

EVOLVED GAS ANALYSIS - A NEW METHOD FOR DETERMINING PYRITE, BICARBONATE, AND ALKALINE EARTH CARBONATES

by

Richard W. Hammack

U.S. Department of the Interior
Bureau of Mines
Pittsburgh Research Center
Cochrans Mill Road
P.O. Box 18070
Pittsburgh, PA 15236

ABSTRACT

An evolved gas analysis technique has been developed that may be useful for the simultaneous determination of pyrite, bicarbonate, and alkaline earth carbonate in geologic materials. Although the technique has only been applied to ideal, reagent grade samples and its applicability to actual geological samples with complex matrices is untested, the technique may potentially improve conventional methods of predicting acid mine drainage potential. The technique employs a programmable tube furnace for heating samples in a 10 percent oxygen atmosphere. The evolution of sulfur dioxide from the oxidation of pyrite and carbon dioxide from the decomposition of carbonate and bicarbonate are monitored with respect to time and temperature using a quadrupole mass spectrometer. Sulfur dioxide peaks attributable to the oxidation of coal-derived pyrite occur between 380°C and 440°C; sulfur dioxide peaks attributable to the oxidation of hydrothermal pyrite are present between 475°C and 520°C. Carbon dioxide evolution resulting from the decomposition of bicarbonate is present between 100°C and 200°C; carbonates decompose with carbon dioxide evolution between 250°C and 700°C. Alkaline earth carbonates can be distinguished from transition metal carbonates and organic combustion on the basis of higher temperatures of carbon dioxide evolution. Calibration curves prepared by plotting evolved gas peak areas versus the concentration of pyrite, bicarbonate, and alkaline earth carbonate were linear.

INTRODUCTION

Acid mine drainage (AMD) is one of the most persistent and serious sources of industrial pollution in the United States. Premining prediction of acid mine drainage alerts mine operators to sources of potential acid discharges and allows them to plan mining operations and reclamation to minimize water quality degradation. In geographical areas or coal seams

that have historically been sources of AMD, mine operators are required by law (1) to identify possible hydrologic consequences prior to opening a new mine. Concern, particularly in the Appalachian region, regarding the possibility of acidic drainage has led to the requirement that an assessment of acid discharge potential accompany each new mine permit application. Overburden analysis to determine acid discharge potential includes chemical tests to quantify the acidic or alkaline weathering products from each stratum overlying or directly underlying the coalbed to be mined.

There are many proposed overburden analysis techniques ranging from direct chemical determinations to simulated weathering methods. However, the acid/base account, a direct chemical technique, is the most widely accepted because of its simplicity and low cost. The method is based on measuring the total sulfur content of each lithologic unit and converting that value to an acid potential based on the stoichiometry of complete pyrite oxidation. The neutralization potential is determined for each lithology by its ability to neutralize strong acid. The two values, acid and neutralization potential, are represented as calcium carbonate equivalents for calculation of net excess or deficiency of neutralizers.

The acid/base account was originally developed as a quick method of identifying acid or alkaline weathering material for revegetation planning. Use of the acid/base account to predict drainage quality from heterogeneous mine spoils without considering the various other contributory factors (mine type, reclamation, climate, and hydrology) is a serious overextension of the originators' intent. A recent study (2) has indicated that the acid/base account as typically applied to overburden analysis has little predictive capability.

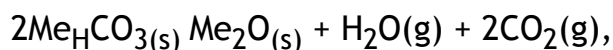
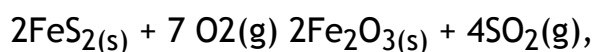
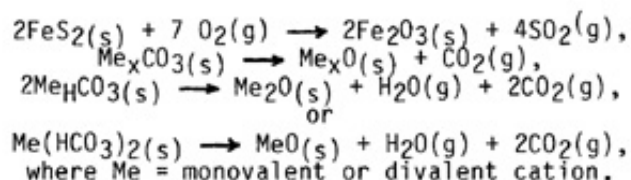
The predictive failure of the acid/base account is partially the fault of the technique. The acid/base account tends to overestimate both the acid potential and the neutralization potential. Because only pyritic sulfur contributes to acid drainage, the acid potential should be calculated from the pyritic sulfur rather than the total sulfur content. The total sulfur content has traditionally been used because it is simpler to determine.

The overestimation of the neutralization potential results from the fact that although all carbonate forms are soluble to some degree in strong acid, not all forms are soluble in the mine environment. Therefore, only some unknown proportion of the predicted neutralization potential would actually exist at a given mine site.

