QUANTITATIVE APPLICATION OF THERMO SYNERGY TG-FTIR ON FORMALDEHYDE SOLUTION SAMPLE

Abstract

Quantitative analysis by Thermogravimetry (TG) is very simple for single-step transitions. However, it is impossible to perform quantitative analysis on overlapped TG transitions, by using TG alone. It is then investigated in this paper to utilize TG-FTIR to perform quantitative analysis for overlapped TG transitions. Formaldehyde solution samples were utilized as the examples. Results showed that it is possible to obtain quantitative information of the components in sample, after performing calibration experiments based on the gases evolved from sample.

Introduction

Thermogravimetry (TG) has been widely used as a tool for analyzing the sample's composition.(1,2) One of the problems is that when two or more weight loss steps are overlapped during the TG experiment, it is very difficult for TG to completely separate and quantitatively analyze them. In Fourier Transform Infra-Red Spectroscopy (FTIR), instead, it is easy to identify different components by looking at the FTIR peaks at different wave numbers. When FTIR is used as the Evolved Gas Analyzer (EGA) for TG, referred to as TG-FTIR, it is then possible to identify different evolved gas components from one TG weight loss step.

In FTIR, the peak characteristic, such as peak height, is proportional to the concentration of the gas, according to the Lambert-Beer's law. (3) Therefore, with success in identifying evolved gas components by FTIR, it is possible to quantify the amount of certain gas evolved from TG. Then the amount of corresponding component in the sample can be obtained from calibration experiments. This kind of application is useful for quantifying compositions of samples which have overlapped TG curves, caused by two or more components. Especially for polymers, overlapped TG curves occur very often because of the plasticizers, initiators and terminators presented in polymers.

Formaldehyde is an evolved gas from the decomposition of some polymers. Because it is toxic, it is necessary to determine the amount evolved. Solution samples were then utilized, in order to establish standards. The possibility of quantitative analyzing formaldehyde solutions by TG-FTIR is investigated.

Experimental

Experiments were performed on a Thermo Cahn Synergy TG-FTIR system. Samples were heated under N_2. Temperature profile on TG was: isotherm for 10 minutes at room temperature, ramp to 200 °C at a heating rate of 5 °C/min and then isotherm for another 15 minutes. Sample sizes were 1.0 mL or about 1 gram.

Evolved gases passed the heated gas cell and FTIR spectra were collected. FTIR spectra were collected at a resolution of 4 cm^{-1} and sampling scan number was 64 (about 11 seconds per spectrum). Spectra were saved continuously during the experiments. Background was collected at 500 scans, before the sample was loaded. Transfer lines and FTIR cell of TG-FTIR interface were heated at 250 °C to prevent evolved gases from condensation.

An unknown formaldehyde percentage solution (formaldehyde in water) was used. Formaldehyde calibration standards were prepared at concentrations of 0.0 % (pure water), 0.5 %, 0.74 % and 1.15 % by weight, from formaldehyde solution (Aldrich, 37 % wt.) and distilled water.

Results and Discussion

Formaldehyde has a boiling point of 96 °C, which is very close to that of water, 100 °C. Therefore, the evolution of formaldehyde and water occur at about the same temperature during the TG experiments, Figure 1. It is impossible to obtain quantitative information. By comparing FTIR spectra of formaldehyde and water vapors, it is found that they have distinguishable peaks. Figure 2 shows an evolved gas FTIR spectrum collected for the solution sample at 180 °C, with library-searched formaldehyde and water vapour spectra. It is then possible to quantify the amount of formaldehyde presented in the sample.

