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# DIFFERENTIAL THERMAL ANALYSIS FOR ESTIMATION OF THE THERMAL STABILITY OF NPK FERTILIZERS

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The thermal decomposition of NPK fertilizers was studied by thermal analysis under dynamic and quasi-isothermal-quasi-isobaric conditions in open and labyrinth crucibles.

It was found that under quasi-equilibrium conditions, the thermal analysis reveals mainly decomposition processes. The thermal stability of NPK fertilizers is characterized by the temperature of beginning of the spontaneous exothermic decomposition, at 180–190°.

Under certain conditions (local heating, high environmental temperature, closed storage rooms with insufficient heat exchange, etc.), complex mineral fertilizers containing ammonium nitrate are capable of decomposing spontaneously with evolution of exothermic heat [1]. In a closed system, this leads to overheating of the whole mass of the substance and the decomposition reaction accelerates. As a result, a thermal explosion may occur and the products of the reaction ($N_2O$, $N_2$, $NO_2$, $H_2O$, $Cl_2$ $NH_4Cl$, etc.) escape into the gaseous phase [2]. Decomposition of the fertilizer takes place only when the temperature of the system is higher than a certain value for particular conditions.

For quantitative estimation of the thermal stability of fertilizers, a critical parameter of the process (the temperature of the beginning of exothermic decomposition) may be determined by thermal analysis [3]. The use of quasistatic thermogravimetric techniques leads to a decrease of the distortions caused by the uncontrolled pressure of the gases formed and the continually rising temperature [4].

In this work, we study the use of thermal analysis methods for determination of the critical temperatures of exothermic decomposition of NPK fertilizers.

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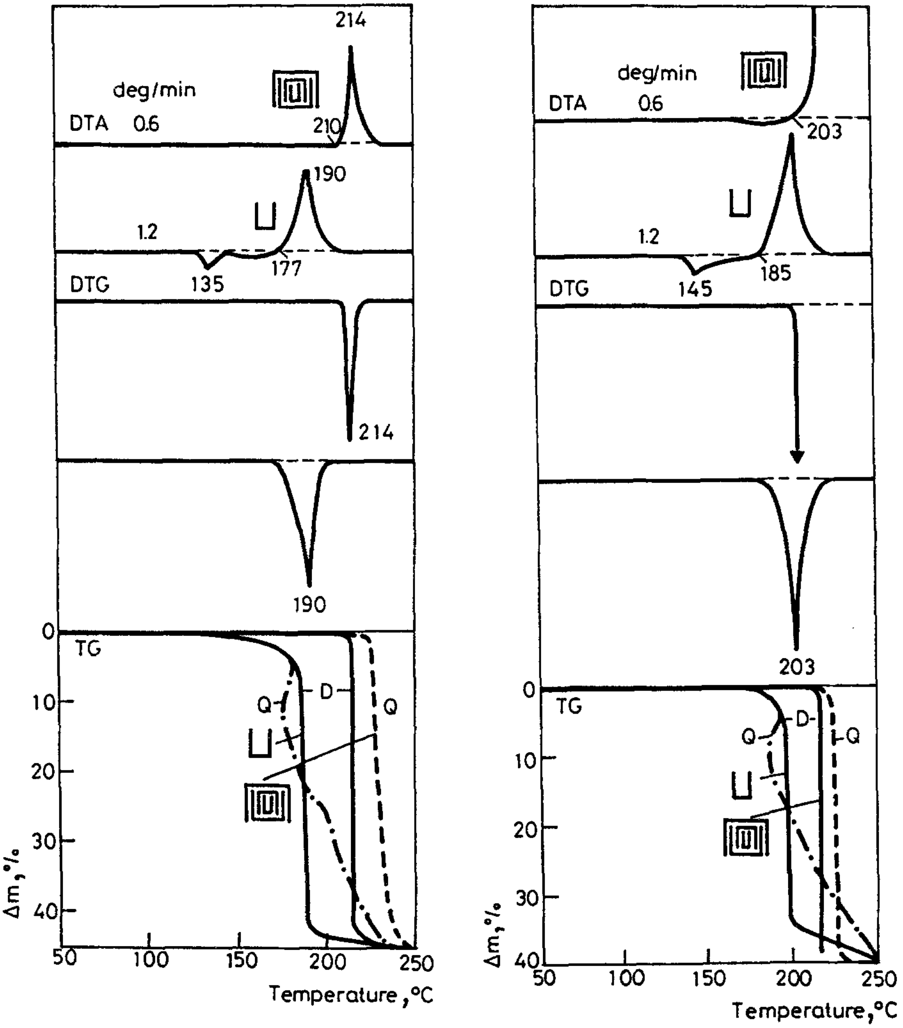
## Experimental

