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THERMAL ANALYSIS FOR CONTROL OF THE PROPERTIES OF MINERAL FERTILIZERS

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Abstract

The development of equipment for thermal analysis has opened up new areas for applications in science, industrial practice and environment studies. On the basis of the literature and information from equipment producers, the directions for the use of thermal analysis in research and practice are classified. Special attention is paid to the possibilities of controlling environmental pollution, and the stability and other properties of intermediate and final industrial products. It is stressed that DSC and DTA systems can be successfully applied to determine enthalpy changes in raw materials and products as control tests for their application. The advantages of coupled thermal systems for complex studies and the control of raw materials, products and wastes are described.

Keywords: ammonium nitrate, ammonium sulphate, fertilizers, phosphates, thermal stability

Introduction

Thermal methods and equipment related have been improved in the past decade and logically their application is currently much wider than previously. The sensitivity and accuracy now available permit the use of thermal methods not only to determine the thermal properties and stabilities of pure compounds, but also to study the influence of impurities and very low quantities of special additives [1–9]. The advanced techniques involving electronic balances and thermogravimetric measurements can distinguish less than 0.01 mg, so it is not a problem to study even monocrystals. DTA and differential TG curves can reveal information on small quantities of volatile impurities in fertilizer products (individual or mixed), intermediates or by-products suitable for use as fertilizers [10–15]. The efforts in this direction started a number of years ago when Paulik's group introduced devices for water vapour measurements. Coupled systems increased the value of thermal analysis in studies relating to chemical safety, secondary pollution due to degradation processes, transformations of hazardous impurities, adsorption capacity and caking processes.

The objective of this work is to demonstrate the possibility of studying the transformations of certain impurities, during the thermal treatment of a new NPS fertilizer, and the heat released during the decomposition of fertilizer mixtures based on ammonium nitrate.

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Experimental

The new NPS fertilizer is produced in the pilot-scale installation at the University of Chemical Technology and Metallurgy, Sofia. The main raw materials are natural phosphate (NP) from Tunisia, urea (U) and acidic solution from methyl methacrylate (MMR) production. The ratio by mass of the components is NP:MMR:U=1:1:0.5. The initial mixture is treated in a triboreactor with a magnetic field [12] and next treated isothermally at 348 K for 2 h. The organic impurity residues in the produced fertilizer were studied by GC-MS techniques: Perkin Elmer GC PE 8700 and GC 8000+VG Quattro MS. CH_3OH and dichloromethane are used for extraction process. Mixtures of standard ammonium nitrate with ammonium sulphate and NPS fertilizer (different quantities) were investigated with a KL-10 calorimeter (produced in Poland), the total heat released during the process of thermal decomposition being determined. The total content of P_2O_3 in the NPS fertilizer was 25.3 mass%, 1.7 mass% N and 3.6 mass% S. Half of the total phosphorus was in citric acid soluble forms.

Results and discussions

The presence of organic impurities in the NPS fertilizer treated isothermally at 348 K was confirmed by mass spectroscopy (Figs 1 and 2). It is obvious that a number of harmful impurities remain in the fertilizer product; these compounds were success-

