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QUANTITATIVE TG/IR *

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ABSTRACT

The relationship of concentration-dependent integrated absorbances of evolved gases and specific chromatogram areas to TG and spectral parameters is examined in an attempt to quantify the spectral information provided by a TG/IR interface. The results suggest that, at present, this technique yields semi-quantitative information which complements the emerging role of this interface as a tool for qualitative evolved gas analysis. The effects of low spectral resolution and changing concentration profiles are factors that must be addressed before accurate spectral quantitation is possible.

INTRODUCTION

The advantages and capabilities of interfacing a thermogravimetric analyzer and Fourier transform IR spectrometer for qualitative evolved gas analysis have been reported [1–4]. This paper describes some initial efforts to quantify the spectral information of TG/FT-IR. Motivating these efforts is the fact that it is not always possible to obtain quantitative results only from TG weight loss data. Stand-alone TG has shortcomings as a quantitative method in several situations, such as: (1) two or more volatiles are evolved simultaneously but only a net overall weight loss is measured; (2) a net weight gain occurs even though volatiles are lost, as seen during reactions (oxidation, carbonation, sulfation, nitridation); (3) TG weight losses of 10 μg or less may be obscured by noise or drift effects, whereas high sensitivity IR detectors can detect strongly absorbing vapors, as CO_2 or NH_3, at lower levels.

In addition to these situations, quantitative IR offers the potential of expanding the capabilities of the thermal analytical laboratory. TG can be used for temperature-programmed desorption, reduction, reaction or pyrolysis of gram quantities of sample, which are larger than the balance

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accommodates. Such samples may be weighed externally in an alumina or platinum boat, which is then placed in the TGA furnace tube. Analyzing larger samples can offer significant improvements in the signal-to-noise ratio of the IR spectra, allowing for qualitative and quantitative trace analysis. The possibility exists of obtaining quantitative elemental analysis (C, H, S) of solid fuels or heavy hydrocarbons by their complete thermal oxidation to CO_2, H_2O and SO_2.

EXPERIMENTAL

Standards (1 to 10 mg) which decompose thermally into gaseous products with known stoichiometries were analyzed. Heating rates of 5 °C min^{-1} or 25 °C min^{-1} were used on an Omnitherm TGA. The standards were heated under helium purge. Standards analyzed were calcium carbonate ($CaCO_3$, Baker, 12.5% carbon, 44% CO_2), ammonium carbonate ($NH_2CO_2NH_4$, EM Science, 15.1% carbon, 43.6% NH_3), barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$, EM Science, 14.7% H_2O), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, EM Science, 36.0% H_2O) and sodium dithionate dihydrate ($Na_2S_2O_6 \cdot 2H_2O$, Fisher, 26.5% SO_2).

TG/IR data were obtained on a Digilab FTS-60 FT-IR spectrometer coupled to the Omnitherm TGA. Experimental details of this interface have been published [1,2].

The data files generated during a TG/IR experiment are as follows. (1) a total IR chromatogram or evolved gas profile, derived from Gram–Schmidt vector reconstruction software. Its intensity is an additive function of the individual concentrations and absorbances of all the IR-active components evolved from the sample. (2) A series of low resolution (32 cm^{-1}) spectra, derived from each spectral scan set. These are computed over the range 600 cm^{-1} to 4000 cm^{-1}. (3) Five specific IR chromatograms or chemigrams. The intensity of these chromatograms is a function of the absorbance within spectral windows characteristic of a specific gas. They are generated from the absorbance values of the low resolution spectra within these windows.

When an experiment is completed, higher resolution spectra are computed from the interferograms. TG–IR spectra for this study have been computed at 8 cm^{-1} resolution, comparable to standard practice for GC–IR spectra. Sixteen interferograms were co-added per spectrum. Relative areas under specific chromatograms and absorbance peaks were calculated with standard software.

Non-linear concentration behavior is encountered when attempting to quantify 8 cm^{-1} spectra of diatomic or triatomic gases because of the narrow linewidths characteristic of the spectral transitions of these small molecules. Absorbance measurements made at resolutions lower than these inherent narrow linewidths show departures from Beer's Law.

RESULTS AND DISCUSSION

The total IR chromatogram of calcium oxalate monohydrate is shown in Fig. 1A. Corresponding to the thermal decomposition of this salt, the first peak in the chromatogram is due to evolution of H_2O, the second due to evolution of CO, which is known to partially disproportionate to CO_2 and carbon, and the third peak to evolution of CO_2. This total chromatogram is decomposed into the three specific chromatograms of H_2O, CO and CO_2, by profiling the 32 cm^{-1} absorbance within appropriate spectral windows as illustrated in Figs. 1B–1D.

