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Applications of thermal methods of analysis to raw and processed minerals

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Abstract

Traditionally, the major areas of application of thermal methods of analysis to minerals are: Assessment of raw material deposits, through characterization, classification and analysis. Investigation of the changes that take place in the mineral resulting from thermal processing. Characterization of products at various stages in industrial processing. In this paper, examples are given in each of the above areas. The need for the use of complementary techniques, such as chemical analysis, X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy, to give qualitative and quantitative assistance in the interpretation of results, are stressed. In addition, recent recommendations on the reporting of details of the sample and experimental variables will be presented. A relatively recent application of thermal techniques is in environmental studies. These can take various forms, form investigations into gaseous emissions which result from the thermal processing of minerals, to studies of the effects of pollutants on the properties of soils.

Keywords: Thermal analysis; Minerals; Recommendations for reporting thermal analysis data; Characterization methods; Analytical methods; Mineral processing; Environmental applications

1. Introduction

The applications of thermal methods of analysis to the earth sciences is one of the more mature fields of study, and the topic has been well reviewed throughout its use (see, for example, [1,2]). In addition, Dollimore [3] has a section on minerals in this biannual reviews of Thermal Analysis published in the Fundamental Review section of Analytical Chemistry. Since the 1960s a series of developments has increased the value of the data obtained enormously as well as enabled the range of applications to be broadened. These developments include:

- increased understanding of the variables that influence the results of thermal analytical experiments
- the development of qualitative and quantitative complementary methods to assist with the characterisation of unreacted and partially reacted minerals
- improvement in the sensitivity of TA equipment
- the development of new techniques, such as the coupling of thermal analysis equipment to various evolved gas detectors.

2. Variables that affect the results of thermal analysis experiments

It has been demonstrated ad infinitum that the results of TA experiments are affected in a major way by variations in the experimental conditions. This includes properties of the sample as well as the parameters used in the control of the TA equipment [4,5]. The ICTAC Standardisation Committee has

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been working on revising the guidelines for reporting TA data [6], and this proposal is before the ICTAC Council for ratification.

One of the major changes relates to the characterisation of the sample under examination. Hence it is suggested that a description of the sample should include: (i) identification of all substances (sample, reference, diluent) by a definitive name, (ii) an empirical formula, or equivalent compositional information, (iii) a statement of the source of all substances, (iv) details of their histories, pretreatments, physical properties, and chemical purities, as far as these are known.

'Histories' includes method of acquisition or manufacture of the sample (how it was isolated or made, manufacturing conditions, e.g. grinding, sizing, etc), previous thermal and mechanical treatments (e.g. repeated grinding, sintering, all experimental conditions), surface modification, and any other physical or chemical treatment: 'pretreatments' includes preparation of the sample prior to the thermal analysis experiment: 'physical properties' includes particle size, surface area, porosity: 'chemical purities' includes elemental analysis, phase composition, and chemical homogeneity of sample.

This list is exhaustive, and it might be difficult to provide some of the information. However, it recognises that the definition of the physical and chemical properties of the sample are of at least equal importance to the definition of the equipment parameters used to carry out the experiment. One of the problems with working with natural minerals is that they frequently contain significant quantities of other minerals. If this is not recognised by a thorough characterisation of the starting material, then there is the possibility of the incorrect assignment of reactions to exotherms/endotherms and mass changes observed in the curves.

The effect of equipment variables is much more appreciated, and has not changed significantly since the first suggestions were published. Hence it is usual to report details of heating rate, atmosphere, sample mass, and sample holder.

In order to illustrate more fully the need to recognise the importance of experimental variables on the thermal analysis record, the oxidation of pyrite will be discussed as a case study. Pyrite is one of the most studied minerals in terms of TA methods, and a wide variety of DTA curves have been published and a variety of intermediate products reported. Early DTA curves showed a very broad exothermic peak in the temperature range 400–800°C (see Fig. 1(a)), with very poor resolution of any structure in the profile. Pyrite is an example of a compound with a reaction rate very much in the range of the usual thermal

