

**EVOLVED GAS COLLECTION FROM A THERMOGRAVIMETRIC ANALYZER AND IDENTIFICATION BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY**

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**ABSTRACT**

The use of spectroscopic techniques (MS and FTIR) to identify the decomposition products from TGA experiments is well known. This work compares the traditional “on-line” method with the alternative “off-line” approach of volatile collection followed by thermal desorption. The desorbed volatiles may then be separated by gas chromatography and identified by mass spectrometry. With this “off-line” approach, complex mixtures (which are often difficult to interpret with the “on-line” method) can be easily analyzed.

**INTRODUCTION**

A major difficulty when using a TGA-FTIR (Thermogravimetric Analysis – Fourier Transform Infrared spectrometry (1)) or TGA-MS (Thermogravimetric Analysis – Mass Spectrometry (2)) system is that there is no separation of the evolved gases prior to detection. This presents few problems when studying simple systems such as clays, minerals and catalysts or where only small molecules (i.e. H<sub>2</sub>O, CO<sub>2</sub>, CO) are being determined. However, when systems that are more complex are studied, such as polymers, the decomposition products can comprise of multiple organic species all being released at the same time. Consequently, interpretation of the MS or FTIR data is difficult or impossible. Trapping the evolved gases using a cold trap is one solution to this problem. The condensed gases may then be separated and identified by GC-MS (3). This paper describes a simple and efficient alternative to the use of cold traps – the use of a sorbent tube to trap the gases evolved during the experiment. This technique is ideally suited to the study of organic decomposition products, and so finds particular utility within the polymer industry. The thermal analyst simply adds a collection tube to the outlet of the TGA furnace and traps any evolved gases. The Evolved Gas Collector (EGC) thermally desorbs the collection tube. The EGC in turn is directly coupled to the inlet of the GC capillary column. Less than 1% of the decomposition products are passed to the GC-MS, the remainder are passed to a second collection tube. In this way, the gases evolved from a single TGA experiment provide enough material for hundreds of GC-MS experiments, in which the separation and identification parameters may be optimized.

## METHODOLOGY

1. The sample is run in the TGA in the usual way.
2. The evolved degradation products are sucked through a collection tube. The organic vapors are trapped on an absorbent contained within the tube (figure 1).
3. At the end of the TGA experiment, the collection tube is thermally desorbed using the Evolved Gas Collector (EGC) and the released volatiles are concentrated in a cold trap.
4. The cold trap is heated and the volatiles released. A controlled percentage of the volatiles are passed onto the end of a GC column. The remainder is re-collected onto another collection tube - should re-analysis be required.
5. After the volatiles have been separated into their individual components they are identified by a mass spectrometer (figure 2.)

## RESULTS AND DISCUSSION

Figure 3. shows typical “on-line” data from a TGA-MS experiment. Here the inclusion of molybdenum trioxide, ( $\text{MoO}_3$  - a smoke suppressant) into poly(vinyl chloride) (PVC) is seen to cause a reduction in the abundance of the m/e 78 ion. However, because of the complex nature of the decomposition products, it is not easy to identify which volatile species are actually created during the TGA experiment. Although m/e 78 is the molecular ion for benzene, the fragmentation of higher molecular weight material can also give rise to a m/e 78 peak.

Figure 4. shows the “off-line” data for the same two PVC samples (the total evolved gasses from approximately 0.5 mg of material was collected in each case). The total ion count from the mass spectrometer detector is plotted against retention time in the gas chromatograph. A list of the major volatiles and their retention times are shown in table 1. Mass peaks below m/e 40 were not collected therefore the evolution of hydrogen chloride was not monitored. Both samples contained plasticizer (dibutyl phthalate) which was detected in the chromatogram directly and as phthalic anhydride. Impurities in the plasticizer were also found.

By selecting a single ion species to display, it is possible to isolate specific chemical species in the chromatogram. A plot of the m/e 78 ion against retention time shows that there is a considerable reduction in the production of benzene brought about by the addition of  $\text{MoO}_3$  to the PVC (figure 5). A plot of m/e 91 (arising from the benzyl group,  $\text{C}_6\text{H}_5\text{CH}_2$ ) detects substituted aromatic molecules such as toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ), xylene ( $\text{C}_6\text{H}_4(\text{CH}_3)_2$ ) *etc.* (figure 6). There are comparable amounts of these materials in both cases. It is the decrease in the amount of benzene from PVC containing  $\text{MoO}_3$  which is thought to contribute to the suppression of smoke generation by this material.

