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A METHOD FOR PREPARING PELLETED CLAY SAMPLES OF SEMI-MICRO QUANTITY FOR DIFFERENTIAL THERMAL ANALYSIS

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Abstract—A semi-micro quantity (10–15 mg) sample of clay is pressed into a 3 mm diameter pellet for differential thermal analysis (DTA) in a STONE-TRACOR ring microsample holder. The pellet is transferred to the sample holder dish with a vacuum tweezers. Platinum sample dishes are also handled by vacuum tweezers to avoid denting the dishes or damaging the thermocouple wires. The DTA curves obtained by the pellet method are highly reproducible. The resolution and sensitivity of reaction peaks are equivalent to or better than those produced by a large sample (200 mg) packed into a nickel block holder.

INTRODUCTION

DIFFERENTIAL thermal analysis is an important analytical technique used in the study of clays and other hydrous minerals. A disadvantage has been that the temperature reported for a particular thermal reaction often may have a range of as much as 100°C, reflecting variations in heating rate, sample size and packing density (Mackenzie and Farquharson, 1953). In order to minimize experimental variations not attributable to the true thermal characteristics of the material, we propose the following method of standardization of sample preparation procedures.

INSTRUMENT AND THE PROBLEM

The Materials Development Laboratory of the State Geological Survey of Kansas recently installed a STONE-TRACOR model 202D DTA system capable of analyzing semi-micro samples weighing between 0·1–20 mg.* The semi-micro sample holder uses a Platinel II ring differential thermocouple with small platinum foil dishes located on the rings. Removal of the platinum dish from the thermocouple ring with needlenose tweezers was somewhat troublesome. Inexperienced operators spilled samples, caught the tweezers on the thermocouple wires and often dented the platinum dish, which caused annealing reaction peaks on the DTA curve. The purpose of this note is to report a method for preparing and handling clay samples of semi-micro quantity that eliminates the use of mechanical tweezers in changing samples and provides a uniform sample area contact with the base of the sample dishes (Fig. 1).

SAMPLE PREPARATION AND HANDLING

Fifteen mg or less of the powdered sample are placed in a 3 mm (0·118 in.) die† and hand pressed into a pellet having a thickness of about 1·1 mm. The pellet can be stored at constant humidity either in a small plastic container or in a small chamber. The pellet is handled by vacuum tweezers so as to avoid excessive mechanical pressure and eliminate chipping of the pellet. Platinum dishes are also handled by the vacuum tweezers to avoid denting the dishes and touching the thermocouple wires. Normally, the pelleted sample is removed from the dish upon completion of the run. The dish remains on the sample holder ring as long as it is not contaminated by the fusion of the pellet.

REFERENCE MATERIALS

The conventional reference material, alumina (Al_2O_3), is difficult to press into a pellet so one part of kaolinite is added to four parts of alumina to improve the pressing characteristics. The mixture makes a satisfactory reference material. Ten milligrams of the mixture is pelleted and calcined to 1050°C before using as a reference pellet.

*TRACOR specifications for the sample holder. The Geological Survey of Kansas does not endorse any equipment or material. Trade names are used only to clarify the experimental work.

†Pellet press manufactured by Parr Instrument Company.

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TEST SAMPLES

Materials used for testing the method were kaolinite (API Ref. Clay No. 7; supplied by Wards Nat'l. Sci. Est. Inc.), quartz (commercial grade St. Peter sand), and their mixtures. Room dried sample of about 40 g was ground in a shatter box for 2 min. The mixtures were prepared after powdering. The prepared powder samples were then divided into two parts; one for DTA, and the other for X-ray diffraction. No impurity was detected by the X-ray diffraction method.

RESULTS AND DISCUSSION

The reproducibility of the pellet method was checked by running three kaolinite samples on three different days, using the same instrument settings and reference material. Agreement of reaction temperatures and area under reaction peaks was within acceptable experimental error (Fig. 2). On subsequent runs it was noted that if the area under low temperature endothermic reaction is of importance, it is necessary to start the furnace at room temperature. A pre-heated or warm furnace will cause partial dehydration before the experiment begins (Fig. 3).

