

# Failure Analysis Using Gas Chromatography/Mass Spectroscopy

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## INTRODUCTION

Failure of polymer formulations may occur in various ways other than fracture, a common type of failure. For example, a material may have unacceptable odor or appearance, or may be of uncertain toxicity. Frequently the cause of the problem is a non-polymeric substance that can be volatilized and analyzed. The non-volatile nature of the host polymer, due to high molecular weight, is an advantage in that the volatile suspect material can be separated from the polymer for analysis. By heating in an inert atmosphere below the decomposition temperature of the polymer, the volatiles produced are only those of volatile non-polymeric materials. The technique is referred to as headspace analysis. For many polymers, heating temperature can be high enough (up to 300-350°C) to drive even relatively high boiling compounds out of the polymer. For example, many antioxidants and plasticizers can be separated this way. By using small samples, of the order of a few mg. or less, and a high enough temperature, volatile compounds can be analyzed quantitatively as well as qualitatively.

A common problem in failure analysis is to determine if there is a particular compound associated with a failure, and if that material was present in the formulation as manufactured, or was picked up in service. In the former case, the manufacturer may be liable for damages, but not in the latter case. A method to isolate and identify possible compounds causing the problem and to determine their origin is a powerful failure analysis method. Identification is done by mass spectroscopy operating on the gas chromatography (GC) effluent.

In this paper examples are given of problems solved by such a technique. An apparatus is described which has been developed to perform such analyses in an advantageous way.

## EXPERIMENTAL - THE DIRECT DYNAMIC HEADSPACE ACCESSORY

The unit is placed directly in the heated injection port of the GC. The sample is transferred automatically on command directly into the heated zone of the injection port and is removed at the end of the desired heating period. By using the injection port as the heated zone and collecting the volatiles at the head of the GC column in a cold oven, good resolution and sensitivity are achieved. Transfer lines or intermediate adsorption tubes, to be desorbed onto the GC column, are eliminated. Precise control of sample desorption time, temperature and column pressure are features of the apparatus.

Figure 1 is a diagram of the accessory. Load and run positions are shown in Figure 2. A closeup view of the sample

tube in the injection port is shown in Figure 3. Samples are contained in small glass tubes (ca. 1"x1/8" OD) held inside by glass wool. Volatiles are swept off onto the head of the GC column continuously, so that overheating effects on the volatiles released are kept to a minimum. The apparatus can be adapted to a sequential multiple sample unit operation, since the time of lowering the sample tube into the injection port and of removing it are controlled automatically.

The "direct" feature of the headspace unit described here refers to the use of the injection port as the heating zone. Transfer lines and other means of placing the headspace volatiles onto the GC column are eliminated. The result is a well focussed narrow band of volatiles that collects at the head of the column.

To appreciate the "dynamic" feature, comparison is made to "equilibrium" headspace devices. In the latter, volatiles are generated in a closed static environment, then transferred to the GC. By continuously sweeping the volatiles away from the sample, the dynamic method achieves a higher percent of the volatiles that can be generated from a sample in a single devolatilization step.

## EXPERIMENTAL - GC/MS CONDITIONS

A Hewlett/Packard 5985 GC/MS System was used with capillary columns. Typical columns used were (1) OV-1 fused silica capillary column 0.32 mm x 50 meters, 1.2  $\mu$ m phase; (2) carbowax 20M, 0.25 mm x 50 m, 2.0  $\mu$ m phase. Injection port temperature was set as required to evolve volatiles completely using the DDHA, typically 150-250°C. Sample heating time in the injection port typically was 5-10 minutes. Column oven temperature was set as low as that of liquid nitrogen, depending on the boiling point of the compounds volatilized and trapped at the head of the column. The chromatography was carried out by temperature programming, such as at 10° or 15° C/min rate of rise up to a top temperature of 250-300°C. The MS has a range of 10 to 1000 atomic mass units. Electron impact ionization was used with 70 electron volts. Scanning rate was 400 atomic mass units per sec. Sample weight varied depending on the type and amount of volatiles to be analyzed. For example, the weight was 18 mg for the blistered rubber case (example 4, below and Figure 4). This is relatively high because the weight of volatiles expected, relevant to the blister condition, was very low.

