THE APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO MINERALOGICAL ANALYSIS

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ABSTRACT

This paper describes the application of DSC to the analysis of a mixture of mineral species, in this instance gypsum, kaolinite and quartz. From pre-determined heat values and instrument parameters, it was possible to determine the amount of each phase in a sample mixture, generally to a relative accuracy of 5–10%. The thermal overlap of kaolinite with quartz was overcome by measuring the β to α transformation of the latter from the programmed cooling curve. This represents a general method for measuring quartz in the presence of thermally interfering mineral species.

INTRODUCTION

The use of differential thermal analysis (DTA) in mineralogical studies is well established [1]. DTA is, however, largely non-quantitative, a limitation overcome by DSC which also produces improved thermal resolution. The fundamental equation governing the latter is

$$\Delta HM = KA \tag{1}$$

where ΔH is the energy (mJ mg^{-1}) involved for a given process. M (mg) is the sample mass, K is the "instrument parameter", and A is the peak area. Earlier [2] we described the measurement of K for a given instrument (Rigaku Denki) over its entire temperature range, and the subsequent determination of ΔH for given pure mineral species.

This paper describes the application of DSC to the quantitative analysis of a mixture of minerals. From eqn. (1) it follows that with pre-determined ΔH of the measured peak area, the percentage of a given mineral phase in a mixture can be established via M.

The system of mineral mixtures chosen for this study was made up of three common minerals, namely gypsum, kaolinite and quartz. The reasons

for this choice embrace the facts that both kaolinite and quartz are essentially ubiquitous, their thermal patterns overlap and that quartz, with its weak α to β transition is difficult to measure; therefore, such a mixture is a realistic mineralogical system to investigate. Gypsum, somewhat less common, is nevertheless thermally far removed from the other phases, and thus allowed a wide temperature range (150–700°C) to be studied. Finally, this tertiary system serves as a simple model for the investigation of mineral matter in coal, which itself consists primarily of clays, quartz, carbonates, sulphides and sulphates.

EXPERIMENTAL

Thermal analysis curves were recorded on a Rigaku Denki Thermoflex 8100 series instrument consisting of TG, DTA and DSC modular units. The DSC unit possessed a range of ± 0.5 to 16 mcal s^{-1} and was operative to a temperature of about 850°C. Runs were performed using platinum pans with corresponding lids. Calcined alumina was used as the thermal reference material. Experiments were carried out in static air.

The chemical analyses for the three mineral species gypsum, quartz and kaolinite are provided in Table 1 as it was felt essential to use materials of proven purity. Sample masses throughout were in the range 5–30 mg and heating rates 10°C min^{-1}. Each weighed sample was heated once only. Chart speed was maintained in the range 5–40 mm min^{-1}. Peak areas were measured using a Planix 7 planimeter.

TABLE 1

Chemical analysis of mineral species

Kaolinite [a] (%), $Al_2Si_2O_5(OH)_4$		Gypsum (%), $CaSO_4 \cdot 2H_2O$		Quartz (%), SiO_2	
SiO_2	44.80	Ca (calc.)	23.28	Si (calc.)	46.74
Al_2O_3	37.20	Ca (found)	23.23	Si (found)	46.35
Fe_2O_3	0.41				
FeO	0.07				
MgO	0.25				
CaO	0.58				
Na_2O	0.40				
K_2O	0.43				
H_2O^+	12.92				
H_2O^-	1.76				
TiO_2	1.26				
Total	100.08%				

[a] Macon, Georgia, U.S.A.

