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# COUNTERFOG system applied inside the warehouse: verification of the counter response against radiochemical attack scenario

**Javier Quiñones**[1,a], **Jose Antonio Domínguez**[2], **Laura Pascual**[2], **Luis Amigo**[2], **Jose Manuel Cobo**[2], **Marta Fernández**[2]

[1] Guardia Civil. Interior Affairs Ministry, Madrid, Spain
[2] Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid, Spain

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**Abstract** Chemical and radiological emergences can be caused by terrorist attacks, such as the use of CWA, as well as from industrial accidents. Whatever the trigger, these events often involve the rapid dispersal of toxic chemical agents that, depending on the scenario and level of exposure, can compromise security and human health. These risks and the associated alarm in the population justify the interest in the development of systems and processes for the efficient capture of toxics airborne released in these incidents. The countermeasure proposed in this work is based on the use of fog (i.e. water dissolution with several additives such as isopropanol, $Ag^+$ compounds even so metallic sorbents solid in suspension). The different combinations of these countermeasures were tested and evaluated in order to achieve maximum cleaning efficiency and speed of action. These tests were performed at different scales comprising laboratory scale, pilot plant, and inside a large building. The effect of the combined countermeasure studied is much greater than that of each of the measures separately, since, as has been shown, the joint interaction favours the reduction of the concentration of the dispersed radiochemical agent in the atmosphere. The capability at real scale of the propounded system for minimising the effect of chemical and/or radionuclide dispersion in the atmosphere has been confirmed.

## 1 Introduction

The growing and widespread use of chemical compounds and radioisotopes [1, 2] in different sectors of the society is made possible through a big interconnectivity of the involved areas: production, research platforms, transports, industry or medicine, among others [3–5].

Although this is an achievement for society, it is necessary to take into account that this interconnectivity can facilitate the access of terrorist groups to these compounds [6, 7], vulnerability of infrastructures or accidental failures [8] that can lead to the release of radiochemical compounds with the consequent panic scenario in the population [9].

The dispersibility of the released toxic agent is one of the main factors that determines the magnitude and impact of these incidents, so it is very important to develop countermeasures

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[a] e-mail: javier.quinones@ciemat.es (corresponding author)

that prevent or reduce this airborne dissemination. This was the goal of the completed COUNTERFOG project, to develop a method of response to an emergency of CBRN (Chemical, Biological, Radiological and Nuclear) nature, capable of collapsing the agent preventing its diffusion even in the possible presence of fire.

The COUNTERFOG technology uses a water-based fog with a distribution size particle in the micrometre range. These water droplets will interact with any dispersed agents in the air dragging them when falling. To increase the interaction between the fog and the airborne agent and therefore, the effectiveness of the countermeasure, different compounds used as additives to the fog water have been studied. These additives aim to modify some physical–chemical characteristic of the fog, such as the surface tension of the water, or to react with the toxic agent forming a compound that facilitates its entrapment (by complexation and/or precipitation) and removal from the atmosphere. Both types of additives have been tested and evaluated in this work.

Another option to improve the effectiveness of the initial COUNTERFOG system is the use of solid particles with large surface area that strongly adsorb the toxic agent. Once trapped, solid particle with CBRN agent is dragged away by fog increasing the reaction rate and decreasing the time necessary to decrease the amount of free agent.

This work shows the effectiveness of the above measures complementing the COUNTERFOG system, evaluating its effectiveness separately and used in different combinations in the scenario of radiochemical attack, paying special attention to the incorporation the $Ag^+$ to minimize the dispersion of iodine as example of radiochemical agent [10–12].

## 2 Experimental procedure

### 2.1 Surrogates selection

One of the principal objectives of the project COUNTERFOG was the selection of the chemical surrogates to use in the trials [13, 14]. To select the surrogates, the following variables (Table 1) have been considered: boiling point, solubility, Henry's law constant ($K_H$), chemical structure, i.e. functional group and molecular weight [15]. The surrogates selected were: triethyl phosphate (TEP) and dipropylene glycol monomethyl ether (DPGME) for G-Agent and methyl salicylate (MS) for Distilled Mustard.

In the case of iodine, a non-radioactive isotope was used.

The dispersion method for Chemical Warfare Agents (CWA) surrogates and iodine was the generation of an aerosol evenly spread in the facility where the experiments were carried out.

