Titration TGA: Application to the calibration of TGA-EGA systems

Introduction

Titration TGA is a method for dosing a gas or a vapor aliquot (i.e. of known amount) on a sample being weighed by a TGA balance. It can be applied to the study of physisorption or chemisorption phenomena and to some extent to all gas-solid reactions (e.g. oxydo-reductions).

In the present case, it has been applied to the calibration of a TG-GC/MS system. It could further be applied to of all TGA-EGA (Evolved Gas Analysis) methods.

Goals

The primary objective of the study was to detect and quantify the Argon desorption from a « TA6V » (Ti based, 6% Al, 4% V) high temperature alloy sample typically used in the space and aircraft industries to make turbine blades and different structure parts. The secondary objective of the study was to additionally detect the evolution of carbon dioxide while heating the samples.

Experimental set-up

Calibration Step

Upstream

An Autoinjector, based on a rotating 6-ways valve and a sample loop of defined volume was used to prepare and inject argon doses in the TGA. The principle of this upstream Autoinjector is depicted on Figure 1 below.

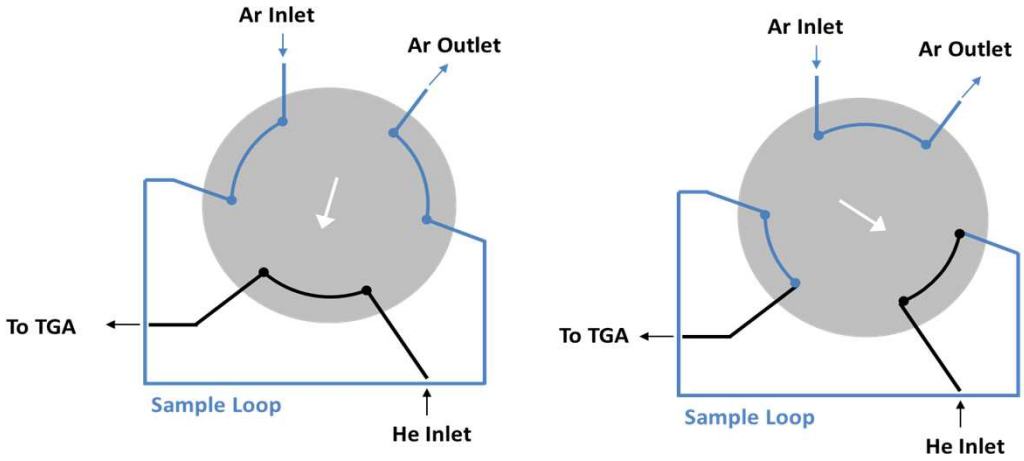

Figure 1 – Principle of the upstream Autoinjector with dose preparation position (left) and dose injection position (right).

In the dose preparation position, argon flows continuously in the sample loop whose volume may be chosen between the 1µl to 1000 µL range ones (1, 2.5 and 5µl in the present study). At a time or with a frequency that can be selected by the user, the injector switches to its injection position and the argon trapped is pushed out of the sample loop and into the TGA gas inlet by an helium flow. The temperature of the Autoinjector, which was chosen to be 30°C in the present case, can be controlled up to 350°C.

Three calibration experiments were run for each sample loop volume.

TGA

A SETSYS Evolution Thermogravimetric Analyzer was used isothermally at 1400°C with an empty alumina crucible and a carrier helium flow. The upstream Autoinjector was connected to the auxiliary gas inlet of the TGA.

Downstream

A second Autoinjector, named GC-MS Autoinjector in Figure 2 was connected to the outlet of the SETSYS Evolution TGA and to the inlet of a Thermo GC/MS. The GC-MS Autoinjector and transfer lines were kept isothermally at 250°C. It was used according to the quasi-continuous mode, which allows for frequent injections, in the present case every 10 seconds. It was equipped with a 1mL sampling loop.

The GC/MS was equipped with a 3m long deactivated silica coated capillary column kept isothermally at 120°C. The MS was programmed to detect ionized molecules in the 10-110 amu range.

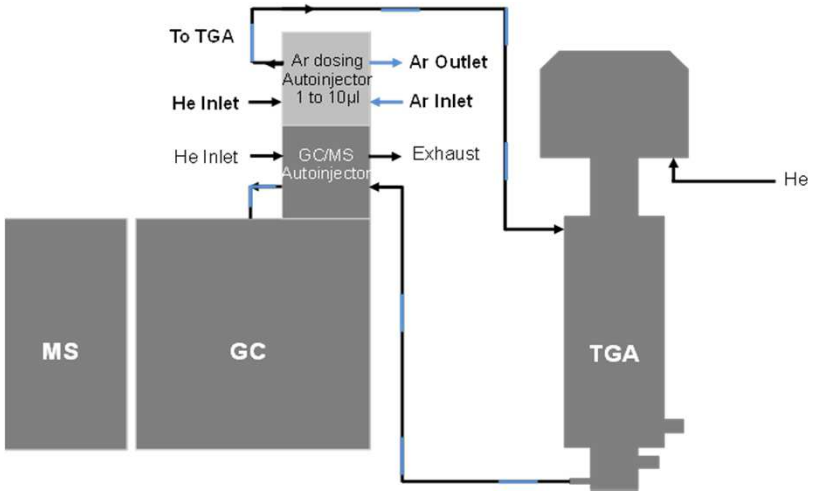

Figure 2 – Schematics of the setup with an idealized representation of the argon doses flow (blue segments).

