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CHARACTERIZATION OF AN EXPERIMENTAL TPD–MS SYSTEM. RELIABILITY PROBLEMS

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ABSTRACT

In the present work, the reliability of the responses obtained using an experimental TPD–MS system with the actual chemical process occurring at the reactor is investigated. The TPD–MS device operates in a flow of helium at normal pressure.

The probable existence of fractioning phenomena was studied by comparing the responses of our system to instantaneous pulses of CO_2 and H_2. In accordance with the results of our study, the analysis of evolved gases is not significantly disturbed by fractioning.

In order to study the distortions induced by the system on the trace recorded at the MS for each of the gases analysed, the stimulus–response technique has been used. Instantaneous pulses of CO_2 were used as probe signals. Analysis of the responses of our TPD–MS system to the CO_2 pulses has been carried out by means of the so-called dispersed flow model. The dispersion moduli of the system were determined under different experimental conditions, which allowed optimization of the working conditions in order to achieve minimum distortion on the signals.

The significance of perturbations induced by the system in a real TPD experiment was discussed by application of the principle of additivity of variances to the trace corresponding to the decomposition of $MgCO_3$.

INTRODUCTION

Mass spectrometry has become a very powerful tool in evolved gas analysis (EGA). In recent years, numerous thermal analyser–MS couplings have been reported [1–3]. Qualitative [4], quantitative [5] and even kinetic information [6] has been obtained from thermal decomposition devices where MS has been used as the analytical technique.

One of the thermal analysis techniques to which MS has been fruitfully applied is temperature programmed desorption/decomposition (TPD–MS) [7–9]. In refs. 7–9, however, no tests aimed at checking the reliability of the signals recorded with the actual processes occurring at the reactor are reported.

In a previous paper, recently appearing in this journal [10], we described a TPD–MS system that operates in a flow of inert gas at normal pressure. In

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ref. 10 it was shown that reliable quantitative analysis of evolved gases can be performed with our device. Likewise, a simple method of obtaining quantitative calibration curves for both organic and inorganic gases and liquids was reported in ref. 10.

In the present work, studies concerning characterization of the TPD–MS system mentioned above are extended to the analysis of reliability problems. In our opinion, this sort of study is necessary in order to obtain meaningful information from the experimental traces recorded on the MS. Some factors affecting the fidelity of the signals will be discussed and the influence of several different operational variables on the shape of the recorded signals tested.

EXPERIMENTAL

The TPD–MS system studied here has been previously described [10]. It essentially consists of a quartz or glass reactor through which an inert gas, helium in this case, flows at normal pressure. A proportion of the flowing gas coming out from the reactor goes to the so-called analytical device through a lateral pipe, connected to which are an auxiliary rotary pump and the mass spectrometer. The remaining fraction of the gas flowing through the reactor goes directly to a vent. The flow of gas through the analytical device as well as the total pressure at the ionization chamber can be modified at will by means of three regulation valves.

High purity helium, hydrogen and carbon dioxide were employed, from SEO. They were used with no further purification.

RESULTS AND DISCUSSION

Concerning reliability problems inherent to any TPD–MS experimental device, two major aspects should be considered. On the one hand, when a mixture of different gaseous products is generated at the reactor, the components of this mixture may reach the MS at different times. This fractioning phenomenon, considered by some authors to be intrinsically associated to the reactor–MS couplings [11], would cause a separation of the gaseous components on their way to the MS, inducing, in brief, a distortion of the qualitative information obtained from the signals recorded on the MS.

The second sort of disturbing effects to be analysed are those related to the deformation of traces obtained on the MS for each of the evolved gases. If this perturbation occurs, kinetic analysis would be carried out on traces which do not represent the true chemical reactions taking place at the reactor, and, therefore, meaningless information would be obtained.

Dealing with the first of the problems considered above, it should be mentioned that, with the present working conditions, both viscous and molecular flow regimes may occur in different areas of the experimental device. Where viscous flow operates, fractioning would be caused by axial diffusion phenomena. Therefore, in order for significant fractioning to occur, it is necessary that the diffusion coefficients in He (the inert gas used here) and those of the components of the mixture are different to each other. We estimated the diffusion coefficients in He of various gaseous products by means of the Hirschelfelder–Bird–Spots equation [12]. According to our calculations, among the gases we usually analyse, CO_2 (5.8×10^{-5} m^2 s^{-1}) and H_2 (15.6×10^{-5} m^2 s^{-1}), are those that show the largest differences in their diffusion coefficients.

When Knudsen (molecular) flow occurs, the magnitude of the fractioning phenomena will depend on the molecular weight of the diffusing gases. In our case, CO_2 and H_2 are again the gases with the largest dissimilarities in their molecular weights.