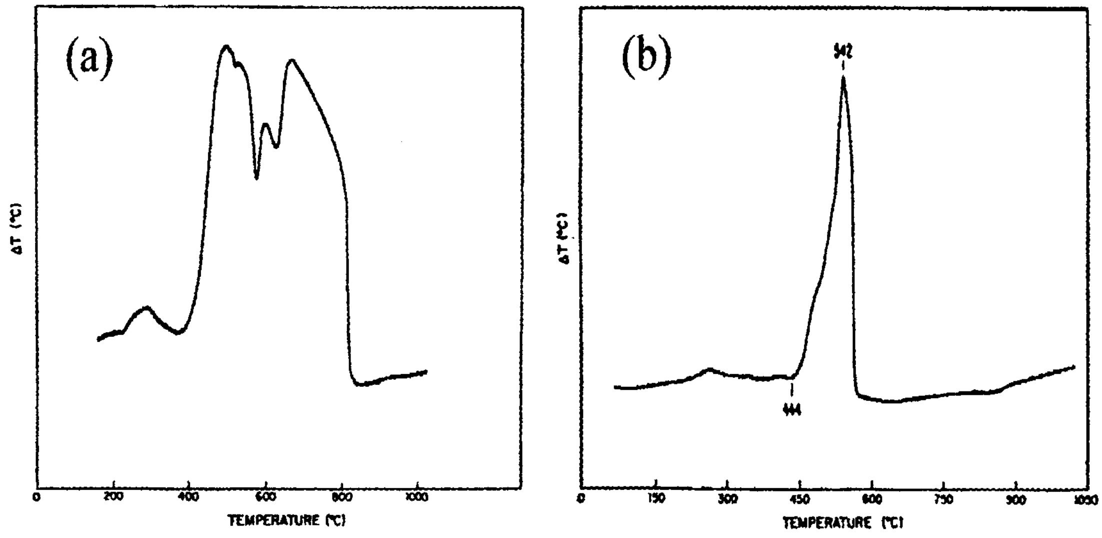

Fig. 1. DTA curves of pyrite heated in air. (a) 20 mg, heating rate 20°C min^{-1}; (b) 6 mg, heating rate 10°C min.

analysis conditions. Hence, at these heating rates what is being measured is the amount of time that it takes to oxidise the pyrite. If the sample mass is increased then the reaction takes place over an even longer time period, and so the exothermic peak broadens even further. If the sample size and heating rate are decreased the DTA curve occurs over a much narrower temperature range, with the main peak appearing between 444–570°C (see Fig. 1(b)) [7]. Some resolution of thermal events is observed, with a shoulder prior to the main exothermic peak which has a peak temperature of 542°C.

Similar studies, but with a variation in the heating rate, particle size and oxygen concentration, have identified three mechanisms which can occur for the oxidation of pyrite, each of which produce markedly different DTA profiles [8,9]. For slow heating rates (2.5°C min^{-1}) with small particles (<45 μm), the oxidation mechanism occurred according to the classical shrinking core model in which the rate of reaction is controlled by oxygen diffusion through product coatings. If sufficient time is allowed, the particles will be completely oxidised by 500°C. Beyond 550°C, an endothermic peak and mass loss are attributed to the decomposition of the iron sulfate phase with the formation of more Fe_2O_3.

If the heating rate is increased to 20°C min^{-1} and the particle size to 90–120 μm, the reaction sequence proceeds by two different mechanism. Up to 500°C the reaction is controlled by oxygen diffusion as before, and the first exothermic peak is due to the direct oxidation of pyrite to Fe_2O_3. However, the faster heating rate combined with the larger particles ensures that the reaction is nowhere near completion at 510°C. Beyond this temperature the pyrolytic decomposition of pyrite begins, and sulfur vapour is evolved. The rate of reaction is now controlled by sulfur diffusion outwards, and no further oxidation is evident until all the sulfur has been evolved. The sulfur burns near the surface of the particle, causing a sharp major exotherm. The resulting pyrrhotite has a very porous structure, and so oxygen diffusion into the particle to oxidise the pyrrhotite to hematite is fast and also contributes to the intensity of the exotherm. The oxidation reaction is complete by 550°C, some 45°C higher than for the smaller particles.

If the heating rate is further increased to 40°C min^{-1} and the atmosphere is changed to oxygen, the smaller particles ignite, and only one intense exothermic peak complete by just above 500°C is evident in the DTA curve.

