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METHODS OF PREPARATION OF MAGNESIUM ORGANIC COMPOUNDS FROM NATURAL DOLOMITE

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A simple method of preparation of organic magnesium compounds (citrate, acetate and aspartate) from natural dolomite with simple apparatus was worked out. In the first stage dolomite was converted into magnesium sulfate and then into basic magnesium carbonate by combination with citric and acetic acids. However, magnesium aspartate was prepared by converting magnesium sulfate into hydroxide and then combining it with aspartic acid. The contents of trace element were determined in the final preparations with ASA. Thermal decompositions of the obtained compounds was studied by means of the thermal analysis. Results could be useful in elaborating method of production of these magnesium compounds from domestic dolomite.

Key words: dolomite, magnesium citrate, acetate and aspartate, ASA, thermal analysis

INTRODUCTION

Dolomite $MgCa(CO_3)_2$, a mineral commonly occurring in nature, finds applications in many fields of industry. For example, it is a fluxing agent in metallurgical, glass and ceramic industry, filling material in paper, rubber and plastic production, a sorbent in desulfurization of exhaust gases as well as a filter for water treatment. Large amounts of dolomite are also used in building industry and agriculture (dolomite fertilizers). In chemical industry dolomite is first of all a source of magnesium compounds - oxide, hydroxide, basic calcium, and magnesium carbonates, which are used as ecological anti-oxide frost agent. It is the subject of many interests and research (Bobolewski, 1982; Łukwiński et al., 1994; Biskupski et al., 1996). Lately, there has been worked out a method for preparing *dolomite sorbent* which exhibits very good adsorbing properties towards dangerous poisons like nitrogen and sulfur

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oxides as well as chromium(VI) ions (Staszczuk et al., 1996; Staszczuk et al., 2000). The presence of magnesium (so-called *life metal*) in dolomite (*life rock*) promoted exploitation of its beds in order to counterbalance the loss of this precious but deficient element in nature. Therefore, we now have dolomite fertilizers, fodder addition and pharmaceutical preparations. Magnesium deficit in the environment and in human organism becomes such serious so that it makes a social problem. This is caused mainly by the environment pollution, diet, stresses, incorporation of lead from exhaust gases. An improvement may come from consumption of full value food or taking special magnesium preparations. A suitable amount of magnesium in human organism protects it against the effects of different pollutions, such as: lead, cadmium, chlorides. Dolomite provides a cheap source of magnesium can be used as a raw material for production of readily available magnesium compounds. The magnesium oxide, hydroxide, chloride, sulfate, carbonate, acetate, citrate, levulinian, ascorbinian, asparginian are widely used in medicine to compensate for magnesium deficit in the organism and to treat many diseases. Basic magnesium carbonate is used for preparation of mixtures and tablets used in deacidification treatment like the hydroxide. Magnesium sulfate (i.e. bitter salt) has been known for a long time as the purgation medication. However, magnesium acetate is a component of the preparations used for parent injections in treatment with magnesium. Magnesium sulfate is used for skin and mucous membrane treatment as well as the antiphlogistic preparation as well as in treatment of keratitis. Magnesium salts are used as transplant preservatives. The above examples of application of magnesium salt indicate great demand for this element. It is believed that the orally administered organic magnesium salts dissolved in water are more readily available and tolerable than insoluble ones. Moreover, it is assumed that organic magnesium salts are more active than inorganic ones (Durlach, 1991; Gumińska Ed., 1990; Staszczuk et al., 1994).

Therefore, an effort has been made to use the domestic dolomite as a raw material for production of readily available organic magnesium compounds. Simple method of preparation of these salts from the domestic natural dolomite has been elaborated.

MATERIALS AND REAGENTS

The domestic dolomite from Odrzychowice-Romanowo (Kłodzko Valley) 0-0.3 mm grain diameter calcinated for 4 hours at 1000° C in laboratory furnace was used. The mineral composition was determined using AAS-3 spectrophotometer (Carl Zeiss, Jena, Germany) (Tables 1 and 2). Thermal decomposition of final compounds was studied using Q-1500 D deriwatograph (MOM Budapest, Hungary) (Staszczuk et al., 1992). Analytically pure reagents from POCH, Gliwice were used.

