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Analysis of $(NH_4)_2SO_4$/$(NH_4)H_2PO_4$ mixtures by thermogravimetry and X-ray diffraction

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Abstract

$(NH_4)_2SO_4$ and $(NH_4)H_2PO_4$ are the principal components in the powder material used in fire extinguishers. In this paper the mutual influence in their thermal decomposition is investigated by thermogravimetry. Two methods for the quantification of both salts in mixtures $(NH_4)_2SO_4$/$(NH_4)H_2PO_4$ are proposed. The first employs thermogravimetry and is based on the measurement of the mass fraction in the 500–550 °C interval, once $(NH_4)_2SO_4$ has totally decomposed to yield gaseous products. The second uses some selected peaks in the X-ray diffractogram.

Keywords: Thermogravimetry; Fire extinguishers; X-ray diffraction

1. Introduction

$(NH_4)_2SO_4$ and $(NH_4)H_2PO_4$ are compounds of considerable economic and industrial importance. Both of them are extensively used as fertilizers or as fertilizer components [1]. These salts are also the principal components in the powder material used in fire extinguishers [2,3]. The thermal decomposition of $(NH_4)_2SO_4$ [4] and $(NH_4)H_2PO_4$ [5,6] are well established and the thermal behaviours of mixtures of $(NH_4)H_2PO_4$ with some inorganic salts or urea have been reported [1,7]. However, the thermal decomposition of mixtures of $(NH_4)_2SO_4$/$(NH_4)H_2PO_4$ has not been investigated.

In this paper the mutual influence of both salts on their thermal decomposition has been studied. Quantitative chemical analysis of $(NH_4)_2SO_4$/$(NH_4)H_2PO_4$ is time consuming and we present here two alternative instrumental analysis methods that yield simultaneously the amount of $(NH_4)_2SO_4$ and $(NH_4)H_2PO_4$ in a mixture, by simple applications of thermogravimetry and X-ray diffraction.

2. Experimental

Representative samples of $(NH_4)_2SO_4$ and $(NH_4)H_2PO_4$ used as raw materials in powder fire extinguishers were ground on a Retsch RM 100 mortar grinder to less than 20 μm diameter and mixed.

2.1. Thermogravimetry

TG and DTG curves were recorded on a Shimadzu TGA-50 thermobalance. The atmosphere used in different experiments was an air flow ($50\,mL\,min^{-1}$). The heating rate was $10\,°C\,min^{-1}$ with a sample mass range of 10.5–14.5 mg, and crucibles of alumina were employed. The evolved products were analyzed by connecting the thermobalance with a spectrophotometer FT-IR Nicolet 550.

2.2. X-ray diffraction

Powder diffraction patterns were recorded on a Bruker D8 Advance diffractometer. The 2θ range was 5–70° with a step of 0.02° and a step time of 2 s, Cu Kα radiation was used. The divergence, antidivergence and reception slits were 2, 2 and 0.2 mm, respectively. The material used as a standard was commercial ZnO (Panreac) dried at 130 °C during 12 h, the proportion of standard in all the mixtures was 20 wt%.

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Table 1
TG and DTG data for $(NH_4)_2SO_4$ and $(NH_4)H_2PO_4$ and mixtures of both salts

Compound	Stage	T range (°C)	DTG_{max} (°C)	Step
$(NH_4)_2SO_4$	1	215–334	304	1S
	2	334–460	416	2S
$(NH_4)H_2PO_4$	1	50–120	88.2	1P
	2	150–200.5	196.5	2P
	3	202–330	210.5	3P
	4	330–420	372.1	4P
	5	420–520	448.2	5P
	6	520–766	635.0	6P
	7	766–990	863.0	7P
20P/80S	1	50–130	80.6	1P
	2	158–240	202.5	2P (includes 3P)
	3	240–340	307.3	1S
	4	340–490	417.1	2S
	5	740–980	835.0	7P
40P/60S	1	50–130	84.2	1P
	2	130–220	197.3	2P (includes 3P)
	3	220–330	294.5	1S
	4	330–500	398.7	2S
	5	730–940	830	7P
60P/40S	1	52–133	87.9	1P
	2	133–225	197.6	2P (includes 3P)
	3	225–334	287.1	1S
	4	334–528	414.4	2S (includes 4P and 5P)
	5	600–774	639.6	6P
	6	774–975	839	7P
80P/20S	1	50–130	85.2	1P
	2	140–202	198	2P
	3	202–223	216.5	3P
	3	223–320	238.88	1S
	4	320–528	386	2S (includes 4P and 5P)
	5	528–774	644	6P
	6	774–980	862	7P

