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Quantitative calibration of a TPD–MS system for CO and CO_2 using calcium carbonate and calcium oxalate

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Abstract

A method is described for calibrating quantitatively a temperature-programmed decomposition, mass-spectrometric (TPD–MS) system by monitoring the gases evolved during the thermal decomposition of a chemical within the TPD reactor. A method for calibrating for evolved CO and CO_2 is described using the thermal decompositions of calcium carbonate and calcium oxalate. The method takes into account the production of CO^+ ions from CO_2^+ ions and secondary reactions in the thermal decomposition of calcium oxalate

INTRODUCTION

Evolved gas analysis by mass spectrometry (MS) has been used increasingly as a tool in thermal analysis, either on its own, where it is particularly useful for temperature-programmed decomposition (TPD) studies, or in combination with other techniques, e.g. thermogravimetry. Advantages of the TPD–MS technique include high sensitivity and specificity, but a disadvantage is that the method is difficult to calibrate for quantitative work. It is possible to calibrate a mass spectrometer against another pressure-measuring instrument by injecting a previously calibrated quantity of gas into the sampling port [1,2]. However, with such methods, it is difficult to simulate the dynamic pressure response and gas flows found in a TPD reactor.

In this paper we report a method for calibrating a TPD–MS system by monitoring the gases evolved during thermal decomposition of a known amount of chemical within the TPD reactor. This allows calibration of the spectrometer without reference to another pressure-measuring device. The method described is based upon calibration of CO_2 and CO evolved by decomposition of calcium carbonate and calcium oxalate. The method is

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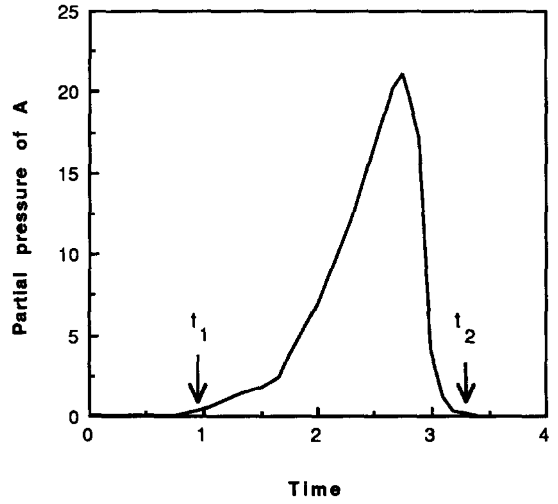

Fig 1. A schematic TPD–MS curve for evolution of a pure gas A.

relevant to quantitative TPD studies of the surfaces of coal chars and other carbon materials where oxygen-containing surface complexes are desorbed as CO and CO_2 [3]. In principle the method can be applied to other gases by following the temperature-programmed decomposition of solids from which they are evolved.

PRINCIPLES OF THE METHOD

Consider the evolution of a pure gas A from a TPD reactor; a schematic of the TPD curve in the form of pressure of A ($P_A(t)$) as a function of time (t) is shown in Fig. 1. Assuming ideal gas behaviour

$$P_A(t)Q_A = n_A(t)RT \tag{1}$$

where Q_A ($m^3\ s^{-1}$) is the pumping speed of the mass spectrometer vacuum system, $n_A(t)$ is the molar flux (mol s^{-1}) of gas A at the sampling port of the mass spectrometer at time t and temperature T, and R is the gas constant. A characteristic of diffusion pumps is that over a wide range of pressure their pumping speed is independent of total pressure [4]. Thus, Q_A can be assumed constant provided that the dynamic range of $P_A(t)$ is within the range where the pumping speed is constant. In such a case

$$Q_A\int_{t_1}^{t_2}P_A(t)\mathrm{d}t = RT\int_{t_1}^{t_2}n_A(t)\mathrm{d}t \tag{2}$$

where t_1 and t_2 are the starting and finishing times respectively of the TPD curve (see Fig. 1). The integral of the left-hand side of eqn. (2) is I_A, the area under the TPD curve, while the integral of the right-hand side of eqn. (2) is