Table 1. Quantitative composition of dolomite (Staszczuk et al., 1992; Staszczuk et al., 1994)

Component	Content, %
CaO	29.54
MgO	19.36
Fe ₂ O ₃	0.30
SiO ₂	3.10
MnO	0.22
Na ₂ O	0.01

Table 2. Contents of trace elements in dolomite (Staszczuk et al., 1994; Stefaniak et al., 2000)

Element	Content, ppm
Mn	286.74 ± 0.99
Zn	50.33 ± 0.10
Pb	24.00 ± 0.36
Cd	3.86 ± 0.30
Al	< 10
Ni	< 0.5

RESULTS AND DISCUSSION

EXPERIMENTAL

Organic magnesium salts were prepared in three stages. The first included formation of magnesium sulfate (separation of Ca and Mg and removal of impurities contained in the raw material). The second one was the synthesis of basic magnesium carbonate and hydroxide from magnesium sulfate. The last stage consisted of combination of basic magnesium carbonate with acetic or citric acid as well as combination of magnesium hydroxide with aspartic acid.

Preparation of monohydrate magnesium sulfate MgSO₄·H₂O

The water magnesium sulfate MgSO₄·H₂O was prepared as follows (Supniewski, 1958; Staszczuk et al., 1994). The 50 g calcinated natural dolomite after heating in laboratory furnace (0-0.3 mm grain size) were dissolved in 180 cm³ of 10% HCl (the amount needed to dissolve half of sample) and then stirred for 7 hours. The resultant mixture was filtrated. The sediment containing mainly magnesium carbonate was washed with a small amount of water and dried at 90° C for two hours. Then, its mass was 26.5 g. Thereafter, it was stirred with 133 cm³ of 20% sulfuric acid at 90° C for 3.5 h. The final mixture was filtered to separate the solid impurities. Then, 2g MgO was added into the clear, heated filtrate for neutralization and adsorption of precipitated impurities (mainly iron) on undissolved magnesium sulfate. Purified filtrate was acidified with sulfuric acid and concentrated until crystallization. Crystals

of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were separated and the filtrate was concentrated until crystallization. The resultant crystals of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were dried for two hours at 150°C . 26.6 g of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ was obtained (Staszczuk et al., 1994).

Preparation of basic magnesium carbonate $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$

The Na_2CO_3 solution (26.5 g , $65\text{ cm}^3\text{ H}_2\text{O}$) was added dropwise into stirred magnesium sulfate solution (26.6 g , $70\text{ cm}^3\text{ H}_2\text{O}$). The reaction mixture was heated slowly at 60°C for one hour. The white precipitate of basic magnesium carbonate was filtered, washed with distilled water till the complete removal of SO_4^{2-} ions was achieved, and dried at room temperature. The 18.7 g of basic magnesium carbonate was obtained (Biskupski et al., 1996).