TABLE 2

Results of quantitative analysis of mineral mixtures

ΔH (gypsum) $= 623$ mJ mg^{-1}; ΔH (kaolinite) $= 664$ mJ mg^{-1}; ΔH (quartz) $= 1.65$ mJ mg^{-1}; K (gypsum) $= 0.92$; K (kaolinite, quartz) $= 1.3$

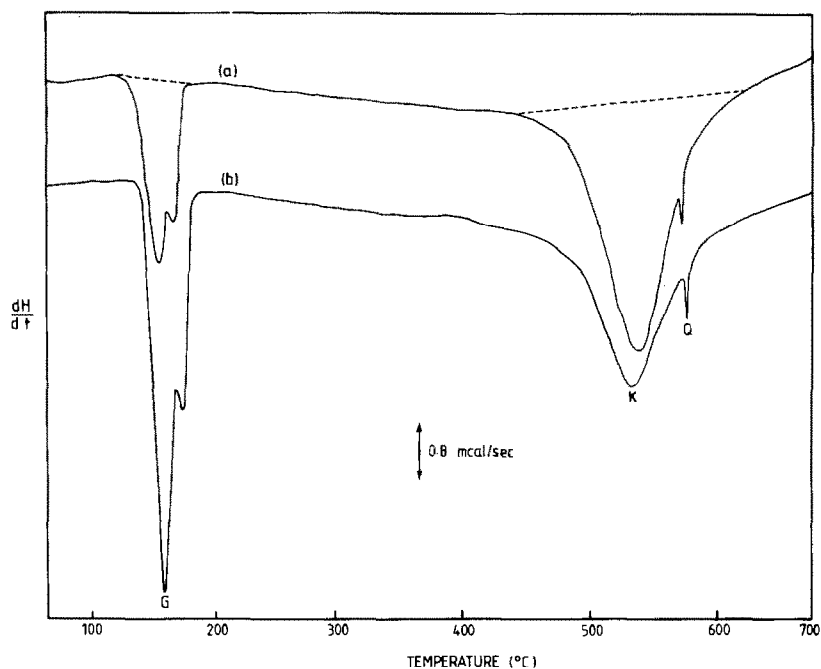| Mineral	% Calc.	% Found	DSC range (mcal s^{-1})	Number of runs
Gypsum	19.9	19.5 ± 0.5	4	8
	15.0	14.7 ± 0.9	4	10
	10.2	10.1 ± 0.5	4	8
	5.0	4.9 ± 0.3	4	8
Kaolinite	79.8	80.9 ± 3.5	8	10
	50.1	51.7 ± 3.0	4	8
	40.1	41.6 ± 0.9	4	8
	30.0	31.5 ± 1.5	4	8
Quartz	50.0	48.9 ± 3.8	2	8
	45.0	46.1 ± 2.5	2	8
	39.9	36.3 ± 1.3	2	8
	30.1	29.8 ± 1.2	1	4
	15.2	12.7 ± 1.7	1	4
	5.0	4.0 ± 0.2	1	4

Fig. 1. DSC curves for mixtures containing gypsum (G), kaolinite (K) and quartz (Q). Curve (a) G/K/Q (10/50/40); curve (b) G/K/Q (20/30/50).

Mixtures of the mineral species were conveniently prepared using a vibratory Specamill. A 100 mg sample mass was placed into an agate cell containing two tiny agate balls and vibrated for 3 min to produce a fine powder of reproducible consistency.

RESULTS AND DISCUSSION

The series of samples studied consisted of intimately mixed amounts of kaolinite, gypsum and quartz. As Table 2 shows the sample content range for kaolinite was 30–80%, gypsum 5–20% and quartz 5–50%. These represent variations not uncommon in a mineralogical environment.