N_A, the total number of moles of gas A evolved in the interval $t_2 - t_1$. Thus, eqn. (2) becomes

$$N_A = Q_A I_A / RT \tag{3}$$

The TPD–MS system may be calibrated by measuring I_A for a thermal decomposition reaction which gives rise to a known amount of gas N_A. In a mass spectrometer, P_A is measured as the ion current of the parent ion of gas A and, on commercial instruments, P_A is presented as a partial pressure of nitrogen. If this is so, eqn. (3) should be corrected for the sensitivity (S_A) of gas A relative to nitrogen [5]

$$N_A = K_A I_A \tag{4}$$

where $K_A = Q_A/RTS_A$. At a given temperature, K_A will be constant for a given experimental system, provided that Q_A and S_A are maintained constant. To apply eqn. (4) to a mixture of gases the interactions between the ionised components of the mixture must be understood so that the system can be calibrated for each evolved gas. This point is illustrated below for the calibration of CO and CO_2 using the decomposition of calcium oxalate.

EXPERIMENTAL

The experimental arrangement is similar to that described previously [6], except that a new quadrupole mass spectrometer (Spectromass Visa, Spectrum Scientific Ltd.) was used and interfaced with a microcomputer (Amstrad, Model PC1512DD) and programs were written for control of the experiments and data acquisition, and for the analysis.

The chemicals used were analytical grade calcium carbonate and anhydrous calcium oxalate. Samples of the chemicals in the range 10–60 μmol were outgassed in a quartz tube reactor to 10^{-5} Pa at 523 K and were subjected to TPD at a linear rate of heating of 150 K h^{-1} to 1273 K under high vacuum. The small sample sizes and low heating rate were chosen to ensure that the maximum total pressure during TPD was less than 10^{-2} Pa, the upper limit for linear response of the mass spectrometer, and to minimise the risk of re-adsorption of desorbed gases. This procedure also facilitates resolution of peaks in TPD curves.

RESULTS AND DISCUSSION

Calibration with calcium carbonate

The decomposition of calcium carbonate has been studied extensively by thermal analysis, e.g. see ref. 7. At high temperatures, CO_2 is evolved by the

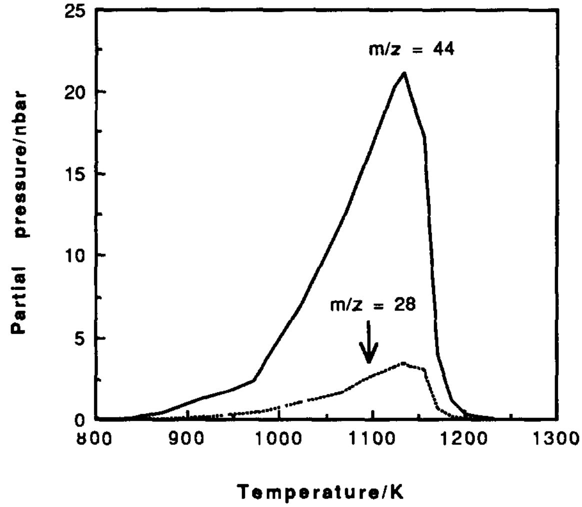

Fig 2 A typical TPD–MS plot for thermal decomposition of calcium carbonate under vacuum Heating rate 150 K h^{-1}.

simple reaction

$$CaCO_3 = CaO + CO_2 \tag{5}$$

In a typical TPD curve for calcium carbonate, Fig. 2, the major peak at $m/z = 44$ is due to the parent CO_2^+ ion and the minor peak at $m/z = 28$ is due to CO^+ ions formed by secondary fragmentation of CO_2^+. The relative abundance of CO^+ ions, f, may be estimated from $f = I_{CO}/I_{CO_2}$, where I_{CO} and I_{CO_2} are the areas under the TPD peaks for $m/z = 28$ and $m/z = 44$ respectively. The mean value and standard deviation of f, 0.114 ± 0.004, is within the reported range of f values for CO^+ ions in CO_2 mass spectra [8].

