Visual and Near Infrared Mass Extinction Coefficient of Five Pyrotechnic Screening Smokes

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Abstract: *The screening properties of five different obscurants were compared at relative humidities of 30%, 50% and 85% and mass extinction coefficients were calculated. The obscurants were five military smokes: 1) a traditional hexachloroethane, Zn powder and TNT based screening smoke, the HC smoke as a reference, 2) a potassium chlorite, Mg powder and azodicarbonamide based screening smoke, the KM smoke, 3) a Mg powder based HC smoke, 4) a potassium chlorate, lactose and terephthalic acid based white coloured screening smoke, the TPA smoke, and 5) a titanium oxide based HC smoke. The apparatus was a CCD (Charge-Coupled Device) detector based dispersive spectrometer with a sample chamber and a humidity generator. The wavelength region was 450 to 850 nm. The important variable in determining how a military smoke retains its screening properties over time is the mass extinction coefficient. According to the results, the Zn based HC smoke has the best screening properties at low relative humidity. When the relative humidity is high the Mg based HC smoke has the best screening properties at first, but the KM type smoke retains its screening properties well, being the best of these three smokes after 20 seconds. After 60 seconds, the mass extinction coefficient of the KM smoke is 33% higher than the mass extinction coefficient of the reference smoke, when the mass extinction coefficient of the Mg based HC smoke is 20% lower than the mass extinction coefficient of the reference smoke.*

Keywords: *Screening smoke, obscurant, extinction coefficient, infrared*

1. Introduction

The reason for measuring transmission is to investigate the extinction properties of obscurants such as military smokes as a function of wavelength in the visual and near infrared region of 450 to 850 nm. The commonly known wavelength limits are 380 to 760 nm for the visual range (VIS) and 0.76 to 1.3 µm for the near infrared range (NIR), respectively. The wavelength limits may vary depending on the reference. Reliable and repeatable laboratory scale transmission measurement of obscurants in the visual and near infrared wavelength region requires an apparatus specially designed for this research.

In practice, humidity noticeably affects the extinction of light in an aerosol medium such as military smokes, and therefore measurements have to be performed in a controlled humidity environment. A humidity generator and the capability to measure the relative humidity and temperature are necessary. On the basis of experience the calculated absolute humidity values for each military smoke using the measured values of relative humidity and temperature should be taken into account when analysing the screening properties.

The extinction research on obscurants such as military screening smokes was performed in the visual and infrared wavelength region using an FTIR spectrometer and an experimental

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chamber with humidity adjustment.[1] Some studies were carried out using the whole broad visual wavelength band of the QTH lamp for the extinction measurements of screening smokes. [,2] An infrared camera was also a very useful instrument for research into the infrared screening capability of military smoke clouds.[3,4] The chemistry of military screening smokes for known compositions has been described by many authors.[5–7]

2. Transmission measurements of aerosols

An aerosol in the gaseous medium consists of solid state particles and/or liquid droplets, which have a particular diametric distribution, e.g. the HC type military smoke has a typical particle diameter of about 0.1 μm,[8] but at high humidity it rises to values of 3 to 7.6 μm after several seconds. As a point of comparison typical natural clouds contain water droplets with mean radii of about 20 μm.[9]

The interaction mechanisms between electromagnetic radiation and aerosol particles in the visible and infrared region are scattering and absorption. In the scattering phenomenon, an electromagnetic wave changes its direction of propagation randomly in every collision with aerosol particles. In absorption a photon loses its energy totally or partly to the vibrational or rotational movement of a molecule. Absorption is a potential interaction mechanism with gaseous molecules and with solid particles or with liquid droplets.

The variables in the transmission of the radiation through a medium containing aerosol particles are spectral radiance $L_\lambda(\lambda,s)$ at a point s with coordinates (x,y,z), mass concentration of the aerosol ρ [g cm^{-3}], spectral mass absorption coefficient $\alpha_a(\lambda,s)$ and spectral mass scattering coefficient $\alpha_s(\lambda,s)$. The wavelength of the radiation is λ. Thus the spectral radiance has the equation:

$$\mathrm{d}L_\lambda(\lambda,s) = -\alpha(\lambda,s)L_\lambda(\lambda,s)\rho\,\mathrm{d}s \qquad (1)$$

where $\alpha(\lambda,s) = \alpha_a(\lambda,s) + \alpha_s(\lambda,s)$ is the spectral mass extinction coefficient. The extinction of the radiation is the combined effect of the absorption and the scattering phenomena.[10,8]

