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THERMOGRAVIMETRY OF POTASSIUM HYDROGEN PHTHALATE, AND ITS USE AS A THERMAL STANDARD

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ABSTRACT

Thermogravimetry of potassium hydrogen phthalate (PHP) by Stanton Redcroft TR02 deflection thermobalance has revealed six thermal events in the range room temperature to 1000°C (200 mg samples in fused-quartz and porcelain crucibles in air atmosphere with heating rate of 280°/hour). DTG peak temperatures give effective definition points, apparently superior to difficult-to-define procedural decomposition temperatures. The spread of events across a relatively wide heating range makes PHP a good standard if drawbacks and limitations are realized and appreciated. Major peaks are located at about 300°(A), 500°(C), 700°(E) and 850°(F). Minor peaks which occur at about 400°(B) and at slightly less than 600°(D) may prove more useful than the major ones for calibration purposes. Reactions A and B were used by Keattch (1967) to define standard temperatures. The temperature range covered is useful for clay mineral thermogravity.

SOMMAIRE

L'analyse thermogravimétrique (TG) du phthalate acide de potassium (PHP) a été conduite sur des prises de 200 mg, chauffées à l'air libre, dans des creusets de quartz fondu et de porcelaine, à raison de 280 degrés par heure. Entre la température ordinaire et 1000°C, six pertes de poids ont été enregistrées au moyen de la thermo-balance Stanton Redcroft TR02. L'analyse thermogravimétrique différentielle (DTG) donne des températures de pic qui fournissent d'excellent points de repère, supérieurs, semble-t-il, à ceux des températures de décomposition qui sont toujours difficiles à fixer. La distribution des pics dans un domaine de température relativement grand fait du PHP un bon composé de référence, pourvu qu'on se rende compte de ses inconvénients et de ses limites d'application. Les pics principaux se trouvent aux environs de 300°(A), 500°(C), 700°(E) et 850°(F). Deux pics secondaires, l'un à ~400°(B) et l'autre un peu en-dessous de 600°(D), seront peut-être encore plus utiles aux fins d'étalonnage. Keattch (1967) a utilisé les réactions A et B pour établir des températures de référence. L'intervalle de température est intéressant pour l'étude thermogravimétrique des minéraux argileux.

(Traduit par la Rédaction)

INTRODUCTION

Thermogravimetry (TG) provides a potentially powerful method for the quantitative analysis of minerals (particularly clay and soil minerals — see Schnitzer *et al.* 1959), and this is laargely because it is possible to measure weight changes with a high degree of accuracy. The modern thermobalance is desiged to give an accurate and reliable record of weight change over a considerable temperature range, but unfortunately the temperature cannot be assessed with the same degree of accuracy as the weight. This has led to the use of thermal standards; these are materials which should undergo a weight-change reaction at a definable temperature, and which could be used by an investigator to characterize the behavior of his apparatus in a way which would be understood readily by other investigators. The basic requirements of thermal standards have been reviewed by McAdie (1972; see also Blazek 1973, p. 57 & 168).

Calcium oxalate monohydrate (COM) has been used as a thermobalance standard, but often as a weight indicator rather than as a thermal measure. Duval (1951) used this material when testing and adjusting thermobalances after they had been assembled, cleaned or repaired. It has been suggested that the extremities of the TG curve might be used as temperature calibration points, but Keattch & Dollimore (1975) have pointed out that this is unwise since these points are not dependent solely on the sample. Simons & Newkirk (1964), however, gave qualified approval of COM as a standard, and Forsyth & Berggren (1965) have used it as an aid to study heavy-element oxalates. The Forsyth & Berggren approach is significant because they use the DTG peak temperature as a critical reference point, rather than trying to define the more elusive point at which the reaction begins on the TG record (the procedural decomposition temperature).

