X-Ray Diffraction Patterns of Ureaforms

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Ureaform fertilizers have a characteristic x-ray diffraction pattern which can be used to identify and determine the amount of ureaform present in mixtures with waste organic fertilizers. Because of the strong interference of the many crystalline components present, less than 25% ureaform in mixtures with ordinary N-P-K fertilizers can not be detected by this method. It was also confirmed that the cold water–soluble portion of ureaform contains comparatively large amounts of urea, methylenediurea, and dimethylenetriurea.

Ureaform fertilizers are composed of a series of low molecular weight condensation products of urea and formaldehyde. Because of their controlled release of nitrogen, they are widely used for direct application and in mixed fertilizers. However, there is no generally applicable method for detecting ureaforms in fertilizer compositions or for determining the amount present. The chief method of characterizing ureaforms and other products containing water-insoluble nitrogen is by solubility tests (Association of Official Agricultural Chemists, 1965), in which the amount of cold water–insoluble nitrogen (WIN) is measured and an indication of its agronomic availability is obtained by the activity index (AI). However, these solubility determinations cannot distinguish ureaforms in mixed fertilizers from other sources of water-insoluble nitrogen such as natural organic materials or urea-formaldehyde plastic-type resins, which are very slowly available, if at all. This research has shown that x-ray diffraction can be used with certain fertilizer mixtures to identify and estimate the amount of ureaform present. Also, x-ray diffraction studies on the fractions separated from a commercial ureaform (Hays and Haden, 1966) have confirmed the chemical composition of some ureaform components.

MATERIALS

Ureaforms. Two commercial ureaforms, A. (Nitroform, Hercules Inc., Wilmington, Del.) and B. (Uramite, E. I. du Pont de Nemours and Co., Wilmington, Del.) were used in these studies. Their solubility properties, as determined by the standard methods (Association of Official Agricultural Chemists, 1965), are given in Table I.

Crystal Urea. (Mallinckrodt, A. R.), 46.65% nitrogen.

Methylenediurea and Dimethylenetriurea. Prepared by the methods described by Hays and Haden (1966).

Ureaform Fractions. The fractions I, II, and III described in Table I were prepared from ureaform A using the method of Hays *et al.* (1965) with slight modification in that a single large sample of ureaform was used, thus avoiding the repetitive procedure used by them. The analyses of the fractions correspond to those obtained by these workers.

Hercules Research Center, Wilmington, Del.

Leather Tankage. Corenco tankage (H. J. Baker Co.) containing 7.6% total nitrogen and having the following solubility properties: WIN, 6.8%; hot-water–insoluble nitrogen (HWIN), 4.2%; and AI, 38.

Sewage Sludge. Chicago sludge containing 4.9% nitrogen with the following solubility properties: WIN, 4.6%; HWIN, 3.4%; and AI, 25.

Leather Tankage–Urea-Formaldehyde Fertilizer. A granular development product made from leather tankage, formaldehyde, and urea. Analysis: N, 21.1%; WIN, 18.6%; HWIN, 11.6%; AI, 38.

Sewage Sludge–Urea-Formaldehyde Fertilizer. A granular development product made from sewage sludge, formaldehyde, and urea. Analysis: N, 17.6%; WIN, 15.7%; HWIN, 11.8%; AI, 25.

Leather Tankage–Ureaform Products of Known Composition. Products containing 10, 20, 30, and 40% ureaform were made by mixing in the desired proportions finely ground (through a U. S. No. 40 sieve) Corenco tankage and ureaform A. These mixtures were remixed by grinding in a mortar and pestle so that all the material passed a U. S. No. 100 sieve.

20–3.4–4.15 (20–8–5). A granulated commercial fertilizer containing 25% of its nitrogen as Uramite, this corresponding to about 13% ureaform by weight (Federal Chemical Co., S. Omaha, Neb.).

METHODS

Activity Index. The procedure of the Association of Official Agricultural Chemists (1965) was used. Samples

Table I. Analysis of Commercial Ureaforms

	Ureaform A	Ureaform B
Nitrogen, %	39.2	37.8
WIN,[a] %	28.3	26.5
HWIN,[b] %	13.7	10.3
Activity Index (AI)	51	61
Fraction I, wt. % cold water sol. (CWS)	28	30
Fraction II, wt. % insoluble in cold, but sol. in hot water (HWS-CWS)	37	43
Fraction III, wt. % insoluble in hot water (HWI)	35	27

[a] WIN, water-insoluble nitrogen.
[b] HWIN, hot water-insoluble nitrogen.

