Thermochimica Acta, 18 (1977) 3–13

ENVIRONMENTAL APPLICATIONS FOR THERMAL ANALYSIS*

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ABSTRACT

A review is presented of the applications of thermoanalytical techniques to problems encountered in the measurement and control of air pollution. A number of suggestions are offered regarding new or extended applications of these techniques.

INTRODUCTION

In 1969, when NATAS was born, concern over the effects of anthropogenic activity upon our environment was already well developed, although the economic consequences of pollution control had not been significantly felt and energy conservation was largely a pious platitude. As NATAS has grown through childhood, concerns over new facets of this loosely defined system we call the environment have increased. Greater knowledge, improved sensitivity of existing analytical methods, development of completely new methods of analysis and detection have all contributed to producing more subjects for public anxiety. Concerns over contamination at the ppm level have given way to the ppb and even ppt levels, and the analytical chemist is increasingly required to measure fewer and fewer molecules of more and more exotic substances.

Unfortunately no area of scientific and technical activity, prior to the "environment", has been subjected to such a continuing series of panics, where so much poor science and technology has resulted from public and political pressure, and where so many instant experts have appeared whose greatest qualifications appear to be a facile tongue, a lack of concern for fact and a genius for oversimplification.

When an area grows as rapidly as that of environmental studies, it is natural that the whole existing armament of scientific methodology will be examined for its potential application. This paper reviews the applications for thermal analysis to those environmental matters involving air pollution.

The study of air pollution involves two primary activities: measurement and control. These may be further sub-divided into four problem areas to which

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*Presented at the 6th North American Thermal Analysis Society Conference, Princeton, N.J., June 20–23, 1976.

thermal analysis may be applied: gaseous measurement—ambient, workroom, stack; particulate measurement—ambient, workroom, stack; atmospheric chemistry—homogeneous and heterogeneous; process control.

Before considering each of these problem areas, however, there are two cautions which thermal analysts should keep in mind.

First, thermal analysis does not involve techniques which can be considered to be "analysis" in the conventional sense of determining what and how much; whereas most environmental studies, and certainly air pollution problems, depend heavily upon analytical techniques, as conventionally defined, for the data on which to base conclusions and actions. Thermoanalytical techniques have been developed for the study of materials, and the vast majority of available technology deals with samples in the solid state.

Secondly, the normal applications of thermal analysis deal with quantities of matter which may be several orders of magnitude greater than those involved in air pollution studies. A ppm is relatively large in air pollution work, yet the best thermobalances are limited to a sensitivity of about 1 part in 10^6. Thermal analysts must be careful not to fall into the trap of trying to adapt a technique to a problem, because of being skilled in that technique, instead of examining the problem objectively and choosing the technique or techniques best suited to providing the information required.

GASEOUS POLLUTANTS

The lowest concentrations of gaseous pollutants usually occur in ambient air, often in the sub-ppm range; similar, or somewhat higher, levels occur in workroom areas; and usually significantly higher concentrations are found in stack emissions, perhaps as much as 10^5 greater than ambient.

Gaseous pollutant measurement involves both wet chemistry—colorimetry, coulometry or conductivity—as well as instrumental methods primarily based on spectral absorption in some form or on chromatographic separation followed by a variety of detectors. The potential application for thermal analysis to the direct measurement of gaseous pollutants is very limited, mainly because of sensitivity and the non-continuous nature of thermoanalytical techniques, i.e., a given sample is studied for a specified time interval or over a specified temperature range.

The application of thermal analysis to gaseous measurement is limited but not impossible. Figure 1 shows the schematic of a commercial portable CO indicator, in which the sampled air passes through an insulated cell containing a Hopcalite catalyst in which are embedded two thermistors. The cell temperature is held constant by the proportional temperature controller and the oxidation of CO on the Hopcalite releases energy which creates an imbalance in the thermistor legs of the bridge. Essentially, this is isothermal DTA. Provided CO concentrations exceed 5–10 ppm, a technique such as this is feasible.