The resolution and sensitivity of reaction peaks

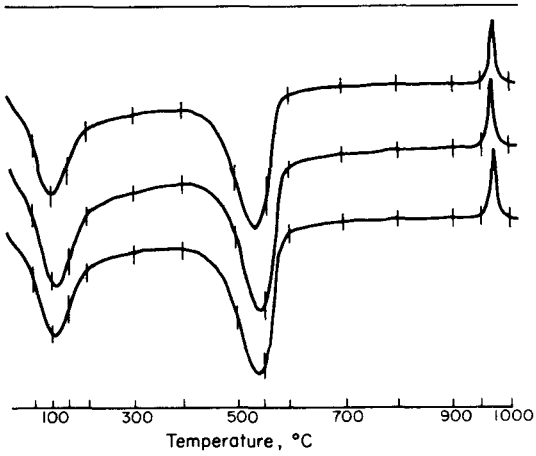


Fig. 2. DTA curves of kaolinite. All curves were made from 15 mg of pelleted samples under the same instrument conditions (300 u.v.; chart speed 0·2 in./min; heating rate 20°C/min; preheat 25 sec).

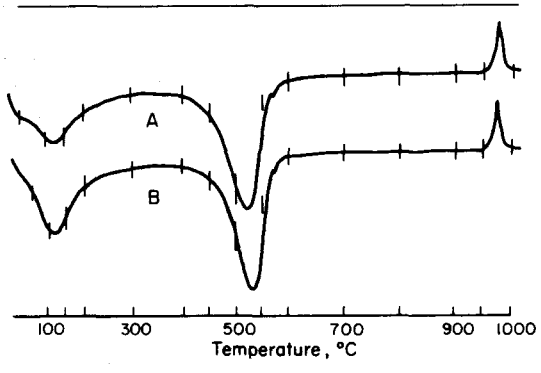


Fig. 3. DTA curves of a mixture of quartz (25 per cent by wt.) and kaolinite (75 per cent by wt.) showing the difference of low temperature endothermic peaks between a sample started with a warm furnace (curve A) and a sample started with a furnace of room temperature (curve B). Other conditions were the same as in Fig. 2.

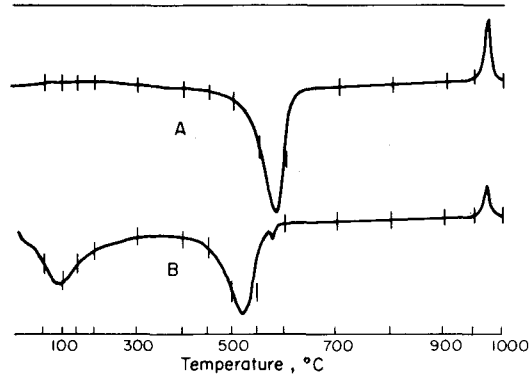


Fig. 4. DTA curves of a mixture of quartz (50 per cent) and kaolinite (50 per cent) showing the difference of reaction temperatures, sensitivity and resolution of the reactions between a large sample (200 mg) packed in a nickel block holder (curve A) and a pelleted sample of semi-micro quantity (15 mg) (curve B). Instrument conditions were the same as in Fig. 2 except curve A, 1200 u.v.

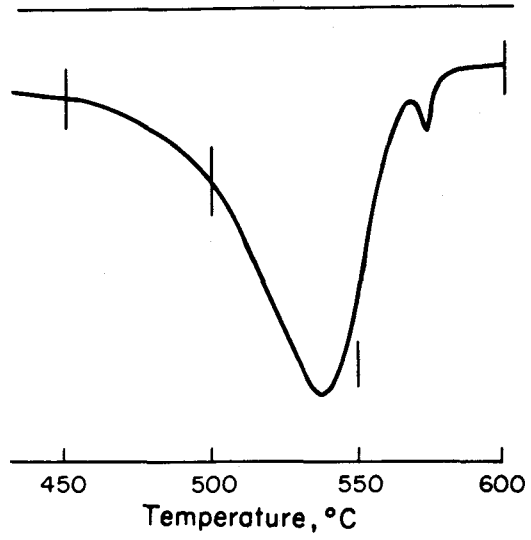


Fig. 5. DTA curve of a mixture of quartz (50 per cent) and kaolinite (50 per cent) packed in a nickel block holder. Sample wt. 200 mg; 1200 u.v.; chart speed 0·1 in./min; heating rate 5°C/min. Compare with Fig. 4.

