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Determination of evolved gas transfer time from a thermoanalyser to a coupled gas detection system using pyrite oxidation

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Abstract

A method is described in which the time taken for molecules evolved during simultaneous TG–DTA analysis to travel from the sample crucible to an evolved gas analysis (EGA) detector, defined as the transfer time, τ, may be determined. It involves heating a <45 μm fraction of pyrite to about 550°C at a rate of 2.5°C $\min^{-1}$ in air flowing at rates ranging from 8 to 91 $\text{cm}^3 \min^{-1}$ in a thermal analyser and passing the SO_2 evolved into a Fourier transform infra-red (FTIR) or mass spectrometer (MS). Two sharp exothermic events occurred in the region 455–475°C which corresponded to equally sharp peaks in the FTIR and MS signals. The time shift between the DTA peak and the corresponding EGA peak was taken to be the transfer time and it was found that this increased with reduction in gas flow rate. For the equipment used in this experiment transfer times of SO_2 produced during the two events agreed within experimental error for gas flows down to 20 $\text{cm}^3 \min^{-1}$ but significant differences were measured for lower flow rates. This method should be useful in determining the transfer times of any combination of thermal analyser and FTIR or MS, provided the thermal analyser has a DTA detector. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Transfer time; Thermal analysis coupled with mass spectrometry; Thermal analysis coupled with FTIR; DTA; Pyrite

1. Introduction

Evolved gas analysis commonly involves the coupling of thermal analysis (TA) instruments to other techniques such as mass spectrometry or Fourier transform infra-red (FTIR) spectrometry. Gas molecules evolved during a desorption or decomposition process are swept through a transfer line connecting the TG equipment with the MS or FTIR detector. The time taken for the molecule to be swept from the sample surface to the detector is defined as the transfer time. This will be determined by the volume of the balance chamber, the length of the transfer line and, in the case of FTIR, by the volume of the gas cell as well as the purge gas flow rate. A molecule detected at a given time t_d would have been generated at time t_s. Hence

$$t_d - t_s = \tau, \qquad (1)$$

where τ is the transfer time.

Kaiserberger and Post [1] have qualitatively described the influence of instrument design and purge gas flow rates on the signals in thermal analysers coupled with mass and FTIR spectrometers and gas chromatographs. Maciejwski and Baiker [2] experimentally determined the effect of the amount of analyzed species, carrier gas flow rate and carrier

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gas properties on the shape and intensity of MS signals in an STA–MS system. They did this by decomposing selected compounds or by injecting slugs of analyte gas into the purge gas stream and found the mass spectrometric signal of a defined volume of CO_2 increased linearly with decrease in purge gas flow rate due to the reduced dilution. It follows that the sensitivity of the system can be increased by reducing the purge gas flow which could be important in analysing samples producing low amounts of evolved gas. Roduit et al. [3] developed a model which interrelated thermoanalytical and mass spectrometric curves based upon experimental studies using the decomposition of $CaCO_3$. They showed that the transfer (or residence) time reduces with increasing flow rate. They also showed the effect of carrier gas and analyte gas diffusivity on DTG and MS curve deviation.

The temperature at which a particular molecule has evolved from the sample at time, t_s, will be less than the sample temperature at the time the molecule reaches the detector, t_d, by an amount determined by the heating rate and τ. In kinetic studies of oil and gas formation from source rocks containing kerogen, evolution studies must be made using at least three different heating rates. In practice these heating rates range from one or two to several tens of degrees per minute [4]. In the case of the higher heating rates the temperature could be several degrees less at t_s than the sample temperature at the time t_d. Failure to account for this temperature difference can result in errors in the kinetic calculations using this information.

The work by Roduit et al. [3] determined theoretical transfer (or residence) times for a particular combination of thermal analyser and mass spectrometer system with different purge gas flow rates. However, experimental confirmation of these calculations requires a discrete decomposition reaction whose temperature is capable of being measured accurately and whose evolved gas is capable of being measured at very low concentrations. This investigation aims to provide a method of determining the transfer times for any combination of purge gas flow rate and thermal analyser and MS or FTIR evolved gas detection systems.