In a careful and critical study of thermal standards for TG, Keattch (1967) considered 26 compounds, including COM and potassium hydrogen phthalate (PHP). More recent consideration of the philosophy of thermal standards by the International Confederation for Thermal Analysis (ICTA: see McAdie 1972) has indicated a certain disaffection with the definable decomposition approach; however, for certain mineralogical studies, and with certain safeguards, it can be recommended and it appears that PHP is one of the most suitable materials. We are particularly concerned with one of the five prime requirements listed by McAdie (1972), namely, to provide a common basis for relating independently acquired data. PHP may be unsatisfactory in many ways, and the philosophy of thermal standards may be faulty, but it is probably the best material available and could be useful until a better approach is devised.

THERMAL DECOMPOSITION OF PHP

The thermal decomposition of PHP has been reviewed by Wendlandt (1964), who has also emphasized some of the hazards involved in using PHP as a standard. In comparing four different investigations concerning the drying and decomposition temperatures of PHP, four different results were obtained. Dupuis & Duval (1951) first reported that the decomposition of PHP began at 172°C. In a later study Duval (1955) found a decomposition temperature of 240°C at 150°/hour heating rate, and 236° at 300°/hour. He also traced the isotherms at 150°, 160° and 170°. Belcher *et al.* (1960) reported that the compound began to decompose at 200°. Newkirk & Laware (1962) reported a procedural decomposition temperature of about 260°, and Keattch (1967) observed reactions beginning at 240-250°, 365-370°, 565° and 670°. Duval (1955) failed to observe an isothermal weight loss which was detected by Caley & Brundin (1953), but Newkirk & Laware (1962) were able to show that the Chevenard thermobalance used by Duval would not have been sensitive enough to detect the weight changes involved. These isothermal weight losses below 200° are so small that they in no way affect the use of PHP as a thermobalance standard in dynamic tests.

There are four major reactions which take place during the heating of PHP: (1) the volatilization of water and phthalic anhydride and the formation of a residue of dipotassium phthalate $C_8H_4O_4K_2$; (2) decomposition of the latter compound to form potassium carbonate and carbonaceous material; (3) the carbonaceous material loses weight slowly and finally burns to a residue of K_2CO_3; and (4) the potassium carbonate decomposes with the evolution of carbon dioxide, and K_2O is formed which reacts with the crucible if it is porcelain or quartz.

Belcher *et al.* (1960) studied the effect of heating rate on thermal decomposition and observed that a heating rate as low as 0.5°/min. (i.e. 30°/hour; c.f. the 300°/hour rate used by Duval) gave an effect much closer to a heating rate ten times as fast than to a zero heating rate. Isothermal heating will bring about reaction at far lower temperatures than is customary in thermogravimetry (Garn 1965, p. 308).

Newkirk & Laware (1962) tested PHP with various crucibles and under different atmospheres. With an air atmosphere and a porcelain crucible (a normal setup for nonspecialist use) they found a slight weight gain between 425° and 450°. This was caused by the evaporation of phthalic anhydride from the furnace walls with increasing temperature and its condensation on the crucible support rod of their Chevenard thermobalance.

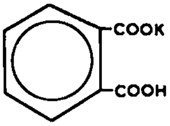
Keattch (1967) used a Stanton deflection balance with a platinum crucible in an air atmosphere. He found that PHP showed a good agreement for reference temperatures of 240°-250° and 365°-370°, but one sample gave a reference temperature of 565° whereas a sample from a different supplier gave an additional reaction at 670°. One of the purposes of the present investigation is to elucidate the behavior of PHP between 500° and 700°.

PHP is listed in the 'Atlas of Thermoanalytical Curves (Liptay 1971-74) as card 123; the data are derived mostly from the work of Belcher *et al.* (1960).

EXPERIMENTS WITH PHP

The ICTA standardization committee has prepared a comprehensive list of suggestions for reporting TG data (see McAdie 1967) and these will be followed as far as possible and relevant. Paragraph numbering follows the ICTA formulation (the omitted paragraphs were not considered to apply):

1. Substances investigated. Potassium hydrogen phthalate $C_8H_5O_4K$ (called by Duval 1963 potassium biphthalate, by Garn 1965 potassium acid phthalate). 200 mg samples used.



