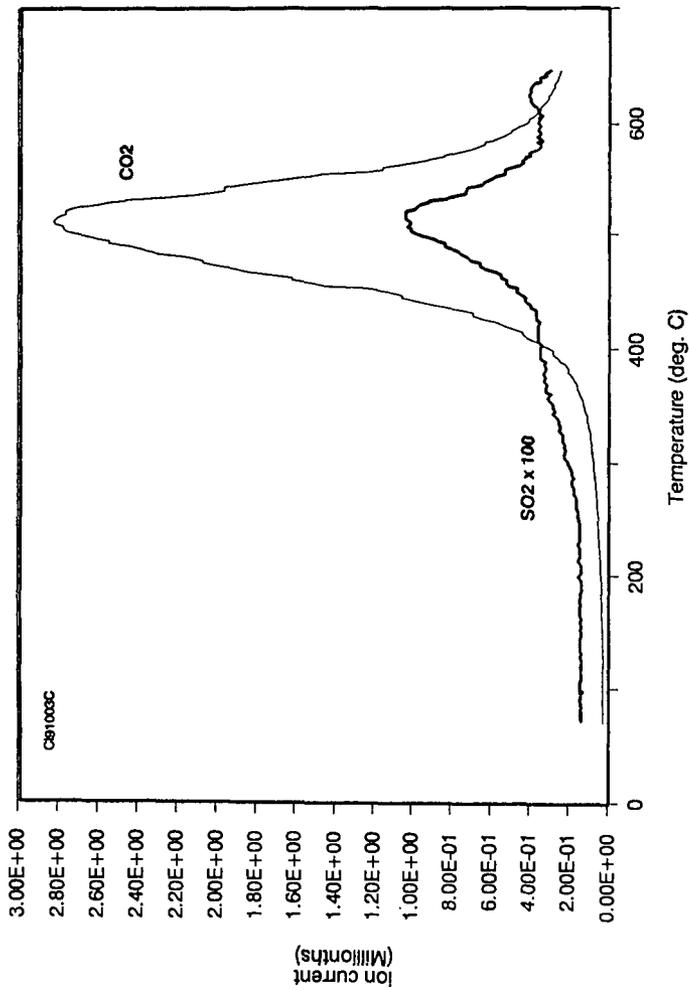


Figure 2. Profiles of CO₂ and SO₂ (X100) in combustion gas under an oxidizing condition at a heating rate of 50°C/min.

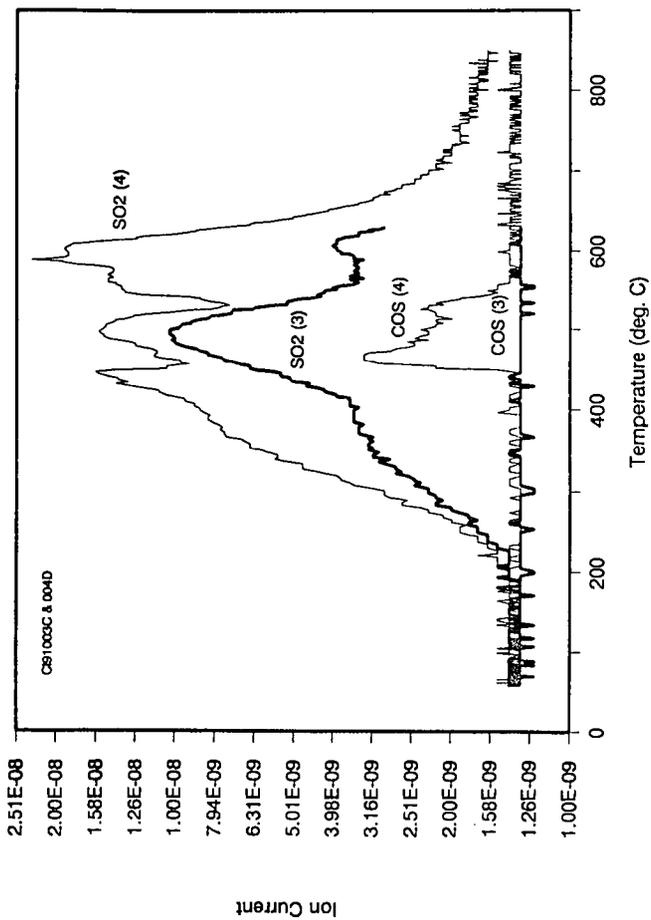


Figure 3. SO_2 and COS profiles when combustion chamber was under oxidizing (Run 3) and reducing (Run 4) conditions.