Most decomposition events occur over too large a temperature range for TG to be useful as "timing marks" in the determination of transfer time. However, Dunn et al. [5] have reported that pyrite of particle size <45 μm heated in air at a heating rate of 2.5°C min^{-1} exhibited a series of sharp exotherms in the DTA curve prior to a larger broad exotherm. Evolved gas analysis using FTIR or MS revealed that SO_2 is detected following each exothermic event; the EGA peak precisely matching the shape and duration of the preceding exothermic peak. The heating rate, atmosphere [5] and particle size [6] all affect the number and size of the sharp exotherms. The number of exotherms reduced as the heating rate increased above 2.5°C min^{-1} and practically disappeared at a heating rate of 20°C min^{-1}. Increasing the pyrite particle size reduced the number and size of the exotherms. For example, the sharp exotherms practically disappeared when the particle size was increased from <45 μm to 90–125 μm.

2. Experimental

A Netzsch STA409C Thermal Analyser equipped with a TG–DSC carrier was connected to a Bruker IFS55 FTIR spectrometer using a transfer line and gas cell heated to 200°C. The DSC detector was used in the DTA mode with an empty reference crucible for the purpose of this experiment. Gas flows were measured using a Fischer and Porter Precision Bore Flowrator FP 1/16 12G flowmeter. The absorbance integrated between 1416.0 and 1288.0 cm^{-1}, corresponding to the SO_2 stretching frequency, was determined every 3.9 s. Alternatively the STA was connected to a Balzers Thermostar quadrupole mass spectrometer (MS) using a 150 μm deactivated quartz capillary also heated to 200°C. The signal at 64 amu was acquired every 1.2 s.

Experiments were conducted using about 2.5 mg of pyrite (FeS_2) heated at 20°C min^{-1} up to 200°C and then at 2.5°C min^{-1} to 600°C. This combination of heating rates was used to reduce the total analysis time while preserving the essential slow heating rate at higher temperatures needed to produce the multiple exotherms. Air was used as a carrier gas flowing at 8, 13, 22, 34, 60 and 91 cm^3 min^{-1}. Since the EGA detectors collect data independently of the thermal analyser the data collection for the two instruments were commenced simultaneously.

3. Results and discussions

The rationalised DTA and FTIR results from the experiment conducted with an air flow of 60 cm^3 min^{-1} are shown together with the sample temperature in Fig. 1a. This figure illustrates a typical output for DTA and FTIR under the prevailing experimental conditions and shows three sharp peaks in the DTA and FTIR outputs in the region between 450°C and 500°C. When experiments are continued to higher temperatures a large exothermic peak appears subsequent to the appearance of the series of sharp peaks. However, this peak occurs over a relatively wide temperature range and is therefore of no use for the determination of transfer time. The peaks in the FTIR signal match the shape and position of the peaks in the