Each sample mixture was heated to a preset value of 750°C at a fixed rate of 10°C min^{-1}. Figure 1 illustrates the DSC pattern for two such mixtures.
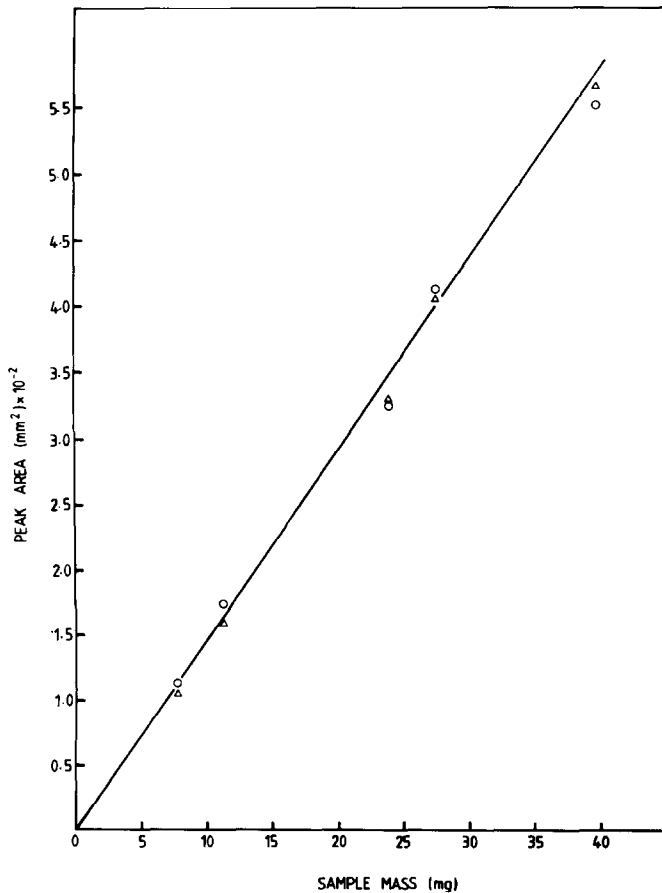

Fig. 2. Peak area versus sample mass for reversible $\alpha-\beta$ quartz transition: ($\bigcirc$) $\alpha-\beta$ transition from heating curve; ($\triangle$) $\beta-\alpha$ transition from cooling wave.
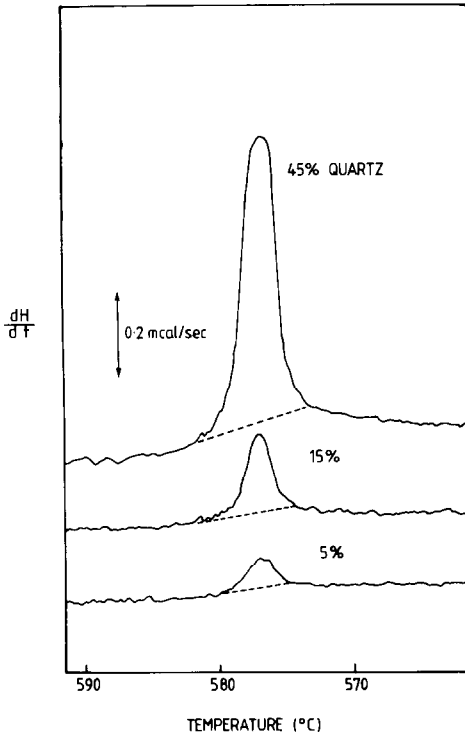
Fig. 3. Cooling curve for gypsum/kaolinite/quartz mixtures containing varying amounts of quartz.

Two strong endothermic peaks occur in the range 140–180°C due to the sequential dehydration of gypsum (losing first 1.5 moles water, and then the remaining 0.5 moles). This is followed by the broad strong peak due to dehydroxylation of the kaolinite, centred at about 550°C. The α–β transition for quartz appears as a sharp spike on the high-temperature side of the kaolinite endotherm.

Measurement of peak area of gypsum and kaolinite posed no problem. This was not true of quartz whose weak sharp transition overlapped with the kaolinite endotherm. This problem was overcome, however, by utilizing the reversible β–α cooling transition of quartz [3]. An exothermic peak of identical area to the heating endotherm is obtained when quartz is cooled below 600°C. Figure 2 illustrates the essential equivalence in peak area for the heating and cooling curves of quartz over a range of sample mass.