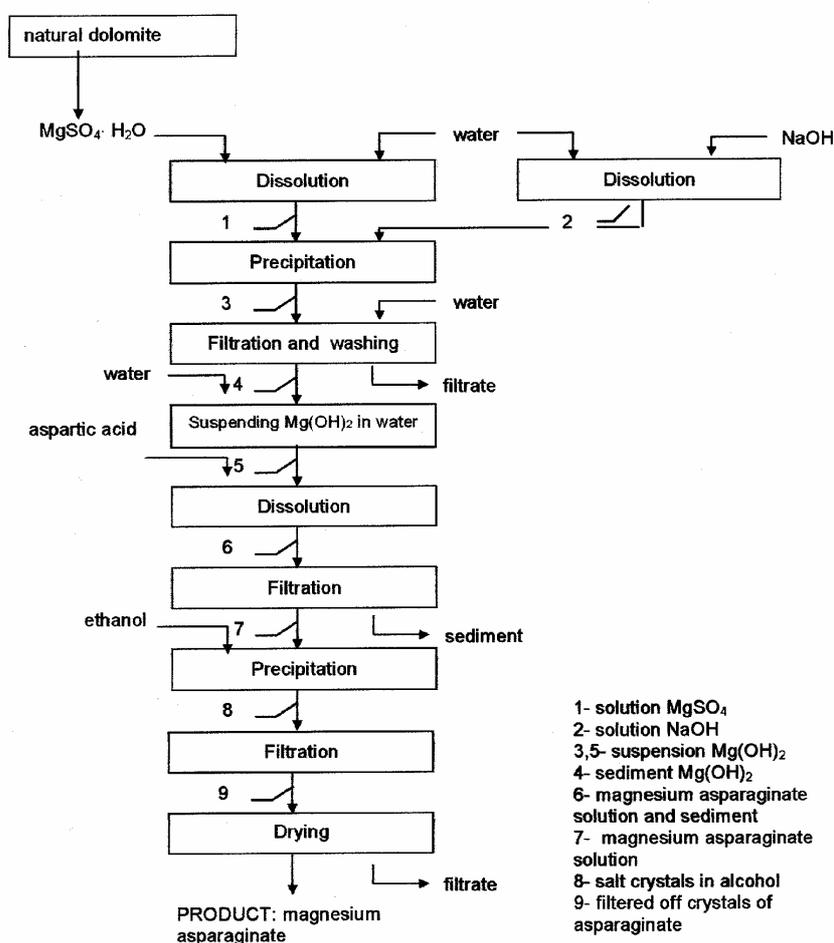


Fig. 1. Scheme of preparation of magnesium acetate

Preparation of magnesium acetate $(\text{CH}_3\text{COO})_2\text{Mg}\cdot 4\text{H}_2\text{O}$

Basic magnesium carbonate (5.5 g) suspended in a small amount of distilled water was added batchwise into 32 cm³ of stirred 20% acetic acid solution to obtain a slightly alkaline solution. The mixture was filtered, concentrated to a thick syrup consistency and dried in the dryer at 70° C for 6 h. The product was refined and dried at 100° C for 1 h. 10.5 g magnesium acetate was obtained at the reaction yield 95% (Fig. 1).

Preparation of magnesium citrate $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2\cdot 9\text{H}_2\text{O}$

4.5 g of basic carbonate were added batchwise into 6 g of citric acid dissolved in 20 cm³ distilled water and stirred to give a slightly alkaline solution. Solution was filtered, then magnesium citrate was precipitated by dropping 80 cm³ of 96% ethanol and stirring. Magnesium citrate precipitates as a resin. The precipitate was filtered, washed with ethanol and dried at room temperature. 10.5 g of magnesium citrate was obtained at the yield 70% (Fig. 2).

