# 5-Amino-1H-Tetrazole-based Multi-Coloured Smoke Signals Applying the Concept of Fuel Mixes

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| Journal: | *New Journal of Chemistry* |
| Manuscript ID | NJ-ART-04-2018-001786.R1 |
| Article Type: | Paper |
| Date Submitted by the Author: | 16-May-2018 |
| Complete List of Authors: | Glück, Johann; Ludwig Maximilians Universität, Department of Chemistry<br>Klapoetke, Thomas; LMU München, Chemistry<br>Küblböck, Teresa; Ludwig-Maximilan University, Chemistry |
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Journal Name

ARTICLE

# 5-Amino-1*H*-Tetrazole-based Multi-Coloured Smoke Signals Applying the Concept of Fuel Mixes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

**www.rsc.org/**

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The development of sugar-free multi-coloured smoke formulations, so-called fuel mixes is reported. These simple four ingredient-based mixtures of dye, potassium chlorate, 5-amino-1*H*-tetrazole and a magnesium carbonate derivative are able to produce a variety of colours by applying the same pyrotechnical system. All components except the dye are pre-mixed; the dye is added in the final step. Based on previous results which indicated an overall higher smoke performance in terms of efficiency and persistence by applying 5-amino-1*H*-tetrazole as fuel in smoke formulations, we developed new coloured smoke formulations. For big producers as well as consumers, the concept of fuel mixes is an effective way to reduce costs and provide a higher degree of safety. In this article, the focus was on dyes applied in the U.S. M18 coloured smoke grenades.

## Introduction

Coloured smoke signals are a non-electronic communication tool for both ground as well as ground-to-air signalling.[1-4] During daytime, the big benefit compared to light-emitting signals is the high visibility over greater distances, when employed against a terrain background of contrasting colour.[2] In this context, the most perceptible colour contrast displaying optimum visibility at a considerable distance is offered by red, green, yellow and violet, thereby creating great research interest.[5] A rather new segment in the market for coloured smokes is the so-called daylight firework.[6] Similar to classical firework displays at night, these formulations create visible effects such as smoke trails or fountains at daytime. Daylight fireworks might be used for any daytime events like sport competitions, religious celebrations and cultural events like museum openings.[6] So far, the biggest consumer of smoke signals still remains the military sector. For decades, coloured smoke signals are valuable in the military for marking unit flanks, target locations, drop zones, and medical evacuation landing sites.[2, 3, 7-10] This also includes marine distress signals, which are an essential part of any safety equipment inventory in the shipping industry as well as sport activities.[11, 12] For both civilian and military application, the formulation compounds remain the same. Typically, smoke-generating compositions consist of an oxidizer/fuel pair providing the heat to vaporize the dye.[13, 14] The coolant keeps the reaction temperature in the desired range, while other additives may be used to modify the mechanical or burning properties.[15] Historically, the old M18 coloured smoke grenades contained an anthraquinone-based dye mixed with sulfur, potassium chlorate and sodium bicarbonate. Further, an optional amount of refined kerosene and tricalcium phosphate for control of dusting and caking could be added.[16, 17]

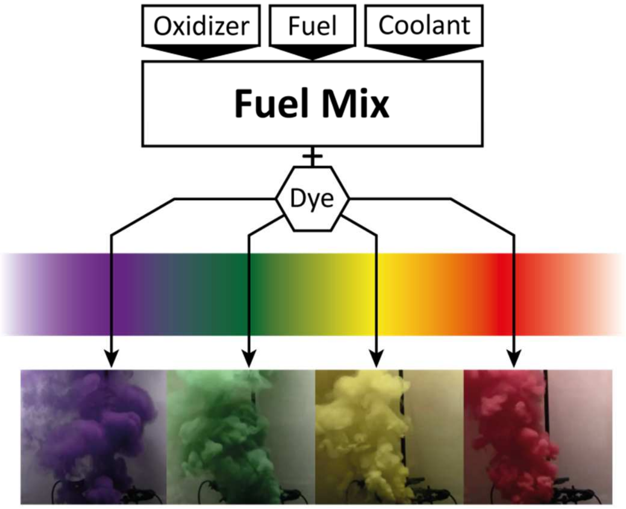

**Figure 1:** The concept of fuel mixes.

However, due to toxicity and health issues, these smoke compositions are no longer produced, since they are suspected to release hazardous $SO_2$ during combustion. An indication for this is provided by soldiers perceiving a burning sensation in their lungs when inhaling such smoke.[9] For this