2. Chemical reagent manufactured by British Drug Houses Ltd. Various purities are available; extra-pure material is available as a pH standard

and also makes a convenient TG standard.

3. Heating rate. 42×5-minute timer periods from room temperature to 1000°C; 980° rise in 210 minutes, about 4.7°/minute or 282°/hour. The chart speed was 152 mm/hour.

4. Furnace atmosphere. Air at atmospheric pressure and temperature at commencement of test.

5. Sample container. Two types of sample container were used and they gave strikingly different results with respect to the amount of K_2O attack experienced: (a) 'Vitreosil' translucent silica, diam. 29 mm, depth 19 mm; (b) 'Royal Worcester' porcelain, diam. 29 mm, depth 19 mm. Type (b) seems to be much more resistant to K_2O attack.

9. Identification of thermal events. This is considered in the discussion section.

10. Thermobalance used. An unmodified Stanton-Redcroft TR02 deflection balance (similar in style, but a later model than that used by Keattch 1967). Full-scale weight loss 20 mg, total weight loss possible without rebalancing: 180 mg. The temperature-measuring thermocouple is located adjacent to, but outside, the sample-containing crucible. Thermal lag at low temperatures has been measured using Newkirk's (1960) method with a drop of water; a constant weight was reached at 122° — exactly the same result at Newkirk achieved.

12. Method of obtaining DTG curve. By plotting the weight variation in successive convenient time periods a useful histogram can be produced; or, provided the time intervals are not too large, a sufficient number of points is produced to enable a smooth DTG curve to be drawn. The weight variation ordinate can be calibrated in units of weight loss % per minute; the abscissa can be presented as a temperature scale; examples are shown in Figures 1 and 2. This appears to be a simple and satisfactory way of obtaining a derivative curve from the TG result produced by a Stanton balance — it depends largely on the accuracy of the balance timer and requires that the heating rate be very close to linear. We feel very strongly that the derivative curve represents a very potent way of presenting TG information and suggest that its neglect by practitioners may have contributed to the relative neglect of the entire range of gravimetric methods in thermal analysis.

Figure 1 is based on the 5-minute timer interval and is presented as a stepped histogram; comparison with Figure 2 shows that this method allows all the salient features to be represented. The inevitable lack of accuracy in the temperature record can be indicated on the temperature axis. ICTA recommendations for presentation of weight loss downwards are followed.

DISCUSSION

The six peaks observed in Figure 1 have been labelled A to F for ease of reference; they are all reasonably symmetrical — except A, the largest — a useful property for a calibration reaction. Reaction A (the transition from $C_8H_5O_4K$ to $C_8H_4O_4K_2$) is extremely rapid. It starts relatively slowly but ends abruptly, which suggests that the end of the reaction interval would be a better reference point than the beginning as used by Keattch (1967), although this point varies more with variation in heating rate. The start temperature in Figure 1 is 260°, as observed by Newkirk & Laware (1962). With this sort of narrow-interval fast reaction, the peak temperature is difficult to assess accurately; it is judged to be 300 ± 10.

The next major reaction (C) is the transition to potassium carbonate and carbonaceous material and the peak is fairly well defined at 510°. The peak shape is distorted by the minor reactions B and D. Reaction E with a peak temperature of 680-700° represents the removal of carbonaceous material and reaction F is the breakdown into K_2O and CO_2 which occurs at 850°C in a quartz crucible, and somewhat higher in a porcelain crucible.