Applied to the evolution of CO_2 by thermal decomposition of calcium carbonate, eqn. (4) becomes

$$N_{CO_2} = K_{CO_2} I_{CO_2} \tag{6}$$

where N_{CO_2} is the molar amount of CO_2 evolved and I_{CO_2} is the area under the TPD curve for $m/z = 44$ in Fig. 2. If the thermal decomposition is quantitative, N_{CO_2} can be replaced by N, the number of moles of calcium carbonate. A plot of N against I_{CO_2}, Fig. 3, shows that the evolution of CO_2 from the TPD of calcium carbonate conforms to eqn. (6), with $K_{CO_2} = 12.00$ μmol Pa^{-1} s^{-1}. (To conform with eqn. (4), I values in this work were obtained by integration of the original partial-pressure–time data obtained from the mass spectrometer.)

Calibration with calcium oxalate

The decomposition of anhydrous calcium oxalate has also been studied extensively by thermal analysis, e.g. refs. 9–13. The reaction proceeds in two

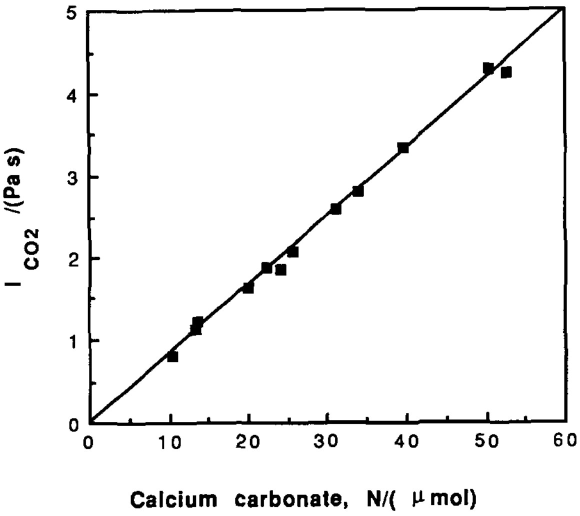

Fig 3 A plot of the area under the $m/z = 44$ curve (I_{CO_2}) in Fig. 2 as a function of the molar amount of calcium carbonate, N

stages

$$CaC_2O_4 = CaCO_3 + CO \quad \text{Reaction I} \tag{7}$$

$$CaCO_3 = CaO + CO_2 \quad \text{Reaction II} \tag{8}$$

In atmospheric air, reaction I is followed by oxidation of CO to CO_2

$$2CO + O_2 = 2CO_2 \tag{9}$$

If the thermal decomposition is carried out under high vacuum, then part of the CO derived from the first stage disproportionates [13]

$$2CO = CO_2 + C \quad \text{Reaction III} \tag{10}$$

Price et al. [13] found that the extent of reaction III varies widely. In agreement with Price et al., we found very fine carbon particles with the calcium oxide remaining after the decomposition of calcium oxalate.

A typical TPD curve for calcium oxalate is given in Fig. 4, which shows that the two stages of the thermal decomposition are resolved at the low heating rates used in this study. The major peak at $m/z = 28$ in the first part of the curve is due to CO produced by reaction I and the minor peak at $m/z = 44$ is due to CO_2 produced by reaction III. In the first stage of decomposition of calcium oxalate, the total molar amount of CO produced, N_{CO}, is given by

$$N_{CO} = N'_{CO} + 2N'_{CO_2} \tag{11}$$

where N'_{CO_2} is the molar amount of CO_2 produced by reaction III and N'_{CO}

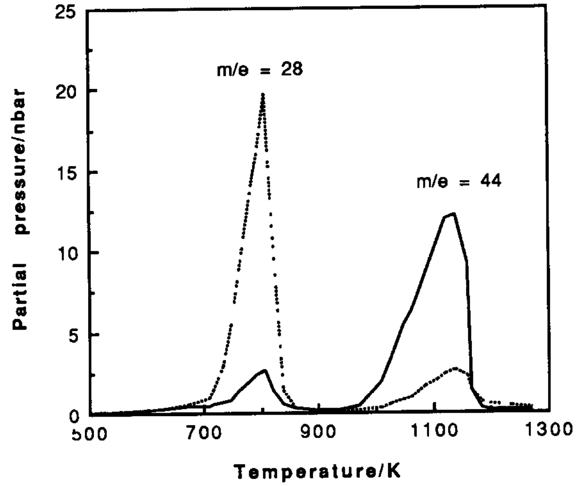

Fig. 4 A typical TPD–MS plot for the thermal decomposition of calcium oxalate under vacuum. Heating rate 150 K h^{-1}.

