Direct Evolved Gas Analysis / FTIR

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by Dr Val Rossiter*, Dr Ray Milward** and Dr Michael Simpson***

DIRECT EVOLVED GAS ANALYSIS / FTIR

The power of Fourier Transform Infrared (FTIR) spectrometers has led to their application in association with a variety of other techniques. The ability of FTIR to identify materials simply, quickly and with a very high degree of certainty, has led to such applications as gas chromatography interfacing (GC/FTIR), liquid chromatography interfacing (LC/FTIR), thermogravimetric interfacing (TGA/FTIR) and other such combined or hyphenated techniques. The contribution of the FTIR is in generating a unique infrared spectrum of the evolved material associated with the GC peak, LC peak or thermogravimetric event. This spectrum can then be compared and often exactly matched to a corresponding spectrum in the computer based FTIR reference library of spectra. Even in the case of the "unknown" not being matched to a reference spectrum already in the library, the FTIR software will enable the analyst to classify the compound through its functional groups and to compare it with its close relatives in the library.

In recent years, FTIR spectrometers have become much more widely available and their growing popularity has been accompanied by remarkable reductions in cost together with much increased instrument power. In this article, we wish to show how many difficult problems can be resolved entirely within the scope of the FTIR spectrometer by using a specially designed "accessory". The new technique of Evolved Gas Analysis (EGA/FTIR) is effectively carried out independently by the FTIR with no reliance on other instruments, unlike GC/FTIR or TGA/FTIR. In many respects EGA/FTIR fulfils the objectives of TGA/FTIR, but EGA/FTIR can also solve additional problems. These would include, for example, the examination of materials for residual solvents or solvent contamination.

INSTRUMENTATION

Evolved Gas Analysis:

Figure 1 shows the new Aabspec EGA/500 System for Direct Evolved Gas Analysis/FTIR. The front section is fitted with a valve and contains a low-volume, high performance Light-Pipe which is gas tight (Aabspec Patent). The rear section contains the Sample Stage. This can accommodate up to a 5ml volume sample and is routinely rated to sample temperatures of 500degC, with even higher temperatures possible if required. The sample loads into a test tube which installs vertically and the Sample Stage temperature is precisely regulated by a Digital Linear Temperature Programmer. This allows the sample temperature cycle to be selected with initial temperature and hold times, variable ramp rate and selectable upper temperature and hold time, etc. The Light-Pipe is separately temperature controlled by a precision Digital Temperature Controller so that the Light-Pipe and Sample Stage temperatures are independent.

The gas volumes in the two sections are interconnected with the valve enabling the exit of the Light-Pipe to be sealed (if required). A choice of blanking cap or gas port at the sample stage configures the system for either closed or flow through operation. If the system is to be operated in the closed mode, then the sample may be contained in vacuum or with a pressurized gas as required. The thermally generated vapour from the sample is continuously released to the Light-Pipe during the experiment and is also in contact with the heated sample. In the flow through mode, a carrier gas is used to stream the released vapour from the sample through the Light-Pipe. Typically the spectra would then be continuously acquired by the FTIR and correlated against a time and temperature profile determined by the sample heating programme.

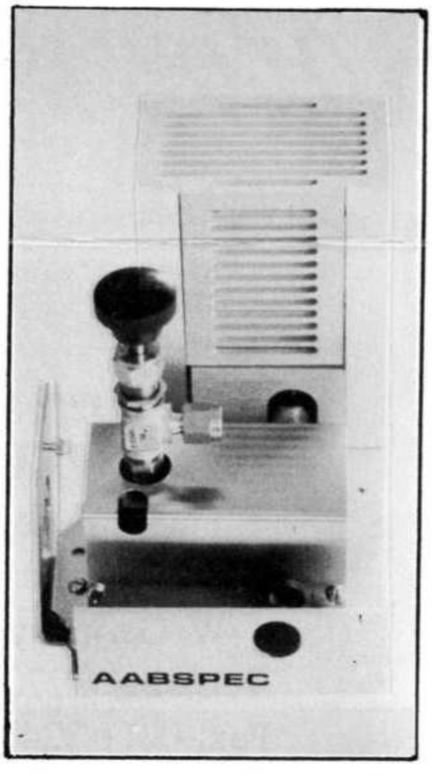

Figure 1. The new Aabspec EGA/500.

The EGA/500 incorporates a mounting system which fits the standard 2″ sample slide in the sample compartment of the FTIR.

