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Introduction

An oxygen combustion, double gold amalgamation system is constructed for the determination of mercury in Alaskan coals. Solutions have been found for certain problems in design and operation. The effect of operating variables have been thoroughly evaluated and analytical procedure is outlined.

The system involves combustion of goal in an oxygen atmosphere and amalgamating mercury on gold coils. The amalgamated mercury is released by heating and measured in an atomic absorption cell.

Previous Investigations

Combustion and gold amalgamation system was first developed by Vaughn[1] and was subsequently modified by Joensuu[2] for the analysis of coal samples. O'Gorman[3] modified the construction details to make it more streamlined. The system described by Diehl[4] is similar to O'Gorman's setup.

The system described here is basically similar to the above. However, some modifications had to be made to make construction sound and operationally simpler.

Analytical System

The essential parts of the system are shown in Figure 1. The tubes are of quartz having 24/40 full length standard taper points with 17mm I.D. shank ends joined to give the desired length. The joints are fitted with teflon sleeves to prevent freezing and make the system leak proof without the use of a lubricant. Each individually heated sections are provided with thermocouple wells, permitting an accurate measurement of the temperature

of the system. The wells are made by locally heating the tube and stretching the area with a 1/8" diameter graphite rod to form a well. A short piece of quartz tube is fitted on the top of the well for supporting a thermocouple.

Previous investigations have heated the chambers by winding 26 gauge Nichrome wire. The wire was protected by means of a titanium paint. It was found that the paint peeled off rapidly exposing the bare wire to rapid oxidation and deterioration. Mixing of quartz wool with the paint has been found to stabilize the paint; however, should the chambers need rewinding, it takes a day or more to rewind it and gradually burn off the vehicle in the paint. In the present construction a beaded wire is wound first and a bare wire is wound in-between the beaded wire by turning direction of winding around over a hook on one end. This has given heating rates of about 275°C/min at 110 volts. Rapid cooling of the amalgamators is accomplished by blowing compressed air. Ten ampere variable resistance transformers are used to regulate heating of the various sections of the system.

The analytical system is divided into four sections: combustion section, catalytic section, amalgamator No. 1 and amalgamator No. 2 all having separate heat controls. Combustion and catalytic sections are contiguous to prevent deposition of tar and other organics. A three way stopcock has been incorporated between the first and the second amalgamator to enable venting of combustion gases without disconnecting amalgamator No. 2. Catalytic section is lined with a gold foil and filled with coils of silver wire. The two amalgamators are filled with coils of gold wire. Amalgamator No. 2 is connected to an 18 cm absorption cell with tygor tubing. Commercial oxygen is used for combustion and sweeping operations. Oxygen flow is controlled by a flow meter and is regulated by means of a needle valve.

Problems of Memory Affects in the Analytical System

During initial runs memory effects were observed. The absorbed mercury was released slowly upon heating. The release was over a long period of time rather rapid release as is the case with silver and gold. This problem was traced to the catalytic section where the quartz tube was corroded forming a brown coating. This could not be cleaned with acids. X-ray power camera studies showed that this consists of α (Low) christobalite, Ag_2SO_4 and AgCl. The material was leached with ammonia to remove silver salts and residue showed the presence of α (Low) christobalite only. The memory affects are now eliminated by lining the catalytic section with a gold foil, which prevents the contact of silver and its salts with the quartz. The deterioration of the quartz tube is then eliminated. Silver and gold, however, should periodically be removed and cleaned.