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Electronic Supplementary Information (ESI) available: see ESI for list of formulations, testing protocol, properties as well as an explanation how to read triangle diagrams.

reason, these early smoke signals, which were already applied during the World War II era, do not meet today's environmental demands anymore and are therefore under constant evaluation for reformulation.[9, 18-23] Sugar was considered as a less toxic alternative to the widely applied sulfur-containing formulations.[18, 24] Compared to the former produced sulfoxides, the now resulting combustion products derived from sugars contain only harmless $H_2O$ and $CO_2$.[9]

A look in the literature revealed, that there is only a limited number of information provided about the percentage of dye actually sublimed upon combustion of the signal.[25, 26] The question arises, whether it is possible to apply alternative fuels, which might improve the smoke dispersal, efficiency, and persistence. As a consequence, the amount of hazardous dyes could be reduced to its minimum, while providing the same colour impression. Unfortunately, each coloured smoke dye has a different enthalpy of sublimation affecting the resulting behaviour and performance of a coloured smoke formulation.[9] For this reason, up to now every single dye needs its own optimized pyrotechnical formulation to meet the requirements for burn time and colour quality. A possible solution to this circumstance might be the development of so-called *fuel mixes* (Fig. 1).[8] Essentially, fuel mixes are combinations of certain components such as the oxidizer/fuel pair and further, other additives like coolant or minor fuels. These ingredients are pre-mixed and subsequently combined with a smoke dye.

The great benefit for producers and consumers is that the need to have a certain number of different smoke formulations in stock serving each colour is gone. In comparison to the conventional smoke signals, the quick-mixing of only two pre-mixed powders (fuel mix + dye) with known quality produces the desired smoke colour. As a result, not only the required space for safe storage is reduced dramatically, but also the total amount of energetic materials stored in the same place drops accordingly. Based on previous work carried out within our group, we investigated the effect of applying 5-amino-1*H*-tetrazole (5-AT) as main fuel in so-called fuel mixes.[25, 26] Hereby, the main combustion product of the fuel would be $N_2$.[27] The slightly higher decomposition temperature compared to sucrose allowed the application as alternative fuel. The small temperature difference itself might be partially explained by the existence of non-oxidized bonds in 5-AT. $KClO_3$ in combination with 5-AT served as the oxidizer/fuel pair; magnesium carbonate hydroxide pentahydrate (MCHP) was the coolant. Most of the applied dyes belong to the anthraquinone group. Disperse Red 9 ((1-methylamino) anthraquinone) was applied for red, Solvent Green 3 (1,4-di-*p*-toluidino-9,10-anthraquinone) for green and Solvent Yellow 33 (2-(2-quinolyl)-1,3-indandione) for yellow. Moreover, to obtain a violet smoke signal the Violet Smoke Dye Mix consisting of the two dyes Disperse Red 9 and Solvent Violet 47 (1,4-diamino-2,3-dihydroxyanthraquinone) were applied.[8]

In a first step different ratios of the pre-mixed powders (oxidizer + fuel + coolant = fuel mix) and the dye were tested to give a coloured smoke cloud. The second step focused on adapting the colour. Diviacchi stated earlier, that the actual colour impression of the emerging smoke may be different from the labelled colour.[8] To overcome this issue, we applied a dye mixture in case the colour was too dark or brighter than intended. The focus of the herein presented results was on the dyes applied in the U.S. M18 coloured smoke grenades and mixtures thereof.[28] At this point, we were not interested in investigating the toxicity issues arising from the dyes or resulting combustion products.[8, 17, 28-32] Instead, we developed three different 5-AT-based fuel mixes (**FM1**, **FM2**, **FM3**) and compared them towards a sucrose-based reference formulation (**Ref-FM**) of the same dye in terms of performance and smoke persistence. HPLC measurements were carried out to quantify the effective amount of dye present in the collected aerosol.