The FTIR Spectrometer:

A standard Mattson FTIR spectrometer (Figure 2) was used in the following experiments to obtain the EGA/FTIR data. The EGA/500 was mounted in the sample compartment. No additional optics were required. In many EGA/FTIR applications, a combination of good sensitivity and wide spectral range are desirable. These features were obtained by using a liquid nitrogen cooled MCT(B) type FTIR detector. If higher sensitivity were required, an MCT(A) detector could have been used. This would have restricted the low

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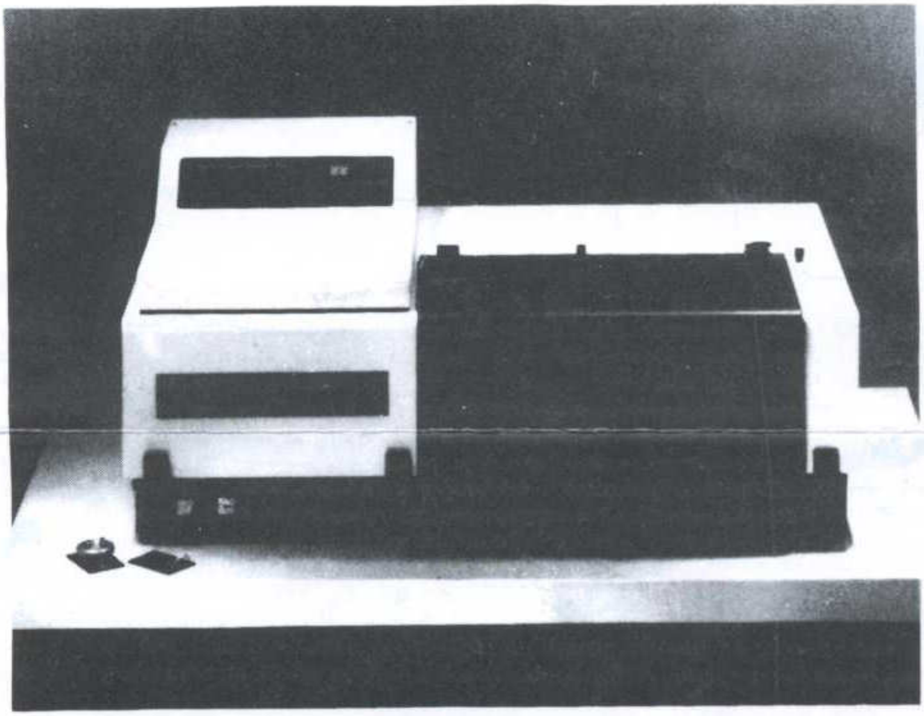

Figure 2. The Mattson Polaris FTIR spectrometer.

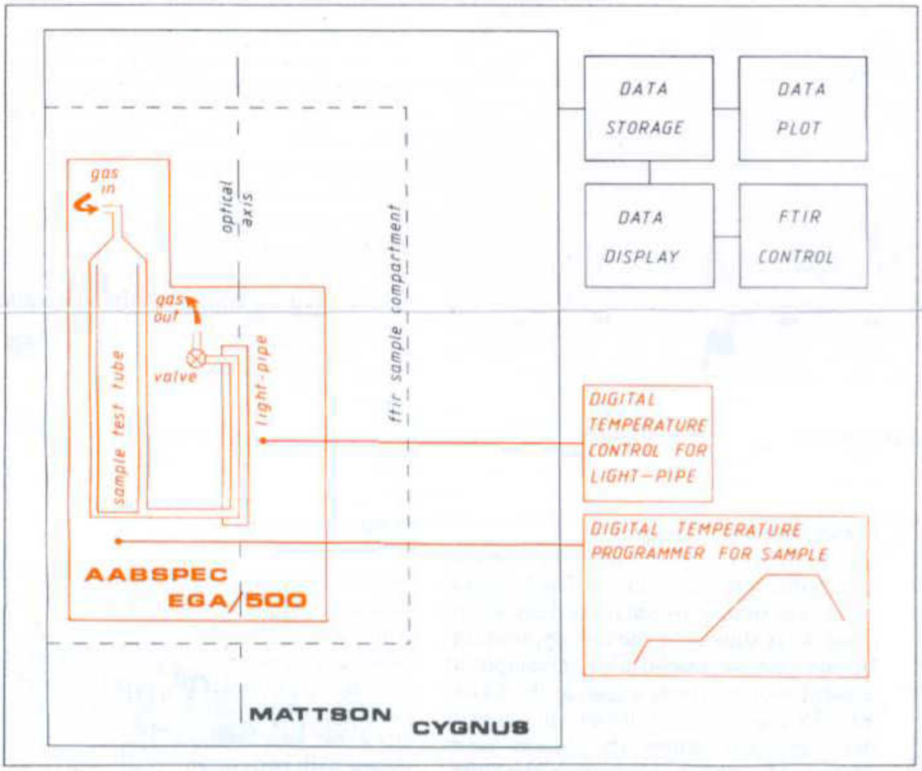

Figure 3. A schematic representation of Direct EGA/FTIR.

