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C.N.TURCANU, M.CORNESCU

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THERMAL ANALYSIS OF IRON

HYDROXIDE MICROSPHERES

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Abstract :

The thermal treatment is an important step in the preparative technology of the iron oxide microspheres with well established mechanical, physical and chemical characteristics. The first indications on the heating procedure have been obtained from the thermal analysis on iron hydroxide microspheres prepared by the support precipitation and internal gelification methods.

1. INTRODUCTION

The iron hydroxide obtained by precipitation of iron soluble salts and represented as $\text{Fe}(\text{OH})_3$, is a nonunitary product, with a variable composition depending on the reactants and the precipitation method.

Generally this is considered to be a hydrated oxide like $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$; OH groups were put in evidence only for some minerals and corrosion products. The iron hydroxide loses the water during the heating and is converted to Fe_2O_3 . The temperature for the complete conversion may characterize the powder, and is depending on the colloidal character of the hydroxide, which is a result of many precipitation parameters.

The iron oxide together with other oxides or transition metal is a component of the catalysts used in chemical and petrochemical industry. A better contact between the reactants and catalysts is obtained with oxide microspheres, optimally used for a fluidised bed technological process.

The preparation of high density metallic oxide microspheres by support precipitation (SNAM), internal gelification (KEMA) and sol-gel method, is used in the nuclear field, to obtain fuel elements. The methods were extended in non-nuclear areas in order to obtain some materials as spinels, ferrites and rare earth oxides (1) having a high density ($>95\%$ from theoretical density, at a lower sintering temperature) and small grain dimensions ($<1\mu\text{m}$). Such characteristics hard to obtained by the conventional methods, determine the large utilisation of these products as microspheres in the areas of the refractory ceramics and of the ceramics with special magnetical and electrical properties. For different nuclear purposes, anorganic ion exchangers were prepared, starting from the aged metallic hydroxides microspheres. These types of ion exchangers present a high irradiation resistance, and can not be replaced by the organic resins.

Besides technology of microsphere preparation, the thermal treatment is very important for acquiring the desired characteristics.

This study was performed for the characterisation by thermal analysis of the microspheres and thus to obtain the informations necessary for the their thermal treatment.

2. EXPERIMENTAL

The support precipitation (SP) method consists of the precipitation of iron hydroxide on an organic support in a concentrated ammonium hydroxide solution. The block diagram of the method is shown

in Fig. 1. A mixture of iron chloride (molar ratio $Cl/Fe < 3$) and support which is an organic macromolecular compound (polyvinyl alcohol, alchil - cellulose etc.) are used. This mixture is dropped in concentrated ammonia with a special device. The rol of the support is to form a perfect spherical matrix in contact with ammonia. Inside the matrix occurs the precipitation reaction of iron hydroxide. The crude microspheres are kept in ammonia for complete precipitations. After washing with water to remove the ammonium chloride and ammonia, the microspheres are dried at $100-120^{\circ}C$.

The thermal treatment is performed in such a way, to obtain the desired final product Fe_2O_3 , Fe_3O_4 or Fe.

By this method iron hydroxide microspheres were obtained using the folloing composition of mixture: 1 M Fe^{3+} with molar ratio $Cl/Fe = 1,8-2, 3, 5-4$ % polyvinyl alcohol.

Iron hydroxide microspheres with a good sphericity and various diameters were realised, Fig. 2, depending on dispersion device parameters (capillary diameter, air flow). The mixture drops were quickly consolidated in contract with ammonia, the precipitation occurring also during the ageing step. The washing with water (three times/15min) removed the most of the ammonia and ammonium chloride, preventing the cracking of microspheres during the thermal treatment.

After drying, the microspherrea were heated for total elimination of water, ammonia, ammonium chloride and support obtaining Fe_2O_3 microspherrea as a final product.

Hydroxide microspherrea were prepared also by the internal gelifications (IG) method, used to obtain ADU microspheres (3). The thermal analysis has been performed using a 10" Derivatograph in a way described previously (4). The samples consisted of single microsphere layers placed in the multiplate sample holder. For the separation of the diffusion effects during the decompositions process, samples consisting of milled microspheres were also analysed.

3. RESULTS AND DISCUSSION

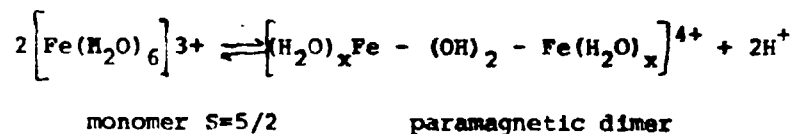
The derivatogram of aged iron hydroxide prepared by precipitation from iron chloride with ammonia, Fig.3, shows that about 90% of water is lost by endothermic process with the minimum close to $130^{\circ}C$. After the loss of an other 5-8%, the hydroxide, initially amorphous, or with a poor crystal-limity chains, shows a structural rearrangement with an exothermal effect (5). The last traces of water are lost towards $700^{\circ}C$. This behaviour coincides within the limits of the instrumentation performances and experimental errors with the published data for iron hydroxide prepared by

precipitation with gaseous ammonia, with ammonia and ethyl alcohol, in the presence of hydrazine or pyridine (6). IR spectra of those oxide are free of water stretching vibrations, but the crystalline lattice shows a variable concentrations of defects for the smaller temperatures.

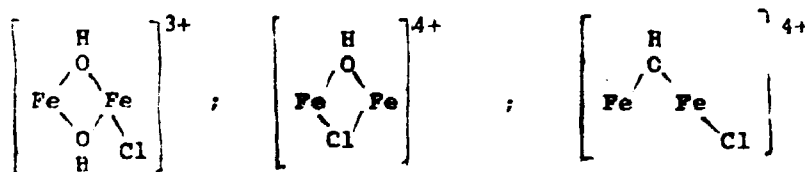
Mössbauer studies have shown that the defects disappear by heating at higher temperatures (above 600°C) when a Fe₂O₃ normal crystalline lattice is obtained (7).

The difference between the iron hydroxide species can be evidenced on the basis of the hyperfine Mössbauer spectra structure recorded at very low temperatures.

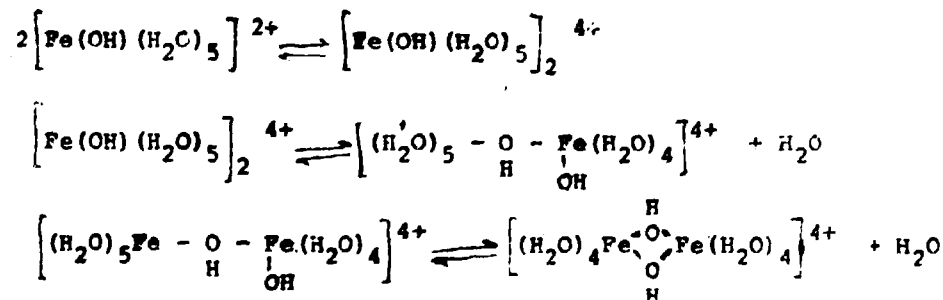
The ferric ion hydrolysis is still an open problem. A diol dimer [Fe(OH)₂]⁴⁺ was presumed to be formed as an initially primary hydrolytical product, by the potentiometric studies. The magnetic measurements data of the hydrolysed iron salts show a decreasing of the magnetic moment, explained by the mechanism (8)



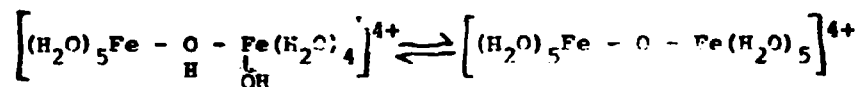
As intermediary steps the formation of some metastable species (experimentally not detected) was postulated (9):



