

Supplementary Data

Co-agglomerated crystals of cyclic nitramines with the sterically crowded molecules

S1 Materials

The chemicals used in the current work, n-butanol, chloroform and dimethyl sulfoxide (DMSO), ethyl acetate, ethyl formate, acetone and n-heptane, are purchased from Lachner. Inc., Neratovice (Czechia) in a pure grade for mixed crystals preparation without further purification. The cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole or bicyclo-HMX (BCHMX) was prepared at the Institute of Energetic Materials as reported [1, 2]. It was recrystallized using solvent/antisolvent technique by acetone/water, and ϵ -2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ϵ -CL20) was a product of the Explosia Co. Pardubice pilot plant, crystallized using ethyl acetate/n-heptane solvents system; by this way the product was obtained with impact sensitivity of 6.4 J (before precipitation its solution in ethyl acetate treated with a little amount of P₂O₅ [3]).

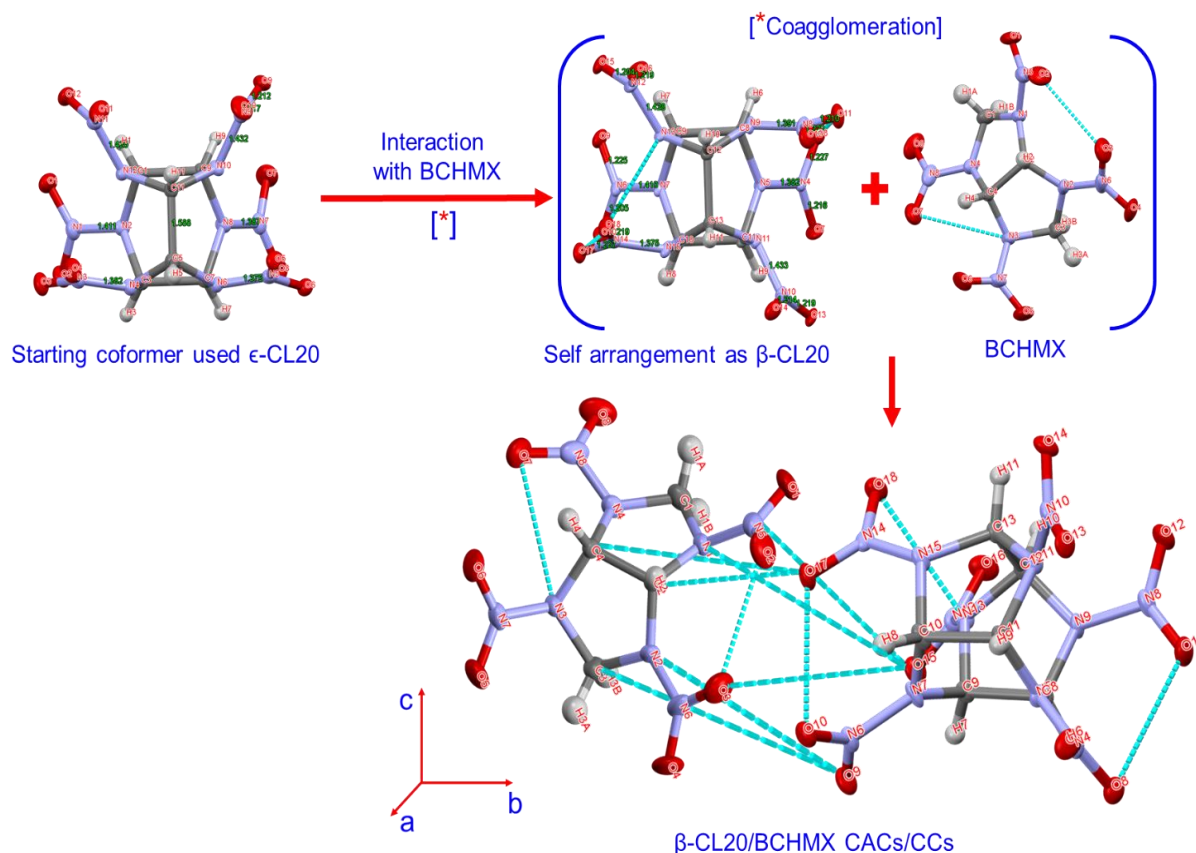
S2 Preparation of Coagglomerated Crystals(CACs)

Basically, two methods have been used to prepare these crystals:

- classical cocrystallization in a solvent/antisolvent system, namely ethyl acetate/n-heptane (sample CCs1) and ethylformate/n-heptane (sample CCs2).
- coagglomeration of the nitramines co-precipitates (from the DMSO/water system) in n-butanol or chloroform - a procedure [4] Similar to the Slurry Method [5].