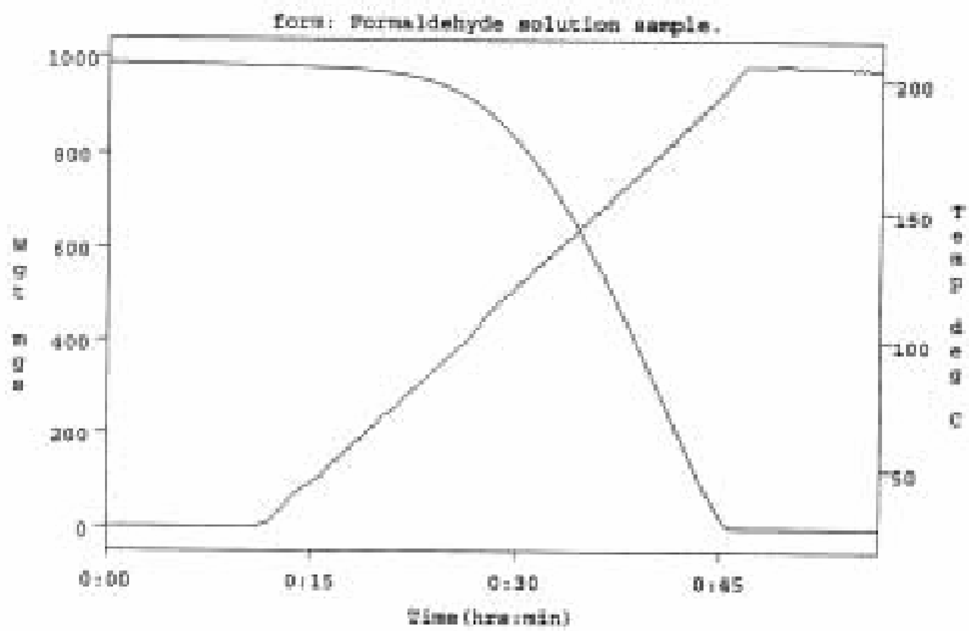

Figure 1. TG curve of unknown sample.

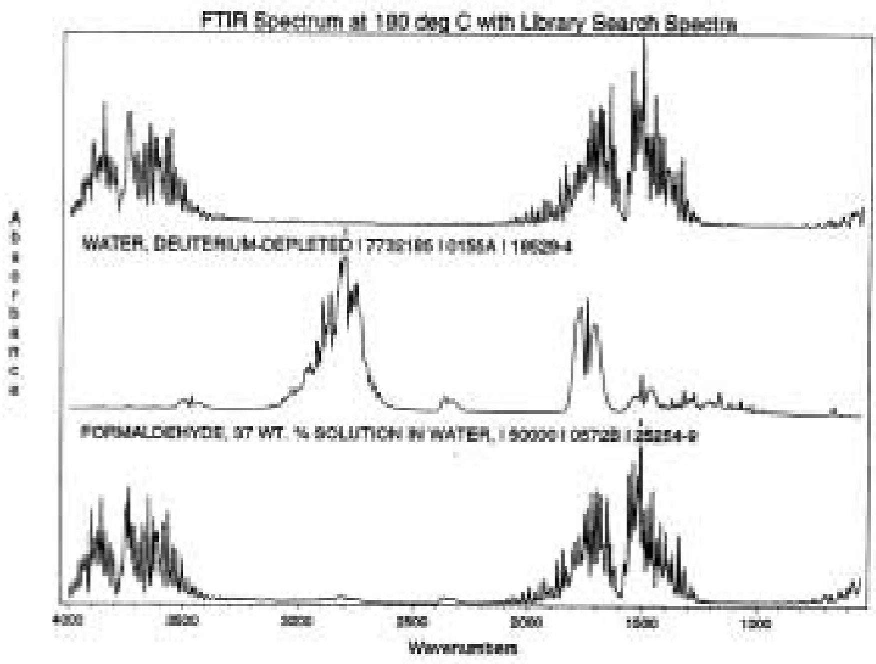

Figure 2. FTIR spectrum of unknown sample at 180 °C with library searched formaldehyde and water vapor spectra.

The frequency windows used to obtain the time-evolved IR traces for water and formaldehyde vapours were from 1280.00 to 1591.00 cm^{-1}, and 2650.00 to 2856.00 cm^{-1} respectively. The net absorbance at frequencies of 1508.43 cm^{-1} (water) and 2802.75 cm^{-1} (formaldehyde) were used to construct the time-evolved IR traces for water and formaldehyde vapours. Figure 3 shows the TG curve and time-evolved IR traces for unknown sample. FTIR spectrum in Figure 2 is shown in Figure 4, with expansion of the formaldehyde peaks. From Figure 4, it can be seen that the maximum peak height for formaldehyde in Figure 3 is only about 0.02. This is because of the low concentration of formaldehyde in the sample.

