Comitetul de Stat pentru Energia Nucleară
INSTITUTUL DE REACTORI NUCLEARI ENERGETICI

IRNE-137-1979

March

C.N.TURCANU, M.CORNESCU

IRNE

THERMAL ANALYSIS OF IRON HYDROXIDE MICROSPHERES

Piteşti - ROMÂNIA

Abstract :

The thermal treatment is an important step in the preparative technology of the iron orids 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 gellification methods.

1. INTRODUCTION

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

Generaly this is considered to be a hidrated oxide like $Fe_2O_3.nH_2O$; 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 coloidal 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 betwen the reactants and catalysts is obtained with oxide microspheres, optimaly 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 obtained 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 μm). Such characteristics hard to obtained by the conventional methods, determine the large utilisation of these products as microspheres in the areas of the refractary 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 resistence, and can not be replaced by the organic resins.

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

This study was performed for the characterisation by thermal analysis of the microspheres and thes 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 (polivynil alcchol, alchil - cellulose etc.) are used. This mixture is droped in concentraded ammonia with a special device. The rol of the support is to from 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 and dried at 100-120°C.

The thermal treatement 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 % polivynil 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 occuring also duirng the ageing step. The washing with water (three times/15min) rémoved the most of the ammonia and ammonium chloride, preventing the cracking of microspheres during the thermal treatment.
After drying, the microspherea were heated for total elimination of water, ammonia, ammonium chloride and support obtaining Fe_2O_3 microspherea as a final product.

Hdroxide microspherea were prepared also by the internal gelifications (IG) method, used to obtain ADU microspheres (3).
The thermal analysis has been performed using a "OM" 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 abuot 90% of water is lost by endothermic process with the minimum close to 130°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°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 streching vibrations, but the crystalline lattice shows a variable concentrations of defects for the smoller temperatures.

Mössbauer studied have shown that the defects desappear by heating at higher temperatures (above 600°C) when a Fe_2O_3 normal crystalline lattice is obtained (7).

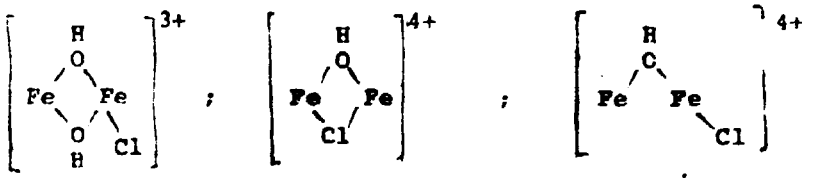
The difference between the iron hydroxide species can be evidenced on the basis of the hyperfine Mössbauer spectra structure recorded at very low temperatures.

The ferric ion hydrolise is still an open problem. A diol dimer $\left[Fe(OH)_2\right]^{4+}$ was presumed to be fromed as an initially primary hydrolitical product, by the potentiometric studies. The magnetic measurements data of the hydrolised iron salts show a decreasing of the magnetic moment, explained by the mechanism (8)

$$2\left[Fe(H_2O)_6\right]^{3+} \rightleftharpoons \left[(H_2O)_x Fe - (OH)_2 - Fe(H_2O)_x\right]^{4+} + 2H^+$$

monomer S=5/2 paramagnetic dimer

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



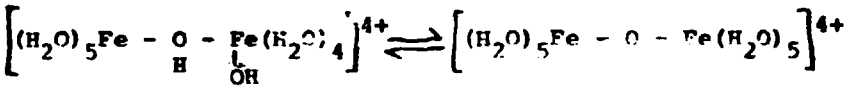
Between the dimer and monomer species the followirgequilibrium existe (9 - 11):

$$2\left[Fe(OH)(H_2O)_5\right]^{2+} \rightleftharpoons \left[Fe(OH)(H_2O)_5\right]_2^{4+}$$

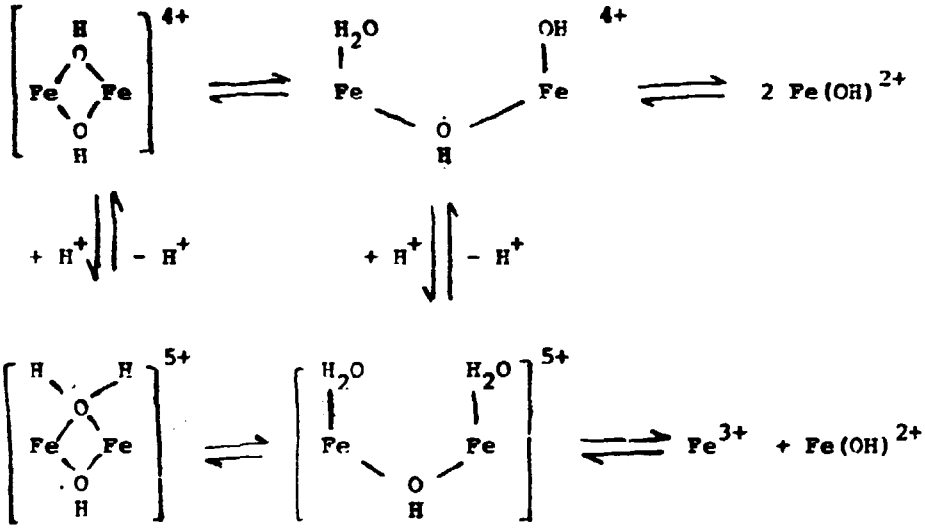
$$\left[Fe(OH)(H_2O)_5\right]_2^{4+} \rightleftharpoons \left[(H_2O)_5 - \underset{H}{O} - \underset{OH}{Fe}(H_2O)_4\right]^{4+} + H_2O$$

$$\left[(H_2O)_5Fe - \underset{H}{O} - \underset{OH}{Fe}(H_2O)_4\right]^{4+} \rightleftharpoons \left[(H_2O)_4Fe\begin{matrix}\overset{H}{O}\\ \diagup\diagdown \\ O\\ H\end{matrix}Fe(H_2O)_4\right]^{4+} + H_2O$$

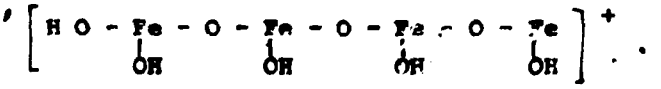
Alternately instead diol-, oxo-complexes can be formed:



Another way for the dimer dissocation occurs by hidrogen ion depending equilibria.



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



The smoller magnetic susceptibility values are explained by the

formation of polimer chaines from dihydroxadimers, bounded by oxo-bridges and keeping the diol structure. The hydrolitical polimerisation which begins with the dimer formation continues during the hydroxide precipitation, but the polimerisation mechanism and the composition of intermediaries remain unknown.

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

For the high molecular weigh polimers, the analytical results sugest a polication as $\left[Fe(OH)_x^{(3-x)+}\right]_n$ 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 beengin 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 normaly obtained from concentrated solutions can be described as an oxide - hydroxide latice where the iron is placed in octahedral and tetrahedral sites.