S2.1 Coagglomeration mechanism prediction of CL20/BCHMX CACs:

The obtained observations from PXRD, FTIR, Raman spectrums and DTA thermograms found that there will be a conversion of ϵ -CL20 to β -CL20 after undergoing interaction with BCHMX during the coagglomeration process. Also shown the predominant N-N stretching vibrations in CL20, equivalently opposite N-N bonding undergone maximum stretching with bending to locate both -NO₂ groups in opposite side sides with Z-order[6,7]. These changes are indicated by taking the 3D structures of both forms of the CL20 molecule in Scheme S1[8-10]. These changes might indicate that CL20 had undergone self-polymorphic modification of the molecule to adjust with BCHMX to form a stable crystal lattice. These stretched N-N bonds showed active intermolecular hydrogen bonds and Van der Waals interactions in CL20 cocrystal earlier reported[4, 6, 8-14]. Based on all these precious observations and other results of earlier reported works, a possible mechanism of co-agglomeration may feasibly be predicted in the sense of proposed the CACs/CCs molecular structure of CL20/BCHMX shown in Scheme S1.



Scheme S1 Possible mechanism of coagglomeration interaction of both conformers in CACs/CCs

S3 Characterizations of CACs

S3.1 Particle size analysis and crystal density specification

The particle morphology, size distribution, crystal structure and composition analysis of the CACS and the conformers were examined using a MIRA3 LMH scanning electron microscope (Tescan, Czech Republic). Density studies by pycnometer were carried to evaluate the change in density after coagglomeration.

Crystal density was measured using the most reliable technique, Gas pycnometer AccuPyc II 1345; this technique is non-destructive as it uses the gas displacement method to measure volume.

S3.2 Chromatographic purity of mixed crystals and hypothetical formulas of CACs

The chromatographic analysis was carried out in Agilent HPLC 1200 Series with a DAD detector. Conditions of measurements, like mobile phase, stationary phase, detector etc., were further modified to improve the separation of EMs [15, 16]. In the present work, determining the purity and composition of co-crystals with concentrations were performed. The isocratic separation mobile phase ratio was used ACN:Water

(60:40) % v/v. The stationary phase was 4.6x250mm BDS Hypersil particle size 5 mm, pore size 112 nm C18 μ m S6 column, and its temperature was 26 °C with 10 mL/min flow. Its absorbance/detection wavelength was 210 nm. The run time of analysis was 15 min. The results are summarized in Table S1.

Table S1 Composition and purity analysis by HPLC

Nitramines (Codes of CACs)	Retention time [min]	Mean area [mAU.s]	Standard Deviation	Percentage of RSD [%]	Content [wt. %]
Pure BCHMX	3.566	501.54	3.362	0.669	100.0
Pure CL20	4.674	365.38	3.391	0.9229	100.0
Co-crystal 1	3.728	299.06	1.867	0.057	52.64
	4.700	275.45	1.112	0.035	47.35
Co-crystal 2	3.727	276.75	1.073	0.040	50.71
	4.699	262.12	1.145	0.037	48.04
S4	3.741	5394.82	1.788	0.033	37.80
	4.728	8879.23	1.480	0.017	62.20
S5	3.743	1171.95	1.254	0.107	27.13
	4.731	3147.49	1.156	0.036	72.86
S4LV	3.718	1212.17	2.983	0.246	30.47
	4.663	4084.09	1.492	0.036	69.53
S4LZ	3.720	1004.06	2.133	0.052	30.61
	4.664	2035.88	1.688	0.168	69.39
S5LV	3.718	1044.99	1.967	0.188	29.85
	4.663	3040.69	1.068	0.035	70.15