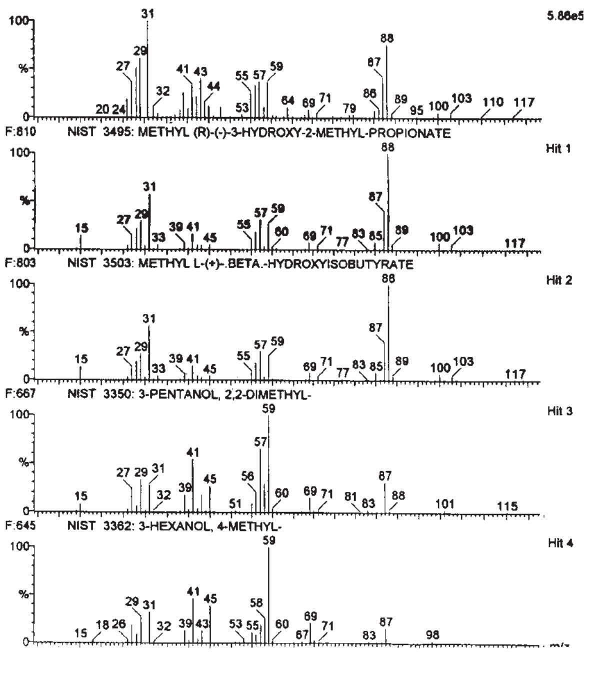

Fig. 1 Mass spectra of NP-fertilizer's impurities extracted with CH_3OH

fully determined through the use of coupled DG-MSS systems. Such impurities may create environmental problems following fertilizer application. Quite often, as in the present case, there are problems with equipment sensitivity, and even MSS techniques demand special care in order to identify most of the impurities. One possible way to decrease the amount of the impurities is thermal treatment of the initial or treated mixtures at higher temperatures. Another way is to use a different type of triboreactor and different treatment conditions. Both directions are subjects of ongoing studies.

The thermal stability of ammonium nitrate demands safety consideration when it is used as a fertilizer or as a component of different explosives. In some countries, for safety reasons the direct application of ammonium nitrate is restricted. Calorimetric studies on the decomposition and heat release are quite difficult because of the high corrosion activity of melted ammonium nitrate. With regard to this tendency, the aim of additive introduction is to avoid possible complications in calorimetric studies and to discover non-explosive fertilizer mixtures with ammonium sulphate, where the practical application of products will not run into safety restriction problems.

Table 1 DSC data on ammonium nitrate (AN)+ammonium sulphate (AS) mixtures

No.	Content/g		Temperature/K				Q/ kJ kg^{-1}
	AN	AS	T_1	T_2	T_3	T_4	
1	9.7	0.3	1.727	1.744	2.126	2.134	4668
2	9.7	0.3	1.629	1.650	2.054	2.063	4873
3	9.5	0.5	1.836	1.842	2.215	2.214	4789
4	9.5	0.5	1.729	1.751	2.138	2.147	4726
5	9.0	1.0	1.691	1.709	2.119	2.129	4873
6	9.0	1.0	1.671	1.697	2.166	2.183	4378
7	8.0	2.0	1.799	1.812	2.244	2.255	5183
8	8.0	2.0	1.970	1.997	2.426	2.434	5175
9	7.0	3.0	1.995	2.014	2.379	2.377	4697
10	7.0	3.0	1.810	1.828	2.243	2.243	4848
11	6.0	4.0	1.691	1.703	2.041	2.053	3892
12	6.0	4.0	1.926	1.945	2.332	2.349	4249
13	4.0	6.0	2.089	2.089	2.080	2.082	147
14	4.0	6.0	1.793	1.827	1.831	1.834	385

Tables 1–4 present experimental results on different mixtures of ammonium nitrate with NPS-fertilizer and ammonium sulphate. From the determined characteristic temperatures (T_1, T_2, T_3 and T_4) in the DSC curves, the total heat released (Q) is calculated. Tables 1 and 2 reveal a sharp decrease in the total Q when the ammonium sulphate or NPS content is about 30 mass%. When the ammonium sulphate content in the mixture with AN is 40 mass%, a high rate of decomposition is not observed and

