ELSEVIER

Thermochimica Acta 329 (1999) 83–88

thermochimica acta

Repetitive pulsed sampling interface for combined thermogravimetry/mass spectrometry

M. Statheropoulos*, S. Kyriakou, A. Pappa

Department of Chemical Engineering, National Technical University of Athens (NTUA),
Sector I, 9 Iroon Polytechniou Str., Athens 157 73, Greece

Received 19 January 1998; received in revised form 26 October 1998; accepted 25 January 1999

Abstract

A pneumatic sampling switch which can be adapted to the outlet of a thermogravimetric analyzer furnace with a horizontal purge gas flow was developed. This system allows a repetitive introduction of short sampling pulses of thermogravimetric analyzer evolved gases to a quadrupole mass spectrometric detector. System performance was evaluated through measuring the level of repeatability under different operation conditions. In addition, pulsed sampling thermogravimetry/mass spectrometry introduced no measurable quantitative or qualitative errors. This system can be used for monitoring thermooxidative decomposition reactions, without accelerating the deterioration of quadrupole mass spectrometric detector performance. Furthermore, it can be used as an inlet system for a future on-line TG/GC/MS system. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetry/mass spectrometry; Pulsed sampling interface

1. Introduction

During the past decade, quadrupole mass spectrometry (QMS) type detectors have been widely used in combined thermogravimetry/mass spectrometry (TG/MS) systems, due to their high sensitivity, fast analysis time and simplicity in construction [1]. Nevertheless, it appears that some TG/QMS systems are not suitable for monitoring oxidation reactions, as the continuous flow of the oxidative purge gas could accelerate the deterioration of the ion source and analyzer performance. Therefore, the oxidative evolved gases should be introduced to QMS detector during short time pulses. Furthermore, on-line TG/GC/MS analysis requires repetitive introduction of short sampling pulses of TG analyzer (TGA) evolved gases into a short chromatographic column, in order to avoid chromatographic peak overlapping [2]. The repetitive introduction of sampling pulses of evolved gases can be achieved using dynamic gas sampling systems. Several gas sampling systems have been previously reported based on mechanical, [3] or fluidic logic devices [4,5]. These systems presented limitations in repeatability and performance, especially with regard to highly polar and low volatile products. To avoid these problems, gas sampling devices based on pressure balance flow switching principles have been reported [6,7].

---

*Corresponding author. Tel.: +30-1-7723109; fax: +30-1-7723188; e-mail: stathero@orfeas.chemeng.ntua.gr

PII: S0040-6031(99)00013-1

When used in TG/MS based evolved gas analysis, such gas sampling systems should meet certain specifications such as: repeatability of sampling duration, sampling period and sampling quantity, quick response, and quick evolved gas transfer from the crucible in the TGA furnace to the QMS detector. In addition, memory effects, degradation or condensation of evolved gases and interferences with the TGA and QMS detector performance need to be avoided. Furthermore, simplicity in construction, easy system decoupling and cleaning, low cost and versatility with respect to TGA and/or QMS detector operation are important [8]. Finally, the operation of such a pulsed gas sampling system should not introduce any quantitative or qualitative error in the results of the TG/MS analysis.

The purpose of this work is to present and evaluate the performance of a repetitive gas sampling system which is adapted to the outlet of a TGA furnace with a horizontal purge gas flow.

2. Experimental

2.1. Instruments

The thermogravimetric analyzer used was a TA Instruments model 2050, the QMS detector used was a Hewlett-Packard 5972 Mass Selective Detector, the TG/MS interface was a single stage capillary system [8]. The TG/MS configuration is shown in Fig. 1. The system consists of: (1) a computer controlled TGA, (2) a heated TG/MS interface and (3) a computer controlled QMS detector. The TG/MS interface is made of a pulsed sampling switch (PSS) and a transfer line. The transfer line consists of a deactivated 2.17 m×0.15 mm i.d. Chrompack capillary and a heating thermomantle. PSS and transfer line can be heated up to 250°C in order to minimize condensation effects. The PSS consists of three coaxial tubes [6–8]. The inner tube is a capillary transfer line connected to the QMS detector ion source. The outer tube is