### 2.2 Sampling and detection

During experiments, compounds were sampled in active mode by drawing the air of laboratory directly, using small suction pumps, into organic solvents (ethanol for MS and hexane for TEP and DPGME) and solid sorbents (Tenax and activated carbon) [16]. For the iodine, air extraction was carried out through a high-volume absorption pump (6 $m^3$/h flow rate) with a circular filter holder. The filters were composed by cellulose and granulated activated carbon (0.5 g) [17, 18] in a sandwich type arrangement.

For detection and/or quantification, different techniques were used in function of the chemical compound used and the characteristics and purpose of the test [19, 20]:

**Table 1** Physicochemical properties of CWA and its potential surrogates

| | Compound | Abbrv. | $M_w$ (g mol$^{-1}$) | $T_B$ (°C) | $P_v$ (mm Hg) | S° (mg l$^{-1}$) |
|---|---|---|---|---|---|---|
| G-agents | Taburn ($C_5H_5N_2O_2P$) | GA | 162.1 | 248 | 0.057 | $7.2 \times 10^4$ |
| | Sarin ($C_4H_{10}FO_2P$) | GB | 140.1 | 158 | 2.1 | $1.0 \times 10^6$ |
| | Soman ($C_7H_{16}FO_2P$) | GC | 182.2 | 198 | 0.4 | $2.1 \times 10^4$ |
| | Diisopropyl methylphosphonate | DIMP | 180.2 | 121 | 0.277 | $1.5 \times 10^3$ |
| | Dimethyl methylphosphonate | DMMP | 124.1 | 181 | 0.96 | $1.0 \times 10^6$ |
| | Dypropyleneglycol monomethyl ether | DPGME | 148.2 | 188 | 0.55 | $1.0 \times 10^6$ |
| | Disiopropyl fluorophosphates | DFP | 184.2 | 183 | 0.58 | $1.5 \times 10^4$ |
| | Triethyl phosphate | TEP | 182.2 | 215 | 0.39 | $5 \times 10^5$ |
| HD | Sulfurd Mustard ($C_4H_8Cl_2S$) | HD | 159.1 | 218 | 0.11 | 684 |
| | 2-Chloroethyl ethyl sulphide | CEES | 124.6 | 157 | 3.4 | 1062 |
| | 2-Chloroethyl phenyl sulphide | CEPS | 172.7 | 257 | $1.9 \times 10^{-2}$ | 84 |
| | Methyl 2-hydroxybenzoate | MS | 152.2 | 223 | 0.04 | 700 |
| VX | VX ($C_{11}H_{26}NO_2PS$) | VX | 267.4 | 292 | $7 \times 10^{-4}$ | $3 \times 10^4$ |
| | 1,2-Bis(ethoxycarbony) ethyl] o,o-dimethyl phosphorodithioate | Malathion | 330.4 | 156 | $3.4 \times 10^{-6}$ | 143 |
| | O,o-diethyl-o,p-nitrophnyl thiophosphate | Parathion | 291.3 | 375 | $6.7 \times 10^{-3}$ | 11 |

Mw is the molecular weight of each substance

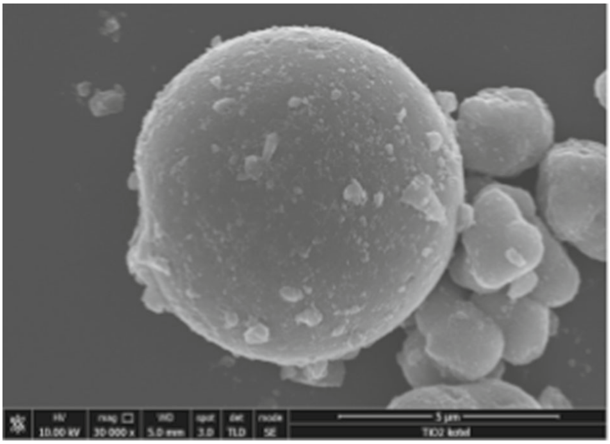

**Fig. 1** Particle of $TiO_2$

- *For MS* Ultraviolet–visible spectroscopy (UV–Vis). This determination is based in a specific colorimetric reaction of MS and, given the simplicity and speed of the method, this compound was used in the design of experiments and in full-scale tests.
- *For DPGME* Gas Chromatography with Flame Ionization Detection (GC-FID). This technique was used since it is the appropriate one for the determination and quantification of semi-volatile organic compounds (SVOCs).
- *For TEP and iodine* GC-FID and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In the case of TEP, the presence of the P atom in the molecule made it possible to use ICP-MS for its determination. The advantages of this technique compared to GC are its lower requirement in sample pre-treatment and the speed of analysis, both important aspects for the design of experiments.