The relation ship 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 deffects in the latice. The excess water associated with chain ends in the most defective sample indicated an average chain lenght of only five FOOH units (13). Obviously, in the case of fast precipitation from a concentrated solution the number of deffects (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 individul reactions on the DTG, DTA and TG curves remain approximate as a result of thermal decomporition process superposition, and of secondary effects given by diffusion and experimental conditions, Fig. 4-6. For a heating rate of 2.6°C/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 liniarly on the TG curve, but the DTG curve present two steps in the range of 130-180°C and respectively 180-225°C. The next 18% are eliminated in three steps at 225-255°C (4%), 255-340°C (10%) and respectively 340-400°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°C/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 exotermic peak occuring at 450°C. The derivatoram of the iron hydroxide microspheres at 19,8°C/min (the highest permited heating rate with MOM 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-volatil 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 esteablished between the decomposition fragments and the solid matix, desplaced the decomposition intervals to higher temperatures. These equilibria are deplaced to the gaseous products generation as a function of the outwards diffusion of the fragments and their oxidation with theatmospheric 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 nonhomogenity, 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 exotermic 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 coresponds 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 rearangement 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 diference 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 show 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 peak appear on the DTA curve at 250 and 360°C, one of them (probably the peak from 360°C) beloging pesumably to the Fe - O - Fe bridges rearrangement.
The behaviour of microspheres in this temperature interval, is very similar to the derivatogram of ageid 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 coresponds to 74% from the initial amount of the sample.

The DTA curve at the heating rate of 10°C/min is poor structured: more evident is the endothermic peak at 150°C with a corresponding peak on the DTG curve at 130°C. The DTG curve show 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 easir 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 Fe_2O_3 microspheres with a good sphericity and free of cracks. The microscopic aspect of a section shows the begining of the sintering process. The sistering was more advanced for the microspheres heated at 950°C. The thermal treatment up to 1200°C, leads to Fe_3O_4 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.

4. 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 elimi... the last traces of carbon are lost between 700 and 750°C.

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

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.

5. REFERENCES

1. .G Facchin ... I.A.E.A Panel on sol-gel processes for ... fabrication, Vienna, May, 1973
2. A.G.Facchini and P.Gerontopoulos, I.A.E.A panel on sol-gel ... s ... o ... u l f brication, Vienna, May, 1 ...
3. ... (will be published)
4. C.M.Turcanu, M.Cornescu and P.Deju, raport extern ITN 107, Ap 1976.
5. C.M.Turcanu, A.Zuda, J.Thermal Anal. (in press)
6. C.Duval, Inorganic thermogravimetric Analysis, Elsevier Publ. Co. 1963, 323.
7. C.M.Turcanu, C.Filoti and ... (will be published)
8. ... , C.Walling, P. ... Tons and M.B.Gray, J.Am. Ch... 89(1967) 3712
9. I.A.Sommer, D.W.Morgerum, Inorg.Chem., 9(1970) 2517
10. H.Wendt, Inorg.Chem. 8(1969) 1527
11. ... , N.Sutin, Inorg.Chem., 10(1971) 428
12. T.G.Spiro, S.E.Allerton, J.Renner, A.Terzio, R.Bils, ... , J.Am.Chem. Soc. 88(1966) 2712

13. K.Kauffman, F.Hazel, J.Inorg.Chem 37(1975) 1139
14. C.N.Turcanu (un published results)
15. P.Gordeș and C.N.Turcanu (un published results)
16. L.Diamandescu, M.Morariu and C.N.Turcanu (un published results)
17. G.Filoti and C.N.Turcanu Proc. Intern. Conf. Mössbauer Spectr. Poland, Cracow 25-30 Aug. 1975 paper 3 A-23
18. G.Filoti, C.N.Turcanu and V.Spînu, International Conferarce on the applications of the Mössbauer effect, Corfu (Greece) September 13-17, 1976.

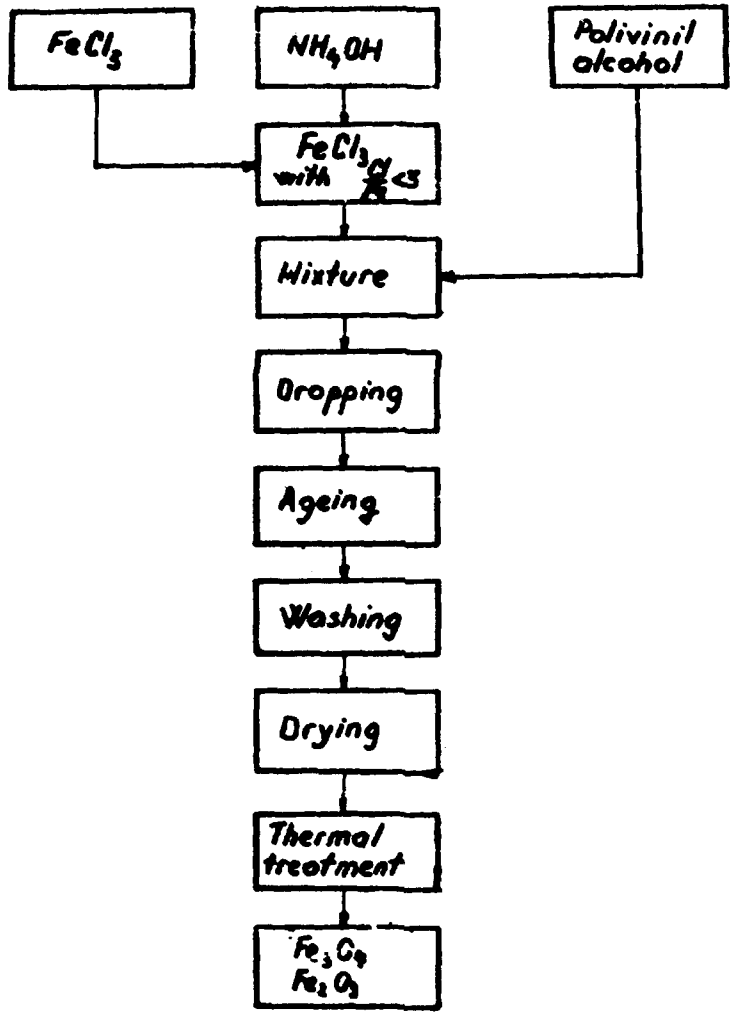


Fig. 1 Flowsheet for iron oxide - sphere preparation.