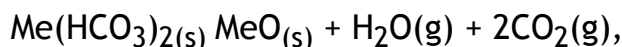
This study was undertaken to develop analytical methods that would improve the predictive capability of the acid/base account. The first step was to improve the selectivity of analyses typically employed by the acid/base account. An ideal analytical procedure would be one that quickly and directly determine the pyritic sulfur responsible for acidity and the carbonate species responsible for alkalinity under field conditions. A previous study (3) has indicated that the technique conventionally used for total sulfur determinations (combustion furnace ignition with infrared SO₂ detection) can be made more selective by operating at lower temperatures. For example, at 5000 C only SO₂ from the combustion of pyritic and organic sulfur is detected because sulfate sulfur is stable at this temperature. In noncarbonaceous samples where the organic sulfur content is negligible, the low temperature technique results in the direct determination of pyritic sulfur. Later studies (4,5) that monitored the evolution Of SO₂ with respect to temperature indicated that samples with low SO₂ initiation temperatures were more reactive and generated more acid in laboratory weathering tests.

A technique capable of distinguishing and quantifying different carbonate minerals has been developed (6). This method distinguishes carbonate minerals on the basis of the different dissociation rate each displays in strong acid. Although effective, this method requires an additional set-up and procedure.

The evolved gas analysis (EGA) technique used in this study is capable of simultaneously quantifying pyrite and various carbonate minerals in a single run. The EGA method monitors the evolution Of SO₂ and CO₂ that results from the following reactions:



or



where Me = monovalent or divalent cation.

The type of gas and temperature of evolution is characteristic of the mineral or compound giving rise to the evolution. Therefore, minerals can be tentatively be identified by the temperatures at which certain gases are evolved. The amount of a particular mineral present in a sample is proportional to the partial pressure of the gas evolved.

Evolved gas analysis may improve the predictive capability of the acid/base account by:

1. determining pyritic sulfur more quickly than conventional ASTM sulfur forms speciation; and
2. providing neutralization potentials based only on carbonates species that are known to be soluble under a given set of field conditions.

METHODS

An instrument designed specifically for evolved gas analysis was assembled for this study. A schematic of this instrument (fig. 1) reveals that it is a improved version of an evolved gas instrument constructed by LaCount and others (7). Major components include an electronic mass flow controller/gas blender, a programmable tube furnace, a quadrupole mass spectrometer, a programmable analog to digital (A/D) converter, and a microcomputer.

The electronic mass flow controller/gas blender can provide selectable flow rates from 0.1 to 200 mL/min. It can also provide two component gas mixtures ranging from 0.1 to 99.9

percent. In this study, a 10.0 percent oxygen/90.0 percent nitrogen mixture was introduced into the tube furnace at a flow rate of 100 mL/min.

Three hundred milligrams of -60 mesh sample was diluted with 3g of tungsten oxide to aid uniform heating. The sample was then placed in a 2.54 cm diameter by 50 cm long quartz tube and secured with either glass wool or quartz wool depending upon the maximum temperature. A 32 mm (1/8 in), Type K thermocouple was inserted into the sample and the tube was placed in the furnace. Output from the thermocouple was conditioned by a linearizer and then an A/D converter.

The tube furnace used for this study was capable of performing two heating ramps with selectable heating rates, dwell temperatures, and dwell times. The heating ramps used in this study are illustrated in figure 2. Initiating at about 70⁰C, the sample was heated at a rate of 6⁰C/min until 380⁰C was attained. The heating rate was then decreased to 3⁰C/min until 720⁰C where each run was terminated.

Evolved gases were detected with a quadrupole mass spectrometer. The inlet to the capillary comprising the atmospheric pressure sampling system was placed immediately downstream from the sample. This placement minimized lag time between gas evolution and detection. The mass spectrometer has the capability of simultaneously monitoring the ion current at 12 user-selected mass to charge ratios (M/e). The ion current is then converted to partial pressure by multiplying by a calibration factor for each gas. Gases typically monitored include: SO₂ (M/e = 64), CO₂ (M/e = 44), COS (M/e = 60), H₂O (M/e = 18), H₂S (M/s = 34), O₂ (M/e = 32 , and C₂H₆ (M/e =30). The partial pressures of all monitored gases were transmitted to a microcomputer upon receipt of a prompt that was generated by the programmable A/D converter for each 1.50 C increase in temperature. Run time, temperature, and gas partial pressures were converted to ASCII files and written to floppy disk. Periodically, these files were transferred to a mainframe computer where graphics, gaussian peak fitting, and peak integration were performed using library functions.

RESULTS AND DISCUSSION

Pyrite Determination

Initial efforts in this study were directed toward resolving SO₂ peaks resulting from the oxidation of pyrite from those attributable to the combustion of organic sulfur. Figure 3 is a SO₂ thermogram of the Rasa Coal from Yugoslavia which contains 8.67 percent organic sulfur and 0.08 percent pyritic sulfur. Because the pyritic sulfur content is two orders of magnitude below the organic sulfur content, this sample provides a good EGA characterization of organic sulfur in coal without the usual pyrite interferences. SO₂ peaks at 325⁰C and 475⁰C are due to the combustion of organic sulfur. A CO₂ thermogram of the same sample (fig. 4) exhibits CO₂ peaks at 325⁰C and 475⁰ C that are known to represent the combustion of aliphatic and aromatic hydrocarbons, respectively (8). The coincident evolution Of SO₂ and CO₂ can be seen by comparing figures 3 and 4. However, less SO₂ evolution accompanies CO₂ evolution at 325⁰C (aliphatic hydrocarbons) than at 475⁰C (aromatic hydrocarbons). A study by LaCount and others (8) has shown that the evolution of sulfur dioxide at 320⁰C is due to the oxidation

of sulfur in nonaromatic structures whereas the SO₂ evolution near 480°C is due to the oxidation of thiophenic and aryl sulfide type structures.