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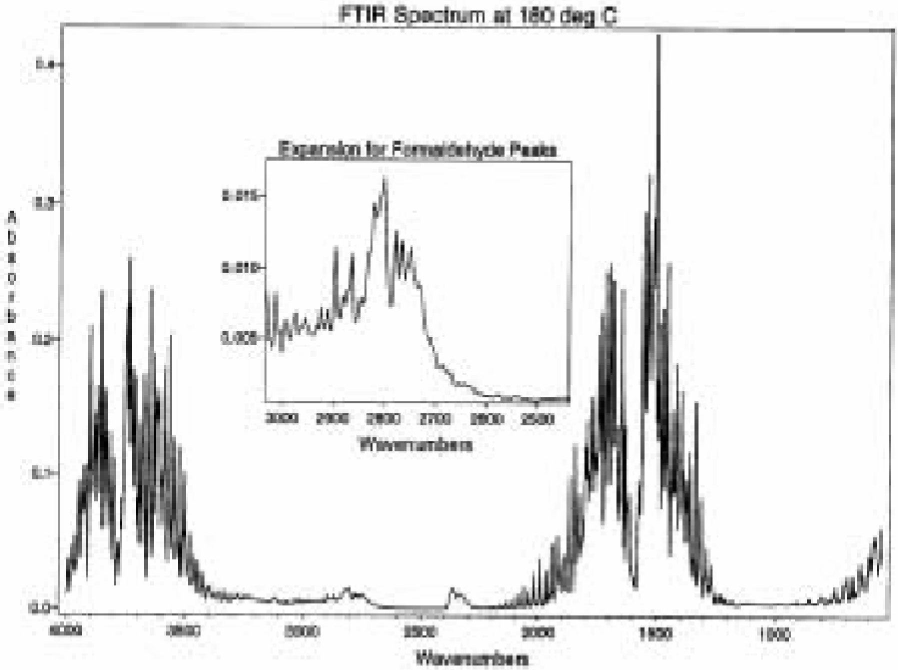

Figure 3. TG curve and time-evolved FTIR traces for formaldehyde sample.

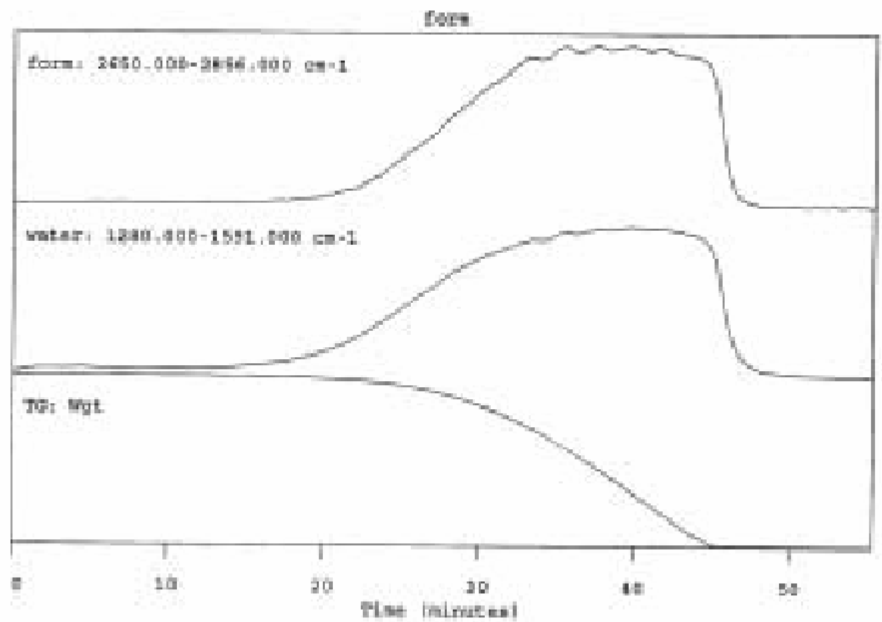

Figure 4. FTIR spectrum of unknown sample at 180 °C.

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Whole curve was integrated, after the baseline was corrected according to the lowest net absorbance value. Integration curve of time-evolved IR trace for formaldehyde vapor in Figure 3 is shown in Figure 5. Integration results for all the samples are listed in Table 1. Calibration curve for formaldehyde is shown in Figure 6. It can be seen that the integration area shows almost linear relationship with weight percentage of formaldehyde in samples. However, there isn't any trend between the integration areas of water and concentration. This is because the water vapour concentration was saturated and the FTIR peaks of water, used to trace water, overlapped with some formaldehyde peaks, Figure 2.

