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THERMOMAGNETOMETRY AND EVOLVED GAS ANALYSIS IN THE IDENTIFICATION OF ORGANIC AND PYRITIC SULPHUR IN COAL AND OIL SHALE

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ABSTRACT

Potential difficulties of using a new TG/TM technique for measuring the pyrite content of coals that also contain siderite are discussed briefly. Direct measurement of the SO_2 evolved on heating pyrite in an oxidizing atmosphere is a possible alternative and this may also provide information on amounts of organic sulphur in the coal

INTRODUCTION

Recently, a new technique combining the proximate analysis/thermogravimetry method with thermomagnetometry has been established for the determination of the pyrite (FeS_2) content of American coals (1). Following conventional proximate analysis, the Fe_2O_3 resulting from pyrite oxidation in the ash is reduced to metallic Fe in flowing H_2. On reheating in O_2 the mass gain corresponding to Fe oxidation can be related to the original pyrite content of the coal. It has, however, been pointed out (2) that siderite ($FeCO_3$) decomposes to Fe-oxides within the same temperature range as pyrite (3) and, when these two minerals occur together in coal, a spuriously high pyrite content will be obtained from the mass gain of the H_2-reduced residual Fe. For American coals this is not a serious problem as it has been shown that Fe-yielding phases other than pyrite are not generally present (4) Siderite and ankerite ($Ca(Mg,Fe)(CO_3)_2$) are common in coals of other countries (4,5), although as the ultimate Fe-bearing decomposition product of ankerite is non-magnetic dicalcium ferrite (6), which is also stable in H_2, the mineral should not affect the TM determination of pyrite.

There is still, therefore, scope for research into new methods for pyrite determination in coal and, as the utilization of coal generally involves heat, the potential for thermo-analytical techniques is considerable. One such method is the direct analysis of SO_2 evolved from pyrite on heating in an oxidizing atmosphere. Studies on oil shales in the BGS laboratories using non-

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dispersive IR detectors to measure evolved volatiles (7) have shown that this is a promising method which has the additional benefit of providing information on the amount of sulphur bound by the organic fraction ('organic S').

MATERIALS AND METHODS

Materials examined were a low-grade oil shale from the Jurassic Kimmeridge Clay Formation of the UK and a suite of Permian bituminous coals from a locality in Australia. Volatile (SO_2, CO_2, CO) evolution profiles were obtained by heating a thin layer of the powdered material in a flowing gas stream (2·1 N_2:O_2) which then passed through non-dispersive IR detectors for the three volatiles arranged in series. The detectors were calibrated using standard gas mixtures and amounts of volatiles evolved calculated from areas under the peaks on the evolution curves (7)

RESULTS

Volatile evolution profiles for the oil shale are shown in Fig 1. The SO_2 profile shows an initial peak at 300°C representing oxidation of organic S. The complex SO_2 evolution peak system above 350°C is related to oxidation reactions of pyrite (8). By measuring the amount of SO_2 evolved below and above the dashed line in Fig.1, a value of 0.19% was obtained for the organic S content and 1.5% for the pyrite content on the basis of the oxidation reaction

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 .$$

The similarity between the SO_2 and CO_2/CO profiles in Figs. 1 and 2 strongly suggests that the rate of SO_2 evolution is dependant on the rate of carbon combustion. It may be seen from the scale on Fig. 2 that the volume of CO_2/CO evolved is at least an order of magnitude greater than that of SO_2 and so may physically 'flush' the SO_2 from the sample

The dependence of SO_2 evolution on the rate of carbon combustion is further illustrated by comparison of the volatile evolution profiles of a fresh coal (stored under N_2) with those of the same coal after four day's exposure to the laboratory atmosphere. In the fresh coal (Fig. 2a) the sharp low-temperature peaks on the CO_2 and CO profiles are matched by an equally sharp peak on the SO_2 profile. However, these peaks are lacking on the volatile evolution profiles for the exposed coal (Fig. 2b), although an initial broad peak occurs on the SO_2 evolution profile within the same temperature range as that assigned to oxidation of organic S in Fig. 1 The large, sharp peak on the SO_2 profile at ~380°C on both Figs. 2a and b could be due to pyrite oxidation but, if so, it occurs at an appreciably lower temperature than in the oil shale. This is a consequence of the strongly exothermic nature of the carbon oxidation which causes the sample temperature to rise much faster than programmed at the heating rate used, with a subsequent loss of the strict temperature control which is probably necessary to differentiate between the SO_2 generated from organic and inorganic (pyrite) S. However, values for total S determined from the areas under the SO_2 evolution profiles for the seven coals examined showed good agreement with total S (organic and inorganic) values determined chemically (Fig 3).

