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COMBINED THERMOGRAVIMETRY AND FOURIER TRANSFORM INFRARED SPECTROSCOPY TECHNIQUES FOR GAS EVOLUTION ANALYSIS

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ABSTRACT

The usefulness of thermogravimetry has been amply demonstrated for a wide variety of material analysis applications. In many instances, however, additional information is required for adequate characterization of the sample and its thermal decomposition behaviour. In this respect, the analysis of evolved gases, or condensed liquids, has proven a highly useful approach. Among the various physical methods used for analysis of the thermal degradation products, infrared spectroscopy has often been found very powerful, being versatile, rapid and widely accessible. In this study, we report a simple new approach in which the evolved gases and condensed liquids from the thermal decomposition of various products are recuperated in an infrared gas cell and on a PVC membrane filter, respectively. The gaseous components were analysed by transmission FT–IR, and the condensed liquid products were examined directly on the PVC membrane by FT–IR in the internal reflexion mode. The technique was used, for example, to examine the pyrolysis products (gases and liquid) of Koberit, a proposed substitute for asbestos. The method was also applied to the study of chemically derivatized asbestos materials in an attempt to unravel the surface chemical modifications.

INTRODUCTION

The application of Fourier transform infrared spectroscopy to the analysis of gaseous products evolved upon thermogravimetric analysis (FT–IR–EGA) was initially suggested by Low [1] in 1967. The Low method was later explored by Liebman et al. [2] in studies of the combustion and pyrolysis behavior of polyvinyl chloride. Since the later work, a number of investigations have been reported in which the combined thermogravimetric and evolved gas analysis using FT–IR was demonstrated to be highly useful [3,4,etc]. In many of the studies described, however, it was reported that this combination of methods was often limited because of overlapping infrared bands which originated from condensable liquid products as well as of the evolved gases.

To alleviate this problem, two types of solutions could be envisaged. In a first approach, liquid condensation could be prevented by heating the

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transfer tube connecting the TGA apparatus to the infrared gas cell, and heating the cell itself. While these measures can be achieved, although with some difficulties, the spectra of the higher molecular weight gases are usually quite complex. For the analysis of the latter compounds, the liquid spectrum is usually more useful; this suggests the alternate approach of condensing some fractions of the evolved products in a cold finger. This approach presents technical difficulties in addition to requiring substantial manipulations of the decomposition products, making the method rather less attractive.

In this paper, we offer an alternative procedure in which the higher molecular weight components are condensed on a PVC membrane located in the transfer tube. The room temperature condensable gases are thus collected on the PVC membrane and can be analysed directly on a membrane by FT–IR spectroscopy in the internal reflection mode. The other components are collected as usual in an infrared gas cell and analysed in the transmission mode. We report below several applications of this technique which illustrate that the separation of component greatly simplifies the spectrum interpretation, retaining the attractive simplicity of the TGA–EGA combination using FT–IR for analysis of the thermal decomposition compounds.

EXPERIMENTAL

Instrumental methods

The thermogravimetric analyser used in this work was a Perkin-Elmer TGS-2 and the FT–IR instrument was a Nicolet model MX-1. To optimize the recuperation of the gases evolved during the thermal analysis, the TGS-2 was modified as illustrated in Fig. 1. First, the dead volume was minimized by installing a stainless baffle plate to limit the escape of gases to the upper tube. The standard pyrex glass side-arm tube from Perkin-Elmer was modified by adding a sintered glass filter; the latter served as support for a PVC 25 mm diameter membrane. The outlet from the filter was connected to the infrared cell using minimum length tubing, again in order to minimize the dead volume. This also reduces the risk of condensation.

For these types of investigation, the sample pan used was three times larger than those used in routine TGA analysis. To further prevent condensation in the upper part of the furnace tube, the latter was maintained at 250°C using a heating tape.

Experimental procedures

The following experimental conditions were used throughout the study: weight of sample: 30–60 mg; sweep gas flow rate: 20 $\text{cm}^3\ \text{min}^{-1}$; heating rate: 20°C min^{-1}.

