Society of Plastics Engineers, ANTEC Conference Proceeding, 1992, p.1717-1719

Application of Direct Dynamic Headspace GC/MS to Plastics Compositional and Failure Analysis

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INTRODUCTION

In 1991 Ezrin and Lavigne[1] described a direct dynamic headspace device they designed for use in GC/MS (gas chromatography/mass spectroscopy) of plastics materials. Examples of its application in failure analysis were also given. Continued experience with the device and with the method of headspace GC/MS has further demonstrated their versatility and usefulness for both compositional analysis and for failure analysis. In this paper additional examples are given. The advantages of the device are (1) rapid placement of sample in the heated zone and removal after a predetermined time; (2) the tube containing sample sits directly on the head of the GC column itself, eliminating the need for a transfer line or other secondary means of introduction of sample into the GC in a separate step. In a typical run the GC column oven starts at or below room temperature, and is temperature programmed to as high as 350° C, depending on the particular GC column. Using capillary columns, excellent resolution of separated compounds is obtained. Identification is made on the basis of GC retention time and mass spectra.

What the continued work with the method has shown is that it is possible to see by GC compounds whose boiling point would seem to make then too low in volatility to be evolved by the headspace technique. Yet the method proved adequate for even very high boiling compounds. The work has also affirmed that it is ideal for isolating trace level compounds that would have been much more difficult to determine by extraction methods. It avoids having to sort out the compound of interest from extraction solvent impurities. Also, the danger of losing the compound being sought, because it may have reacted with solvent or other compounds in the long period usually involved, is minimized. Even though the headspace method employs high temperature to release volatiles, the volatiles are immediately swept into a cool zone, so that total heat history, in inert atmosphere, is not great. Furthermore, analysis time is much shorter than by extraction.

EXPERIMENTAL

Presently we have been using a Hewlett Packard 5890 Series II GC with the 5971A MSD (mass selective detector). The same direct dynamic headspace device is used as was described in 1991. Temperature range for release of volatiles is up to 400° C, the upper limit of the injection port of the GC. The instrument includes a reference compound MS search capability for identification of unknown mass spectra.

Typically a sample of only about 5–25 mg is used, placed directly in the hot zone of the GC injection port. But it is also possible to analyze the volatiles from much larger quantities, by collecting them on an adsorbent column (Tenax) and subsequently thermally desorbing from Tenax onto the GC column.

EXAMPLES OF APPLICATIONS

The examples are of two types – (1) those in connection with failure analysis, using GC/MS to identify materials and thus aid in determining the cause of a failure, and (2) compositional analysis, i.e., analysis of an unknown composition. These two situations are very similar – they differ mainly in the purpose of the analysis. Analysis for determining an unknown composition for the purpose of matching competition could even be considered a type of failure analysis – failure to match a competitive product.

A. FAILURE ANALYSIS

1. Identification of Source of Oil in Oil Contaminated Electrical Systems

One example of this type was given before[1]. This appears to be a common type of failure, as evidenced by the fact that two other electrical type failures attributed to oil contamination have occurred since then. In one case, involving a submersible pump, oil had leaked onto the neoprene jacket of the cable causing it to swell. GC/MS identified the source of the oil in two ways – by the several peaks in GC and by the mass spectra of peaks from the unknown and the suspected source.

2. Exudation Problem at Soldered Locations

In this case a wax–like compound separated from a polyolefin type insulated wiring used in circuitry for a military application. The manufacturer of the equipment was reluctant to release it for service without knowing the nature of the exuded material and the cause of the exudation. The exuded material was identified by infrared spectroscopy as the antioxidant, but that gave no clue as to the cause of the exudation. GC/MS not only confirmed the identification of the antioxidant, but more importantly for the cause of the effect, was the identification of low levels of both isopropanol and a Freon type CFC (chlorofluorocarbon) solvent. Both the latter compounds were used in degreasing/cleaning of circuit boards prior to soldering. Their retention and entrapment in the insulated wiring to be soldered was due in part to wicking along the cable at cut locations where soldering was to occur. The two cleaning fluids, being solvents for the antioxidant, tended to carry antioxidant along with them as they responded to the heat of soldering.

As a result of the analysis, the manufacturer of the cable in question was absolved of responsibility for the exudation and the manufacturer of the equipment learned that it would be necessary to dry the degreased boards further before soldering.

3. Electric Power Cable Suspected as Cause of Worker Health Problem

[1]M. Ezrin and G. Lavigne, "Failure Analysis Using Gas Chromatography/Mass Spectroscopy", 1991 SPE–ANTEC, Montreal, p. 2230–2233.

