What's In Vial No. 3?

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Last weekend I taught a special two-day course on the identification of explosives to a young lady from San Salvador. She is a forensic microscopist newly assigned to the "Bomb Squad". Her problem was to determine what explosives were used after terrorist bombings. Fortunately, some small particles of the explosive substance usually remain after a detonating. Careful examination of a bomb crater or of bomb fragments usually uncovers these tiny residues.

My problem was to teach her the microscopical characteristics of the most likely explosives she might encounter. These include common inorganic nitrates, chlorates and percholorates and less common organic (military) explosives such as TNT, RDX, HMX, PETN and tetryl. Each of these compounds is easily recognized by a microscopist trained in crystal morphology and optics, fusion methods and microchemical analysis. Thom Hopen[1]; John Kilbourn[2] and I[3,4] have published useful procedures for doing so.

Table 1 shows some of the data that are helpful in identifying the inorganic high explosives. With a little practice any of these compounds can be recognized, often at sight. Still, it is necessary to confirm the identification in order to convince others (non-microscopists). One can then check refractive indices and interference figures, take melting points, characterize the crystals from the melt, and do microcrystal tests. Figure 1 shows crystals of $KClO_3$, KNO_3 and $KClO_4$ from a droplet of water by the hugging procedure. A tiny particle (10-100 ng) on a slide picks up moisture from one's breath and dissolves when huffed. On drying for about 5 seconds, the droplet usually crystallizes to form characteristic, well-formed crystals. Figure 2 shows the characteristic crystallization patterns of TNT from the melt. Curiously, most inorganic explosives can also be crystallized from the melt and yield distinctive patterns.

So, my student, Dulce Flores, did very well and by noon of day-two I gave her four unknowns. She did well on three but said No. 3 didn't fit any explosive we had covered. I told her it *was* one of the ones she had studied. She looked puzzled and went back to her 'scope. Ten minutes later she reported that she couldn't identify it. I sat down to show her it was NH_4NO_3 and found, at once, that it wasn't NH_4NO_3 or any of the possible compounds she had studied.

I was embarrassed because it came from one of our classroom reagent blocks in a vial labeled NH_4NO_3. But what was it? I gave her another unknown and retreated to my den to identify my new unknown. The crystals melted below 100^0 C and evolved H_2O at 100^0 C and resolidified while still hot; it was, therefore, a hydrate. I got a good whiff of the vapors as I heated the micro sample and it was acrid like NH_4NO_3 so I surmised it might be a nitrate.

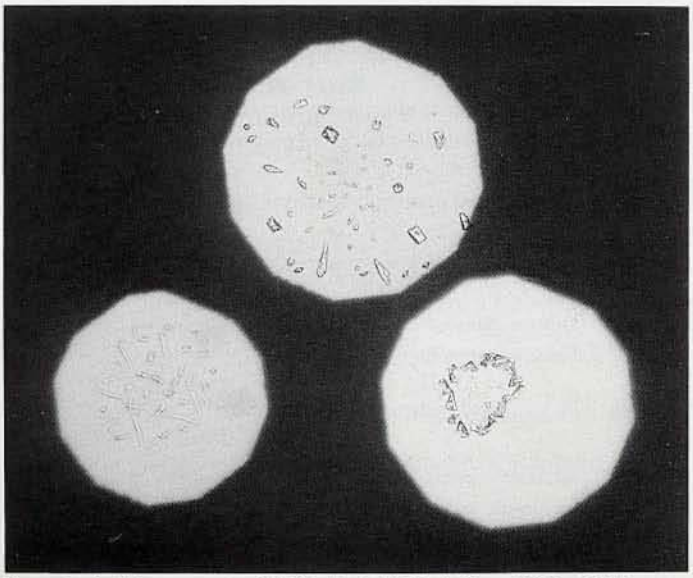

Figure 1. A triple exposure of $KClO_4$ (top), $KClO_3$ (left) and KNO_3 (right) crystallized by huffing single 90 ng particles, 50X.

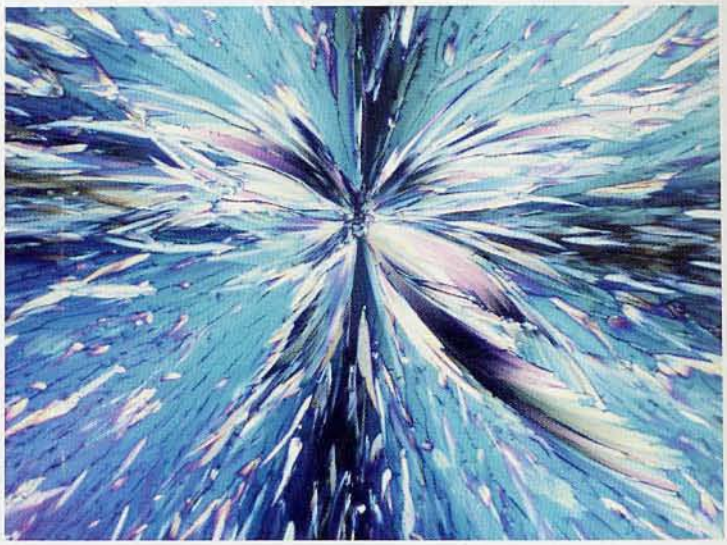

Figure 2. TNT recrystallized spontaneously from a supercooled (to room temperature) melt, crossed polars, 80X.