Fig. 2. $Fe(OH)_3$ microsphere S(x60)

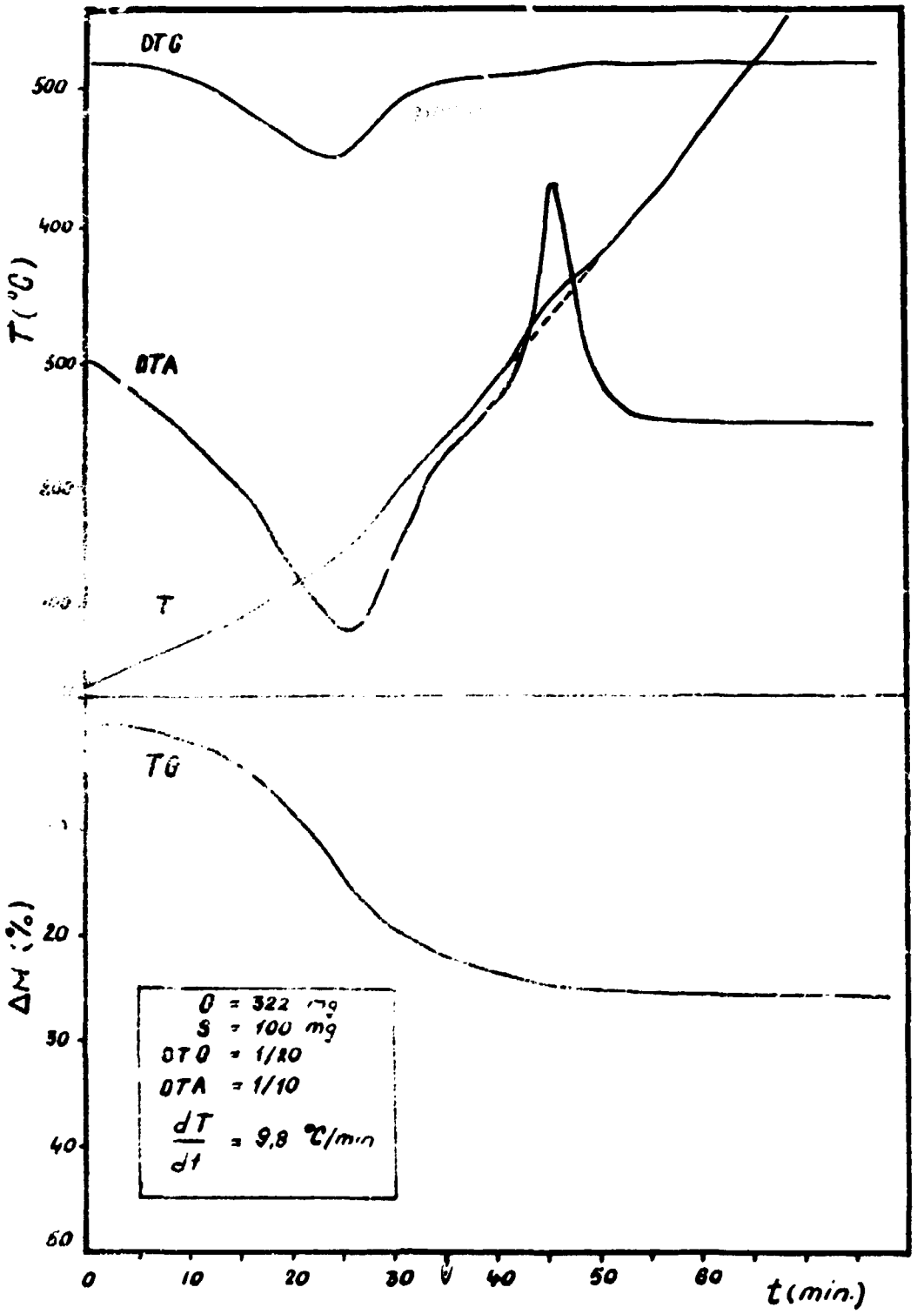


Fig. . Derivatogram of $Fe(OH)_3$.

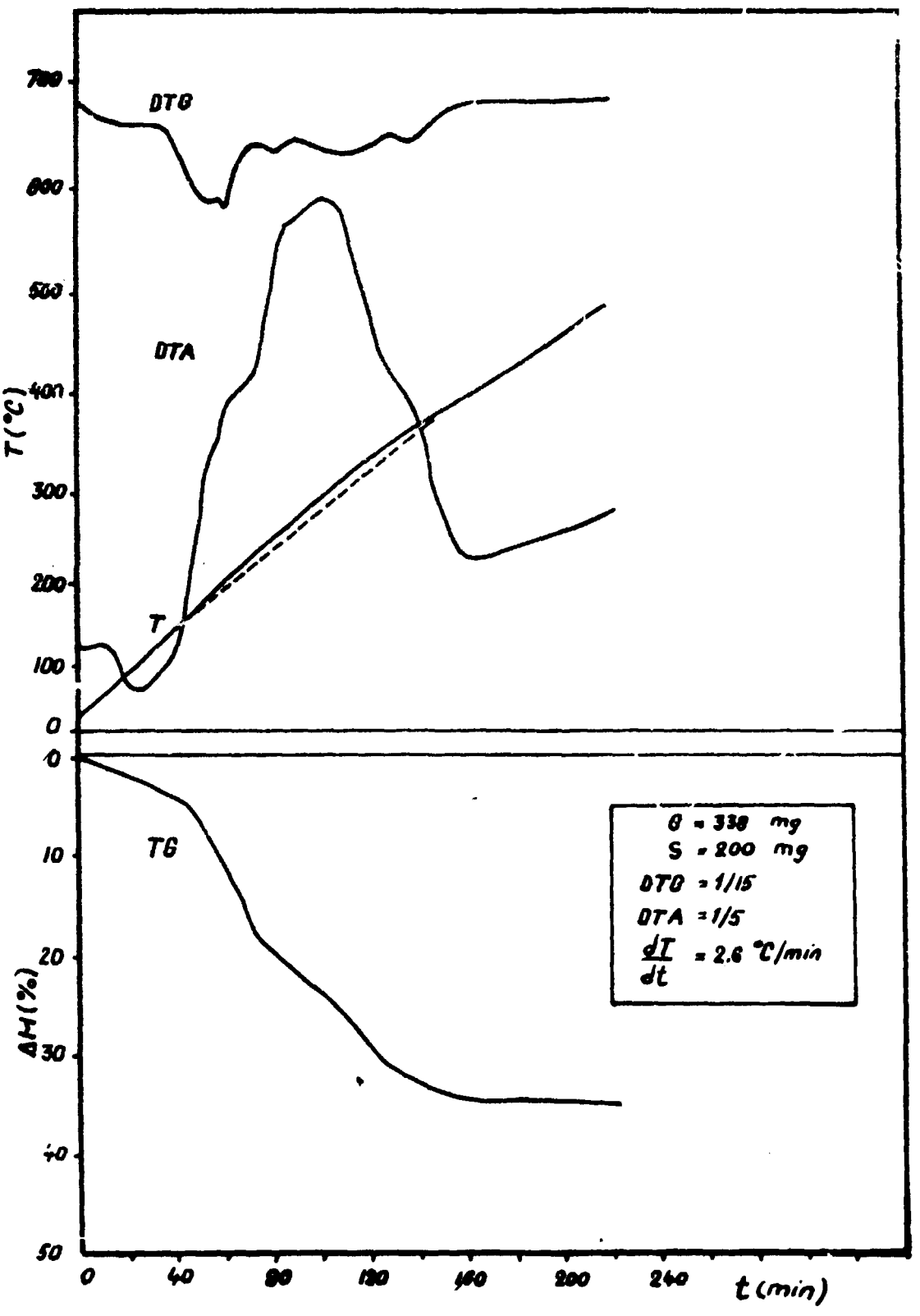


Fig. 4 Derivatogram of $Fe(OH)_3$ microspheres.

