Modelling the effect of humidity on obscurant performance

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Abstract

New obscurant compositions are needed with a performance that is comparable to currently used compositions, based on environmentally benign ingredients, and with a low toxicity of the reaction products. A variety of compositions were prepared; small scale performance tests were carried out at 20 °C and 35 or 60% relative humidity in a 2 m^3 chamber volume and large scale tests in outdoor conditions. Also in-vitro toxicity tests were carried out. A difference in hygroscopic behavior was noted and the effect of humidity on obscurant performance is modelled for a selection of tested compositions. All three compositions generate substantial amounts of condensed products, referred to as primary smoke. Secondary smoke generation (condensation of water/acid vapor) through homogeneous nucleation does not explain the experimentally observed humidity dependence of light extinction. Heterogeneous nucleation, however, seems a plausible hypothesis for secondary smoke generation.

1. Introduction

Hexachloroethane / aluminum / zinc oxide is a traditional obscurant composition. During combustion of this composition, the zinc chloride formed readily condenses water from the atmosphere at low relative humidity. The formed aerosol droplets are acidic, corrosive and may even dissolve organic tissue [1]. In an effort to replace hexachloroethane / zinc oxide as obscurant composition, new pyrotechnic compositions are needed with a performance that is comparable to currently used compositions, based on environmentally benign ingredients, and with low toxicity reaction products. A variety of compositions were prepared, small scale performance tests were carried out in a 2 m^3 chamber volume, and large scale tests in outdoor conditions. Also in vitro toxicity tests were carried out. Experimental results were presented in [2], including the performance (Figure of Merit) of 15 compositions at 20 °C and 60% relative humidity. A selection of 8 compositions was further tested also at a reduced 35% relative humidity. A difference in hygroscopic behavior was noted, which was the direct motivation for the modelling of the effect of humidity on obscurant performance.

The starting point for the analysis is STANAG 6016 [3], developed to classify solid propellant smoke. The standard recognizes the need for a uniform classification of smoke signatures as more generic terms like “reduced smoke”, “minimum smoke”, *etc.* were being used. The concept of primary smoke and secondary smoke generation that is introduced in [3] will be applied here to some of the pyrotechnic compositions in [2]. The principles underlying the distinction between primary smoke and secondary smoke are not *per se* limited to solid propellant smoke, but might be extended to any decomposing energetic material. A recent example of the use of primary and secondary reactivity in smoke compositions is found in [4], where the thermodynamics of boron phosphide – potassium nitrate and boron carbide – potassium nitrate binary systems are studied. In particular the adiabatic reaction temperature of pure red phosphorous, white phosphorous and M819 are calculated as a function of the amount of air (25 ºC temperature and 50% relative humidity) participating in the combustion as well as the reaction products for the case of 77 or 73 wt.% of air.

Thermodynamic calculations are presented here for the smoke generated by three compositions. Primary and secondary smoke generation is quantified. In particular the degree of dilution of smoke into a volume of air, and the effect of relative humidity, is studied in detail. Furthermore, the effect of particle size on secondary smoke generation is discussed.

2. Smoke compositions

Three different smoke compositions from [2] were studied. The reference composition is 11EM0745 containing 70 wt.% $NaClO_3$, 22% cellulose, 5% $CaCO_3$ and 3% Mg. The compositions 15EM280 and 15EM281 contain the ingredients $NaClO_3$, $CaCO_3$, Mg as well as another component to replace the cellulose.

Small scale performance tests were carried out in a 2 m^3 chamber volume, and large scale tests in outdoor conditions. The extinction of visible light and near infrared radiation was measured with a 1 m travel distance for light inside the chamber. A known amount of composition was burnt in the chamber and reaction products are homogenized by enforced air recirculation in the chamber. The Figure of Merit of the smoke compositions, see Table 1, was calculated applying Lambert Beer's law. The higher the Figure of Merit, the better the obscurant performance of a smoke composition.

$$Figure\ of\ Merit = \frac{-Volume_{chamber} \ln\left(\frac{Intensity\ radiation_{with\ extinction\ by\ smoke}}{Intensity\ radiation_{witho\ \ \ extinction\ by\ smoke}}\right)}{Mass_{composition} \cdot Travel\ distance\ radiation}$$

Table 1: Figure of Merit determined in a 2 m^3 chamber for 3 compositions at indicated temperature and humidity.