CONCLUSIONS

From the limited results recorded above, continuous analysis of SO_2 generated on heating coal or oil shale in an oxidizing atmosphere should give reasonably values for total S contents but difficulties may be experienced in differentiating between organic and inorganic sulphur contents. Peak deconvolution techniques applied to the SO_2 evolution profile may help to some extent but it is apparent that the configuration of this is markedly affected by the rate of release from the sample of CO_2 and CO resulting from combustion of the organic material. In addition, the markedly exothermic nature of this combustion causes a rapid increase in sample temperature, resulting in premature oxidation of pyrite and consequent merging of SO_2 peaks due to organic and inorganic S Work is continuing to resolve these problems

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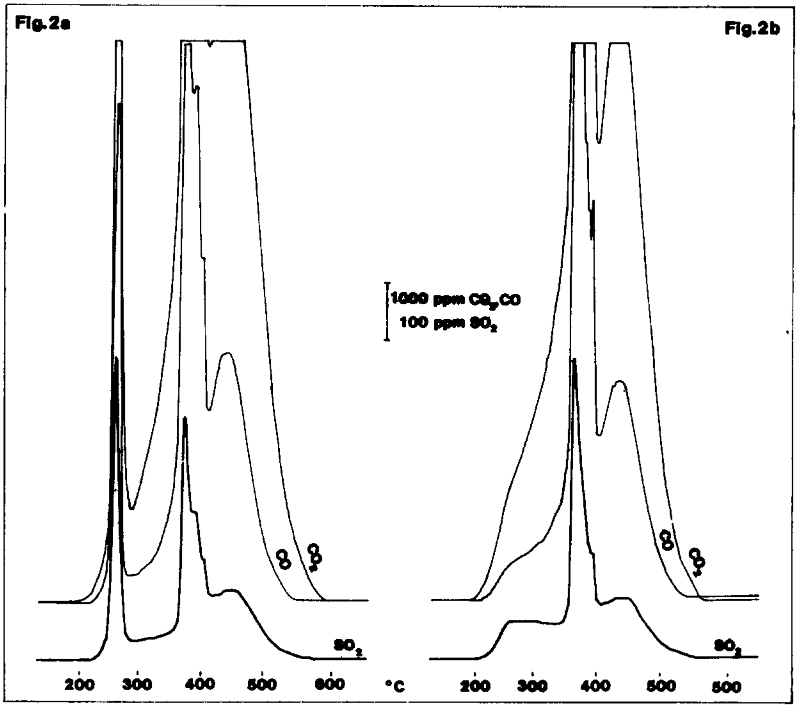

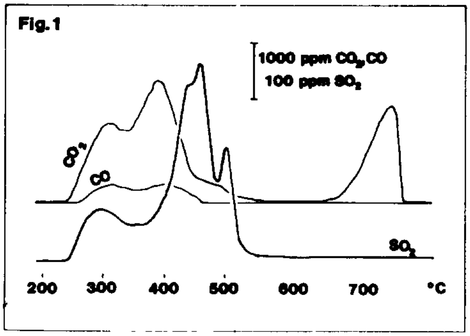

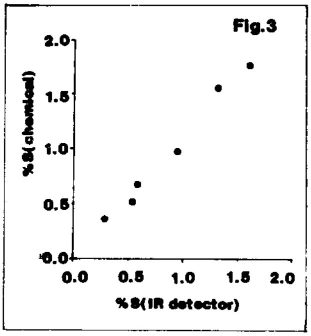

FIG.1. Volatile evolution profiles for oil shale Sample weight 119 mg, heating rate 10°C/min, carrier gas 2:1 $N_2:O_2$ at 300 ml/min. Sensitivity ranges of detectors : CO_2, CO 10,000 ppm fsd; SO_2 1000 ppm fsd.

FIG.2. Volatile evolution profiles of (a) 'fresh' and (b) 'exposed' bituminous coals. Sample weight 70 mg, other experimental details as in Fig. 1.

FIG.3. Total S from chemical analysis vs. total S from SO_2 evolution curves for bituminous coals.