Table 1. Decomposition products of PVC samples

Compound	Retention Time (min)*
Benzene	3.5
Toluene (Methylbenzene)	7.8
Ethylbenzene	14.3
1,3-Dimethylbenzene	14.7
Styrene (Ethenylbenzene)	15.9
1,2-Dimethylbenzene	16
Propylbenzene	19
Ethylmethylbenzene	19.4
Trimethylbenzenes	20.1 & 20.7
Propenylbenzene	22.4
Indene	22.7
Methylpropylbenzene/Butylbenzene	23.2
Phthalic Anhydride	31.9
Diethyl Phthalate	39.4
Dipropylbenzene	41.1
Dibutyl Phthalate	47.8

\* Column: HP-5 MS capillary column (30 m x 0.25 mm i.d. x 1.0  $\mu$ m d.f.).  
 Carrier: Helium (24 psi)  
 Oven program: Initial: 40°C (10 min. isotherm), Ramp 5°C/min to 250°C (20 min. isotherm).  
 MS parameters: Mass Range: m/e 45-500, Scan rate: 3.21 scan/s

## CONCLUSIONS

The combination of TGA with either MS or FTIR is very useful and powerful. However, this configuration is best suited when simple (or few) gases are evolved during the TGA experiment. For materials that breakdown to give multiple organic species (e.g. most polymers) the use of an “off-line” technique allows the volatiles to be separated and identified conclusively by GC-MS. The ability to save some of the evolved gases for repeated GC-MS experiments allows optimization of experimental conditions and it is possible to use change collection tubes to sample the evolved gases from individual steps of multi-stage decomposition reactions.

## REFERENCES

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2. S. Materazzi; *Appl. Spectrosc. Rev.* **1998** 33(3) 189-218.
3. J. Mullens; *Calorim. Anal. Therm.* **1997** 28 73-77.

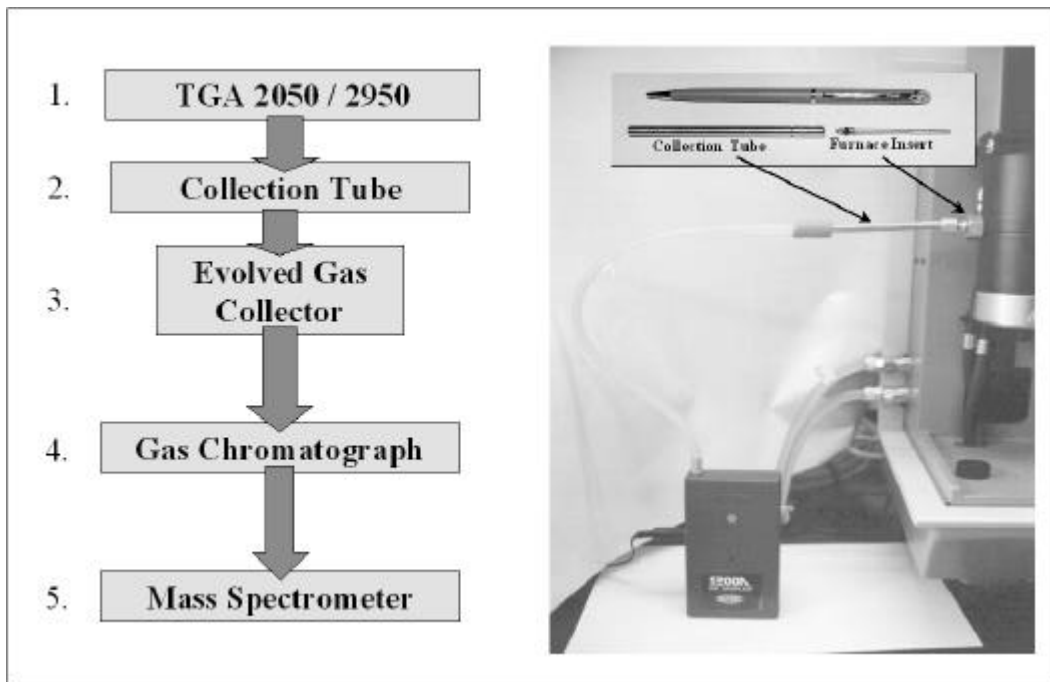


Figure 1. Overview of Evolved Gas Collection.