Composition	Figure of Merit Visible light m^2/gr	Figure of Merit Near infrared m^2/gr	Relative humidity %	Temperature ºC
11EM0745	0.47	0.41	60	20
	0.24	0.18	35	20
15EM280	0.57	0.54	60	20
	0.44	0.40	35	20
15EM281	0.67	0.65	60	20
	0.65	0.62	35	20

The Figure of Merit, thus obscuring performance, increases going from the reference to the new compositions 15EM280 and 281. The composition 15EM281 has the best performance both in the visible and near infrared regime. The effect of relative humidity is noticeable for both the reference composition and 15EM280. For composition 15EM281, the transmission of radiation in the visible and near infrared regime is hardly effected by the change in relative humidity, despite chemical similarity of 15EM280 and 15EM281.

Outdoor experiments were performed at Edgewood Chemical and Biological Centre. In those experiments each sample contained 400 g of the study composition and 5 g of a starter composition. The observation of "nice, even burn, dense and persisting smoke cloud" was reported.

3. Primary and secondary smoke generation

In [3] a distinction is made between the generation of condensed materials in the exhaust plume, and the condensation of water vapor and/or acid vapors.

- Primary smoke: the result of condensed materials (metals, oxides, carbon, etc.) in the exhaust plume.
- Secondary smoke: the result of condensation of water vapor alone or of water and acid vapor.

Acid vapor is known to depress the saturated water vapor pressure [5]. The effect of humidity is therefore related to the secondary smoke generation.

Thermodynamic calculations were performed using the ICT-code [6]. Reaction products are calculated at 25 °C for a combustion at a very low loading density of less than 0.00020 g/cm^3. Results are presented in Table 2. The reference compositions 11EM0745 produces almost twice the number water molecules per unit weight of composition. Both compositions 15EM280 and 15EM281 produce an overwhelming amount of HCl in comparison to composition 11EM0745.

Table 2: Calculated reaction products with ICT-code.

	11EM0745	**15EM280**	**15EM281**
Density kg/m^3	$2.18 \cdot 10^3$	$2.13 \cdot 10^3$	$2.06 \cdot 10^3$
Gas volume w/o water m^3/kg	0.2393	0.2596	0.2953
Products mol/kg			
Total	24.842	22.833	24.011
Solids	8.309	8.498	8.009
Gases with water	16.533	14.335	16.001
Gases without water	9.782	10.613	12.071
Liquid mol/kg			
H_2O	6.751	3.722	3.930
Gas mol/kg			
CO_2	8.640	6.900	6.964
CO	0	0	1.236
O_2	1.106	1.517	0
N_2	0	0	0
HCl	0.032	2.154	3.600

3.1 Primary smoke generation

The primary smoke evaluated according to the parameter [7]

$$1 - \exp\left(-\sum_i (\%M_{pi}N_i/SG_i)\right)$$

with $\%M_{pi}$ the mass percentage of the condensable product, N_i the optical property constant (assumed to be 1.0), and SG_i the specific gravity, and i each of the condensable metallic products CaO, $CaCl_2$, MgO, NaCl and NaOH. This parameter equals 1.00000 for all three compositions. All three obscurant compositions are assessed as generating substantial primary smoke, and no distinction between the compositions can be made.

3.2 Secondary smoke generation

The secondary smoke generation is quantified using the same physical principles as described in [3]. In the standard the assessment of secondary smoke generation is based on mixing of exhaust gases into a 1000-fold volume of gases of ambient relative humidity.

The secondary smoke generation is quantified here by calculating the required relative humidity of the ambient atmosphere at which the water saturation pressure will be exceeded. The required relative humidity is calculated as a function of the dilution from no dilution at all, up to a 1000-fold dilution. The dilution is the volume of the ambient atmosphere divided by the volume of produced smoke.