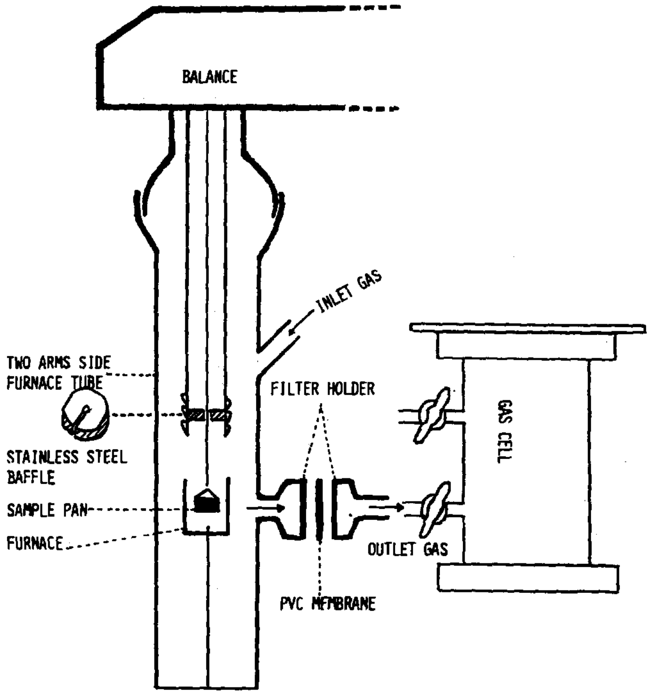

Fig. 1. Schematic of the TGS-2 furnace tube after modification.

The manipulations involved in the proposed method are relatively straightforward. After weighing a given amount of sample, the TGA analysis is performed in the usual way, and the gaseous decomposition products are swepted out of the furnace, toward the infrared cell. The room temperature condensable gases readily condense on the PVC membrane while the remaining gases are carried through to the infrared gas cell. The PVC membrane is then removed and affixed against an attenuated total reflectance (ATR) KRS-5, 45° element. The infrared spectrum of the membrane and adsorbed liquids is then recorded in the 400–3800 cm^{-1} range. The infrared spectra of the gases were recorded in the usual transmission mode.

RESULTS

Thermal decomposition of fibrous organic materials

To illustrate the possibilities of the method proposed, we report in Fig. 2 the observations recorded for several organic polymers (Figs. 2 and 3). In Fig. 2A, we illustrate the thermogravimetric recording (TGA, DTG) obtained with a commercial polymer known as Koberit; the latter is one of many proposed substitutes for asbestos and is derived from natural organic