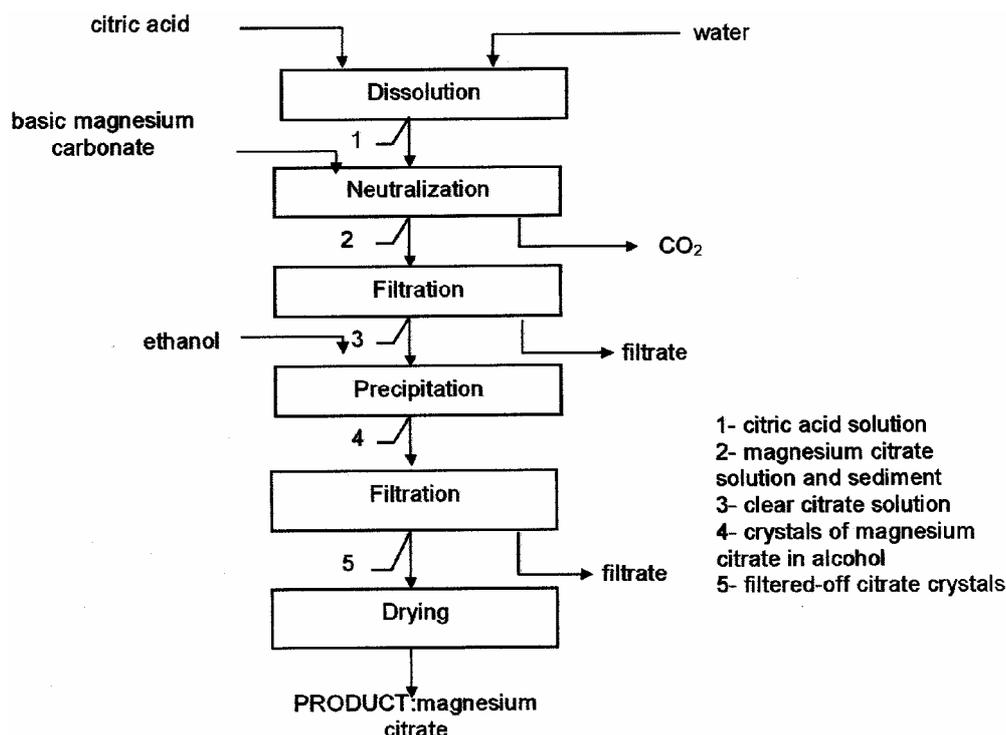


Fig. 1. Scheme of preparation of magnesium citrate

Preparation of magnesium aspartate $[\text{HOOCH}(\text{NH}_2)\text{CH}_2\text{COO}]_2\text{Mg}\cdot 4\text{H}_2\text{O}$

Sodium hydroxide solution (1.2g, 10 cm³ H₂O) was dropped into stirred magnesium sulfate solution (2g MgSO₄·H₂O, 15 cm³ H₂O). The precipitate of magnesium hydroxide was filtrated and washed with distilled water in order to remove SO₄⁼ ions. Solution of aspartic acid solution (1.2g, 10 cm³ H₂O) was added to moist sediment Mg(OH)₂ suspended into 20 cm³ of distilled water. The final solution was treated with 96% ethanol (70 cm³) dropped in slowly at continuous stirring. Magnesium aspartate precipitates as a resin was ground with a glass rod. The obtained precipitate was filtered, washed with ethanol and dried at room temperature. 2.5 g of magnesium aspartate was obtained at the reaction yield 75.8% (Fig. 3).

THE ASA AND THERMOGRAVIMETRIC ANALYSES

Quality and composition of preparations

The quantitative composition (mainly a number of crystalization water molecules) of the final preparations was determined from the thermal analysis while the contents of trace elements were determined with AAS-3 spectrophotometer. Content of Ca, Fe, Zn, Mn, Pb, Cu, Ni, Cd, Cr and Sr are shown in Table 3 (Stefaniak et al., 2000).

Table 3. Results of AAS analysis of produced compounds

Compound	Content, ppm									
	Ca	Fe	Zn	Mn	Pb	Cu	Ni	Cd	Cr	Sr
Magnesium sulfate	277	6.68	0.86	17.5	<0.10	<0.03	<0.05	<0.02	<0.05	<0.10
Basic magnesium carbonate	2044	24.6	10.5	97.0	<0.10	<0.03	<0.05	<0.02	<0.05	<0.10
Magnesium acetate	1396	7.6	2.45	1.47	<0.10	<0.03	<0.05	<0.02	<0.05	<0.10
Magnesium asparaginate	112	17.8	15.6	16.8	<0.10	<0.03	<0.05	<0.02	<0.05	<0.10
Magnesium citrate	1289	22.0	23.7	84.0	<0.10	<0.03	<0.05	<0.02	<0.05	<0.10

From Table 3 it follows that there a very low content of Pb, Cu, Ni, Cd, Cr and Sr were found. Their concentrations were below the detection limit, so that our preparations might be called *spectral purity* compounds.