## Experimental

**Chemicals and Sample Preparation.** Sucrose (≥ 99 %), and magnesium carbonate hydroxide pentahydrate (BioXtra) were purchased from Sigma-Aldrich. 5-AT (98 %) was purchased from abcr chemicals. Potassium chlorate (≥ 99 %) was purchased from Grüssing GmbH. Disperse Red 9, Solvent Green 3, Solvent Yellow 33 and the Violet Mix Smoke Dye were purchased by Nation Ford Chemical. For initial testing, small mixtures (2 g) were carefully mixed manually for 5 min in a mortar by combining the dry compounds. If those tests were successful, larger mixtures (40 g) were prepared by combining the dry components in a cylindrical rubber barrel and rolling for 120 min. The rotatory rock tumbler (model 67631) was built by "Chicago Electric Power Tools" and operated with steel balls. To remove any clumps, the compositions were passed through an 800 μm screen. 2 g of this so prepared composition was pressed into a cylindrical steel compartment (diameter 2.0 cm), with the aid of a tooling die and a hydraulic press. The used consolidation dead load of 3000 kg was applied for 3 s, if not stated otherwise. Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, 2.9 $\Omega\ m^{-1}$). For each composition, three pellets were tested and the results were averaged.

**Aerosol Quantification.** The experimental setup to collect the aerosol was described previously.[25, 26] A Thermo Scientific™ DIONEX™ UltiMate™ 3000 HPLC System (accucore RP-MS column (3.0 x 150.0 mm, particle size 2.6 μm) with a DAD-3000 photometer and Chromeleon® 7.2 Chromatography Management Software was used to quantify the amount of dye (see ESI for exact method). The measurements were performed in cooperation with the *CBRN Defense, Safety and Environmental Protection School* of the German *Bundeswehr* (CDSEP-School), Sonthofen (Germany).

**Burn Rate.** The testing protocols as well as pellet sizes are given in the ESI. However, we were facing serious problems to determine the burn rate at different pellet sizes. Some formulations which produced smoke on a rather small height/diameter ratio burned with an open flame at higher height/diameter ratios. The collected data for two different pellet sizes is provided in the ESI.

**Sensitivities and Thermal Stability.** The impact and friction sensitivities were determined using a BAM Drophammer and a BAM Friction Tester (method 1 of 6). The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+): impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive 360 N > x > 80 N, very sensitive < 80 N, extreme sensitive < 10 N.[1] Thermal stability measurements. Onset temperatures were measured with an OZM Research DTA 552-Ex Differential Thermal Analyzer at a heating rate of 5 °C $\text{min}^{-1}$. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive < 0.1 J, insensitive > 0.1 J.

## Results and Discussion

**Development of Coloured Smokes.** A suitable starting point to fulfil the concept of fuel mixes is an exactly stated testing protocol as outlined by Domanico (see ESI).[7] Due to the existing differences in terms of physical behaviour and chemical stability, a screening of several different fuel mix ratios was performed. Therefore, the amount of dye (30 %) was fixed, while the remaining 70 % was the respective fuel mix. The first step of this presented study was the investigation of working smoke compositions for each dye separately. Subsequently, the optical performance evaluation included the emerging colour impression, smoke thickness as well as burning behaviour. The most advanced formulations were selected for further testing and evaluation, such as yield, burn time and rate, transfer rate and sensitivity towards mechanical stimuli as well as thermal stability (Table 1). A fuel mix might be more sensitive than the final coloured smoke formulation. To ensure safe handling in every single manufacturing step, e.g. the mixing and grinding of fuel mixes starting from the single components or the final coloured smoke formulations, the sensitivities have to be determined also for all intermediate steps.

The most promising fuel mixes for further characterization are illustrated within a ternary diagram (Fig. 2). The first fuel mix **FM1** consisted of 50 wt% 5-AT, 30 wt% $KClO_3$ and 20 wt% MCPH and therefore, contained the highest amount of oxidizer. **FM2** had a ratio of 50 wt% 5-AT to 20 wt% $KClO_3$ to 30 wt% MCPH and **FM3** had the highest amount of the fuel 5-AT (60 wt%) and equal contents of $KClO_3$ and MCPH (20 wt%). The reference fuel mix **Ref-FM** contained 40 wt% sucrose, 40 wt% $KClO_3$ and 20 wt% MCPH (see ESI for a complete listing of formulation ingredients and weight percentages). Further, the properties of the resulting coloured smoke formulations (Table 2/Table 3) based on these fuel mixes are summarized in Table 1.