In accordance with the considerations above, if fractioning phenomena are significant in our experimental device, the separation of hydrogen and carbon dioxide should be observed. When instantaneous pulses of these two gases were injected into the system, no fractioning could be observed, both gases showing a maximum-intensity signal recorded on the MS at quite similar times.

Concerning the second of the problems outlined above, i.e., distortion of the trace corresponding to a single product, it should be mentioned that, in order to prevent such a problem, it is necessary that the amount of a specific product, generated at the reactor at a given instant, and the corresponding signal at the MS are always linearly related to each other. As discussed in ref. 10, in order that such a condition is fulfilled, the pumping rate (volume per unit time) at every point along the pipes must be constant throughout the whole TPD experiment. This requirement, which is satisfied by our experimental device [10], guarantees that quantitative analysis of evolved gases can be carried out. However, this condition, though necessary, is not sufficient to ensure that the recorded signal reliably represents the processes occurring at the reactor. In effect, phenomena associated with the transport of gases from the reactor to the MS may also induce undesirable distortions of the signals.

In order to investigate the magnitude of the distortions induced by our experimental system on the signal generated at the reactor, the so-called stimulus–response technique has been used. This technique essentially consists of injecting into the system a signal, the function of which is well known, and studying the response of the system. In our case instantaneous pulses (time of injection < 1 s) of 0.5 cm^3 of CO_2 were injected, and the response at the MS studied.

Analysis of the recorded signals thus obtained was carried out by application of the dispersed flow model [13]. According to this model, a single parameter, the dispersion modulus, D, is used to describe the perturbation induced by the system on the signals generated at the reactor.

After ref. 13, the dispersion modulus can be determined by the equation

$$D = \sigma_\theta^2/2 \tag{1}$$

where σ_θ^2 accounts for the variance of the recorded trace referred to adimensional time

$$\sigma_\theta^2 = \sigma^2/\bar{t}^2 \tag{2}$$

where σ^2 is the experimentally determined variance of the curve, and $\bar{t}$ is the residence mean time of the injected gas probe.

The last two parameters, σ^2 and $\bar{t}$, can be determined from the equations

$$\bar{t} = (\Sigma t_i C_i \Delta t)/(\Sigma c_i \Delta t) \tag{3}$$

$$\sigma^2 = \left[(\Sigma t_i^2 C_i \Delta t)/(\Sigma C_i \Delta t)\right] - \bar{t}^2 \tag{4}$$

where C_i represents the signal recorded on the MS at the instant $t = t_i$ ($t = 0$ is considered to be the instant of the injection).

The experiments were performed by substituting the TPD reactor by a piece of pyrex glass with analogous geometric characteristics.

Figures 1–3 account for the responses obtained when the CO_2 pulses were

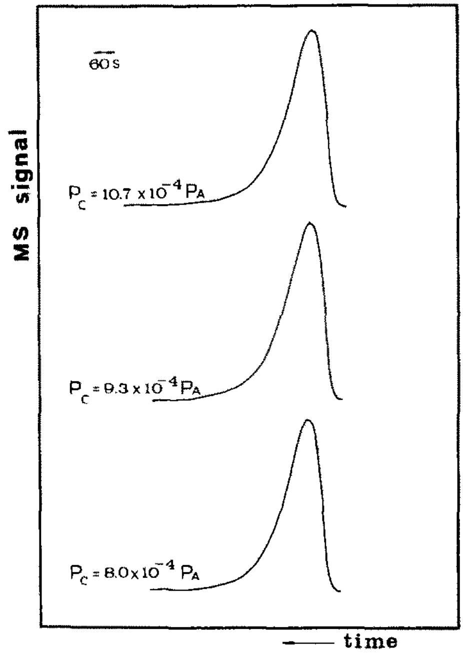

Fig. 1. Responses of the TPD–MS system to instantaneous pulses of CO_2 at three different values of pressure at the ionization chamber (P_c).

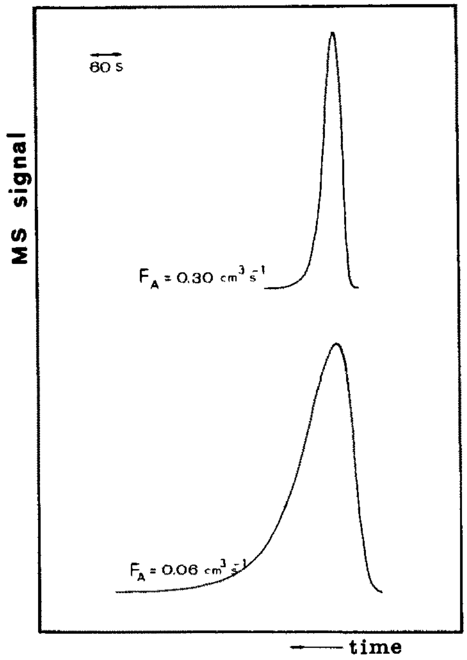

Fig. 2. Influence of the flow through the analytical device (F_a) on the response of the TPD–MS system.

injected into the system under different pressures at the ionization chamber (P_c), different flows of gas through the analytical device (F_a) and different flows of gas through the reactor (F_r), respectively.