The peak temperatures of events A, C and E agree well with those observed by Belcher *et al.* (1960), and these workers have provided some observations which may explain the small peak B at about 410°. They have shown that two types of reaction take place in the decomposition of dipotassium phthalate, and observed a very marked DTA peak at 440°. Although they observed no weight loss corresponding to this DTA peak, some small weight loss may possibly occur at this point. Peak B is more significant than its size suggests because it defines the reaction interval (with start temp. 370°) which Keattch (1967) listed as a temperature reference. He had problems with the higher temperature peaks but B was always detected.

Previous investigators such as Belcher *et al.* (1960) and Newkirk & Laware (1962) have only presented direct TG data; they did not determine the DTG curves and seem to have overlooked small-scale reactions B and D. Keattch (1967) also neglected the DTG approach but he did list what appears to be the start temperature for reaction D as one of his elusive reference points (not always obtained). We always detected D although its position between large peaks C and E makes it rather less than obvious on the direct TG record. However, on the extended ordinate DTG plots (Fig. 2) it shows up very clearly. In Figure 2 the D start temperature corresponds

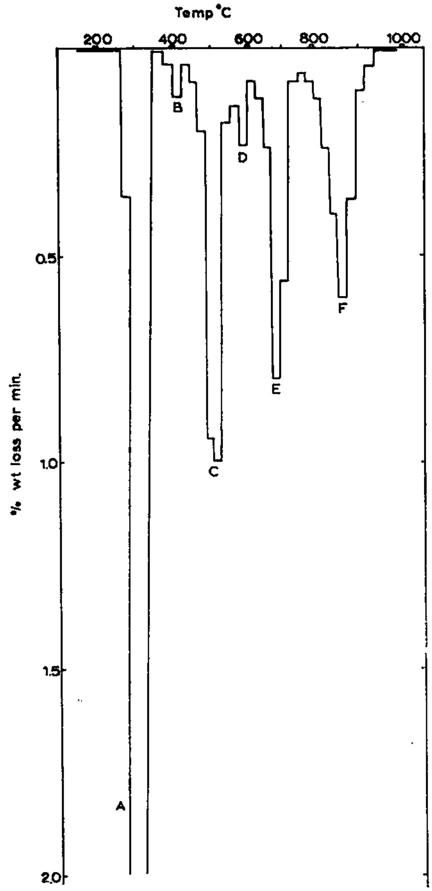


FIG. 1. (left). DTG histogram for PHP: 200 mg sample, air atmosphere, fused-quartz crucible, heating rate about 280°/hour. Histogram intervals defined by 5-minute balance marker.