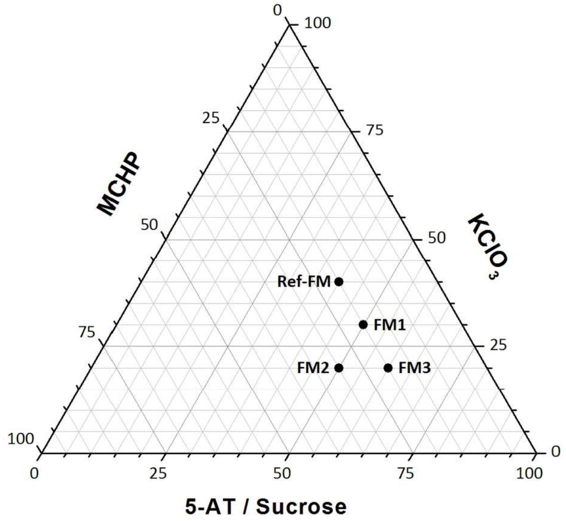

**Figure 2:** Developed fuel mixes. **FM1** = 5-AT (50 wt%), $KClO_3$ (30 wt%), MCHP (20 wt%); **FM2** = 5-AT (50 wt%), $KClO_3$ (20 wt%), MCHP (30 wt%); **FM3** = 5-AT (60 wt%), $KClO_3$ (20 wt%), MCHP (20 wt%); **Ref-FM** = sucrose (40 wt%), $KClO_3$ (40 wt%), MCHP (20 wt%). See Table 2 and Table 3 for for a complete listing of formulation ingredients, weight percentages and the ESI for brief explanation of the triangle diagram.

**Properties of Coloured Smoke Formulations.** In this context, formulations **Y1**, **G1**, **R1** and **V1** were referred to **FM1**, while **FM2** was the basis for **Y2**, **G2**, **R2** and **V2**. The compositions **Y3**, **G3**, **R3** and **V3** were based on **FM3** and fuel mix **Ref-FM** resulted in coloured reference formulations.

**Table 1:** Properties of yellow-, green-, red- and violet-coloured smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

| | **BT** /s | **Y** /% | **T%** /% | **$m_{HPLC}$** /mg | **ESD** /J | **$T_{onset}$** /°C |
|---|---|---|---|---|---|---|
| **Y1** | 15 | 29 | 59 | 354 | 1.0 | 184 |
| **Y2** | 26 | 21 | 56 | 233 | 0.4 | 189 |
| **Y3** | 29 | 30 | 49 | 292 | 0.5 | 187 |
| **Ref-Y** | 13 | 33 | 73 | 435 | 0.3 | 178 |
| **G1** | 20 | 36 | – | – | 0.4 | 192 |
| **G2** | 45 | 24 | – | – | 0.2 | 198 |
| **G3** | 31 | 31 | – | – | 0.5 | 194 |
| **Ref-G** | 19 | 32 | – | – | 0.2 | 172 |
| **R1** | 20 | 29 | 76 | 457 | 0.5 | 184 |
| **R2** | 75 | 25 | 58 | 351 | 0.7 | 182 |
| **R3** | 41 | 28 | 72 | 432 | 0.5 | 189 |
| **Ref-R** | 21 | 36 | 86 | 514 | 0.6 | 172 |
| **V1** | 23 | 29 | – | – | 0.2 | 182 |
| **V2** | 27 | 26 | – | – | 0.3 | 186 |
| **V3** | 27 | 29 | – | – | 0.3 | 180 |
| **Ref-V** | 15 | 32 | – | – | 0.7 | 178 |

*Annotation: measured for 2.0 g pellet; BT = burn time; Y = yield; T% = transfer rate; $m_{HPLC}$ = dye content present in aerosol; ESD = electric discharge sensitivity; $T_{onset}$ = onset temperature of decomposition; impact sensitivity = 40 J for all measured formulations (only Ref-G/Ref-V = 30 J); friction sensitivity = 360 N for all measured formulations; see ESI for summary of all determined properties.*

**Table 2:** Yellow- and green-colored smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM** in weight percent [wt%].