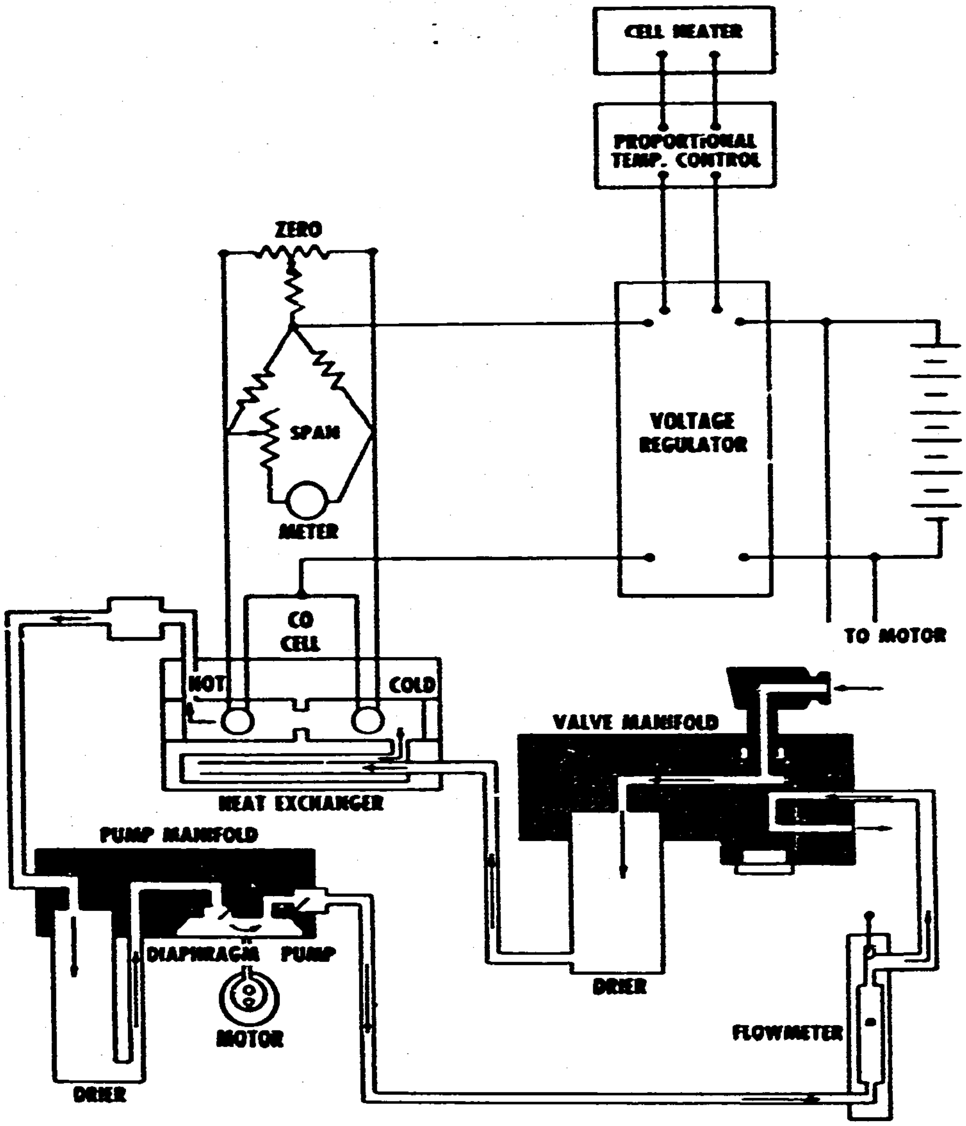


Fig. 1. Schematic of a commercial portable CO indicator.

Perhaps there are other thermally intensive gas–catalyst interactions which could form the basis for other types of portable or workroom monitors. Alternatively, well-documented applications of DTA to the study of catalyst activity could be extended to assist in developing new catalysts having higher rates of reactivity for the gas in question, thus compressing the time period over which a temperature change occurs and hence improving the sensitivity. Another application, related particularly to those who enjoy developing new thermal analysis instrumentation, would be the development of simple, rugged and sensitive thermal detection devices to improve sensitivity and reduce cost.

Another indirect application of thermal analysis relates to chemiluminescence techniques which have found wide application, particularly for the measurement of oxides of nitrogen (Fig. 2). The reaction between NO and O_3 produces an electronically excited form of NO_2 which chemiluminesces on reversion to its ground state. This chemiluminescence is monitored through a narrow band-pass optical filter by a high sensitivity photomultiplier tube positioned at one end of the reactor.