The following steps are needed in the calculation:

- The saturated vapor pressure of water p^0_{H2O} at a specific temperature is calculated using the Antoine equation.
- The HCl (acid gas) pressure in the reaction product volume at standard conditions is calculated.
- The actual HCl pressure p_{HCl} is a function of dilution according to

$$p_{HCl}(dilution) = \frac{p_{HCl,volume\ of\ reaction\ products\ at\ 298K}}{dilution}$$

- The saturated vapor pressure of water is suppressed by the presence of acid gases. Data to describe this relation is found in [5], and a 3rd order polynomial fit is made of the relation between the logarithm of HCl vapor pressure and the depression factor K of saturated vapor pressure of water.

$$K(HCl) = \frac{p^o_{H2O}(p_{HCl})}{p^o_{H2O}(according\ to\ Antoine\ equation)}$$

- The required relative humidity RH_{req} to reach the saturated vapour pressure of water in the presence of HCl is calculated, taking into account 1) water and HCl already present in product gas composition, 2) dilution and homogeneous mixing into ambient gas volume, and 3) depression of saturated vapor pressure of water. The requirement for homogeneous condensation is:

$$p_{H2O,ambient} + p_{condensable\ gaseous\ products\ after\ dilution} = K(HCl)p^{o}_{H2O}(according\ to\ Antoine\ equation)$$

or

$$\frac{p_{H2O,ambient} + \dfrac{(p_{H2O} + p_{HC}\ )_{in\ product\ gasvolume\ @\ dilution=1}}{dilution}}{p^{o}_{H2O}(according\ to\ Antoine\ equation)} = K(HCl)$$

This is then rewritten as

$$RH_{req} = 100\% * \left(K(HCl) - \frac{(p_{H2O} + p_{HC}\ )_{in\ product\ gasvolume\ @\ dilution=1}}{dilution * p^{o}_{H2O}(according\ to\ Antoine\ equation)}\right)$$

Figure 1 contains the data for the depression factor *K*(HCl) of saturated vapor pressure of water versus absolute HCl vapor pressure. Experimental data from [5] is fitted data at 15, 20 and 25 °C. The fitted curve with constants as well quality of the fit (R^2) for the 20 °C case is presented in Figure 1. One can see that for HCl vapor pressures as low as 10^{-7} bar the value of *K*(HCl) deviates from 1 and HCl vapor has an effect on the saturated vapor pressure of water.

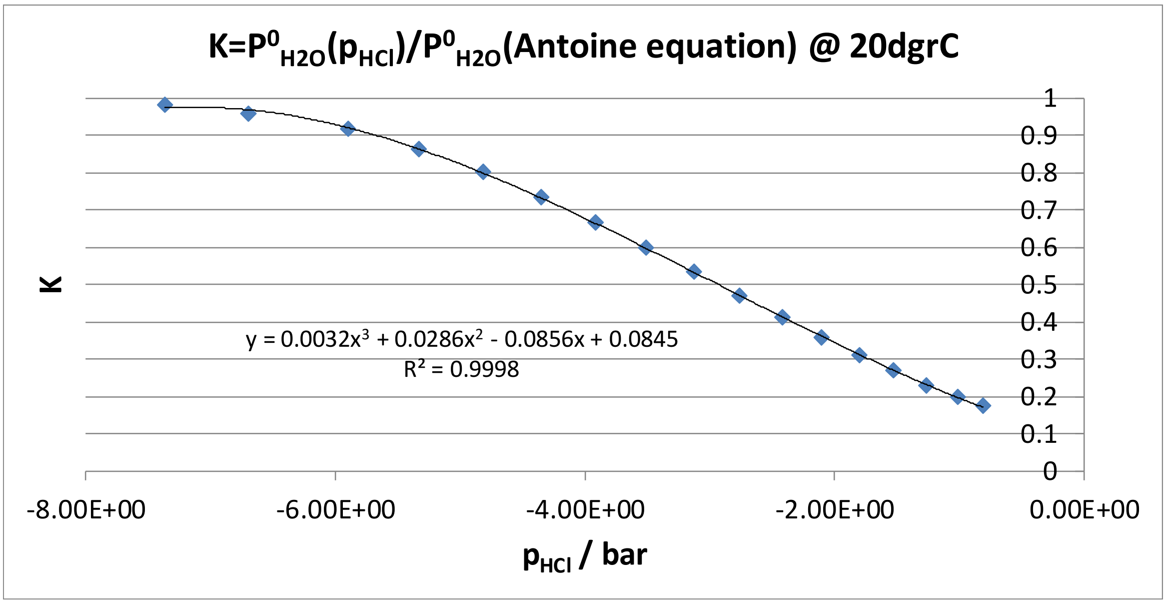

Figure 1: Depression factor *K* of water saturated vapor pressure at vertical axis and logarithm of HCl vapor pressure (in bar) at horizontal axis. Temperature is 20 °C. Data is extracted from [5].