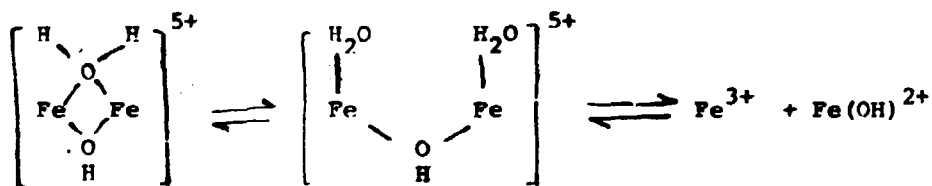
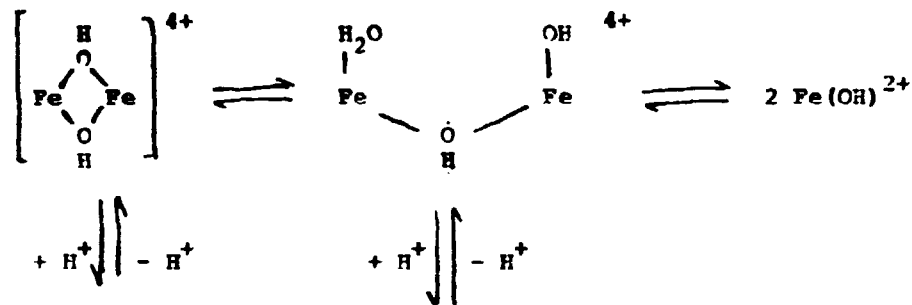
Between the dimer and monomer species the following equilibrium exists (9 - 11):



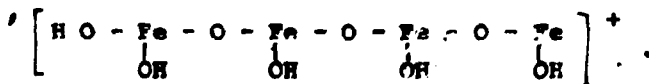
Alternately instead diol-, oxo-complexes can be formed:



Another way for the dimer dissociation occurs by hydrogen ion depending equilibria.



In weak acid solutions at higher concentrations of ferricions, the existence of tri- and tetrapolymers is presumed, in linear or cyclic forms (9):



The smaller magnetic susceptibility values are explained by the

formation of polymer chains from dihydroxadimers, bounded by oxo-bridges and keeping the diol structure. The hydrolytical polymerisation which begins with the dimer formation continues during the hydroxide precipitation, but the polymerisation mechanism and the composition of intermediaries remain unknown.

Diffusion, ultracentrifugation and dialysis experiments (12) show the formation of the polinuclear and polydisperse iron hydroxo complexes which contain always small molecular weight fractions. The increasing of the polymerisation degree and the precipitation are two independent processes that may occur in the same time or not.

For the high molecular weight polymers, the analytical results suggest a polymerisation as $\left[\text{Fe}(\text{OH})_x^{(3-x)+} \right]_n$ formed by ferric ions chains bounded by two hydroxi bridges. Electron microscopy results show discrete spheres not bound as in the case of iron hydroxide gels.

A tridimensional structure of twisted chains bounded by hydroxi groups can be presumed, these groups being in excess beside the diol bridges.

Such a structure respects the normal octahedral configuration of iron and does not impose restrictions to diol or oxo bridges which may be linear or not.

The dried precipitates normally obtained from concentrated solutions can be described as an oxide - hydroxide lattice where the iron is placed in octahedral and tetrahedral sites.

The relationship among the structures is revealed by studying the interconversions they undergo, using thermal analysis, electron microscopy, X-ray diffraction, IR and Mössbauer spectroscopy (13 - 16). The variations in TG and DTA behaviour are explained by the presence of variable concentrations of chain ends and defects in the lattice. The excess water associated with chain ends in the most defective sample indicated an average chain length of only five POOH units (13). Obviously, in the case of fast precipitation from a concentrated solution the number of defects (including chain ends, excess water, precipitating agent, initial anion, etc.) will be very large. The same phenomena will be found in the metal hydroxide microspheres precipitation. For these reasons, a single particle might contain regions which are similar to different oxide or hydroxide phases. By the combination of the analytical techniques, it will be shown that the initial amorphous gel obtained by precipitation from concentrated solutions is metastable and by ageing is transformed in poor crystalline products.

When the iron hydroxide microspheres are prepared by the support precipitations method the precipitate includes both the organic support and anorganic foreign ions. The thermal behaviour of the microspheres is very complicated by the presence of a large number of compounds with different thermal properties. The separation of the individual reactions on the DTG, DTA and TG curves remain approximate as a result of thermal decomposition process superposition, and of secondary effects given by diffusion and experimental conditions, Fig. 4-6. For a heating rate of $2.6^{\circ}\text{C}/\text{min}$, the TG curve shows four decomposition steps, while the DTG curve shows five, well enough separated. The DTA curve is poor structured, thermal effects being overlapped. Up to 130°C part of the water is eliminated (4%). Between 130 and 225°C , 13% from the weight are lost linearly on the TG curve, but the DTG curve present two steps in the range of $130-180^{\circ}\text{C}$ and respectively $180-225^{\circ}\text{C}$. The next 18% are eliminated in three steps at $225-255^{\circ}\text{C}$ (4%), $255-340^{\circ}\text{C}$ (10%) and respectively $340-400^{\circ}\text{C}$ (4%). Thermal decomposition practically ends at 400°C , the resulting non-volatile product being 65% from the initial amount. At higher heating rate ($5^{\circ}\text{C}/\text{min}$), Fig. 5, the DTG curve shows six elimination steps; the thermal effects resulting from the DTA curve are exothermic, with the exception of the first step which is endothermic. The increase of the heating rate leads to a better separation of the processes, but in the same time to a displacement at higher temperatures. The final non-volatile product (65%) is obtained at 500°C , the last exothermic peak occurring at 450°C . The derivatoram of the iron hydroxide microspheres at $19,8^{\circ}\text{C}/\text{min}$ (the highest permitted heating rate with MCM Derivatograph), Fig. 6, shows only five decomposition steps in the TG and DTG curves. For the DTA curve a minimum of the exothermic effect appears at 410°C .

An important difference beside the smaller heating rate is related to the final amount (only 64%). This diminution can be correlated with the reduction of the trivalent iron to divalent or metallic iron.

The reducing character of the organic fragments generated during the thermal decomposition in the reactions between fragments and solid matrix was evidenced for iron complexes with 8-hydroxyquinolin, by thermal analysis (5) and by Mössbauer effect studies on the non-volatile residual product (17,18). The microsphere can be considered a nearly closed system, where the thermal decomposition of the components included in the iron hydroxide matrix, occurs in a

poor oxygen atmosphere.

The diffusion of oxygen from the furnace atmosphere is delayed by the solid wall of the microsphere and by the over pressure of the gaseous fragments generated inside. Equilibria which are established between the decomposition fragments and the solid matrix, displaced the decomposition intervals to higher temperatures. These equilibria are displaced to the gaseous products generation as a function of the outwards diffusion of the fragments and their oxidation with the atmospheric oxygen, or in the case of the strong reducing fragments, with the oxygen from the iron oxo-hydroxide matrix. The gaseous fragments generated inside the particle, during the outwards diffusion, can reestablish the decomposition equilibria, thus enlarging the temperature range where the process occurs. The decomposition is not uniform because the composition, density, and porosity nonhomogeneity, which leads to a nonuniform temperature in different points of the microsphere. The temperature differences can reach 50-100°C, in the higher temperature points other reactions being initiated, in contrast with the normal process induced by the furnace temperature. The overlapping of the reactions on the thermal curves is explained by the influence of all these factors which are depending by the particular state of the thermal sample as a microsphere.

A more exact evaluation of the decomposition processes is possible on the milled microspheres samples, Fig. 7-10. The shape of the TG, DTA and DTG curves allow a better separation of the thermal reactions.

The final temperature when the amount of this non-volatile product remains constant (the sample is totally converted in Fe_2O_3), for the heating rate of 4.9°C/min is 400°C, nearly 100°C less than for the normal microsphere derivatogram. The water elimination with endothermic effect, occurs up to 150-180°C, followed by a strong exothermic process associated with a rapid loss of weight. The peak of this process on the DTG curve is at nearly 180°C, independently of the heating rate used. Exothermic character of the reaction leads to an increase of the temperature on the T-curve with nearly 50°C, which corresponds to a violent decomposition. The next processes have smaller exothermic effects.

All the thermal curves of the milled microspheres samples show a diminution or overlapping of the exothermic effects which characterize the rearrangement of the Fe - O - Fe bridges in iron hydroxide after the water elimination, Fig. 4-10.

The derivatograms of the iron hydroxide microspheres prepared by internal gelification (IG) show a better marked endothermic character on the DTA curve, compared to derivatograms of the microspheres prepared by support precipitation. The difference of the thermal effects during the heating is given by the specific thermal behaviour of the compounds enclosed in the hydroxide matrix. For a heating rate of 5°C/min, the TG curve shows that 20% from the initial amount is lost, associated with a minimum at 120°C on the DTG and DTA curves. At 200°C the DTA curve shows an inflexion (present also on the DTG curve) which does not change the character of the process. Small exothermic peaks appear on the DTA curve at 250 and 360°C, one of them (probably the peak from 360°C) belonging presumably to the Fe - O - Fe bridges rearrangement.