| | **Y1** | **Y2** | **Y3** | **G1** | **G2** | **G3** | **Ref-Y** | **Ref-G** |
|---|---|---|---|---|---|---|---|---|
| **$KClO_3$** | 21 | 14 | 14 | 21 | 14 | 14 | 28 | 28 |
| **5-AT** | 35 | 35 | 42 | 35 | 35 | 42 | – | – |
| **MCHP** | 14 | 21 | 14 | 14 | 21 | 14 | 14 | 14 |
| **Sucrose** | – | – | – | – | – | – | 28 | 28 |
| **Solvent Yellow 33** | 30 | 30 | 30 | 10 | 10 | 10 | 30 | 10 |
| **Solvent Green 3** | – | – | – | 20 | 20 | 20 | – | 20 |

**Table 3:** Red- and violet-colored smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM** in weight percent [wt%].

| | **R1** | **R2** | **R3** | **V1** | **V2** | **V3** | **Ref-R** | **Ref-V** |
|---|---|---|---|---|---|---|---|---|
| **$KClO_3$** | 21 | 14 | 14 | 21 | 14 | 14 | 28 | 28 |
| **5-AT** | 35 | 35 | 42 | 35 | 35 | 42 | – | – |
| **MCHP** | 14 | 21 | 14 | 14 | 21 | 14 | 14 | 14 |
| **Sucrose** | – | – | – | – | – | – | 28 | 28 |
| **Disperse Red 9** | 30 | 30 | 30 | – | – | – | 30 | – |
| **Violet Smoke Dye Mix** | – | – | – | 30 | 30 | 30 | – | 30 |

In detail, **FM1**- and **Ref-FM**-based formulations resulted in rapid, strong smoke generation, while **FM2**- and **FM3**-based compositions produced smoke continuously over a longer period of time. This trend was also reflected in terms of burn time (**FM1** or **Ref-FM**: 12–23 s compared to **FM2** or **FM3**: 26–45 s) as well as burn rate. An exception was **R2** with the overall longest burn time of 75 s.

All tested coloured smoke formulations were insensitive towards impact and friction except of **Ref-G** and **Ref-V**, which were classified as less sensitive. Moreover, all compositions were insensitive towards electrostatic discharge. The decomposition temperatures were in the range of 172–198 °C.

The measurements of all coloured smoke formulations and their references were carried out on approximately similar humidities (see ESI). More precisely, the performance and in particular the yield *Y* of hygroscopic smoke mixtures is strongly dependent on the relative humidity, since at higher humidity levels higher yields are obtained.[25] It is noticeable, that the yield of **FM2** was significantly worse for all tested dyes in the range of 21–26 %. In contrast, formulations based on **FM3** were approximately as efficient as **FM1** (28–31 %) with the exception of **G1** (36 %). However, the yield of **Ref-FM**-based smoke compositions was slightly higher for yellow, red and violet smoke in the range of 32–33 %.

It has to be stated, that not all produced aerosol disseminated by coloured smoke formulations is in fact the implemented dye. More precisely, the term *aerosol* describes the total amount of produced non-gaseous reaction products including soot, water, dye and all other resulting combustion products. Whereas the information about the collected aerosol is sufficient for obscurants to calculate the yield (quotient between the amount of collected aerosol divided by the pyrotechnical payload), we were interested in the exact amount of dye present in the aerosol. The so-obtained values were used for the calculation of the previously introduced term of the *"transfer rate"* by the authors (quotient between the amount of actually dispersed dye divided by the amount of dye in the pellet).[25] Dye which remains in the pyrotechnical device or is consumed by the flames does not contribute to the optical performance. The optimized ratio between the amount of applied dye and successfully dispersed dye would contribute to a more sustainable material life-circle, since less unburned material is spread into the environment. Due to the high solubility in organic solvents, HPLC analysis of the collected aerosol was performed and revealed the dye concentration in the aerosol (Table 1).

### Discussion Transfer Rate / HPLC

HPLC measurements revealed a transfer rate of 49–73 % for the yellow smoke formulations. **Ref-Y** based on sucrose achieved the highest transfer rate, followed by **Y1** with 59 %.

Compared to the yellow smoke compositions, an increase of the transfer rate was observed for the red dye. Formulations **R1**–**R3** and **Ref-R** displayed transfer rates in the range of 58–86 %. Here again, the sucrose-based fuel mix achieved the best value followed by **R1**.