is the residual, molar amount of CO formed by reaction I. N'_{CO_2} is calculated from

$$N'_{CO_2} = K_{CO_2} I'_{CO_2} \tag{12}$$

where I'_{CO_2} is the area under the $m/z = 44$ curve in the first part of Fig. 4 and K_{CO_2} is obtained from the decomposition of calcium carbonate. Assuming that reaction I is quantitative, N_{CO} in eqn. (11) can be replaced by N', the molar amount of calcium oxalate. Values of N'_{CO_2} and N'_{CO} obtained from eqn. (11) are plotted as a function of N' in Fig. 5. The mean value of the ratio N'_{CO}/N' is 0.53, indicating that almost half of the CO produced in the first stage of decomposition of calcium oxalate disproportionates. Figure 5 also shows that the extent of disproportionation is insensitive to sample size.

Equation (4) applied to the evolution of CO in reaction I requires correction for the contribution to the $m/z = 28$ peak produced from secondary fragmentation of CO_2^+ ions

$$N'_{CO} = K_{CO}\left(I'_{CO} - fI'_{CO_2}\right) \tag{13}$$

where I'_{CO} is the area under the $m/z = 28$ curve in the first part of Fig. 4; the value $f = 0.114$ is obtained from the decomposition of calcium carbonate. Figure 6 shows that the evolution of CO in the first stage of the decomposition of calcium oxalate conforms to eqn. (13) with $K_{CO} = 10.67$ μmol Pa^{-1} s^{-1}.

In the second part of the TPD curve in Fig. 4, the major peak at $m/z = 44$ is due to CO_2 formed during reaction II, and the minor peak at $m/z = 28$ is partly due to CO^+ ions formed by secondary fragmentation of CO_2^+ ions, as in the case of the decomposition of calcium carbonate.

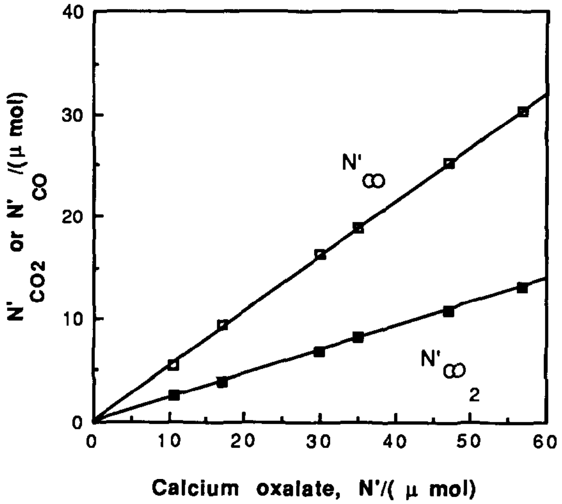

Fig. 5 A plot of the molar amounts of CO and CO$_2$, N'_{CO} and N'_{CO_2}, respectively, evolved during the first stage of the decomposition of calcium oxalate, Fig 4, as a function of the molar amount of calcium oxalate N'.

However, the relative abundance of CO$^+$ in the second part of the decomposition of calcium oxalate is higher than for the decomposition of calcium carbonate. This indicates that there is an additional source of CO in the second stage of decomposition of calcium oxalate. The source is most