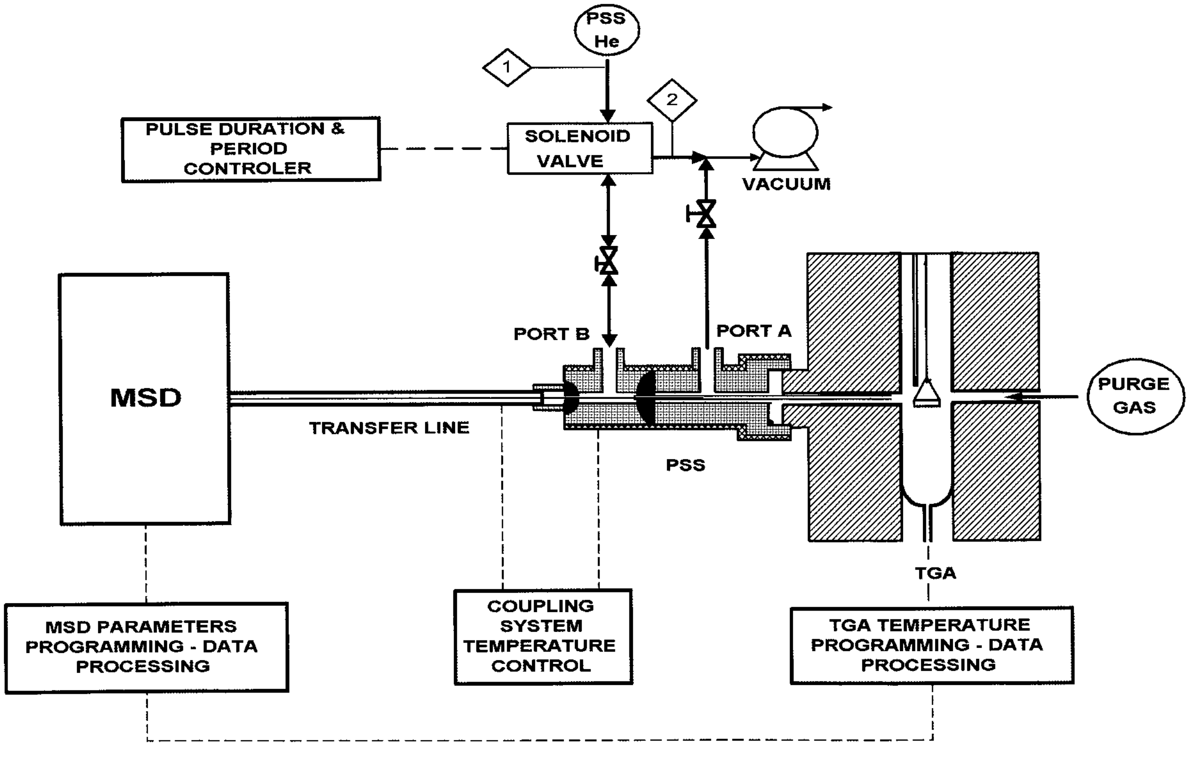

Fig. 1. Pulsed sampling TG/MS interface configuration: (1) idle mode, (2) sampling mode.

connected to a vacuum source, in order to produce stable laminar flow conditions in the PSS. The flow through the intermediate tube has two modes of operation: (1) the idle mode, when the intermediate tube is flushed with an inert gas (PSS He) in order to prevent evolved gases from reaching the capillary, and (2) the sampling mode, when the intermediate tube is connected to vacuum in order to direct the evolved gases to the head of the capillary. Sampling period and duration are adjusted by an electronically controlled solenoid valve. When the sampling duration is adjusted to be infinite, then the system operates in a continuous sampling mode.

2.2. Materials

TA Instruments provided $CaC_2O_4 \cdot H_2O$ 99.9% (w/w) standard.

2.3. Methods

1. System repeatability was examined, by monitoring repetitive sampling pulses of an inert purge gas (argon) at: (i) different TGA furnace temperatures using a specific PSS He flow and sampling duration and (ii) different sampling durations and different PSS He flow rates at a specific TGA furnace temperature. The pulsed sampling TG/MS (PS-TG/MS) signal at different TGA furnace temperatures was monitored using a heating rate of 20°C min^{-1} from ambient temperature up to 1000°C, a PSS helium flow of 27.7 cm^3 min^{-1}, a sampling duration of 1.18 ms and a sampling period of 40 s. The influence of different sampling durations and PSS He flow rates was studied using: sampling durations of 0.77, 0.86, 1.18, 1.74 and 2.20 s; PSS He flow rates of 16.6, 21.2, 27.7, 34.8 and 44.1 cm^3 min^{-1} and no heating of the TGA furnace. In all the above cases an argon purge gas flow of 100 cm^3 min^{-1} was used.
2. System accuracy was examined by comparing the CO_2 (m/z 44) QMS detector signal during continuous and PS-TG/MS analysis of standard calcium oxalate decomposition in helium. Continuous TG/MS analysis of calcium oxalate in helium was performed using: a TGA heating rate of 20°C min^{-1} up to 800°C and a helium purge gas flow of 100 cm^3 min^{-1}. PS-TG/MS analysis of calcium oxalate in helium was performed using: a TGA heating rate of 20°C min^{-1} up to 800°C, a helium purge gas flow of 100 cm^3 min^{-1}, a PSS helium flow of 27.7 cm^3 min^{-1}, a sampling duration of 1.18 ms and a sampling period of 40 s.