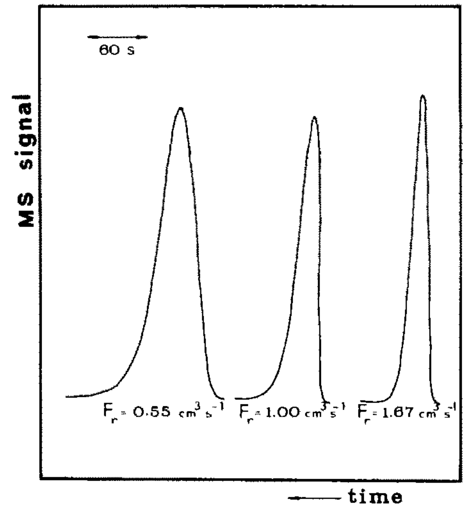

Fig. 3. Responses of the TPD–MS system to instantaneous pulses of CO_2 at three different flows through the reactor (F_r).

TABLE 1

Dispersion moduli (D), residence mean times ($\bar{t}$), and variances (σ^2), corresponding to the responses of our TPD–MS to instantaneous pulses of CO_2 injected at the operational conditions indicated

Operational conditions				Results		
P_c (Pa×10^4)	F_a (cm^3 s^{-1}×10^2)	F_r (cm^3 s^{-1}×10)	T (K)	σ^2 (s^2)	$\bar{t}$ (s)	D
10.7	5.8	5.5	298	4347	190	0.050
9.3	5.8	5.5	298	3756	190	0.044
8.0	5.8	5.5	298	4072	185	0.050
9.3	30.0	5.5	298	361	100	0.017
9.3	35.8	10.0	298	163	71	0.015
9.3	38.5	16.7	298	56	53	0.011

Likewise, Table 1 reports the variances (σ^2), residence mean times ($\bar{t}$), and dispersion moduli (D) calculated by application of the equations above to the traces given in Figs. 1–3.

From the analysis of Table 1 it can be deduced that the working conditions at our experimental device can be easily optimized in order to achieve the best fitting of the experimental curves to the true chemical processes occurring at the reactor. Among the experimental conditions tested here, in effect, the lowest dispersion modulus, and, therefore, the minimum distortion on the recorded signal, is obtained when $P_c = 9.3 \times 10^{-4}$ Pa, $F_a = 38.5 \times 10^{-2}$ cm^3 s^{-1} and $F_r = 167 \times 10^{-2}$ cm^3 s^{-1}.

Taking into account that throughout the whole TPD experiment the temperature is continuously rising, the influence of the temperature at the reactor on the reliability of the recorded signal has also been investigated. Three different temperatures (291, 388 and 468 K) have been studied. As can be seen in Fig. 4, the higher the temperature the lower the distortion of the response of the system to the pulses of CO_2. Accordingly, the reliability tests reported in Table 1 have been carried out under conditions less favourable than those operating in real TPD experiments. In other words, perturbations smaller than those predicted by the reliability essays performed at room temperature ought to be expected in TPD experiments.

Assuming that the principle of additivity of variances [13] can be applied to our system, the magnitude of the distortion induced by the system on an actual thermal decomposition trace can be estimated. Thus, from Table 1, when the operational conditions are $P_c = 9.3 \times 10^{-4}$ Pa, $F_a = 30 \times 10^{-2}$ cm^3 s^{-1} and $F_r = 55 \times 10^{-2}$ cm^3 s^{-1}, the variance corresponding to the response to an instantaneous injection is 361 s^2. Since the variance for the instantaneous pulse is assumed to be zero, from the principle of additivity of variances, the increase in the variance induced by our system is, under working conditions specified above, $\Delta\sigma^2 = 361$ s^2.

