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APPLICATION OF THERMAL ANALYSIS FOR QUANTITATIVE NITROGEN DETERMINATION IN FERTILIZERS

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DSC and DTA techniques have been used to determine nitrogen present in the form of ammonium nitrate in fertilizers. The optimum conditions for the investigations were determined for both techniques. By determining peak area, i.e. the enthalpy of the ammonium nitrate crystal transformation II →I, it was possible to determine the nitrogen content in ammonium nitrate and in lime ammonium nitrate by DSC with average deviations of 0.44 and 0.91%, respectively. Using DTA and the enthalpy of the ammonium nitrate crystal transformation IV →III, the average deviation of nitrogen determination in lime/ammonium nitrate was 1.09%.

Ammonium nitrate is the most widely used nitrogen fertilizer and is the basic nitrogen component in mixed and complex fertilizers. In the USA and the USSR, technically pure salt is used as a nitrogen fertilizer, whereas in most European countries the material generally used is a granulated mixture of ground limestone or dolomite with ammonium nitrate, i.e. lime/ammonium nitrate, which contains 60–77% of ammonium nitrate.

The complexity of the fertilizer production process requires a very frequent control of the chemical composition of the product in the different production phases. The classical analytical methods for total nitrogen content determination, as fertilizer nutrient component, are based on the distillation procedure of Kjeldahl. As the distillation procedure takes a long time, the information on the fertilizer chemical composition, i.e. on its nitrogen content, is obtained after the fertilizer has already reached the storage stage.

This paper reports an attempt to determine the nitrogen present in the form of ammonium nitrate in fertilizer through the application of differential thermal analysis and differential scanning calorimetry.

In the temperature interval from $-20°$ to the melting temperature, 169.6°, ammonium nitrate exists in five stable crystal forms [1]. The crystal transformations from the rhombic into the monoclinic (IV →III), from the monoclinic into the trigonal (III →II) and from the trigonal into the cubic (II →I)

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form of ammonium nitrate are possible during the production, storage and transport of fertilizers; they occur at 32.3°, 84.1° and 125.2°, respectively. The enthalpies of these transformations are 19.89, 16.75 and 52.83 J/g, respectively [2–4].

During heating, the DTA curves of ammonium nitrate show the transformations IV →III →II →I and melting. Except for the temperature of the transformation IV →III, which appears, according to different authors, in the interval from 31° to 55°, the temperatures of the crystal transformations are in good accordance with the data in the literature [3, 5–13]. The DSC curves point to discrepancies in the temperatures and enthalpies of the ammonium nitrate crystal transformations IV →III and III →II [14–16]. The best agreement of the DTA and DSC curves has been observed for ammonium nitrate transformation II →I. Therefore, attempts have been made to use this transformation enthalpy to determine the ammonium nitrate content in fertilizers [17–18]. By determining the peak areas of the transformations IV →III, III →II, II →I and melting from the DTA curves, it is possible to calculate the enthalpies of all the transformations, and on the basis of the enthalpies the nitrogen contents of fertilizers that contain ammonium nitrate. From the DSC curves, the enthalpy and hence the nitrogen content determination is possible only for the ammonium nitrate crystal transformation II →I.

Experimental

The investigations were carried out with ammonium nitrate p.a. from Merck (Table 1), with samples of lime/ammonium nitrate, a commercial fertilizer, immediately after production (Table 2) and with samples of lime ammonium nitrate prepared under laboratory conditions (Tables 3 and 4).

The ammonium nitrate p.a. samples contained 0.12% of moisture. The samples of lime/ammonium nitrate contained calcium nitrate as a result of unwanted reaction between ammonium nitrate and limestone, and ammonium sulphate which had been added to the melt of ammonium nitrate to inhibit this reaction. The content of calcium nitrate in lime ammonium nitrate usually ranges between 0.50 and 1.70%, while that of ammonium sulphate is 0.15%. The varying calcium nitrate contents point to the disturbance of the production process. We have investigated some such samples to establish the influence of high contents of calcium nitrate on the enthalpies of ammonium nitrate crystal transformations, i.e. the nitrogen contents.

The third series of investigated samples were samples of lime ammonium nitrate prepared in the laboratory with approximately the same calcium nitrate contents, but without ammonium sulphate, and with different limestone grain sizes, in order

Table 1 Nitrogen contents in the samples of ammonium nitrate determined according to the enthalpy of the transformation II →I on the DSC (vessel for solid sample)

Sample no.	Nitrogen contents determined by DSC %, mass	Conditions on the DSC	Deviation	
			average, %	standard, %
1	34.50			
2	34.75	4 deg/min	0.44	±0.72
3	34.40	R=16		
4	33.44			
5	33.95			
6	35.28			
7	34.72	8 deg/min	0.68	±0.82
8	33.74	R=8		
9	33.65			
10	33.85			
11	33.97			
12	32.79	16 deg/min	0.85	±1.19
13	34.23	R= 8		
14	34.21			

to investigate the influence of the limestone grain size on the enthalpies of ammonium nitrate crystal transformations. Sample I in Tables 3 and 4 is an ammonium nitrate sample subjected to the same thermal pre-treatment as that for the samples of lime/ammonium nitrate in the same Tables.