Standards of hydrothermal and coal pyrite were tested to determine the temperature range for sulfur dioxide evolution. Hydrothermal pyrite from the Noranda Mine in Quebec, Canada evolved SO₂ between 430°C and 520°C with the predominant peak at 485°C (fig. 5). A sample of hydrothermal pyrite from Rico, Colorado also displayed a prominent SO₂ peak at 485°C (fig. 6). Unlike the Noranda Mine sample, this pyrite also exhibited a small but well-resolved SO₂ peak at 440°C. Because hydrothermal pyrite evolves SO₂ in the same temperature range as organic sulfur, the two species could not be distinguished if present in the same sample.

Coal pyrite standards were obtained as the sink fraction from the heavy media (bromoform) separation of pyritic coal. Combustion furnace analysis indicated that these concentrates contained greater than 90 percent pyrite. Two SO₂ peaks attributable to the oxidation of coal pyrite (fig. 7) occur at about 380°C and 430°C. One or both peaks may be present but the 430°C peak generally predominates. Exceptions have been noted where the 380°C peak is the sole peak (fig. 8) or the predominant peak (fig. 9). EGA studies of bituminous coal (9) and pyritiferous shale (10) have shown similar results despite the fact that different experimental conditions were used (33 percent O₂, 300 mL/min. flow)

Initially, samples in this study were heated at a constant rate of 60°C/min. At this heating rate, the SO₂ peak due to organic sulfur (fig. 8, 475°C) was barely discernable and not suitable for quantitation. By reducing the heating rate to 30°C/min at temperatures above 380°C, the organic sulfur component was partially resolved (fig. 10). The application of a gaussian peak fitting routine may result in the resolution of two pyritic sulfur and one organic sulfur peak.

There are two ways to calculate the pyrite content from EGA data. The first method is to determine the amount of SO₂ evolved that is attributable (based on temperature of SO₂ evolution) to pyrite and from that value calculate the amount of pyrite present. The advantage of this method is that only a SO₂ standard gas is required for calibration. This method does not account for the SO₂ adsorption/desorption effects from the sample matrix, tube walls, or capillary. Adsorption/desorption effects are compensated for in the second calibration technique. For this technique, a set of pyrite standards are prepared and run in the same manner as actual samples. A calibration curve (fig. 11) is made by plotting the SO₂ peak area attributable to pyrite versus pyrite content. The plot approached linearity over the range of 0.01 to 0.10 g pyrite.

Carbonate Determination

EGA can be used to distinguish three basic carbonate types. These include: the bicarbonates with CO₂ peaks between 100 and 200°C (fig. 12), the transition metal carbonates (fig. 13) which decompose between 220°C and 520°C, and the alkaline earth carbonates (fig. 14) that yield CO₂ between 220°C and 440°C and between 520°C and 660°C. Only the bicarbonates and alkaline earth carbonates are important to the acid/base account because the transition

metal carbonates are only slightly soluble under field conditions.

Bicarbonate determination is straightforward with adsorbed CO_2 being the only possible interference. At worst, the adsorbed CO_2 results in a sloping baseline on which the bicarbonate peak is imposed. The interference may be completely eliminated by holding the temperature at 1000°C until CO_2 desorption abates before beginning the bicarbonate analysis. A calibration curve plotting CO_2 peak area ($100\text{--}200^\circ\text{C}$) and sodium bicarbonate content (fig. 15) is linear indicating that EGA may be a useful technique for bicarbonate determination.

The quantitation of alkaline earth carbonates (CaCO_3 , Na_2CO_3 and K_2CO_3) is more difficult. All alkaline earth carbonates evolve CO_2 above 550°C and in the same temperature range as transition metal carbonates and organic combustion ($300\text{--}500^\circ\text{C}$) (Fig. 16). The decomposition peak at 600°C is solely attributable to alkaline earth carbonates. Therefore, any quantitation of alkaline earth carbonates without interference must be made using this peak. However, if only this peak is used for quantitation, not all CO_2 evolution attributable to alkaline earth carbonates is determined. Accurate quantitation can only be achieved if the CO_2 peak at 600°C is proportional to the alkaline earth carbonate content. This would indicate that the ratios of the 600°C peak area to the peak area for the 300°C to 500°C peak is constant for all alkaline earth carbonate standards. A linear relationship between the peak area for the 600°C CO_2 peak and the alkaline earth carbonate content indicates that the ratio is constant and EGA may be used for this analysis.

