

## TECHNICAL NOTE

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# A Field Diagnostic Test for the Improvised Explosive Urea Nitrate

**ABSTRACT:** A sensitive, specific and simple color test for the improvised explosive urea nitrate is described. It is based on the formation of a red pigment upon the reaction between urea nitrate and p-dimethylaminocinnamaldehyde (p-DMAC) under neutral conditions. Urea itself, which is the starting material for urea nitrate, does not react with p-DMAC under the same conditions. Other potential sources of false positive response e.g., common fertilizers, medications containing the urea moiety and various amines, do not produce the red pigment with p-DMAC. Exhibits collected from 10 terrorist cases have been tested with p-DMAC. The results were in full agreement with those obtained by instrumental techniques including GC/MS, XRD and IR.

**KEYWORDS:** forensic science, field test, explosives, urea nitrate, color test, p-dimethylaminocinnamaldehyde (p-DMAC), p-dimethylaminobenzaldehyde (p-DMAB)

Urea nitrate **1** (Fig. 1) is a powerful improvised explosive, frequently prepared and used by terrorists. It can be prepared quickly and easily by adding nitric acid to a cooled aqueous solution of urea (Scheme 1). The white precipitate thus formed is filtered, washed with cold water and dried in air. Even unskilled workers can prepare large amounts of this material in “back-yard” facilities (1). Urea nitrate, in its pure form, is a white, crystalline powder, which, just by looking at it, cannot be distinguished from e.g., sugar. It is assumed that about half a ton of this material was used in the first World Trade Center bombing, in February 1993 (1). In Israel, urea nitrate is believed to be one of the most widespread explosives used by Palestinian terrorists, which is responsible for the loss of many lives. Large improvised mines, suspected of containing urea nitrate, have seriously damaged several Israeli Merkava tanks (2), which are considered to be the safest and best-protected tanks in the world. Quantitative data on the explosive performance of urea nitrate have been reported recently by a joint group of researchers from the Defense Evaluation and Research Agency (DERA, UK) and the FBI (3). It is, therefore, imperative to develop a detection capability for urea nitrate in various scenarios, particularly for fieldwork. An optimal diagnostic device must be simple, sensitive and specific.

Based on our positive experience with simple field tests, for military as well as for improvised explosives (4–6), we decided to apply a chemical color test for urea nitrate too. The main candidate for color reaction was p-dimethylaminocinnamaldehyde (p-DMAC), **2** (Fig. 2), a commercially available chemical, recently suggested for urea determination in biological fluids (7). Another candidate

was the one-vinyl-shorter analogue, p-dimethylaminobenzaldehyde (p-DMAB) **3** (Fig. 2), which was suggested for measuring urea in pharmaceutical formulations (8).

## Methods

### Materials

Urea—99.5% was purchased from Riedel-de Haën.  
Nitric acid—69–70% C.P. was purchased from Palacid Ltd. (Israel)  
p-DMAC **2**—98% was purchased from Aldrich. Chemical Company Inc.  
p-DMAB **3**—99% was purchase from B.D.H. Chemicals Ltd.

### Color Tests

Batches of 1–20 g urea nitrate **1** were synthesized without difficulty from urea and nitric acid, according to literature procedure (9,10). For crystallographic studies small amounts were carefully recrystallized from the mother liquor, after addition of nitric acid (11), to provide large colorless crystals. Solutions of reagents **2** and **3** were prepared in four alcohols: methanol, ethanol, iso-propanol and n-butanol, at concentrations ranging from 0.1 to 0.5%.

Color formation was visually observed. After initial optimization of the technique was accomplished, spray cans containing reagent solution under compressed air were prepared for further experimentation.

### Trials in Solution

One drop of reagent solution (**2** or **3**) was added to a dilute aqueous solution of urea-nitrate **1** (1 mL) and the color change was observed.