wavenumber range, a region which is important, for example, in identifying chlorinated hydrocarbons. In practice, the overall system proved to be extremely sensitive with the MCT(B) detector. Spectra were recorded at $8cm^{-1}$ wavenumber resolution, taking 32 sample scans per spectrum. The overall EGA/FTIR arrangement is schematically illustrated in Figure 3.

APPLICATIONS

Thermal Decomposition of Materials:

One of the applications of Thermogravimetric analysis (TGA) is to study the thermal breakdown of materials. The use of FTIR to form a combined TGA/FTIR system greatly enhances the TGA data by identifying the gaseous breakdown products. There is then available much more specific information on the chemistry of the process than can be obtained from the TGA alone. A simpler way of obtaining much of this information is with Direct EGA/FTIR. Here all the data is provided by the FTIR where the released vapours are identified as a function of the time/temperature heating profile used for the sample. As an example of the type of information obtainable, Figure 4 shows two superimposed spectra for the vapour released during the thermal decomposition of a commercial adhesive tape at 400 degC. The upper spectrum is obtained when the sample is heated in a nitrogen atmosphere, while the lower spectrum shows the decomposition product when the sample is heated in air.

Head Space Analysis:

The analysis of the head space over a solid or liquid is a useful technique with important commercial applications. For example, it is possible to quickly check the character of the solvent system used in commercial samples by this method. To illustrate the application of EGA/FTIR for head space analysis, the spectra of the head space of three liquids are shown in Figure 5. The spectra were obtained by placing a small quantity of the liquid in the EGA/500 sample stage and heating the sample to 60degC. The upper spectrum is that for a commercial turpentine. The middle spectrum is for a commercial solvent based paint sample and the lower spectrum is for a varnish sample. Further analysis of the data is, of course, possible with the FTIR. For example, the software provides spectral subtraction routines which can be used to subtract these spectra in a variety of ways and so examine the differences between the samples.

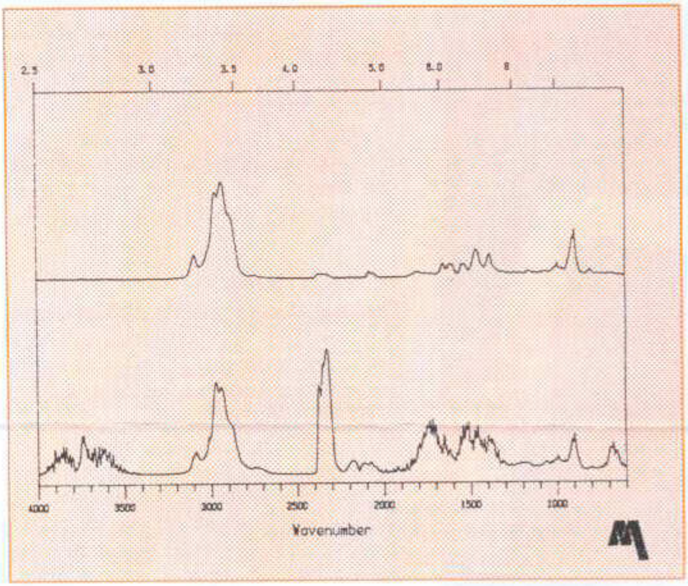

Figure 4. Decomposition products of an adhesive tape.

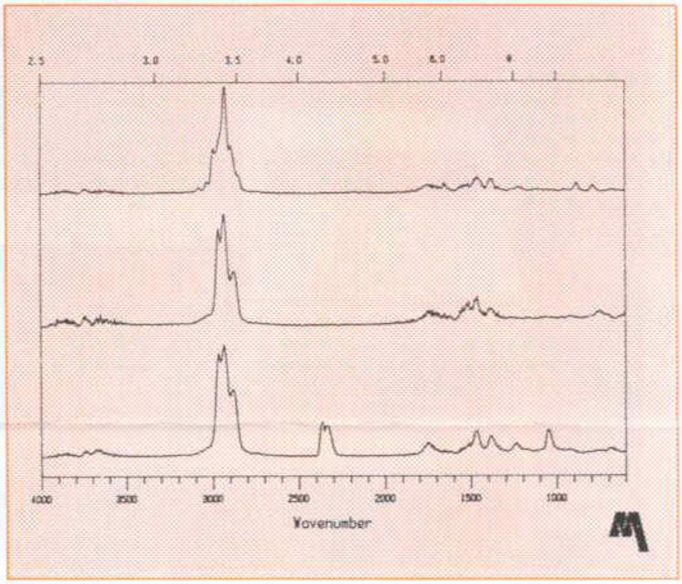

Figure 5. Head space composition of paint related products.

