

## CHARACTERIZATION OF AN EXPERIMENTAL TPD–MS SYSTEM. QUANTITATIVE CALIBRATIONS

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### ABSTRACT

A simple TPD–MS device, which operates in a flow of helium at normal pressure, is described.

The system was checked to ensure that it was capable of performing quantitative analysis of evolved gases. Quantitative calibrations were obtained for a number of substances, both organic and inorganic. The influence of several operational variables, which were easily modified in our device, on the response of the system has also been studied.

Calibrations were obtained by fast injection into the system of the substances to be analysed. Since these calibrations were obtained in an unusual way, under conditions which are not exactly the same as those operating in real TPD experiments, their applicability to EGA has been tested.

### INTRODUCTION

Analysis of evolved gases (EGA) provides the source of information in temperature programmed desorption (TPD) studies. Accordingly, the analytical device ought to be considered one of the most important components of any TPD system. Three aspects are important in relation to EGA: the qualitative identification of desorbed products, their quantitative analysis, and, lastly, the fidelity of the recorded spectra to the chemical process occurring at the reactor.

Conventionally, gas chromatography (GC) has been the analytical technique used in TPD [1,2]. However, when more than one product is simultaneously desorbed, the application of GC has obvious limitations. In this case, EGA is necessarily discontinuous, which makes reliable quantitative and/or kinetic analysis difficult. Moreover, some problems may even arise in the qualitative identification of desorbed products.

For the past decade, mass spectrometry (MS) has proved to be an advantageous alternative to GC. On the one hand, MS allows an almost continuous pursuit of evolved gases, and on the other, structural information

concerning the desorbed gases can be obtained. Furthermore, MS is a suitable technique for isotopic studies of surface reaction mechanisms [3]. In fact, this technique has been used fruitfully in thermal decomposition studies of inorganic solids [4,5] and polymers [6].

Nevertheless, because MS requires low operation pressures, restrictive interfaces in the reactor-MS chain must be used, and, therefore, perturbations are introduced in the gas flow. These perturbations may disturb kinetic, quantitative and even qualitative information obtained from the TPD spectra. As a consequence, many TPD-MS experimental devices, operating both in vacuum [7-9] and in an inert gas flow at normal pressure [3,10], have only been used for qualitative purposes. Sometimes, kinetic parameters have been obtained from TPD-MS experiments: however, the fidelity of the recorded diagrams to the chemical reactions under study was not checked in these studies [11,12].

In the present paper, a simple TPD-MS device which allows reliable kinetic and quantitative studies of thermal desorption processes is described and a number of quantitative calibrations reported. Likewise, the influence of the operational variables on the response of the system has been studied. Finally, since the calibrations were made in a rather unconventional way, their applicability to the real TPD experiments is also discussed.

## EXPERIMENTAL

Solid ( $\text{MgCO}_3$ ), liquid (water, acetone) and gaseous ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{H}_6$ ) chemicals were used for the calibrations reported here. The chemical analysis of  $\text{MgCO}_3$  showed:  $\text{SiO}_2$ , 1.73%;  $\text{Fe}_2\text{O}_3$ , 1.12%;  $\text{Al}_2\text{O}_3$ , 0.32%;  $\text{CaO}$ , 0.98%;  $\text{MgO}$ , 43.55%: the weight loss by calcination was 50.50%. Water was distilled in our laboratory; the acetone was Merck AR grade. The gases were supplied by SEO.

The mass spectrometer was a Vacuum Generator, model 201. This magnetic deflection instrument, which incorporates a Faraday detector, can sweep the  $m/e$  range 12-240.

### *TPD-MS experimental device*

The experimental device described here operates in a flow of helium at normal pressure. As can be seen in Fig. 1, it basically consists of a primary circuit through which helium flows at 101.3 kPa (1 atm). The gas flow is regulated by valve  $V_1$ . This circuit includes the TPD reactor, R, heated by a furnace, F, the temperature of which may be controlled by a thermocouple, T. Connected to the so-called primary circuit, there is a device for preparation of the adsorbed phases in situ, i.e. box 1 within dotted lines, and the analytical device, box 2. The analytical device includes two valves,  $V_2$  and  $V_3$ .