Decomposition of magnesium compounds

Studies of mechanism and kinetics of decomposition of the magnesium compounds were carried out with derivatograph Q-1500 D. A conventional method was applied (platinum measuring crucibles) at the rate of heating 10 °/min. Temperature T, mass loss TG, differential DTG as well as DTA curves were registered. Figures 4-7 present thermal analysis curves for magnesium acetate, citrate and aspartate, respectively. On the DTG and DTA curves one can observe peaks or inflexions resulting from the stage decomposition of the compounds due to the sample heating. The peaks on the DTG curves are very distinct and of good resolving power. They a 3-stage decomposition processes of studied compounds result from:

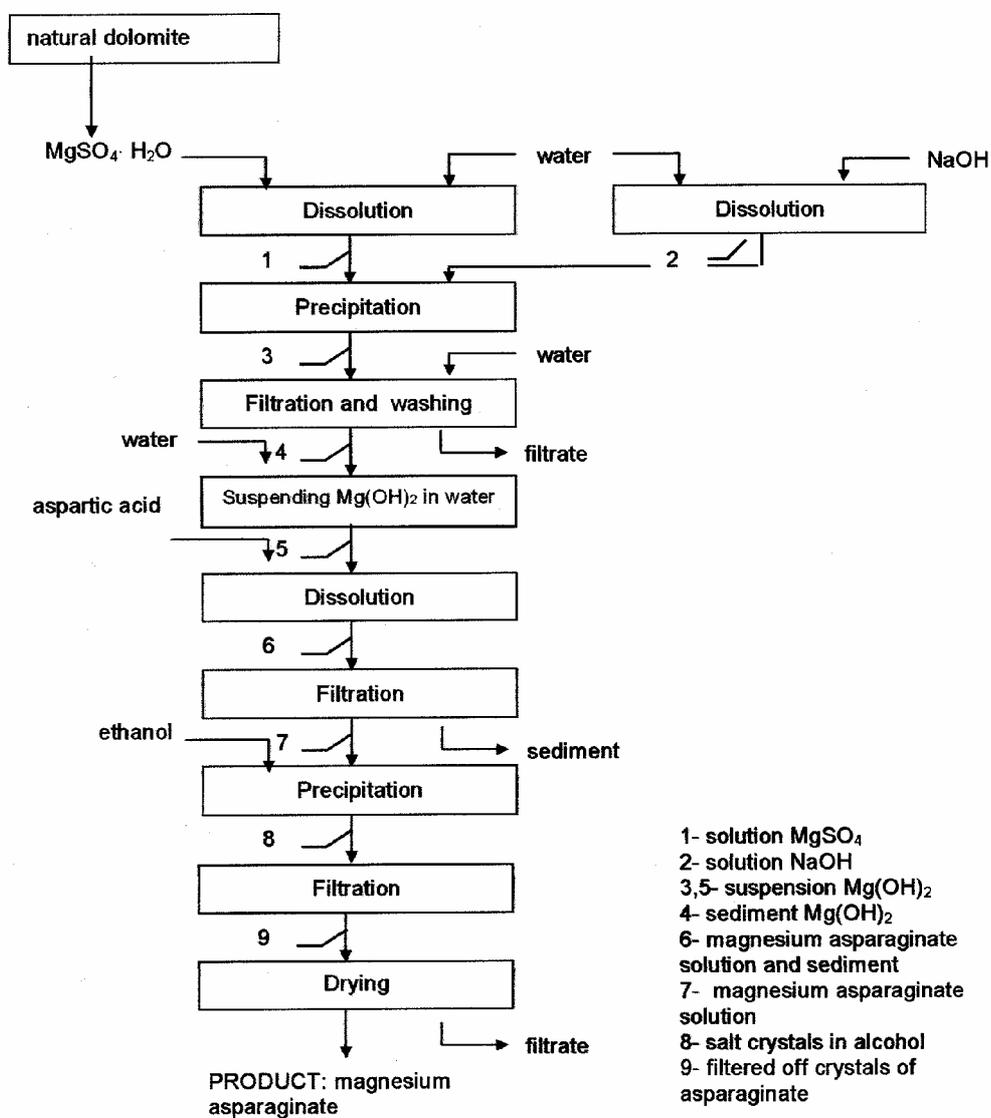
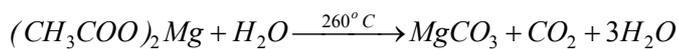


Fig. 3. Scheme of preparation of magnesium asparaginate

a) decomposition of magnesium acetate (Fig. 4):