Crosslinked polyethylene power cable being installed in an electric utility plant was suspected of having caused workers handling the cable to become ill. Two samples were submitted – one that had been handled in the case in question, and another that had not caused any such difficulty. Both were from the same shipment to the utility, so that it was not likely that a difference existed that would cause a health problem. But, as often happens in failure cases, the product supplier is immediately suspected, even when it is very unlikely that the fault lies with the product in question, as in this instance.

Since the nature of the health problem was such that a volatile material was suspected, headspace GC/MS was a logical choice. The two cables submitted, one suspected as the cause of the problem, and the other not under suspicion, showed identical chromatograms and spectra. Where there were differences, it was in relative amount of traces of acetophenone and cumyl alcohol, the suspect cable having more of both. These compounds are decomposition products of the crosslinking agent, dicumyl peroxide, used to crosslink PE. A cable made in this way has a substantial content of decomposition products, as evidenced by odor. Cable manufacturers are well aware of these and other decomposition products of dicumyl peroxide – the odors are strong and well recognized. The concentration decreases with time as the volatile compounds are evolved. The concentration remaining in the cable in question was a very small fraction of what is formed when the cable is manufactured and in storage. Yet there is no significant history of health effects (nausea, etc.) from the compounds at much greater concentration than in the cable in question.

It was concluded that the cables were not likely to have caused the problem. Suspicion was then placed on a more likely cause – a natural gas leak in the work area.

4. Compounds Adsorbed on Fiber Reinforcing Agents for Composites

Reinforcing fibers, such as glass and carbon, which are used in composites, generally use a coupling agent to effect a good bond between fiber and the matrix resin. Ideally, there should be little else adsorbed or bonded to the fiber prior to application of the coupling agent. With carbon fiber, in particular, the strongly adsorbing characteristic of the fiber makes it difficult to eliminate undesired compounds entirely before addition of the coupling agent. Headspace GC/MS was used to analyze for adsorbed compounds. The results are in Figure 1. In spite of the fact that the fiber was thought to be substantially free of adsorbed compounds, it actually had many volatile compounds. These might interfere with the contact of the coupling agent. They may also exert vapor pressure at elevated temperature, either in curing or in service, tending to weaken the bond between fiber and resin. Headspace GC/MS is an effective way of monitoring the condition of the fiber prior to processing.

In Fig. 1, the peak near 28 minutes is for di–2–ethylhexyl phthalate. Being unexpected, its presence was traced to plasticizer in the plastic wrapping in which the carbon fiber had been received. This is a common problem which can lead an analysis astray if not realized. Samples placed in low density polyethylene bags, for example, have been found to transfer surface material from the bag to the samples.

Together with the example in B1 below, this is also a case of a high boiling compound (384°C) being detected readily by headspace GC/MS.

5. Analysis of Volatiles Collected from a Large Quantity of Material

Instead of using small samples (usually up to ca. 25mg) introduced directly into the heated zone, volatiles from some materials have been collected over periods of about a month while exposed to heat. Two such instances were epoxy resin electrical spacers used in high voltage applications, and EPR cable (ethylene propylene rubber) insulation for medium voltage distribution. Volatiles are collected on a Tenax column ca. 3" long x ca. 1/4" diameter. The adsorbed volatiles were thermally released from the Tenax and swept with carrier gas onto the GC column. In the case of the epoxy resin, interest was in volatile material that might contribute to void formation. For cable insulation, interest was in learning about mechanism of thermal degradation.

B. COMPOSITIONAL ANALYSIS

1. Identification of a High Boiling Trace Compound

The purpose was to determine what the resin was in an impregnated fabric. The fabric was part of a system in which bond strength to material added thereto was of critical importance. Infrared spectroscopy of extracted samples was inconclusive and there was interference from extractables of the fabric. Headspace GC/MS was used primarily to identify the resin, on the assumption that it was a relatively uncured thermosetting resin. That was accomplished successfully by GC/MS and confirmed by infrared spectroscopy of a tiny particle of resin picked off from the substrate, and by wet chemical analysis. What was not expected was a bonus – identification of very low levels of triphenylphosphine and somewhat larger amounts of nitromethane. TPP had apparently been used to improve wetting of fabric, thus improving the bond of resin to fabric. Garton[2,3] has reported on the use of TPP to improve wettability of polyethylene.

What is remarkable about finding TPP by GC/MS is that its value of boiling point is 377°C. Yet at 150°C headspace temperature, there was no difficulty in obtaining a sharp GC peak (Figure 2). The mass spectrum matched that of TPP well, and the retention time was also confirmed. Based on analysis for phosphorus, the approximate content of TPP was of the order of 0.1% or less. Furthermore, nitromethane, which was also found, was probably the solvent for introducing TPP onto the fabric. By means of GC/MS, an otherwise difficult to determine trace compound was identified along with the solvent with which it had been applied.