Desorption experiments

Desorption experiments were run without the use of an upstream Autoinjector. All of the other elements of the previously described setup were used.

Three samples of TA6V with initial masses ranging between 3400 and 3500mg were hung in a SETSYS Evolution TGA alumina crucible. Two preliminary primary vacuum / helium purge cycles were applied followed by a heating sequence from 50°C to 1700°C at a rate of 10°C/min. The TGA was flowed with helium as a carrier gas. All of the other test conditions were identical to the ones described above.

Results

Calibration

The GC/MS data treatment software allows plotting the chromatogram corresponding to a given mass spectrum of a given gas. In the present case, figure 3.a. shows the chromatogram corresponding to the amu 40, i.e. to argon.

A calibration line was plotted from the three sets of peaks envelopes area versus injected argon volume, leading to Figure 4 below. The peaks envelopes were preferred for integration as their area is related to the total amount of argon flowing out of the TGA, while the sum of the retention peaks areas is related only to the part that has been injected in the GC column.

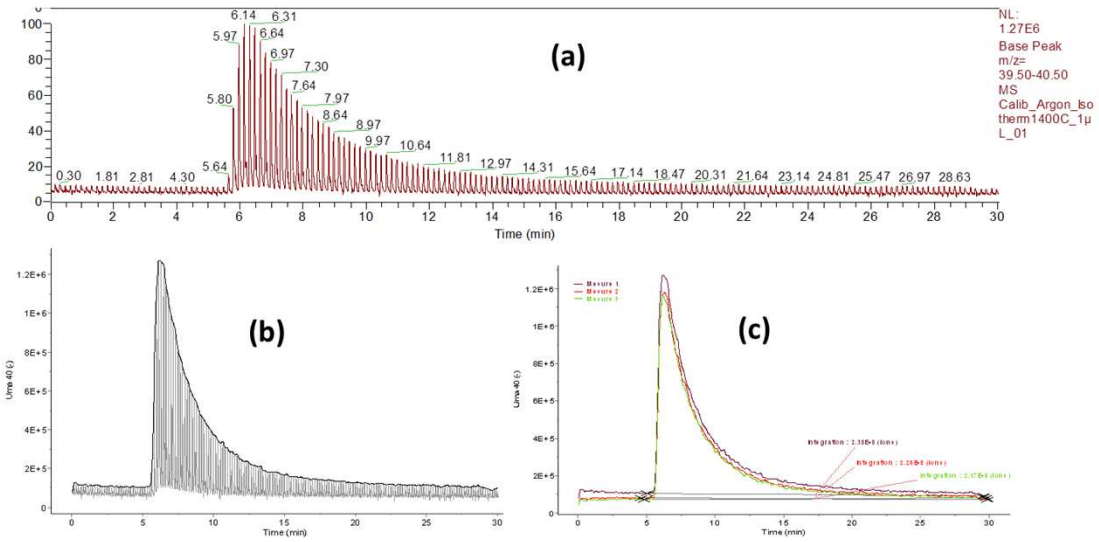

Figure 3 – Contribution of Argon to the Total Ion Current signal during the calibration run with a 1µl argon dose (a) Drawing of the peaks envelope for the same run (b) Overlay of the three peak envelopes for the three runs with a 1µl argon dose (c).