## EXAMPLES OF FAILURE ANALYSIS BY GC/MS

1. In this first case, the apparatus described above was not required. It was used in all the following examples. The problem was a large blister on a printed circuit board. The

blister space was sampled with a syringe and fine needle plunged into the blister. The gas was injected directly into the GC, and found by MS to be carbon dioxide. This information was helpful in controlling the problem.

2. A tar-like roofing product had a strong odor which was particularly objectionable when the material was hot, as in a closed hot truck. GC/MS showed the presence of morpholine, a solvent used in manufacture. Incomplete removal of morpholine was the cause of the problem odor. Modifications in processing gave an acceptable product.

3. An electrical cable stored in a warehouse had abnormal spots on the outside when it was taken to be used. This is an example of a point in the Introduction, i.e., did the questionable or unacceptable condition originate in the product as made, or did it occur in service. In this instance, it would be in storage prior to service.

Analysis of samples cut from spots and from non-spotted areas showed that the spots contained compounds not present in normal areas. That, in itself, is a good indication that the manufacturer was not at fault. Furthermore, the nature of one of the compounds in spots suggested a rodenticide, i.e., a material used to control rats and mice. It developed that the warehouse had sprayed such a control substance. Apparently the spots were the locations of droplets that fell on the cable.

4. In a similar case to example 3 above, described in the 1991 ANTEC paper of M. Ezrin, "Case Studies of Failures Due to Unintentional Service Conditions", a rubber electrical cable jacket developed blisters in service. The cable lay on the ground in a cornfield and provided power and control to a radar antenna. The cable manufacturer did not know that the cable would be on the ground in a cornfield. Agricultural chemicals sprayed on the corn would have also contacted the cable jacket. Samples of jacket were taken from blisters and from unblistered jacket. The analysis showed at least 5 compounds in the blisters not present otherwise. Some of these seemed reasonable as having probably originated from agricultural chemicals. In any case, the GC/MS of the volatiles using the Direct Dynamic Headspace Accessory clearly showed that the blisters were caused by an external source.

Figure 4 is part of the chromatogram of blistered and unblistered jacket, showing two compounds present in the former that are absent in the latter. Figure 5 is the mass spectrum of one of the compounds, identified as cyclopropane, 1-ethenyl, 2-hexenyl.

5. An underwater electrical transmission cable removed from service was found to have an unusually soft, weak jacket instead of the usual firm, rubbery, jacket. Analysis by GC/MS showed the presence of hydrocarbon oil that corresponded to oil that had spilled in the vicinity of the cable in question.

By showing that there was a close correspondence between the spilled oil and the contaminant in the cable jacket, it was concluded that the unusual condition of the cable was from contact with spilled oil. In this case, too, the responsibility could not be assigned to the manufacturer, but to service conditions.

Figure 6 is the chromatogram of an oil sample recovered from ocean bottom soil, dried and devolatilized at 260°C for 5 minutes. Several peaks of the oil were also found in the chromatogram of the cable.

6. In food and medical applications, there is little or no room for uncertainty as to possible toxic substances in a product that may be ingested or transferred to skin, as from adhesive tape. In the latter case, GC/MS, using devolatilization of the product in question, was able to identify residual solvent and residual monomer from the adhesive layer. Knowing what is present and the level permits modifying processing and/or formulation so that only acceptable trace materials are present.

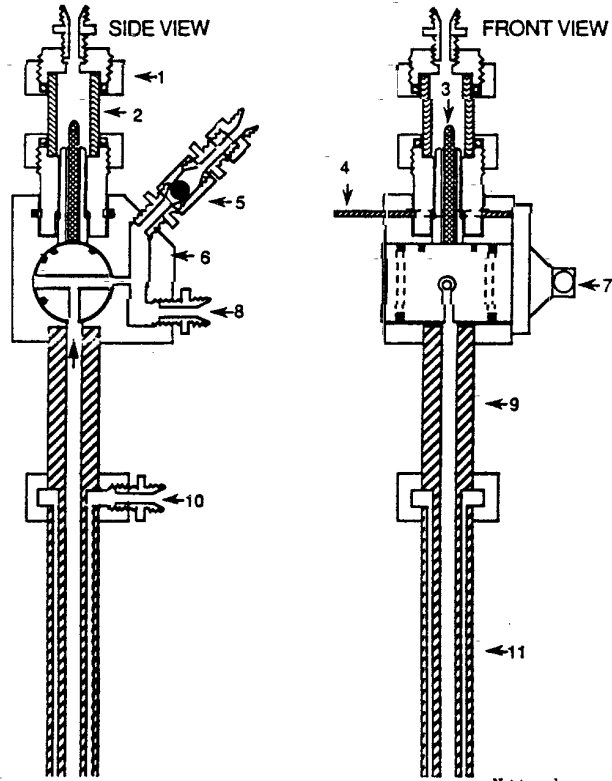
The direct heating method is advantageous over solvent extraction, followed by injection of the extract. Not only is the procedure simpler and faster, but detectability may be improved and there are no complications from the extracting solvent.