The required relative humidity of the ambient atmosphere to reach the saturated vapor pressure of water, taking into account the presence of HCl in the reaction products, is plotted in Figure 2 for the three obscurant compositions as a function of dilution. Data are shown only for HCl pressures that are within the range of experimental data in [5]. This is done at the three indicated temperatures. The scale of relative humidity is from 0 to 100%, the scale of dilution is from 1 (no dilution) to 1000. As expected a decrease in temperature lowers the required relative humidity to reach the condensation condition for each composition, especially at low dilution numbers.

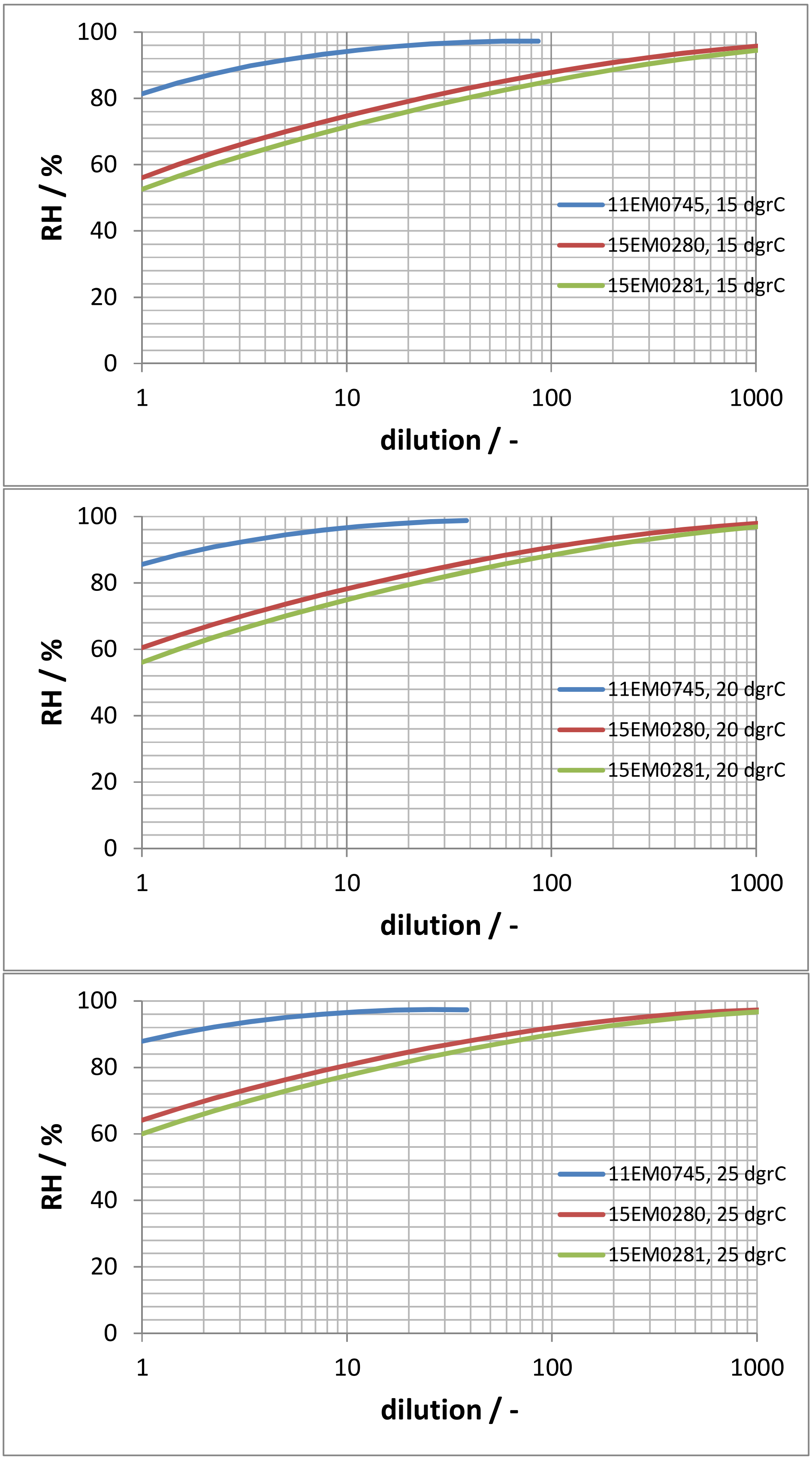

Figure 2: Required relative humidity versus dilution of combustion gases into ambient atmosphere for indicated compositions. Temperature is 15 ºC (top), 20 ºC (middle) and 25 ºC (bottom).

There is a clear distinction in these graphs between the reference composition and the other two compositions. Even though more moles of water are produced by the reference composition, the required relative humidity to reach the saturated water vapor condition is higher than for 15EM280 and 15EM281. Therefore, when only regarding the production of water by the composition, this cannot explain the required relative humidity for secondary smoke generation.

Hydrogen chloride is a gas in the 15-25 °C range, with a saturated vapour pressure of HCl that is 3 orders of magnitude larger than the saturated vapor pressure of water. In the product composition at ambient temperature, the HCl pressure is of the order of 10^{-6} bar when not diluted. The pure condensation of HCl cannot explain secondary condensation.

The presence of HCl in product gases has a strong effect on the saturated vapour pressure of water as the H_2O and HCl molecules have a large affinity. This has been introduced explicitly in the modelling and it is not strange that this effect is noticed. The magnitude of the effect was not known up front however. The presence of HCl in the product gas for studied compositions has decreased the saturated vapor pressure of water to such a degree that the required relative humidity needed to condense water in the ambient atmosphere is significantly lowered.

The above arguments are qualitative and intuitively explain experimental observations. Even if compositions 15EM280 and 15EM281 are more prone to secondary smoke generation the question remains whether this will explain the experimental results in a quantitative manner.