Table II. X-Ray Diffraction Interplanar Spacings of Ureaforms and Some of Their Components

Interplanar Spacings, dA.[a]	Relative Intensities (I/I_2) Ureaform A	Ureaform B	Urea	Methylene-diurea	Dimethylene-triurea	Fraction I Ureaform A	Fraction II Ureaform A	Fraction III Ureaform A
6.4	<1	...	...	8	..	8	...	...
4.8	...	...	...	<1	..	..	...	...
4.7	...	...	<1	...	..	..	...	...
4.6	1	1	...	...	..	..	<1	...
4.50–4.55	...	...	...	...	10	8	...	...
4.4	...	...	...	2	..	..	...	...
4.2	...	...	...	6	10	10	...	...
3.95–4.05	10	10	10	10	8	10	10	10
3.80–3.85	...	...	...	...	2	..	...	...
3.72	...	...	...	...	3	..	...	...
3.6	...	...	6	5	..	9	...	...
3.5	4[b]	3[b]	...	...	..	..	3[b]	7
3.40–3.45	...	...	...	1	4	1	...	...
3.30–3.33	...	...	...	1	..	1	...	...
3.15–3.20	2[b]	...	...	10	9	10	...	...
3.02–3.05	...	...	7	<1	..	9	...	...
2.9	...	...	...	<1	5	2	2[b]	...
2.85	2[b]	2[b]	...	...	..	..	...	...
2.8	...	...	3	<1	..	3	...	4
2.6	...	...	...	...	2	1	...	...
2.50–2.53	...	...	5	1	..	5	...	...
2.40–2.45	1[b]	...	4	1	4	5	<1[b]	...
2.32–2.35	...	...	<1	1	..	5	...	2[b]
2.27	...	...	...	...	2	..	...	...
2.21	...	...	...	...	2	1	...	...
2.14–2.17	<1[b]	1[b]	2	1	1	3	...	2[b]
2.00	<1[b]	...	1	...	3	3	...	2[b]
No. of additional weak spacings	0	0	11	2	5	15	0	0

[a] To simplify tabulation, two or more spacings were sometimes grouped in a very narrow range.
[b] Spacings were broad and diffuse.

for both cold and hot water solubility tests were crushed to pass a U. S. No. 40 sieve (35-mesh).

X-Ray Diffraction. The samples were run on a Phillips x-ray diffraction unit using a standard copper target tube with a nickel filter.

The samples were very finely ground in a mortar and pestle, packed by tamping into a 0.5-mm. glass capillary tube, and "backed" (stoppered) with a 0.3-mm. glass capillary tube. Exposure times of two hours were used for the chemically pure compounds and ureaforms, but four-hour exposures were necessary to obtain good patterns with the products containing natural organic waste materials.

RESULTS AND DISCUSSION

X-ray diffraction patterns were obtained on two commercial ureaforms, A and B (Figure 1). From these patterns, the interplanar spacings in Angstrom units (A.) and their relative intensities (I/I_2) were obtained (Table II). These data show that both these ureaforms have the same characteristic pattern which must be caused by the same chemical compounds. The definite, unique patterns shown by these commercial ureaforms indicate that x-ray diffraction may be a useful tool for analysis of fertilizer materials containing ureaforms.

Ureaform fertilizers are generally considered to consist of a continuous series of polymethyleneureas (Clark *et al.*, 1956), the lower molecular weight members, methylenediurea and dimethylenetriurea having been synthesized in pure form (Hays and Haden, 1966). A small amount of free urea is also usually present. The interplanar spacings and relative intensities of urea and methylenediurea have been reported (Index to the Powder Diffraction File, 1968) but those of dimethylenetriurea have not. As shown in Figure 2 and Table II, dimethylenetriurea has now been characterized by its x-ray diffraction pattern. Included also are the data on urea and methylenediurea and these agree with those published (Index to the Powder Diffraction File, 1968).