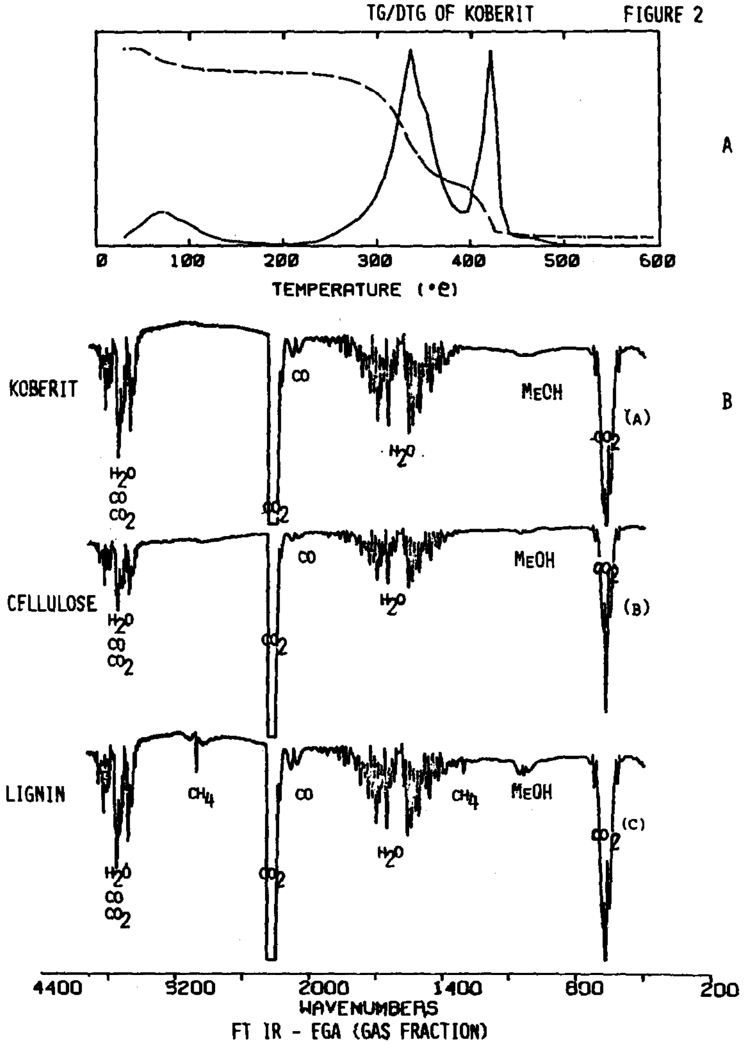

Fig. 2. TG/DTG curve and evolved gases spectra for Koberit, cellulose and lignin.

fibers. This thermal curve is analogous to that of cellulose so the thermal decomposition products of Koberit were examined in comparison to those of cellulose and lignin. The infrared spectra of the gaseous fractions collected are shown in Fig. 2B (A)–(C), and the corresponding spectra for the condensable liquids are illustrated in Fig. 3.

In the IR spectra of the gaseous components (Fig. 2B), we note, for the three compounds examined, the appearance of absorption bands which correspond to CO_2, CO, H_2O and methanol. In the case of lignin an additional and specific band is observed which corresponds to small quantities of methane. From the spectra of the collected gases, the thermally degradable fraction of Koberit then appears to consist largely of cellulose.

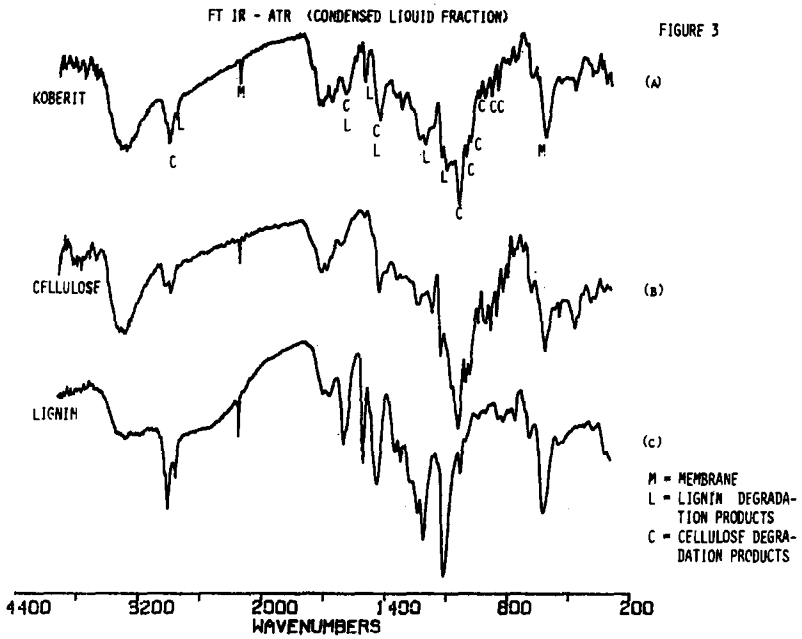

Fig. 3. Infrared spectrum of the condensed liquids fraction for Koberit, cellulose and lignin.

The components of Koberit can be still better identified from the spectra of the condensable gases shown on Fig. 3. The IR spectrum of the liquid products collected on the PVC membrane during the thermal decomposition of Koberit closely ressembles that of cellulose in most aspects. However, by comparing with the thermal degradation liquids derived from lignin, it is also apparent that the thermal degradable fraction of Koberit also contains some minor amount of lignin. The presence of cellulose and lignin is readily identified from their thermal degradation products: for cellulose, the levoglucosan with characteristic absorption bands in the 900–1100 cm^{-1} region; for lignin, the aromatic species with characteristic bands between 1450–1620 cm^{-1} and also the phenolic OH absorption bands near 1210 cm^{-1}. Hence, for studies of this type of polymer, the method proposed here can be quite specific.