CONCLUSIONS

Evolved gas analysis may provide a relatively simple and quick method for determining the pyrite, bicarbonate, and alkaline earth carbonate content of overburden samples. All analyses are performed on single sample in one run. The method can discriminate species that are critical to the acid/base account (pyrite, bicarbonates, and alkaline earth carbonates) from species that should be excluded (organic sulfur and transition metal carbonates). Use of the EGA technique may improve the predictive capability of the acid/base account.

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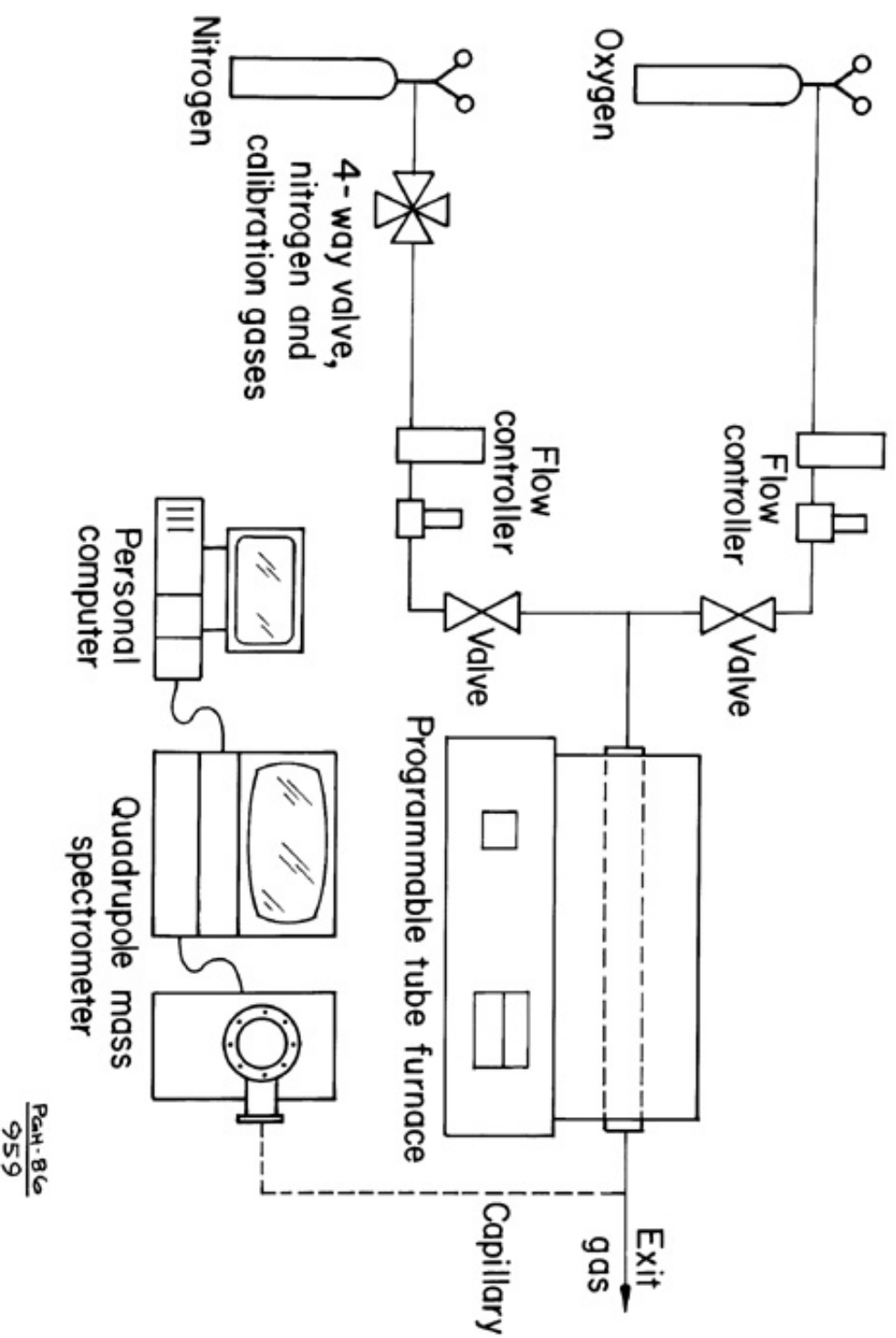


Figure 1. Diagram of an evolved gas analysis instrument.

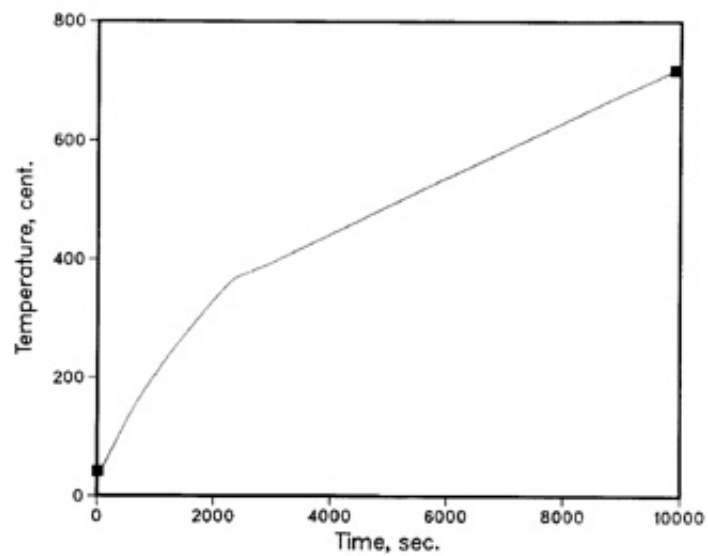


Figure 2. Furnace Program.

