

# Time of Flight mass spectrometry for quantitative data analysis in fast transient studies using a Temporal Analysis of Products (TAP) Reactor

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## Introduction

The Temporal Analysis of Products (TAP) [1] technique has been successfully applied to transient kinetic characterization of model and industrial catalysts in many areas of chemical kinetics and engineering [2]. Vacuum pulse-response TAP experiments are characterized by the sub-millisecond time resolution and low pulse intensity. This provides an opportunity to test activity of the catalyst with particular surface composition that does not change significantly during a single pulse experiment. [3].

Quadrupole mass spectrometers (QMS) have been traditionally used as detectors in various transient experiments including TAP. QMS provide a good time resolution, are inexpensive and relatively easy to operate and quantify. The key drawback of QMS is that in order to keep a sub-millisecond time resolution in a TAP pulse-response experiment, the QMS must be locked to a single atomic mass unit (AMU). To observe a number of different AMUs for reactants/products, the corresponding number of one-pulse experiments must be performed.

Time of flight (ToF) mass spectrometers offer a great opportunity to observe all masses simultaneously. Until recently, ToF MSs were not well suited for observing fast time dependencies. Contemporary ToF MSs can provide reasonable time resolution and sensitivity, which makes them potentially very useful for fast transient experiments. For a TAP experiment ToF can provide possibility to easily observe the complete fragmentation pattern; to identify unexpected products and to broaden the range of pulse intensity in use.

Herein, a TAP reactor equipped with a Time of Flight (ToF) mass spectrometer suitable in terms of sensitivity, detector response and time resolution is reported.

## Materials and Methods

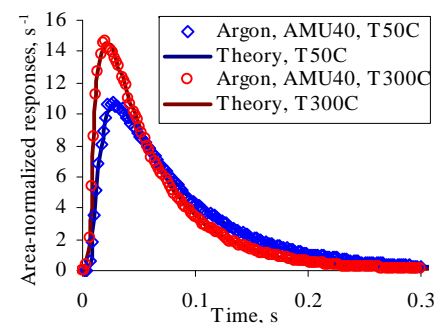
Technical difficulties associated with the adaptation of ToF spectrometry to TAP application as well as the solutions implemented are disclosed and commented, including electronics modification, shaped field buncher, ion source improvement, magnetic field shielding, detector linearization etc.

The performances of the ToF and the linearity of the specific detector over the full dynamic range were tested using partial pressure measurements and pulse response experiments. Different gases (mixtures) were pulsed in different amount at different temperature over the one-zone TAP reactor packed with silicon-carbide particles. The responses observed for different molecules/fragments were used to unravel complex fragmentation patterns and to deconvolute saturated-unsaturated hydrocarbon mixture.

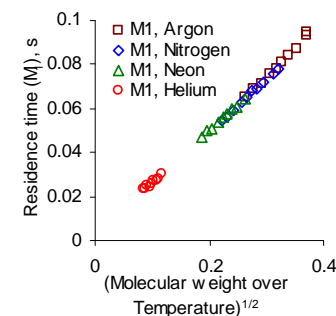
## Results and Discussion

The traditional procedures to validate that all the components of a TAP system work properly is to observe an agreement between the observed diffusion responses and TAP Knudsen diffusion theory. This includes fitting the observed responses with model responses and checking a correct dependence of diffusional residence time (or diffusivity) on temperature and molecular weight.

Figure 1 demonstrates typical agreement between theory and experimental responses recorded for argon at  $T = 50$  and  $300$  °C. Remarkably, similarly good agreement was observed for other molecules/fragments in a wide range of intensities. Figure 2 shows the residence times (first moment) calculated for responses for different molecules pulsed at different temperatures over the same reactor packing. According to Knudsen theory the residence time should be proportional to the square root of the ratio of molecular weight to temperature. It is evident that all the data points follow a single straight line as expected from the theory.



**Figure 1: Comparison of theoretical curves and argon responses observed at AMU=40 at temperature 50°C and 300°C**



**Figure 2: Residence time ( $M_1$ ) plotted versus the square root of the ratio of molecular weight to temperature**

## Significance

The reported TAP-ToF setup is the first system that achieves the high level of sensitivity allowing monitoring the full 0-300 AMU range simultaneously with sub-millisecond time resolution. This achievement is expected to stimulate an application of the modified ToF mass spectrometers to other fast transient experiments.

## References

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