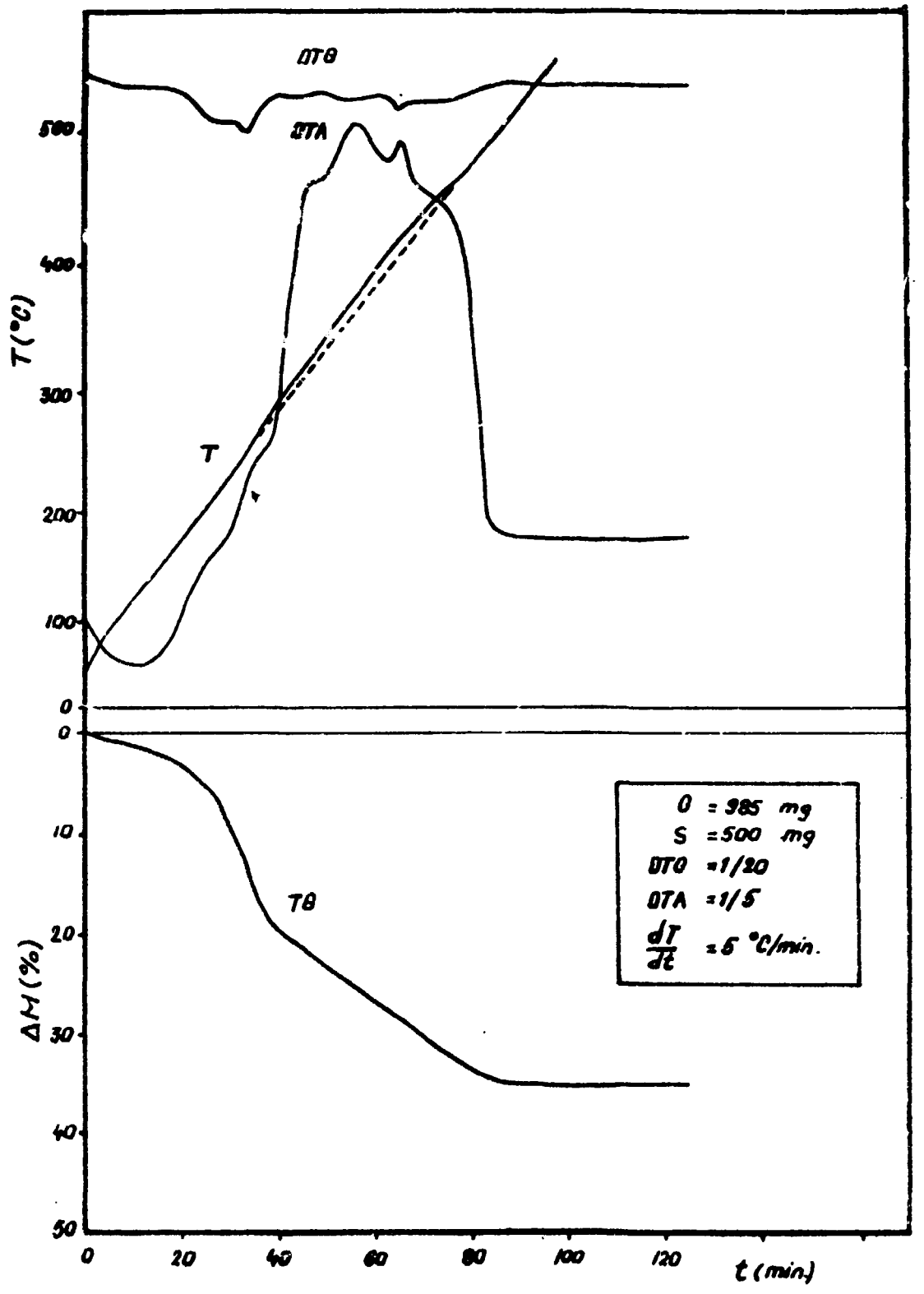


Fig. 5 Derivatogram of $Fe(OH)_3$ microspheres.

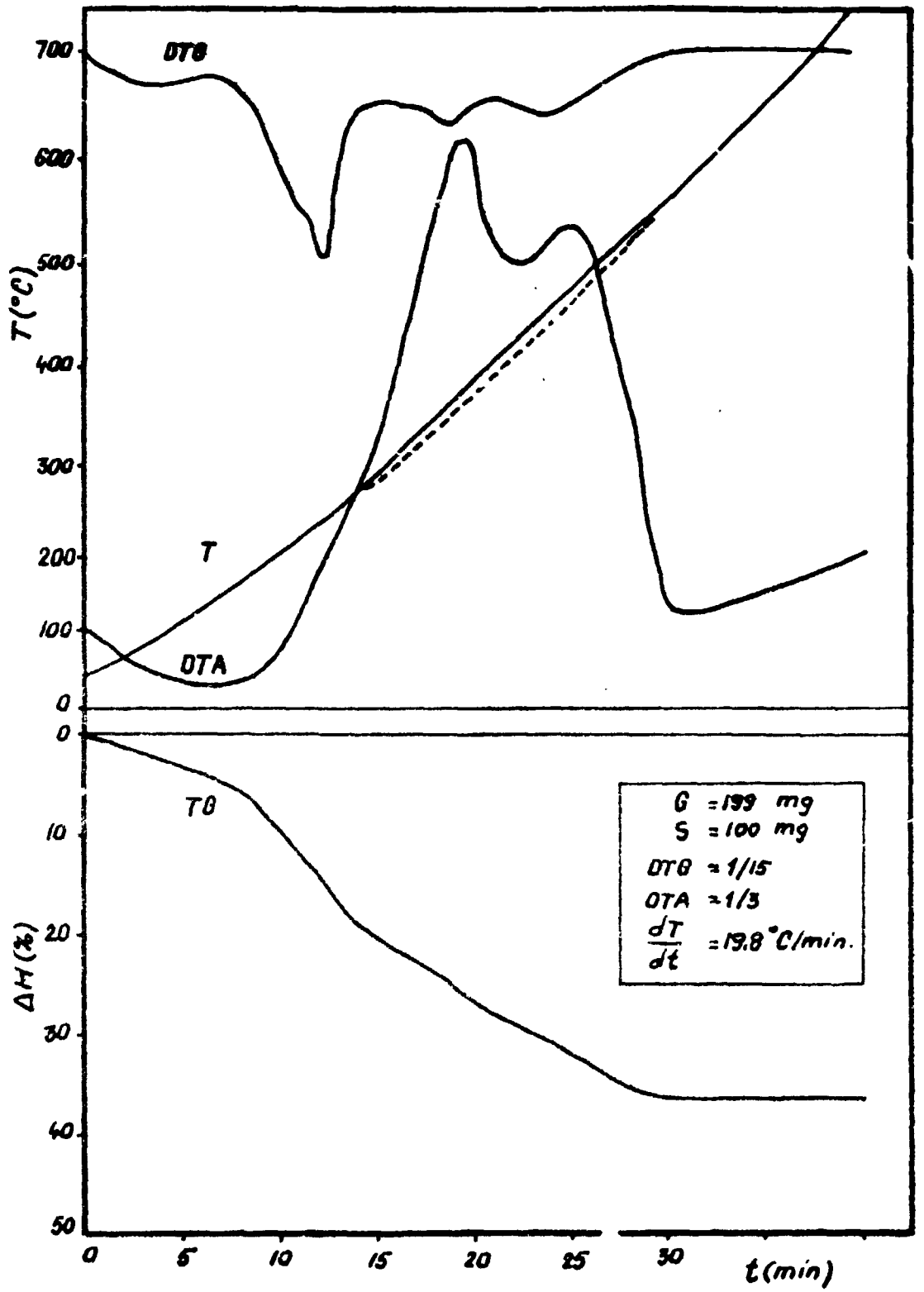


Fig. 8 Derivatogram of $Fe(OH)_3$ microspheres.