The dilution number corresponding to the experiments performed in the 2 m^3 box, is calculated for each composition, see Table 3. The required relative humidity for condensation is larger than any of the experimental conditions, i.e. either 35 or 60% relative humidity. This means that no liquid droplets will form. Furthermore, in the experiments a change in light extinction was noticed for 11EM0745 and 15EM280 as function of relative humidity. Secondary smoke generation through homogeneous nucleation of liquid droplets in ambient atmosphere therefore appears not able to (fully) explain the experimental results.

Table 3: Required relative humidity (RH) for secondary smoke generation through depression of saturated vapor pressure by the presence of water for experiments presented in [2], see Table 1.

	11EM0745	15EM280	15EM281
Dilution at 20 °C	1700	1567	1378
Required RH	>98.8%	≈98.8%	≈98.8%
Experimental RH	35/60%	35/60%	35/60%

4. Discussion on heterogeneous nucleation and secondary smoke generation

In the analysis above, only primary smoke generation (due to solid particles in reaction products) and secondary smoke generation based on homogeneous nucleation, were taken into account. Secondary smoke generation based on heterogeneous nucleation was not part of the assessment. All three obscurant compositions were assessed as generating substantial primary smoke, and therefore nuclei are present onto which water and acid vapor might condense.

Here the effect of solid particles and the eventual condensation of the condensable gases onto these particles is discussed. Suppose a liquid droplet, or a solid particle with a liquid film cover, of diameter D is in a vapor environment. The equilibrium vapor pressure at the liquid and vapor interface, is different for the droplet as compared to a planar interface. The change in equilibrium vapor pressure is due to the increased energy of a curved surface. Growth of the surface will decrease curvature, thus energy of the total aerosol system, and may be realized if condensable vapor is present in the ambient atmosphere.

In case of an obscurant smoke it is hypothesized that H_2O and HCl condensable products in the combustion products (i.e. regardless of relative humidity of the ambient atmosphere) are condensing on small solid particles already. The consequence is that particles are larger than the dry particles only.

The thus formed liquid film might attract humidity from the environment, and let the aerosol particles grow further until equilibrium with the vapor phase is reached. This equilibrium depends on surface curvature, the amount of acid in the liquid film, the relative humidity of the ambient atmosphere and vapor concentrations of condensable products in the surrounding air.