Studies of physisorption and chemisorption on chrysotile asbestos

In other applications of the instrumental methods described here, we have investigated the solid phenomena (adsorption, reaction) occuring between chrysotile asbestos and several gaseous compounds. The results given below pertain to chrysotile samples to which several gaseous products (SO_2, NO_2, $POCl_3$) had been adsorbed or reacted under conditions described elsewhere [5, 6]. The interest in this case is to determine to what extent the gaseous compounds undergo chemisorption (chemical reaction) versus physisorption,

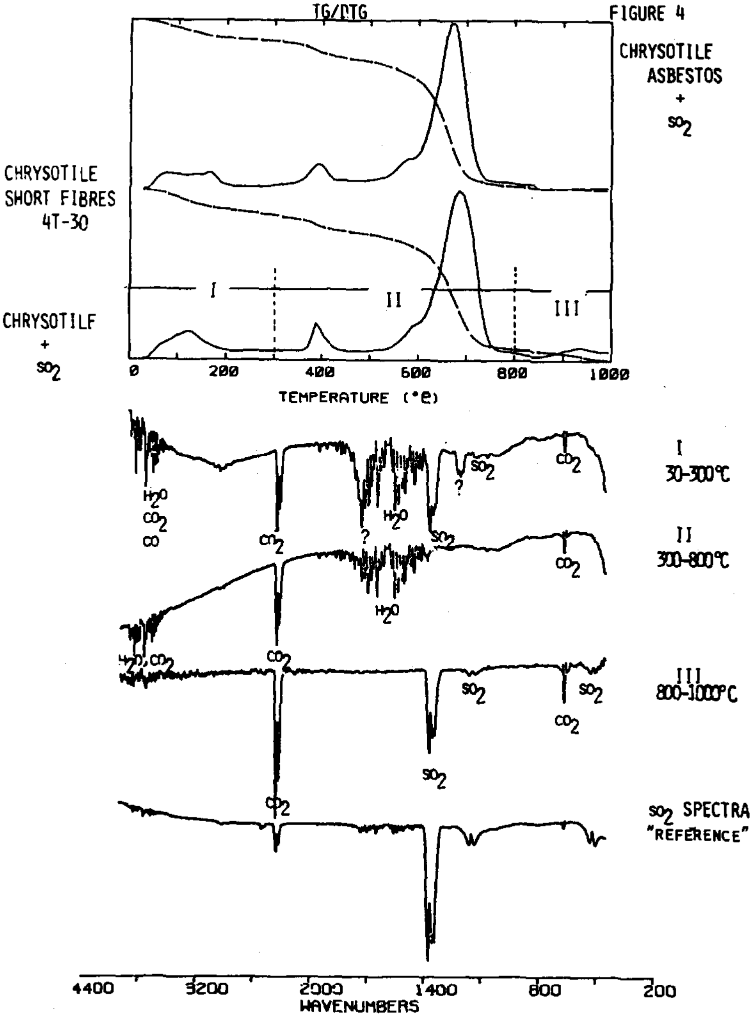

Fig. 4. TG/DTG curves and evolved gases spectra for chrysotile asbestos reacted with SO_2.

and in the cases where chemisorption occurs, identify the surface complexes formed.

In Fig. 4, we illustrate first the thermal curves obtained during thermogravimetric analysis of native chrysotile asbestos and asbestos after adsorption of SO_2. The gaseous decomposition products collected at the temperatures indicated are also shown on Fig. 4. The gases evolved at the lower temperatures consist of H_2O (physisorbed water and brucite decomposition) CO_2 from carbonate impurities and in all spectra, SO_2 bands. For the spectrum of the gases evolved in the temperature interval 30–300°C, additional features were observed near 1730 cm^{-1}; these components have not been formally identified but are presumed due to formation of S_xO_y species during the gas–solid reactions, or during the thermal degradation. The appearance of SO_2 bands in this temperature interval is clear evidence that SO_2 can be physically adsorbed on chrysotile asbestos.

In the temperature range 300–800°C, the evolved gases IR spectra exhibit no significant SO_2 bands while there remains strong adsorption from H_2O and CO_2. Interestingly, for the gases collected in the 800–1000°C interval, the infrared spectrum again shows strong SO_2 absorption. The latter behaviour, is typical of the thermal decomposition behaviour of magnesium sulphate ($MgSO_4$). Therefore, it can be concluded that a significant part of the adsorbed SO_2 was chemisorbed on the asbestos brucite surface, yielding magnesium sulphate.

