

## DIFFERENTIAL THERMAL ANALYSIS OF ARTIFICIAL MANGANESE COMPOUNDS

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A previous paper [2] dealt with the examinations of the DTA of natural manganese minerals. The present measurements carried out on artificial manganese compounds, manganese-oxides and carbonates supplement partly the work mentioned above and are also associated closely with the examinations of *Gy. Grasselly* and *E. Klivényi* [1].

*Grasselly* and his co-worker prepared three manganese-oxides the thermal properties of which they studied in detail in addition they also prepared manganese carbonate and a mixture series in which the proportion of the prepared oxides and carbonates varied. The authors mentioned above described in their paper in detail the manner of preparation and the change which the prepared oxides and their mixtures undergo on the action of heat.

Authors also carried out their DTA examinations on the samples prepared by *Grasselly* and *Klivényi*, in this way well defined and chemically thoroughly examined compounds could be studied and our DTA curves supplemented the work of *Grasselly* and co-worker.

The detailed description of the DTA equipment used for the examinations has been already reported elsewhere [3]. The DTA examinations were carried out at a temperature ranging between room temperature and 1000°C. The results of the examinations are shown on the figures.

Fig. 1. shows the DTA curves of the four prepared manganese compounds. The first curve was prepared from  $MnO_2$ . The curve corresponds with that of pyrolusite the only difference being that particularly the first peak illustrating the transformation of  $MnO_2$  to  $Mn_2O_3$  appears in the present case at a temperature about 60—80°C below the one it appears as in the case of natural pyrolusite. This phenomenon which can be frequently observed on comparing DTA curves of artificial and natural substances can obviously be explained by the fact that the size of the granule of the artificially produced compound is more minute than that of the natural mineral. The second peak of  $MnO_2$  indicates the transformation of  $Mn_2O_3$  into  $Mn_3O_4$ .

The second curve of Fig. 1. was prepared of  $Mn_2O_3$ , until 1000°C it only shows a single peak a little below 1000°C at this peak  $Mn_2O_3$  transforms into  $Mn_3O_4$ .

The third curve was prepared from artificial  $Mn_3O_4$ . Until 1000° C the curve does not show any characteristic peak, at the most, only an insig-

nificant endothermic bend between 950—1000° C. This bend may be either due to a small part of the  $Mn_3O_4$  having oxidised during the heating to  $Mn_2O_3$  and that over 950°C this is retransformed into  $Mn_3O_4$ , or it may be the consequence of a transformation  $\alpha \rightarrow \beta$ , a fact which is also referred to in the book of Rode [4].

The fourth curve is the artificial curve of  $MnCO_3$ . The endotherm peak indicating the decomposition of the carbonate and the exotherm peak following it appear earlier than in the curve of the natural  $MnCO_3$  mineral. The small peaks appearing between 900—1000° C are striking they could not be detected on the DTA curves of natural rodochrosite.

The other Figs. illustrate the DTA examinations of mixtures of the four ground substances mentioned above and their investigation purposes the establishment to what extent these compounds may be determined simultaneously and to what an extent they interfere or influence one another.

Fig. 2. shows the DTA curves of the mixtures containing  $MnO_2$ ,  $Mn_2O_3$  and  $Mn_3O_4$  in different proportion. The curves form as anticipated, it should only be remarked that the duplicated broadening of the peaks appearing between 950—1000° C is in agreement with the establishment of *Grasselly* and co-worker that if the size of the granules of  $MnO_2$  and  $Mn_2O_3$  varies they do not transform into  $Mn_3O_4$  at exactly the same temperature.

Fig. 3. illustrates the DTA curves of the  $MnO_2$  and  $MnCO_3$  mixtures. In the case of these curves it is striking that the peak indicating the decomposition of  $MnCO_3$ , particularly in the case of mixture 3, decreases irregularly.

The curves of the mixtures visible on Fig. 4. seem to support the establishments of *Grasselly* and co-worker that if  $Mn_3O_4$  is present together with other manganese-oxides it oxidises into  $Mn_2O_3$  at the stability temperature range of  $Mn_2O_3$  and that the whole  $Mn_2O_3$  only retransforms into  $Mn_3O_4$  at temperatures exceeding 950° C. This statement seems also to be supported by the fact that e. g. the peaks between 950—1000°C appear to be duplicated too, furthermore that if the mixture contains 25 per cent of  $Mn_2O_3$  the peak mentioned is higher than if it would only derive from  $Mn_2O_3$ . However, the question arises why the DTA curve does not indicate the oxidation of  $Mn_3O_4$ ? The blunting of the exothermic peak following the decomposition of  $MnCO_3$  on curve No. 4 of Fig. 4. can be attributed to the reducing effect of  $Mn_2O_3$ . A similar phenomenon can be seen on curves 2 and 3 of Fig. 5. on which the oxidation following the decomposition of the manganese carbonate appears also to be less distinct.