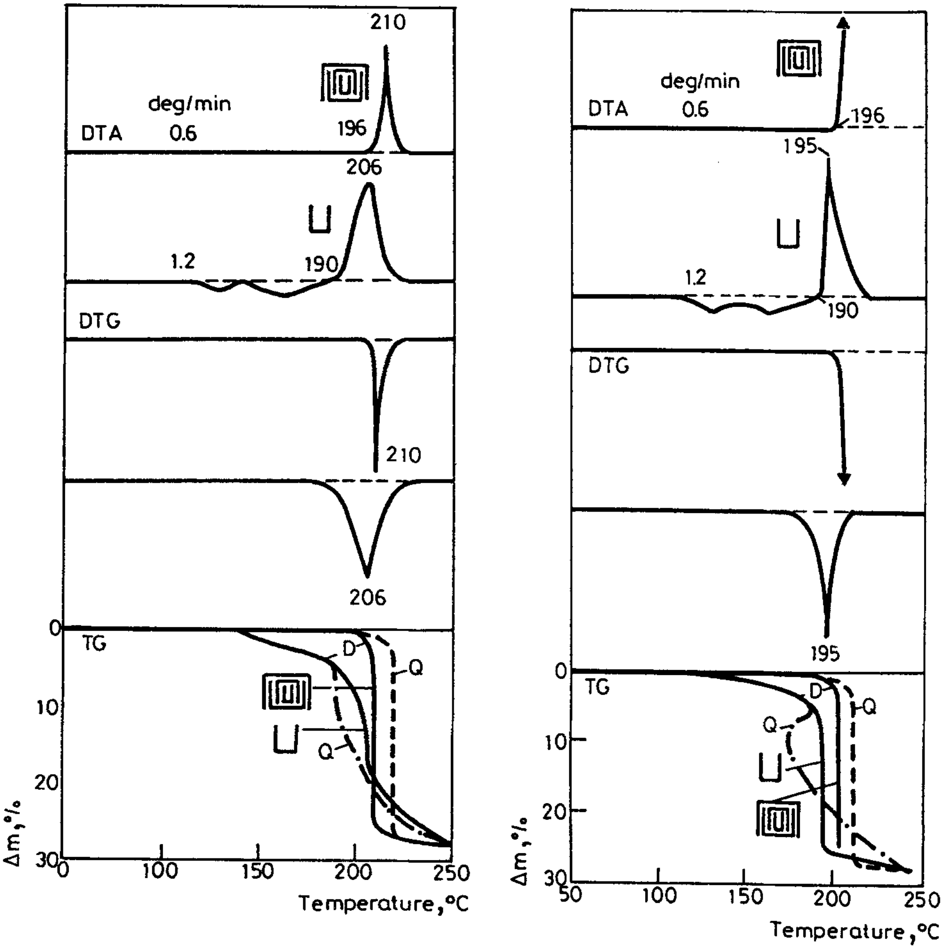
Dynamic (DTA-DTG-TG) and quasi-isothermal-quasi-isobaric (Q-TG) heating conditions were applied using a Q-derivatograph (MOM, Budapest) in stationary air. The heating rate was 0.6 or 1.2 deg/min and the rate of mass loss in the quasi-equilibrium state was 0.5 mg/min. The gas-exchange



**Figs 1/1, 1/2** Decomposition of NPK-fertilizers in open and in labyrinth crucibles. Heating: dynamic (D – 0.6 and 1.2 deg/min) and quasi-isothermal (Q). Sample mass about 200 mg. The composition of samples look at the table.

conditions in the system were modified by means of different sample holders: an open crucible (with a partial pressure of gases of 5 kPa) and a labyrinth crucible (with a partial pressure of reaction products of 100 kPa [4]). The sample mass varied from 100 to 500 mg.