Nessler's reagent gave needles and rods confirming that guess. I tried various microchemical reagents to identify the cation: zinc metal, CsCl, H_2PtCl_6 and $K_2Hg(SCN)_4$, but these only told me a lot of elements it wasn't. However, NH_4MoO_4 gave $Al(MoO_4)_3$, as square plates so I looked up $Al(NO_3)_3$ and found it is a nonahydrate melting at 73^0 C but no crystallographic data could be found. A mixed fusion with known $Al(NO_3)_3 \cdot 9H_2O$, however, showed our "NH_4NO_3" was indeed $Al(NO_3)_3 \cdot 9H_2O$.

I decided to do the crystal morphology and optics on it to help other microscopists who might have the same problem. This turned out to be a real jkob (Figure 3). The crystals are extremely soluble in water and the temperature coefficient of solubility is very high. So you keep adding solute until crystallization occurs. the microscope then shows very complex nearly equal crystals lying on any one of up to 26 different faces. There is no way to figure them out before the drop goes to dryness, so I added a coverslip to the drop and sealed it with fingernail polish. The drop is saturated only below a definite temperature. Any rise in temperature of a few tenths of a degree rounds off the crystals to near-spherical shapes. The microscope illuminator rounds them off. Your fingers on the slide or your breath also round them off. The crystal forms are very complex; there are 6 different crystal forms (1 bypyramid, 2 prisms and 3 pinacoids). It is monoclinic so there are 13 different views, each with alarmingly different distortions. After laboriously achieving a general idea of the forms I decided to resort to dried-drop crystals. This often works well if, when good crystals are obtained but still under the drop surface, the H_2O is soaked into a few layers of Kleenex pressed on the slide drop. This removes most of the solution and some of the crystals. Most of the remaining solution is removed by a corner of filter paper touched to the slide near each good-looking crystal. This may require several quick dabs under the stereo until no more solution appears to be present. The slide is then dried carefully at only 40-50^0 C. I then covered the crystals with a coverslip and Cargille liquid 1.50 to cut down the contrast and maybe, just maybe, come close to one refractive index. The crystal morphology, optical sectioning and use of interference figures showed it to be monoclinic with $\alpha = b = BX_a$. I could also see α was much less than 1.50 and β and γ were close together but somewhat higher than 1.50. I washed the crystals free of 1.50 liquid with successive drops of amyl acetate over a waste basket, dried the slide and added new cargille liquids with amyl acetate washing in between, until I had α = 1.404, β = 1.522 and γ = 1.528 with the optic axial angle 2V = 25^0(-) with strong dispersion r>b.

With that information I went back to the crystal forms. Mounting the crystals in 1.404 I could find any crystal showing α. If it also showed a nearly centered BX_o or a flash figure, it had to show also β or γ respectively. This helped in looking for these three principal views (Figure 4a or b). Choosing the locations of the axes was then the next problem. The *b* axis, of course, is perpendicular to the plane of

TABLE I.
IDENTIFICATION OF INORGANIC HIGH EXPLOSIVES

Compound	Crystal System	a or w	b or n	g or e	Biref.	m.p.°C	Micro-xtal tests, page
$Ba(NO_3)_2$	Cubic	---	1.571	---	0	592	Ba, 125; NO_3, 324
$Pb(NO_3)_2$	Cubic	---	1.781	---	0	470	Pb, 203; NO_3, 324
$NaClO_3$	Cubic	---	1.515	---	0	248	Na, 51; ClO_3, 381
$KClO_3$	Monocl.	1.415	1.517	1.523	0.108	368	K, 65; ClO_3, 381
$NaClO_4$	Orthorh.	1.461	1.462	1.473	0.012	482	Na, 51; ClO_4, 386
$KClO_4$	Orthorh.	1.473	1.474	1.477	0.004	610	K, 65; ClO_4, 386
NH_4ClO_4	Orthorh.	1.482	1.483	1.488	0.006	>480	NH_4, 73; ClO_4, 386
KNO_3	Orthorh.	1.335	1.506-	1.506+	0.172	333	K, 65; NO_3, 324
$NaNO_3$	Hex.	1.587	---	1.336	0.251	308	Na, 51; NO_3, 324
NH_4NO_3	Orthorh.	1.413	1.611	1.637	0.224	169	NH_4, 73; NO_3, 324

*The tests are described in Chamot & Mason Vol. II[5] on the pages noted.