The three last curves of Fig. 5. show the oxide mixtures with three components. In these the duplicated broadening of the second peak appears, its presumable reason has already been referred to.

The investigations lead to the conclusion that with due care carbonate and manganese oxide may be determined simultaneously by means of DTA curves, however, owing to their interaction quantitative determinations based on the DTA peaks may become unreliable.

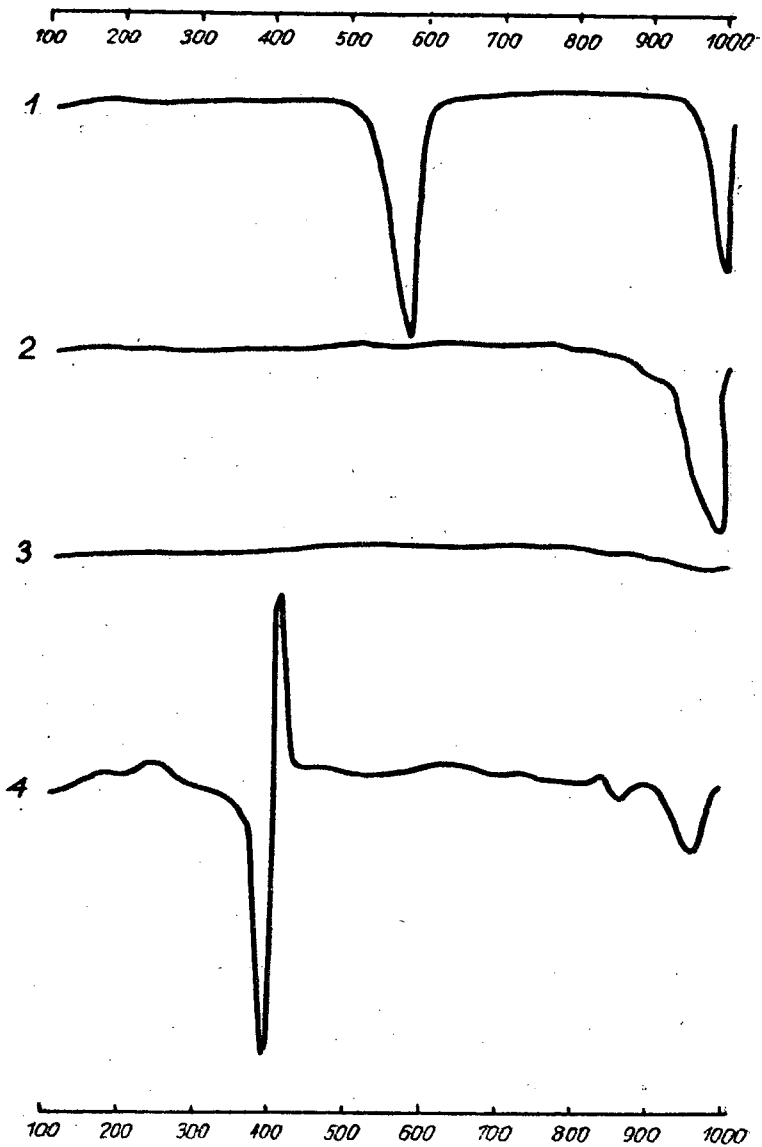


Fig. 1.

DTA curves of artificial manganese oxides and that of manganese carbonate.