The behaviour of microspheres in this temperature interval, is very similar to the derivatogram of aged iron hydroxide (Fig. 3). At higher temperature, the TG curve presents a pseudolinear decrease of the sample weight, with a small endothermic effect at 480°C, followed by a small exothermic peak at 800-820°C, given probably by the physical transformations. The final amount of the non-volatile product corresponds to 74% from the initial amount of the sample.

The DTA curve at the heating rate of 10°C/min is poorly structured: more evident is the endothermic peak at 150°C with a corresponding peak on the DTG curve at 130°C. The DTG curve shows a minimum at 240°C, better separated than for the heating rate of 5°C/min. On the DTA curve the exothermic peaks are present at 300 and 380°C.

The derivatogram of milled microspheres prepared by internal gelification method shows (Fig. 13) the similar shape for the TG and DTG curves, with a better separation of the reactions because of the easier diffusion of volatile decomposition products. A larger difference shows the DTA curve, where the exothermic peak from 230°C is very strong and very well correlated with the DTG curve peak at 240-250°C.

After the thermal analysis data of the microspheres, the first thermal treatment at 450°C leads to Fe₂O₃ microspheres with a good sphericity and free of cracks. The microscopic aspect of a section shows the beginning of the sintering process. The sintering was more advanced for the microspheres heated at 950°C. The thermal treatment up to 1200°C, leads to Fe₃O₄ microspheres.

A detailed study of the thermal treatment correlated with other physico-chemical analysis, X-ray diffraction and Mössbauer spectroscopy will permit to obtain microspheres for different purposes.

3. CONCLUSIONS

- The support precipitation and internal gelification methods are suitable to obtain iron hydroxide and iron oxides microspheres.

- The thermal analysis of the iron hydroxide microspheres shows that during precipitation, big quantities of foreign compounds are enclosed from reaction system.

- All decomposition reactions are exothermic, with the exception of water elimination. The exothermic effects are stronger for the microspheres prepared by the support precipitation method.

- Up to 500°C nearly all the thermal unstable compounds are eliminated, the last traces of carbon are lost between 700 and 750°C.

- The thermal treatment of hydroxide microspheres must have a small heating rate up to the temperature when the majority of volatile products are eliminated. The microspheres obtained in this way are free of cracks.

These two preparation methods will be used to obtain microspheres of different metal (or mixtures) hydroxides and oxides which are of interest in nuclear or non-nuclear fields.

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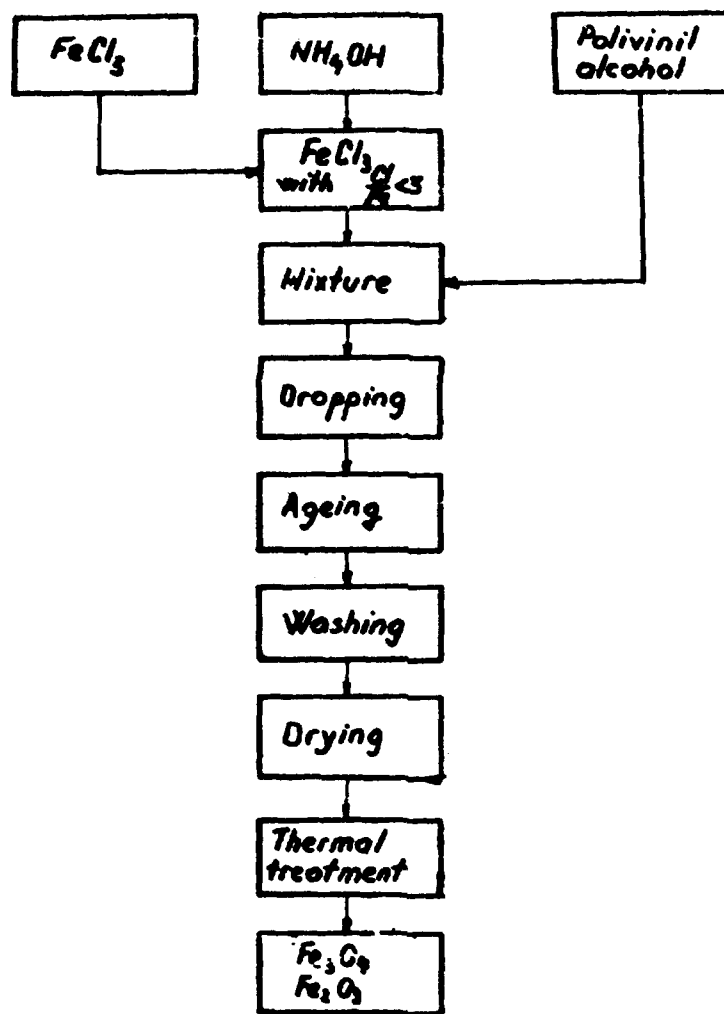


Fig. 1 Flowsheet for iron oxide-sphere preparation.

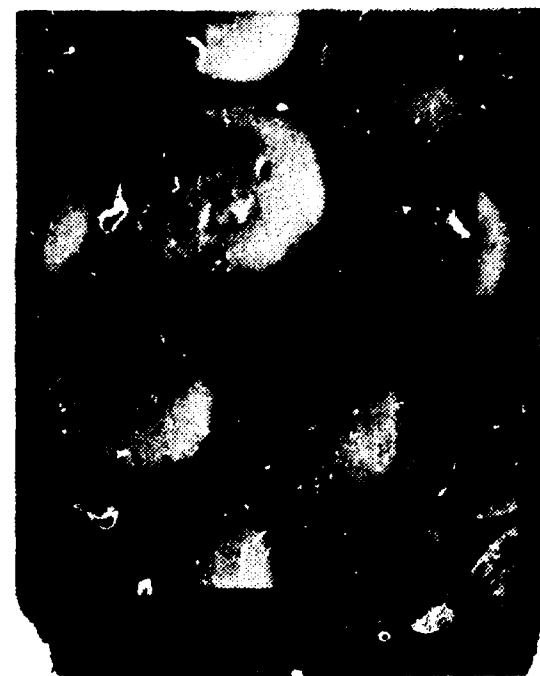


Fig. 2. $Fe(OH)_3$ microspheres (x60)