The DSC investigations were carried out on a Perkin–Elmer differential scanning calorimeter model DSC–1B, for the first two series of samples, in the interval from ambient temperature to 160°. The heating rate was 4, 8 or 16 deg/min and the sensitivity was 16 or 8 mcal/min in a dynamic atmosphere of nitrogen and in the vessels for solid or volatile samples. The mass of the sample lay in the interval 10–22 mg.

Differential thermal analysis was carried out on a derivatograph (MOM) in the interval from ambient temperature to 250°, at a heating rate of 2.5, 5 or 10 deg/min at a TG sensitivity of 200 mg, in a small platinum crucible and in a static atmosphere of air. The mass of the samples ranged from 240 to 280 mg.

DTA was used only for the samples prepared in the laboratory. Because of the different cooling conditions in the bulk of the sample, there was a possibility of crystal inhomogeneity, and in order to get better and more correct results we used a larger sample and the DTA technique.

Potassium nitrate crystal transformation, silver nitrate melting and $BaCl_2 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$ and $CaSO_4 \cdot 2H_2O$ dehydration were used for derivatograph constant determination, and indium melting for the calorimeter constant.

Table 2 The results of nitrogen contents determination in the lime ammonium nitrate from industrial production by the DSC analyses (heating rate 8 deg/min, sensitivity R = 8 mcal/min)

Sample	Chemical analysis of samples, %				N, % by DSC	Deviation	
	N	$Ca(NO_3)_2$	H_2O	SO_4		aver., %	stand., %
a) vessels for solid sample							
1	32.23	1.17	0.39	0.09	34.62		
2	27.30	1.42	0.46	0.11	27.56		
3	27.09	1.57	0.44	0.11	29.13		
4	27.32	1.67	0.48	0.09	27.00		
5	26.26	1.70	0.49	0.13	28.11	2.32	±3.01
6	29.11	1.71	0.46	0.10	31.10	1.56*	±1.88*
7	28.20	1.87	0.50	0.14	30.44		
8	26.72	1.87	0.37	0.13	28.96		
9	27.44	4.02	0.69	trace	32.45		
10	26.40	4.07	0.62	trace	32.05		
* deviations for the samples from 1–8							
b) vessels for volatile sample							
1	27.34	0.65	0.46	0.38	26.39		
2	28.34	0.77	0.38	0.14	28.89		
3	27.71	0.98	0.41	0.19	27.50		
4	28.27	0.89	0.44	0.09	26.23		
5	27.29	1.12	0.38	0.09	26.64		
6	26.60	1.17	0.59	0.13	27.50		
7	27.99	1.18	0.53	0.08	27.56	0.99	±1.24
8	26.94	1.22	0.63	0.12	26.30		
9	26.59	1.37	0.45	0.09	25.47		
10	27.57	1.37	0.64	0.08	25.56		
11	25.40	1.44	0.45	0.09	27.43		
12	25.50	1.58	0.73	0.08	26.08		
13	28.13	1.66	0.49	0.05	26.14		
14	27.19	2.60	0.74	0.02	26.62		

Results and discussion

From the enthalpy of the ammonium nitrate crystal transformation II →I, the contents of nitrogen were determined by DSC at different heating rates. The result of chemical analysis (34.65% of nitrogen for the ammonium nitrate sample) was taken as the real nitrogen content of the samples investigated.

Table 3 Lime ammonium nitrate samples composition, synthetized in the laboratory and grain size of calcium carbonate used

Sample	NH_4NO_3	$CaCO_3$	$Ca(NO_3)_2$	H_2O	N	Grain size of used $CaCO_3$ μm
	%	%	%	%	%	
I	99.70	—	—	0.30	34.90	—
II	76.64	22.55	0.51	0.30	26.42	−250+149
III	76.49	22.48	0.67	0.36	26.77	−149+ 74
IV	76.40	22.55	0.76	0.29	26.74	− 74+ 43
V	76.33	22.56	0.83	0.28	26.72 30	− 43+ 30
VI	76.22	22.49	0.94	0.35	26.68	− 30

The results of nitrogen determination by DSC at different heating rates show the absolute error to vary from −1.84 to +0.63% [19–20]. With increase of the heating rate from 4 to 16 deg/min, the average deviation increases from 0.44 to 0.85%, and the standard deviation from 0.72 to 1.19% (Table 1).