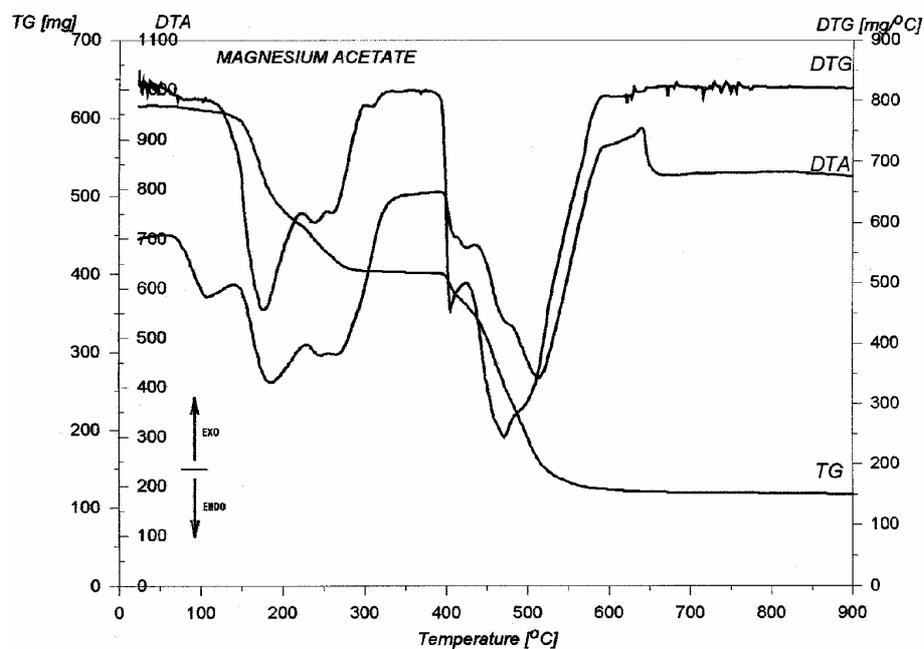
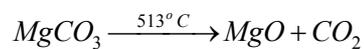
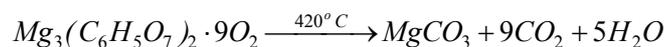
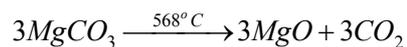
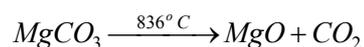
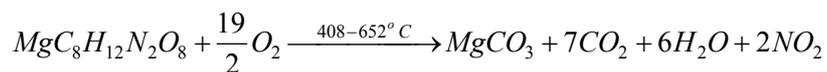
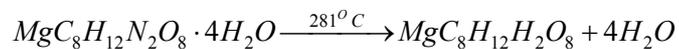


Fig. 4. Thermal decomposition of magnesium acetate

b) decomposition of magnesium citrate (Fig. 5):



c) decomposition of magnesium aspartate (Fig. 6):