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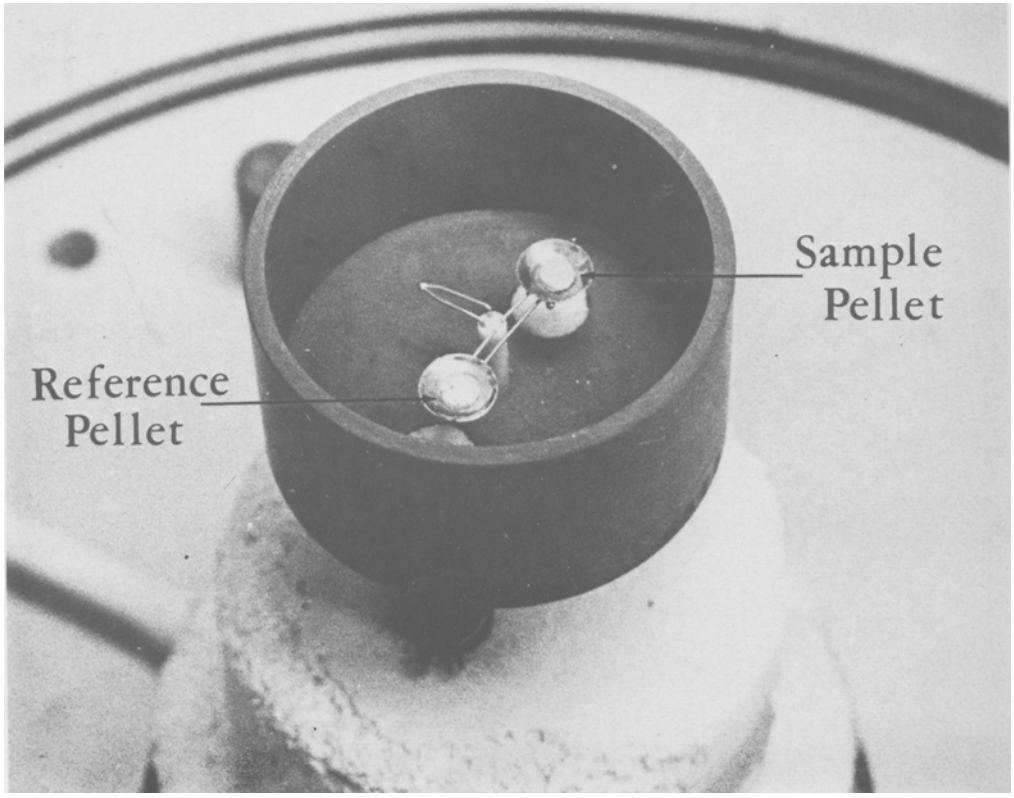


Fig. 1. Pelleted sample and reference material on the platinum dishes in a micro sample holder. Holder diameter 4 cm.

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produced from pelleted sample of semi-micro quantity (15 mg) composed of a mixture of quartz and kaolinite (1 : 1 by weight) was compared with that from a large sample (200 mg) packed into a nickel block holder. No quartz was detected in curve A (Fig. 4) from the large sample with a heating rate of 20°C/min (Fig. 4). Only after the heating rate was reduced to 5°C/min was the separation of quartz and kaolinite reactions between 500 and 600°C from the large sample (Fig. 5) as clear as that from the pelleted sample with a heating rate of 20°C/min (curve B, Fig. 4). The sensitivity of low temperature endothermic reaction on the DTA curve from the large sample was also very low in comparison with that from the pelleted sample.

