Thermochimica Acta, 8 (1974) 197–204

THE DETECTION OF CHRYSOTILE ASBESTOS AT LOW LEVELS IN TALC BY DIFFERENTIAL THERMAL ANALYSIS*

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(Received 27 August 1973)

ABSTRACT

Currently, there is a great deal of interest in the determination of asbestiform minerals in cosmetics and foods. A sensitive and reliable technique was sought for the detection of small quantities of chrysotile asbestos in talc. X-ray diffractometry is limited in the identification of trace amounts of the serpentine minerals in talc because of interfering diffraction peaks of the chlorite minerals which are usually present. A Robert L. Stone Differential Thermal Analyzer, utilizing a high temperature powder sample holder with exposed-loop thermocouple, has been used to detect chrysotile added in varying amounts to pharmaceutical grade talc. The minimum level of detection by this method is 1% by weight of chrysotile. This is possible because of the intense dehydroxylation endotherm and recrystallization exotherm exhibited by chrysotile. Mineral impurities normally found in high grade talc do not interfere. The preparation of homogeneous chrysotile–talc standards is discussed.

INTRODUCTION

Recent concern about the possible presence of asbestos minerals in the environment has resulted because some of these materials are suspected of causing adverse effects on health. There is a great deal of interest, for example, in the examination of talc dusting powders where the presence of asbestos in significant amounts could pose a problem through accidental inhalation. Nenadic and Crable[1] have reviewed several X-ray diffraction techniques for both qualitative and quantitative determinations of asbestos minerals and other materials considered hazardous in certain occupational environments. Other methods[2,3] have recently been developed for the determination of sub-milligram quantities of asbestos particulates collected by membrane filters in studies of urban atmospheres.

Asbestos minerals consist principally of chrysotile, of the serpentine group of minerals, and certain fibrous varieties of amphibole. Talc, the base of some common household items, is not an asbestos mineral. However, geologic investigations have indicated that talc may result from hydrothermal alteration of such minerals as serpentine, tremolite, and chlorite. Hence, it is theoretically possible that traces of these minerals may occur as impurities in talc. Equations (1) and (2) indicate several modes of paragenesis of talc:

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*Presented at the 4th North American Thermal Analysis Society Meeting, Worcester, Mass., June 13–15, 1973.

$$\underset{\text{Serpentine}}{2Mg_3Si_2O_5(OH)_4} + 3CO_2 \xrightarrow[\text{pressure}]{\text{heat}} \underset{\text{Talc}}{Mg_3Si_4O_{10}(OH)_2} + 3MgCO_3 + 3H_2O \qquad (1)$$

$$4SiO_2 + \underset{\text{Dolomite}}{3CaMg(CO_3)_2} + H_2O \xrightarrow[\text{pressure}]{\text{heat}} \underset{\text{Talc}}{Mg_3Si_4O_{10}(OH)_2} + 3CaCO_3 + 3CO_2 \qquad (2)$$

In the first, talc is thought to be formed by the action of carbon dioxide, heat, and pressure on the mineral serpentine, so that magnesite might occur as an impurity. In the second, talc is formed from the reaction of silica with dolomite, leaving calcite as an impurity.

X-ray diffraction and differential thermal analysis are effective and complimentary techniques for the characterization of talc. X-ray diffraction can be used to identify mineral impurities which may be finely interspersed or intercalated with talc. However, the diffraction characteristics of many clay minerals have considerable similarity so that unequivocal identification by the use of diffraction data only is frequently not possible. In addition, certain inherent characteristics of these minerals, such as their variable composition, crystal imperfections caused by randomly oriented layers, and tendency toward preferred particle orientation can cause shifting of diffraction peak maxima and variation in relative peak intensities. This can result in misinterpretation of the X-ray diffractogram.