S3.3 FTIR and Raman spectral studies

A Nicolet Protege 460 FTIR spectrometer was used to record the IR spectral measurements of the samples using the transmission technique. Raman spectra were measured with Nicolet Is50 Raman, Thermo scientific, using an Ar laser ($\lambda = 514.5$ nm) and a semiconductor laser ($\lambda = 785$ nm). The maximum output power is 1.7 mW of the light spot of the Raman spectrometer, and the spectral resolution is 1 cm^{-1} . For a detailed understanding of the structural aspects of the CACs prepared and the interactions between their components, the FTIR and Raman spectroscopic techniques were used. Outputs from FTIR spectroscopy the Fig. S1 and Table 2 represent, from Raman spectroscopy results are summarized in Fig. S2 and Table 3 (both these Tables in the main paper text).

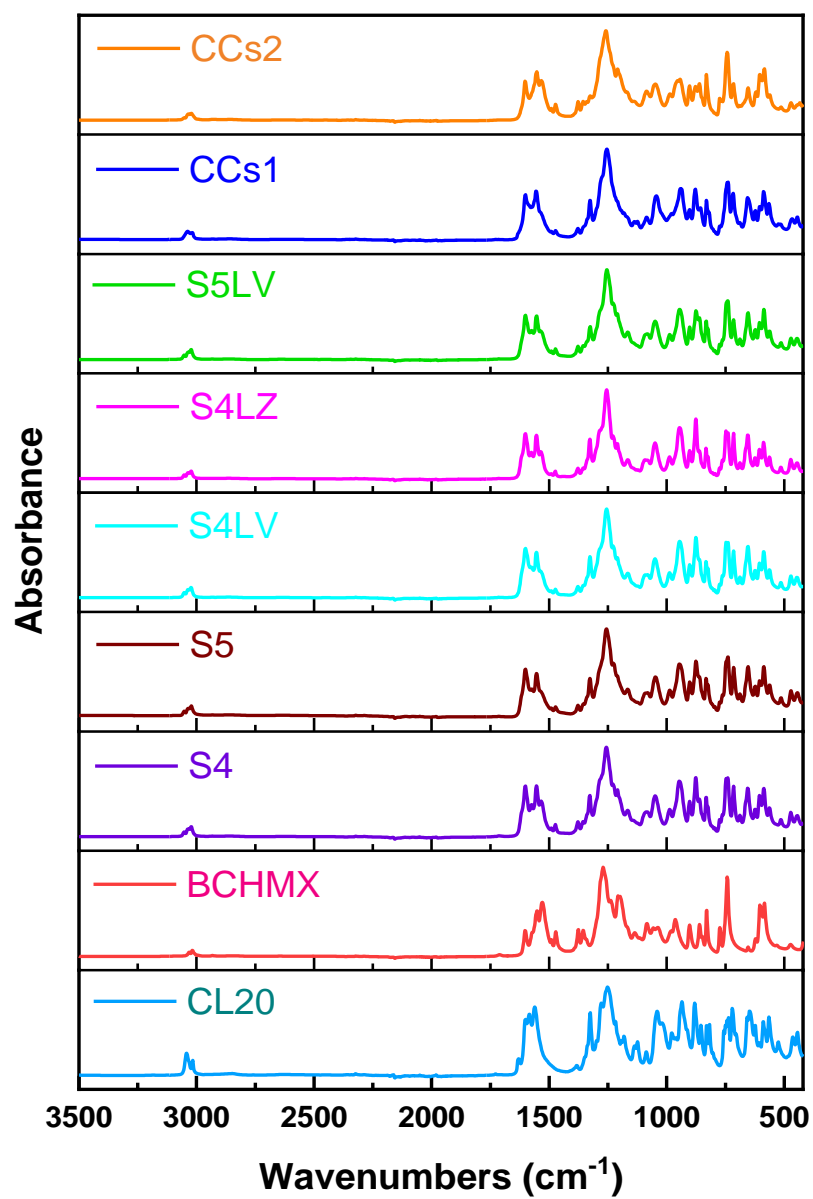


Fig. S1 FTIR spectra of CCs/CACs and their cofomers

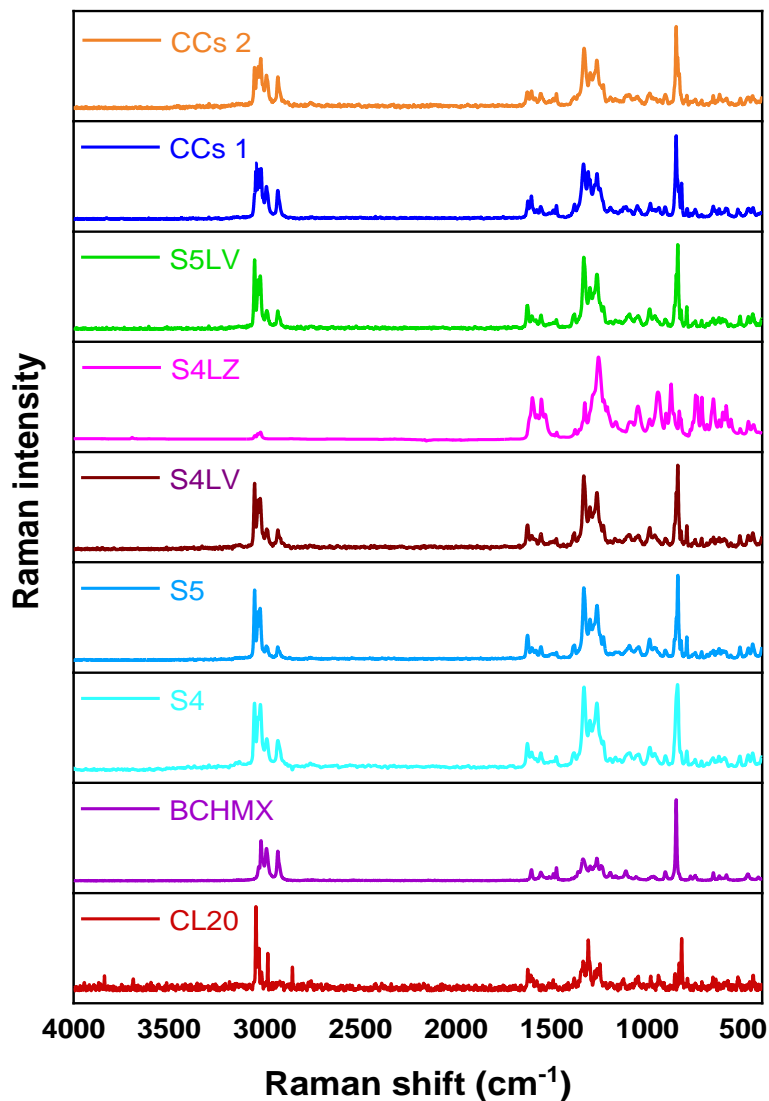


Fig. S2 Raman spectra of CCs/CACs and their cofomers

S3.4 Powder X-ray diffraction (PXRD)

To understand the morphology and phase purity by PXRD studies and the Scanning electron microscope (SEM) using a nano-layer gold coating(Tuscan, Czech Republic). The PXRD data were collected at room temperature with a Rigaku MiniFlex 600 powder diffractometer with Bragg-Brentano θ - 2θ geometry using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, $U = 40\text{kV}$, $I = 15 \text{ mA}$). Data were scanned with an ultrafast detector Dtex ultra over the angular range 2 - 50° (2θ) with a step size of 0.02° .

S3.5 Heat of combustion

The heat of combustion was measured with IKA C 200 Bomb-type calorimeter. The increase of temperature in the calorimeter barrel can be converted into the heat of combustion. The calorimeter was calibrated using benzoic acid. Enthalpy of formation was calculated according to Hess law. To get exact purity of individual and composition of CACs, a chromatographic analysis was carried out in Agilent HPLC 1200 Series with DAD detector. Results are summarized in Table S2.

Hypothetical formulas of CACs were calculated from the HPLC outputs. So, that number of nitrogen atoms in the formula of the given the BCHMX/CL20 CACs/CCs is the same, as there is in the CL-20) molecule (i.e. of 12). Results are summarized in Table S2.