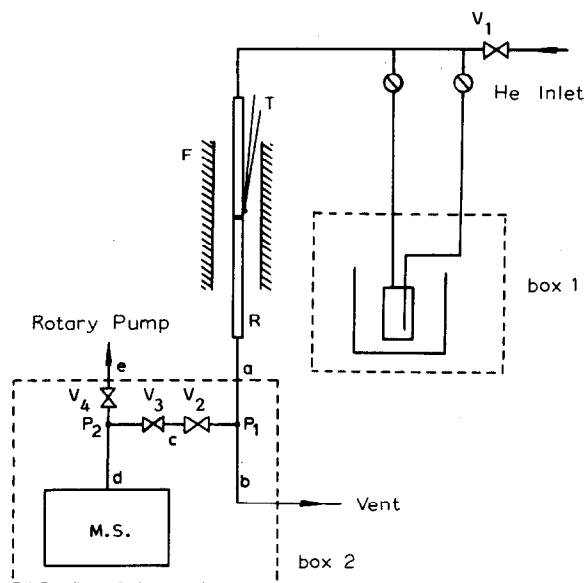


Fig. 1. TPD-MS experimental system. Box 1 device for preparation of the adsorbed phases in situ; box 2, analytical device.

the mass spectrometer and an auxiliary rotary pump, which is connected to the primary circuit-MS line through valve  $V_4$ . Valves  $V_2$  and  $V_3$  regulate the inflow to the analytical device, whereas the total pressure at the ionization chamber of MS is controlled by valve  $V_4$ .

The pipeline joining the reactor and MS is about 50 cm long and 2 mm in diameter. Conventional valves for fine regulation of gas flow were used.

## RESULTS AND DISCUSSION

### *Requirements for the quantitative analysis of evolved gases in a TPD-MS device*

The conditions to be fulfilled by a TPD-MS device in order to obtain reliable kinetic and quantitative results will be discussed on the basis of the following material balance.

For the device described in Fig. 1, at the initial instant,  $t = t_0$ , when the rate of desorption is zero and only the inert gas flows through the system, at point  $P_1$

$$S_{a0} = S_{b0} + S_{c0} \quad (1)$$

and at point  $P_2$

$$S_{c0} = S_{d0} + S_{e0} \quad (2)$$

$S_{i0}$  represents the helium flow rate (in mole per unit time) throughout  $i$  at  $t = t_0$ . Because  $S_{i0} = (P_{i0}B_{i0})/RT$ , where  $B_{i0} = (dV/dt)_{i0}$  is the rate of flow, eqn. (1) may be written

$$S_{a0} = \frac{P_{b0}B_{b0}}{RT} + \frac{P_{c0}B_{c0}}{RT} \quad (3)$$

If the desorption rate of  $x$  becomes significant, for  $t = t_1$ , at point  $P_1$

$$S_{a1} = \frac{P_{b1}B_{b1}}{RT} + \frac{P_{c1}B_{c1}}{RT} \quad (4)$$

which, when referred to the desorbed product  $x$ , becomes

$$S_{a1}(x) = \frac{P_{b1}(x)B_{b1}}{RT} + \frac{P_{c1}(x)B_{c1}}{RT} \quad (5)$$

A rather similar material balance might well be formulated at point  $P_2$ .

If flow is considered to be ideal, some desorbed product at a given instant,  $[dn(x)/dt]$ , will attain the point  $P_1$  without distortion, and therefore, for the general case  $t = t_i$

$$\left[ \frac{dn(x)}{dt} \right]_i = \frac{P_{b_i}B_{b_i}}{RT} + \frac{P_{c_i}B_{c_i}}{RT} \quad (6)$$

Taking into account that the thermal evolution of  $x$  is experimentally studied by its partial pressure at the ionization chamber of the MS,  $P_{MS}(x)$ , reliable desorption data will be obtained easily only if  $S_{ar}(x)$  and  $P_{MS}(x)$  are continuously linearly related. In this case,  $P_{MS}(x)$  would constitute a measurement of the desorption rate,  $dn(x)/dt$ , and therefore, upon integration of the  $P_{MS}(x)$  trace, an area linearly related to the amount of desorbed product,  $x$ , will be obtained. In accordance with eqn. (6), the foregoing requirement will be fulfilled when  $B_{ii}$  is constant for every  $i$  and  $t$ . In effect, since the distribution of the desorbed products along the different pipes depends on the corresponding  $B_{ii}$  values, the amount of  $x$  that reaches the MS will be linearly related to the amount of  $x$  generated at the reactor if  $B_{ii}$  is constant during the whole experiment.

When the TPD-MS device operates in an inert gas flow at normal pressure, the desorption reaction represents small changes on the total pressure, and, therefore, the foregoing condition may be easily satisfied.

It must be pointed out, however, that factors other than the variation of  $B_{ii}$  during the TPD experiment, which might also introduce distortions on the signal generated at the reactor, have not been considered. Nevertheless, factors like those related to the non-ideal behavior of the gas flow, although they can modify the shape of TPD diagrams, causing fidelity problems, do not affect the area under them and, therefore, the quantitative analysis of the evolved gases.