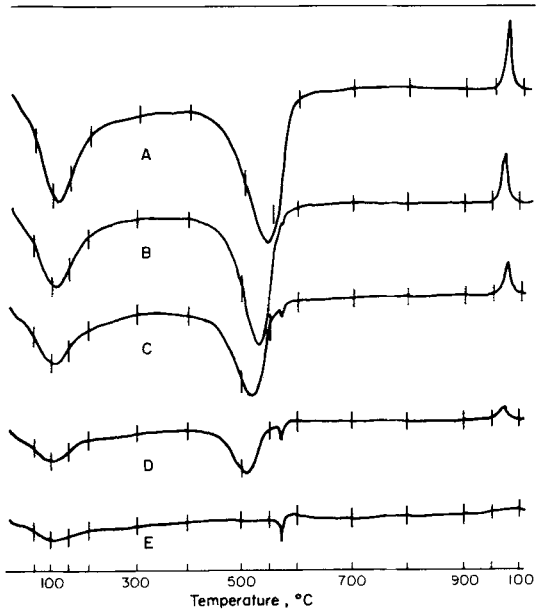


Fig. 6. DTA curves: A, kaolinite 100 per cent; B, kaolinite 75 per cent; quartz, 25 per cent; C, kaolinite 50 per cent; quartz, 50 per cent; D, kaolinite 25 per cent; quartz, 75 per cent; E, quartz, 100 per cent. Sample weight and instrument conditions were the same as in Fig. 2.

The results from mixtures of different amounts of quartz and kaolinite indicated that there is a possibility for an estimation of the quantity of each component in the mixture (Fig. 6).

CONCLUSIONS

From the results, we conclude that a pellet method:

(1) Eliminates the handling problem encountered with a small size; (2) Avoids damaging the thermocouple wires and denting the platinum dishes; (3) Provides a sample that is easily stored under any atmospheric conditions; (4) Saves time owing to a fast heating rate; (5) Permits highly reproducible curves, high sensitivity of the reactions and high resolution of the reaction peaks.

Acknowledgments—Mr. T. C. Waugh of the State Geological Survey of Kansas took the picture for Fig. 1 and allowed the senior author to use his laboratory in evenings and weekends to prepare some of the samples for this study. Professor L. F. Dellwig of The University of Kansas reviewed the manuscript.

REFERENCE

Mackenzie, R. C., and Farquharson, K. R. (1953) Standardization of differential thermal analysis technique: *Proc. 19th Session Intern. Geol. Cong., Algiers*, 1952, 183–200.

Résumé—Une semi-micro quantité (10-15 mg) d'argile est compressée en une pastille de 3 mm de diamètre pour l'analyse thermale différentielle (ATD) dans un anneau Stone-Tracor. La pastille est transférée avec des pinces à vide dans la capsule. Les capsules de platine sont également manipulées avec des pinces à vide pour éviter de les denteler ou d'endommager les fils du thermocouple. Les courbes ADT obtenues par la méthode des pastilles sont hautement reproductibles. La résolution et la sensitivité des crêtes de réaction sont équivalentes ou supérieures à celles produites par un grand échantillon (200 mg) pressé dans un support de nickel.

Kurzreferat—Eine Tonprobe semimikroskopischer Grösse (10–15 mg) wird zu einem Plätzchen mit 3 mm Durchmesser gepresst um in einem STONE-TRACOR Ringmikroprobenhalter einer differentiellen thermischen Analyse (DTA) unterzogen zu werden. Das Plätzchen wird mittels einer Vakuumpinzette in die Schale des Probehälters überführt. Die Platinprobenschalen werden ebenfalls mit Vakuumpinzetten behandelt um jede Verbeug ung der Schalen oder Beschädigung der Thermoelementdrähte zu verhindern. Die mittels der Plätzchenmethode erhaltenen DTA Kurven sind sehr gut reproduzierbar. Die Schärfe und Empfindlichkeit der Reaktionsspitzen sind gleichwertig oder besser als die mittels einer grossen Probe (200 mg) in einem Nickelblockgerät erhaltenen.

Резюме — Из полумикроколичества (10–15 мг) глины под прессом получается таблетка для дифференциального термического анализа (ДТА) в специальном кольцевом держателе. Таблетка помещается в держатель с помощью вакуумного пинцета. Последний употребляется и для манипулирования с платиновым держателем, чтобы избежать его повреждения и повреждения термопары. Кривые ДТА, полученные с помощью этой методики, характеризуются высокой воспроизводимостью. Разрешение пиков и чувствительность не отличаются от таковых для больших новесок (200 мг) в никелевом блокодержателе или превосходят их.

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