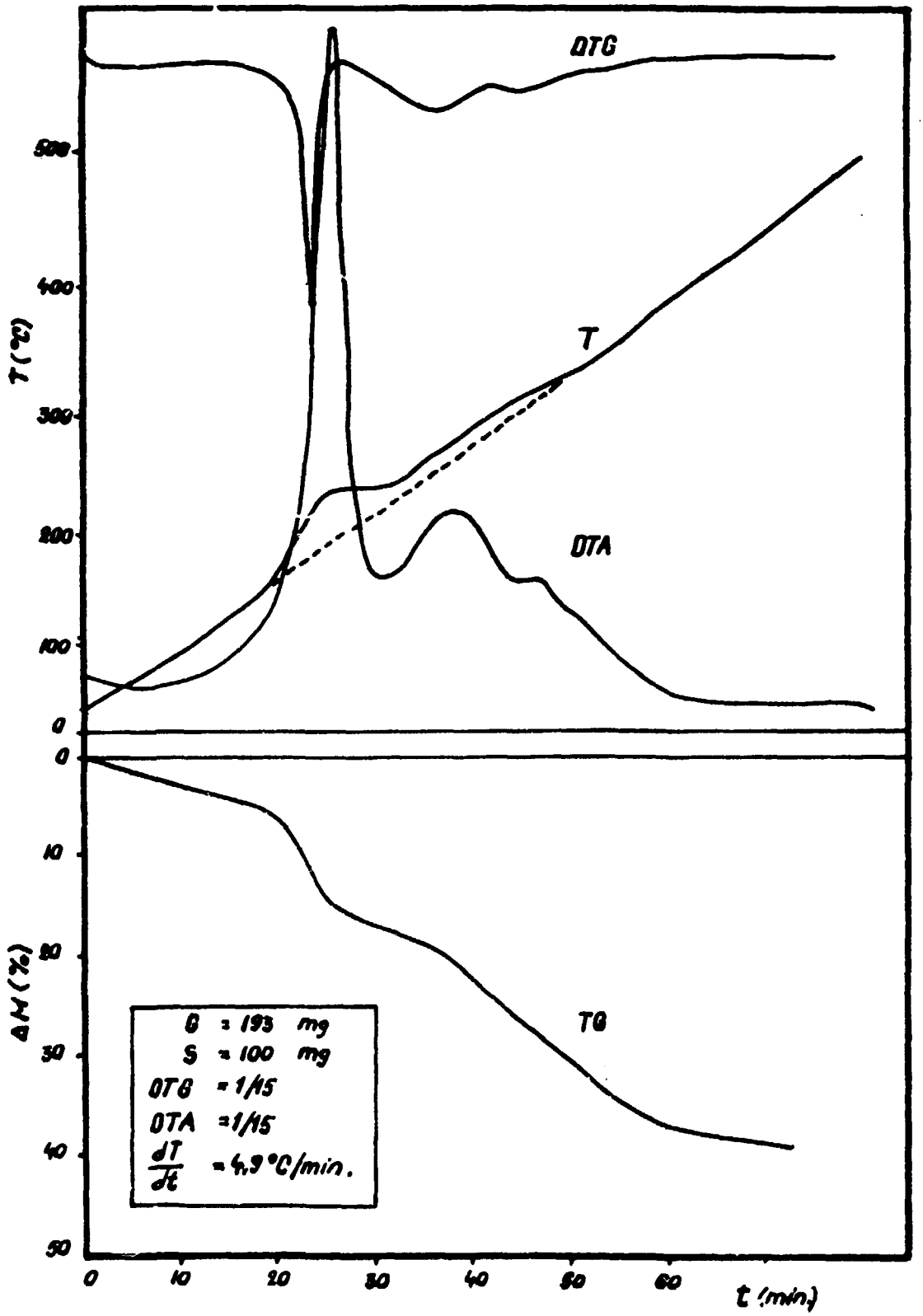
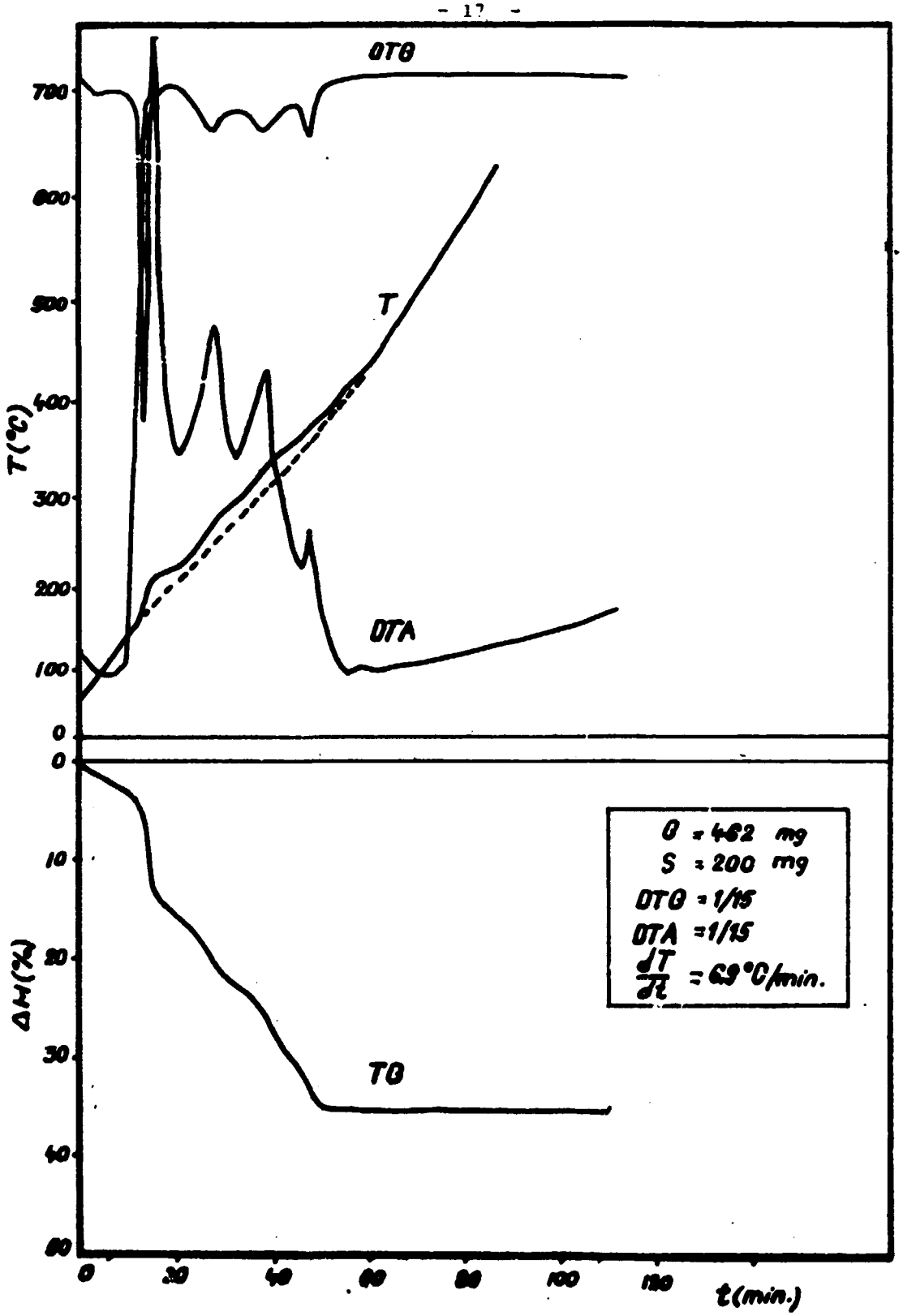