*Quantitative calibrations. Influence of the operational variables*

In order to verify that our TPD-MS device fulfilled the foregoing conditions, the response of the system against the injection of variable amounts of a number of different substances was studied (Table 1).

The quantitative calibrations were obtained by substituting the reactor, R, by a piece of pyrex glass with analogous geometric characteristics. At the height of the reactor bed, this piece has a small lateral pipe through which the gases and liquids to be analysed were injected into the so-called primary circuit. When solid samples were studied, the calibrations were obtained using the TPD reactor.

The following conditions, hereafter referred as to standard conditions (SC), were selected in order to obtain the corresponding calibrations: reactor temperature ( $T_r$ ), 298 K; flow of helium through the reactor ( $F_r$ ),  $0.55 \text{ cm}^3 \text{ s}^{-1}$ ; flow through the analytical device ( $F_a$ ),  $0.05 \text{ cm}^3 \text{ s}^{-1}$ ; total pressure at the ionization chamber ( $P_c$ ),  $9.3 \times 10^{-4} \text{ Pa}$ ; voltage at the ionization source, 70 V. These calibrations were drawn by fast injection into the primary circuit of variable amounts of the substances to be analysed. In every case, integration was performed upon the signal corresponding to the  $m/e$  values for which the maximum response was obtained. The amounts injected were always within the required range for analysing the desorbed products in real TPD experiments [13].

Since  $F_r$ ,  $F_a$  and  $P_c$  can easily be modified in our TPD-MS device, the influence of these variables on the quantitative response of the system may be studied, allowing optimization of the operational conditions in order to

TABLE 1

Quantitative response of the TPD-MS system to the fast injection of variable amounts of  $\text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_6\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{C}_3\text{H}_6$

Volume <sup>a</sup> ( $\text{cm}^3$ or $\mu\text{l}$ )	Area under the MS signal ( $\text{mV s}$ ) $\times 10^{-2}$				
	$\text{H}_2\text{O}$	$\text{C}_3\text{H}_6\text{O}$	$\text{CO}_2$	$\text{CH}_4$	$\text{C}_3\text{H}_6$
0.3		66			
0.4	230		360		
0.5			470	510	460
0.6	380	136	590		
0.8	530		750		770
0.9		203			
1.0	650	223	1000	960	950
1.5			1580	1410	1510
2.0			2090	1880	1930
2.5			2720	2290	2310
3.0			3140		
4.0			3850	3690	

<sup>a</sup> Water and acetone were injected as liquids (volume in  $\mu\text{l}$ ).

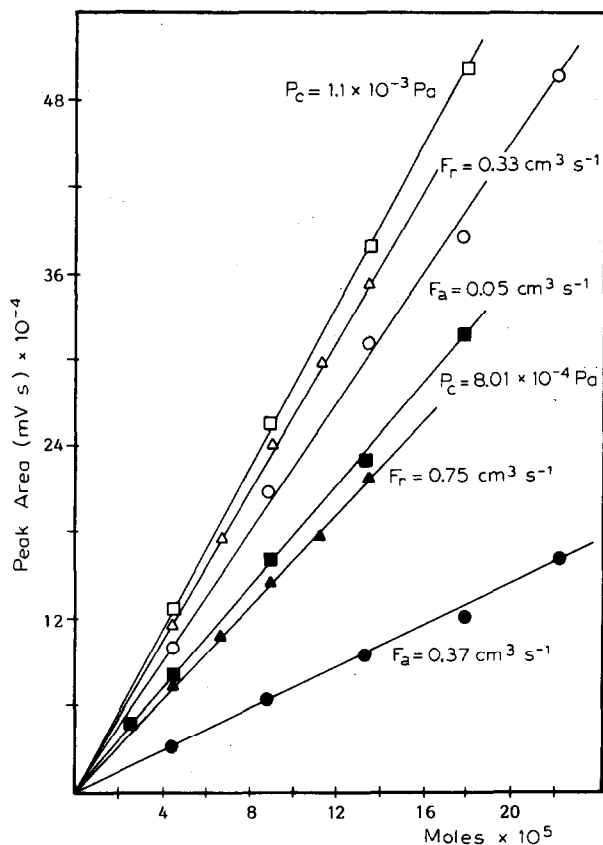


Fig. 2. Influence of the operational variables,  $F_r$ ,  $F_a$  and  $P_c$ , on the quantitative response of the system to the injection of variable amounts of  $\text{CO}_2$ .  $\circ$ , SC (standard conditions).