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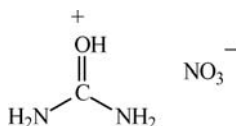
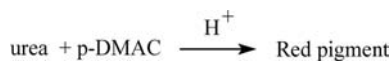
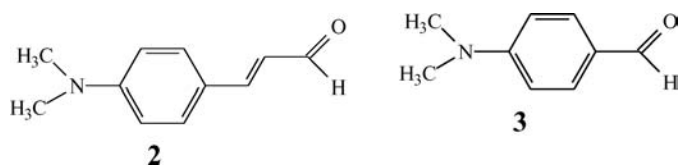


FIG. 1—Structure of urea nitrate.

SCHEME 1—Urea reaction with *p*-DMAC **2** under acidic conditions.FIG. 2—Structures of the two potential color-reagents for urea nitrate *p*-DMAC **2** and *p*-DMAB **3**.

### Trials with Solid Urea Nitrate

A tiny crystal of urea nitrate **1** was placed on a circle of filter paper. One drop of the reagent was pipetted onto the crystal and the color change was observed.

### Detection Limit

Drops containing known amounts of urea nitrate **1** in descending order were pipetted on circles of filter paper and dried in air. The

strips were then sprayed with the reagent solution and the color change followed until reaching a stain that provided no observable color change. The threshold for detection was defined as the smallest detectable amount per cm<sup>2</sup>.

### Trials Imitating “Operational Conditions”

Hands of volunteers were swabbed by filter paper 5 min after they had lightly touched urea nitrate **1** crystals. Door handles were swabbed after being opened with hands that had touched urea nitrate crystals. The swabs were developed by spraying with reagent solution.

### Casework Trials

Exhibits from 10 terrorist cases have been tested by the above technique. One of the exhibits contained particles recovered from post-blast debris and the rest have been intact materials collected from various scenes. A few solid particles from each case were placed on circles of filter paper and the reagent was pipetted onto them. Color change was recorded.

### Potential Interferences

Two groups of potential interfering materials that might confuse the test have also been tried under similar conditions. They were tested separately and admixed with urea. The first group included urea itself and compounds that contain urea or urea-analogue moiety in their molecule (Table 1, compounds **4–9**). The second group included ammonium and hydroxylamine salts, and acidic salts, all of which are likely to be found in industrial and agricultural environments (Table 1, compounds **10–25**). Another potential source

TABLE 1—*p*-DMAC's reaction to some potential interferences.

Compound Number	Compound Name	Compound Structure	pH in Aqueous Solution	Reaction with <i>p</i> -DMAC	Reaction with <i>p</i> -DMAC in Presence of Urea
4	Urea		6	N.R.*	
5	Thiourea		5	N.R.*	N.R.*
6	Guanidine hydrochloride		6–7	N.R.*	N.R.*
7	Alloxan		4	N.R.*	N.R.*
8	5,5-Diethylbarbituric acid		5–6	N.R.*	N.R.*
9	Phenobarbital		5–6	N.R.*	N.R.*
10	Hydroxylammonium chloride	HONH <sub>2</sub> · HCl	3	light pink**	N.R.*
11	Ferric ammonium sulfate	FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	7	N.R.*	N.R.*
12	Ferrous ammonium sulfate	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	4	light pink**	N.R.*
13	Hydroxylammonium sulfate	(H <sub>2</sub> NOH) <sub>2</sub> · H <sub>2</sub> SO <sub>4</sub>	3–4	light pink**	N.R.*
14	Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	6–7	N.R.*	N.R.*
15	Ammonium chloride	NH <sub>4</sub> Cl	6–7	N.R.*	N.R.*
16	Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	6–7	N.R.*	N.R.*
17	Ammonium dihydrogen phosphate	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	5	N.R.*	N.R.*
18	Potassium dihydrogen phosphate	KH <sub>2</sub> PO <sub>4</sub>	4	light pink**	N.R.*
19	Sodium dihydrogen phosphate monohydrate	NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O	4	light pink**	N.R.*
20	Sodium hydrogen phosphate heptahydrate	Na <sub>2</sub> HPO <sub>4</sub> · 7H <sub>2</sub> O	9	N.R.*	N.R.*
21	Sodium hydrogen sulfate monohydrate	NaHSO <sub>4</sub> · H <sub>2</sub> O	1–2	light pink**	Positive, like urea nitrate
22	Sodium hydrogen sulfite	NaHSO <sub>3</sub>	8	N.R.*	N.R.*
23	Sodium hydrogen carbonate	NaHCO <sub>3</sub>	9	N.R.*	N.R.*
24	Potassium hydrogen carbonate	KHCO <sub>3</sub>	8	N.R. <sup>1</sup>	N.R.*
25	Potassium hydrogen sulfate	KHSO <sub>4</sub>	1–2	light pink**	Positive, like urea nitrate
26	20-20-20 fertilizer	Urea, potassium nitrate and ammonium phosphate	4–5	N.R.*	N.R.*