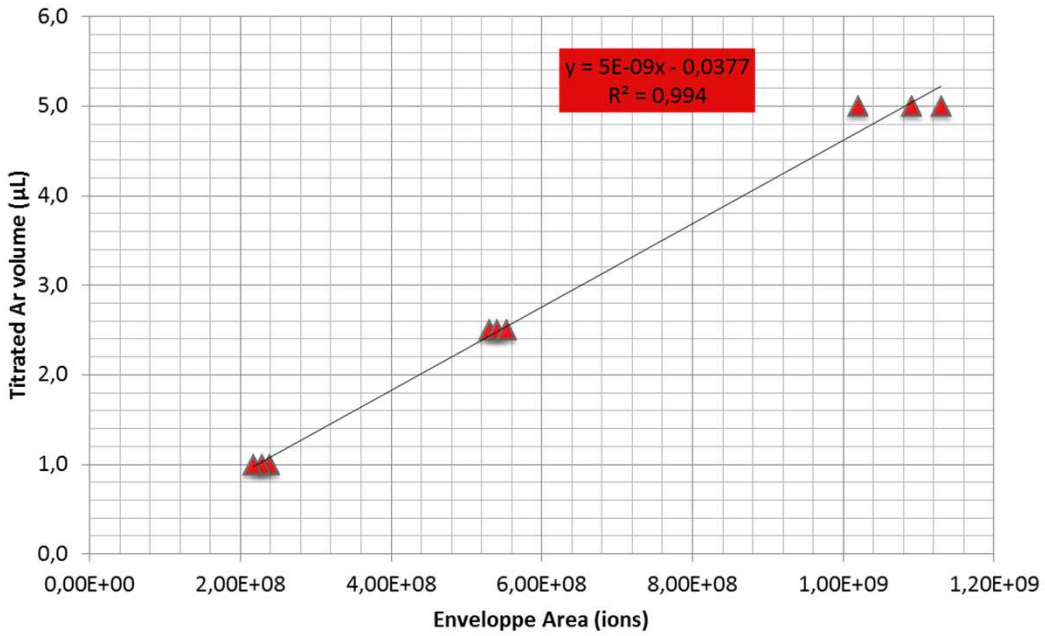

Figure 4 – Calibration plot.

Desorption experiments

Figure 5 represents the overlay of the signals of interest for the first sample tested. All the tested samples followed the same trend. The mass change signal exhibits 3 main steps in the process:

- A first mass loss between 100°C and 600°C is linked to a significant increase of the TIC and of the contribution of CO_2 to the TIC, meaning that it is at least partly linked with the evolution of carbon dioxide from the sample.
- A second mass loss occurs between 600°C and 1300°C but is not linked to one of the molecules of interest.
- A third mass loss starts at around 1300°C and ends at around 1700°C. The TIC and the contributions of CO_2 and Ar to the TIC show that both gases were evolved during that step.

In order to quantify the argon evolved during the high temperature mass loss, the envelope of the GC signal corresponding to amu 40, i.e. signal (v) on Figure 5 has been drawn and integrated. From the obtained area value in ions and the calibration curve, it was possible to determine the argon amount evolved by the sample (see Table 1 below). The same procedure has been applied to the two other samples.

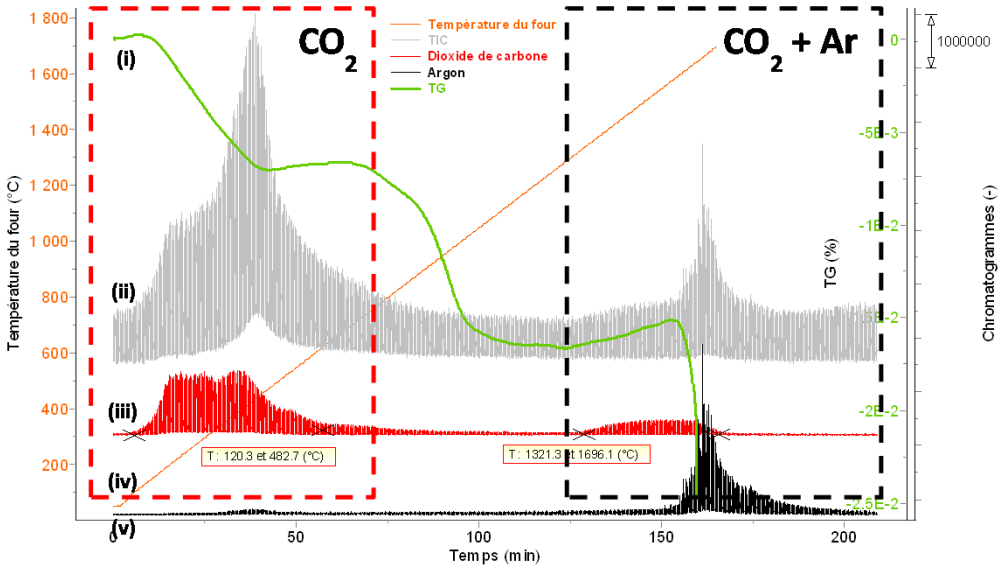

Figure 5 – Overlay of the mass change (i), total ion current (ii), contribution of CO_2 to the TIC (iii) temperature (iv), and contribution of Ar to the TIC (v) as a function of time for the experiment run with sample 1 (initial mass 3492.1mg).

Sample	Area (ions)	Ar volume (µl)	Ar qty (mmol)	Ar concentration (ppm)
1	$9{,}60.10^8$	4.76	0.192	2.2
2	$1{,}23.10^9$	6.11	0.247	2.9
3	$1{,}16.10^9$	5.76	0.232	2.7

Table 1 – Argon amounts evolved by the three tested samples.

Conclusion

This testing method, which allows quantifying small amounts of an evolved gas within a gas blend, is applicable to a wide range of TGA-EGA techniques and of sample materials, providing that an adapted calibration method is developed.

The Autoinjector is able to work with a large number of dosing volumes from 1µl to 1ml (more on request), meaning that the method can be adapted to samples that lead to the evolution of larger amounts of gases. Moreover the Autoinjector and transfer lines being temperature controlled, injection of vapors of high boiling point (water, solvents, volatile organic compounds,…) can be achieved.