Here it is assumed that: 1) the aerosol medium is homogenous and thus $\alpha(\lambda,s) = \alpha(\lambda)$; 2) the scattering originating from the side radiation by the aerosol is insignificant and 3) the intrinsic thermal emission of the aerosol and the medium atmosphere is insignificant. The Lambert–Beer law can be written as:

$$\alpha(\lambda)\rho l = -\ln L_\lambda/L_{o\lambda} = \ln L_{o\lambda}/L_\lambda \qquad (2)$$

The transmittance at the wavelength λ is:

$$T_\lambda = L_\lambda/L_{o\lambda} = e^{\alpha(\lambda)\rho l} \qquad (3)$$

The spectral mass extinction coefficient can be calculated from the equation:

$$\alpha(\lambda) = \ln(L_{o\lambda}/L_\lambda)/\rho l = -\ln T_\lambda/\rho l \qquad (4)$$

The variables $L_{o\lambda}$ and L_λ, describing the intensity of the transmitted radiation without aerosol and with aerosol, respectively, can be measured as a function of wavelength. The mass concentration of the aerosol ρ is calculated and the path length of radiation l is known from the geometry of the experimental setup.

The models for the scattering of electromagnetic radiation by a single particle are based either on an exact solution to Maxwell's wave equations or, if there is no analytical solution, on approximative numerical solutions. The Mie theory is an analytical solution to Maxwell's equations in the case of scattering by spherical and ellipsoidal particles. In the case of more complicated geometrical forms of particles, some approximative methods were developed.[11–14]

3. Technical description of the apparatus

The basic setup of the apparatus is a dispersive spectrometer with a multichannel detector for the visible and the near infrared wavelength region. The apparatus is depicted schematically in Figure 1. The monochromator is the 1/8m Oriel 77400 with a 400 lines/mm ruled grating (Oriel 77417). The usable wavelength range of the grating is 270 to 1600 nm, having a primary wavelength range 300 to 1200 nm and a blaze wavelength of 500 nm. Before the exit slit of the monochromator there is a 50 mm diameter diffusing sphere assembly (the integrating sphere Oriel 70505). The CCD (Charge-Coupled Device) detector has 1024 × 256 channels (Oriel model 77193-5 InstaSpec IV) and 180 to 1100 nm spectral response. The usable wavelength region of the spectrometer is thus 270

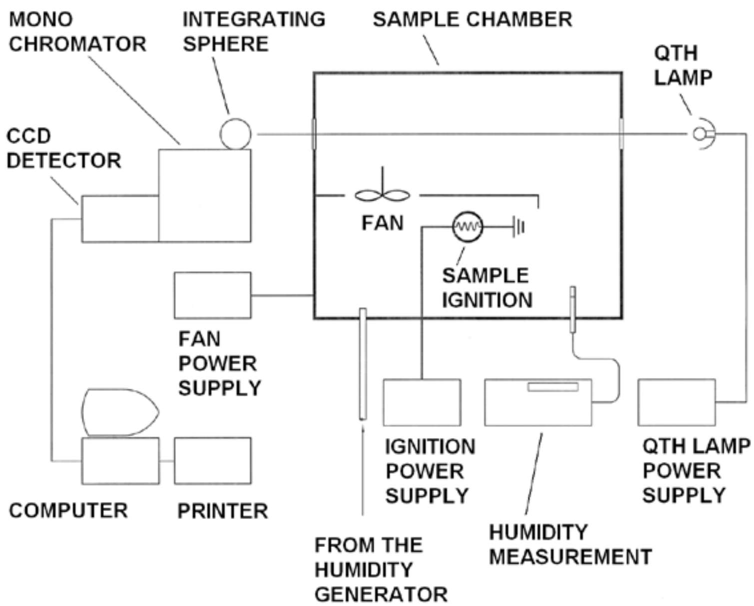

Figure 1. *Schematic picture of the spectrometer for the transmission measurements of aerosols.*

to 1100 nm. The software for the CCD detector system is InstaSpec System IS 401 Version 1.0.

The light source is a QTH lamp, 100 W/12 V Oriel 6358, connected to a stabilized power supply. The sample chamber has a volume of 150 L with dimensions of 840 × 300 × 600 mm. The material is stainless steel AISI 314 with a wall thickness of 1 mm. The optical windows are made of quartz glass. The wavelength calibration of the spectrometer was performed using the well-known mercury lines of a fluorescent lamp.