Differential thermal analyses of the clay minerals show characteristic endothermic reactions due to dehydration and loss of crystal structure, and exothermic reactions due to formation of new phases at elevated temperatures. DTA curves are generally not diagnostic enough to permit absolute identification of these minerals in a mixture. The variable composition and thermal history of the minerals can lead to variations in the appearance of their thermograms. As would be expected, peak temperatures vary somewhat with the amount present. The thermal profile of talc [Equation (3)] shows one predominant endothermic peak at greater than 900°C which is attributed to the dehydroxylation, yielding enstatite, with the evolution of amorphous silica and

$$Mg_3Si_4O_{10}(OH)_2 \xrightarrow{>900^{\circ}C} \underset{\text{Enstatite}}{3MgSiO_3} + SiO_2 + H_2O \qquad (3)$$

chemically combined water. Thermograms of talc, run under sensitive and carefully controlled experimental conditions, can provide information concerning the mineral impurities present. It then became apparent that, due to the presence of these trace mineral impurities, DTA could be used to characterize and identify a talc by the unique nature of its thermogram. Assignment of the thermal transitions attributed to mineral impurities was accomplished by the direct addition of small quantities of these minerals to the talc sample. Therefore, a DTA curve coupled with supporting X-ray diffraction evidence is sufficient to positively identify the trace mineral impurities. The minerals which have been most frequently encountered in the analysis of pharmaceutical grade talcs are indicated in Table 1. The ideal formula has been given in each case, although few minerals are found with the theoretical composition. An extensive amount of isomorphous substitution can occur, resulting in numerous mineral species which complicate the analysis.

TABLE 1

MINERALS COMMONLY ASSOCIATED WITH TALC

Species	*Ideal formula*
chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$
phlogopite	$KMg_3(Si_3Al)O_{10}(OH)_2$
magnesite	$MgCO_3$
calcite	$CaCO_3$
dolomite	$CaMg(CO_3)_2$

The asbestos minerals, given in Table 2, consist of certain varieties of the serpentine and amphibole groups. Since the amphiboles do not exhibit intense thermal transitions distinguishable from talc, DTA is not applicable for the detection of these minerals at low levels in talc. However, using the step-scanning technique of X-ray diffractometry, we have been able to detect amphibole at less than 0.5% by weight in a talc matrix. By this method, the individual amphibole species present cannot be determined.

TABLE 2

ASBESTOS MINERALS

Group	*Ideal formula*
Serpentine group	
chrysotile	$Mg_3Si_2O_5(OH)_4$
Amphibole group	
tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
actinolite	$Ca_2(Mg, Fe^{2+})_5Si_8O_{22}(OH)_2$
anthophyllite	$Mg_7Si_8O_{22}(OH)_2$
amosite	$(Mg, Fe^{2+})_7Si_8O_{22}(OH)_2$
crocidolite	$Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$

The serpentine minerals are related structurally both to the kaolinite minerals and to the chlorites. This, coupled with the variable chemical composition of the serpentines, leads to great difficulty in their detection in trace amounts by X-ray diffractometry. A sensitive and reliable technique was sought for the detection of small quantities of chrysotile asbestos in talc. Thermograms of the serpentine minerals show a dehydroxylation endotherm at approximately 650°C, followed with very little intermediate phase by an exotherm at 820°C associated with the formation of forsterite. These intense thermal transitions suggest DTA as a method for detecting chrysotile in a talc matrix. Mineral impurities normally found in pharmaceutical grade talc do not interfere.

EXPERIMENTAL

A Robert L. Stone Differential Thermal Analyzer (Model LA-XYH), utilizing a high temperature powder sample holder with exposed-loop differential thermocouple (Model SH-8BE2-NIZ) is particularly suited for this work. It permits direct contact of thermocouple wire and sample, yielding maximum sensitivity in the thermogram. The sample cavity may be packed with 130–140 mg of talc. The packing technique must be as consistent as possible and loose enough to prevent thermocouple stress. All talc samples, mineral standards and the aluminum oxide used as reference material were ground to pass a 325-mesh sieve. The samples were heated at 10 °C/min in a dynamic helium atmosphere in order to sweep out gaseous mineral decomposition products and to prevent oxidative reactions. By holding the above factors constant, reproducible DTA curves were obtained. In most cases, however, duplicate thermograms were run to protect against spurious heat effects caused, for example, by slight shifting of the sample, which can occur with this type of sample holder. Determination of the minimum level of detection of chrysotile in talc by DTA was accomplished by the preparation of standard samples. The finely fibrous, silky nature of chrysotile made the preparation of homogeneous chrysotile–talc standards difficult. The talc was first slurried in ethanol in a Waring Blender. The chrysotile was then added to the solution, and the mixture was blended for 20 minutes. The ethanol was then evaporated on a steam bath, and the resulting caked sample was broken and mixed by shaking for 20 minutes in a Spex Mixer/Mill. The homogeneity of the chrysotile–talc standards prepared in this way was verified by two optical microscopists.