1. MnO<sub>2</sub>, 2. Mn<sub>2</sub>O<sub>3</sub>, 3. Mn<sub>3</sub>O<sub>4</sub>, 4. MnCO<sub>3</sub>.



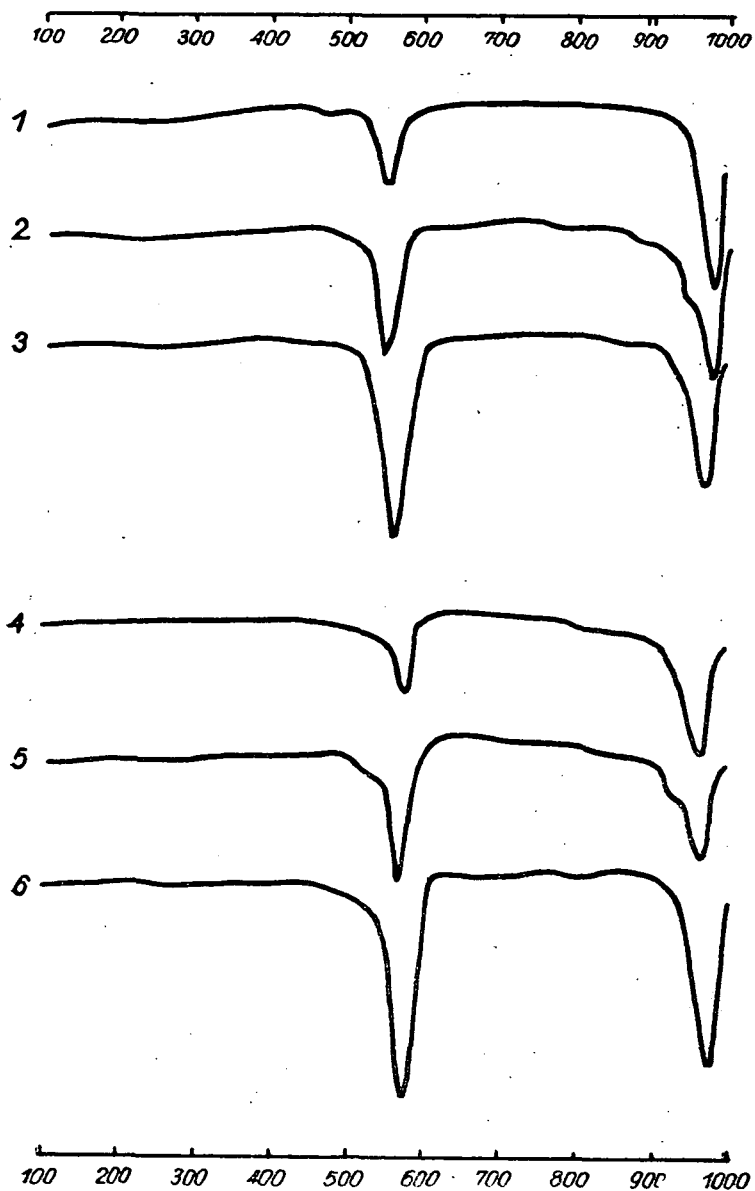


Fig. 2. DTA curves of mixtures of manganese oxides.

1. 25%  $\text{MnO}_2$  + 75%  $\text{Mn}_2\text{O}_3$
2. 50%  $\text{MnO}_2$  + 50%  $\text{Mn}_2\text{O}_3$
3. 75%  $\text{MnO}_2$  + 25%  $\text{Mn}_2\text{O}_3$
4. 25%  $\text{MnO}_2$  + 75%  $\text{Mn}_3\text{O}_4$
5. 50%  $\text{MnO}_2$  + 50%  $\text{Mn}_3\text{O}_4$
6. 75%  $\text{MnO}_2$  + 25%  $\text{Mn}_3\text{O}_4$