S3.6 Calculation of detonation parameters

The theoretical detonation parameters (detonation velocity D , detonation pressure P and detonation energy E_{det}) for the compositions tested as well as pure explosives were calculated using the CHEETAH code [17] with the BKWS set of parameters for the BKW (Becker-Kistiakowsky-Wilson) equation of state, that is, $\alpha = 0.5$, $\beta = 0.298$, $\kappa = 1050$, $\Theta = 6,620$ [18]. The detonation energy is a sum of mechanical and thermal energies released during the detonation process. The mechanical energy represents the amount of energy available to do mechanical work, and it is equal to the expansion work of detonation products and determined for the volume of detonation products corresponding to a pressure of 1 atm. In contrast, thermal energy is the heat in the detonation products under this pressure [19]. For these calculations, the composition of detonation products was frozen at a temperature of 1800 K on the isentrope beginning at the CJ point. The final thermal energy determined for all compositions and explosives was zero. The calculated detonation parameters for the compositions and for the pure explosives are presented in Table 5 (in the main text of paper).

Table S2 Hypothetical formulas of the BCHMX/CL20 CACs and their heats of combustion

Sample code	Molecular formula	Molecular weight	Heat of combustion ($\text{J}\cdot\text{g}^{-1}$)	
			determined Q_c	averaged Q_c
S4	$\text{C}_{6.00}\text{H}_{7.23}\text{N}_{12.00}\text{O}_{12.00}$	439.44	8429	8475±33
			8573	
			8424	
S4LV	$\text{C}_{6.00}\text{H}_{6.91}\text{N}_{12.00}\text{O}_{12.00}$	439.12	8433	8446±23
			8481	
			8424	
S4LZ	$\text{C}_{6.04}\text{H}_{6.89}\text{N}_{12.00}\text{O}_{12.00}$	439.58	8379	8379± 3
			8375	
			8385	
S5	$\text{C}_{6.00}\text{H}_{6.78}\text{N}_{12.00}\text{O}_{12.00}$	438.99	8391	8343±32
			8333	
			8305	
S5LV	$\text{C}_{5.99}\text{H}_{6.89}\text{N}_{12.00}\text{O}_{12.00}$	438.98	8315	8318± 6
			8327	
			8312	

CCs 1	C _{6.03} H _{7.21} N _{12.00} O _{12.00}	439.78	8468	8447±13
			8432	
			8442	
CCs 2	C _{6.00} H _{7.46} N _{12.00} O _{12.00}	439.70	8667	8655± 7
			8651	
			8649	

S3.7 Impact Sensitivity

The sensitivity was determined employing a standard impact tester with exchangeable anvil (Julius Peters [20, 21]), with the amount of the tested substance being 40 mm³ [20]; the detection was based on sound effect [21]; drop hammers of 2 kg weight were used [20, 21]. The new method/algorithm, called FEST [22] (an innovative method of probit analysis [23]), was utilized to determine the probability levels of the initiation. The obtained sensitivity was expressed as the drop energy, E_{dr} , versus the percentage of initiation. The 50% (E_{dr} 50 %) and 95% (E_{dr} 95 %) probabilities of initiation are specified in this article.

S3.8 Differential thermal analysis (DTA)

This analysis was carried out to understand the CACs samples thermal behaviour was measured using a differential thermal analyzer. A DTA 550 Ex apparatus (OZM Research) was used for thermal analysis of the samples [24]. The measurements were carried out at atmospheric pressure, with the tested sample in direct contact with the air. The tested sample (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm long. The reference standard was 0.05 g aluminium oxide. A linear heating rate of 5 °C min⁻¹ was used.

S3.9 Test of the initiation efficiency of coagglomerates in detonators

The test of the initiation strength of coagglomerates (CACs) of CL20 with BCHMX was carried out according to standard [20] with weights from 51 to 300 mg of selected CACs, in aluminium shells of 7.5 mm diameter, with a pressure of 60 kg per pressing pin, with a secondary charge of 720 mg pentythritol tetranitrate (PETN), pressed by a pressure of 180 kg per pressing pin. The adjusted detonator was then placed on a 5 mm thick lead plate, and the detonator was initiated according to the standard procedure [20]. Figure S3 shows the measurement setup and the result of two tests with an amount of S4LZ from 50 to 300 mg sample weight: in neither of these two tests, the initiation of the secondary charge of the detonator occurred with a charge. In all cases, the aluminium tubes were ruptured, and PETN residues were found; the lead plates were not punctured effectively.