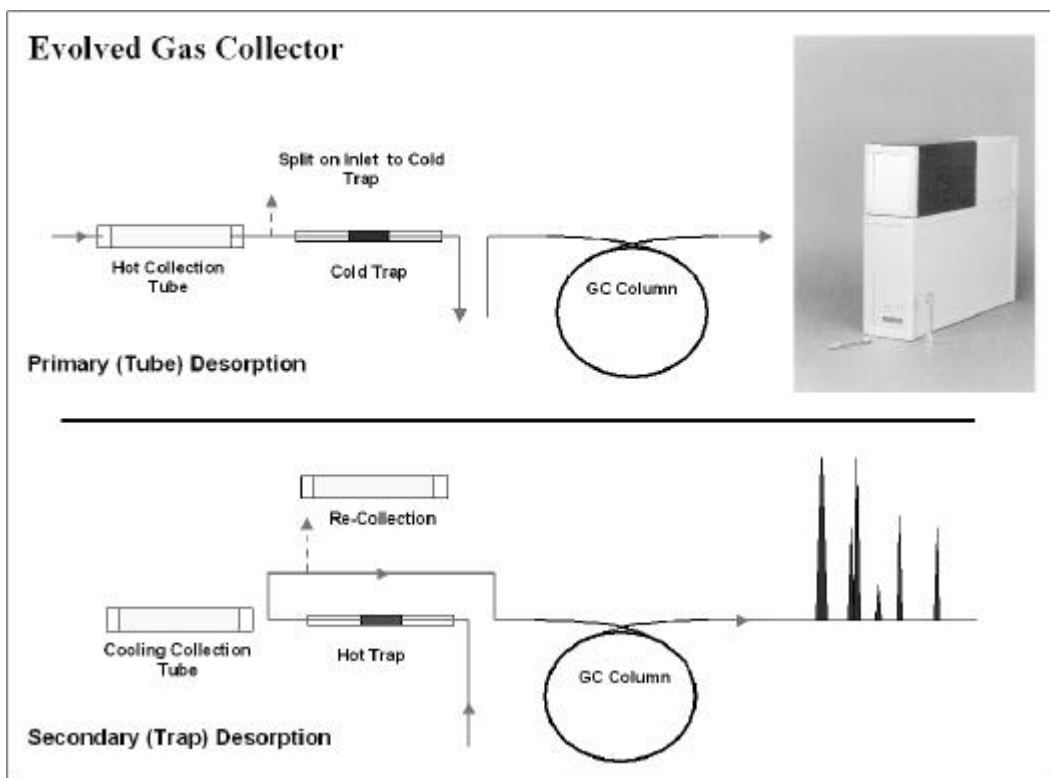


Figure 2. Overview of Evolved Gas Collector.