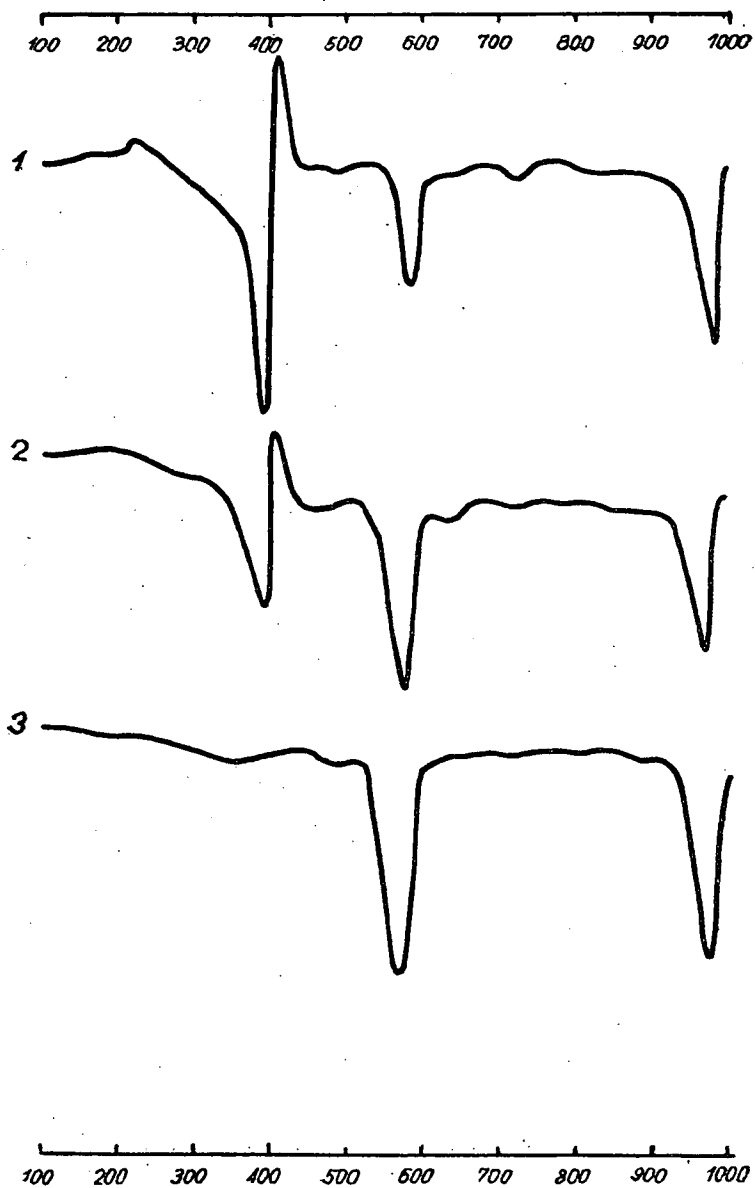


Fig. 3.

DTA curves of mixtures of  $\text{MnO}_2$  and  $\text{MnCO}_3$

1. 25%  $\text{MnO}_2$  + 75%  $\text{MnCO}_3$
2. 50%  $\text{MnO}_2$  + 50%  $\text{MnCO}_3$
3. 75%  $\text{MnO}_2$  + 25%  $\text{MnCO}_3$

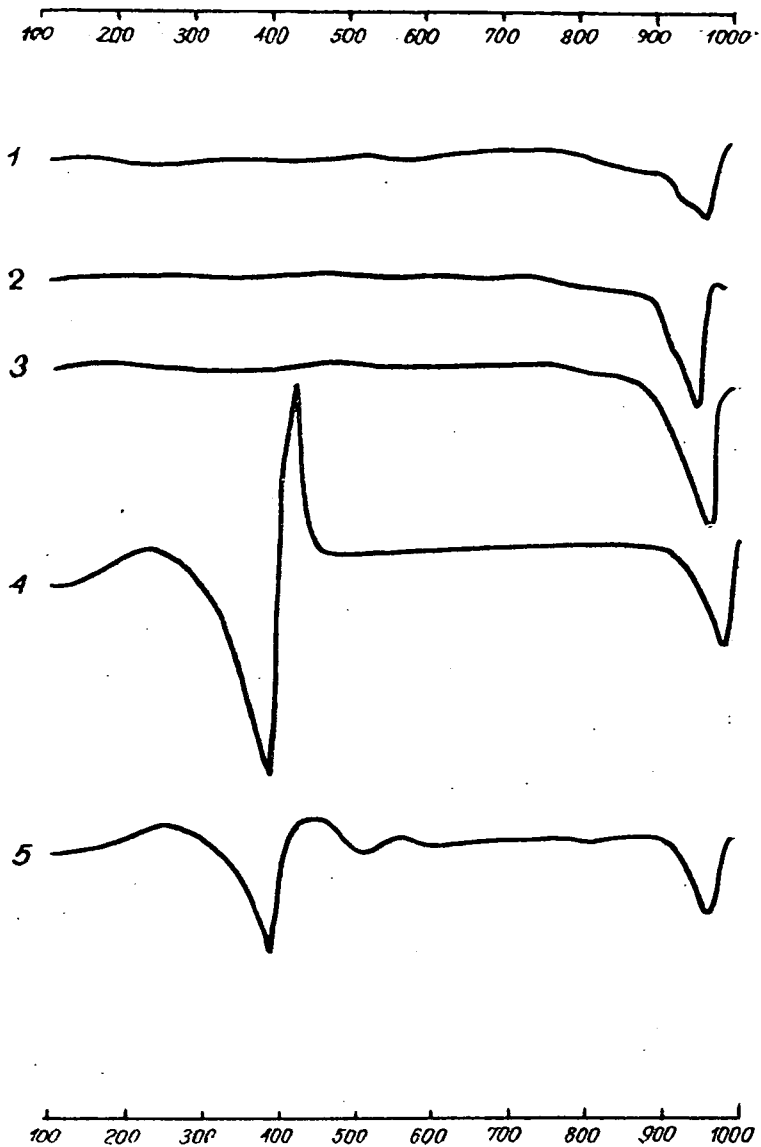


Fig. 4. DTA curves of mixtures of manganese oxides and carbonate, respectively.