The weight of a military smoke sample was 2 g. The specific weight of the military smoke mixture varied depending on the specific weight of the used components. Typically the net weight of the military smoke canister is 425 g. That's why it is reasonable to use constant sample weight for all studied obscurants. The pressed sample pellets have been ignited with electric current using 0.25 mm thick AlCr wire.

4. Humidity of air and humidity generator

The relative humidity RH of an air and water vapour mixture is defined as the ratio of the partial vapour pressure of water P_w to the saturated vapour pressure of water P_{ws} at a prescribed temperature. It is normally expressed as a percentage according to the equation RH = $P_w/P_{ws}\times 100\%$.

The saturated vapour pressure can be calculated from the equation[15]

$$P_{ws} = A \cdot 10^{\left(\frac{m \cdot t}{t+T_n}\right)}$$

where temperature dependent variables A, m and T_n are given values from Table 1

The absolute humidity α is the quantity of water in a particular volume of air. Usually it is the mass of water vapour m_w in grams per cubic meter of air V_a: $a = m_w/V_a$.

The absolute humidity is a function of temperature and can be expressed using the saturated vapour

Table 1. Values of variables A, m and T_n at temperatures from −40 to +180 °C.

t/°C	A	m	T_n
−40 to +50	6.1078	7.5000	237.3
+50 to +100	5.9987	7.3313	229.1
+100 to +150	5.8493	7.2756	225.0
+150 to +180	6.2301	7.3033	230.0

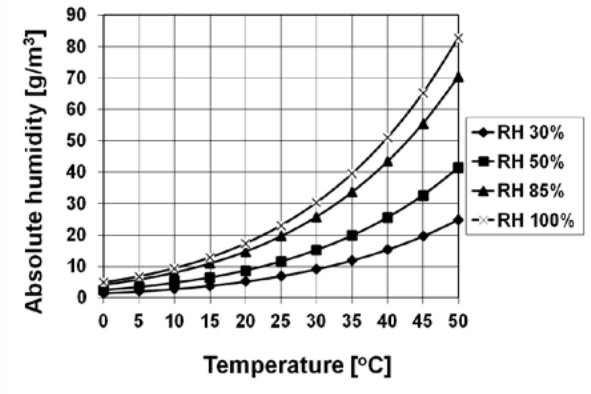

Figure 2. *Absolute humidity of air as a function of temperature calculated using equation of α when relative humidity is 30%, 50%, 85% and 100%.*

pressure of water and the relative humidity of air in the form

$a = 216.68 \cdot \mathrm{RH} \cdot P_{ws} / (100 \cdot p - \mathrm{RH} \cdot P_{ws})$.[12]

Figure 2 describes the absolute humidity of air as a function of temperature calculated using this equation for *a* when the relative humidity is 30%, 50%, 85% and 100%.

The setup of the humidity generator is represented in Figure 3. It consists of three 500 ml electrically warmed gas washing bottles connected in series using silicone rubber pipes.

The adjustment of humidity is performed by mixing dry air and damp air in a three way valve. The air, having suitable humidity for the research, is connected to the sample chamber. The humidity is measured in the condensed water extraction container and in the sample chamber using humidity transducers (Vaisala HMP230).

5. Results

Several transmission measurements of military screening smokes have been performed by varying the humidity in the sample chamber. In Figure 4, a transmission spectrum of HC smoke in the visible and very near infrared region of 402 to 884 nm is depicted, when the relative humidity was 30%. The maximum intensity of the spectrum in this setup is typically 266 000 counts. Measuring the spectrum without extinction, the background spectrum, it is possible to work out the net effect of an aerosol. It is the difference between the background spectrum and the extinction spectrum of the aerosol. Typically the maximum intensity of a background spectrum is 4.5×10^6 counts, which