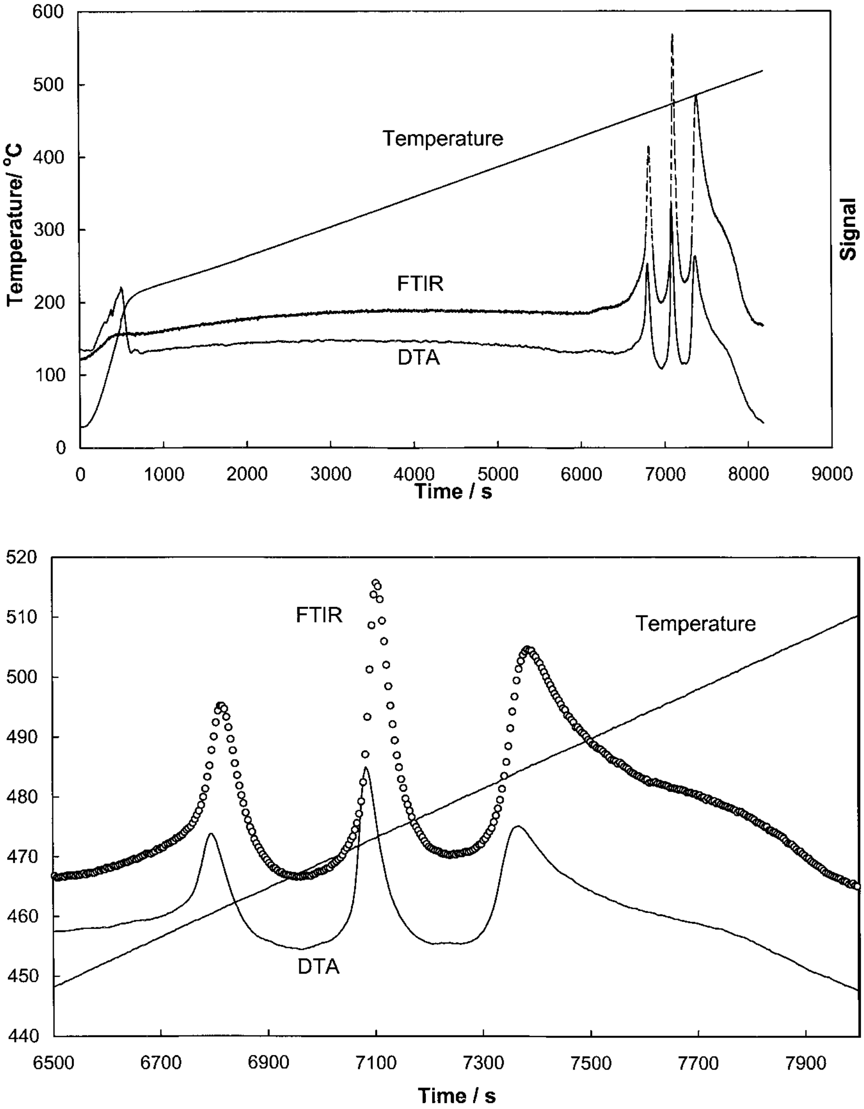

Fig. 1. Comparison of DTA and FTIR signals during pyrite oxidation from ambient to 520°C in an air flow of 60 cm^3 min^{-1}: (a) all data, (b) data from 6500 to 8000 s.

DTA signal confirming that the "bursts" of SO_2 correspond to the observed exothermic events. Expansion of the time scale in the region 6500–8000 s reveals a time displacement between the relevant FTIR and DTA peaks as illustrated in Fig. 1b. Here the difference between time of DTA peak 1, t_{s1} time of the FTIR peak 1, t_{d1} relates to the transfer time, τ_1,by:

$$t_{d1}-t_{s1}=\tau_1. \tag{2}$$

Similarly the second DTA and FTIR peak are used to calculate τ_2.

An experiment replacing the FTIR spectrometer with a mass spectrometer as evolved gas detector produced results shown in Fig. 2. This shows that oxidation of the pyrite once again resulted in three peaks in the MS signal matching the DTA exotherms closely in shape. It can be concluded that the resolution of evolved gas detection using either MS or FTIR matches that of the DTA detection system used.

The results for experiments using FTIR and MS spectrometers with an air flow of 13 $cm^3\ min^{-1}$ are shown in Figs. 3 and 4 respectively. When compared with the experiments conducted at an air flow of 60 $cm^3\ min^{-1}$ there was a larger displacement between the DTA and EGA peaks indicating a longer transfer time, τ. Broader EGA peaks resulting from experiments at the lower flow rate may be the result of the air flow being insufficient to sustain the rapid rate of oxidation. The third peak was most affected by this broadening with the result that it would not give reliable transfer times so has not been used in subsequent calculations.

The transfer times were determined by subtracting the peak of the relevant gas detector signal from the peak maximum of SO_2 exotherm. The transfer times at six different purge gas flow rates are given in Table 1 along with the results of replicate experiments that were performed. The results are depicted graphically in Fig. 5.

Where duplicate transfer times were determined they agreed within the data acquisition intervals of the EGA detector used, i.e. 1.2 s for the MS and 3.9 s for the FTIR. The transfer time for peak 2 would be expected to be the same as that of peak 1. While close agreement was observed for gas flow rates of 20 $cm^3\ min^{-1}$ and higher, the transfer times for peak 2 differed significantly from peak 1 at lower flow rates, being 25 s higher for the MS detector at 8 $cm^3\ min^{-1}$. Such differences may arise from back diffusion.