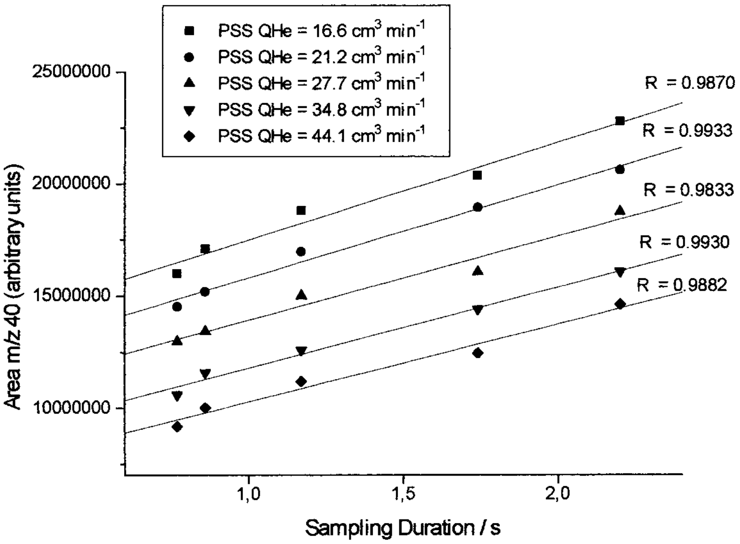

Fig. 2. Area of m/z 40 signal (arbitrary units) vs sampling duration at different PSS He flow rates.

3. PS-TG/MS analysis of calcium oxalate in air was performed using: a heating rate of 20°C min^{-1} up to 800°C, an air purge gas flow of 100 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, a PSS Helium flow of 27.7 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, a sampling duration of 1.18 ms and a sampling period of 40 s.

In all cases the suction flow in port A was of 60 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, while the flow in port B, during sampling mode, was 39 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. The weight of the calcium oxalate samples analyzed was 7 mg.

3. Results and discussion

Provided that the gas flow through the capillary is stable, the amount of evolved gas introduced in the QMS detector ion source is mainly affected by the TGA furnace temperature, the sampling duration and the PSS He flow rate. The area of repetitive short sampling pulses of argon at increasing TGA furnace temperature, showed a relative standard deviation (RSD) better than 2%. The sampling period showed a RSD of less than 0.40%. Furthermore, the PSS He flow through the intermediate tube caused a disturbance in TGA weight measurement of less than 0.005 mg. No disturbance in TGA temperature measurement was observed. Figs. 2 and 3 show that a linear relationship exists between argon (*m/z* 40) area, sampling duration and PSS He flow rate, respectively. This indicates that plug flow conditions exist in the pneumatic switch. In every case the observed RSD was less than 2%. The values of argon area at zero sampling duration are due to argon back diffusion in the PSS He flow stream.

In order to evaluate the ability of PS-TG/MS to give accurate results, a continuous TG/MS and PS-TG/MS analysis of thermal decomposition of standard calcium oxalate in He was performed. Fig. 4 shows the weight loss curve, the differential thermogravimetric curve and the temperature of the calcium oxalate decomposition. The first decomposition stage (15–23 min) is attributed to the formation of $CaCO_3$ and CO, while the second (24–31.5 min) produces CaO and CO_2. In Fig. 5 the QMS detector signal of *m/z* 44 (CO_2) from continuous TG/MS analysis is shown. The amount of CO_2 detected during the 15–23 min time window is due to CO disproportionation and residual oxygen trapped in the TGA furnace [9]. Fig. 6 shows the *m/z* 44 QMS detector signal of repetitive sampling pulses. A very good time agreement exists between the *m/z* 44 signal, from continuous TG/MS and PS-TG/MS analysis. In addition the ratio of the *m/z* 44 signal area during 15–23 min time window to that of *m/z* 44 signal area during 24–31.5 min window is 0.33 with an RSD of 5% for continuous TG/MS and 0.35 with an RSD of 4% for PS-TG/MS. At a 95% confidence level