3. Results and discussion

The thermal decomposition of $(NH_4)H_2PO_4$ has been described [5] as taking place in several stages with loss of ammonia and water (Table 1), involving a polycondensation process that yields a variety of polymers. Thermal dissociation above 100 °C leads to the regular liberation of ammonia while water of constitution begins to be liberated at 170 °C and evolution increases sharply at 220 °C (the maximum quantity of combined water is liberated in the range 220–350 °C). At 600 °C, intensive decomposition of the polycondensation products begins, accompanied by a rapid loss in mass as can be seen on the TG curve. Fig. 1 shows the TG–DTG curve of the thermal decomposition of $(NH_4)H_2PO_4$ in dynamic air atmosphere at 10 °C/min.

Ammonium sulphate decomposes by heating in two stages [4] that can be summarized as:

$$2(NH_4)_2SO_4\,(s) \rightarrow (NH_4)_2S_2O_7 + 2NH_3\,(g) + H_2O\,(g) \quad (1)$$

$$3(NH_4)_2S_2O_7 \rightarrow 2NH_3\,(g) + 6SO_2\,(g) + 2N_2\,(g) + 9H_2O\,(g) \quad (2)$$

Fig. 1 shows the TG–DTG curve of the thermal decomposition of $(NH_4)_2SO_4$ in dynamic air atmosphere at 10 °C/min.

The nature of the evolved gases was confirmed by the IR frequencies: 1152 cm^{-1} for SO_2; 1595, 3652 and 3756 cm^{-1} for H_2O; 932, 968 and 1628 cm^{-1} for NH_3.

3.1. Thermal decomposition of $(NH_4)_2SO_4$/$(NH_4)H_2PO_4$ mixtures

In order to study the thermal decomposition of mixtures of ammonium sulphate (hereafter S) and ammonium dihydrogen orthophosphate (hereafter P) samples containing different mass proportions (20P/80S, 40P/60S, 60P/40S and 80P/20S) of these salts were analyzed by thermogravimetry in air atmosphere at 10 °C/min. The results are shown in Fig. 2 and Table 1.

The mixtures exhibit complex TG curves but they can be usefully compared using the temperatures of maximum decomposition rate (DTG_{max}). As can be seen in Table 1 pure $(NH_4)_2SO_4$ shows two maxima in the DTG curve while pure $(NH_4)H_2PO_4$ exhibits seven maxima in the range studied. In the mixture with the highest proportion of $(NH_4)_2SO_4$ the two maxima of ammonium sulphate can be easily recognized, while only three maxima belonging to the decomposition of $(NH_4)H_2PO_4$ are