achieve the highest sensitivity. Figure 2 shows some results from this study. As can be deduced from this figure, by regulating valves  $V_1$  to  $V_4$ , significant changes in the response of the device to the injection of variable amounts of  $\text{CO}_2$  is accomplished. However, modification of the operational variables also has influence on the fidelity of the recorded signal. Accordingly, the working conditions should be set when both the sensitivity and fidelity aspects of the TPD-MS response are taken into account. A further paper,

TABLE 2

Influence of the reactor temperature ( $T_r$ ) on the quantitative response of the TPD-MS system

Amount of $\text{CO}_2$ (mole) $\times 10^5$	$T_r$ (K)	Area under the MS signal (mV s) $\times 10^{-2}$
13.4	298	1605
13.4	388	1498
13.4	468	1563

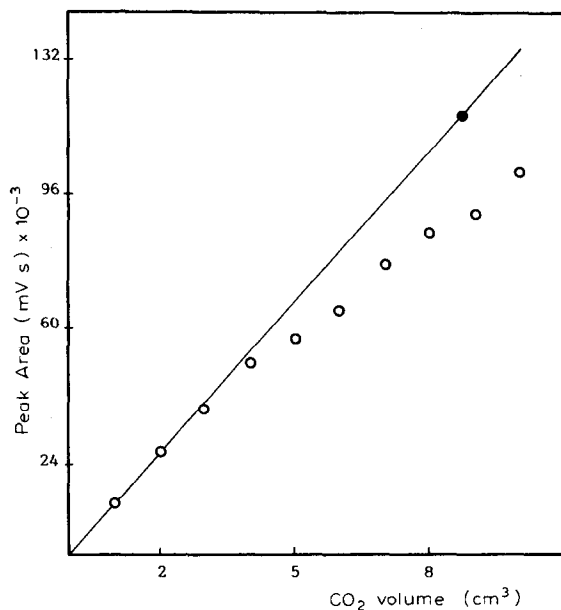


Fig. 3. Effect of the injection time on the quantitative response of the system. Signal recorded under the following conditions:  $F_r$ ,  $1.7 \text{ cm}^3 \text{ s}^{-1}$ ;  $F_a$ ,  $0.4 \text{ cm}^3 \text{ s}^{-1}$ ;  $P_c$ ,  $9.3 \times 10^{-4} \text{ Pa}$ . ●, Data corresponding to the decomposition of 32.8 mg of  $\text{MgCO}_3$ .

which will also concern the characterization of our TPD-MS device, will deal specifically with the fidelity problems.

Calibrations carried out in the way described have some advantages over the usual methods, i.e. thermal decomposition of solids [14] or the method reported in ref. 5. Firstly, less time is needed in order to obtain the corresponding calibrations. Secondly, a higher number of substances, both organic and inorganic, are easily calibrated. Nevertheless, these calibrations are obviously obtained under conditions which are not exactly the same as those operating in TPD experiments. In the latter case, in effect, the temperature rises continuously, and the evolution of the desorbed products takes place in hundreds of seconds, while injections are carried out in about one second. Therefore, the likely effect of these variables ought to be considered.

With regard to the influence of the reactor temperature, Table 2 shows the results corresponding to the injection of  $1.3 \times 10^{-4}$  moles of  $\text{CO}_2$  ( $3 \text{ cm}^3$ ) at 298, 388 and 468 K. According to these data no significant influence on the area under the recorded signal can be observed for variation of  $T_r$ .

With regard to the injection time, it is apparent that the smaller this variable, the higher the perturbation introduced into the flow. This perturbation will also depend on the amount injected. In this study, when increasing volumes of  $\text{CO}_2$  were injected under the conditions reported in Fig. 3, the response of the system was found to be linear up to  $4 \text{ cm}^3$  ( $1.8 \times 10^{-4}$

moles). For larger volumes, it cannot be considered to be linear, which suggests that the perturbation on the flow is strong enough to prevent the fulfilment of the condition  $B_{it} = \text{constant}$ . This interpretation seems to be confirmed by the results obtained when known weights of  $\text{MgCO}_3$  were thermally decomposed. In this case, since the length of the injection time is much longer, about 1200 s, an amount of  $\text{CO}_2$  equivalent to  $8.7 \text{ cm}^3$  can be injected without deviation of the response from the linearity, see Fig. 3. In accordance with these results, the range of linear response of our TPD-MS device in real experiments is higher than in the case of fast injection of the sample, which guarantees the applicability of calibrations obtained in the way reported here.

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