\* No reaction.

\*\* Quickly disappears.

of interference was a very common chemical fertilizer, “Ecogan,” manufactured in Israel and known also as “20-20-20,” which contains urea, potassium nitrate and ammonium phosphate.

### Instrumentation

Gas chromatography/mass spectrometry (GC/MS) was carried out on Agilent 6890 PLUS gas chromatograph, coupled with an Agilent MSD 5973N. The GC column was a J&W fused silica capillary column, 15 m × 0.25 mm (i.d.) coated with DB-5MS (0.25 μm film). Injector temperature was 180°C. Column temperature was programmed from 60°C to 280°C at a rate of 25°C/min. Transfer line was held at 180°C. Ion source temperature was 230°C and quadrupole temperature was 150°C. Scan range was 40–500 daltons. Scan rate was 3.11 scans/sec. Electron energy was 70 eV and the carrier gas was helium. Injections were carried out in split mode.

Infra red (IR) spectroscopy was carried out on Nicolet 460 ESP Protégé using KBr pellets.

X-ray diffraction (XRD) measurements of casework samples were carried out on Scintag, Advanced Diffraction System X2, Cu tube.

### Results

Both reagents, **2** and **3**, produced distinct colors within one minute from contact with urea nitrate, in solution or in crystalline form. p-DMAC **2** produced a red-orange pigment ( $\lambda_{\max}$  514 nm) shown in Fig. 3A, while p-DMAB **3** changed from colorless to

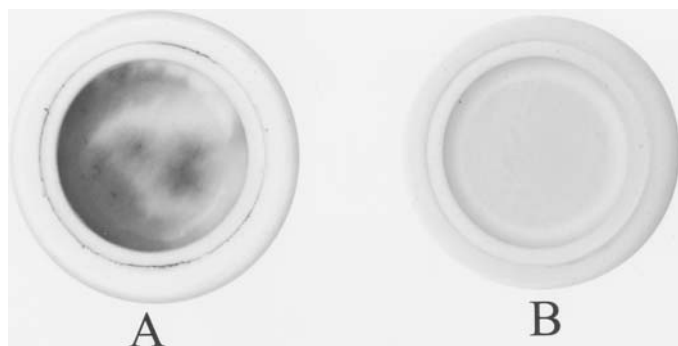


FIG. 3—Color developed in the reaction between p-DMAC **2** and A. urea nitrate (“positive”) B. potassium nitrate (“negative”).

TABLE 2—Instrumental analyses and color reaction results of real cases.