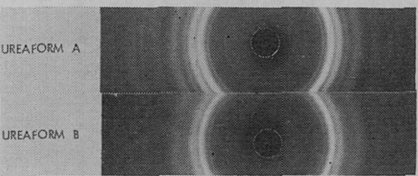

Figure 1. X-ray diffraction patterns of commercial ureaforms

On the basis of their solubilities in cold (25° C.) or hot (100° C.) water, ureaforms can be separated into three fractions (Hays *et al.*, 1965). Fraction I is that portion which is soluble only in cold water; fraction II is the portion which is insoluble in cold water, but soluble in hot water; and fraction III is that portion insoluble in hot water. The weight per cent portions of the fractions of ureaforms A and B are given in Table I. A commercial ureaform of the A type was separated into three such fractions and the x-ray diffraction pattern of each fraction was obtained; the characteristic pattern of fraction I is shown in Figure 2, and the interplanar spacings are given in Table II. On the basis of the presence of the more intense interplanar spacings, it can be deduced that fraction I contains comparatively large amounts of urea, methylenediurea, and dimethylenetriurea. Thus, the

Table III. X-Ray Diffraction Interplanar Spacings of Fortified and Unfortified Organic Waste Fertilizers

Interplanar Spacings, dA.[a]	Relative Intensities (I/I_2): Sewage Sludge	Fortified Sewage Sludge	Leather Tankage	Fortified Leather Tankage	α-Quartz
7.0	...	...	<1	<1	..
5.3	...	...	<1	...	..
4.5	<1	...	...	...	..
4.2–4.3	2	<1	3	1	7
4.0	...	10	<1	10	..
3.5	...	<1[b]	5	2[b]	..
3.3–3.35	10	8	10	3	10
3.2	...	...	1	<1	..
2.8–2.9	2	<1[b]	1	2[b]	..
2.7	<1	...	2	...	..
No. of additional weak spacings	7	0	4	0	24

[a] To simplify tabulation, two or more spacings were sometimes grouped in a very narrow range.
[b] Spacings were broad and diffuse.

Table IV. X-Ray Diffraction Interplanar Spacings of Fortified Leather Tankage and Leather Tankage Containing Various Amounts of Ureaform

Interplanar Spacings, dA.[a]	Relative Intensities (I/I_2): Leather Tankage	10% Ureaform Leather Tankage	20% Ureaform Leather Tankage	Unknown, Ureaform Leather Tankage	30% Ureaform Leather Tankage	40% Ureaform Leather Tankage	Ureaform A
7.0	<1	<1	<1	<1	<1	<1	...
6.4	...	...	...	...	...	...	<1
4.5–4.6	...	<1	...	...	<1	<1	1
4.3	3	1	<1	1	1	<1	...
4.0	<1	1	9	10	10	10	10
3.5	5	5	5	2[b]	3	1	4[b]
3.33	10	10	10	3	7	4	...
3.2	1	...	...	...	...	2	2[b]
2.8–2.9	1	<1	1	2[b]	1	<1	2[b]
2.7	2	2	...	...	<1	...	...
2.45–2.50	2	...	<1	...	...	...	1[b]
2.2	3	<1	<1	...	<1	<1	...
2.13–2.15	...	...	...	<1	...	...	1
2.0	...	<1	<1	...	1	...	<1

[a] To simplify tabulation, two or more spacings were sometimes grouped in a very narrow range.
[b] Spacings were broad and diffuse.

seven most intense spacings of fraction I correspond to the three most intense spacings of urea, the four most intense spacings of methylenediurea, and the four most intense spacings of dimethylenetriurea. The presence of as much as 20% free urea has been chemically measured previously in fraction I (Hays *et al.*, 1965), but this is the first time that methylenediurea and dimethylenetriurea have been specifically identified in the cold water–soluble portion of ureaform.

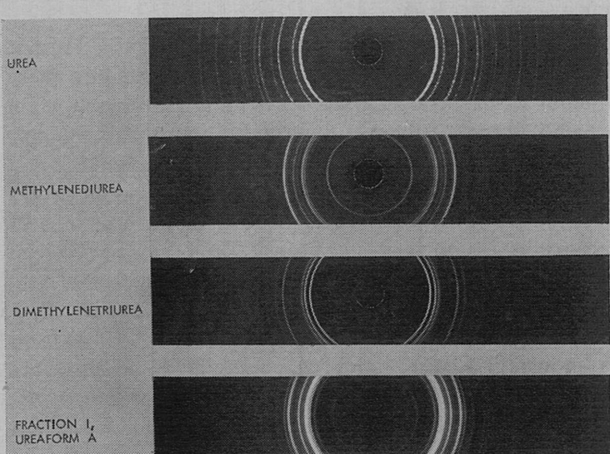

Figure 2. X-ray diffraction patterns of ureaform components

As shown in Table II, x-ray diffraction patterns were also obtained for fractions II and III of ureaform A. The patterns of both fractions are very similar to each other and to the original ureaform; therefore, the components of fractions II and III are closely similar in chemical structure and contribute strongly to the total x-ray diffraction pattern of ureaform.