7. GC/MS has been used to determine what volatile compounds form during thermal aging of crosslinked polyethylene electrical insulation. Such substances are not only informative as to the mechanism of aging, but are relevant also to explosion hazards because of flammable gases that accumulate and may be trapped in restricted conduits, etc. Figure 7 shows chromatograms for aged and unaged XLPE insulation. The differences are numerous, and many were identified by MS.

#### CONCLUSIONS

There are many instances in polymer research and problem solving wherein GC/MS can be useful. The isolation and identification of compounds that relate to or are the cause of a problem or failure can be accomplished readily provided that they are sufficiently volatile to pass through a GC column. The apparatus described herein, Direct Dynamic Headspace Accessory, has been found advantageous as a means of releasing volatiles from samples directly in the GC injection port. Chromatograms of good resolution were obtained, enhancing the chances of making identification by MS. The temperature limit for devolatilization is that of the GC injection port, ca. 350°C in this case. In many instances the method is the best and most direct way of proving if an unusual or unacceptable condition developed from an external service condition or is related to the composition as manufactured.

# Direct Dynamic Headspace Accessory



Not to scale  
Gay Levine 4/1090

Figure #1 Diagram of Direct Dynamic Headspace Accessory 1. Loading Area Cover and Window assembly; 2. Glass Window; 3. Sample Tube; 4. Loading area Interlock; 5. Check Valve; 6. DDHA Valve Body; 7. Valve and Handle assembly; 8. Vented Carrier Gas Outlet; 9. Sample Transport Tube; 10. Carrier Gas Inlet; 11. Injection Port Insert assembly

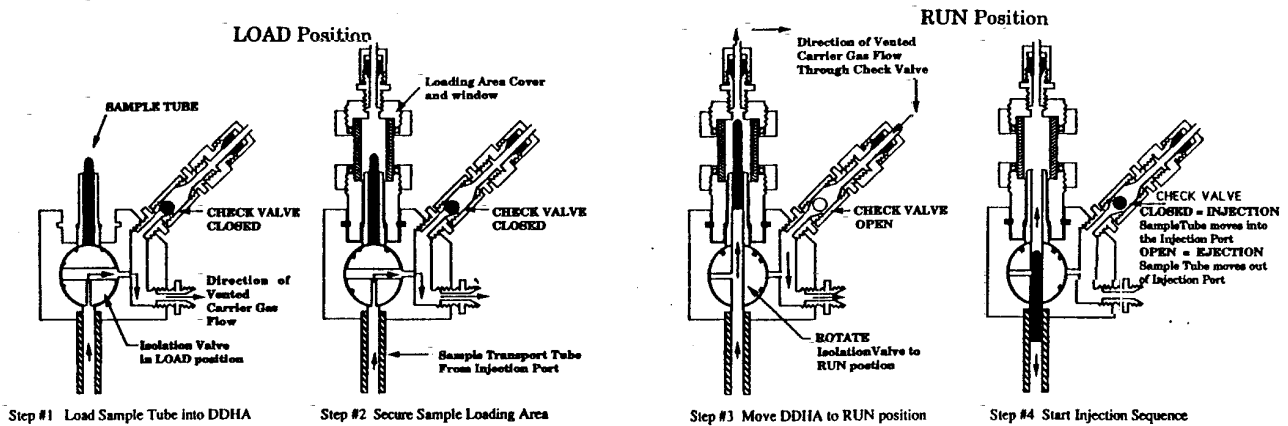


Figure 2 - Load and run positions of direct dynamic headspace accessory.