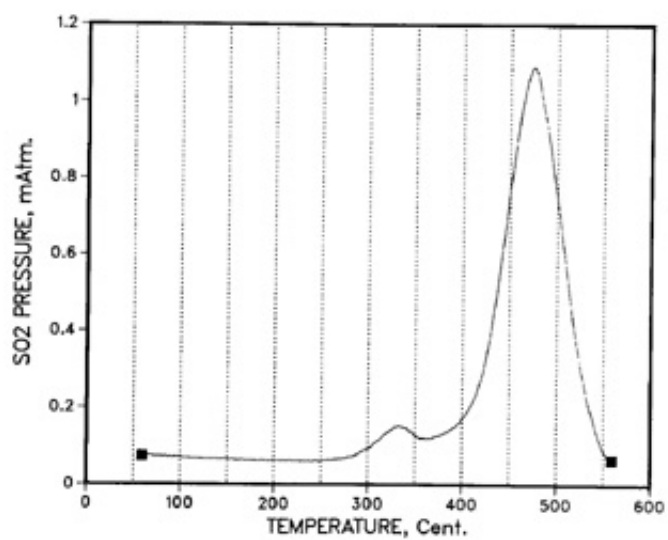


Figure 3. SO₂ thermogram of a coal containing 8.67 pct. organic sulfur.

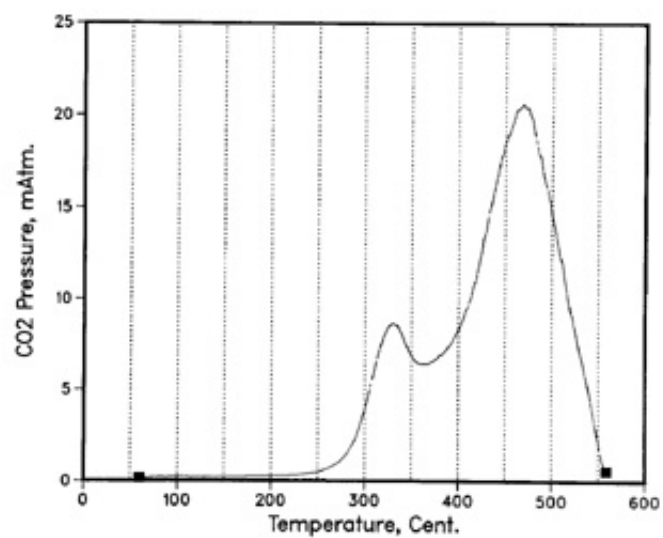


Figure 4. CO₂ thermogram of same coal as figure 3.

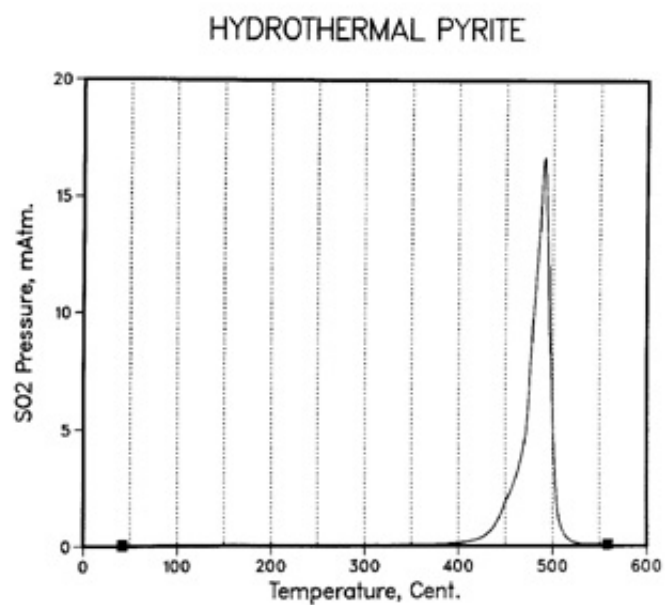


Figure 5. SO₂ thermogram of hydrothermal pyrite from Noranda Mine, Quebec, Canada.