RESULTS AND DISCUSSION

In Fig. 1, DTA curve (1) represents the thermogram of talc as it is normally

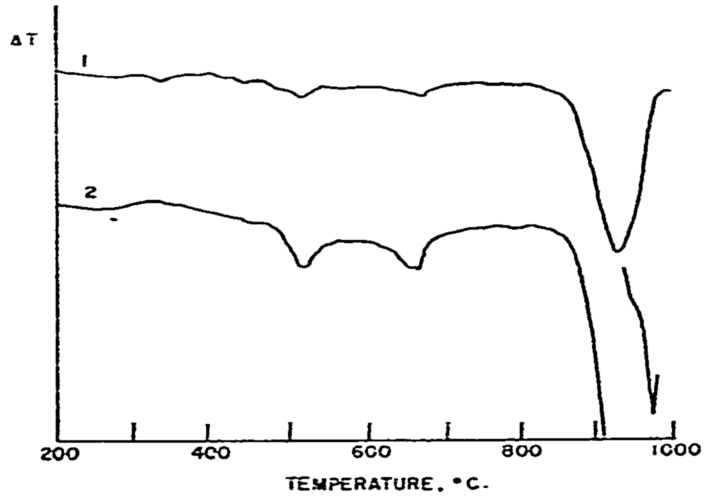

Fig. 1. DTA curves for talc run under normal (1) and more sensitive (2) conditions.

found in the literature. The endothermic dehydroxylation of talc is the only evident thermal transition. Curve (2) is a thermogram of the same pharmaceutical grade talc, run under the more sensitive, standardized experimental conditions. Two mineral impurities are indicated, each at a level of about 1% by weight. Both peaks represent the decomposition of carbonates: the first is magnesite, the second is dolomite or a mixture of dolomite and calcite. The major endotherm for talc shows an interesting asymmetry. This is an unresolved doublet suggesting structural variations such as isomorphous substitutions within the talc lattice, which would modify bond strengths[4].

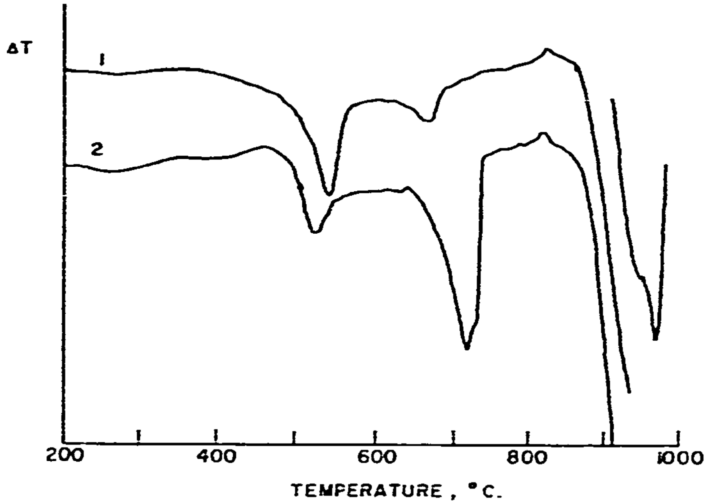

Fig. 2. DTA curves showing the effect of adding 1% magnesite (1) and 2% dolomite (2) to talc.

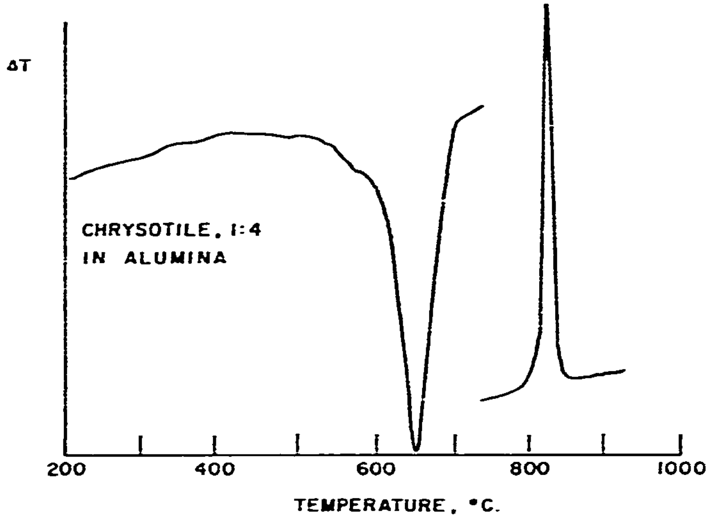

Fig. 3. DTA curve for chrysotile asbestos.