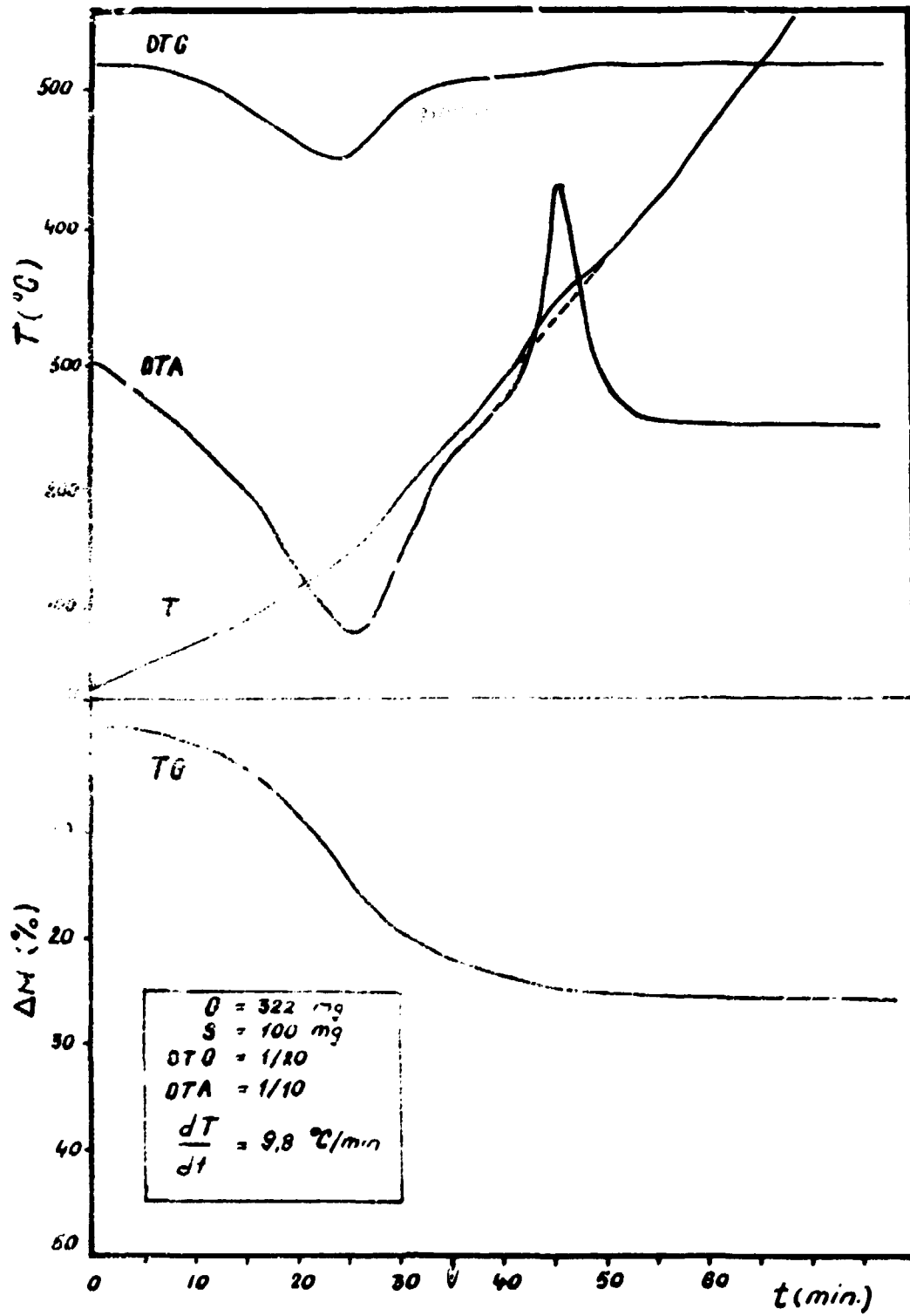


Fig. Derivatogram of $\text{Fe}(\text{OH})_3$.

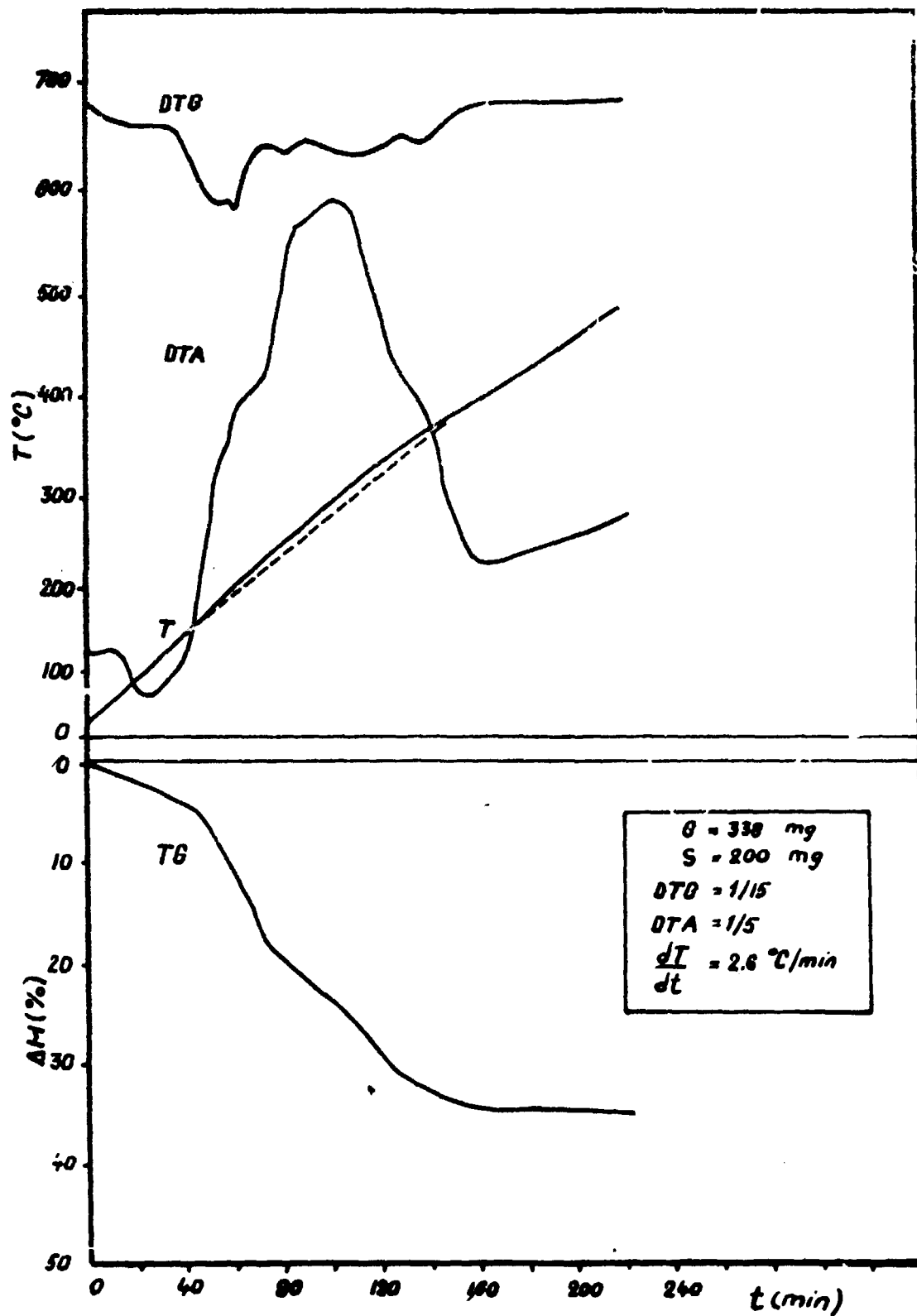


Fig. 4 Derivatogram of $\text{Fe}(\text{OH})_3$ microspheres.

