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DIFFERENTIAL THERMAL ANALYSIS OF COMMERCIAL FERTILIZERS

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ABSTRACT

Commercial fertilizers were analyzed via DTA. Characteristic endotherm patterns were noted for virtually all samples. The endotherms were identified, and characterized by comparison with known compounds. This relatively simple and fast method yields qualitative and semiquantitative data amenable to identification or quality control.

INTRODUCTION

Commercial fertilizers are analyzed for nitrogen (% N), phosphorous (% P_2O_5) and potassium (% K_2O). Minor constituents such as sulfur, iron and trace minerals may or may not be reported. The variety of chemical species which may be used to prepare a fertilizer is large. Common constituents of the NPK analysis include urea, substituted ureas*, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, NH_4NO_3, KNO_3, KCl and many others. As a result, a listing of the NPK analysis may tell very little about the fertilizer. For example, ammonium salts provide nitrogen rapidly to plants affecting a rapid greening. This effect is short-lived since ammonium ions are quickly used or leached from the soil. Urea provides a longer lasting effect since nitrogen is released slowly as a result of hydrolysis. Urea is highly soluble and, therefore, it may be leached rather rapidly also. Substituted ureas which are insoluble provide long-term sources of nitrogen. A single value for nitrogen content does not discriminate between these possibilities. Since analysis for each type of nitrogen may involve lengthy procedures, the use of DTA as a rapid qualitative and semiquantitative tool was investigated. This report concerns the observation and identification of DTA endotherms for a wide variety of fertilizers. The quantitative use of these data will be discussed elsewhere.

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*"Insoluble ureas" or methylene ureas are a complex and presently uncharacterized mixture of compounds formed by reacting urea with formaldehyde. Two possible but soluble byproducts of this process are shown as curves D and E in Fig. 1.

EXPERIMENTAL

DTA curves were obtained on a Stone Thermoanalyzer (Columbia Scientific Industries Corp., Austin, Texas) with a LB-202 controller unit and JB-202 furnace platform. All heating rates were 10°C per min with a recorder chart speed of 5 min per in. Determinations were run in air, and the detection system was of the ring-disc type using Pt–Rh thermocouples. Melting points of pure compounds generally agree to within ±5°C of the literature values.

Samples of fertilizer were obtained from commercial sources and from O. M. Scotts and Sons (Marysville, Ohio). Ammonium phosphate (monobasic), ammonium sulfate, urea, ammonium nitrate, potassium nitrate, potassium chloride and potassium phosphate were reagent grade materials used without further purification. Methyl