2. Identification of a Polymer Not Readily Identified by Other Methods Due to Interference From Additives Present

A flame retardant product had been identified as containing a uncrosslinked elastomer by solvent extraction. The problem was that the extracted polymer and flame retardant (alumina trihydrate), together with carbon black, accounted for only about 60–70% of the product. The question was whether a crosslinked polymer was also present. Infrared spectroscopy, differential scanning calorimetry and thermogravimetric analysis were unable to establish the identity of the insoluble polymer. Alumina trihydrate interfered with IR and with TGA. DSC of the material after removal of the soluble polymer gave a melting point of 85°C, but that was not enough to identify the material in question. While there was reason to suspect EVA (ethylene vinylacetate) as the crosslinked polymer, IR and TGA could not confirm that. A well known method[4] for determining vinyl acetate content of EVA is by TGA. The first decomposition step corresponds to acetic acid released by the vinyl acetate portion. Using slow rate of rise, resolution is good enough to use the weight loss of the first decomposition step as a quantitative measure of VA. In this case, however, alumina trihydrate decomposes over the same temperature range, so that TGA cannot be used as an indication of VA.

Headspace GC/MS was used, setting the temperature at 325°C. At that temperature, acetic acid was released and readily identified by GC retention time and by mass spectra. An attempt had been made to identify acetic acid qualitatively by heating sample in a test tube and smelling for the typical pungent odor. This was not successful, probably because acetic acid may have reacted with alumina trihydrate (a base) as it formed by decomposition of EVA. Using high temperature (325°C) in the injection port to rapidly decompose EVA and carrying off volatiles as formed, at least some of the acetic acid passed into the GC column without reacting with the trihydrate.

Having confirmed EVA as the crosslinked polymer, the melting point of 85°C (DSC) permitted selection of a grade of EVA very close to that in the competitive material.

CONCLUSION

The examples presented further illustrate the versatility and wide applicability of headspace GC/MS to problems of plastics analysis, both for failure cases and for compositional analysis. The direct dynamic headspace device described in 1991 has continued to perform well and to expand the applications for headspace GC/MS. Compounds of high boiling point, thought to be too non–volatile for analysis by this method, have been evolved and identified by the method. The design of the device probably contributes to this capability, there being no transfer lines and the sample tube being located directly at the head of the GC column. The continuous (dynamic) nature of the method also helps in the transfer of volatiles to the column. Thereafter, programmed heating at high temperature brings about resolution of compounds.

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[2]J. Yang and A. Garton, "Primers for Polyolefin Surfaces", ACS Preprints, PMSE Div., 62, 1990, Boston, p. 916–919.

[3]J. Yang and A. Garton, "Aging of Primed Polyolefin Surfaces", ACS Preprints, PMSE Div., 65, 1991, New York, p. 255–256.

[4]A. Krause, A. Lange, and M. Ezrin, "Plastics Analysis Guide – Chemical and Instrumental Methods", Hanser, 1983, p. 267.

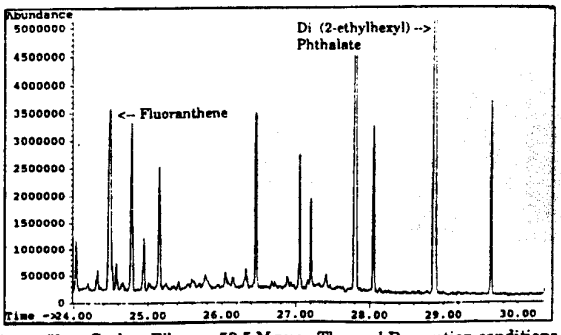

Figure #1 Carbon Fibers 59.5 Mgms., Thermal Desorption conditions 4 mins. at 250°C, Column HP-1, 15 M x 0.25 mm , 0.2 µm film thickness, Temperature program 0°C to 300°C at 10°C /min.

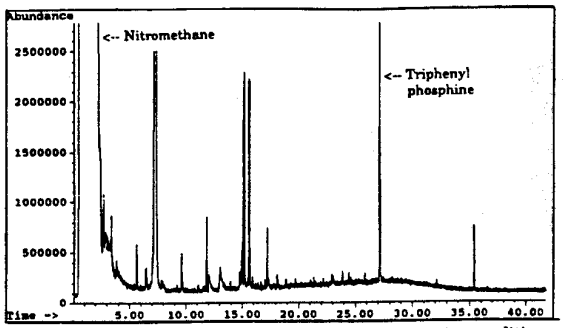

Figure #2 Coating on cloth 5.4 Mgms., Thermal Desorption conditions 2 mins. at 150°C, Column HP-1, 15 M x 0.25 mm, 0.2 µm film thickness, Temperature program 35°C to 325°C at 15°C /min.