1. 25%  $Mn_2O_3$  + 75%  $Mn_3O_4$
2. 50%  $Mn_2O_3$  + 50%  $Mn_3O_4$
3. 75%  $Mn_2O_3$  + 25%  $Mn_3O_4$
4. 25%  $Mn_2O_3$  + 75%  $MnCO_3$
5. 50%  $Mn_2O_3$  + 50%  $MnCO_3$

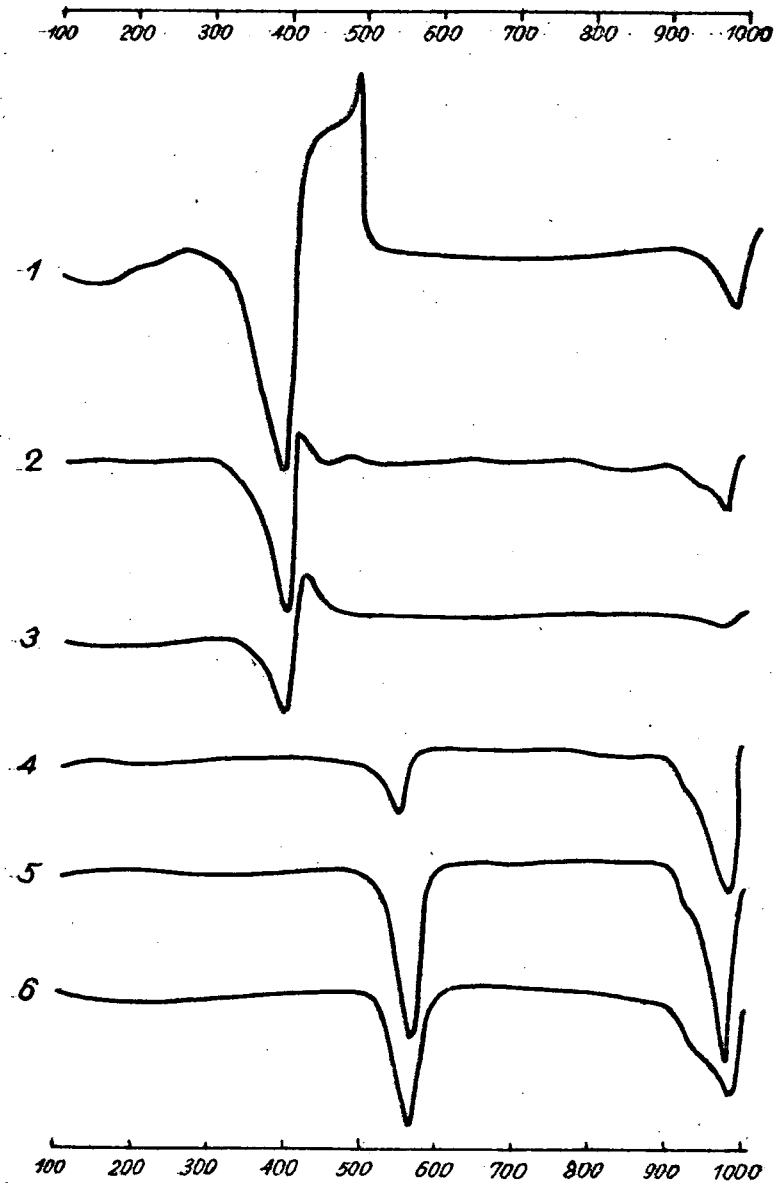


Fig. 5. DTA curves of mixtures of manganese oxides and carbonate, respectively.

1. 25%  $Mn_3O_4$  + 75%  $MnCO_3$
2. 50%  $Mn_3O_4$  + 50%  $MnCO_3$
3. 75%  $Mn_3O_4$  + 25%  $MnCO_3$
4. 20%  $MnO_2$  + 30%  $Mn_2O_3$  + 50%  $Mn_3O_4$
5. 50%  $MnO_2$  + 30%  $Mn_2O_3$  + 20%  $Mn_3O_4$
6. 40%  $MnO_2$  + 20%  $Mn_2O_3$  + 40%  $Mn_3O_4$

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