Nitrogen determination on the industrially produced lime ammonium nitrate samples was carried out in the vessels for solid and volatile samples with the same heating rate and sensitivity conditions.

For each sample of lime ammonium nitrate, a complete chemical analysis was performed to determine the real nitrogen content, in order to explain the influence of chemical composition changes on nitrogen determination results by DSC.

The absolute error in the nitrogen determination by DSC ranges in the interval from −0.23 to +5.65% in the vessel for solid sample, and from −2.04 to +2.03% in the vessel for volatile sample. The average deviation amounts to 2.32% and 0.99%, respectively, in vessels for solid and volatile samples (Table 2).

Analysis of the results obtained shows extremely high absolute errors of 5.01 and 5.65% for two lime ammonium nitrate samples. They contain 4.02 and 4.07% of calcium nitrate, which is unusually high for fertilizer. If these two results are excluded, then the absolute error in the vessel for solid sample ranges from −0.23 to 2.39%, with an average deviation of 1.56%, and a standard deviation of ±1.88%.

Further investigations of the influence of calcium nitrate on ammonium nitrate behaviour during thermal analysis showed that the presence of calcium nitrate reduces the ammonium nitrate melting temperature. The melting process begins before the crystal transformation finishes, and the peaks of melting and crystal transformation overlap, which causes the error in peak area determination, i.e. in transformation enthalpy and nitrogen content (Fig. 1).

From the nitrogen determination results by DSC on the same sample of lime ammonium nitrate, the reproducibility of the method was determined. For ten

Table 4 The results of nitrogen contents determination in ammonium nitrate and in lime ammonium nitrate prepared in laboratory conditions by the DTA analysis

Sample	N cont., % determ. by DTA IV →III	Abs. error, %	Rel. error, %	N cont., % determ. by DTA III →II	Abs. error, %	Rel. error, %	N cont., % determ. by DSC II →I	N cont., % determ. by DTA II →I	Abs. error, %	Rel. error, %	N cont., % determ. by DTA melt	Ab. error, %	Rel. error, %
I	27.49	−7.41	−21.23	42.79	+7.89	22.61	33.00	37.40	+2.50	7.16	46.52	+11.62	33.30
	37.17	+2.27	6.50	41.29	+6.39	18.31		34.56	−0.34	0.97	41.52	+6.62	18.97
II	25.73	−1.09	4.06	26.98	+0.16	0.60	26.16	23.31	−3.51	13.09	25.62	−1.20	4.47
	26.44	−0.38	1.42	27.96	+1.14	4.25		22.51	−4.31	16.07	25.81	−1.01	3.77
III	26.99	+0.22	0.82	27.83	+1.06	3.96	24.56	22.72	−4.05	15.13	24.81	−1.96	7.32
	27.93	+1.16	4.33	27.72	+0.95	3.55		22.76	−4.01	14.98	26.39	−0.38	1.42
IV	23.62	−3.17	11.83	25.28	−1.51	5.64	24.24	21.35	−5.44	20.31	22.95	−3.84	14.34
	26.84	+0.05	0.19	26.36	−0.43	1.61		21.27	−5.52	20.60	22.11	−4.68	17.47
V	29.18	+2.46	0.21	28.63	+1.91	7.15	24.50	21.81	−4.91	18.38	20.37	−6.35	23.76
	27.60	+0.88	3.29	27.81	+1.09	4.08		22.67	−4.05	15.16	24.41	−2.31	8.64
VI	28.15	+1.47	5.51	25.55	−1.13	4.24	24.18	18.09	−8.59	32.20	21.22	−5.46	20.46
	26.62	−0.06	0.22	28.96	+2.28	9.55		18.87	−7.81	29.27	18.05	−8.63	32.35
Average deviation for lime ammonium nitrate, %		1.09			1.17				5.22			3.58	
Standard deviation for lime ammonium nitrate, %		±1.55			±1.38				±5.76			±4.63	

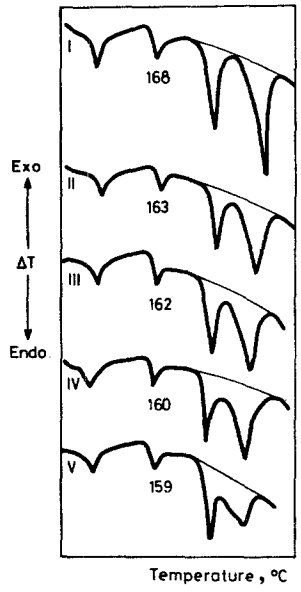

Fig. 1 DTA curves of NH_4NO_3 in the presence of increasing amount of $Ca(NO_3)_2$

different industrial samples of lime ammonium nitrate, ten nitrogen determinations were carried out in the vessel for volatile samples. The standard deviation of these determination ranged from ± 0.44 to ± 1.24%.