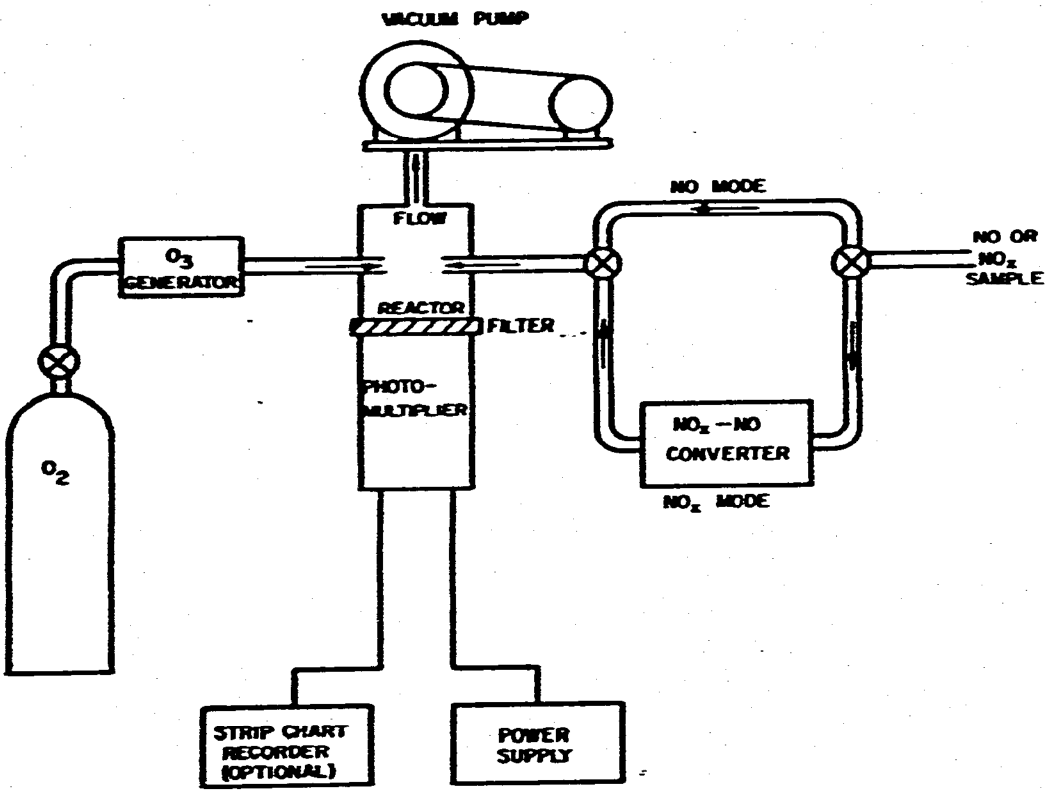


Fig. 2. Instrumentation for the measurement of nitrogen oxides.

This technique is specific to NO and if one wishes to use it to monitor NO_2 the sample steam is diverted through a high-temperature catalytic cell which decomposes NO_2 to NO. Different instruments employ different catalysts, having varying efficiencies and life times. Another suggested application for thermal analysis would be to study the efficiency of NO_2 reduction on various catalytic surfaces as a function of temperature, age and prior dosage of NO_2. The objective would be to develop a reproducible, high performance, stable reduction catalyst, with a long life, which can function at the lowest possible temperature. The problem for the thermal analyst is: how many DTA units can handle up to 10,000 ppm levels of moist NO_2 at several hundred degrees centigrade?

Even before measuring gaseous pollutants there is often concern over the volatility of a particular material and whether, in fact, significant quantities of it could be inhaled. Here, thermal evolution analysis, a Knudsen cell attached to a thermobalance, or similar thermal techniques can be employed to produce a Clausius–Clapeyron plot in a fraction of the time required by other methods[1].

PARTICULATE POLLUTANTS

The second problem area is that of particulate measurement. Here, again, the applications of thermal analysis to direct measurement are limited. Despite the fact the Krakatoa erupted in 1883, about the same time as Le Chatelier was developing the first automatic registration of a heating curve, measurements of atmospheric particulates and thermal analysis have not greatly intertwined.