Due to dispersion of the smoke in time, the aerosol becomes diluted and the equilibrium conditions that led to a stable liquid film may change, probably leading to its evaporation. The lower the ambient relative humidity the larger the driving force for evaporation, and the shorter the effect of secondary smoke persistence. However, the higher the acid content absorbed into the liquid film, the smaller the driving force for evaporation and the longer the effect of secondary smoke persistence.

The saturation ratio *S* for an aqueous droplet is described for example in [8].

$$S = a_{H2Oinsolution}\exp(\frac{4\gamma M_{wH2O}}{RT\ {}_{H2O}D})$$

With a the activity of water in solution, γ the surface tension of the solution/air interface, M_w the molecular weight water (18.02 g/mol), R the gas constant (8.31 J/molK), T the absolute temperature, ρ the density water (1.0 kg/m^3) and D the diameter of the aerosol particle.

In order for a smoke like 15EM0281 to show independence on relative humidity in the 35-60% range, is that the aerosol particles are so small that also at 35% relative humidity the saturation condition is reached over a curved surface.

The following are preliminary calculations with the aim to check the feasibility of the heterogeneous nucleation hypothesis, assuming that the temperature is 20 °C, the activity of water in a liquid film covering a solid nucleus is 1 (it should be less as HCl will dissolve into it), the surface tension is 0.072 N/m (water) and that the depression of the saturation pressure of water in the presence of HCl is not influenced by the aerosol particles.

The required saturation ratio S_{req} to reach heterogeneous nucleation is calculated using

$$S_{req} = \frac{RH_{req}}{RH_{ambient}}$$

The maximum aerosol particle to meet the required saturation ratio is then calculated. Results are presented in Table 4, 5 and 6 for a dilution of 1, 10 and 100 respectively.

Table 4: Required saturation ratio *S* and maximum aerosol particle size for secondary smoke generation through heterogeneous nucleation. No dilution of combustion products in ambient atmosphere, i.e. dilution =1.

Dilution=1	**11EM0745**	**15EM280**	**15EM281**
Required *S*	2.33	1.68	1.55
Maximum aerosol particle size	2.52 nm	4.11 nm	4.86 nm

Table 5: Required saturation ratio *S* and maximum aerosol particle size for secondary smoke generation through heterogeneous nucleation. 10-Fold dilution of combustion products in ambient atmosphere, of indicated relative humidity (RH).

Dilution=10	**11EM0745**	**15EM280**	**15EM281**
Required *S*			
35% RH	2.75	2.23	2.13
65% RH	1.48	1.20	1.15
Maximum aerosol particle size			
35% RH	2.11 nm	2.26 nm	2.82 nm
65% RH	5.38 nm	11.5 nm	15.1 nm

Table 6: Required saturation ratio *S* and maximum aerosol particle size for secondary smoke generation through heterogeneous nucleation. 100-Fold dilution of combustion products in ambient atmosphere, of indicated relative humidity (RH).

Dilution=100	**11EM0745**	**15EM280**	**15EM281**
Required *S*			
35% RH	2.81	2.59	2.52
65% RH	1.52	1.40	1.36
Maximum aerosol particle size			
35% RH	2.06 nm	2.24 nm	2.30 nm
65% RH	5.12 nm	6.39 nm	6.94 nm

It is clear that it is easier to have heterogeneous nucleation in the reaction products (dilution is 1) in case of 15EM281 than for the other two compositions as the required particle size is larger. Still, the absolute value of the aerosol particle size needs to be quite small, less than 4.86 nm, and one may debate if condensation really occurs.

At a 10-fold dilution it is noted that only particles as small as 15.1 nm are needed for condensation in 65% relative humidity. This particle size is getting intuitively closer to realistic particle sizes. It is concluded that the “easiness” of heterogeneous nucleation has an optimum between a dilution of 1 and 100, in case of 15EM281. If all compositions produce solid particles with the same particle size distribution, then it is understandable that humidity has a tendency to wet the particles in particular those of composition 15EM281.

The particle sizes were monitored in the 0.3-20 µm range during in vitro experiments [9]. Most particles were measured at the small particle size of the measurement range, i.e. near 300 nm, and particles above 1.6 µm were only present in very small numbers, see Figure 3. The measurement range however, did not extend below 300 nm. This means approximately 1 to 2 orders of magnitude difference with the calculated particle size required for heterogeneous nucleation.