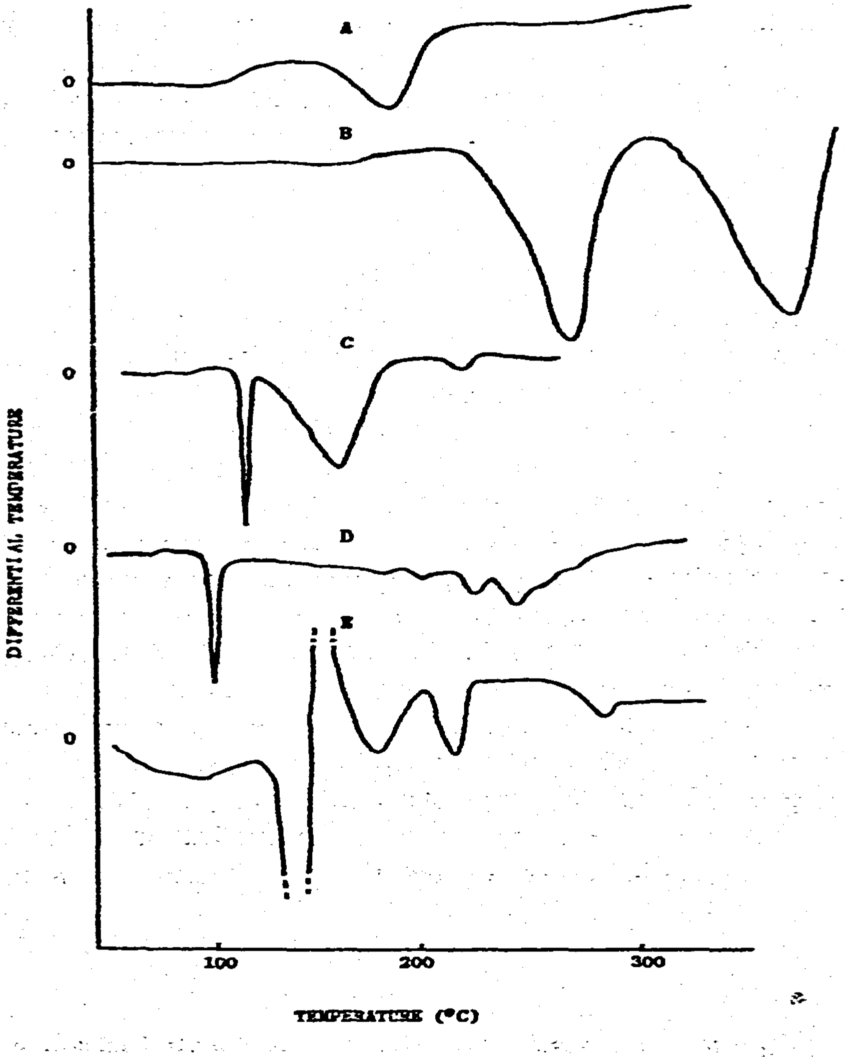

Fig. 1. DTA curves of (A) $NH_4H_2PO_4$, (B) $(NH_4)_2SO_4$, (C) urea, (D) 1,3-bis(hydroxymethyl)urea, (E) 1-hydroxy urea. Sample weights vary from 2–10 mg, positions and shapes of peaks are important.

urea, bis(hydroxy methyl)urea and hydroxy urea were run as is although they may not have been pure.

Samples were treated three ways. First, a ground portion was run without further treatment. Sample sizes ranged from 3 to 9 mg. Second, a weighed portion of the fertilizer (usually 1 or 2 g) was added to 10.0 ml of distilled water, shaken for 30 min. After the particulates settled, 20-μl aliquants of the clear solution were placed on the sample plates, and dried in a dessicator at room temperature overnight. The third treatment involved taking the above solutions and adding a large amount of urease (Sigma Chem. Co., St. Louis) and allowing the reaction to proceed for a day. Then 20-μl aliquants were taken and dried as above. The samples obtained from evaporated solutions gave uniform deposits on the plates.

RESULTS

Figure 1 is a set of the relevant DTA curves of compounds found in the fertilizer samples studied. Although many compounds were tried, only those found in