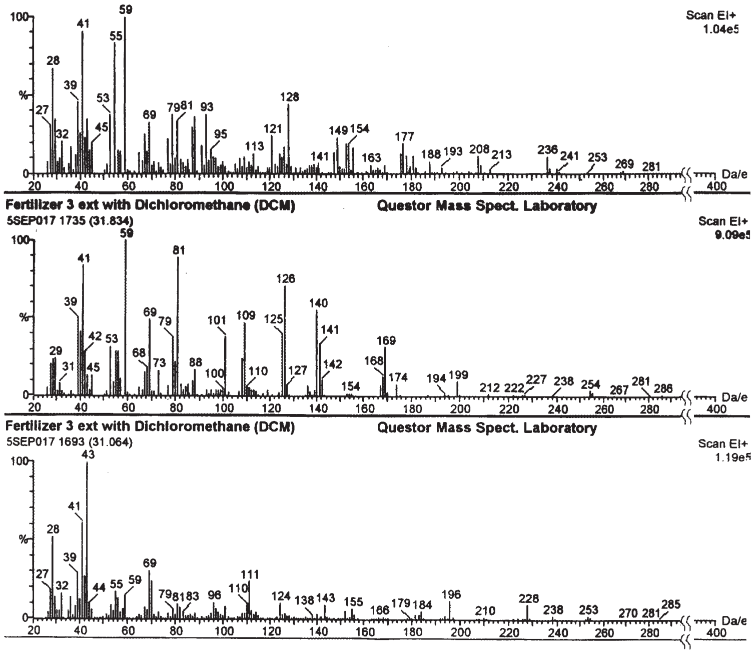

Fig. 2 Mass spectra of NP-fertilizer's impurities extracted with Dichloromethane

the DTA curves show that Q is very low. This means that, when mixtures with such additives are prepared ammonium nitrate can be safely applied as a fertilizer and can not be used illegally as an explosive component.

Table 2 Calorimetric data for AN – NPS-fertilizer mixtures

No.	Content/g		Temperature/K				Q/ kJ kg^{-1}
	AN	NPS	T_1	T_2	T_3	T_4	
1	9.7	0.3	1.831	1.845	2.256	2.266	4865
2	9.7	0.3	1.672	1.695	2.375	2.400	7764
3	9.5	0.5	1.781	1.802	2.243	2.261	4760
4	9.5	0.5	1.507	1.543	1.983	2.009	4617
5	9.0	1.0	1.780	1.820	2.259	2.281	4575
6	9.0	1.0	1.867	1.899	2.317	2.339	4487
7	8.0	2.0	1.782	1.787	2.157	2.170	4274
8	8.0	2.0	1.625	1.645	2.028	2.045	4241
9	7.0	3.0	1.542	1.555	2.019	2.014	4261
10	7.0	3.0	1.542	1.555	2.019	2.014	4068

Table 3 Standard deviation for measurements of AN-AS mixtures

No.	Q/ kJ kg^{-1}	Temperature/K				d/%	S_x/%
		T_1	T_2	T_3	T_4		
1	4768	1.681	1.704	2.103	2.089	2.15	3.04
2	4756	1.778	1.801	2.182	2.178	0.7	0.93
3	4626	1.678	1.703	2.142	2.163	5.34	7.56
4	5179	1.882	1.998	2.331	2.342	0.08	0.11
5	4772	1.904	1.921	2.314	2.311	1.6	2.23
6	4068	1.811	1.821	2.181	2.204	4.37	6.19
7	264	1.942	1.962	1.952	1.961	45	63.4

Our findings correspond fully to the standard test results for pure AN, AS and their mixtures. The statistical calculations (Tables 3 and 4) on the standard average deviation (d, S_x) confirm that the accuracy is mostly higher than 95% and it is sufficient for practical use and control. The significant change in Q facilitates a ready distinction of explosive from non-explosive mixtures.

Table 4 Standard deviation for measurements of AN+NPS mixtures

No.	Q/ kJ kg^{-1}	Temperature/K				d/%	S_x/%
		T_1	T_2	T_3	T_4		
1	6398	1.751	1.770	2.315	2.333	24	34
2	4688	1.644	1.672	2.113	2.135	1.52	2.15
3	4529	1.823	1.859	2.288	2.310	0.97	1.37
4	4257	1.703	1.716	2.092	2.107	0.39	0.56
5	4165	1.542	1.555	2.009	2.014	2.31	3.27

Conclusions

The results of these investigations demonstrate that different techniques of thermal analysis can be successfully used for the development of new environmentally friendly fertilizer technologies and for control of the safety properties of the fertilizers produced. Coupled analytical systems lend additional strength to the studies, and future extension of their application in this area is promising.

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