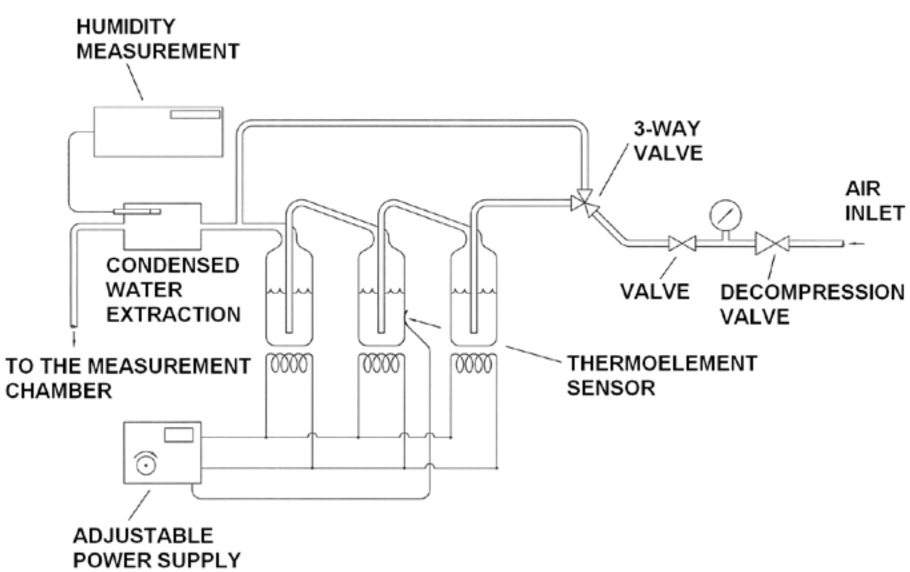

Figure 3. *The schematic picture of the humidity generator.*

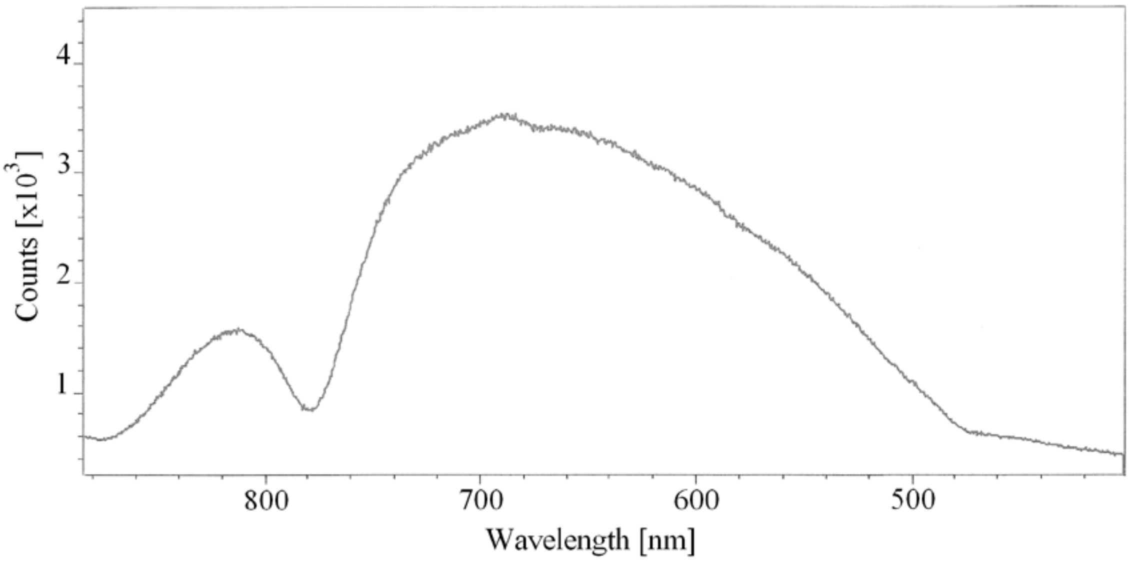

Figure 4. *A single spectrum of an HC/Zn type military smoke in the wavelength region 884 to 402 nm.*

corresponds to zero absorption. Those values are relative and depend on the intensity of the QTH lamp and on the setup of the apparatus.

The measurement of the kinetic series of an aerosol gives the extinction coefficients as a function of time. In Figure 5, a kinetic series of a HC/Zn type military smoke is depicted on a time scale of up to 190 s. The aerosol pellet is ignited between 30 and 40 seconds after the start of the measurement.

Details of the military smoke compositions studied are given in Table 2. HC/Zn is the traditional hexachloroethane, metallic Zn powder and TNT based military smoke, which was usually used as a reference.