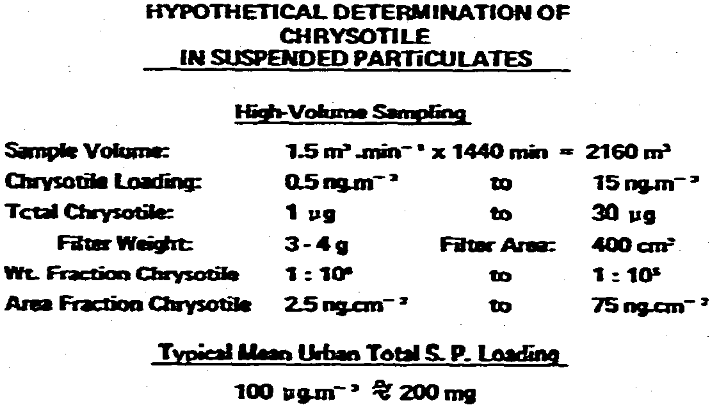
In any of the three sampling situations, ambient, workroom or stack, most measurement methods involve collection of discrete samples over periods of up to 24 h. Various filter media are employed, including paper, glass fibre, teflon, polycarbonate, etc. The collection is then subjected to some form of mass measurement, either direct weighing or β-particle attenuation. For certain measurements the optical density of the filter plus collection may be compared to that of the unexposed filter and a form of particulate loading inferred.

Particulate measurement may be automated[2], although truly continuous particulate monitors are still largely undeveloped and those that are available primarily involve light scattering over various wavelength ranges and path lengths.

From a thermoanalytical standpoint, a solid particulate collection on a filter is a more customary type of sample. The obvious application for thermal analysis, then, is to assist in the identification of specific constituents within the grab-bag of total atmospheric suspended particulates. Many of the constituents may be of natural origin, such as re-entrained dirt or soil (is not it interesting that clay mineralogists were among the first users of DTA); they may be of industrial origin, such as fly ash or oil soot from a power house; or they may result from atmospheric reactions between gases and/or other primary particulates coupled with moisture and sunshine.

At first glance, then, thermal analysis might be useful in particulate constituent identification. However, care must be exercised. Thermal analysis may have some use for this purpose, but there are a number of other techniques which are better and the best tool for the purpose should be chosen rather than reshaping another tool to "make do".

Figure 3 illustrates this, and also the problems of sensitivity and specificity encountered when applying thermal analysis to air pollution measurement, by the example of asbestos. Today there is wide-spread concern for asbestos in the ambient air and its potential for causing mesothelioma and gastrointestinal carcinoma. Current methods of measurement rely upon visual microscopic examination and counting, infrared spectrometry and X-ray diffraction, all of which tend to neglect the fibres <5 μm considered to be important causes of these diseases, leaving only electron microscopy supported by electron diffraction and X-ray spectrometry as approaches having adequate sensitivity and specificity.



HYPOTHETICAL DETERMINATION OF
CHRYSOTILE
IN SUSPENDED PARTICULATES

High-Volume Sampling

Sample Volume:	$1.5\ m^3.min^{-1} \times 1440\ min = 2160\ m^3$		
Chrysotile Loading:	$0.5\ ng.m^{-3}$	to	$15\ ng.m^{-3}$
Total Chrysotile:	1 μg	to	30 μg
Filter Weight:	3 - 4 g	Filter Area:	$400\ cm^2$
Wt. Fraction Chrysotile	$1 : 10^6$	to	$1 : 10^5$
Area Fraction Chrysotile	$2.5\ ng.cm^{-2}$	to	$75\ ng.cm^{-2}$

Typical Mean Urban Total S. P. Loading

$100\ \mu g.m^{-3} \approx 200\ mg$

Fig. 3.

Consider sensitivity first. A normal high-volume sampler used in most ambient measurements of suspended particulates, and in some workroom measurements, operates for 24 h at a flow-rate of about $1.5\ m^3\ min^{-1}$ and passes $2160\ m^3$ of air per day. Chrysotile loadings recently measured in Ontario[3] range from $0.5–15\ ng\ m^{-3}$, so that the total 24-h particulate collection would include 1–30 μg chrysotile, allowing for less than 100% collection efficiency. This collection is made on a filter with a tare weight of 3–4 g and an exposed area of $400\ cm^2$. Thus, the problem becomes that of finding 1 part of chrysotile in $10^5–10^6$ parts by weight of matrix or, if it is desirable to aliquot the filter, that of identifying 2.4–75 ng of chrysotile per cm^2 of filter area.