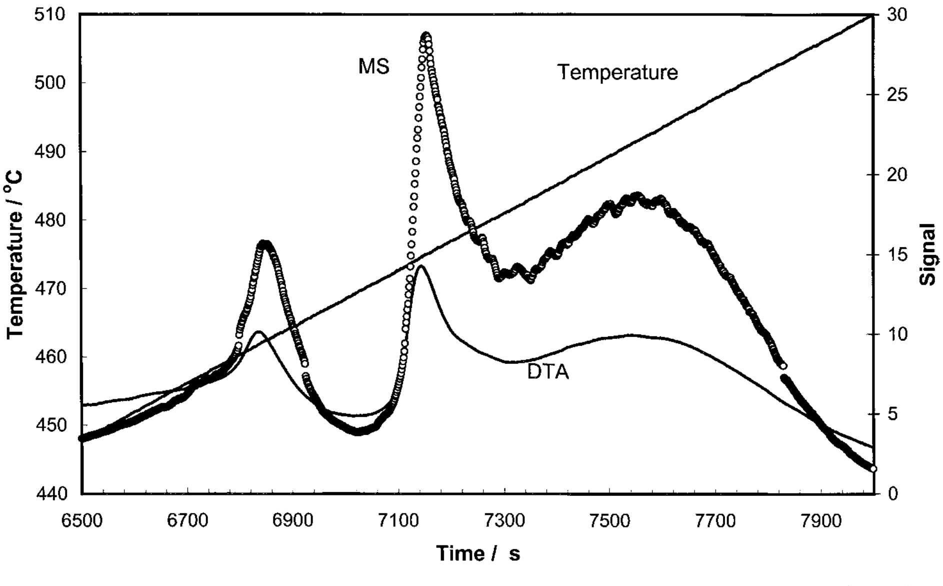

Fig. 2. Comparison of DTA and MS signals during pyrite oxidation from ambient to 520°C in an air flow of 60 $cm^3\ min^{-1}$ (data from 6500 to 8000 s).

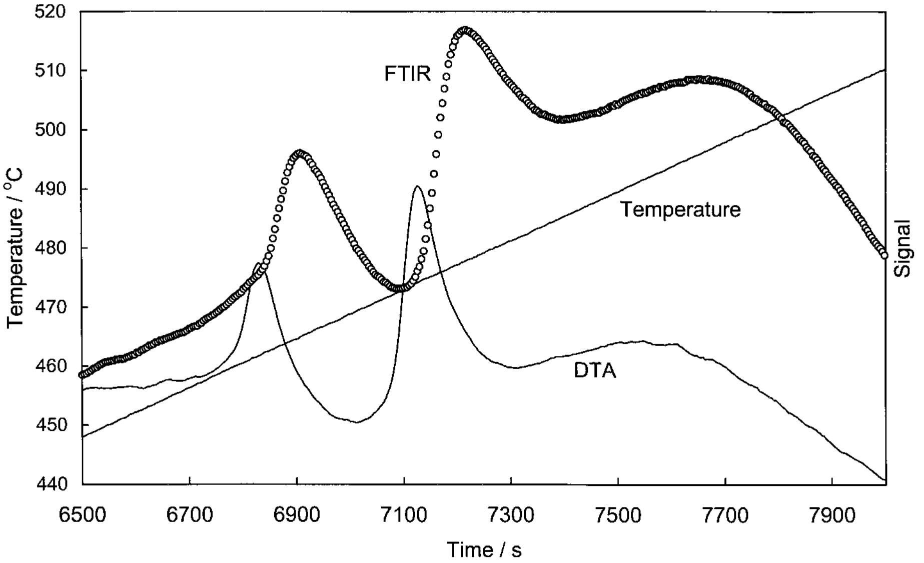

Fig. 3. Comparison of DTA and FTIR signals during pyrite oxidation from ambient to 520°C in an air flow of 13 cm^3 min^{-1} (data from 6500 to 8000 s).