The samples of NPK fertilizers were prepared in the laboratory by mixing different amounts of the initial components (industrial products) superphosphate, ammonium nitrate and sodium chloride. Some samples were made with the addition of microelements. The chemical compositions of the samples studied and the main thermal analysis data under the investigated



**Figs 1/3, 1/4** Decomposition of NPK-fertilizers in open and in labyrinth crucibles. Heating: dynamic (D – 0.6 and 1.2 deg/min) and quasi-isothermal (Q). Sample mass about 200 mg. The composition of samples look at the table.

conditions are shown in the Table and in Figs 1/1–1/4. As a criterion of the thermal stability, the critical temperature of the beginning of exothermic decomposition was used. For comparison, thermal curves of the original components (ammonium nitrate and superphosphate) are shown in Figs 2 and 3.

## Results and discussion

The thermoanalytical results in Fig. 1 show that under dynamic heating the courses of the decomposition of NPK fertilizers differ only in the temperature of the beginning of exothermic decomposition (5–15 deg) in the

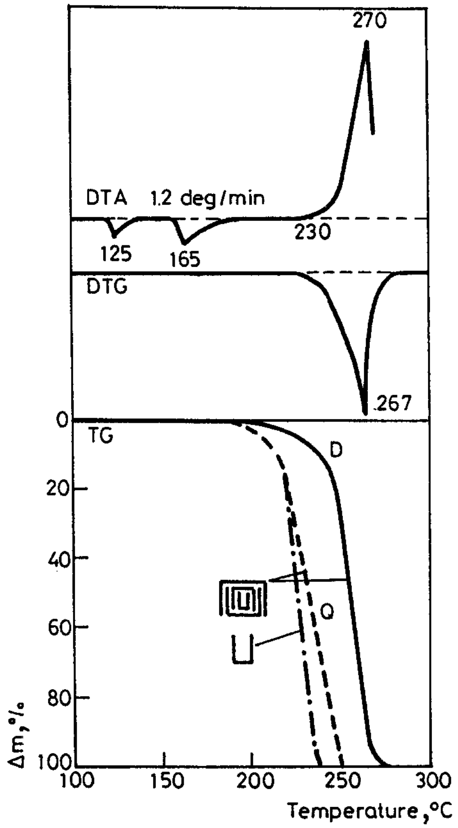


Fig. 2 Decomposition of $NH_4NO_3$ in open and in labyrinth crucibles. Heating: dynamic (D-1.2 deg/min) and quasi-isothermal (Q)

Table 1 Characteristics of samples

| No. | Chemical composition, % | | | | | | | | | Type of fertilizer, N:P:K | Heating conditions | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Dynamic | | | | Quasi-equilibrium | | | |
| | | | | | | | | | | | Crucible | | | | | | | |
| | $P_2O_5$ | N | $K_2O$ | $H_2O$ | B | Cu | Mo | Co | Mn | | Open | | Labyrinth | | Open | | Labyrinth | |
| | | | | | | | | | | | $T_c$ | $\Delta m$ | $T_c$ | $\Delta m$ | $T_c$ | $\Delta m$ | $T_c$ | $\Delta m$ |
| 1 | 7.9 | 15.3 | 16.6 | 0.4 | - | - | - | - | - | 1:0.5:0.9 | 177 | 2.5 | 210 | 1.8 | 183 | 3.9 | 225 | 1.2 |
| 2 | 7.7 | 15.4 | 16.2 | 0.8 | 0.03 | - | 0.015 | 0.01 | - | 1:0.5:0.9 | 185 | 1.0 | 203 | 0.8 | 185 | 1.9 | 220 | 2.6 |
| 3 | 11.7 | 8.5 | 17.0 | 0.4 | - | - | - | - | - | 1:1.5:2.0 | 190 | 5.1 | 203 | 2.5 | 190 | 4.5 | 220 | 2.0 |
| 4 | 11.6 | 8.6 | 14.5 | 0.5 | 0.03 | 0.2 | - | - | 0.15 | 1:1.5:2.0 | 190 | 5.3 | 197 | 0.8 | 187 | 4.8 | 212 | 3.1 |

$T_c$ – critical temperature, °C

$\Delta m$ – mass loss established at the moment of the beginning of exothermal effect, %

different crucibles. In comparison with $NH_4NO_3$ (Fig. 2), the process is particularly affected by volatile chlorine components, known to be catalysts of the exothermic decomposition of $NH_4NO_3$ [5]. In the closed system (in the labyrinth crucible), gaseous reaction products block the active centres and retard the reaction, thereby increasing the critical temperature. In NPK fertilizers, the higher total nitrogen content decreases the thermal stability to some extent (see Table).