Fig. 7 Derivatogram of $Fe(OH)_3$ (milled microspheres)


DTG
T
DTA
T(°C)
700
600
500
400
300
200
100
0
0
10
20
30
40
60
ΔH(%)
TG
0
30
40
60
80
100
110
t(min.)
O = 462 mg
S = 200 mg
DTG = 1/15
DTA = 1/15
dT/dt = 6.9 °C/min.

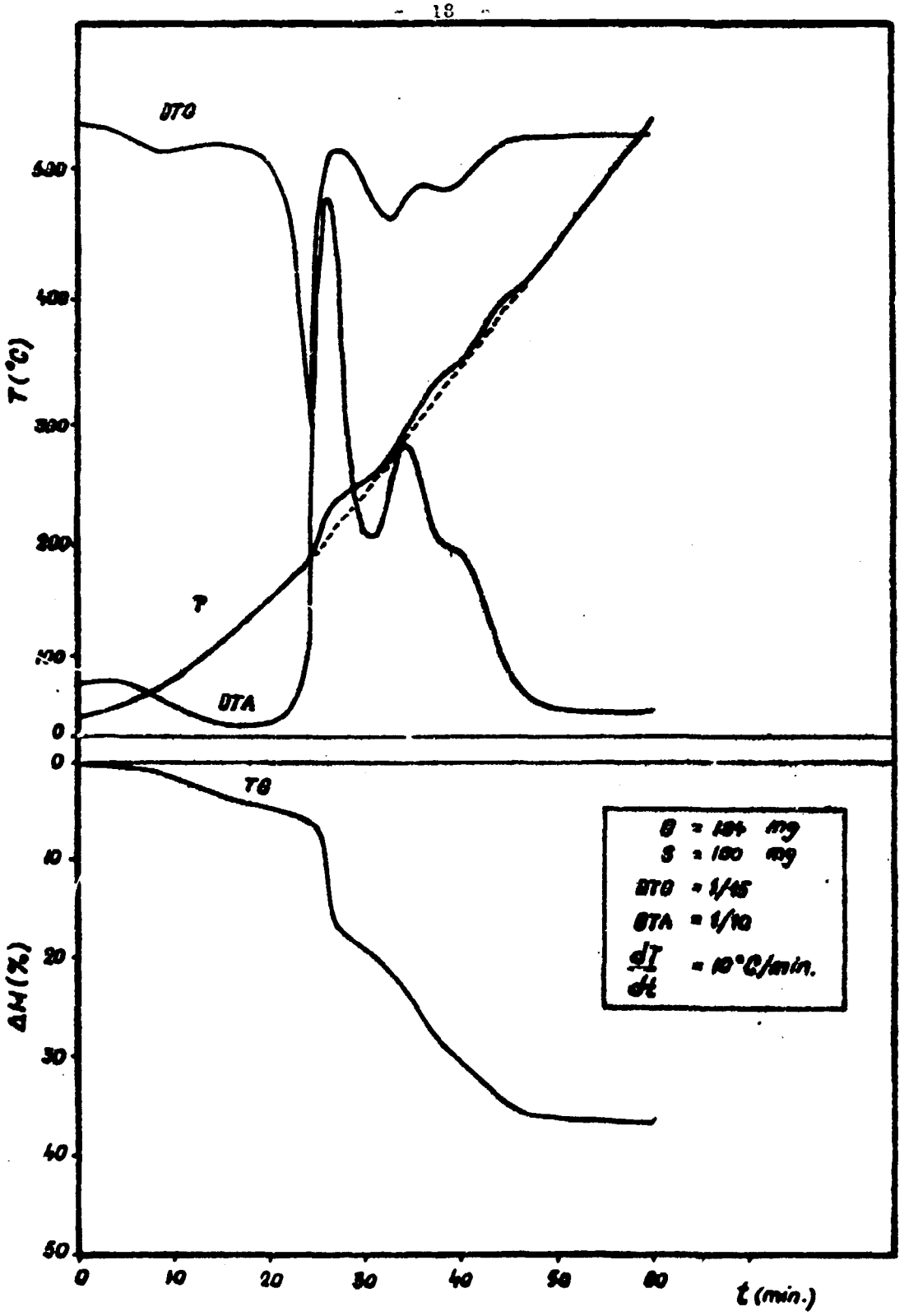


Fig. 9 Derivatogram of $Fe(OH)_3$ (milled microspheres)