Since the high-volume sampler collects all suspended particulates, not just chrysotile, each 24-h collection will total approximately 200 mg. Even if it is possible to dissolve the filter, as can be done with some media, the problem remains that of determining 1 part chrysotile in 10^4 to 10^5 parts of other particulates. While this is not an impossible thermoanalytical task, it leads directly to the next problem: specificity.

Detection of chrysotile by DTA can be based upon the dehydroxylation endotherm with a peak temperature of approximately 685 °C. However, in the grab-bag of real world air samples there is both a heterogeneous mess and mass of primary particulates, i.e., finely divided fragments of original composition, and secondary particulates found through atmospheric interactions. Naturally occurring clays, minerals, etc. usually form a significant proportion of these particulates and, unless clear specificity can be introduced through atmosphere control, it is questionable that thermal analysis would be a valid tool for this measurement.

It might be useful as a screening tool to reduce large volumes of samples to more manageable numbers for more detailed study.

It should also be noted that current criteria are tending towards concentration units of fibres per cubic meter. Each fibre is made up of a widely varying number of fibrils and rough estimates[3] suggest 10^5–10^7 fibrils ng^{-1}. Thus, a mass-dependent method of identification is considerably less attractive than a number and size-dependent method.

ATMOSPHERIC CHEMISTRY

Thus far, only limited applications for thermal analysis to problems of air pollution have been identified. Let us now examine what might be considered a new thermoanalytical approach and then an area for research where an established thermoanalytical technique might have significant impact.

Both these topics relate to atmospheric chemistry which, in the real world, involves a largely uncontrollable reactor of constantly changing temperature and proportions containing an horrendous melange of homogeneous and heterogeneous processes. One of the most famous products from such a reactor is the Los Angeles smog aerosol, which arises from a complex series of interactions between, primarily, the products of automobile exhaust and which comprises largely a mass of liquid droplets. Recently, Husar and Shu[4] have studied the volatility of this aerosol mass to determine how much may be driven from the aerosol form to the gas phase at various temperatures: Using essentially a stepwise isothermal approach, in which real-world aerosol passes through a heated section to a cooling section and hence to a nephelometer which measures the total light scattering coefficient, the so-called thermonephelograms (not an ICTA-approved term!) appear to vary with the level of photochemical reactivity in the atmosphere. On hazy days of low reactivity a relatively linear decrease in scattering coefficient was observed up to 150°C, while on smoggy days a reverse "S" curve suggested that a substantial portion of Los Angeles smog aerosol is comprised of matter which is volatile below 150 °C. This type of information provides a further clue as to the complex mixture of secondary reaction products involved in this smog.

Schuetzle et al.[5] have used mass spectrometric thermal analysis to study aerosol samples collected in the 1972 California Aerosol Characterization Study A single-stage impactor was employed to collect particles >1–$2\,\mu m$ on 0.30-in. diameter gold plates. The remainder of the particulate matter was collected on glass fiber filters and a temperature-programmed probe was designed to accommodate both of these receptor surfaces. This probe was inserted into the vacuum lock of an AEI-MS9 high-resolution mass spectrometer interfaced with a PDP-12 digital computer, and programmed over the range 20–400 °C. In this case MSTA was used as another approach for determining the relative volatility of various aerosol collections, which could then be related to time and place of collection, and the area under each total ion intensity curve can be related to the total quantity of material volatilized, including mainly organic compounds plus inorganic nitrates and sulphates.

This is only one relatively limited application of MSTA, a technique which is capable of considerably more application to atmospheric chemistry because of its inherent sensitivity.