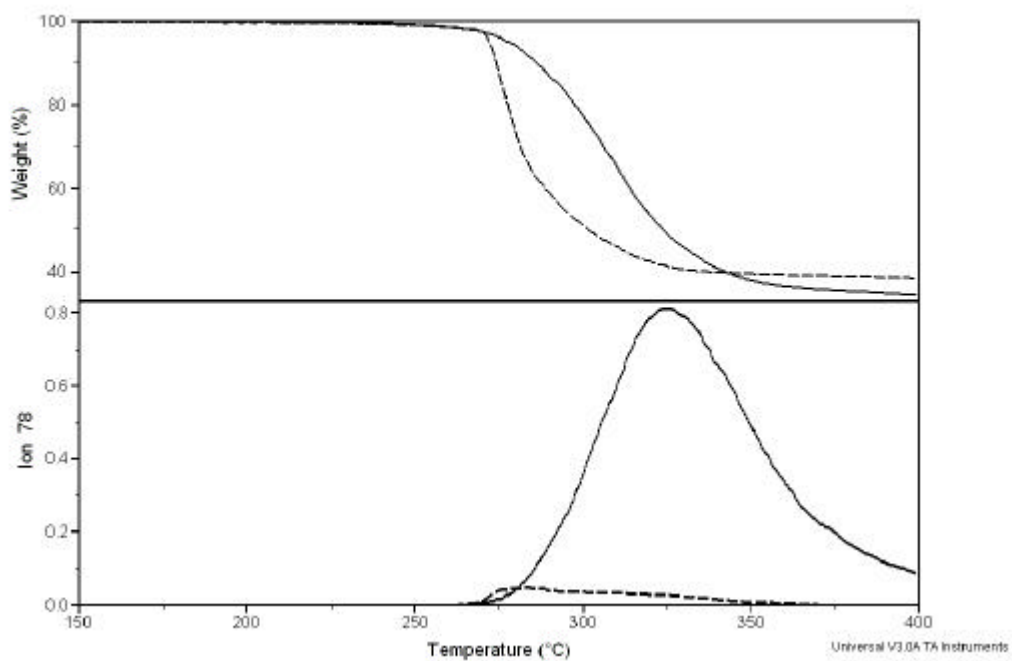


Figure 3. “On-line” TGA-MS data for PVC without (solid line) and with added MoO<sub>3</sub> (broken line).

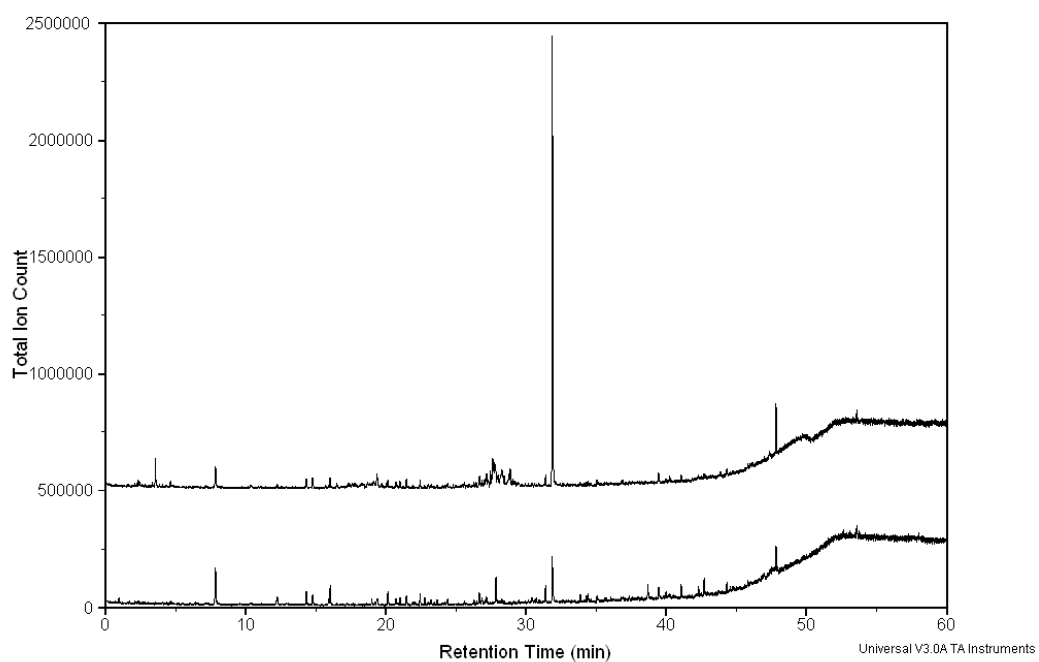


Figure 4. “Off-line” EGC data for PVC (see text).