Fig. 2 illustrates the effect of particle size on the appearance of the TG-DTA curves [9]. All three

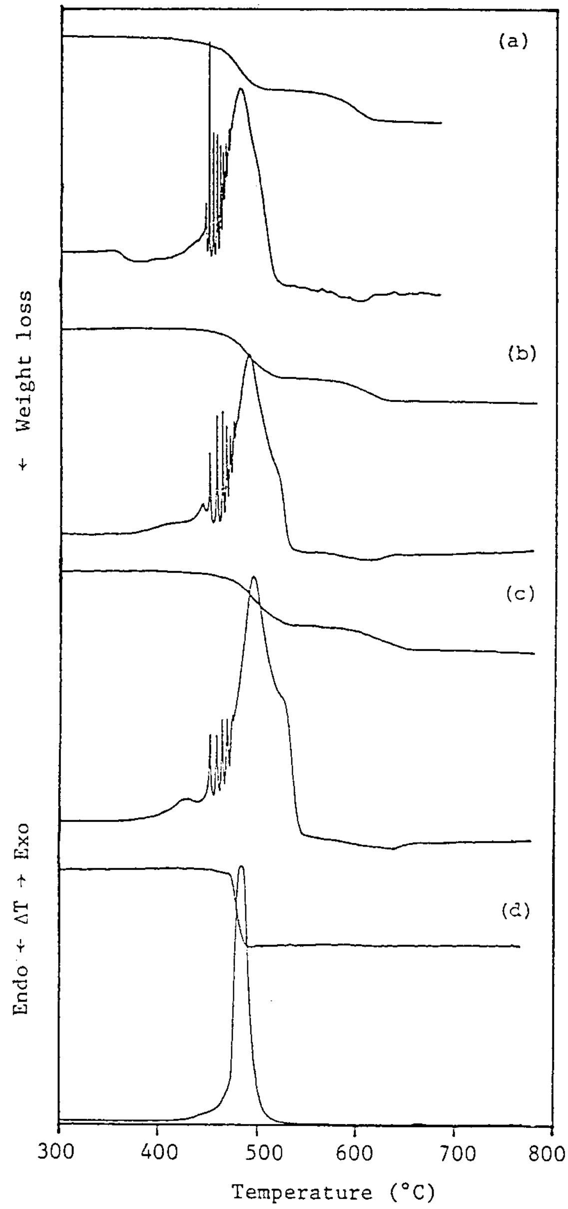

Fig. 2. Effect of particle size on the TG-DTA curves of pyrite. (a) <45; (b) 45–74; (c) 75–90. 1.8 mg sample, heating rate 10°C min^{-1}, in flowing air [9].

Table 1
Determination of Cu_2O by quantitative XRD in partially oxidised samples of chalcocite as a function of temperature

Temperature (°C)	Cu_2O content (%w/w)	Mean	Standard deviation
435	0.7, 0.9, 0.7, 0.8, 1.5, 2.0, 1.5, 1.7	1.2	0.5
470	2.0, 2.5, 1.9, 3.5, 4.4, 3.3	2.9	0.9
570	42.5, 40.5, 52.6, 50.7, 48.3, 45.9	46.8	4.7
670	38.1, 37.6, 40.6, 34.3, 33.3, 36.4, 40.6, 39.5, 43.1	38.2	3.2

Heating rate, 10°C min^{-1}; particle size, 45–63 µm; air atmosphere [10].

samples are heated at 10°C min^{-1} in an air atmosphere. The number of DTA peaks changes, as well as shift in temperature, as the particle size increases from <45 to 90 µm. For the smallest particles the main mechanism is the first one described above, and the DTA peaks are all associated with the oxidation of pyrite to hematite through oxygen diffusion into the particle. As the particle size increases the second mechanism becomes more important, simply because it takes longer for the oxygen to diffuse into the unreacted core. Hence less pyrite is directly oxidised, and more and more remains to be decomposed to form pyrrhotite. Consequently the DTA peaks below 500°C decease in magnitude and the peak above 500°C becomes more pronounced. Eventually for the 90–120 µm fraction (not shown) only an exothermic drift is observed below 500°C followed by a single sharp exotherm between 520–540500°C. The quantity of iron sulfate formed decreases as the particle size increases, as evident from the decreasing mass loss above 500°C with increase in particle size.

These results indicate the wide variation that can be observed in DTA traces with variation in the properties of the sample and change in experimental conditions.

3. Complementary qualitative and quantitative characterisation techniques

The determination of the above mechanisms could not have been made without the use of complementary techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe microanalysis (EPMA), chemical analysis, and Fourier transform infrared (FTIR) spectroscopy. The TA experiment can be stopped at any thermal event and the products isolated and characterised by one of the above methods. If the technique is quantitative then the appearance and disappearance of a particular phase can be followed as a function of temperature.