It seems that heterogeneous nucleation might be the working hypothesis to explore, in order to explain the independence on relative humidity for composition 15EM0281. The same working hypothesis should also be able to explain the relative humidity dependence of the other compositions.

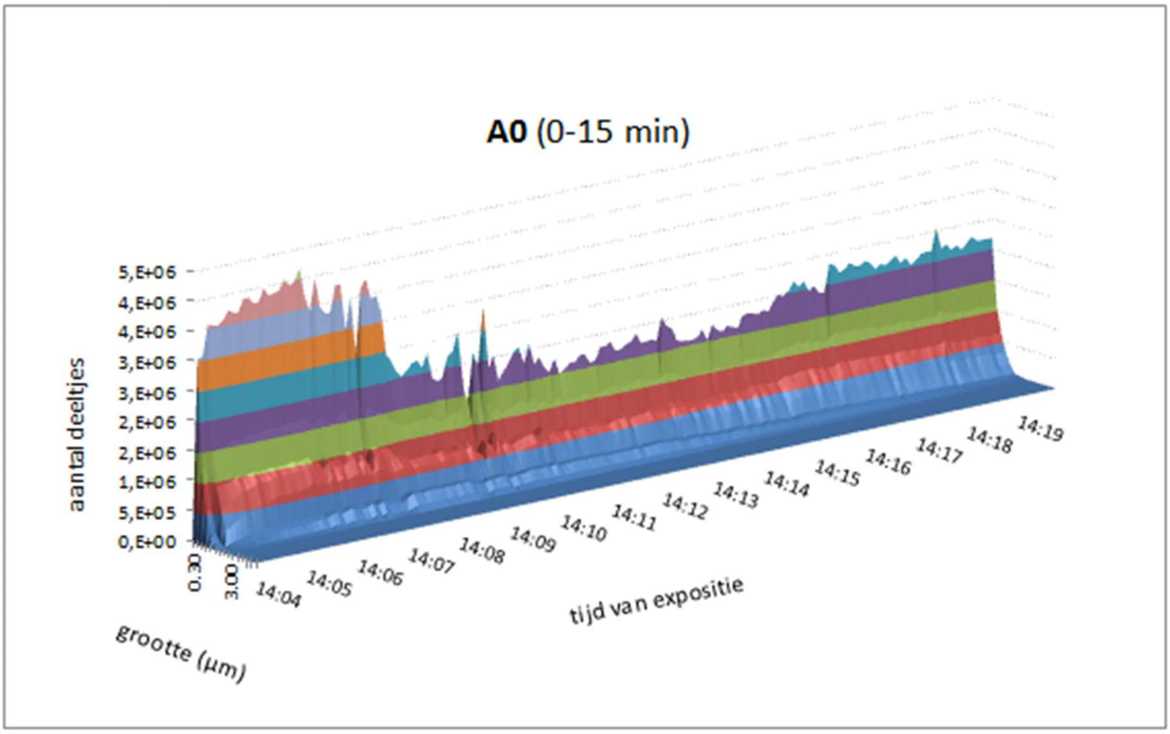

Figure 3: Particle number of reaction products composition 15EM281 (vertical axis), particle size distribution (short axis in horizontal plane) and 15 minute duration of particle size distribution measurement (long axis in horizontal plane) [9].

Conclusions

The performance of three obscurant compositions was measured in the visible light and near infrared, at ambient temperature and at a relative humidity of 35 or 60%. Thermodynamic calculations were performed to support the experimental data. Conclusions regarding the thermodynamic calculations are:

- All three compositions generate substantial condensed products, referred to as primary smoke generators.
- Secondary smoke generation through homogeneous nucleation cannot explain the experimentally observed humidity dependence of light extinction.
- Heterogeneous nucleation seems a plausible hypothesis for secondary smoke generation, as 1) required seed particle sizes for the condensation of water and acid vapors are near 10 nm at a moderate ten-fold dilution of reaction products in ambient atmosphere, and 2) measured particle numbers of the best performing smoke composition are highest near the lower size detection limit of 300 nm.

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