CO_2

The strong 2350 cm^{-1} stretching band of CO_2 has a narrow linewidth of 0.15 cm^{-1}. Thus, data derived from the 32 cm^{-1} specific chromatograms of CO_2 might be expected to show a non-linear concentration dependence. The concentration of CO_2 was varied by heating 1–10 mg of $CaCO_3$ in the TGA to 900 °C, at rates of 25 °C min^{-1} and 5 °C min^{-1}. Provided that heating and flow rates are kept constant, the specific chromatogram area from 2200 cm^{-1} to 2400 cm^{-1} can be calibrated to the milligrams of CO_2 generated by the $CaCO_3$. The calibration curves in Fig. 2 show that, under constant conditions, acceptable linear correlations can be obtained. At 25 °C min^{-1} and 50 cm^3 min^{-1}, a good correlation of 0.99 was found. This was also seen

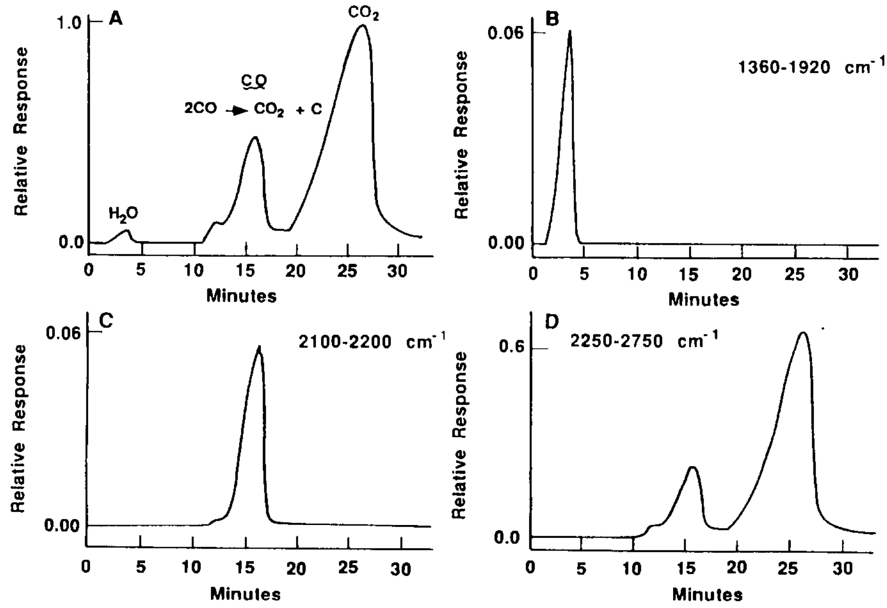

Fig. 1. A, Total chromatogram of calcium oxalate monohydrate; B, H_2O profile; C, CO profile; D, CO_2 profile.

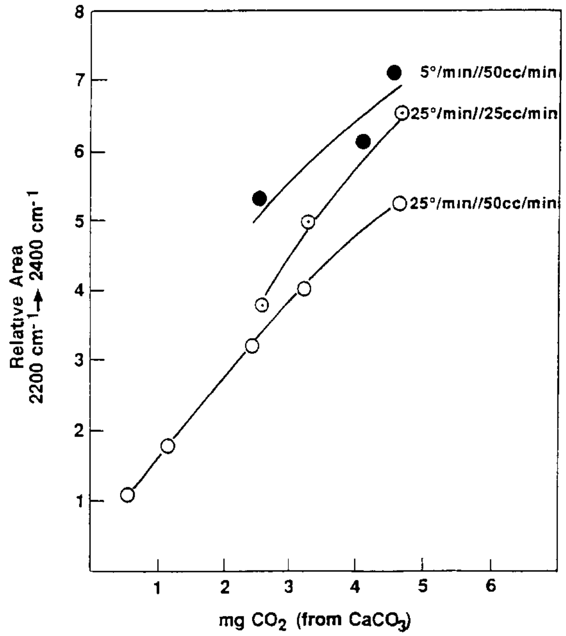

Fig. 2. Calibration curves for CO_2 generated by heating $CaCO_3$.

at 25 °C min^{-1} and 25 cm^3 min^{-1}. The more scattered data at 5 °C min^{-1} and 50 cm^3 min^{-1} showed a lower correlation of 0.85. The heating rate dependence of the calibration curves is evident in this figure. At 5 °C min^{-1}, for a given amount of CO_2, a larger area is measured than at 25 °C min^{-1}. A larger area was also measured when the flow rate of the helium purge was reduced from 50 cm^3 min^{-1} to 25 cm^3 min^{-1}, effectively increasing the instantaneous CO_2 concentration. Profiling the weaker CO_2 bending band at 670 cm^{-1} still shows this heating and flow rate dependence, a reflection of the non-linear absorbance versus concentration measurements.