Quantitative XRD can be carried out with small sample masses in the milligram range, which makes it applicable to TA studies. By using ratios of several interference-free peaks in the XRD record of the partially reacted mineral against some internal standard, it is possible to produce several results from one experiment which can be averaged to produce a reasonably reliable value. An example is shown in Table 1, which gives the Cu_2O content of partially oxidised chalcocite as a function of temperature [10]. It is evident that wide variation can occur between individual values, but the average value has an acceptable standard deviation.

The combination of Fourier transform methods and infrared spectroscopy has caused a major resurgence of interest in this technique. The quality of the spectrum has been vastly improved even for very small samples in the milligram range, and so again this is a useful method for TA. One significant advantage is that compounds with the cation in different oxidation states can often be differentiated. This technique has been used to follow the formation of iron(II) and iron(III) sulfates during the oxidation of pyrite [11]. Although sulfate is known to be formed in significant quantities it is often difficult to even detect by XRD perhaps because it is amorphous. The FTIR technique is very sensitive to the detection of sulfate vibrations, and so the formation and decomposition of the iron(II) and iron(III) sulfates in quenched samples of partially oxidised pyrite can be followed as a function of temperature. It was found that $FeSO_4$ was the major species formed, and that very little conversion of Fe(II) to Fe(III) took place under the experimental conditions used (see Fig. 3).

The technique was similarly used to determine $CuO{\cdot}CuSO_4$, which is one of the products formed

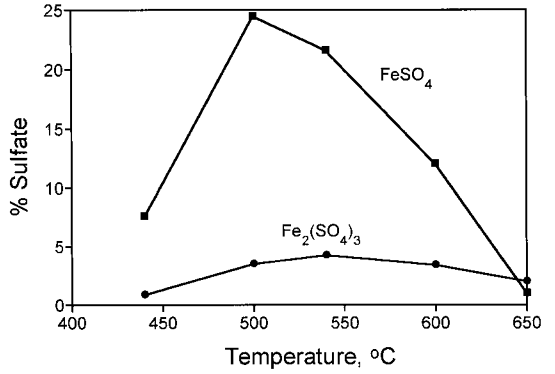

Fig. 3. Concentration of iron(II) and iron(III) sulfates as a function of temperature during the oxidation of pyrite determined by quantitative FTIR analysis [11].

during the oxidation of chalcocite. The FTIR pattern of CuO·$CuSO_4$ is shown in Fig. 4. The peak at 439 cm^{-1} was not interfered with by any of the other compounds present in the partially oxidised sample, and the measurement of its peak height for a set of standard samples was used to construct the calibration curve given in Fig. 5. Excellent quantitative result were achieved, and the method had better detection limits than XRD [10]. $CuSO_4$ was also determined, but the data were confused by the rate at which the sulfate adsorbed water once removed from the TG-DTA apparatus. At low temperatures of around 400°C water was adsorbed quite rapidly, with the formation of $CuSO_4 \cdot H_2O$, with a related decrease in the peak intensity of $CuSO_4$. At higher temperatures of around 600°C the rate of adsorption was much slower, and therefore the decrease in peak size was not so significant. This made the construction of a calibration graph impossible, and the only solution was to bracket each sample with standards heated to the same temperature, and then ratio the standard and unknown values. This is a very time consuming process. The results from the compositional analysis by XRD (Table 1) and the FTIR are plotted for partially oxidised samples of chalcocite against temperature in Fig. 6. Summation of the data for those samples in which all the phases were determined by these methods, i.e., at 570°C, 670°C and 775°C, gave values that were better than ±10% relative error (Table 2). Hence these analytical methods provide a reasonable estimation of the phase composition of the sample at any particular temperature.

The use of these characterisation methods permits the reaction scheme to be written with some confidence.

4. Improvement in the sensitivity of TA equipment

Various improvements in the technology associated with heat sensing, and the adoption of the electronic microbalance as the most popular weighing device, has seen considerable improvement in the sensitivity of thermal analysis equipment.