Kinetic measurements make it possible to compare the extinction properties of aerosols in a certain fixed wavelength as a function of time. The mass concentration of the aerosol ρ was calculated using a sample chamber of 0.150 m^3 in volume and a mass of 2 g for the pressed smoke pellet. Here it was assumed that the smoke pellet burns perfectly without producing any ash. The path length l of the radiation was 0.84 m. The relative

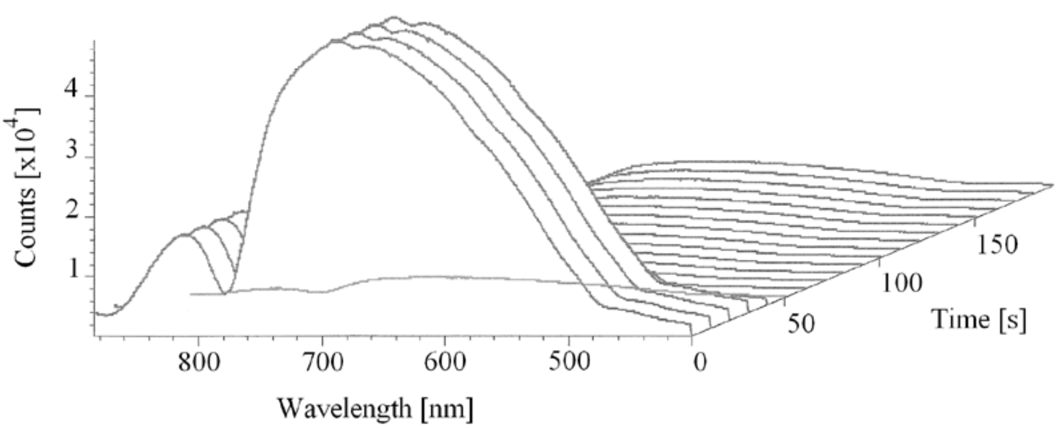

Figure 5. *The kinetic series of a HC/Zn type military smoke between 0 and 190 seconds. The time difference between the two spectra is 10 seconds. The ignition took place between 30 s and 40 s after the start of the measurement.*

Table 2. *The studied military smoke compositions.*

Symbol	Type	Composition	Manufactured by
HC/Zn	HC smoke	C_2Cl_6, Zn, TNT [a]	Haapajärvi Ordnance Depot, Finland
KM	KM smoke	KCl, KNO_3, Mg, $NH_2CON{=}NCONH_2$,[b] $KClO_4$[16]	NICO GmBH, Germany
HC/Mg	HC smoke	C_2Cl_6, Mg[17]	TNO, Netherlands
TPA	White coloured smoke	$KClO_3$, lactose, terephthalic acid (TPA)[18]	PVTT
TIO	HC smoke	C_2Cl_6, Al, TiO_2	Haapajärvi Ordnance Depot, Finland

[a] C_2Cl_6 is hexachloroethane (HC), TNT is trinitrotoluene. [b] Azodicarbonamide.

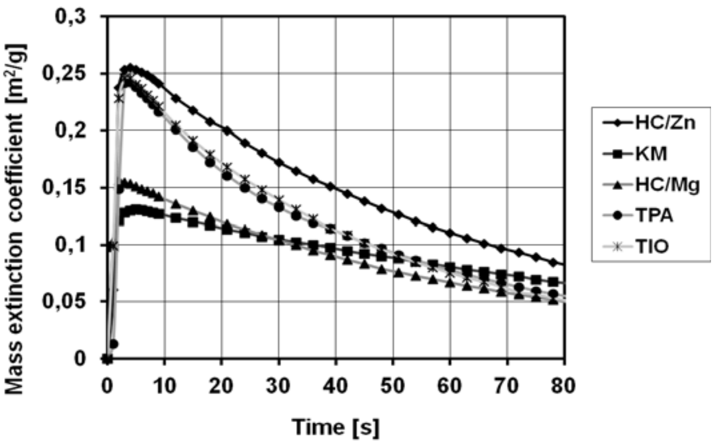

Figure 6. *The relative mass extinction coefficient of five military smokes as a function of time with a fixed wavelength of 600 nm and relative humidity of 30%.*

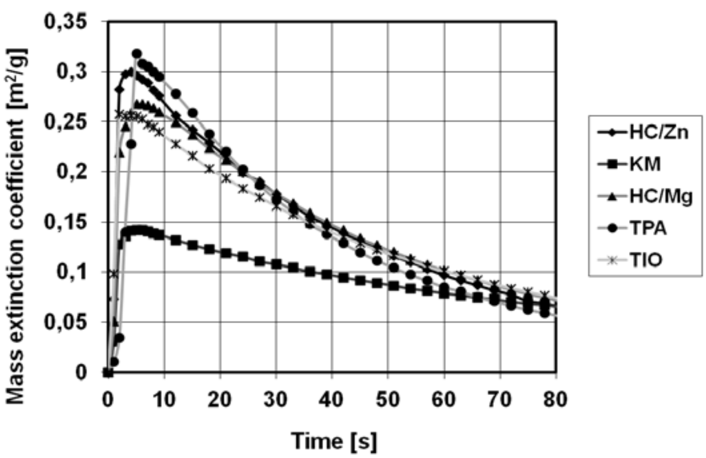

Figure 7. *The relative mass extinction coefficient of five military smokes as a function of time with a fixed wavelength of 600 nm and relative humidity of 50%.*

mass extinction coefficient was calculated using equation (4) for $\alpha(\lambda)$ as in section 2.