Analytical Procedure

Fifty to 100 mg of finely pulverized coal sample is weighed into a quartz combustion boat. One flake of SM-1 powder is added to the sample, (supplied by Perkin Elmer Corporation). The three way stopcock is kept in a position to vent the combustion gases out. Oxygen flow is adjusted by means of the needle valve to 700 cc/min. Too low flow rates will result in excessive condensation o moisture at the exit end. Catalytic section is preheated 500°C and the amalgamator are set at about 150°C. The heat for the combustion section is now turned on. SM-1 powder has a flash point of 200°C and the combustion starts at this tempreature. Without this, combustion will only start with an explosion aided by the volatiles evolved from the coal at about 300°C with the resultant formation of smoke. With SM-1 addition, however, combustion starts very smoothly. It takes about 90 seconds to start combustion and an additional 120 seconds for complete combustion. Mercury is picked up by gold in amalgamator No. 1 while venting combustion gases out.

Keeping the amalgamator at 150°C prevents condensation of moisture and volatile organics on gold. Now the three way stopcock is turned to sweeping position and heat is turned on for amalgamator No. 1. Mercury is released from amalgamator No. 1 and reamalgamated on amalgamator No. 2 while venting interfering moisture and organics out of the system. Oxygen flow is now adjusted to 450 ml/min and heat is turned on for amalgamator No. 2. A sharp peak is observed as the mercury is released from gold. It has been determined that mercury is released from gold at about 280°C. The entire analytical procedure takes from 8 to 10 minutes.

Affect of Operating Variables on Absorption Signal

The two principal operating variables that affect the absorption signal are heating rate determined by the voltage setting of the variable transformer, and oxygen flow rate. These are shown in Figure 3. Increase in heating rate results in a larger and sharper signal. A heating rate of 275°C/min has been chosen for the system. Increase in flow rate result in a smaller signal but the peak is sharper.

Acknowledgements

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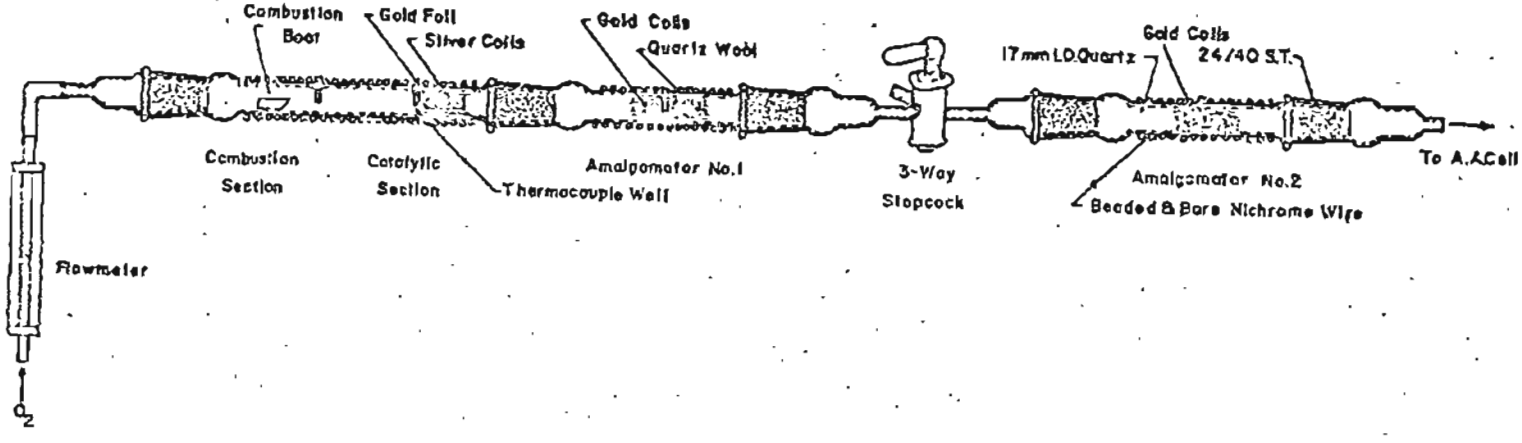