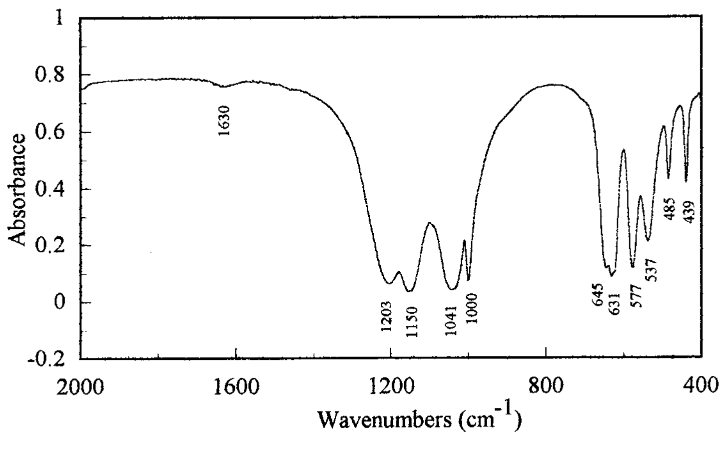

Fig. 4. FTIR pattern of copper oxysulfate, CuO·$CuSO_4$.

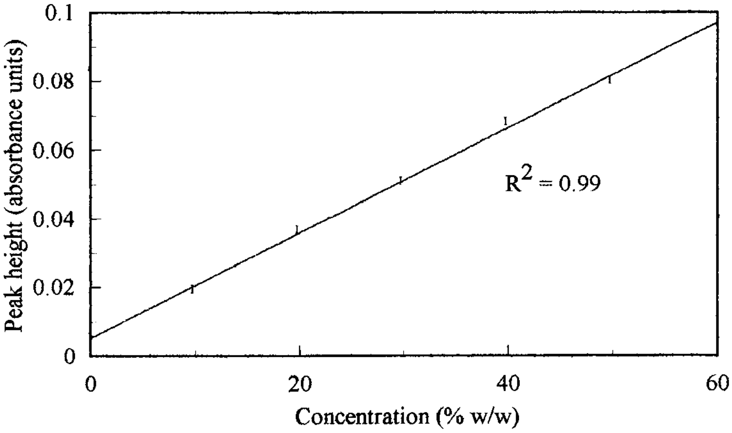

Fig. 5. Calibration curve for CuO·CuSO$_4$.

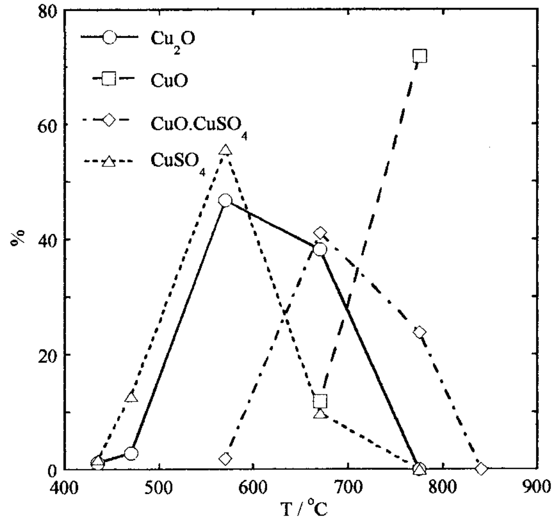

Fig. 6. Phase composition of products (%w/w) isolated at various temperatures during the oxidation of chalcocite [10]

Advantage can be taken of this for quantitative phase analysis, which in some cases proves to be the most appropriate analytical method available.

It is useful to sometimes remind ourselves how sensitive thermal analysis techniques are. Fig. 7 is a DTA record taken some 20 years ago of a sample of 1% $Mg(OH)_2$ and $Ca(OH)_2$. The first endotherm, which is due to the dehydroxylation of the $Mg(OH)_2$, is easily detectable and a reasonable attempt could be made to integrate the area under the peak. The sample mass was about 5 mg, so the DTA peak represents 50 μg of $Mg(OH)_2$. This was by no means the most sensitive setting on the instrument, and so the real detection limit is probably 5–10 μg. Since the energy of a given reaction can be easily quantified by a calibrated DTA or DSC apparatus, it then becomes easy to estimate the detection limit.

One example of a quantitative analysis is taken from the alumina industry [12]. In the Bayer process, the precipitated gibbsite ($Al(OH)_3$) is heated in a fluidised bed to produce alumina. This process is never totally efficient, and so some technique is needed to measure the quantity of unreacted gibbsite left in the calcine. Several methods were attempted, including XRD, FTIR and DSC.