Organic waste products are frequently used as sources of slow release nitrogen fertilizers, but because of their generally low total nitrogen contents of 5 to 7%, such materials are more useful when fortified with other sources of nitrogen. Two such materials reportedly made from sewage sludge and leather tankage by addition of formaldehyde and urea and containing 18 to 20% total nitrogen were studied. Solubility tests showed that the added nitrogen was of the water–insoluble type, possibly from ureaform. X-ray diffraction patterns of these unknown materials as well as those of a typical sewage sludge and leather tankage were obtained as shown in Figure 3. The pattern for α-quartz is also included in Figure 3 because quartz was detected in the leather tankage and

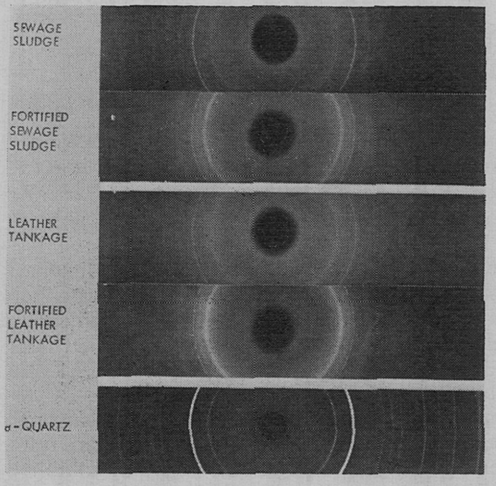

Figure 3. X-ray diffraction patterns of organic waste fertilizers

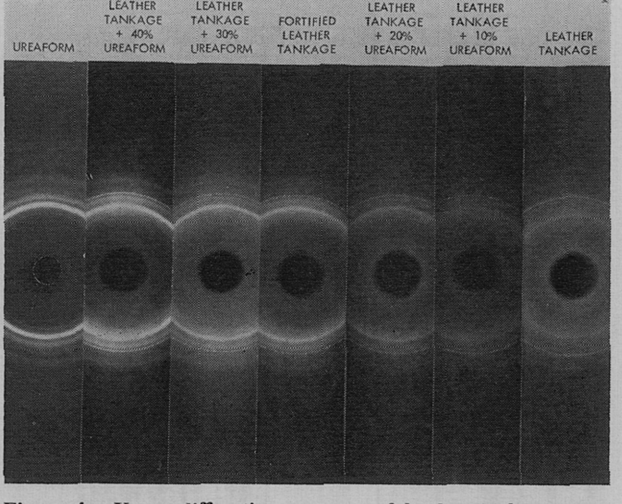

Figure 4. X-ray diffraction patterns of leather tankage–ureaform mixtures

sewage sludge materials. Comparisons of these patterns and the interplanar spacings given in Table III with the corresponding patterns and spacings for ureaforms (Figure 1 and Table II), confirm that both of these waste organic fertilizers contain ureaform. The characteristic pattern for ureaform with its most intense spacing at 4.0 A. is clearly seen when compared with the very weak patterns of the largely noncrystalline waste products with an intense spacing corresponding to the most intense spacing of α-quartz at 3.33 A.

Having shown that the presence of ureaform can be qualitatively detected in mixtures with organic materials, it was of interest to establish that x-ray analyses of these materials can be put on a more quantitative basis. A comparison was made of the fortified leather tankage product, shown to contain ureaform, with a series of known mixtures containing 10, 20, 30, and 40% of solid ureaform with leather tankage. The photographs in Figure 4 show that the leather tankage product is similar to the leather tankage material containing 30% ureaform. The interplanar spacings given in Table IV confirm this conclusion. As the concentration of ureaform increased, the most intense ureaform spacing at 4.0 A. increased from a relative intensity of <1 for the leather tankage to the maximum of 10 for the 30% ureaform mixture, and the most intense leather tankage spacing at 3.33 A., which was due to a high concentration of α-quartz, decreased in a corresponding manner as the leather tankage was diluted with ureaform.

An attempt was made to use the x-ray diffraction method to determine ureaform in a commercial 20–3.4–4.15 (20–8–5) granulated fertilizer stated to contain 13% ureaform by weight (25% of its N as ureaform nitrogen). Because of the strongly crystalline components of this fertilizer, it was not possible to detect the characteristic pattern of ureaform. Limits of detection of ureaform by this x-ray method are estimated to be 10% or greater in fertilizers of low crystallinity and 25% or more in fertilizers of high crystallinity.

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