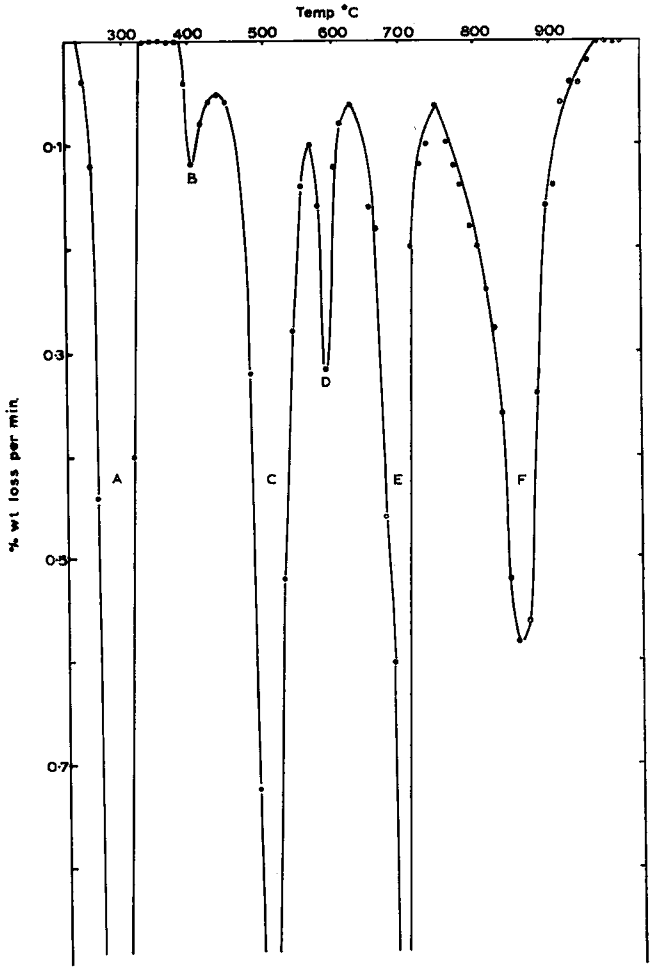


FIG. 2. (right). DTG curve for PHP: same conditions as Figure 1. Weight loss over each 2.5 minutes recorded and used in plotting rate-variation points.

almost exactly with the Keattch result of 565°.

Keattch's other elusive point at 670° presumably corresponds to the start of reaction E; since reaction E is so significant in the PHP breakdown sequence it is difficult to see why it appeared in Keattch's results as such an elusive point. It was explained as being due to the variability of materials from different suppliers but this variability has not been reported by other workers and it may be that Keattch was the victim of a very unlikely accident, and that most PHP is reliable.

PHP is already in use as a standard reagent. A 0.05*M* solution has a pH of 4.000 at 15° and is used in Britain as the primary pH standard (BS 1674: 1961). This established use means that very pure PHP is available from chemical supply companies, and in fact should already be possessed by most chemical laboratories. All thermobalance users should have ready access to PHP of sufficient purity. It stores well; Duval (1963, p. 267) described it as "anhydrous, and quite dry" — a statement which cannot be made about COM, which tends to become damp under normal laboratory storage conditions; in fact all hydrates tend to have irregularities of water content. PHP can be stored in a laboratory cupboard, without special conditions.

SOME WIDER IMPLICATIONS

An analytical machine for use in clay mineralogy should ideally identify the clay minerals present in a sample, *and* give a quantitative estimate of their absoute amounts. The thermobalance can partly meet this dual requirement, but to operate effectively a set of acceptable standards is required; these should be temperature standards (such as PHP and COM) and mineral standards which allow comparative estimates of mineral content. The comparative standard technique has been applied to the St. Jean Vianney quickclay to give a numerical determination of clay-mineral content (Smalley *et al.* 1975) and the very low value obtained allows certain useful geotechnical conclusions to be drawn.

The DTG curves for PHP appearing in this paper were determined on the same Stanton Redcroft machine that was used for the investigations of the St. Jean Vianney quickclay and should be considered as characterizing that particular apparatus. It would be useful if future investigations which utilize TG techniques could include a DTG determination of PHP which, published with the major results, would — as McAdie proposed — provide a common basis for relating the data.

It would be useful if a simple and relatively straightforward TG method were available which could be incorporated in the series of tests carried out by soil engineers when assessing the suitability of soil materials for construction purposes. Normally the 'clayeyness" of the soil is determined by measuring plasticity parameters after the fashion of Atterberg — a method which is very susceptible to operator variation and which does not directly distinguish among the types of clay mineral present in a sample. It is so universally useful, despite its many drawbacks, only because it is a completely standard method. The TG method, using a readily available autonomous balance such as the Stanton, could provide invaluable data for the soils engineer. Bidlo (1971) has shown how this concept can be applied in his studies of loess from the site of the 1964 embankment collapse at Dunaujvaros.

CONCLUSIONS

Six thermal events are detectable with a Stanton Redcroft TR02 thermobalance when potassium hydrogen phthalate is heated from room temperature to 1000°C in an air atmosphere and a porcelain or fused-quartz crucible. Since very pure PHP is readily available and it is already in use as a pH standard it is proposed as a convenient TG standard. Its behavior is fairly well understood and recorded and it goes some way to meeting the ICTA requirements. If PHP is to be used as a thermal standard, the peak temperatures of the DTG curve provide convenient reference points.

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