Table 2
Summation of oxide and sulfate phaes present in partially oxidised chalcocite determined by XRD and FTIR

Temperature (°C)	Cu_2O	$CuSO_4$	$CuO{\cdot}CuSO_4$	CuO	Total
570	46.8 ± 5.3	55.6 ± 2.8	1.9 ± 0.1		104 ± 6.0
670	38.2 ± 3.8	9.8 ± 1.0	41.2 ± 1.4	11.9 ± 2.8	101 ± 5.0
775			23.8 ± 0.8	71.9 ± 9.4	95.7 ± 9.4

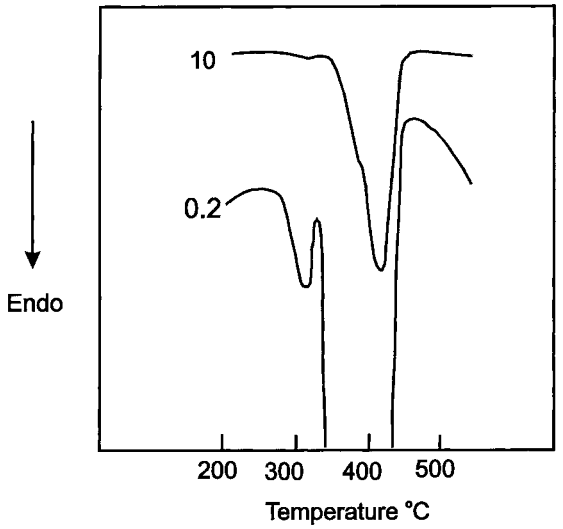

Fig. 7. DTA of 1% $Mg(OH)_2$ in $Ca(OH)_2$. 5 mg sample heated at 10°C min^{-1}. The numbers 10 and 0.2 refer to the relative sensitivities of the DTA scales.

The first two methods are very dependent on the crystallinity of the material, and unsatisfactory results were obtained. On the other hand, the specific enthalpy for the dehydroxylation of gibbsite was found to vary by only up to 10% across a series of samples of quite different crystallinity (see Table 3). Hence integration of the peak area of the endotherm in the vicinity of 250°C, due to the dehydroxylation reaction, enables gibbsite to be determined with a detection limit of about 0.25%. For a 10 mg sample, this corresponds to the detection of 250 μg gibbsite. The analytical results obtained for the gibbsite analysis by the three different methods are presented in Table 4. The DSC procedure has been adopted by some of the alumina producers, who have purchased automated TA equipment for routine analysis of alumina products.

Table 3
Specific enthalpy for the dehydroxylation of gibbsite samples of different degrees of crystallisation

Sample	
1	10.6, 11.3, 11.0
2	10.6, 10.7
3	11.2, 10.5
4	10.7, 11.1
5	10.1, 10.1
6	10.9, 10.9
7	9.95, 10.5

Table 4
Analytical data for the determination of gibbsite in calcined alumina by three different methods [12]

% w/w Gibbsite		
DSC	XRD	FTIR
0.44	0.33	0.13
0.72	0.67	0.54
1.26	0.88	0.87
1.00[a]	0.90[a]	0.80[a]
1.00	0.97	0.53

[a] 1.0% gibbsite standard.

Another example is from the cement industry. About 5% gypsum is added to cement clinker in order to retard the rate of setting. During the milling of the clinker and gypsum, some heat is generated which can dehydrate the gypsum to the hemihydrate, which reduces the concentration and therefore the effectiveness of the gypsum. Accurately determining the quantity of the two phases is a very difficult thing to do except by DSC [13]. The equations for the dehydration of gypsum are

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 0.5H_2O \rightarrow CaSO_4$$

If the reaction is carried out in a sealed pan, the water released in the first step delays the second dehydration by some 40° which allows each endothermic event to be separated sufficiently to be integrated and related to the quantity of each phase. This analysis takes about 30 min to carry out, and gives values which have relative standard errors of 3.7% for gypsum determination and 9.1% for the hemihydrate determination.

5. The development of new techniques

The development of new techniques has been mainly in the coupling of other measurement techniques with thermal methods of analysis. Probably the most common is the addition of evolved gas analysis methods, such as FTIR and MS, to TG-DTA apparatus. A recent symposium was devoted to this topic

[14]. Apart from the obvious advantage of being able to confirm the reactions that are taking place for a given exo- or endothermic event or mass change during the decomposition or oxidation of a mineral, the techniques can also be used to examine the evolution of material that is a minor component or contaminant of the mineral. Increased attention is being given to the environmental effect that industrial organic waste has on soils, which include clay minerals. The adsorption of organic compounds by clay minerals affects their mechanical properties, and can lead to a change in the stability of the organic compound.