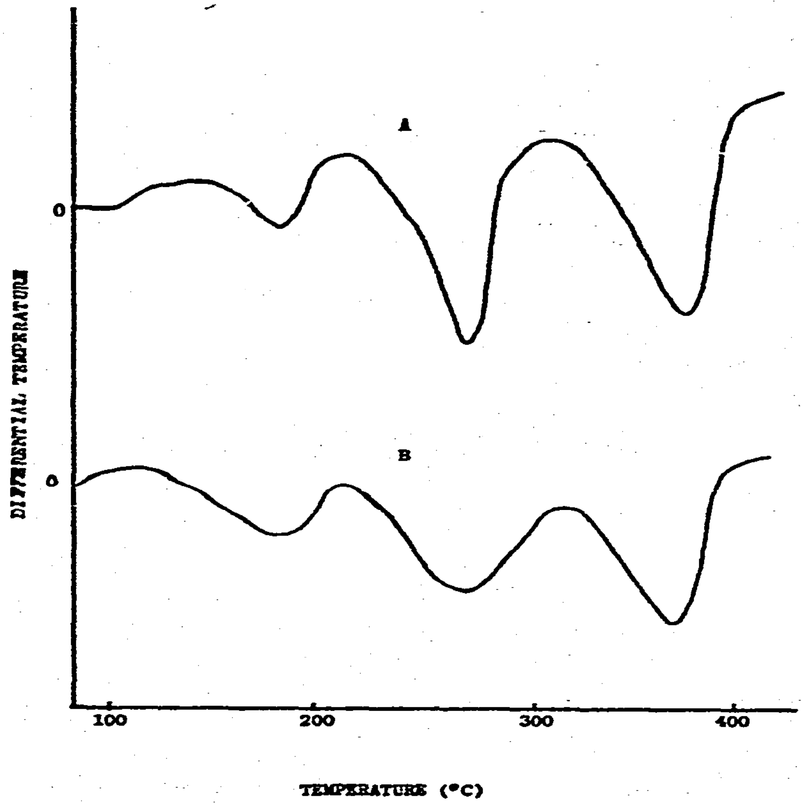

Fig. 2. DTA curves of fertilizers containing only $NH_4H_2PO_4$ and $(NH_4)_2SO_4$ which react in the temperature range studied. Curve A residue from soluble portion of fertilizer (ca. 4 mg), curve B same sample after urease hydrolysis. Two samples, NPK = 12-8-4 and 12-6-6 give virtually identical curves.

actual fertilizer samples are shown. By comparison of these curves with the fertilizer samples the compounds responsible for the peaks were deduced. To be sure that the peaks did not interact, mixtures of the pure compounds were studied but are not shown here. Figure 2 shows DTA curves for the simplest fertilizers studied. They are apparently mixtures of $NH_4H_2PO_4$ and $(NH_4)_2SO_4$ as evidenced by the peak at about 190°C and the two peaks at 275 and 360°C, respectively. Addition of urease does not alter the curves to any significant extent. Figure 3 illustrates two fertilizers containing urea. The first has urea as the main nitrogen source, while the second contains an

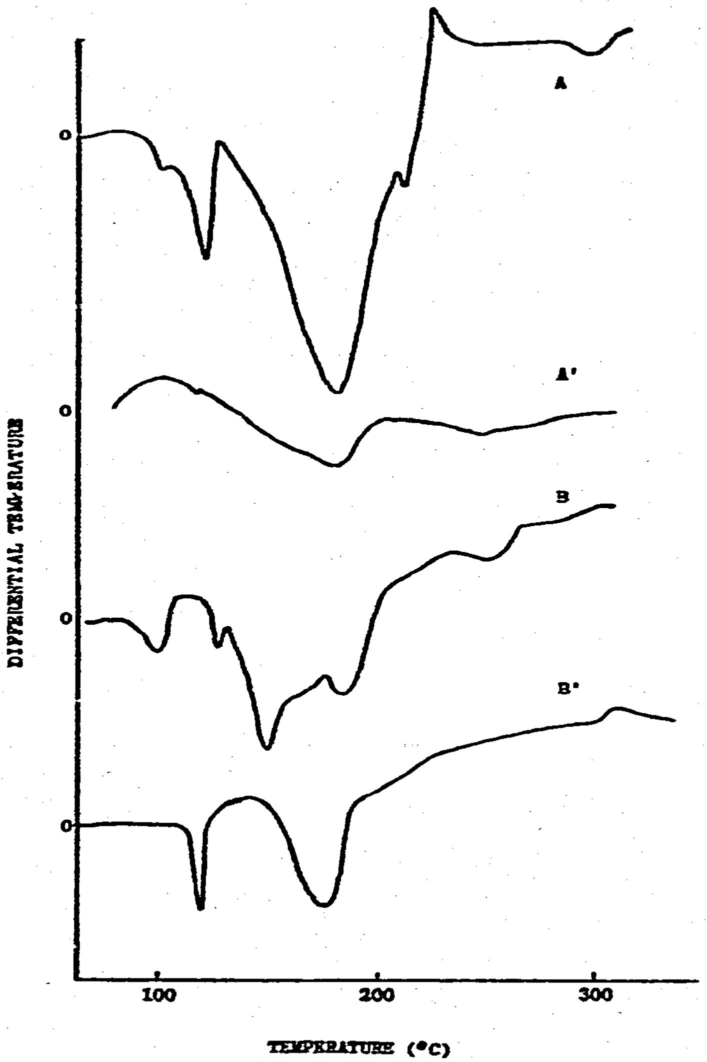

Fig. 3. DTA curves of fertilizers containing mixtures of urea and appreciable amounts of ammonium phosphate. Curves A and A', before and after urease hydrolysis (note small residual peak on A' which may be ammonium phosphate). Curves B and B' before and after urease hydrolysis (note clear peak for ammonium phosphate in B', and a strong suggestion of it in B). Sample A, NPK = 20-4-4; sample B, NPK = 23-19-17.