The foregoing analysis of evolved gases shows rather conclusively that SO_2 adsorption on chrysotile is both a chemical phenomena and a physical

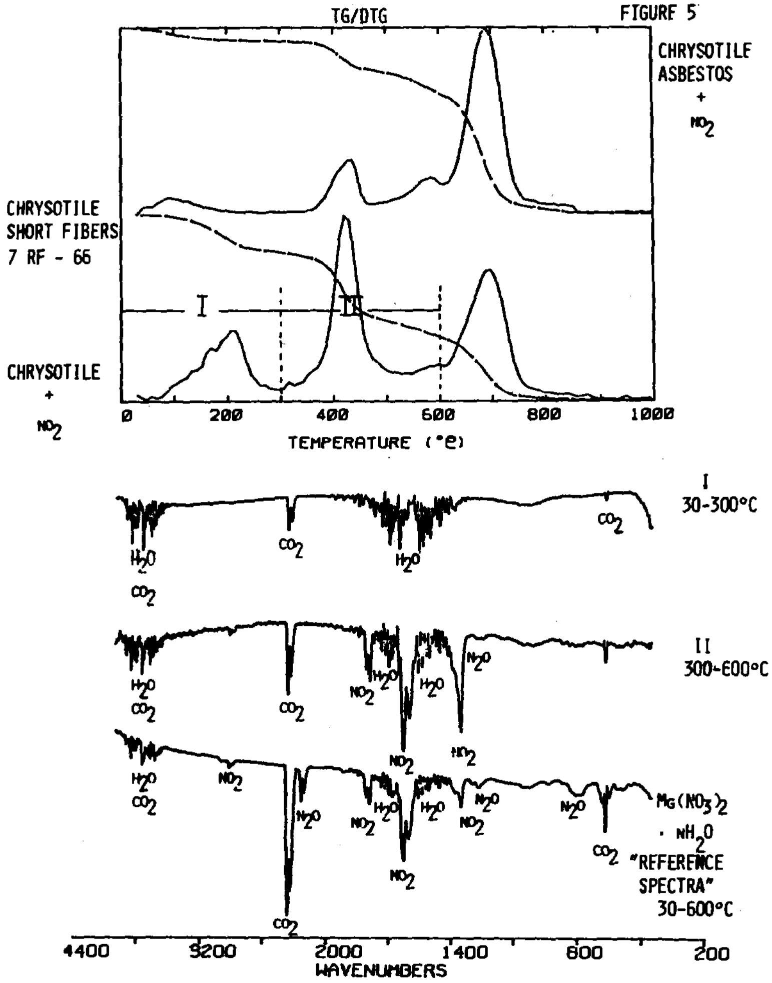

Fig. 5. TG/DTG curves and evolved gases spectra for chrysotile asbestos reacted with NO_2.

adsorption process. Since the quantities of surface compounds involved are very small compared to the total mass, the TGA analysis alone is incapable of providing this type of detailed information, the TGA curves of asbestos and SO_2-treated asbestos being nearly identical.

The results of a similar study are reported on Fig. 5, which illustrate the TGA curve for a chrysotile asbestos sample and the same material after reaction with NO_2 gas. The infrared spectrum of the gases evolved upon thermal decomposition of the NO_2 treated chrysotile material are also illustrated.