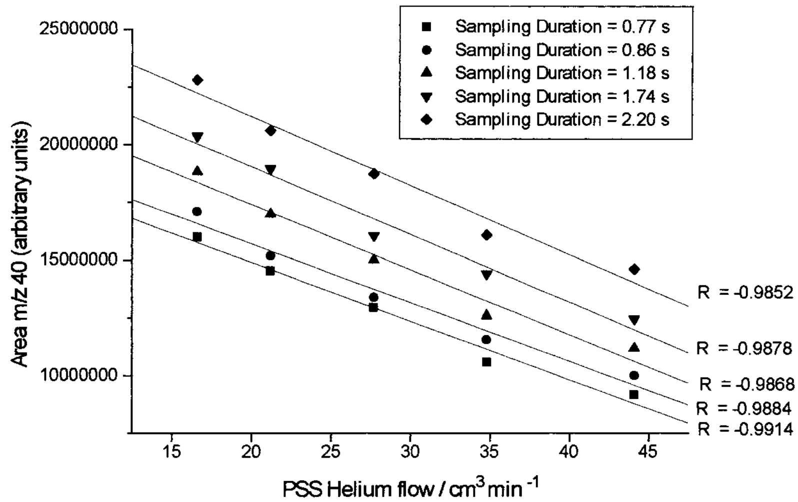

Fig. 3. Area of *m/z* 40 signal (arbitrary units) vs PSS He flow rates at different sampling durations.

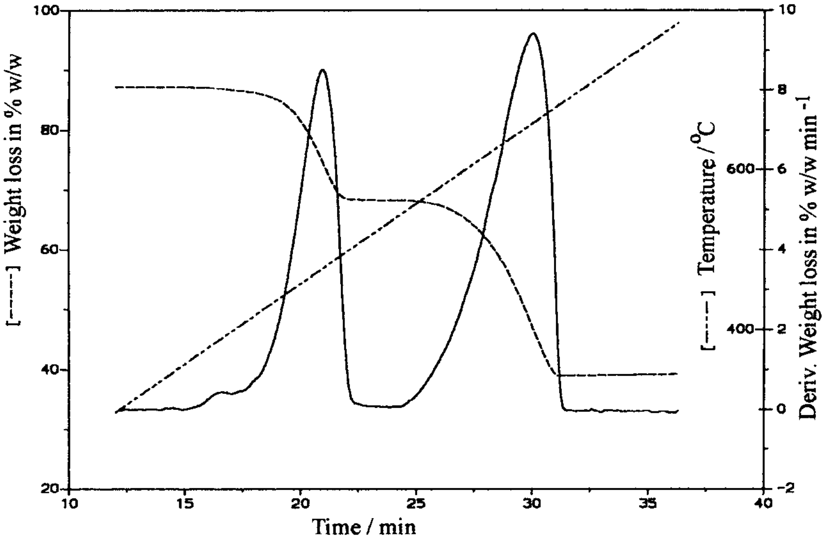

Fig. 4. Weight loss, DTG and temperature curve of standard calcium oxalate decomposition.

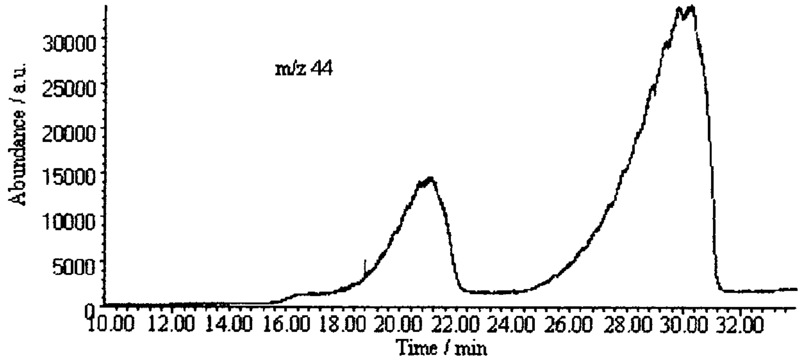

Fig. 5. *m*/*z* 44 signal (arbitrary units) from continuous TG/MS analysis of standard calcium oxalate decomposition in He.