FIGURE 1. Double Gold Amalgamation System For The Detetermination Of Hg In Coals

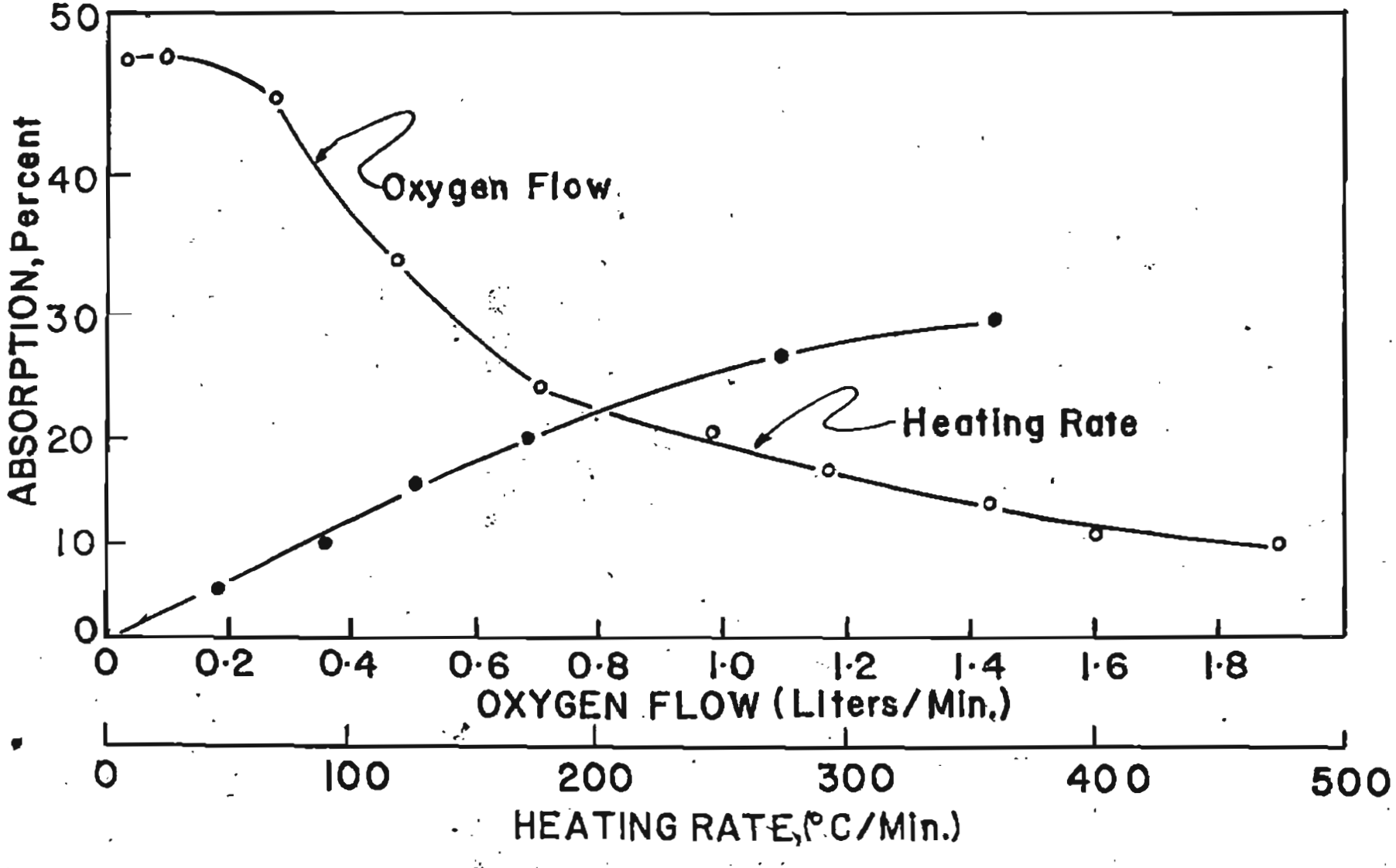

FIGURE.2. Effect Of O_2 Flowrate And Heating Rate On Absorption Signal