A change of the solution colour was observed for the violet dye mix in acetonitrile upon measurement. Re-running the measurements in darkened glass showed the same result displaying additional peaks. It was concluded, that the dye mix is not stable in solution and was therefore excluded from the HPLC measurements. The green formulations applying a mixture of two dyes proofed to be more difficult than expected and will be addressed in the future.

**Properties of Fuel Mixes.** The characterization of sensitivity data is mandatory for producers as well as consumers, since the handling, preparing and in particular storing of such fuel mixes need to be safe. Therefore, the sensitivities were determined additionally for the novel fuel mixes (Table 4).

**Table 4.** Sensitivity data of fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

| | **IS** /J | **FS** /N | **ESD** /J | **$T_{onset}$** /°C |
|---|---|---|---|---|
| **FM1** | 6 | 252 | 1.5 | 331 |
| **FM2** | 20 | 360 | 0.3 | 342 |
| **FM3** | 20 | 360 | 0.1 | 337 |
| **Ref-FM** | 20 | 360 | 1.5 | 172 |

*Annotation: IS = impact sensitivity; FS = friction sensitivity; ESD = electric discharge sensitivity;* $T_{onset}$ *= onset temperature of decomposition.*

In detail, the tested fuel mixes were sensitive towards impact, where the impact sensitivity of **FM1** was comparatively higher with 6 J. It is literature known that higher amounts of $KClO_3$ lead to higher sensitivities. Besides that, the exothermic decomposition process of $KClO_3$ causes an acceleration to the rate of reaction.[33] In contrast to this, **FM2**, **FM3** and **Ref-FM** were classified as insensitive towards friction, while **FM1** was sensitive. All samples were insensitive towards electrostatic discharge except of FM3 reaching the transition between sensitive and insensitive material. The onset temperatures of decomposition of 5-AT-based fuel mixes were significantly higher in the range of 331–342 °C in comparison with the sucrose-based reference **Ref-FM** (172 °C). Therefore, these fuel mixes are potentially sensitive energetic materials and must be handled with care and caution.[34]

## Conclusions

The successful demonstration of 5-AT-based fuel mixes to produce green, yellow, red and violet smoke is presented. The developed formulations revealed that non-traditional high-nitrogen fuels can produce smoke of high colour quality. More precisely, **FM1**-based mixtures resulted in a rapid, strong smoke generation in a short time, while **FM3**-based compositions were characterized by a slow, continuous smoke generation over a much longer period of time. 5-AT is only one of the potential candidates, which should be considered for future investigations. Sensitivity measurements revealed that all developed formulations are insensitive towards friction. In addition, all developed 5-AT-based coloured smoke formulations are completely insensitive towards impact. The fuel mixes were more sensitive towards mechanical stimuli. A comparison of the collected aerosol revealed similar yields for **FM1**-based and sugar-based formulations. The superiority of prepared sugar-based reference formulations was displayed by the measured transfer rates. The obtained baseline (yield, transfer rate) are the first literature-reported values for sugar- and 5-AT-based coloured smoke formulations. Future investigations in our group will focus on providing even more coloured smoke formulations, e.g. blue and black, applying the same fuel mixes. To secure a proper evaluation, new strategies to characterize aerosol produced by a mixture of two dyes (e.g. green dye mix) has to be established.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Office of Naval Research (ONR) under grant no. ONR.N00014-16-1-2062, is gratefully acknowledged. We thank Mr. Andreas Bertsch (*Schule ABC-Abwehr und Gesetzliche Schutzaufgaben*) for running the HPLC measurements and Mr. Jay Dickson (Nation Ford Chemical) for providing the applied dyes. In addition, we thank Dr. Anthony P. Shaw for many inspiring discussions and his help for the last few years.

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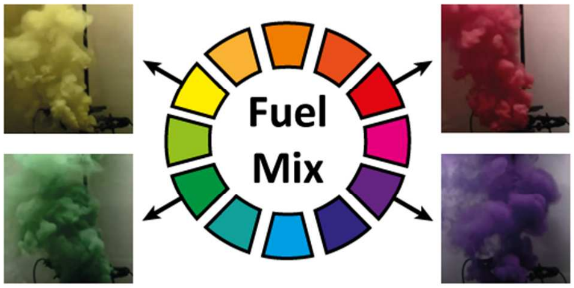
Synopsis:

The development of 5-amino-1H-tetrazole-based fuel mixes providing access to multi-coloured smoke signals is reported.



TOC

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