In Figures 6–8, the relative mass extinction coefficient of the five military smokes with a fixed wavelength of 600 nm is depicted up to 80 s after ignition, when the relative humidity was 30%, 50% and 85%.

In Figures 9–13, the maximum value of relative mass extinction coefficient for five military smokes is depicted as a function of wavelength 450 to 650 nm, when the relative humidity was 30%, 50% and 85%. The mass extinction coefficient has been calculated as a mean value of three measurements.

In Tables 3–5, the absolute humidity values α for each military smoke are calculated using the measured values of relative humidity RH and temperature t. The nominal value of relative humidity was 30%, 50% and 85%.

According to the equation for α and Figure 2 the absolute humidity mean value of 22.1 g m^{-3} in Table 5.4 corresponds to a relative humidity of 100% when the temperature is 24.3 °C.

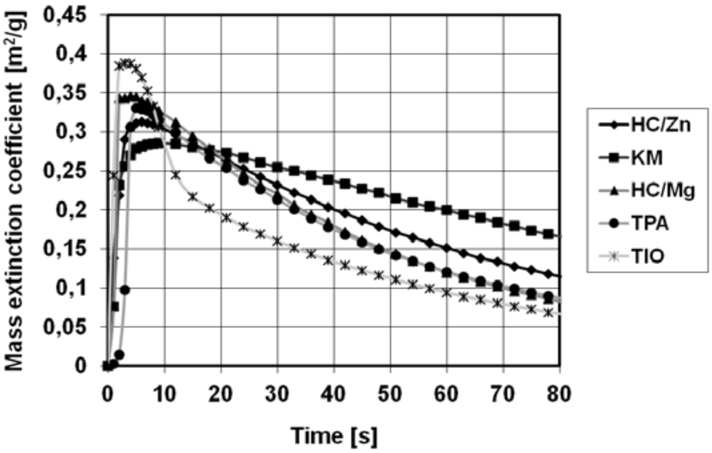

Figure 8. *The relative mass extinction coefficient of five military smokes as a function of time with a fixed wavelength of 600 nm and relative humidity of 85%.*

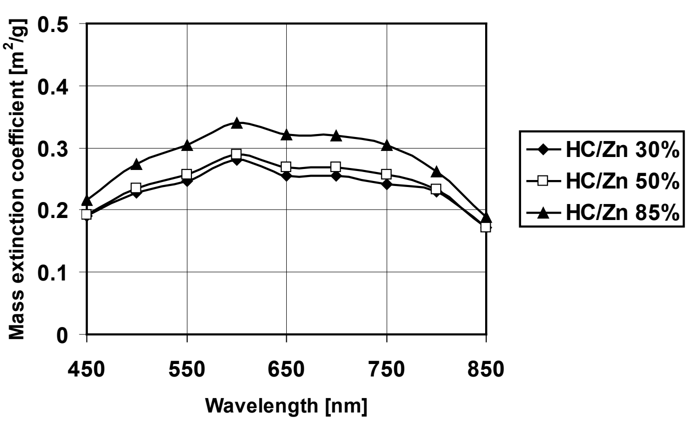

Figure 9. *The relative mass extinction coefficient of HC/Zn military smoke as a function of wavelength, when the relative humidity was 30%, 50% and 85%.*

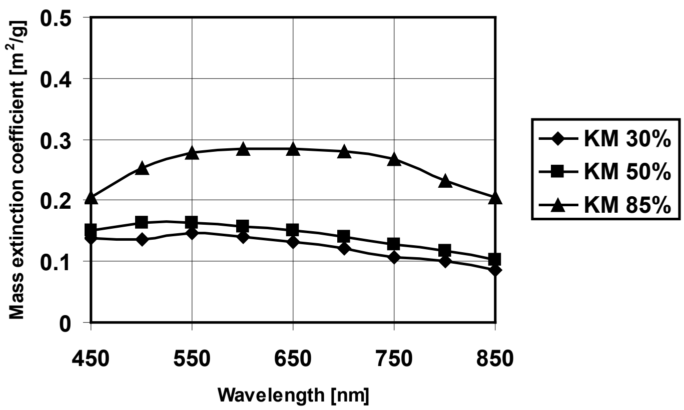

Figure 10. *The relative mass extinction coefficient of KM military smoke as a function of wavelength, when the relative humidity was 30%, 50% and 85%.*