One such area of atmospheric chemistry which is poorly understood is the adsorption or absorption of gases on particulates. Most atmospheric particulates have significant surface areas and may be coated with films of moisture, hydrocarbons, or other contaminants formed through secondary interactions, such as the oxidation of SO_2 to H_2SO_4. Alternatively, these particulates may absorb or adsorb gases such as SO_2. On being inhaled, most gases are trapped in the upper respiratory tract, and cause relatively minor irritation at low concentrations unless infection already exists in this area. However, fine particulates of approximately $2\,\mu m$ and less in diameter can pass through the upper respiratory tract and eventually deposit at various depths within the lungs. Such fine particulates will have surface forces suitable for the adsorption or absorption of gases. Even a perfectly smooth spherical particulate of $2\,\mu m$ diameter and density of 2.5 would have a surface area of about 1 $m^2\,g^{-1}$, so that a gaseous pollutant sorbed on a particulate carrier could penetrate further into the respiratory tract than might otherwise be possible.

The problem, then, is to determine small quantities of gases sorbed on particulates. This could be an ideal problem for mass spectrometric thermal analysis employing a quadrupole mass spectrometer with a fast scan rate of mass number to about 100 and slow heating rates of about 1°C min^{-1}. There will be experimental problems. For instance, it will be necessary to characterize the desorbed particulate substrate first to be aware of any potential thermal decomposition of this substrate. For example, hydrocarbon gases sorbed on power house oil soot would be difficult to differentiate from the substrate itself. However, SO_2 sorbed on power house flyash would be relatively simple to determine. The mass spectrometer has both the sensitivity and the specificity to overcome many of the interference problems and a technique, such as MSTA, which can operate on mg or μm of sample, could provide a significant advance in our understanding of the extent to which hazardous pollutants are sorbed on atmospheric particulates.

PROCESS CONTROL

The final air pollution application area to review is that of process control, the area where thermal analysis can probably be most useful. It is also familiar territory for the thermal analyst because many such processes involve catalysis, heterogeneous solid–gas interactions, thermal stability ranges of materials, effects of atmospheric pressure and composition, and so forth.

In a large number of cases solid systems are involved, for which thermoanalytical instrumentation is primarily designed. However, again, there is a practical problem of instrumentation. How many sample holders will withstand atmospheres of moist SO_2, NO_x, CO or Cl_2 up to 1000°C? Either within individual laboratories, or those of the instrument manufacturers, it will be necessary to redesign and re-construct sample holders from materials with possibly less desirable thermal characteristics but more desirable chemical and mechanical characteristics. In most cases, such sample holders must be used in a combination of DTA and TG with a relatively sophisticated gas analysis and detection system.

Catalytic control processes for reducing air pollutant emissions are numerous, the best known being those for vehicular emissions. It is amazing that comparatively few investigators have chosen to study such catalytic processes by dynamic thermal methods, preferring the classical step-wise isothermal approach. One notable exception has been Gallagher[6] who has long recognized the value of DTA for rapidly screening potential catalysts, for evaluating the effects of various pretreatments, and for determining the poisoning tendencies of agents added to either the gas stream or to the catalyst. No experimental complexity is involved—just a logical application of well-known DTA practice. Relatively rapid heating rates can be used to reduce the time required for screening a large number of catalysts, however slower rates should be employed if one wishes to correlate DTA curves with percentage conversion. The sensitivity of the technique can be increased by increasing the gas flow-rate through or over the sample depending upon holder configuration, but sensitivity will be diminished by the instrument blank due to reactions on the surfaces of the sample holder or homogeneous gas phase reactions, both of which will vary with temperature.

Perhaps more important than the screening aspect is Gallagher's finding[6] that the "results of DTA experiments and the conclusions therefrom are in agreement with other more detailed work using supported samples in a catalytic reactor". This conclusion may not apply in every case, but the inherent advantages of DTA suggest a much greater use of it in pollution control process development.

Another example involves the limestone injection method for control of SO_2. Ingraham and Marier[7] defined the mechanisms of this heterogeneous solid–gas interaction by a simple combination of DTA and TG experiments and published more information in a one-page paper than in many expensive publications on the same subject involving over 200 pages.