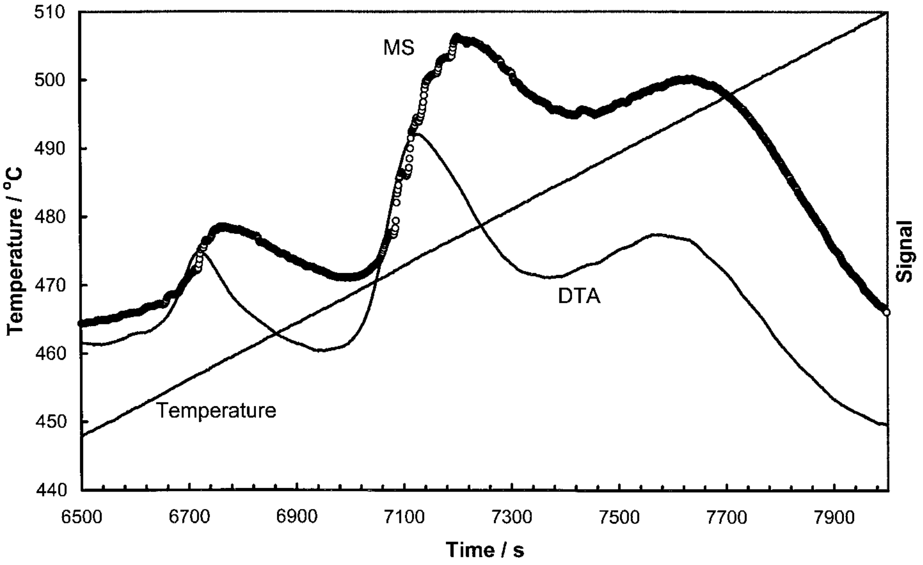

Fig. 4. Comparison of DTA and MS signals during pyrite oxidation from ambient to 520°C in an air flow of 13 cm^3 min^{-1} (data from 6500 to 8000 s).

4. Conclusion

The DTA of pyrite oxidised using the experimental conditions described combined with either FTIR or MS has been used to determine the transfer time of SO_2 evolved. When gas flows were increased from 8 to 91 cm^3 min^{-1} the transfer times reduced as did the reproducibility which became acceptable around flow rates of 20 cm^3 min^{-1} and higher. It should be possible to use this method for any combination of thermal and evolved gas analyser which includes a DTA detector.

Table 1
Effect of purge gas flow on transfer time for mass and IR spectrometers coupled to STA409C simultaneous thermal analyser

Flow rate (cm^3 min^{-1})	Transfer time (s)							
	STA–MS				STA–FTIR			
	Peak 1		Peak 2		Peak 1		Peak 2	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
8	64		89		131		156	
13	44		66		77		88	
22	37		42		45	41	45	45
34	25	26	29	28	37		37	
60	15		15		18	17	18	17
91	8		8		10	9	11	9

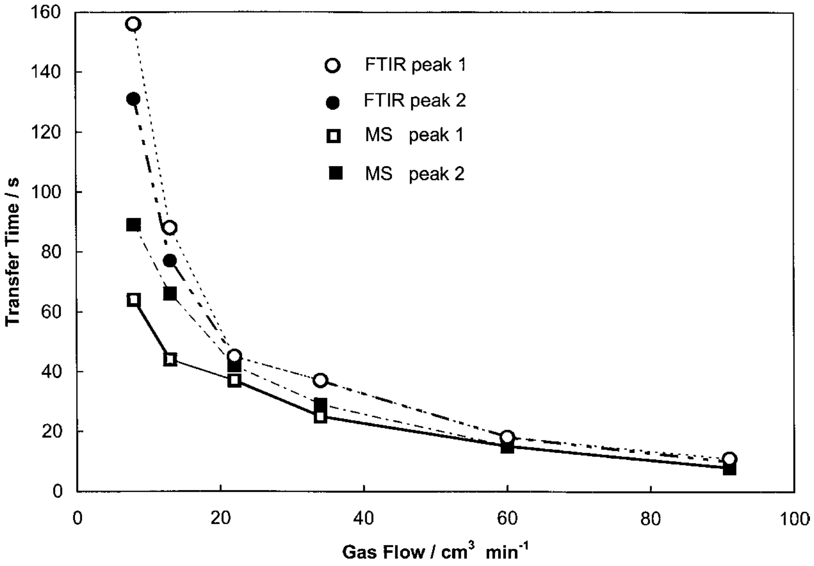

Fig. 5. Effect of purge gas flow rate on the transfer time of SO_2 evolved during pyrite oxidation.

Acknowledgements

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