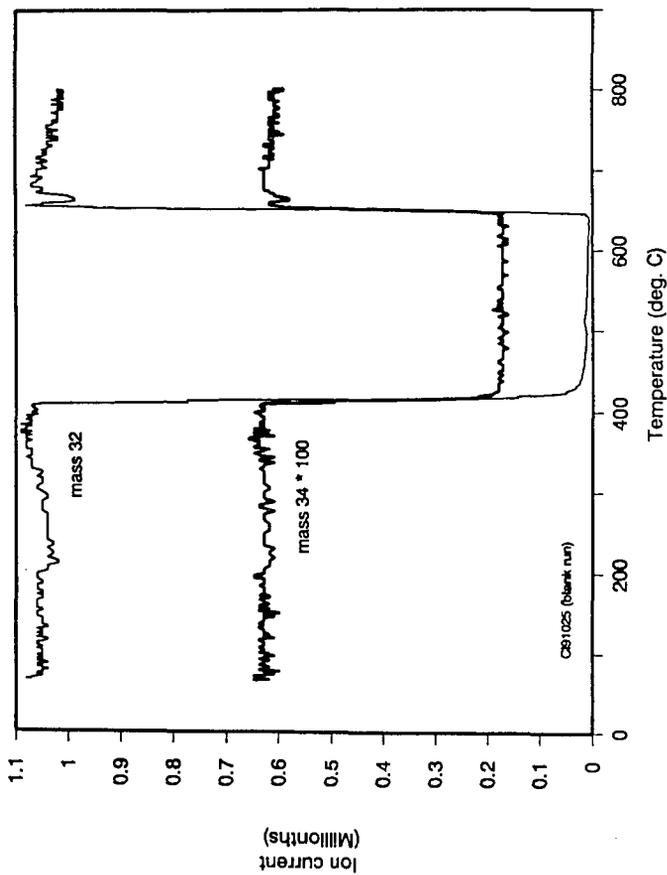


Figure 4. Profiles of masses 32 and 34 ($\times 100$) during a blank run where O_2 flow was shut off between 400° and $625^\circ C$.

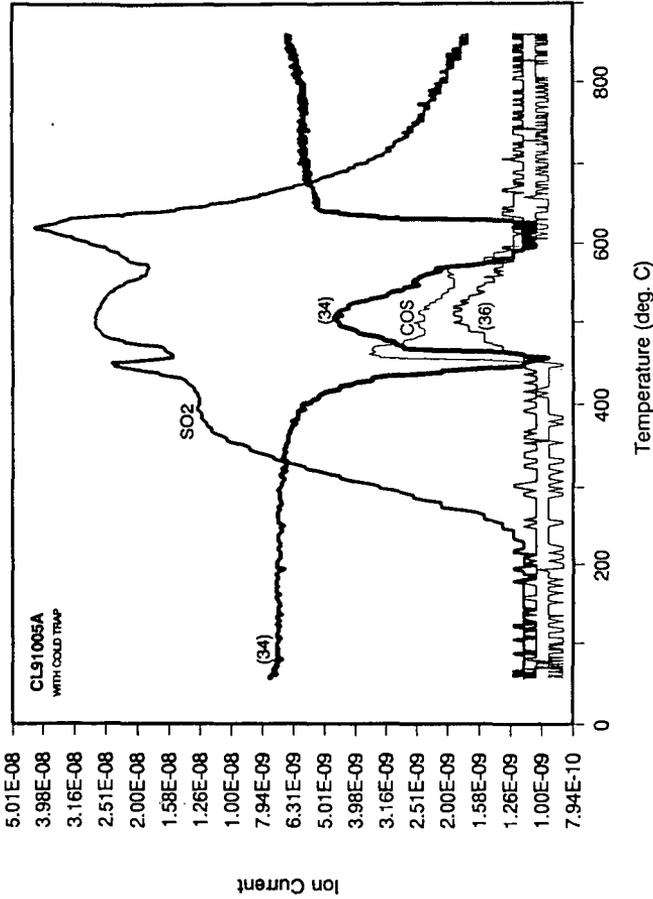


Figure 5. Gas release profiles obtained when combustion chamber was under a reducing condition. Mass numbers in parentheses are used for profiles that possibly represent more than one gaseous species.