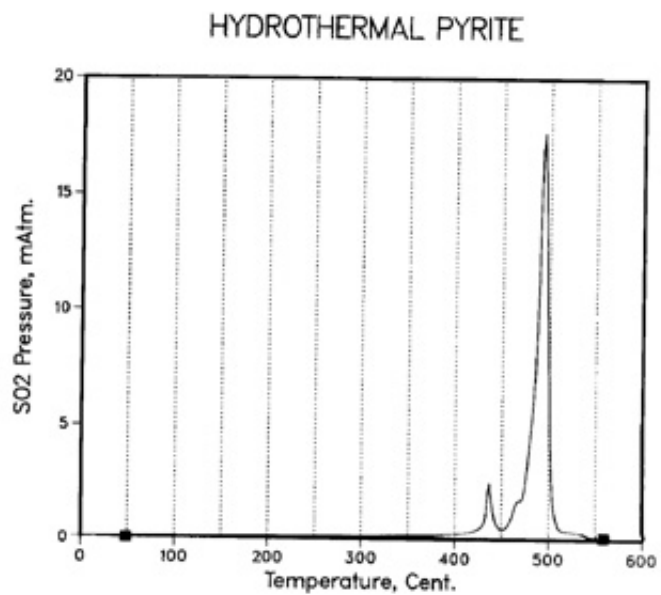


Figure 6. S₀₂ thermogram of hydrothermal pyrite from Rico, Colorado.

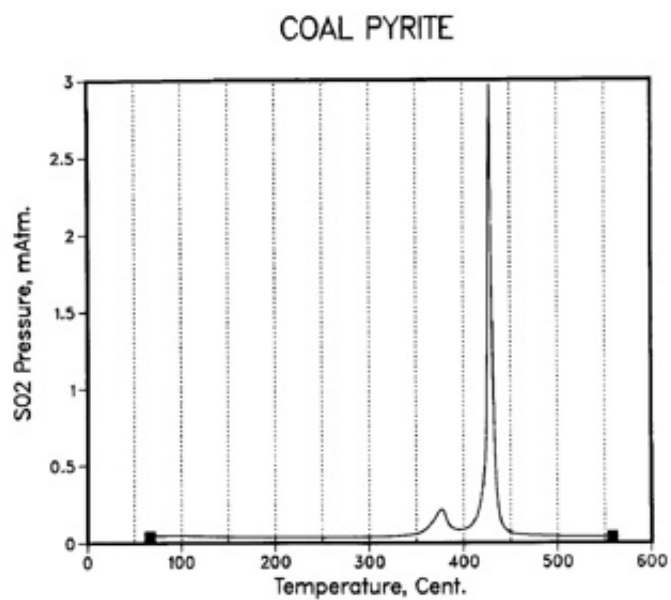


Figure 7. S₀₂ thermogram of coal pyrite concentrate.

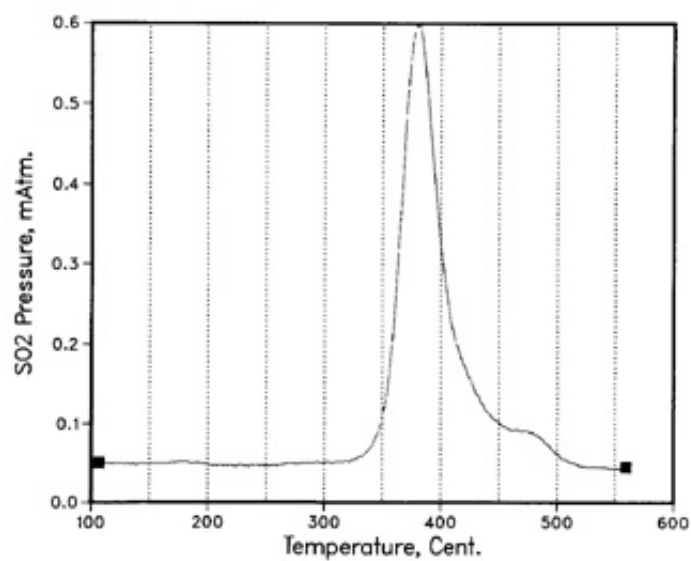


Figure 8. SO₂ thermogram of carbonaceous shale.

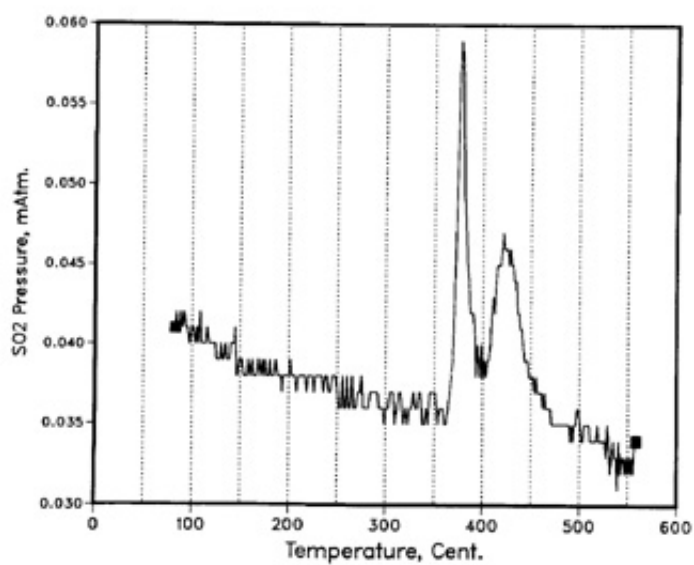


Figure 9. SO₂ thermogram displaying a predominant pyrite peak at 380° C.