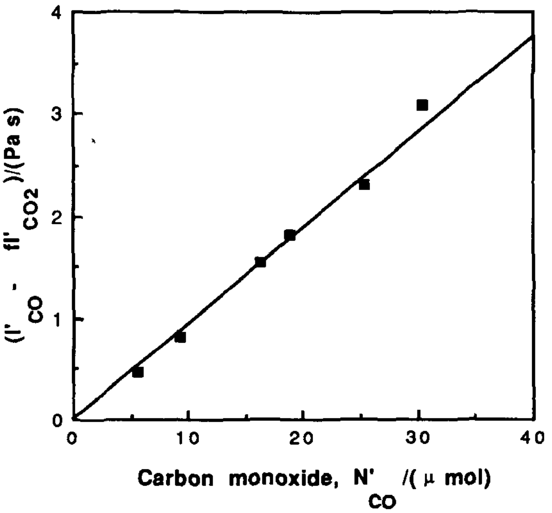

Fig. 6 The molar amount of CO evolved in the first stage of the decomposition of calcium oxalate N'_{CO} plotted as a function of eqn (13) I'_{CO} and I'_{CO_2} are the areas under the $m/z = 28$ and $m/z = 44$ curves, respectively, in the first stage of the decomposition

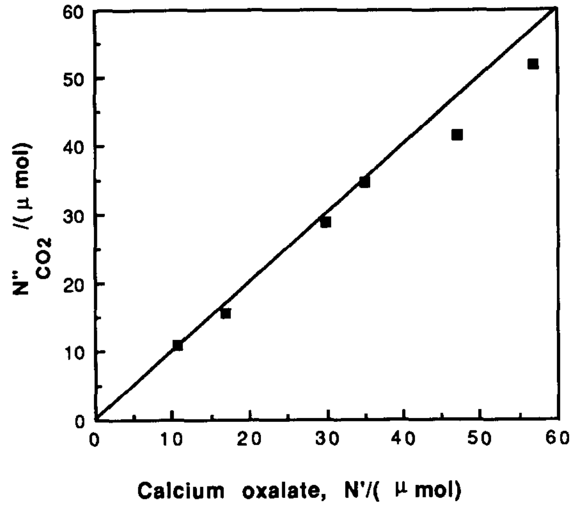

Fig. 7 The molar amount of CO_2 evolved in the second stage of the decomposition of calcium oxalate N''_{CO_2} as a function of the molar amount of calcium oxalate N'. Slope of the line = 1

probably gasification of carbon particles remaining after the first stage of decomposition, i.e. by the reverse of reaction III

$CO_2 + C = 2CO$ Reaction IV (14)

which is catalysed by calcium salts [14].

If gasification of carbon occurs in the second stage of the decomposition

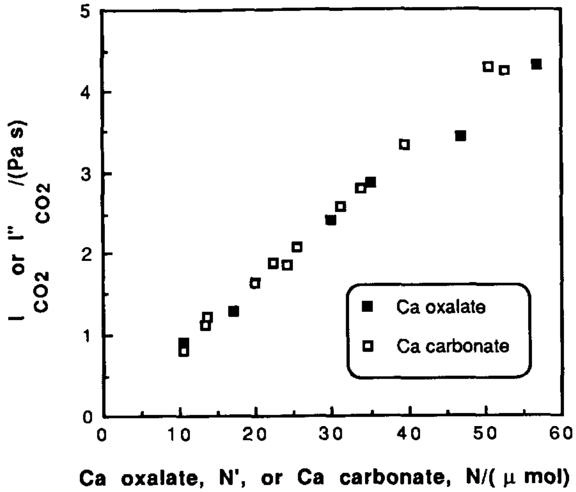

Fig. 8 A plot of the area under the $m/z = 44$ curve (I''_{CO_2}) for the second stage of the decomposition of calcium oxalate as a function of the molar amount of calcium oxalate (N') compared to the data in Fig 3 for the thermal decomposition of calcium carbonate.

of calcium oxalate, then the total molar amount of CO_2 formed, N_{CO_2} is given by

$$N_{CO_2} = N''_{CO_2} + 0.5N''_{CO} \tag{15}$$

where N''_{CO} is the molar amount of CO produced from reaction IV and N''_{CO_2} is the residual molar amount of CO_2. N''_{CO_2} is obtained from

$$N''_{CO_2} = K_{CO_2} I''_{CO_2} \tag{16}$$

where I''_{CO_2} is the area under the $m/z = 44$ curve in the second stage of the decomposition of calcium oxalate, Fig. 4. Values of N''_{CO_2} are plotted against molar amount of calcium oxalate N', in Fig. 7. N''_{CO_2} is clearly less than N', particularly when larger samples of calcium oxalate are used. The mean value of the ratio N''_{CO_2}/N' is 0.93, indicating a small extent of gasification of the carbon particles. If gasification of carbon is neglected, eqn. (16) becomes