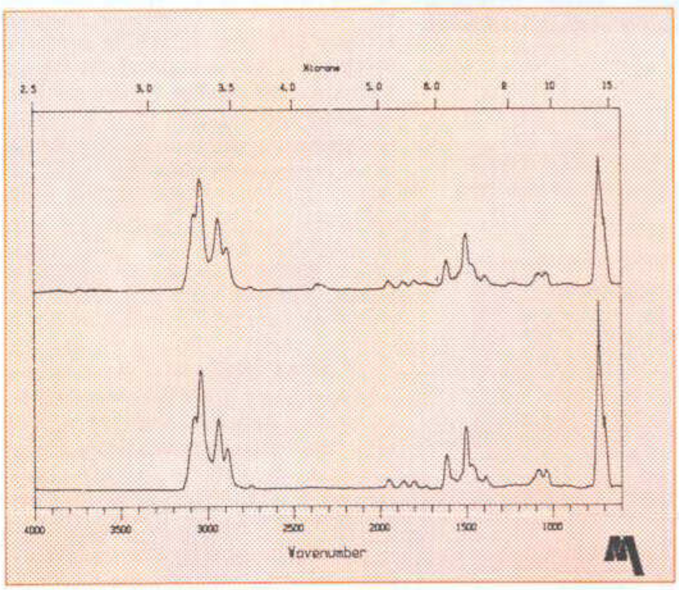

Figure 6. O-Ring failure as a result of toluene absorption.

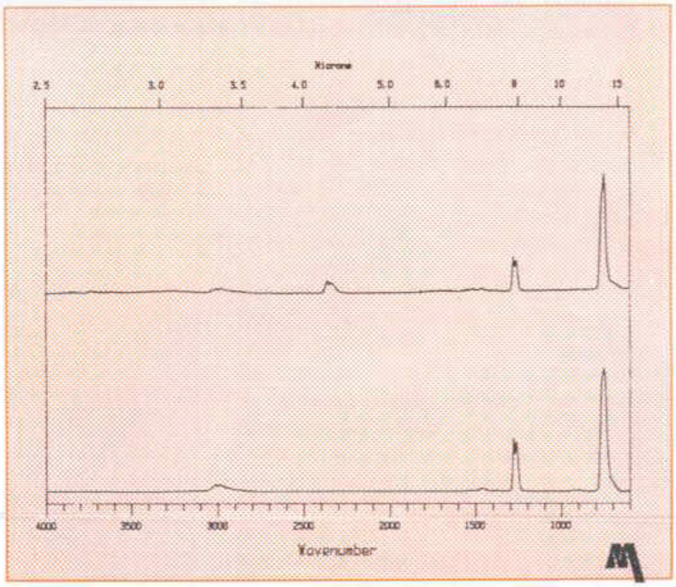

Figure 7. Dichloromethane contamination of polypropylene beads.

Component Failures:

Failure analysis can be a difficult and time consuming business. We wish to illustrate here how Direct EGA/FTIR can provide rapid solutions to some such problems. The failure of an O-Ring Seal in service can often provide only residual small fragments for subsequent analysis. We took such a small fragment and heated it in the EGA/500. The resulting spectrum is shown in the lower trace in Figure 6. The upper trace is the spectrum of toluene and is an excellent match obtained from the computer based spectral library search routine.

Material Contamination:

The problems of contamination of materials (either raw materials or finished product) and that of residual solvents are in some ways similar to the last application. In this case we placed a small sample of suspect polypropylene beads in the EGA/500. In Figure 7, the lower spectrum is that obtained when the beads were heated. The upper spectrum is the reference library spectrum for dichloromethane. In this example, the low wavenumber range of the MCT(B) detector proves to be useful in identifying this chlorinated hydrocarbon contaminant.

CONCLUSIONS

We have outlined the basis of a new FTIR technique for Direct Evolved Gas Analysis/FTIR. The simplicity of the technique, essentially requiring familiarity only with the FTIR, together with its problem solving power make this a most attractive new method. The data was obtained with two commercially available instruments the Aabspec EGA/500 and the Mattson FTIR. Many more applications of commercial and environmental importance will be found for this attractive and cost effective analytical method.