Utilizing this property of quartz all samples were cooled to 500°C at a controlled rate ($10°C$ min^{-1}) following the initial heating to 750°C. Because the kaolinite has been irreversibly dehydrated at 550–600°C, the cooling curve exhibits no pattern for the clay and only the quartz exotherm appears (Fig. 3). Indeed for most mineralogical situations no cooling pattern is
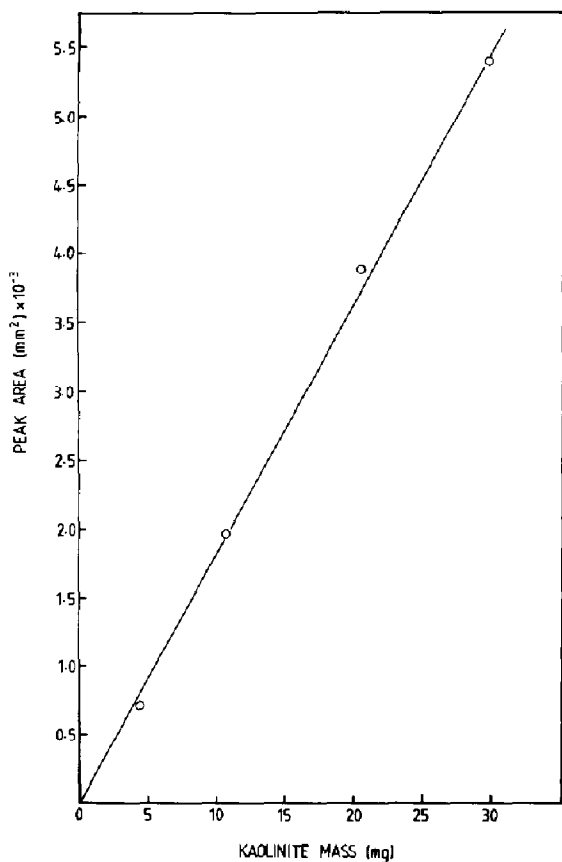
Fig. 4. Peak area versus sample mass for kaolinite.

obtained so that quartz should be generally measurable in the presence of other minerals by this method.

In order to use DSC analytically the enthalpic values, ΔH, of the species involved must be known, as indicated by eqn. (1). For this study, the values for gypsum, kaolinite and quartz were measured using pure minerals as outlined earlier [2]. Figure 4 shows a plot of peak area versus sample mass for the kaolinite endotherm from which ΔH was determined. The results obtained for each phase in a given mixture using measured peak areas and pre-determined ΔH and K values are shown in Table 2. All samples were analysed at least four times.

Figures 5 and 6 are instructive in showing the agreement between the calculated and observed percentage values for each of the three phases. It is clear that DSC yields satisfactory results but that accuracy and precision vary with the mineral species and its concentration. Gypsum and kaolinite produced the most accurate results within about 5% relative. However, from Fig. 6 it is apparent that a bias to higher values occurs for kaolinite. This
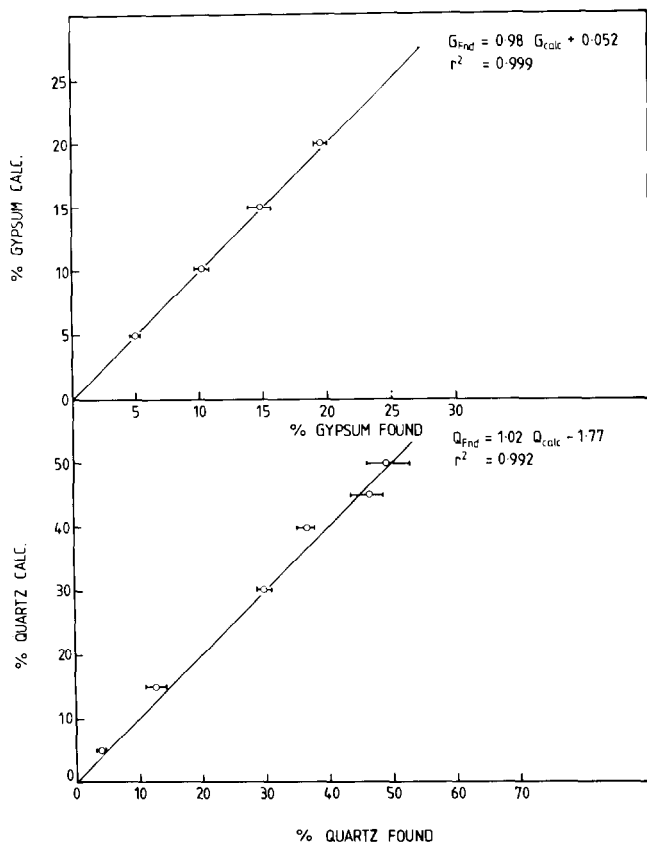
Fig. 5. Plots of percentage calculated values versus percentage found for gypsum (top) and quartz (bottom).