$$N_{CO_2} = K_{CO_2} I''_{CO_2} \tag{17}$$

If the overall decomposition of calcium oxalate is quantitative, then N_{CO_2} can be replaced by the molar amount of calcium oxalate, N'. In Fig. 8, a plot of N' against I''_{CO_2} is compared with the data from Fig. 3 for the thermal decomposition of calcium carbonate. There is reasonable agreement between the two data sets when smaller amounts of the salts are used. However, for larger sample sizes the data for calcium oxalate fall below those for calcium carbonate as a result of reaction IV. Thus, although it is small, the extent of gasification of the carbon particles must be considered if an accurate calibration is to be achieved.

CONCLUSIONS

A method is described for calibrating a TPD–MS system by monitoring the gases evolved during the thermal decomposition of chemicals within the TPD reactor. The thermal decompositions of calcium carbonate and calcium oxalate are used to calibrate for evolved CO and CO_2. The two-stage thermal decomposition of calcium oxalate under vacuum is more complex than previously thought. Disproportionation of CO occurs during the first stage of the decomposition, as noted by Price et al. [13]. During the second stage of the decomposition, there is evidence for gasification of the carbon particles produced by disproportionation of CO in the first stage of the decomposition, particularly with large sample sizes. In addition to the above secondary reactions, it is necessary to correct for the production of CO^+ ions by secondary fragmentation of CO_2^+ ions, if a quantitative calibration is to be made.

The calibration constants, K_{CO_2} and K_{CO}, obtained in this study may be used, for example, to calculate the amounts of CO_2 and CO desorbed from a carbon or coal char surface by TPD of surface oxides [3]. The calibration constants are specific to the experimental system used in this study because, from eqn. (4), K_A is a function of the pumping speed of the mass spectrometer vacuum system, Q_A, and the sensitivity of the mass spectrometer to the gases being measured. However, the principles of this method can be applied to quantitative calibration of a TPD–MS system for any gas or gas mixture which can be evolved from a TPD reactor, provided care is taken to correct for any secondary reactions.

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APPENDIX· LIST OF SYMBOLS

f	relative abundance of CO^+ in mass spectrum of pure CO_2
I_A	area under TPD peak for pure gas A
I_{CO}, I_{CO_2}	area under $m/z = 28$ and 44 peak, respectively, for TPD of $CaCO_3$ (Pa s)
I'_{CO}, I'_{CO_2}	area under $m/z = 28$ and 44 peak, respectively, for 1st stage TPD of CaC_2O_4 (Pa s)
I''_{CO_2}	area under the $m/z = 44$ peak for 2nd stage TPD of CaC_2O_4 (Pa s)
K_A, K_{CO_2}, K_{CO}	proportionality constants for eqns. (4), (6) and (13), respectively (mol Pa^{-1} s^{-1})
$n_A(t)$	molar flux of gas A at time, t (mol s^{-1})
N, N', N_A	amounts of $CaCO_3$, CaC_2O_4 and pure gas A, respectively (mol)
N_{CO}, N'_{CO}	total and residual amounts of CO evolved in 1st stage TPD of CaC_2O_4, respectively (mol)
N_{CO_2}	total amount of CO_2 evolved in TPD of $CaCO_3$ (mol)
N'_{CO_2}	amount of CO_2 evolved by disproportionation in 1st stage of TPD of CaC_2O_4 (mol)
N''_{CO}	amount of CO evolved by gasification of carbon in 2nd stage TPD of CaC_2O_4 (mol)
N''_{CO_2}	residual amount of CO_2 evolved during 2nd stage TPD of CaC_2O_4 (mol)
$P_A(t)$	partial pressure of gas A at time t (Pa)
Q_A	pumping speed of mass spectrometer vacuum system (m^3 s^{-1})
R	gas constant (J K^{-1} mol^{-1})
S_A	mass spectrometer sensitivity for gas A

t	time (s)
T	temperature (K)

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