Figure 2 demonstrates the addition of known mineral impurities for the purpose of assigning thermal transitions. The same talc sample used for the DTA curve in Fig. 1 was employed. Curve (1) shows the effect of adding 1% by weight of magnesite; curve (2) represents the addition of 2% dolomite.

Figure 3 represents the thermogram of chrysotile asbestos. The intensities of the dehydroxylation endotherm and the recrystallization exotherm are evident since the sample was only a 20% mixture of chrysotile with alumina. Thermograms of chrysotile asbestos obtained from 33 locations throughout the world exhibited these same two thermal transitions. The DTA curve of the talc used for the standard

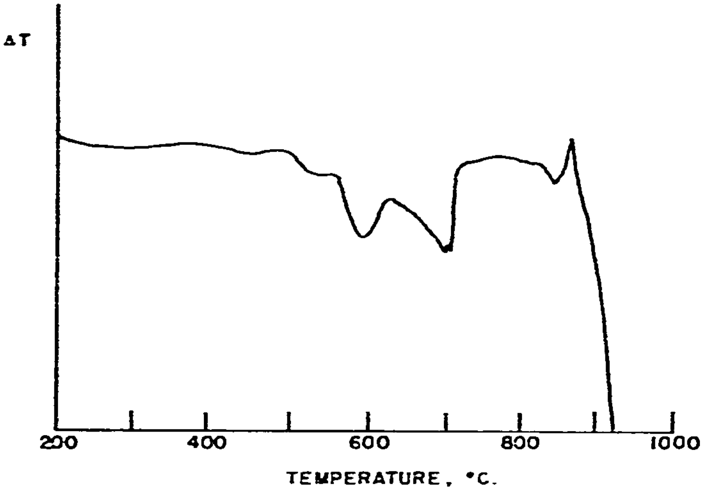

Fig. 4. DTA curve for talc used to prepare chrysotile-talc standards.

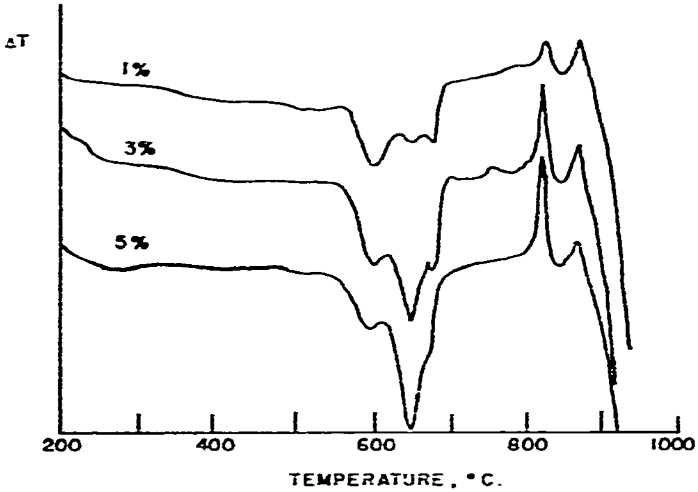

Fig. 5. DTA curves for 1, 3, and 5% by weight of chrysotile in talc.

samples is shown in Fig. 4. This particular talc was selected because of the presence of several mineral impurities in the region of interest. These include chlorite in addition to the carbonates previously described. This chlorite mineral shows a dehydroxylation endotherm at approximately 600°C, followed at 850°C by an endothermic–exothermic effect attributed to further dehydroxylation and recrystallization to olivine. More than one variety of chlorite may frequently be present. Figure 5 shows thermograms obtained for the chrysotile–talc standards. Although this talc is from the same source as that in Fig. 4, it is a different sampling; hence, a difference in the quantity of carbonates present can be detected. In the case of 5% by weight of