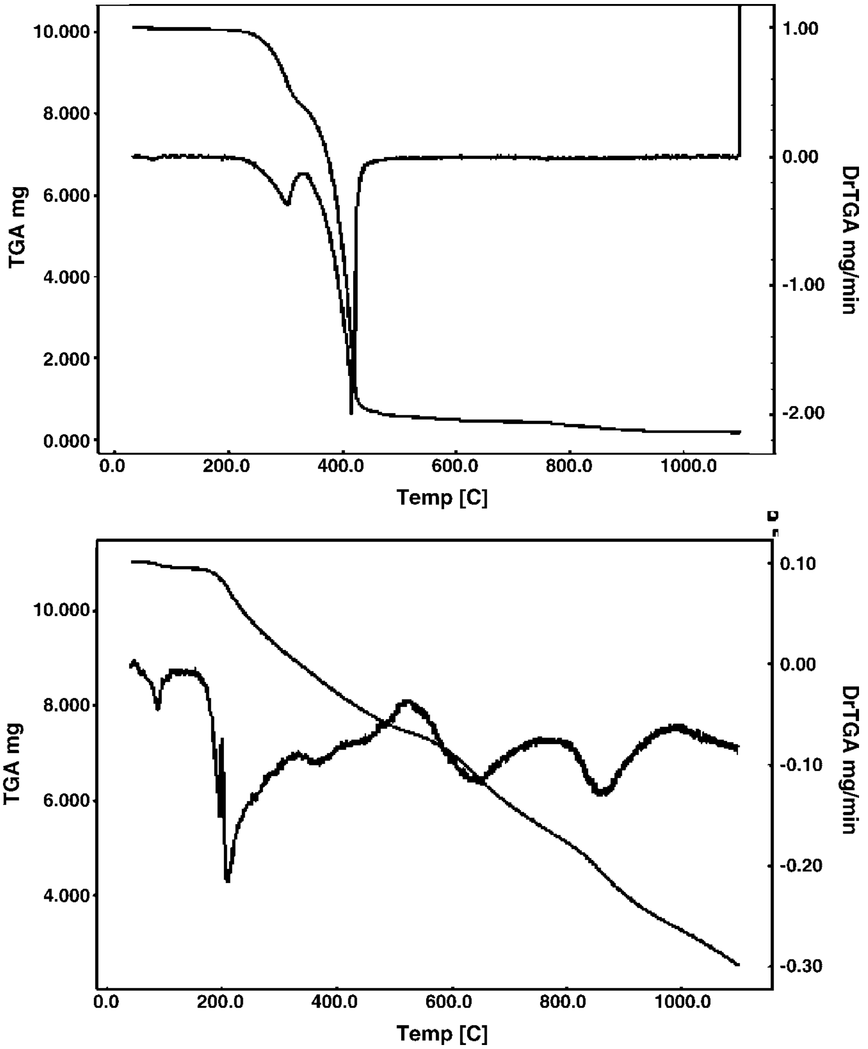

Fig. 1. TG and DTG curves of $(NH_4)_2SO_4$ (top) and $(NH_4)H_2PO_4$ (bottom).

observed. Similar features are detected in the decomposition of the 40P/60S. In mixtures having a $(NH_4)H_2PO_4$ proportion higher than 50% it is possible to recognize the phosphate maximum that appears around 640 °C. In all the cases maxima 4P and 5P are overlapped with the second stage from the ammonium sulphate decomposition.

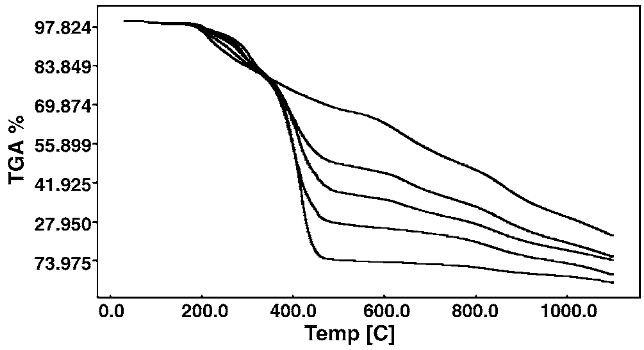

Fig. 2. TG curves of $(NH_4)H_2PO_4/(NH_4)_2SO_4$ mixtures (20P/80S, 40P/60S, 60P/40S and 80P/20S) and pure $(NH_4)H_2PO_4$.

As can be seen in Fig. 2 and Table 1 no significant mutual influence on the peak positions of sulphate or phosphate are observed. In addition, it is also important to note that the last stage in the decomposition of $(NH_4)H_2PO_4$ (step 7P in Table 1) is present in all the mixtures.

3.2. Thermogravimetric quantitative analysis of mixtures $(NH_4)_2SO_4/(NH_4)H_2PO_4$

As can be seen in Fig. 1 the thermal decomposition of $(NH_4)_2SO_4$ is complete at 500 °C without any mass residual (the products of decomposition are gaseous). The TG curves of mixtures (Fig. 2) in the 500–550 °C range are approximately parallel and there is a linear correlation between the mass of this fraction and the amount of phosphate in the sample at any temperature in that interval. As an example Fig. 3 shows the plot of mass fraction versus initial phosphate fraction at 515 °C, the linear coefficient correlation being 0.9928.

An alternative method of calculating the mass of $(NH_4)H_2PO_4$ in the sample is the mass loss in the step 7P using the 7P step in pure $(NH_4)H_2PO_4$ as reference.

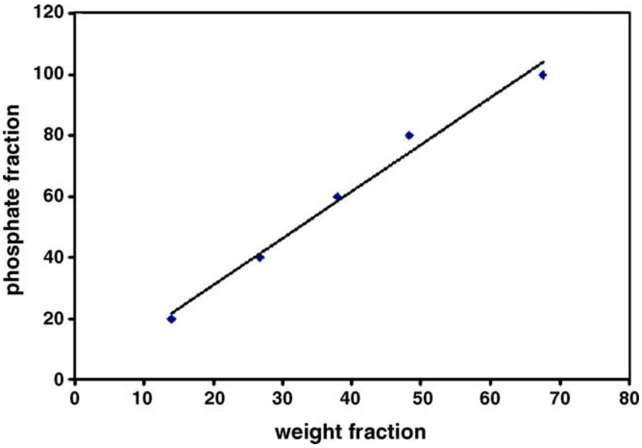

Fig. 3. Plot of mass fraction vs. phosphate fraction at 515 °C.