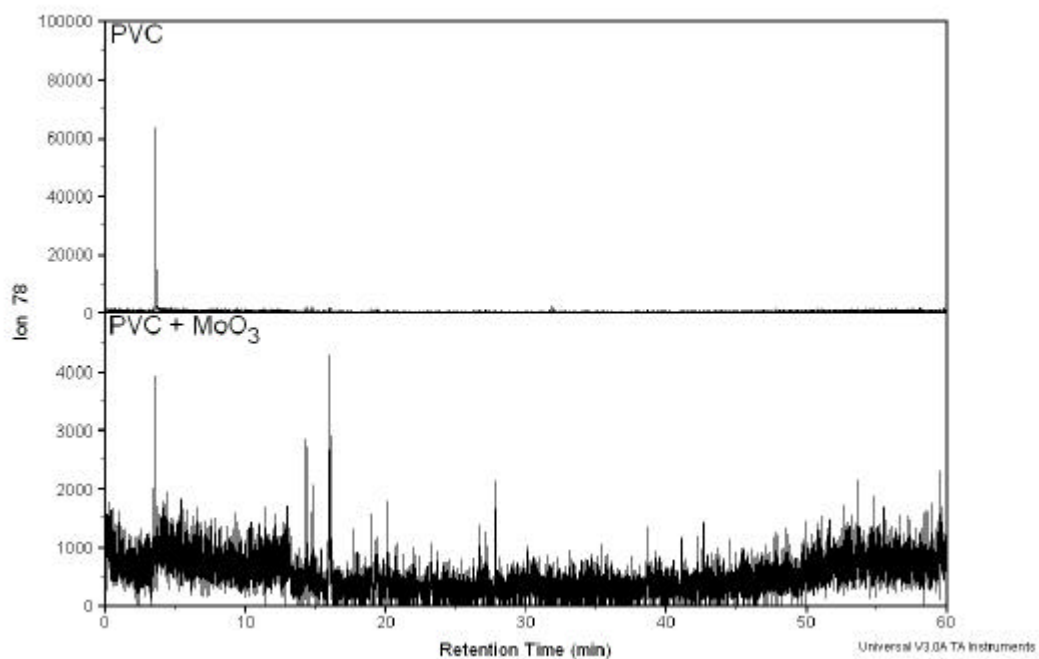


Figure 5. Single ion chromatograms for PVC samples (m/e 78).

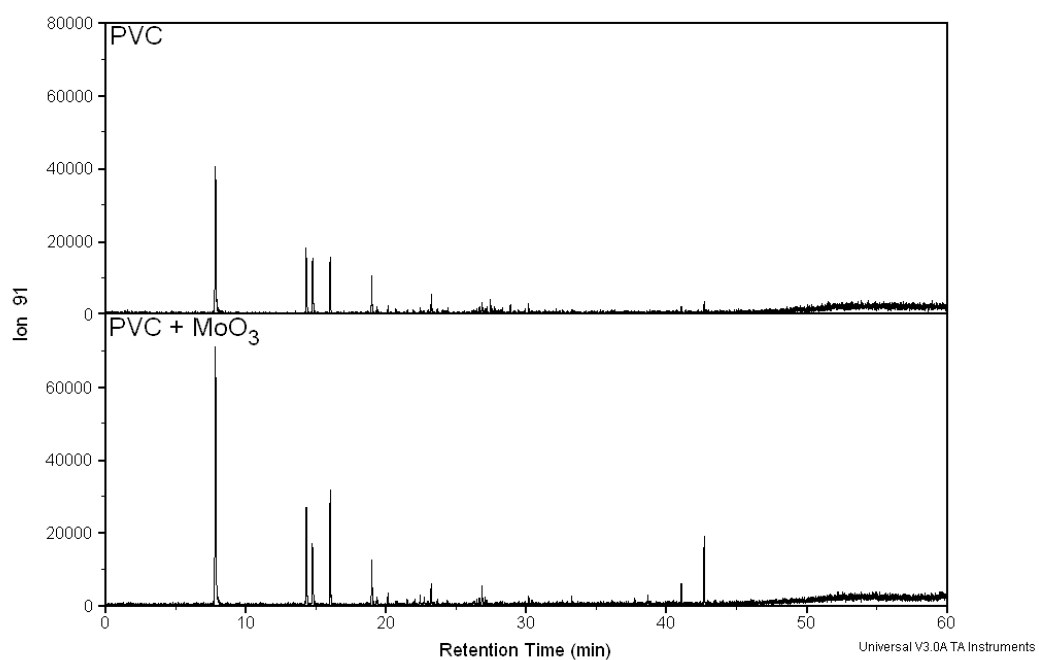


Figure 6. Single ion chromatograms for PVC samples (m/e 91).