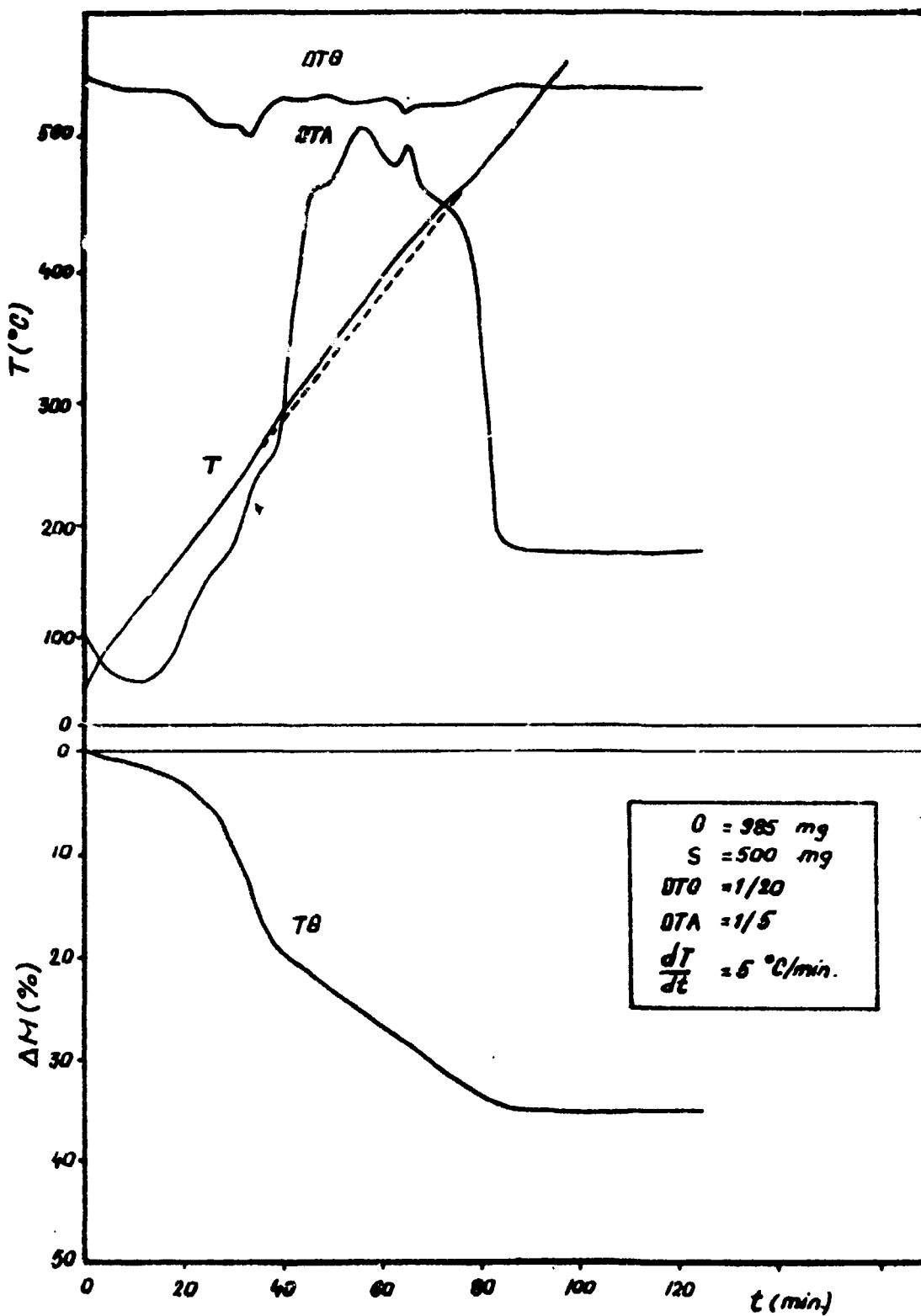


Fig.5 Derivatogram of $\text{Fe}(\text{OH})_3$ microspheres.

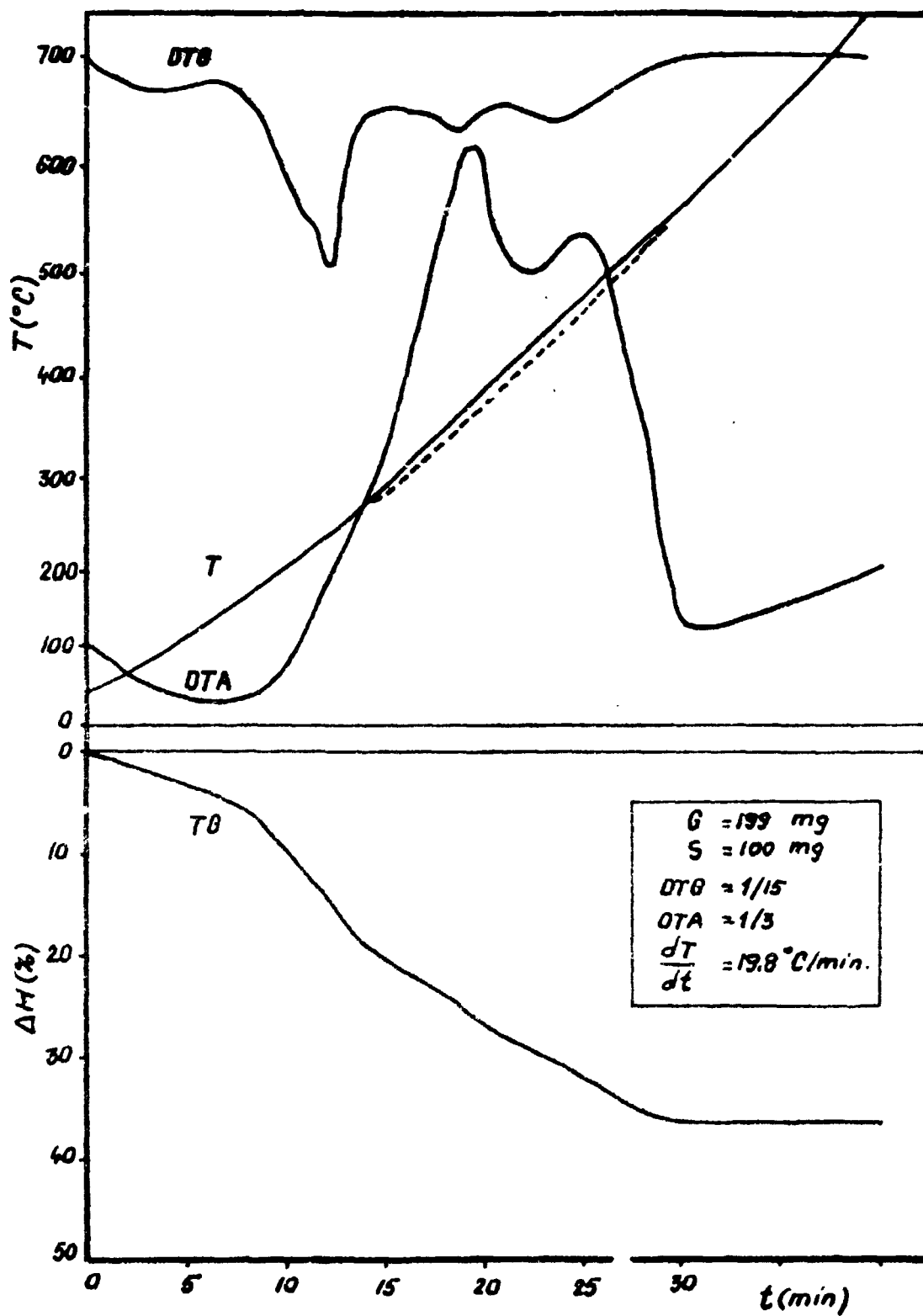


Fig. 8 Derivatogram of $\text{Fe}(\text{OH})_3$ microspheres.