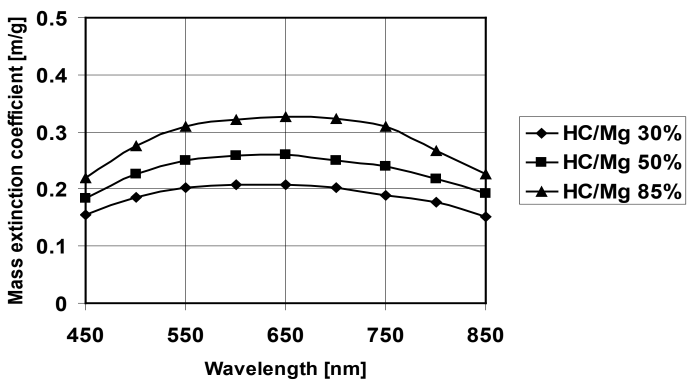

Figure 11. *The relative mass extinction coefficient of HC/Mg military smoke as a function of wavelength, when the relative humidity was 30%, 50% and 85%.*

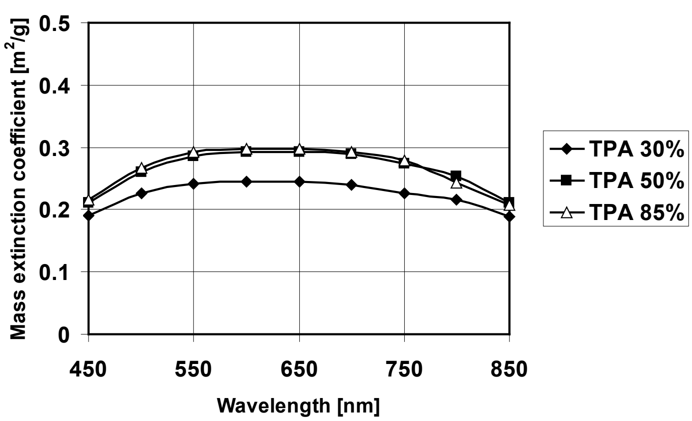

Figure 12. *The relative mass extinction coefficient of TPA military smoke as a function of wavelength, when the relative humidity was 30%, 50% and 85%.*

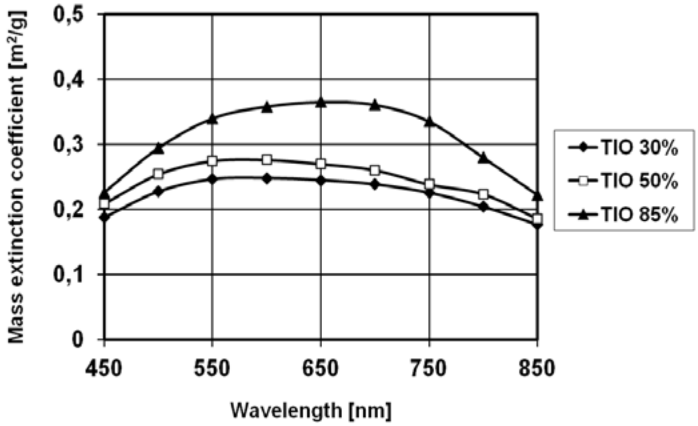

Figure 13. *The relative mass extinction coefficient of TIO military smoke as a function of wavelength, when the relative humidity was 30%, 50% and 85%.*

Table 3. *Measured values of relative humidity and temperature and calculated absolute humidity values for each military smoke with mean value and variation of absolute humidity α when the nominal value of the relative humidity was 30%.*

	RH (%)	t/°C	α/g m^{-3}
HC/Zn	50.5	24.2	11.1
KM	50.7	24.3	11.2
HC/Mg	50.2	23.3	10.5
TPA	50.4	24.7	11.4
TIO	50.3	24.4	11.2
Mean value			**11.1**
Variation (%)			**8.2**