The ratio of chromatogram area to milligrams of evolved CO_2 (response factor, RF) varies inversely with heating rate as shown in Fig. 3. The dependence of the chromatogram width at half-height ($W_{\frac{1}{2}h}$) on heating rate is also plotted. This reveals that at slower rates, the CO_2 profile broadens. CO_2 has a longer net residence time in the 10 cm flow-through gas cell that is being scanned spectrally. At 5 °C min^{-1}, $W_{\frac{1}{2}h}$ for this profile was about 19 min as compared to only 4 min at 25 °C min^{-1}.

The volume of the gas cell is 6 cm^3, so that at a purge rate of 50 cm^3 min^{-1} it takes 7 s to replace completely the volume element of CO_2 in the gas cell. At 8 cm^{-1} resolution and 16 co-added scans per scan set, 5 s are needed to record a spectrum. Thus, some fraction of CO_2 from the previous ($N-1$) scan set is still in the cell and its absorbance is again co-added into the Nth scan. This fraction is larger for the slower heating rates. The overlapping of the CO_2 signals contributes to the heating rate dependence of their areas.

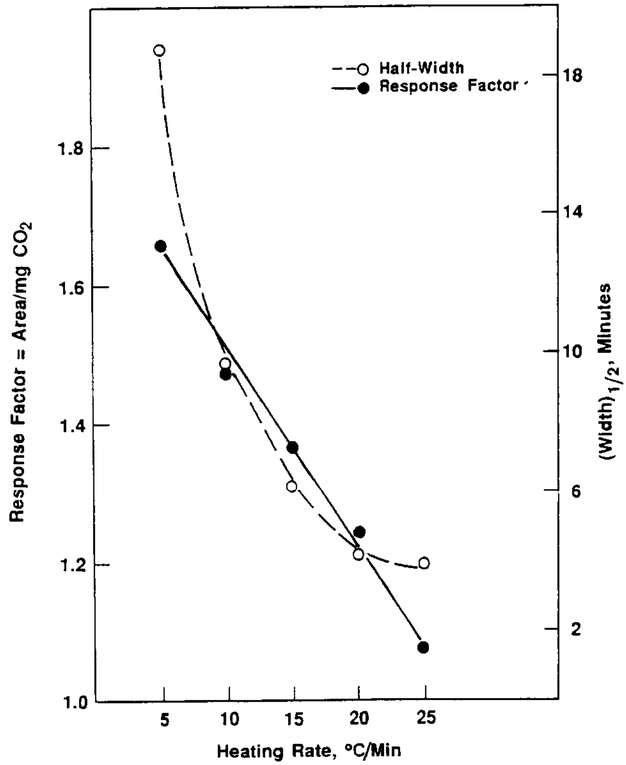

Fig. 3. Response factor and profile widths for CO_2 generated from $CaCO_3$.

The effect of such non-linear absorbance was reduced by working at lower concentrations of CO_2, as might be expected from Beer's Law. When the $CaCO_3$ is diluted with Al_2O_3, so that smaller weighed quantities are heated, the areas for the 25 °C min^{-1} and 5 °C min^{-1} scans approached each other. At lower concentrations, however, the sensitivity of the interface becomes a concern.

An underlying question relative to the heating rate effect is that, even at the same rate, CO_2 evolved from compound A at a given inherent rate, depending on its energetics of decomposition, will have a different response than CO_2 evolved from compound B at its own inherent rate. If this is the case, separate calibration curves would have to be used for CO_2 generated from each compound at a given heating rate. Indeed, some preliminary data indicate different response factors for the CO_2 evolved from ammonium and calcium carbonates, the latter being approximately 20% larger.

Other gases

Calibration curves for gases other than CO_2 were also prepared. None showed as severe a heating rate dependence as CO_2.

NH_3

NH_3 generated from ammonium carbonate was analyzed by measuring the area of the specific chromatogram between 900 cm^{-1} and 1000 cm^{-1}. The same inverse relationship between area and heating rate was seen as for CO_2 but with a smaller difference between the areas measured at 5 °C min^{-1} and 25 °C min^{-1}. In fact, all the data points combined, for both heating rates, fell reasonably well in a linear plot with a correlation of 0.94.

Another possible approach to quantitation is to integrate the absorbances under characteristic 8 cm^{-1} bands as a function of concentration. This was done for the N–H bending mode of NH_3, absorbing between 780 cm^{-1} and 1250 cm^{-1}. The average integrated absorbances over the N scan sets that make up the total IR chromatogram were plotted versus NH_3 concentration. The dependence of these average integrated absorbances on heating rate is opposite to the dependence of the specific chromatograms—the 25 °C min^{-1} scans show a larger area. The reason for this is that the 25 °C min^{-1} absorbances are integrated over fewer total scan sets—the same amount of NH_3 is evolved over less time.