Sample <sup>1</sup>	IR	XRD	MS	p-DMAC
1	Urea nitrate	Urea nitrate	Urea	Positive
2	Urea and nitrate salt	Urea nitrate	Urea and EGDN <sup>2</sup>	Positive
3	Urea nitrate		Urea and TNT <sup>3</sup>	Positive
4	Urea and nitrate salt	Urea nitrate	Urea, TNT and RDX <sup>4</sup>	Positive
5	Urea nitrate		Urea and HNO <sub>3</sub>	Positive
6	Potassium nitrate and sugar	Potassium nitrate		Negative
7	Urea and nitrate salt	Urea		Negative
8	TATP <sup>5</sup>		TATP	Negative
9	Potassium nitrate and sugar	Potassium nitrate		Negative
10	Urea			Negative

<sup>1</sup> A brief description of the exhibits' origin appears in Table 3.

<sup>2</sup> EGDN—Ethylene glycol dinitrate.

<sup>3</sup> TNT—2,4,6-Trinitrotoluene.

<sup>4</sup> RDX—Hexahydro-1,3,5-trinitro-1,3,5-triazine.

<sup>5</sup> TATP—Triacetone triperoxide (3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexaoxocyclonane).

TABLE 3—Description of cases from which exhibits were taken and tested with **2**.

Case	Description of the Exhibits' Origin
1	Recovered from a metal fragment found in the debris after a suicide bomber had exploded in a car in the Sharon region.
2	Found in an explosive device which did not explode, on a suicide bomber.
3	Recovered from an improvised mortar shell fired in Gaza.
4	Recovered from the contents of an improvised bomb in Gaza.
5	Recovered from an improvised bomb near a police station in the Old City of Jerusalem.
6	An explosive device submitted to the police.
7	Found in an improvised rocket fired at a city in the Negev region.
8	Found in a belt carried by a suicide bomber in the Sharon region.
9	Recovered from a pipe bomb in Gaza.
10	Recovered from a clandestine laboratory.

bright yellow ( $\lambda_{\max}$  420 nm). The formation of the red-orange color was much more noticeable to the naked eye, so experiments were continued only with **2**.

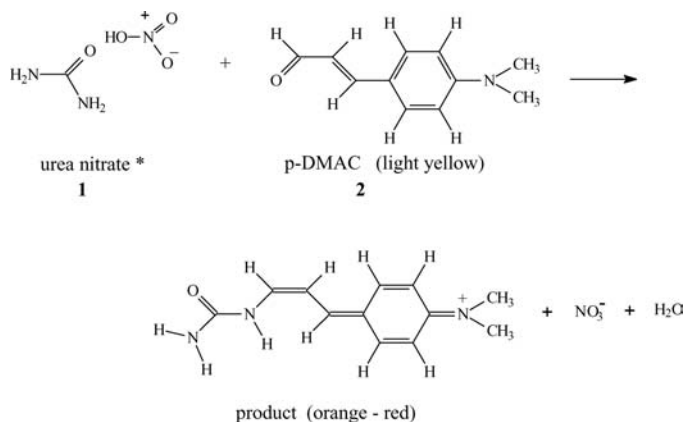
An optimal working solution was composed of **2** (0.4%) in ethanol. The detection limit on paper was found to be about 100 μg/cm<sup>2</sup> (subjective to the observer's eye). Hand-swabs, as well as swabs collected from door-handles after being handled with hands contaminated with urea nitrate, all provided positive responses.

Neither of the potential interferences (Table 1) produced the typical red pigment with **2**. Acidic salts, whose pH was lower than 4, produced a light pink color, which quickly disappeared. When admixed with urea, however, the two acidic salts, potassium hydrogen sulfate **25** and sodium hydrogen sulfate **21**, did produce the positive response in a similar fashion to urea nitrate.

The exhibits from 10 actual terrorist cases produced 5 positive and 5 negative responses, which fully matched the results obtained by instrumental analyses: GC/MS, XRD and IR (Table 2 and Table 3).

### Discussion

The reaction between urea and p-DMAC **2** to produce a red pigment, was suggested in the forensic literature for the detection of



SCHEME 2—The reaction of p-DMAC 2 with urea nitrate (7).