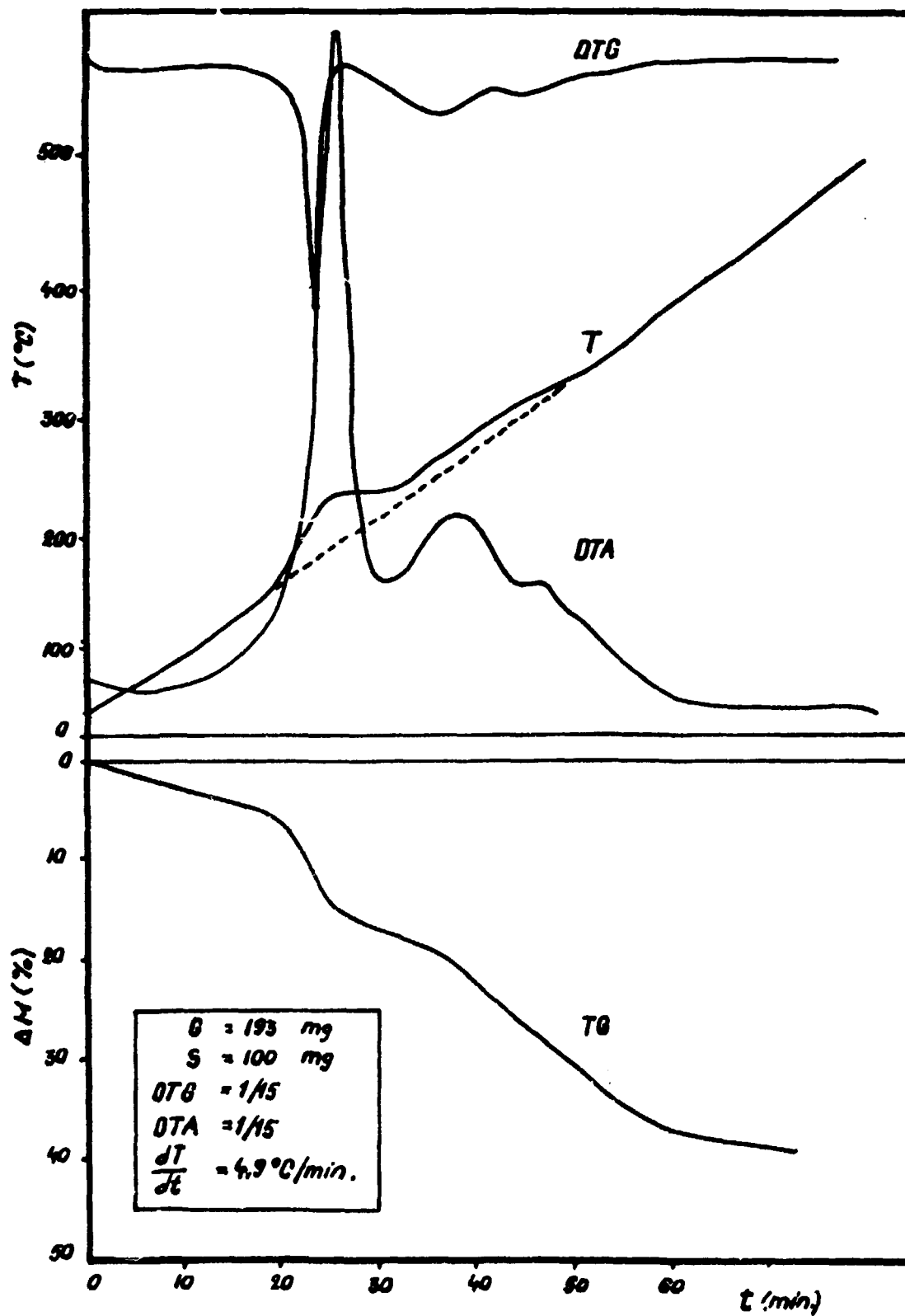
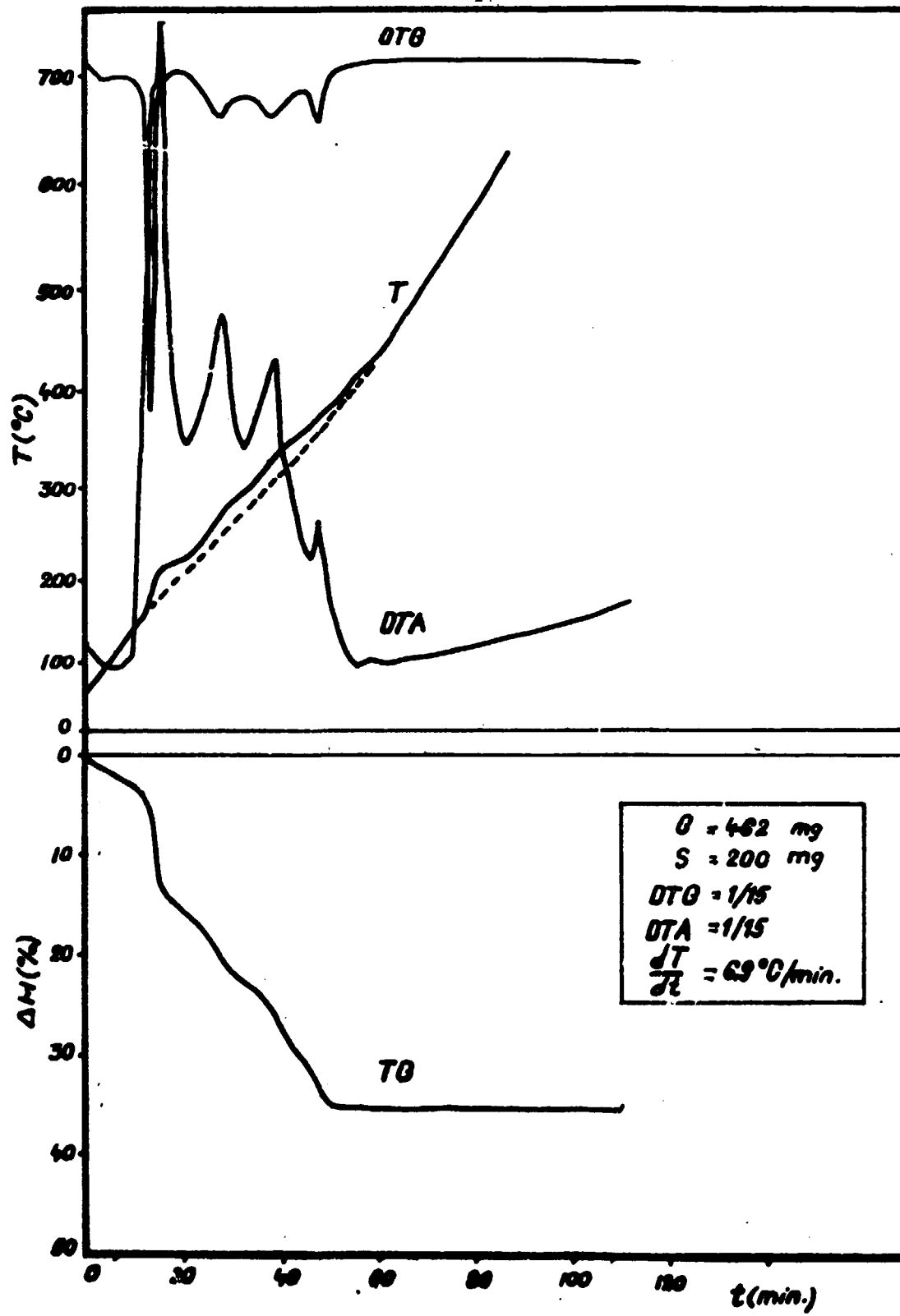


Fig. 7 Derivatogram of $\text{Fe}(\text{OH})_3$ (milled microspheres)



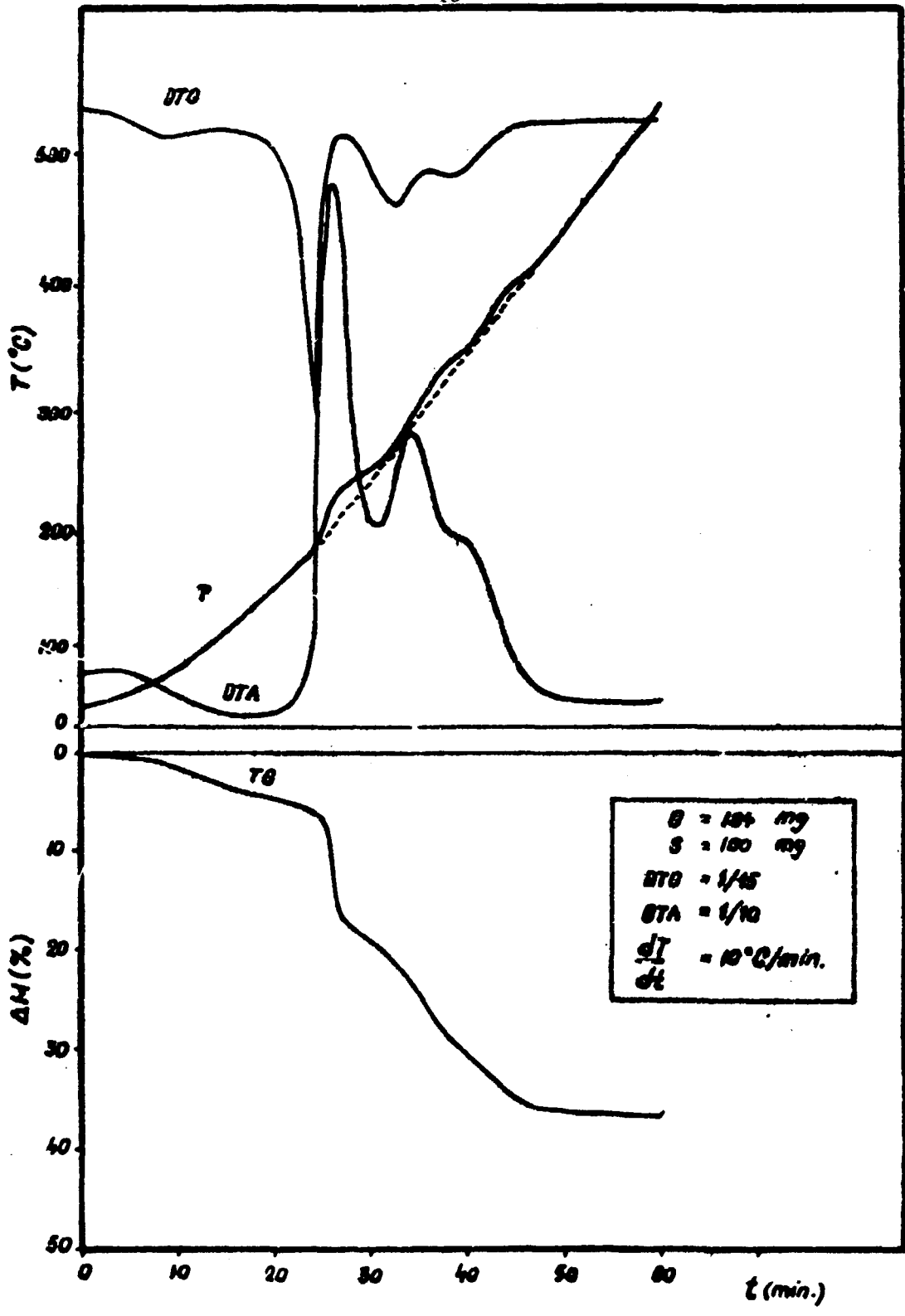


Fig. 9 Derivatogram of $\text{Fe}(\text{OH})_3$ (milled microspheres)