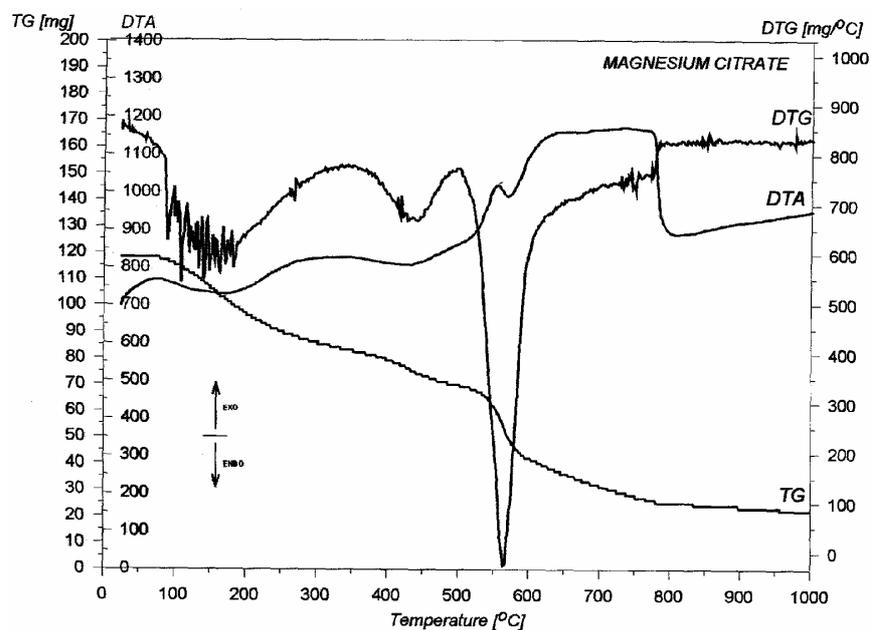


Fig. 5. Thermal decomposition of magnesium citrate

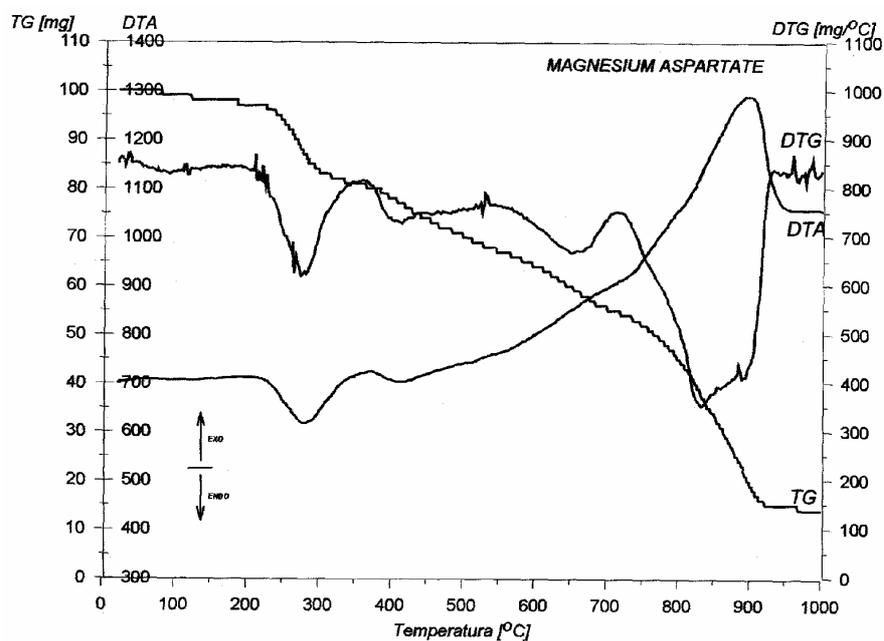


Fig. 6. Thermal decomposition of magnesium aspartate

It is worth to note that the second stage of decomposition of anhydrous aspartate proceeds in two steps within a wide temperature range (408-652 °C). Mechanism of this decomposition is very similar to that of thermal decomposition of hydrated calcium oxalate (a standard reagent used for calibration of derivatographs (MOM Instruction, 1980), which also proceeds in two stages in the temperature range from 425 to 533 °C. This may result from a similar chemical structure of both compounds (presence of carboxyl groups in a molecule).

CONCLUSIONS

As it comes from the above studies, simple method of synthesis of magnesium compounds synthesis from natural dolomite can be successfully applied to produce cheap preparations. Owing to their spectral purity, these organic magnesium compounds can be used as preparations counteracting magnesium incorporation of dangerous poisons by organisms.

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W pracy opisano prostą metodę otrzymywania cytrynianu, octanu i asparagianu magnezu z dolomitu naturalnego, która nie wymaga skomplikowanej aparatury. W pierwszym etapie dolomit został przekształcony w siarczan magnezu, a następnie w zasadowy węgiel magnezu, który poddano reakcji z kwasem cytrynowym lub octowym. Asparagian magnezu otrzymano po przeprowadzeniu siarczanu magnezu w wodorotlenek i po reakcji z kwasem asparaginowym. Śladowe zawartości metali ciężkich w otrzymanych preparatach określono metodą ASA. Ponadto, wykonano analizy rozkładu termicznego preparatów za pomocą derywatografu. Otrzymane wyniki badań mogą być użyteczne w opracowaniu metody produkcji magnezowych związków organicznych z krajowego dolomitu.