These problems have been studied by coupled techniques. Examples include characterisation of hydrocarbon-sludge-soil mixtures [15], conversion of hydrocarbons on solid matrices [16], and reactions of hydrocarbons during thermodesorption from sediments [17]. For complex mixtures of evolved gases it is not sufficient to have a MS or FTIR coupled to the thermal analysis equipment, and a separation method is required between the thermal analysis apparatus and the detector system. GC-MS is the method of choice. One of the problems with determining minor components in the host matrix is that large samples are required to give appropriate detection levels, as well as a representative sample. Some manufacturers have started to make available large sample pans capable of holding 500–1000 mg sample. One thermal analysis system has been designed to take sample volumes of 170 ml, which overcomes problems of inhomogeneous masses such as material in rubbish dumps. This equipment has an interface to a GC-MS analyser [18].

An excellent review by Yariv [19] of the interaction between organic compounds and clays gives details of the use of Thermo-IR-spectroscopy to study interactions of organic pollutants with clay minerals. In this technique, the IR spectrum of the sample is recorded as a function of temperature in specified atmosphere at a specified programmed heating rate. The test sample can be examined in a pressed alkali halide disc, or in a specially built vacuum cell. The layer of contaminated clay can be heated to various temperatures and the IR or FTIR spectrum obtained.

6. Conclusions

This paper demonstrates that the field of thermal analysis continues to evolve. More tools are now available for a fuller characterisation of the starting sample and reaction intermediates, which enables a more reliable interpretation of the results. Improved quality of instrument coupled with the development of new, more powerful combinations of techniques, permits broader application into new areas of interest to those involved with minerals.

References

[1] S.St.J. Warne, Thermochim. Acta 192 (1991) 19–28.

[2] S.St.J. Warne, Minerals to Fossil Fuels, in: E.L. Charsley, S.B. Warrington (Eds.) Thermal Analysis: Techniques and Applications, Royal Society of Chemistry Special Publication No. 117, UK, 1992, pp. 217–237.

[3] D. Dollimore, Anal. Chem. Fund. Rev. 66 (1994) 17R–25R.

[4] P.J. Haynes, Thermal Methods of Analysis, Blackie, London, UK, 1995, Ch. 1.

[5] J.G. Dunn, J.H. Sharp, Thermogravimetry, in: J.D. Winefordner (Ed.), Treatise on Analytical Chemistry, Part 1, vol. 13, Wiley, New York, 1993, pp. 127–266.

[6] J.G. Dunn, J. Therm. Anal. 40 (1993) 1431–1436.

[7] C.M. Earnest, Thermochim. Acta 75 (1984) 219–232.

[8] J.G. Dunn, G.C. De, B.H. O'Connor, Thermochim. Acta 145 (1989) 115–130.

[9] J.G. Dunn, G.C. De, B.H. O'Connor, Thermochim. Acta 155 (1989) 135–149.

[10] J.G. Dunn, A.R. Ginting, B. O'Connor, J. Therm. Anal., in press.

[11] J.G. Dunn, W. Gong, D. Shi, Thermochim. Acta 208 (1992) 293–303.

[12] G. Roach, J. Cornell, J.G. Dunn, C. Kleppe, 3rd Int. Alumina Quality Workshop, October 1993, NSW, Australia.

[13] J.G. Dunn, K. Oliver, G. Nguyen, I. Sills, Thermochim. Acta 121 (1987) 181–191.

[14] J.G. Dunn, K. Oliver, G. Nguyen, I. Sills, Thermochim. Acta 195 (1997) 1–183. (Note this a complete issue of TA with papers from a symposium on environmental topics).

[15] M. Remmler, F.-D. Kopinke, U. Stottmeither, Thermochim. Acta 263 (1995) 101–112.

[16] M. Remmler, F.-D. Kopinke, Thermochim. Acta 263 (1995) 113–122.

[17] F.-D. Kopinke, M. Remmler, Thermochim. Acta 263 (1995) 123–140.

[18] A. Kettrup, G. Matuschek, H. Utschick, Ch. Namendorf, G. Brauer, Thermochim. Acta 295 (1997) 119–133.

[19] S. Yariv, Thermochim. Acta 274 (1996) 1–35.