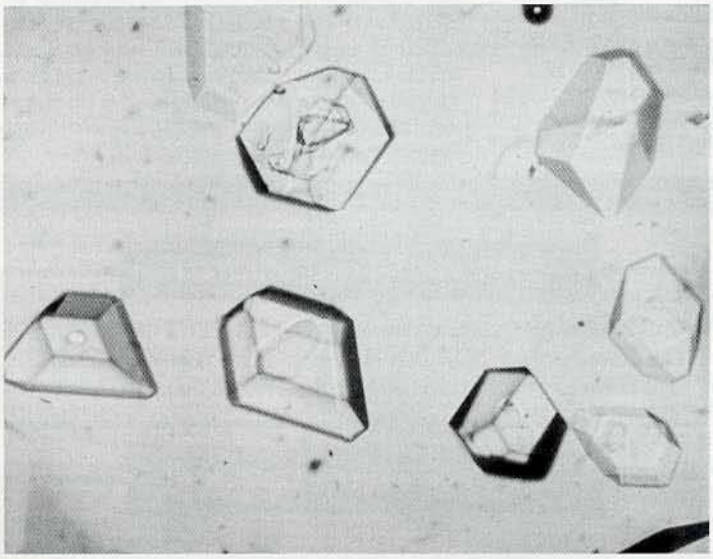

Figure 3. A representative group of $Al(NO_3)_3 \cdot 9H_2O$ crystals from a drop of water on a microscope slide.

symmetry since the crystals are monoclinic. The axes *a* and *c* lie in the plane of symmetry separated by the β angle. However, a microscopist can only choose their orientations by placing them so that simple Miller indices result. In this case there are two such choices; one based on a bipyramid and the other based on two prism forms. My preferred set of views are those lying on the three pinacoid faces (Figure 4a) since these show the three principal interference figures (BX_a, BX_o and flash). X-ray diffraction would be required, however, to decide between the two choices. ■

1. Hopen, Thomas; Kilbourn, John. "Characterization and Identification of Water-Soluble Explosives"; *The Microscope* **1985**, 33, 1-22.
2. Kilbourn, John; and McCrone, Walter. "Fusion Methods Identification of Inorganic Explosives"; *The Microscope* **1986**, 34, 107-118.
3. McCrone, Walter "Solubility, Recrystallization and Microchemical Tests on Nanogram Single Particles"; *The Microscope* **1986**, 34, 107-118.
4. McCrone, Walter, Andreen, J.H., and Tsang, Sien-Moo "Identification of Organic High Explosives"; *The Microscope* **1993**, 41, 161-182.
5. Chamot, Émile; Mason, Clyde. *Handbook of Chemical Microscopy*, Vol. II; Wiley: New York 1940; reprinted by McCrone Research Institute; Chicago, 1989.

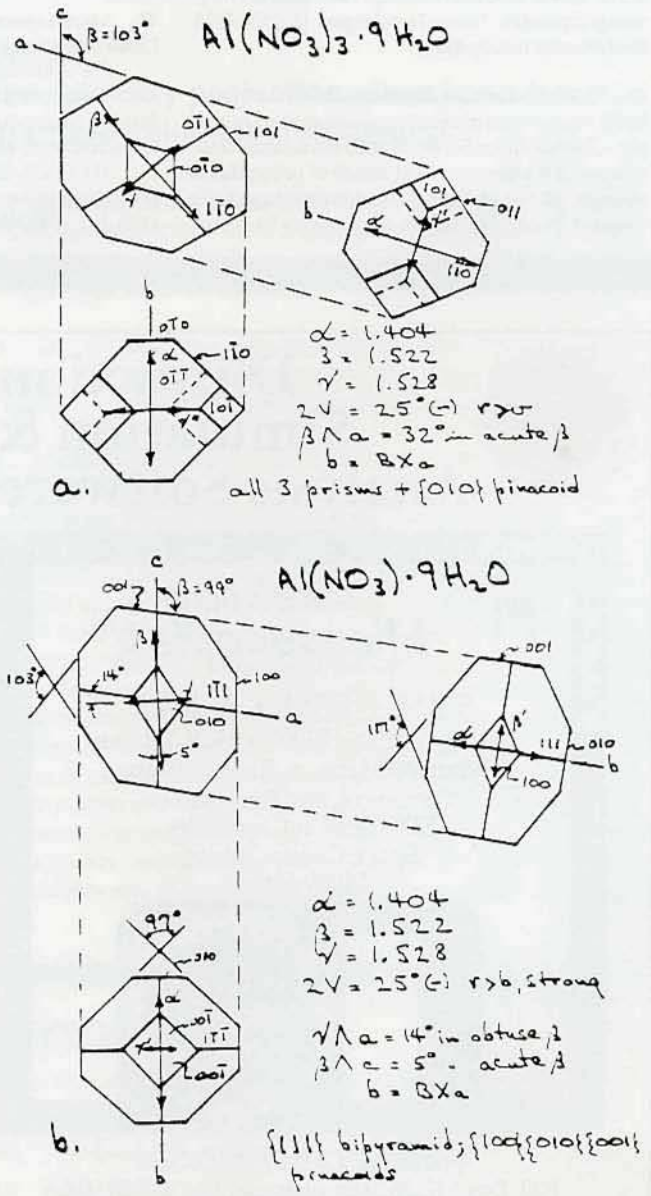

Figure 4. $Al(NO_3)_3 \cdot 9H_2O$ shown as bipyramid and pinacoids (a) and prisms and pinacoids (b).