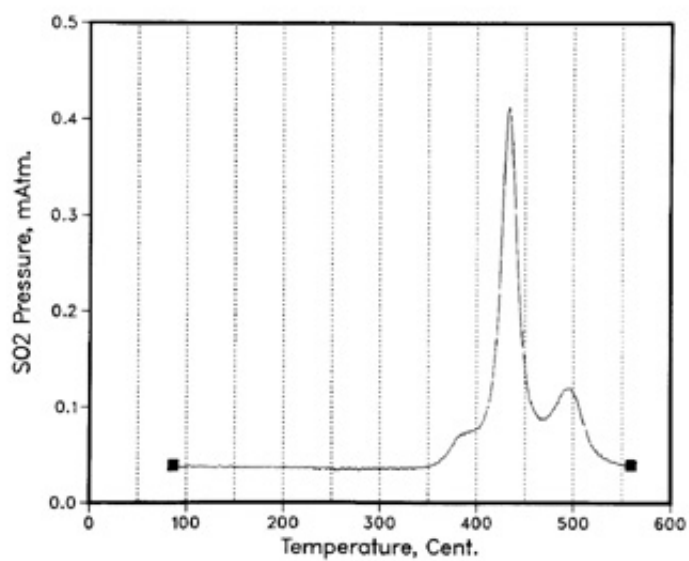


Figure 10. SO₂ thermogram of carbonaceous shale exhibiting two pyrite peaks (380° C, 440° C) and one organic sulfur peak (490° C).

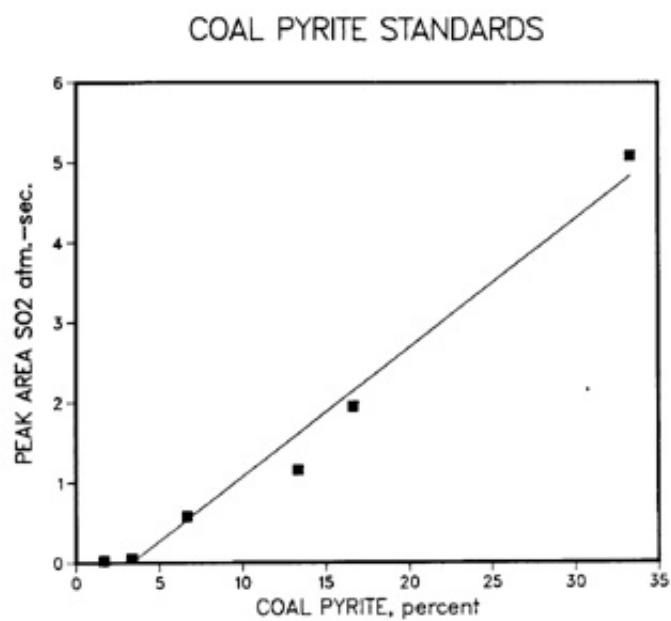


Figure 11. Calibration curve for pyrite standards.

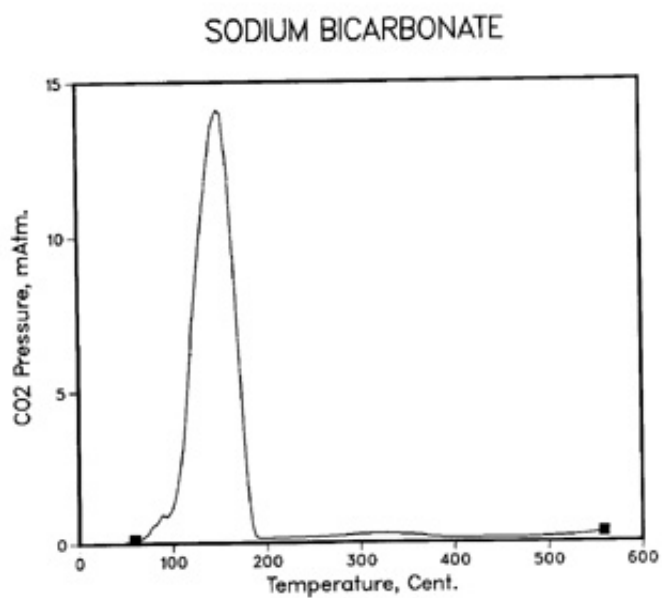


Figure 12. CO₂ thermogram of sodium bicarbonate standard.