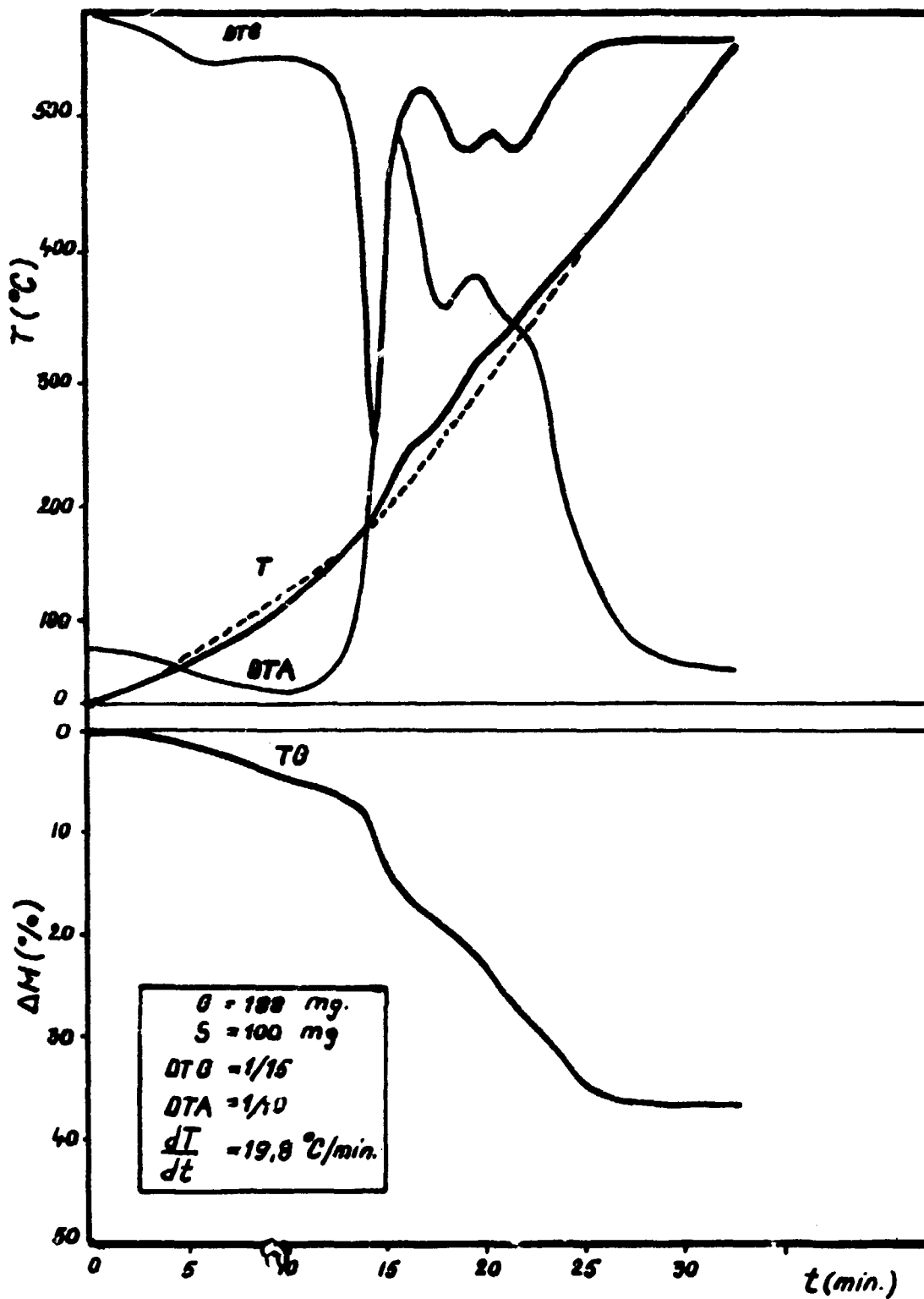


Fig.10 Derivatogram of $Fe(OH)_3$ (milled microspheres)

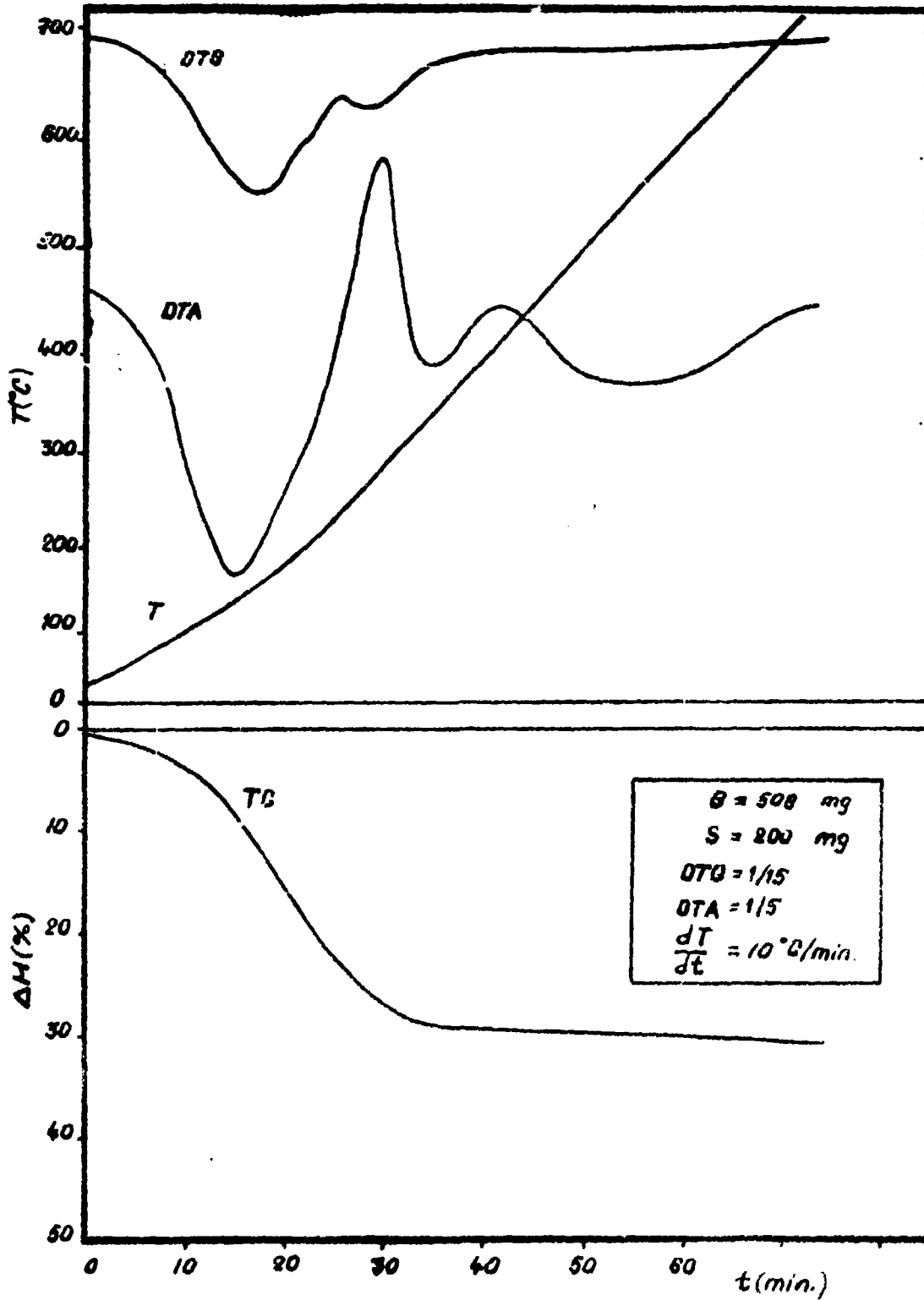


Fig. 11. Derivatogram of $Fe(OH)_3$ microspheres.