observable amount of $NH_4H_2PO_4$ along with the urea. After the addition of urease to both, peaks corresponding to the position of $NH_4H_2PO_4$ show up clearly. In Fig. 4, fertilizers which contain appreciable amounts of insoluble urea derivatives are shown. Urea is apparent from the first two curves where it is observed that urease just about completely eliminates the first peak. Note that the peaks at 250 °C show very similar structure to that of 1,3-bis(hydroxymethyl)urea (cf., Fig. 1). The insoluble ureas show up in the curve run on the solid fertilizer sample as a large peak at 250 °C*. There is apparently little ammonium phosphate present since a peak for this species does not appear (at 190 °C) even after treatment with urease. Of the fifteen fertilizers studied, they all fell generally into the above categories (i.e., Figs. 2–4), yet the curves were distinctly different.

DISCUSSION

From the results shown here, it is evident that a relatively large amount of information may be deduced about a fertilizer from DTA curves. Only very simple

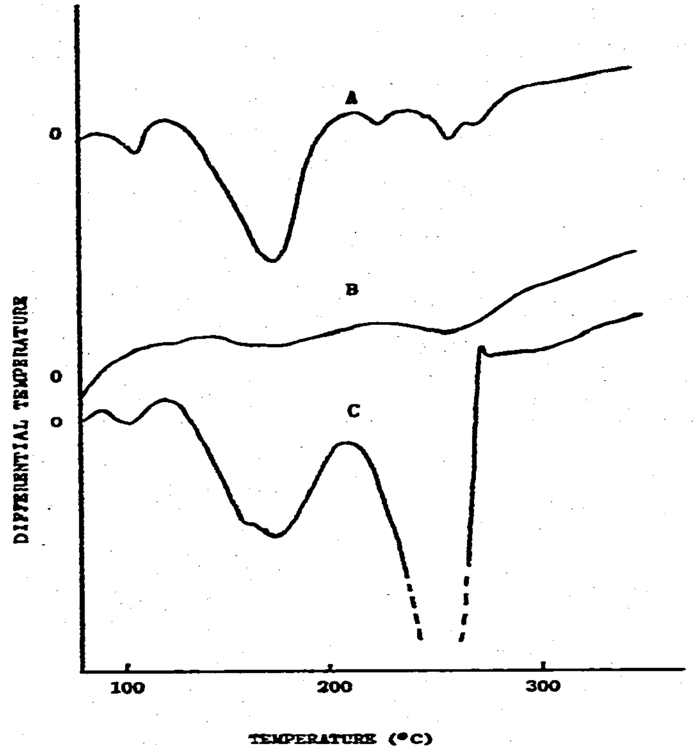

Fig. 4. DTA curves of fertilizer containing soluble and insoluble ureas. Curve A, residue from fertilizer solution (ca. 4 mg). Curve B, same as A except treated with urease. Curve C, solid sample (note appearance of the large peak corresponding to insoluble ureas). NPK of this fertilizer is 26-5-3.

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*Although not shown, it has been observed that the size of the peak at 270 °C is roughly proportional to the amount of nitrogen content not accounted for by urea.

procedures are used to separate constituents whose peaks may overlap. Qualitative analysis of fertilizers with respect to the nitrogen-containing species is relatively straightforward. In addition, the phosphate is also apparently determinable since virtually all of the phosphate comes from ammonium phosphates.

Two obvious applications for DTA in this area are (a) qualitative analysis and identification of fertilizers, and (b) the possible use of this method as a rapid quality control check on finished products. In the first case, it was found that after analyzing fifteen fertilizers, only two gave the same DTA curve (i.e., Fig. 2). All others were different in terms of the peak size or placement due to the differing compositions. The second possibility is more attractive. Since fertilizers are blends of several constituents, a DTA curve can quickly be used to spot irregularities in the finished product. Omission or any change in the amount of a particular constituent will quickly and specifically show up on the DTA curve. In contradistinction, a NPK analysis may show that something is wrong, but not reveal where the error occurred.

CONCLUSIONS

DTA curves of fifteen fertilizers were analyzed via DTA. The endotherms observed up to 350°C are all due to nitrogen-containing species, and they are readily identifiable. Virtually all samples studied gave different patterns with DTA suggesting the feasibility of qualitative identification. In addition, it seems reasonable that DTA could be used to advantage in quality control.

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