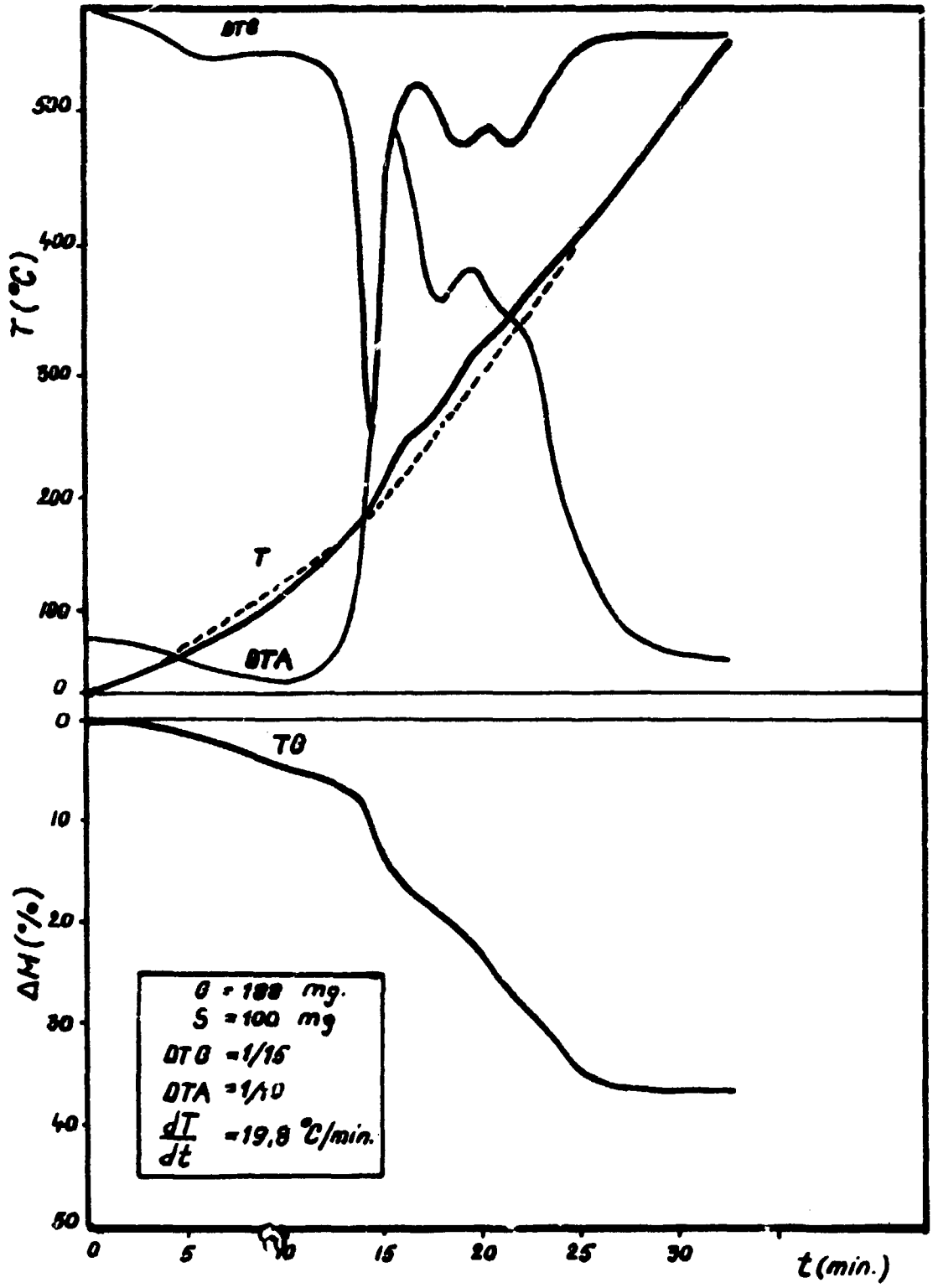


Fig.10 Derivatogram of $Fe(OH)_3$ (milled microspheres)

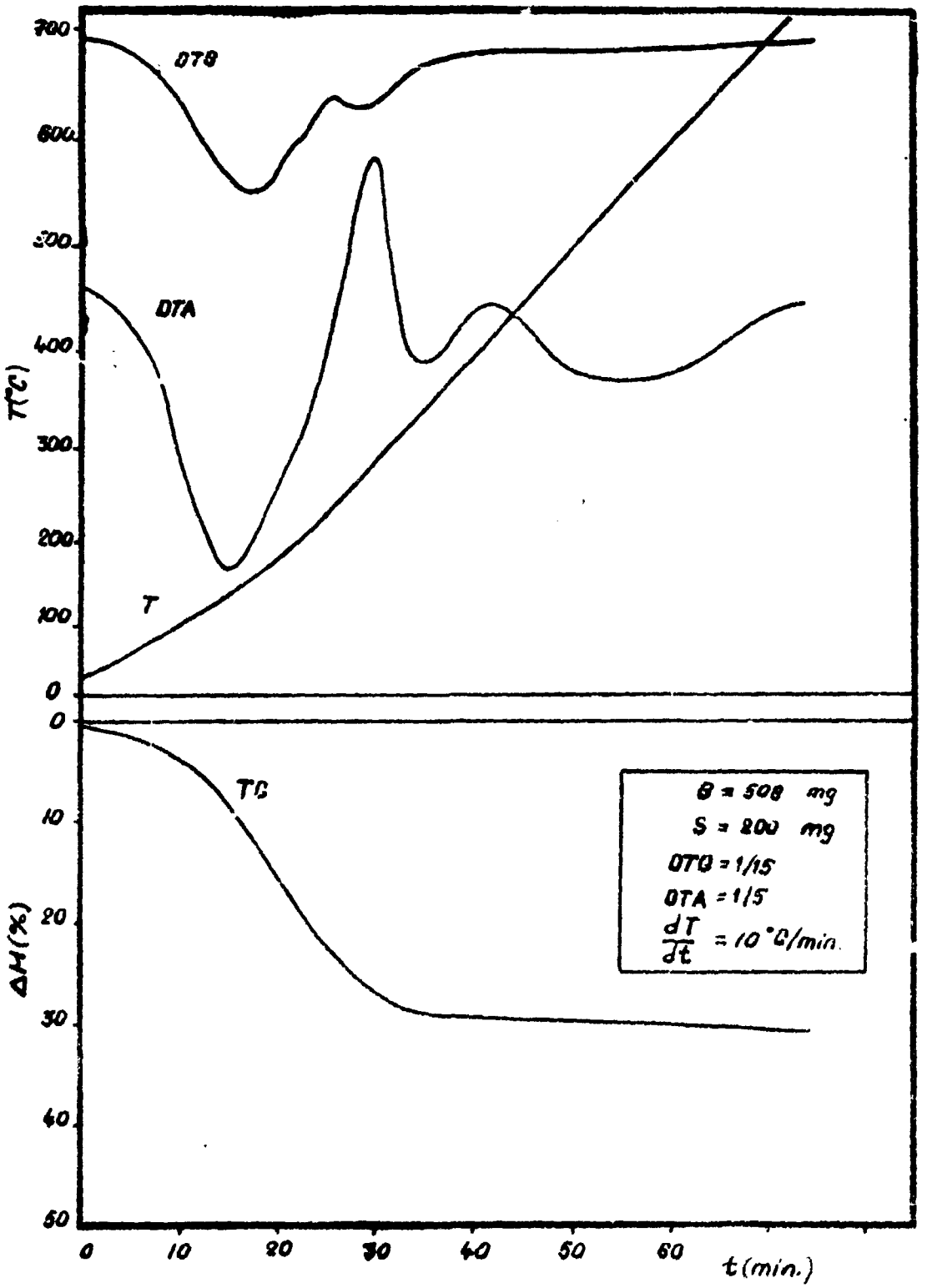


Fig. 11. Derivatogram of $Fe(OH)_3$ microspheres.