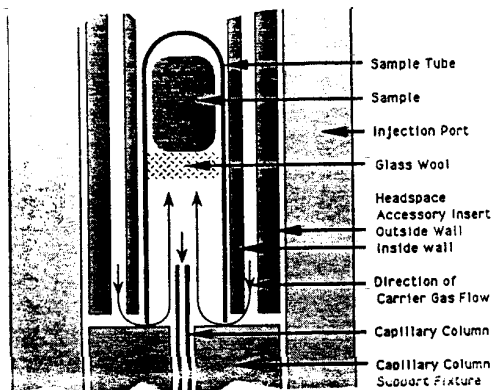


Figure 3 - Position of sample tube in injection port during collection of headspace gases onto column.

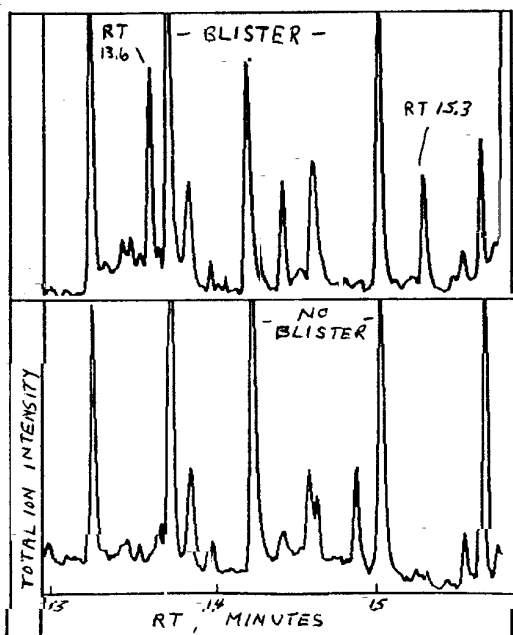


Figure 4 - GC chromatograms of blister (top) on rubber electrical jacket and unblistered area (bottom).

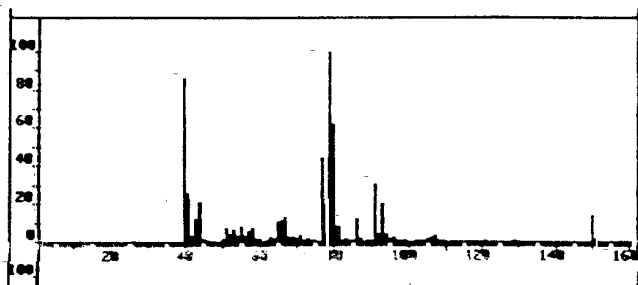


Figure 5 - Mass spectrum of peak RT 13.6 min. of blistered rubber (see Figure 4).

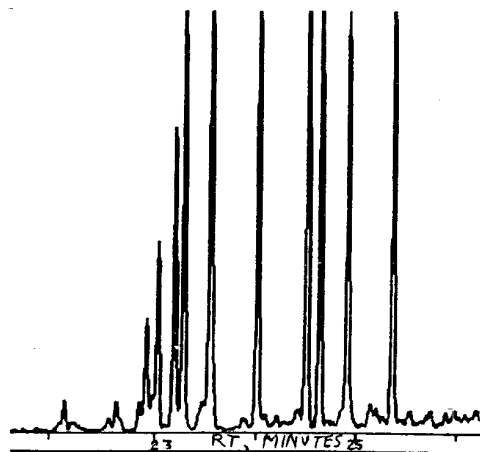


Figure 6 - GC chromatogram of volatiles from dried ocean bottom soil samples. Comparison with volatiles from underwater cable showed the damage to the cable was due to an oil spill.

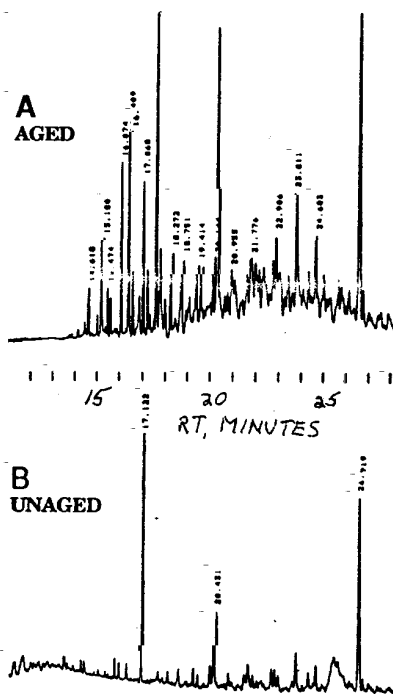


Figure 7 - GC chromatograms of volatiles from aged and unaged crosslinked polyethylene insulation.