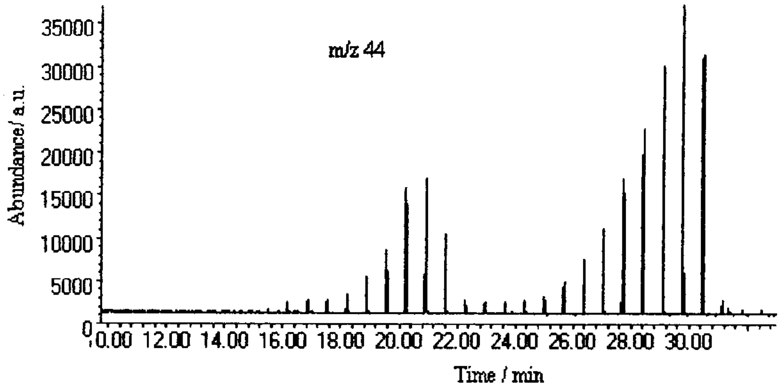

Fig. 6. *m*/*z* 44 signal (arbitrary units) from PS-TG/MS analysis of standard calcium oxalate decomposition in He.

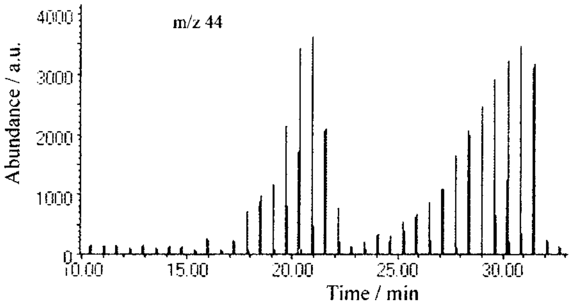

Fig. 7. *m*/*z* 44 signal (arbitrary units) from PS-TG/MS analysis of standard calcium oxalate decomposition in air.

the two ratio values are statistically the same. Therefore, it appears that PS-TG/MS does not introduce any qualitative or quantitative error in the analysis results.

During thermal degradation of standard calcium oxalate in air, no temperature shift was observed in the weight loss curve. On the assumption that any CO evolved during the 15–23 min window was totally oxidized to CO_2, the amount of CO_2 theoretically expected from the two decomposition stages must be the same. Fig. 7 shows the *m*/*z* 44 signal resulting from PS-TG/MS analysis of standard calcium oxalate oxidative decomposition. The ratio of the total *m*/*z* 44 area during 15–23 min window to the total area during the 24–31.5 min is 1.01 with a RSD of 4%, which is in very good agreement with the theoretically expected value. It should be noticed that a small background of *m*/*z* 44 signal pulses exist before and after the decomposition stages. The background, as measured during the 10–15 min time period, is nearly 2.5% of the maximum *m*/*z* 44 signal. This background was subtracted from the pulse signal before calculating the ratio of *m*/*z* 44 area during 15–23 min and 24–31.5 min. In addition, it should be noted that after a testing period with PS-TG/MS experiments using oxidative purge gas, no deterioration of ion source filaments or electron multiplier performance was recorded.

4. Conclusions

A pneumatic gas sampling switch which can be adjusted to the outlet of TGA furnace with a horizontal purge gas flow was developed and evaluated. This switch allows the repetitive introduction of short sampling pulses of TGA evolved gases into QMS system. Pulsed sampling TG/MS proved to work effectively according to the criteria established, giving repeatable and accurate results in both inert and oxidative environment. The system can be used to study the thermooxidative decomposition of both inorganic and polymeric materials without causing any deterioration to QMS ion source or electron multiplier performance. Furthermore, it can be used as an inlet technique for a future system of TG/GC/MS analysis.

Acknowledgements

The authors wish to acknowledge Prof. H.L.C. Meuzelaar from Center of Microanalysis and Reaction Chemistry, of University of Utah, for his helpful comments on this work.

References

[1] K.G.H. Raemaekers, J.C.J. Bart, Thermochim. Acta 295 (1997) 1.
[2] W.H. McClennen, R.M. Buchanan, H.L.C. Meuzelaar, Anal. Chem. 65 (1993) 2819.
[3] G. Schomburg, H. Hysmann, F. Weeke, J. Chromatogr. 112 (1975) 205.
[4] R. Wade, S. Cram, Anal. Chem. 44(1) (1972) 131.
[5] G. Gaspar, P. Arpino, G. Guiochon, J. Chromatogr. Sci. 15 (1977) 256.
[6] D.R. Deans, J. Chromatogr. 289 (1984) 43.
[7] N.S. Arnold, W.H. McClennen, H.L.C. Meuzelaar, Anal. Chem. 63 (1991) 299.
[8] M. Statheropoulos, S. Kyriakou, N. Tzamtzis, Thermochim. Acta 322 (1998) 167.
[9] T. Leskelä, M. Lippmaa, L. Niinistö, P. Soininen, Thermochim. Acta 214 (1993) 9.