H_2O

H_2O was generated using $BaCl_2 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$. The results from both samples show only a slight heating rate dependence of the specific chromatogram integrated between 1360 cm^{-1} and 1920 cm^{-1}. The $BaCl_2 \cdot 2H_2O$ data, obtained at both heating rates, fell in a linear plot with a correlation of 0.99. The H_2O evolved from dehydration of $CuSO_4 \cdot 5H_2O$ gave about a 10% lower response factor than that from $BaCl_2 \cdot 2H_2O$.

SO_2

SO_2 was generated from sodium dithionate dihydrate. The chromatogram area integrated from 1270 cm^{-1} to 1410 cm^{-1} shows little dependence on heating rate. Using the combined data gives a linear correlation of 0.98.

$Ca(OH)_2$–clays mixture

Illustrative of situations where quantitative TG/IR can be of value, a mixture of $Ca(OH)_2$ and clays was studied. As illustrated in Fig. 4A, thermal decomposition of the mixture under inert argon showed a TG weight loss of 14% H_2O from 360 °C to 460 °C. The H_2O profile peak in Fig. 4B had a maximum at 446 °C with an integrated area corresponding to 12% H_2O loss. Under a reactive CO_2 purge, the $Ca(OH)_2$ transformed to $CaCO_3$ between 250 °C to 575 °C with a net weight gain of 16%. The area of the H_2O profile under CO_2 purge now integrated to only 4% loss weight and the temperature of maximum evolution rate shifted up to 517 °C as shown in Fig. 4D. This suggests that during reaction with CO_2, some of the hydroxyl groups are incorporated in the partially carbonated mixture to

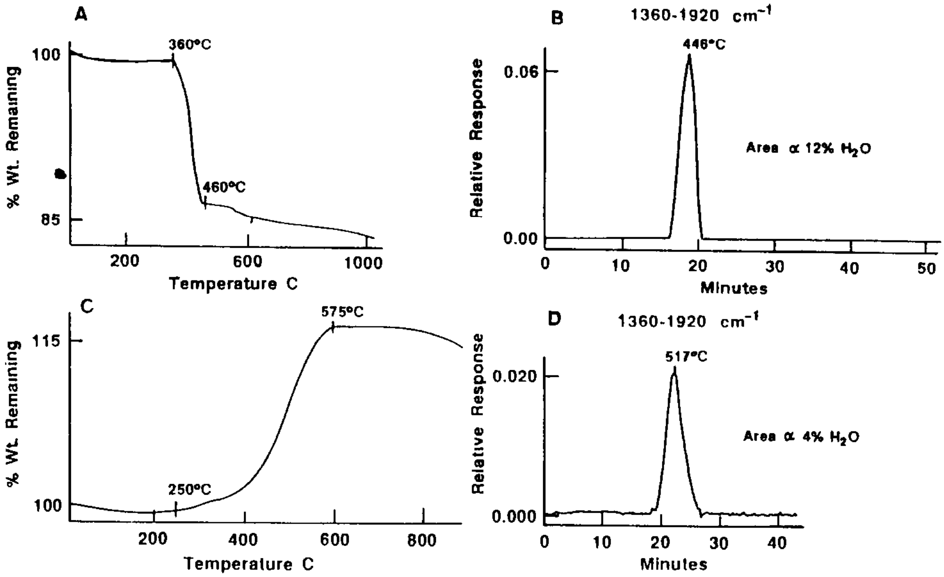

Fig. 4. A, TG curve for lime under argon, 20 °C min^{-1}; B, H_2O profile under argon; C, TG curve for lime under CO_2, 20 °C min^{-1}; D, H_2O profile under CO_2.

hydroxy-carbonate structures that are stable to higher temperatures. Without the IR data, it would not have even been possible to recognize that water is lost.

CONCLUSIONS

The results presented here point to two major difficulties in obtaining quantitative data from TG/IR. First is the problem of a non-linear absorbance versus concentration dependence because of the low resolution at which specific chromatograms and spectra are collected. The second complication arises from the dynamic nature of the technique—the fact that changing concentration profiles are being measured, with possible overlap of co-added scan sets. Until these problems are resolved, caution must be exercised in applying quantitative IR results. However, this should not detract from the technique's ability to provide an approximate value in otherwise untenable situations such as the example of H_2O evolved during lime carbonation.

Quantitative data ($\pm 10\%$) may be obtained via calibration of gases evolved from specific material at constant heating rate, purge rate, spectral resolution, and data acquisition time.

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