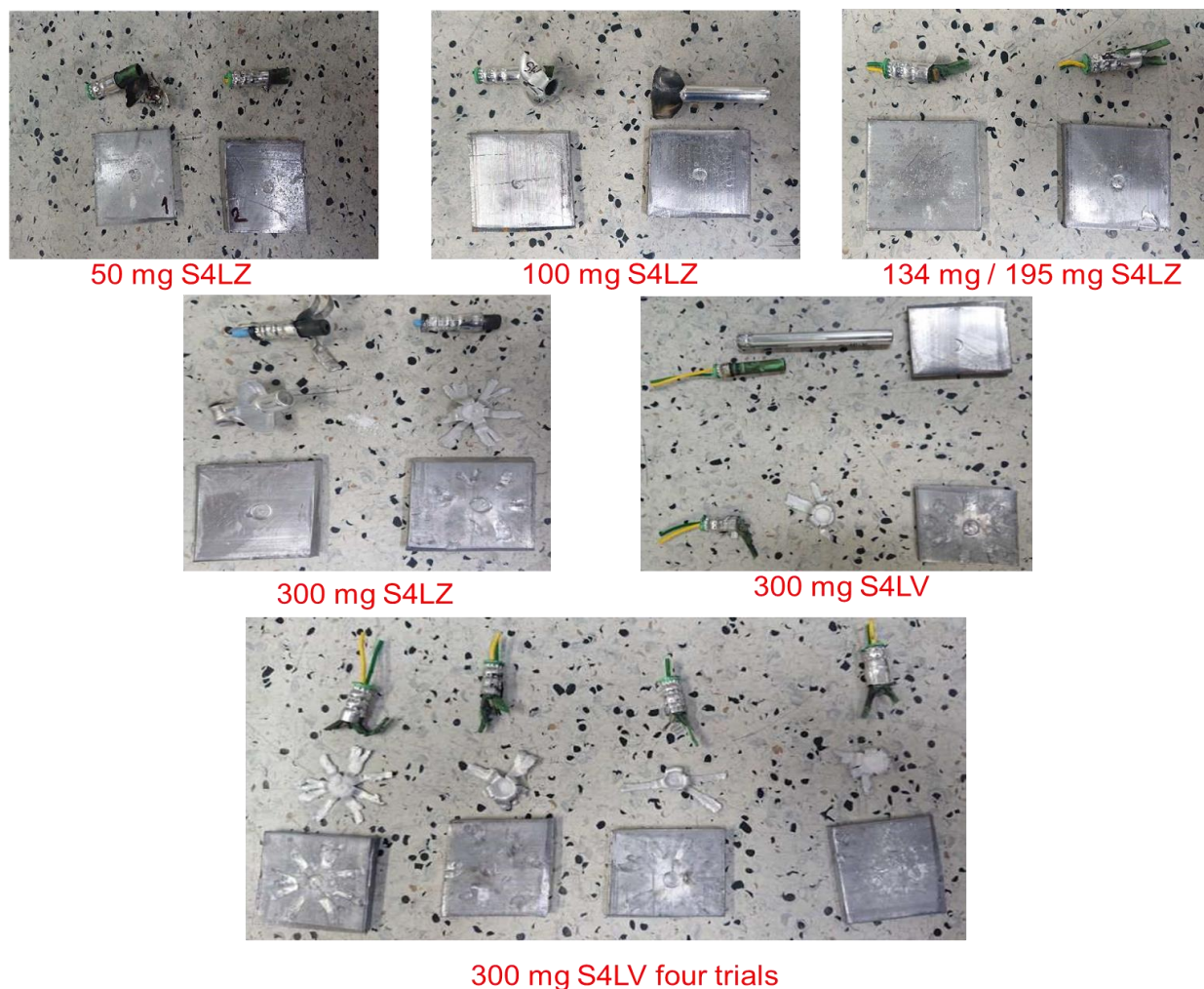


Fig. S3 The initiation efficiency determination of detonators with CACs as primers results of two tests for each weighed amount - the lead plates pictures.

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