Because SO_2 does not displace CO_2 from limestone below its calcination point, it is the reactions of CaO, not those of $CaCO_3$, which are important. If CaO is heated in SO_2 at 5 °C min^{-1} (Fig. 4a), both DTA and TG show reaction beginning at 100 °C and reaching a maximum rate at 330 °C when approximately 30% of the CaO is converted to $CaSO_3$ and the compactness of this product layer prevents further reaction. From DTA curves for $CaSO_3$ in N_2, O_2 or SO_2 (Fig. 4b), coupled with product identification, it was established that the exotherms at

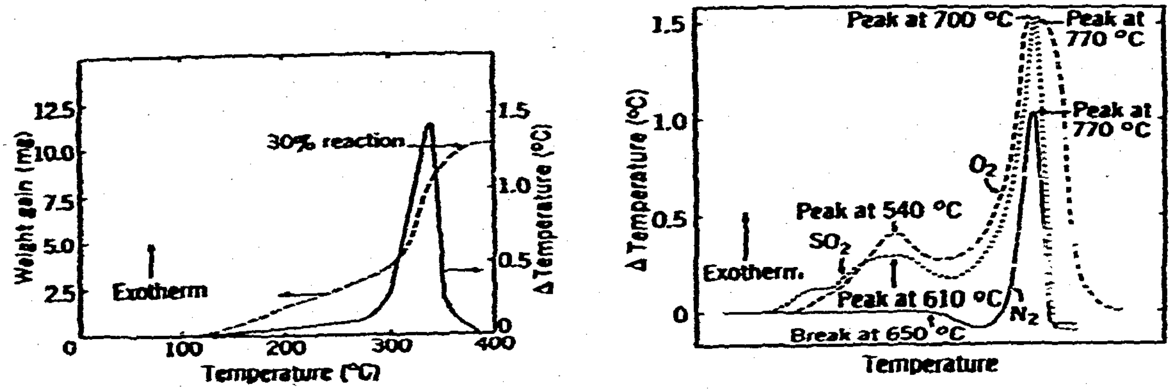


Fig. 4. (a) DTG and TG curves for CaO heated in SO_2 at 5 °C min^{-1}. (b) DTA curves for $CaSO_3$ heated in: ——, N_2; – – –, O_2; and ·····, SO_2.

540 °C in O_2 and 610 °C in SO_2 were due to the oxidation of $CaSO_3$ to $CaSO_4$. The endotherm beginning at 650 °C in N_2 was the dissociation of $CaSO_3$ to CaO and SO_2 confirmed by vacuum TG. The large exotherm occurring in all three atmospheres was due to a binary peritectoid decomposition producing CaS and $CaSO_4$.

Thus, by well-chosen thermoanalytical experiments it was possible to define the reaction systems involved in the conversion of $CaCO_3$ and the temperature ranges over which they occur. One can only wonder why more investigators have not chosen such direct approaches to process control studies.

The final example relates to air pollution problems arising from thermal degradation. A particular industrial process may involve a drying or curing oven at some stage. This industry may be primarily concerned to operate the oven so as to maximize production rate consistent with product quality. However, rapid curing at high temperatures may produce secondary reactions in the evolved volatiles which could lead to an objectionable effluent (Fig. 5). For example, suppose a product involves n-butanol in its formation and the solvent must be removed. Operating the drying oven at a relatively low temperature allows n-butanol to evolve undecomposed, and possibly, to be recovered. Local concentrations of 10,000 ppb could be present before the odour threshold for n-butanol is reached.

ODOURS

	Odour Threshold Concentration	Description
n-Butanol	10,000 ppb	sweet
n-Butraldehyde	70 ppb	sour
n-Butyric Acid	1 ppb	sweaty

Fig. 5. Relative odour thresholds.

Even then, at this ambient concentration, the general reaction may not be unpleasant. However, if the over temperature is increased there is an increasing tendency for n-butanol to decompose to n-butraldehyde and thence to n-butyric acid, with sharp reduction in the corresponding odour thresholds of these secondary products. n-Butyric acid will be detected at only 1 ppb and the reaction of most people will be less than agreeable.

This type of situation might be avoided, and product quality maintained, by a time–temperature study of the curing cycle, which can often be done directly by TG as in the same manner that polymer thermal analysts have been doing for years, coupled with evolved gas analysis of the voltailes.

CONCLUSION

This discussion has attempted to present examples of both critical and optimistic interfaces of thermal methods of analysis with air pollution problems. Thermal analysis does have a significant role to play in certain important aspects of air pollution, although its value is limited in others. Thermal analysts have always been ingenious—they should not overlook their role in better understanding and controlling our environment.

ACKNOWLEDGEMENT

This work was supported by funds received through a grant to the Ontario Research Foundation from the Ministry of Industry and Tourism, Province of Ontario.

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