arises due to overestimation of the clay peak area as a result of ambiguity in the commencement and ending of the peak itself. The point of departure from the tangent drawn parallel to the baseline was taken to be the commencement of dehydration. Quartz yielded reasonable accuracy at high concentration levels (> 30%) but this quickly declined at lower levels. Below levels of 20% the accuracy is observed to be within 10–20% relative. Nevertheless, this is favourably comparable with powder X-ray diffraction analysis which routinely boasts no better than 10% relative error. The precision of measurement for gypsum and kaolinite was in the range 3–6%, and somewhat higher for quartz, about 4–10%.

The variability in precision and a common source of error, especially in dealing with such phases as quartz, is the delineation of the baseline [4]. In this study a suitable baseline, including part of the asymmetric peak tail, was found to yield more accurate results, and therefore was used consistently throughout (Fig. 3). Moreover, because of the inherent weakness of the
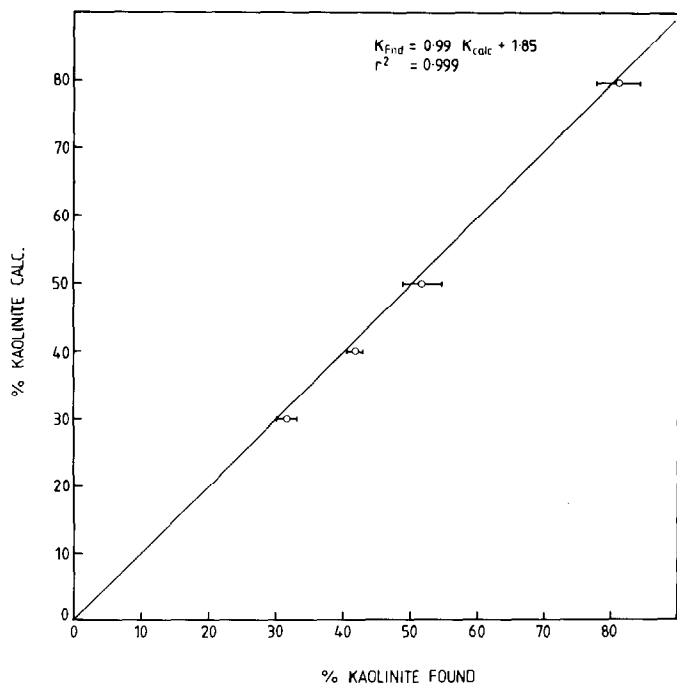
Fig. 6. Plot of percentage calculated value versus percentage found for kaolinite.

quartz peak, high DSC sensitivity (± 1–2 mcal s^{-1}) and fast chart speeds (40 mm min^{-1}) were necessary to obtain large peaks whose areas could be measured with confidence. The thermal behaviour of quartz, therefore, poses a problem for accurate measurement by DSC and its sensitivity by this technique remains inferior to that of XRD, the common method for identification [5].

In conclusion it is clear that DSC can be used for the quantitative analysis of a mixture of mineral species. The accuracy of the determination will depend on the reliable measurement of ΔH and peak area. Taking gypsum as a straightforward case and quartz as a difficult one, it would appear that the general accuracy lies in the range of the 5–20% relative error.

ACKNOWLEDGEMENTS

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