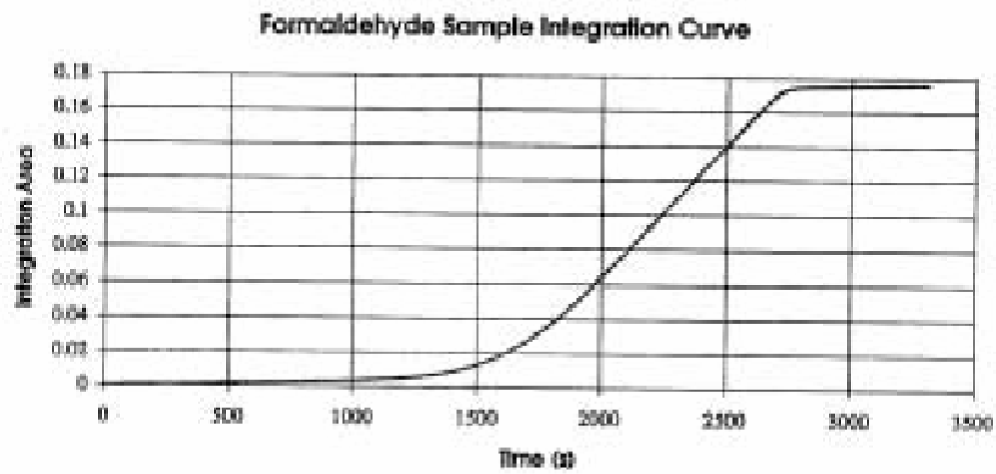

Figure 5. Integration area of the time-evolved curve of formaldehyde in unknown sample.

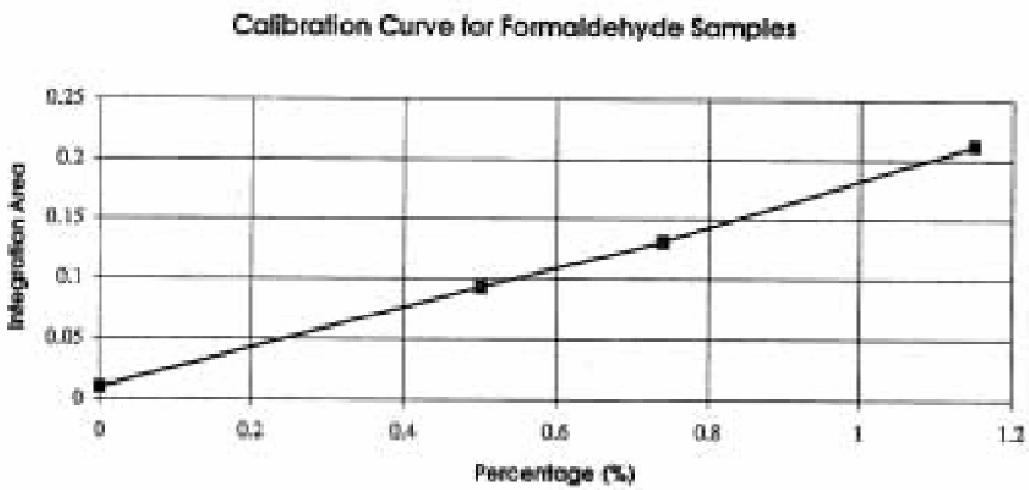

Figure 6. Calibration curve for formaldehyde.

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Sample ID	Area for Formaldehyde	Area for Water
Unknown	0.176	8.49
0.0 % solution (water)	0.00962	8.31
0.5 % solution	0.0927	8.41
0.74 % solution	0.131	8.41
1.15 % solution	0.212	8.45

Table 1. Integration results for all solution samples

From the calibration curve, the percentage of formaldehyde in the unknown sample is determined as 0.97 % ±0.02 % wt.. This demonstrated the ability of performing quantitative analysis from FTIR.

Conclusions

Overlapped TG curves won't be able to provide any quantitative information about each component, by using TG alone. By using TG-FTIR, it is then possible to quantitatively trace different components, if the evolved gases have distinguishable peaks in FTIR.

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