In this case, substantial differences can be seen between the thermograms

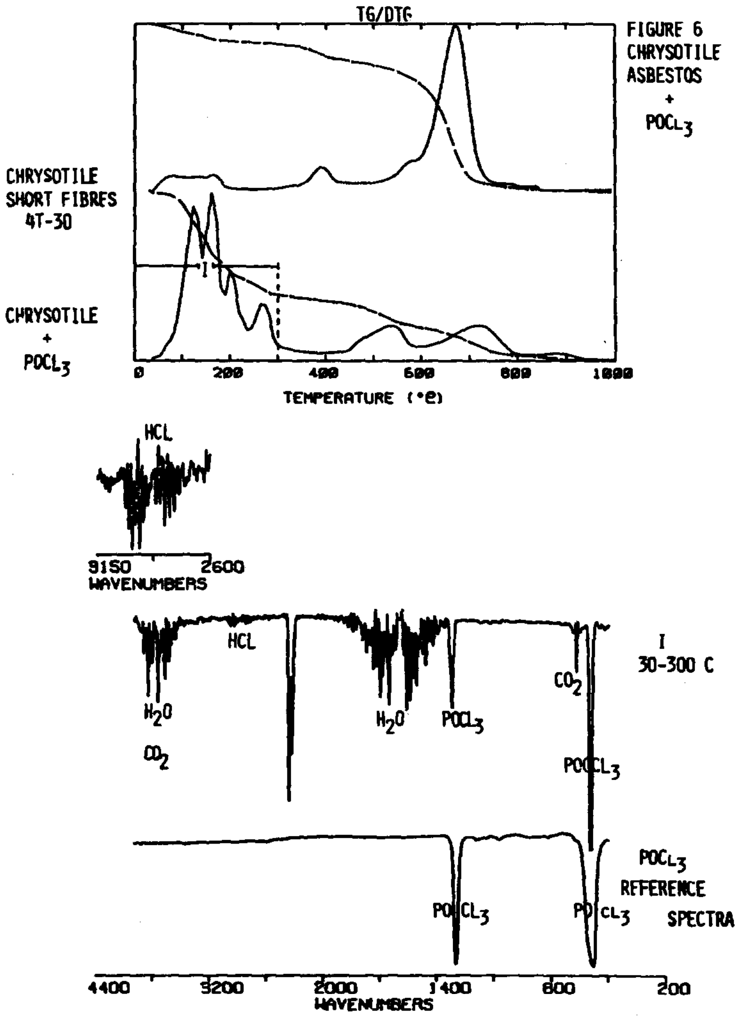

Fig. 6. TG/DTG curves and evolved gases spectra for chrysotile asbestos reacted with $POCl_3$.

recorded with the treated and native chrysotile samples. However, in spite of a significant weight loss in the temperature range 30–300°C, the spectrum of the evolved gases show only the presence of H_2O and CO_2; the significant weight loss observed in this temperature interval must result from a large amount of physisorbed and chemisorbed water. The spectrum of the gases evolved in the temperature range 300–600°C, however, shows strong NO_2 bands and an overall spectrum very similar to that observed with hydrated magnesium nitrate also shown as reference. Hence, in this case, it appears that the amount of NO_2 adsorbed on the chrysotile samples was largely chemisorbed, yielding magnesium nitrate.

In Fig. 6, we illustrate the thermogram and evolved gases spectra obtained from chrysotile asbestos samples reacted with $POCl_3$; the latter compound has been shown to react with the brucite layer of chrysotile yielding surface phosphate groups upon elimination of HCl. The chrysotile sample reacted with $POCl_3$ exhibits a markedly different TGA curve compared to the native chrysotile. As shown from the spectra of the evolved gases, the weight loss in the temperature interval 30–300°C is largely due to H_2O, HCl and $POCl_3$. The occurence of $POCl_3$ in the evolved gases would seem to be due to an unreacted excess of this compound. The evolution of HCl is readily explained from the nature of the reaction between $POCl_3$ and chrysotile asbestos; the HCl evolved during the latter reaction can in turn react with the brucite to give magnesium chlorite [5, 6]. Since $POCl_3$ is a liquid at room temperature, the PVC membrane condensation technique could also be used to examine the evolution of reactions involving this compound.

CONCLUSION

The results reported here again show the usefulness of the combined TGA–EGA analytical methods. The modifications proposed here which consist in collecting separately, the condensable liquids on a PVC membrane filter have proven highly adequate to characterize the thermal behaviour and composition of organic polymer materials such as those derived from wood pulp. The proposed procedure eliminates the need for a heated gas transfer tube, and the recorded spectra of the separated gas and liquid fractions are greatly simplified. The system has also been found useful in investigations of surface solid–gas reactions or interactions. The procedure is currently used to study the reaction products formed on the surface of chrysotile asbestos after reacting with various inorganic and organic gaseous reactants.

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