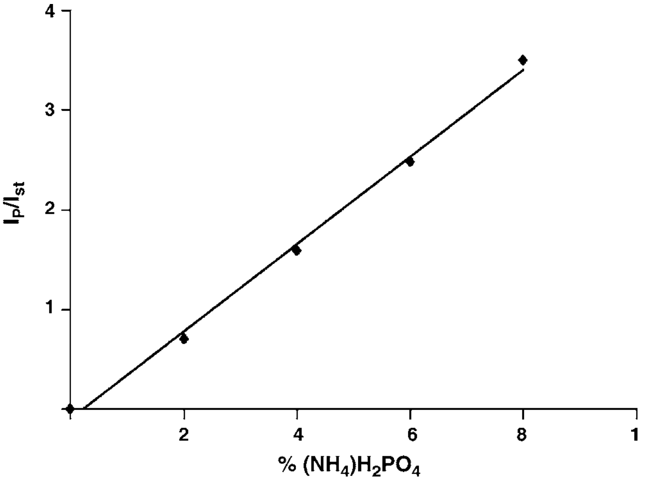

Fig. 5. Calibration curve of $(NH_4)H_2PO_4$.

3.3. Quantitative X-ray diffraction

The presence of impurities in the sample may decrease the accuracy of the thermogravimetric analysis described above. An alternative method for fast and simple quantitative analysis is X-ray diffraction.

Quantitative methods of analysis based on X-ray diffraction have been described using selected peaks or whole fitting pattern [8]. The whole-pattern fitting approach is capable of greater accuracy and precision but some peak-intensity methods are faster and require less computing time.

In the internal standard method [9] the intensity of a diffraction line from the phase being determined is compared with a line from a standard substance mixed with the sample in known proportions. In the mixture studied in this paper the chosen standard was ZnO in a proportion of 20 wt%. Fig. 4 shows the diffractogram of a mixture of $(NH_4)_2SO_4$, $(NH_4)H_2PO_4$ and ZnO.

The intensity ratio of a line from the analyte phase and a line from the standard is therefore a linear function of the mass fraction of analyte in the original sample. In order to determine the amount of $(NH_4)H_2PO_4$ in the mixtures that linear relationship is:

$$\frac{I_P}{I_{st}} = kW_P$$

where I_P is the intensity of a peak from $(NH_4)H_2PO_4$ and I_{st} is the intensity of a peak from the standard, ZnO. The peak used for $(NH_4)H_2PO_4$ had $d = 3.7498$ Å corresponding to the 2 0 0 reflection ($(NH_4)H_2PO_4$ crystallizes in the tetragonal system, Powder Diffraction File entry 85-0815). The peak used for ZnO had $d = 2.8137$ Å corresponding to the 1 0 0 reflection (Powder Diffraction File entry 89-0511). The intensities were obtained by a Pawley extraction using Topas V. 2.0 [10].

A calibration curve (Fig. 5) was prepared from measurements on a set of samples containing known concentrations of $(NH_4)_2SO_4$ and $(NH_4)H_2PO_4$, in addition to a constant concentration of standard (20 mass%). The correlation coefficient was $r = 0.9981$. Once the calibration curve is established, the concentration of analyte in an unknown mixture of P and S is obtained simply by measuring the ratio I_P/I_{st} of a sample containing the unknown and the same proportion of standard used in the calibration.

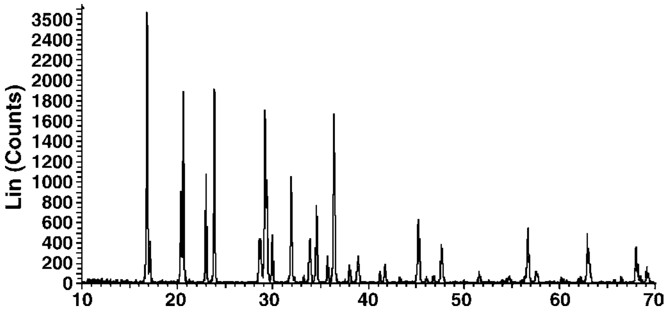

Fig. 4. Diffractogram of a sample containing 40% of $(NH_4)H_2PO_4$, 40% of $(NH_4)_2SO_4$ and 20% of ZnO in the 2θ range 10–70°.

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