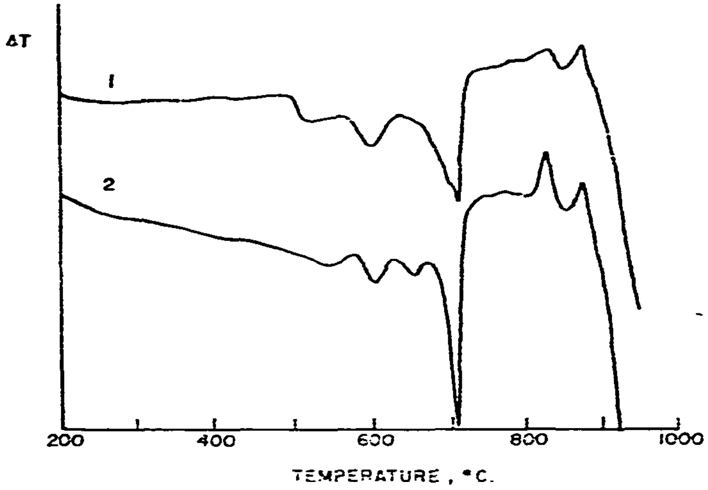

Fig. 6. DTA curve for an adult dusting powder (1) and the addition of 1% chrysotile to this product (2).

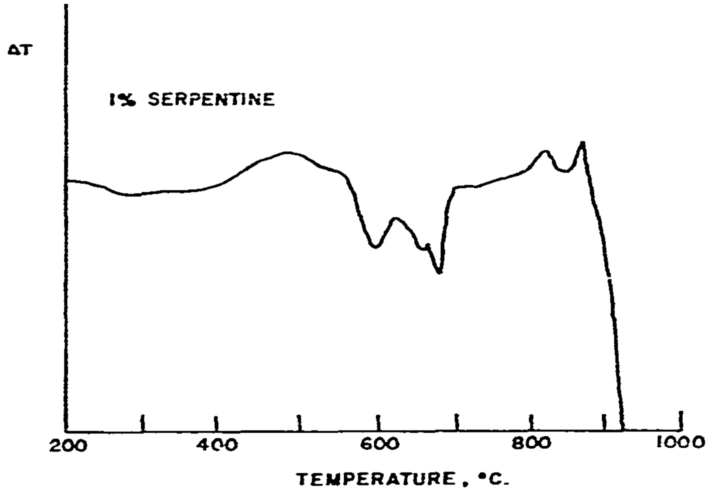

Fig. 7. DTA curve representing the addition of 1% of the serpentine mineral, antigorite, to talc.

chrysotile in talc, the intensity of the chrysotile endotherm causes a poorly resolved doublet between the chrysotile and dolomite. The 1% level represents the practical limit of detection of chrysotile in talc by this method.

DTA curve (1) in Fig. 6 is that obtained for an adult dusting powder. The mineral impurities which could be detected in this sample are magnesite, chlorite and dolomite. Curve (2) shows the same commercial product to which has been added 1% chrysotile. Note that the thermal transitions of the serpentine mineral are easily detectable. The thermogram shown in Fig. 7 was obtained from a high grade talc with a known addition of 1% of a serpentine mineral, thought to be the non-fibrous, platy variety called antigorite. The thermal transitions of this serpentine are indistinguishable from those of chrysotile at this concentration level, as indicated by the characteristic endotherm and exotherm.

In conclusion, the minimum level of detection by this method is 1% by weight of chrysotile asbestos in pharmaceutical grade talc. This is more sensitive than the X-ray diffractometry technique, where even step-scanning procedures show a 2–3% limit of detection for serpentine because of interfering diffraction peaks of the chlorite minerals normally present. The DTA method, using suitable instrumentation and carefully controlled experimental conditions, appears to be reliable and specific for the presence of serpentine mineral. A talc sample showing serpentine in its DTA curve would be subjected to microscopic examination to establish the presence of the fibrous variety.

ACKNOWLEDGMENTS

The author wishes to thank Mrs. Marion Martin and Mr. Roger Bartholomew for their invaluable assistance in performing the experimental work and Mr. Robert Allara for his assistance in preparing the figures.

The author is indebted to the Johns-Manville Corporation for kindly supplying him with the samples of chrysotile asbestos.

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