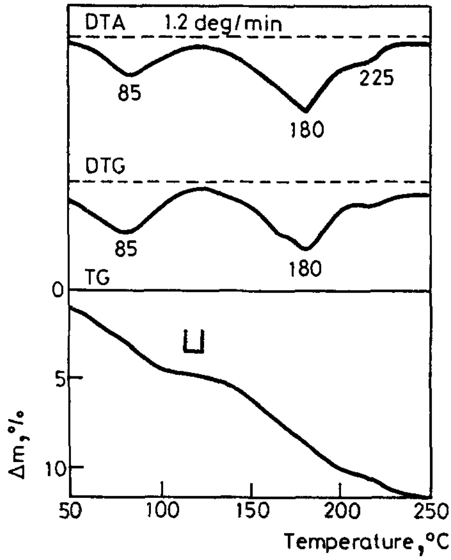


**Fig. 3** Decomposition of superphosphate in open crucible. Heating rate 1.2 deg/min

The thermoanalytical curves registered under quasi-equilibrium conditions have a more complicated character, due to the simultaneous occurrence of several reactions, which are almost irreversible. The course of the decomposition process depends on the pressure of the gaseous reaction products (see the curves for the different crucibles). The indication of overheating regions in some Q-TG curves demonstrates the possible existence of an induction period for the decomposition processes. The partial deviation of the process from isothermal conditions can be explained by a crust forming on the surface of the particles, so that mass transfer is hindered.

When labyrinth crucibles were used, the decomposition process went out of control after the critical temperature was reached and all the NPK fertilizer samples decomposed with an explosion. In open crucibles, a thermal explosion occurred during the analysis only under dynamic heating conditions.

It was established that the exothermic peaks in the thermoanalytical curves, and also the critical temperature, depend on the mass of the sample (Fig. 4). For a relatively small sample mass, the increase in temperature as a result of exothermic heat is insignificant and the reaction products cause practically no acceleration of the reaction of self-decomposition. When the mass of the sample is increased, the critical temperature of the beginning of exothermic decomposition decreases. The temperature difference was 10–15 deg when the sample mass was varied from 100 to 500 mg.

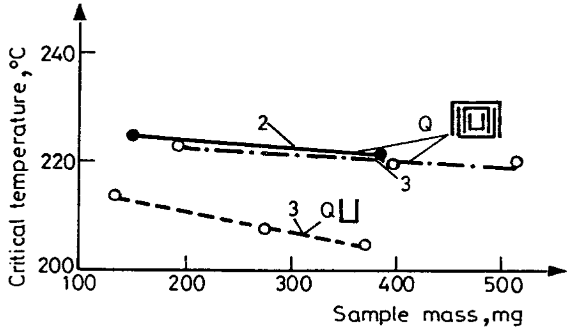


**Fig. 4** The critical temperature of exothermic decomposition as a function of the mass of the sample. Heating: quasi-isothermal in open and labyrinth crucible. Probes nr. 2 and 3

The effects of certain microelements, (B, Cu, Mo and Mn) in the studied amounts on the decomposition of NPK fertilizers and on their critical temperatures were negligible.

It was found that, at the beginning of spontaneous decomposition, the critical temperature was 180–190° for NPK fertilizers, i.e. 40–50 deg lower than for $NH_4NO_3$.

## Conclusions

The thermal stability of NPK fertilizers can be characterized by their critical temperature at the beginning of their spontaneous exothermic decomposition, identified by means of thermal analysis.

The dependence of the thermal decomposition reaction on the heating conditions (open or labyrinth crucibles as sample holders) was established.

The difference results from the effect of the escaping gaseous products on the nature and rate of the decomposition process.

Thermal analysis under quasi-equilibrium conditions reveals mainly decomposition processes, occurring due to exothermic reactions and self-heating of the samples.

## References

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**Zusammenfassung** — Mittels Thermoanalyse unter dynamischen und quasi-isothermen-quasi-isobaren Bedingungen in offenen und Labyrinthtiegeln wurde die thermische Zersetzung von NPK-Düngern untersucht.

Man fand, daß die wichtigsten Zersetzungsprozesse durch die Thermoanalyse unter quasi-Gleichgewichtsbedingungen charakterisiert werden. Die thermische Stabilität von NPK-Düngern wird durch die Temperatur gekennzeichnet, bei der eine spontane exotherme Zersetzung einsetzt (180–190°C).