From ref. 14 we were able to estimate the variance associated with the

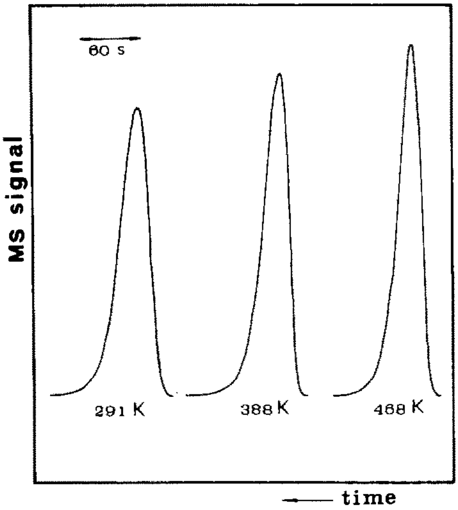

Fig. 4. Influence of the temperature at the reactor on the response of our TPD–MS system to the instantaneous pulses of CO_2.

DTG trace corresponding to the decomposition of $MgCO_3$, at a heating rate of 0.2 K s^{-1}, which was found to be 90.000 s^2. Since in ref. 14 the thermal decomposition of $MgCO_2$ was studied by means of a thermobalance, the recorded trace can be considered free of the disturbing effects investigated here. Therefore, the variance associated with the trace reported in ref. 14 can be considered to be the variance of the signal generated at the TPD reactor when $MgCO_3$ is decomposed at 0.2 K s^{-1}. Assuming this, when our system operates under the conditions specified above, the variance of the trace recorded at the MS should be 90.361 s^2, which suggests that the distortion of the decomposition trace obtained on our device for the decomposition of $MgCO_3$ would be rather small. In other words, reliable kinetic analysis from the signals recorded at the MS should be expected. This has been experimentally tested by comparing, with good results [15], the kinetic law and kinetic parameters (activation energy and pre-exponential factor) reported in ref. 14 for the decomposition of $MgCO_3$ to those obtained by us from the corresponding DTP–MS trace.

In summary, in the present work, on the grounds of the so-called stimulus–response technique, the reliability of the responses obtained by our TPD–MS device, under different experimental conditions, has been tested. As deduced from Table 1, the reliability of the response of our system can be easily optimized. Furthermore, by comparison of the variance data obtained on our system for instantaneous injections of the gas to be analysed to those corresponding to real TPD traces, the feasibility of the kinetic analysis to be carried out on the TPD–MS experimental curves can be estimated, at least to a first approximation.

Finally, it should be noted that in the present work, factors other than those associated with physical phenomena due to the transport of the gases from the reactor to the MS, which may also cause reliability problems, have not been considered. Thus, chemical interaction of the evolved gases with the walls of the pipes or their simple condensation should also be taken into account. In order to prevent these effects, materials for making the pipes should be carefully selected. Likewise, heating the pipes at a convenient temperature can also contribute to the elimination of undesirable adsorption and condensation phenomena on their walls.

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REFERENCES

1 D. Price, C. Lukas, G.J. Milnes and R. Whitehead, Eur. Polym. J., 19 (1983) 219.
2 D. Dollimore, J.P. Gupta and D.V. Nowell, Thermochim. Acta, 30 (1979) 339.
3 D. Price, N.S. Fatemi, R. Whitehead, J.H. Lippiatt and D. Dollimore, Dynamic Mass Spectrometry, Vol. 5, 1978, Chap. 20, p. 216.
4 M.L. Aspinal, H.J. Madoc-Jones, E.L. Charsley and J.P. Redfern, in H.G. Weidemann (Ed.), Proc. 3rd Int. Conf. Thermal Anal., Vol. 1, Davos, 1971, Birkhaeuser Verlag, Basel, 1972, p. 303.
5 B. Courtault, Analusis, 7 (1979) 481.
6 P. Forzatti, N. Kotzev, L. Gencheva, I. Pasquon, D. Shopov and P.L. Villa, J. Catal., 65 (1980) 369.
7 R. Hierl, H. Knözinger and W. Schubart, Z. Phys. Chem., Neue Folge, 106 (1977) 109.
8 J.B. Moffat, E.E. Chao and B. Nott, J. Colloid Interface Sci., 67 (1978) 240.
9 D.C. Foyt and J.M. White, J. Catal., 47 (1977) 260.
10 S. Bernal, R. García and J.M. Rodríguez-Izquierdo, Thermochim. Acta, 70 (1983) 249.
11 W.D. Emmerich and E. Kaiserberger, J. Therm. Anal., 17 (1979) 197.
12 C.R. Wilke and C.Y. Lee, Chem. Eng. Sci., 47 (1955) 1253.
13 O. Levenspiel, Chemical Reaction Engineerings, 2nd edn., Wiley, New York, 1972.
14 J.M. Criado, R. García and F. González, An. Quim., 75 (1979) 179.
15 S. Bernal, R. Garcia and J.M. Trillo, React. Kinet. Catal. Lett., 10 (1979) 125.