\*For clarification, urea nitrate is drawn here as a combination of urea and nitric acid, but its actual structure is that of uronium salt, in which the proton is attached to the carbonyl oxygen (Fig. 4) (9,10,17).

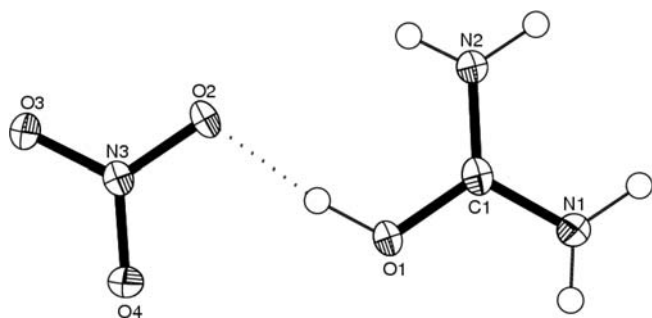


FIG. 4—Urea nitrate crystal structure (17). Empty circles represent hydrogen atoms. Notice that the proton is attached to the urea oxygen (9,10,17).

urine stains (12) and for fingerprint visualization (13,14). This reaction takes place only under strong acidic conditions (Scheme 1, 12–14). The structure of the pigment was determined recently, and the color development was ascribed to the formation of a long conjugated system between urea and the unsaturated aldehyde (Scheme 2, 7). The essence of the technique proposed in this work lies in the fact that as opposed to urea, urea nitrate is strongly acidic (pH 1–2) thanks to the nitric acid moiety within its molecule (Fig. 4). Thus, while neutral urea does not react with p-DMAC 2, urea nitrate does, since it provides the necessary acidity for the reaction to occur. p-DMAC actually does not detect urea but uronium ion (Scheme 2). The visual detection limit on swabs, which was found to be ca. 100 µg/cm<sup>2</sup>, is sufficient for many operational purposes such as the examination of hand swabs, door handles, suspicious materials and, sometimes, even post blast debris. The potential interferences, which have been evaluated, are the materials suspected of providing false positive results due to their structural resemblance to urea. The list includes: urea itself; organic molecules containing a urea moiety such as allofan, barbiturates, or urea analogues such as thiourea and guanidin; ammonium salts, including ammonium nitrate; amines in salt form, inorganic nitrates and acidic salts (Table 1). From the entire list, only urea in presence of acidic salts, whose pH is lower than 2, produced the color reaction, thus confirming that the p-DMAC reaction actually detects the uronium ion.

“Uronium” like “ammonium” is the correct term for the positive ion, which is derived from urea by addition of a proton or another positive ion (9,15,16). Hence the correct name for urea nitrate would be uronium nitrate.

In presence of strong mineral acids, urea would also produce the same color reaction. However, since most mineral acids are liquids, this possibility is less likely to be of great concern. The crystalline salts of urea with mineral acids, e.g., uronium sulfate (15), which would also give a false positive response, are very rare and are not likely to impose an operational problem. It is noteworthy that the fluorescence mode for detection was also tried, in a similar manner to that suggested for fingerprint detection with p-DMAC (18,19): illumination at 530 or 555 nm and watching through 590 nm cut-off filter. Spots of urea nitrate product with p-DMAC fluoresced intensely, but there was also strong background fluorescence from the reagent itself, which rendered this mode unsuitable for diagnosing urea nitrate.

## Conclusion

p-DMAC in neutral solution provides a simple, sensitive and reliable diagnostic test for the improvised explosive urea nitrate. It can be used in the field, on hands of suspects, on door handles or packaging devices, and on suspected materials, even in trace amounts. It can also be applied in the laboratory, as a preliminary test, prior to instrumental analysis. A field device based on the p-DMAC reaction is already commercially available, under the name UN-1 (Aphelion Ltd., Innovative Security Technologies and Patent application filed, Israel.) Obviously, p-DMAC results are only preliminary and must be confirmed by instrumental analyses such as IR, XRD or MS.

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