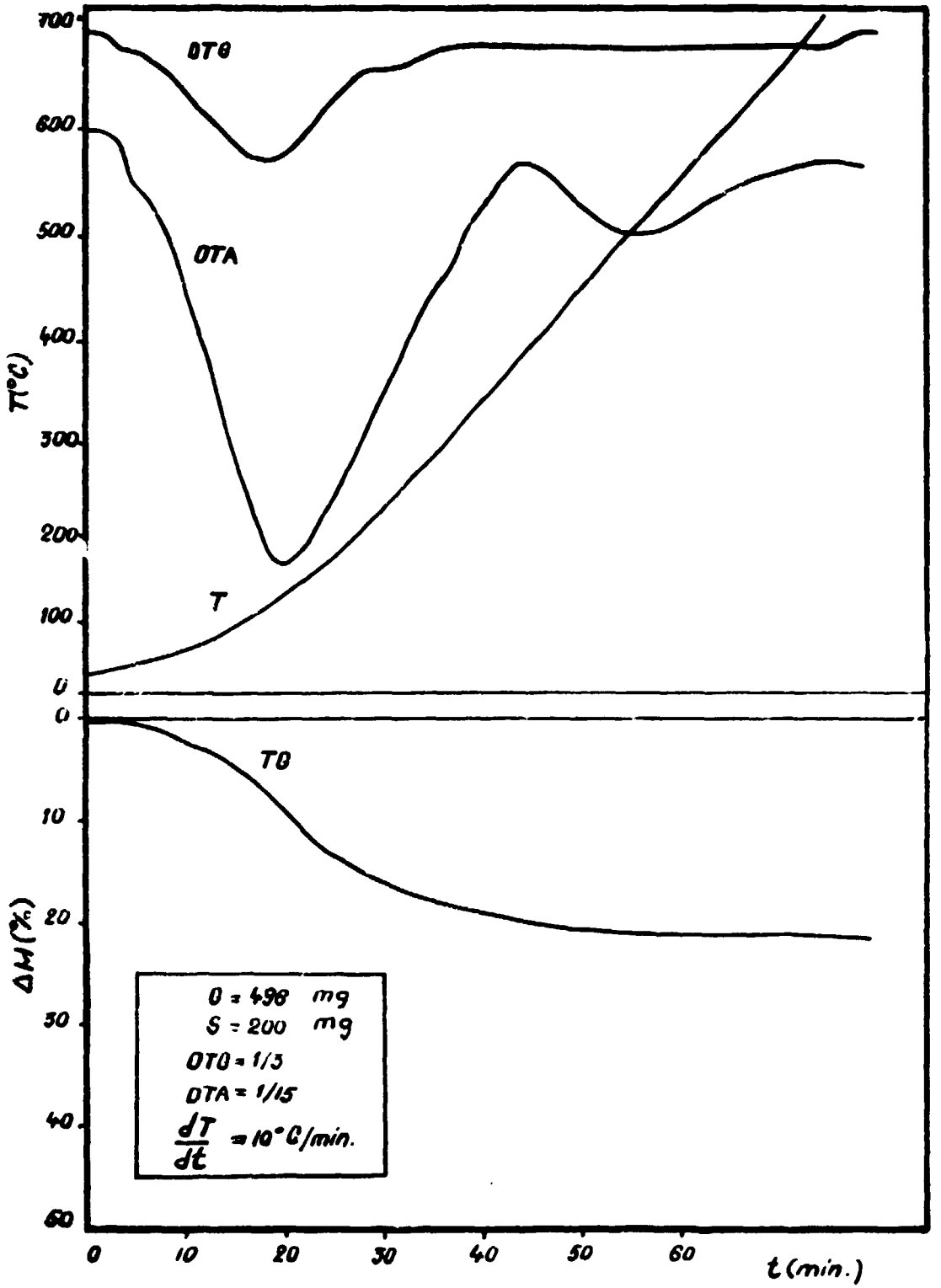


Fig. 12 Derivatogram of $Fe(OH)_3$ microspheres.

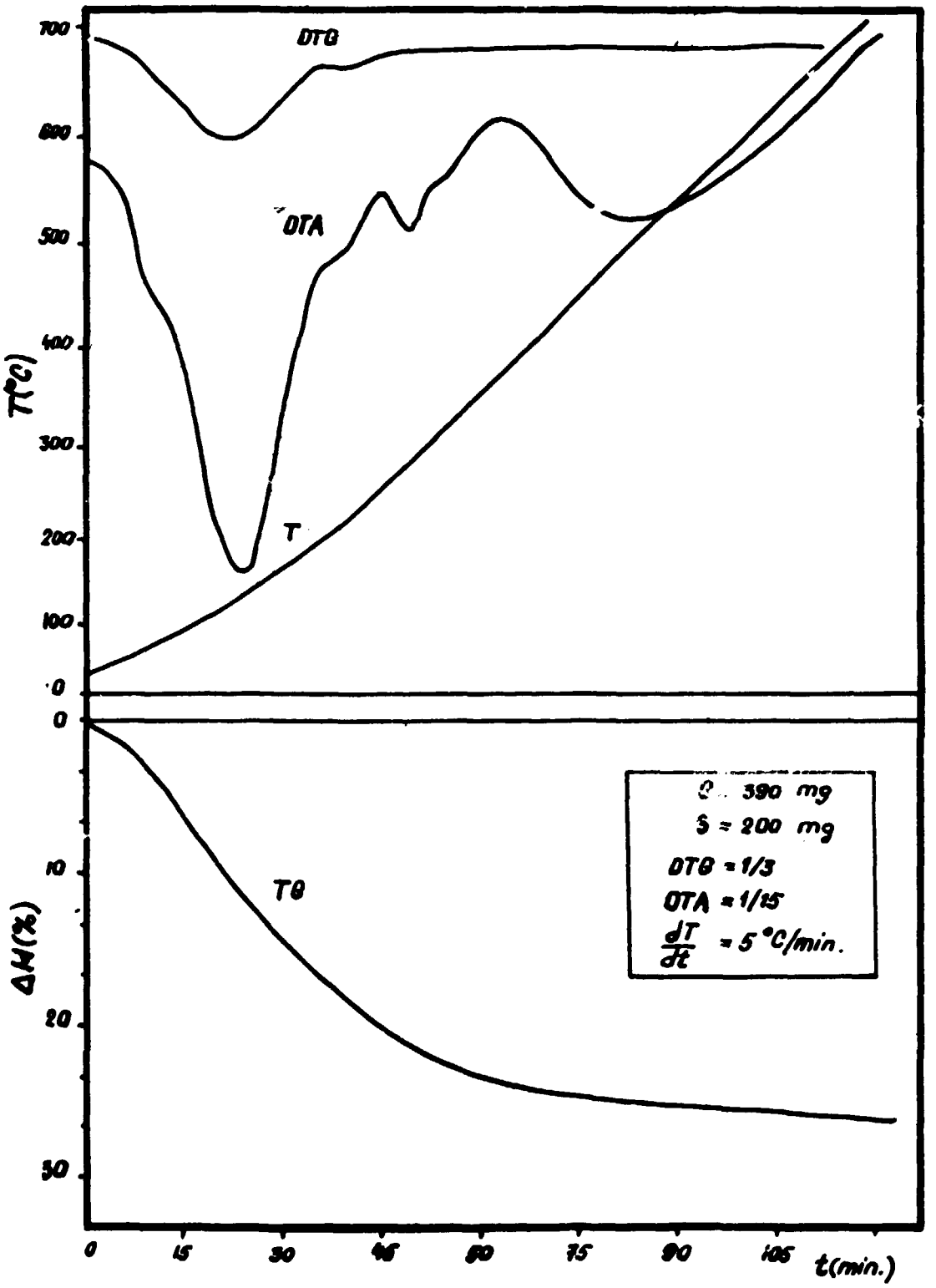


Fig. 13 Derivatogram of $Fe(OH)_3$ (milled microspheres).

Comitetul de Stat pentru Energia Nucleară

INSTITUTUL DE REACTORI NUCLEARI ENERGETICI

Piteşti — c.p.nr 78 — telefon 1 26 10 — telex 1 82 72