For nitrogen determination in ammonium nitrate and lime ammonium nitrate by means of DTA, the enthalpies of crystal transformations IV →III, III →II, II →I and ammonium nitrate melting were used (Table 4). As we expected, the absolute errors in these determinations are far bigger than those for DSC, and range from −8.63 to +11.62%.

Analysis of the results obtained reveals the differences in behaviour between the samples of lime ammonium nitrate and the sample of ammonium nitrate undergoing the same pre-treatment as the lime ammonium nitrate. The average deviation in the determination of the nitrogen content in ammonium nitrate is less only for the transformation II →I enthalpy, at 1.42%, while tie average deviations for the lime ammonium nitrate samples are 1.09, 1.17, 5.22 and 3.58% for the enthalpies of crystal transformations IV →III, III →II, II →I and melting, respectively. The reason for such behaviour may be the different heat transfer in the sample of lime ammonium nitrate.

The increase in the absolute error with decrease of the limestone grain size is distinctly noticeable for samples II to VI. Such behaviour can be explained by the reaction of ammonium nitrate with solid calcium carbonate. As the limestone grain size decreases, the contact surface between the ammonium nitrate and the calcium

carbonate increases, which speeds up their reaction, increasing the calcium nitrate content. The use of a platinum crucible, which accelerates the reaction of ammonium nitrate with calcium carbonate during thermal analysis, together with the calcium nitrate content, may be the causes of error in determination of the enthalpies of crystal transformation II →I and melting for ammonium nitrate.

Conclusions

Investigation of the possibility of applying DTA and DSC analysis for determination of the nitrogen content in ammonium nitrate and in lime ammonium nitrate from the crystal transformation enthalpy has led to the following results:

1. DSC analysis can be applied for nitrogen content determination via the enthalpy of ammonium nitrate crystal transformation II →I. The sample for such determinations should be packed into the vessel for volatile samples, its mass should be about 10 mg, and the heating rate should not be higher than 4 deg/min.

2. DTA analysis can be applied for nitrogen content determination in ammonium nitrate and lime ammonium nitrate, but only via the enthalpy of ammonium nitrate crystal transformation IV →III. A small platinum crucible should be used, with a heating rate of 2.5 deg/min.

3. The absolute error in the nitrogen determination in lime/ammonium nitrate by DTA under the given conditions ranges from −3.17 to +2.46%, and its average deviation is 1.09%.

4. The absolute error in the nitrogen determination in ammonium nitrate by DSC under the conditions of investigation ranges from −1.84 to +0.63%; the average deviation ranges from 0.44 to 0.85%, and increases with increase of the heating rate.

5. The absolute error in the nitrogen determination in lime ammonium nitrate by DSC under the conditions of investigation ranges from −2.04 to +2.03%, and the average deviation is 0.99%.

6. The method reproducibility, on the basis of the standard deviation ranges in the interval from ±0.44 to ±0.97%.

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Zusammenfassung — DSC und DTA wurden zur Bestimmung des in Düngemitteln in Form von Ammoniumnitrat vorliegenden Stickstoffs benutzt. Für beide Techniken wurden die optimalen Untersuchungsbedingungen ermittelt. Durch Bestimmung der Peakfläche, d. h. der Enthalpie der Kristalltransformation II →I des Ammoniumnitrats konnte der Stickstoffgehalt in Ammoniumnitrat und in Kalk/Ammoniumnitrat mittels DSC mit mittleren Abweichungen von 0.44 bzw. 0.91% bestimmt werden. Aus der Kristalltransformation IV →III des Ammoniumnitrats ergibt sich bei Benutzung der DTA-Methode eine mittlere Abweichung von 1.09% für die Stickstoffbestimmung in Kalk/Ammoniumnitrat.

Резюме — Использованы методы ДСК и ДТА для определения азота, находящегося в удобрениях в форме нитрата аммония. Установлены оптимальные условия определения азота. Путем определения площади пика, например, энтальпии фазового превращения (II →I) нитрата аммония, представилось возможным методом ДСК определить содержание азота в нитрате аммония и смеси известь — нитрат аммония. Среднее отклонение составляло, соответственно, 0,44 и 0,91%. При использовании метода ДТА и энтальпии фазового превращения IV →III нитрата аммония, среднее отклонение при определении азота в смеси известь-нитрат аммония составляло 1,09%.