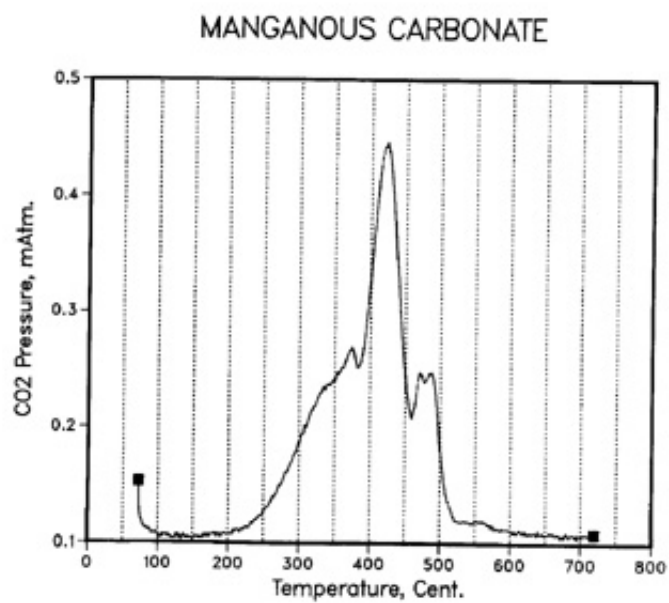


Figure 13. CO₂ thermogram of manganous carbonate standard.

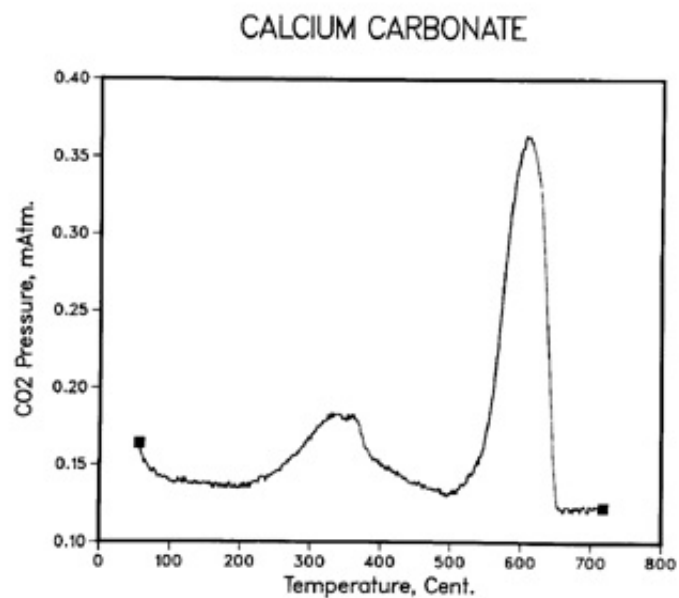


Figure 14. CO₂ thermogram of calcium carbonate standard.

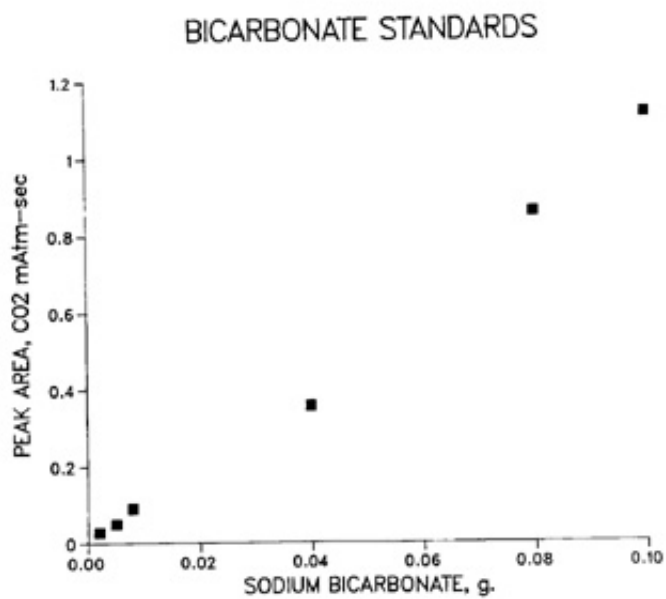


Figure 15. Calibration curve for sodium bicarbonate standards.

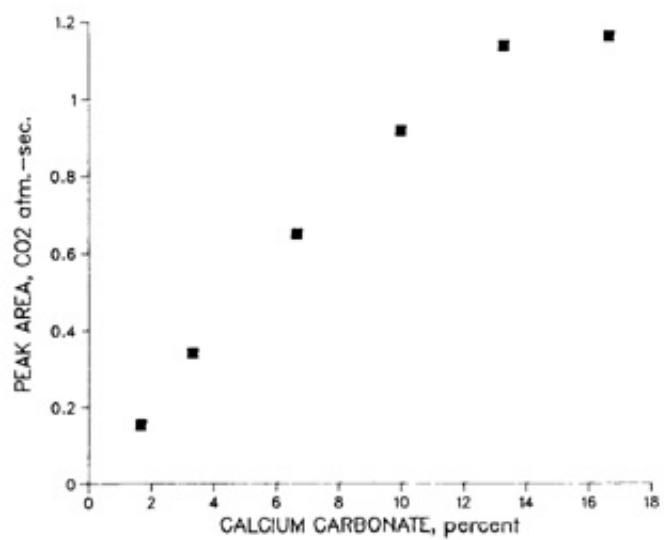


Figure 16. Calibration curve for calcium carbonate standards.