Table 4. *Measured values of relative humidity and temperature and calculated absolute humidity values for each military smoke with mean value and variation of absolute humidity α when the nominal value of the relative humidity was 50%.*

	RH (%)	t/°C	α/g m^{3}
HC/Zn	30.3	24.0	6.6
KM	29.7	23.0	6.1
HC/Mg	30.3	24.0	6.6
TPA	30.3	24.3	6.7
TIO	30.4	23.3	6.4
Mean value			**6.5**
Variation (%)			**9.3**

Table 5. *Measured values of relative humidity and temperature and calculated absolute humidity values for each military smoke with mean value and variation of absolute humidity α when the nominal value of the relative humidity was 85%.*

	RH (%)	t/°C	α/g m^{3}
HC/Zn	85.0	27.9	23.0
KM	85.0	27.8	22.9
HC/Mg	85.0	25.7	20.3
TPA	85.1	27.7	22.8
TIO	85.0	26.8	21.6
Mean value			**22.1**
Variation (%)			**11.9**

6. Discussion

The laboratory scale extinction measurement as a function of wavelength is a method for comparing the screening and protection properties of military smokes. Using the CCD-detector, the whole wide wavelength region was measured simultaneously. Our interest is in comparing the screening properties of military smokes as a function of time and as a function of wavelength. In the real life environment, temperature and humidity change constantly. The measurement of extinction when the relative humidity is, for example, 30%, 50% and 85% provides a useful range for comparing the screening properties of aerosols such as military smokes. The calculated absolute humidity values for each military smoke using the measured values of relative humidity and temperature (Tables 3–5) were taken into account analysing the screening properties. The water has a well known absorption minimum at the wavelength 460 to 480 nm.[8]

Strong absorption by CO_2 exists in the 2.7 µm region, the 4.3 µm region and the region between 11.4 µm and 20 µm. Weaker absorption bands are present at 1.4 µm, 1.6 µm, 2.0 µm, 4.8 µm, 5.2 µm, 9.4 µm, and 10.4 µm. Absorption bands by CO exist in the 2.3 µm and in the 4.7 µm region. Weaker absorption bands are present at the wavelength 1.560 to 1.633 µm.[11] Thus the distinctive absorption bands of CO_2 and CO are outside the wavelength region of 450 to 850 nm.

Analysis of screening properties as a function of time (Figures 6–8) shows, for example, that the traditional HC/Zn smoke and TIO have the best extinction properties inside a time period of 80 seconds when the relative humidity is 30%. Unexpectedly, the traditional HC/Zn smoke, the TPA smoke and the HC/Mg smoke have virtually equal screening properties when the relative humidity is 50%. The screening properties are better compared with the KM smoke and the TIO smoke up to 80 seconds at that relative humidity. At a relative humidity of 85% the TIO smoke has the best screening properties inside the first 7 seconds, but it loses screening properties rapidly compared with the other smokes, the HC/Zn, the KM, the HC/Mg and the TPA smoke. The HC/Mg smoke and the TPA smoke have the second best screening properties inside the first 18 seconds. After that the HC/Mg smoke and the HC/Zn smoke have better screening properties. The TIO based military aerosol is probably better at producing bigger particles when compared, for example, with the other smokes studied here. According to those results (Figure 8), the KM smoke retains its screening properties best when the relative humidity is high. As a general observation one could say that the screening properties of military smokes are better when the humidity of the air is rising, which is in good agreement with other references.

Considering the values of the relative mass extinction coefficient as a function of wavelength 450 to 850 nm (Figures 9–13), when the relative humidity was 30%, 50% and 85%, it can be seen that the extinction properties are, in general, better in the visual range when the wavelength is longer, except for HC/Zn, which seems to have a maximum value at about 600 nm (orange).

In general the measured temperature values were about 3 degrees higher for all five military smokes when the relative humidity was 85% in comparison with the measurements at relative humidity 30% and 50%. The absolute humidity mean value of 22.1 g m^{-3} (Table 5) corresponds to a relative humidity of 100% when the temperature is 24.3 °C. Conversely, the temperature value of 24.3 °C corresponds to the absolute humidity value of 18.8 g m^{-3} when the relative humidity is 85%. The difference is 3.3 g m^{-3}, which is 17.6% of the humidity value of 18.8 g m^{-3}. This may emphasize the relative influence of humidity. The mean variation of the absolute humidity in the measurements was about 10% and it may have influenced the individual extinction coefficient values but not the order of measured military smokes, when the variable was the mass extinction coefficient.

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