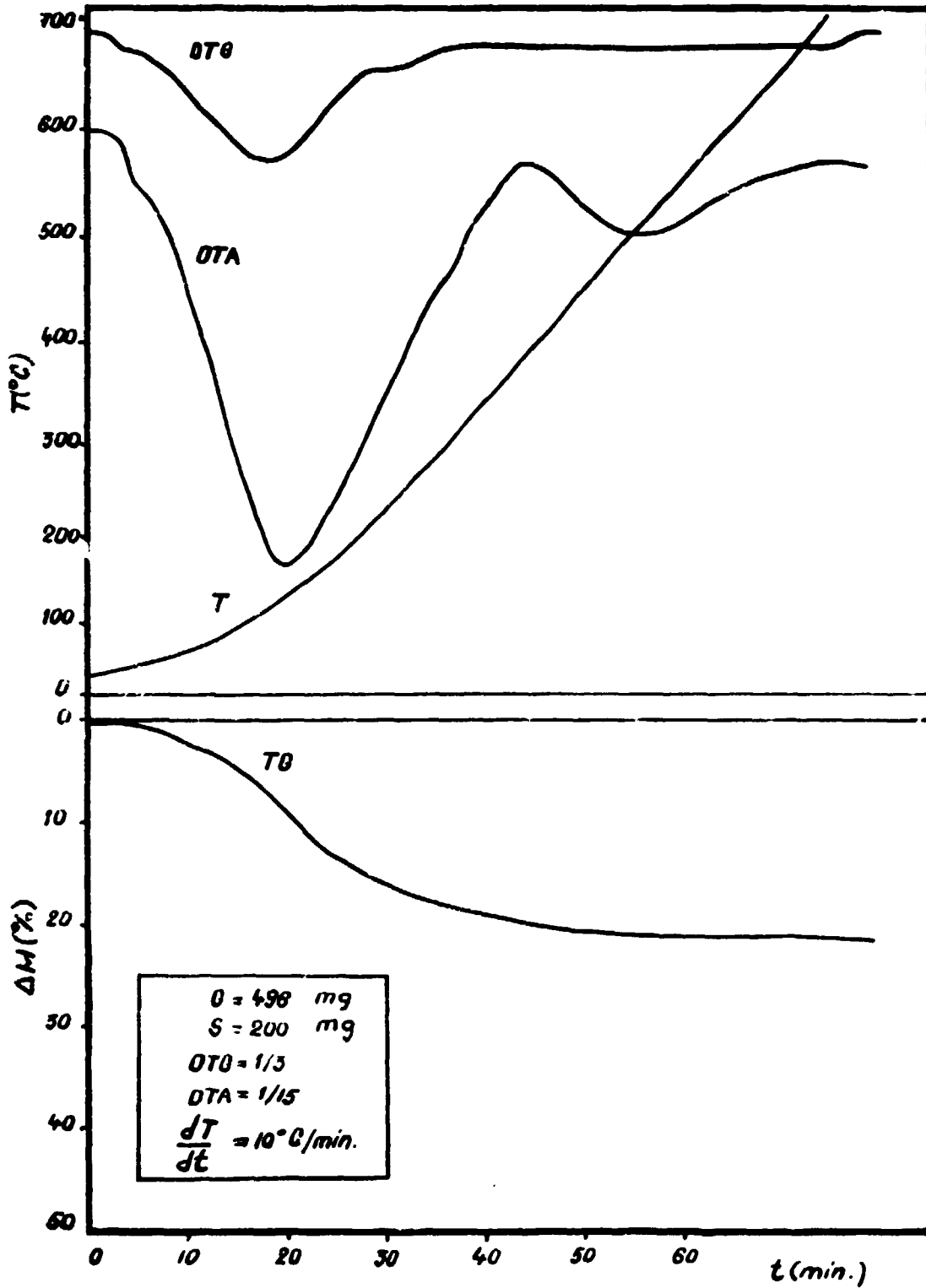


Fig. 12 Derivatogram of Fe(OH)₃ microspheres.

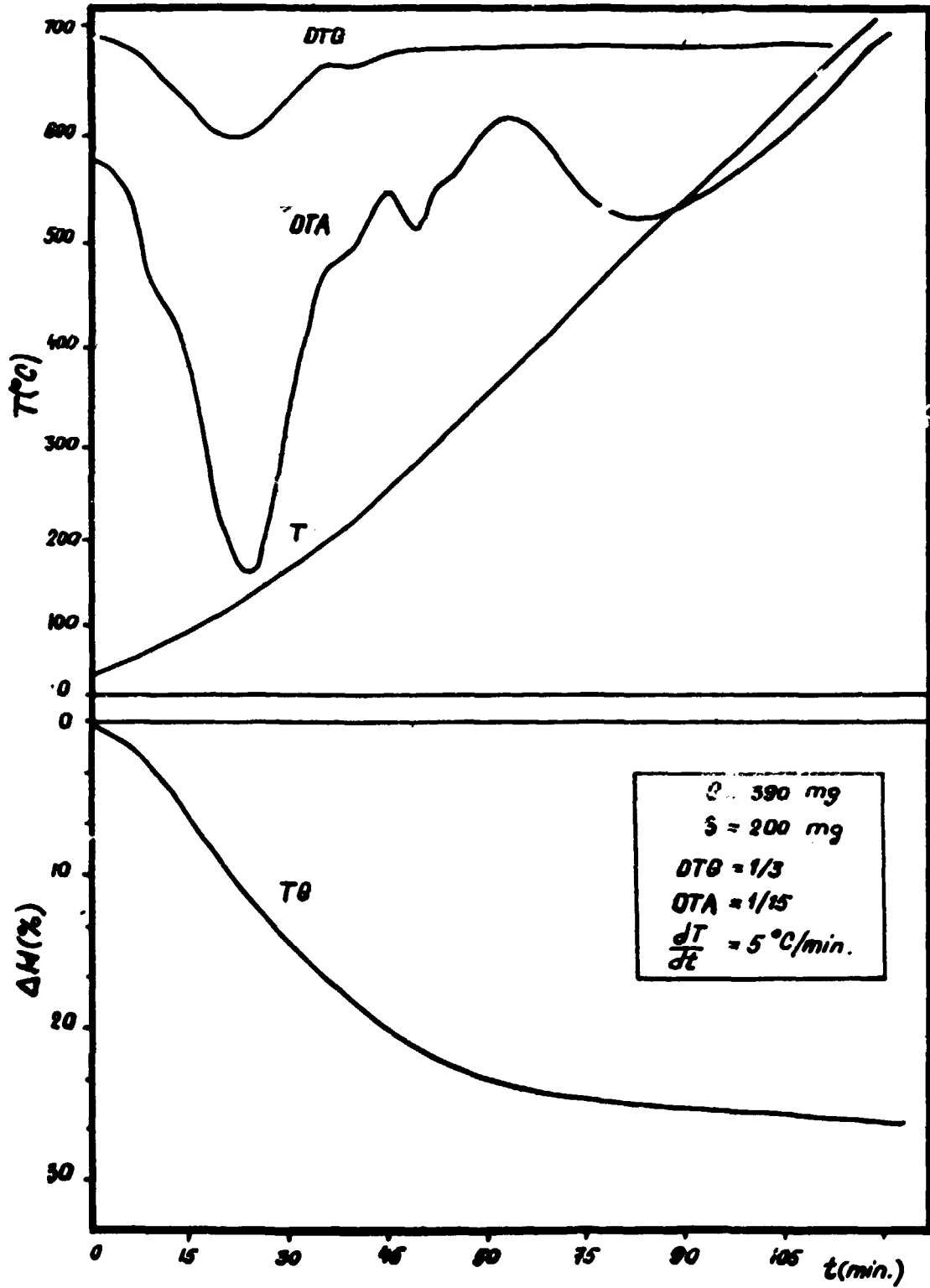


Fig. 13 Derivatogram of $\text{Fe}(\text{OH})_3$ (milled microspheres).

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