### 2.3 Additives

The need of using additives in the fog water was raised when the first tests showed its limited effectiveness in cleaning hydrophobic substances. In order to facilitate the interaction of this type of toxic substances with the fog different additives were evaluated, choosing the isopropanol for this purpose [21].

Then, particles of $TiO_2$ and $TiO_2$–$Al_2O_3$ were selected to trap CWA in their pores [22, 23] and dragging them down. These particles were used to increase the fog efficiency and accelerate the time necessary to remove the agent to the atmosphere. The characterization of these particles is shown below (Figs. 1, 2, 3, 4 and Table 2). In Figs. 3 and 4, the particle size distribution of the ceramic particles used in the different set up is plotted. The data are summarised in a histogram (plotted in black) and frequency diagram (in red and right values). These data allow determining the particle size distribution using the average diameter of the particles (Table 2).

In some of the experiments done in the presence of iodine, the $Ag^+$ ion (as dissolution of AgCl added to water) was used, which will produce the iodine precipitation as AgI(s) [24] when fog and $I_2(g)$ interact.

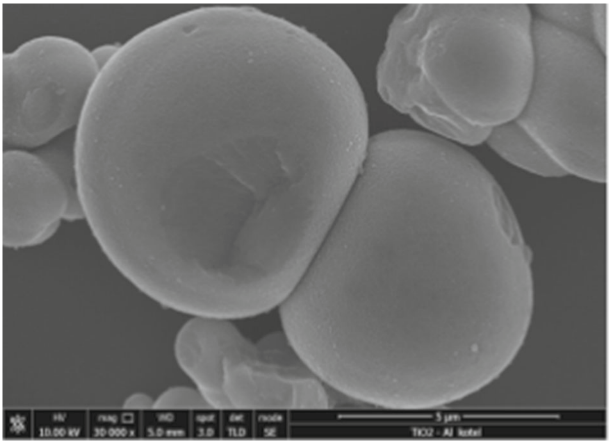

**Fig. 2** Particle of $TiO_2$–$Al_2O_3$

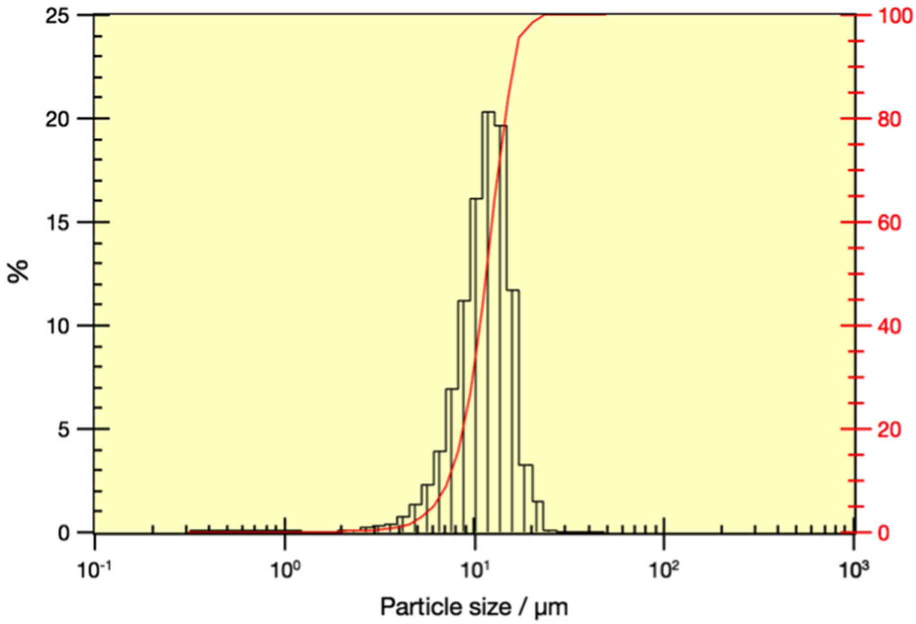

**Fig. 3** Particle size distribution $TiO_2$

## 2.4 Test carried out

Many tests with the selected surrogates of CWA (methyl salicylate, dipropylene glycol methyl ether and triethyl phosphate) and the different combinations of countermeasures were performed in order to assess their response to the fog generated by the nozzle in these circumstances. Further, the countermeasure system was tested and evaluated at different scales in order to achieve the most efficient combination depending on the hazardous substance. The scales tested were the following:

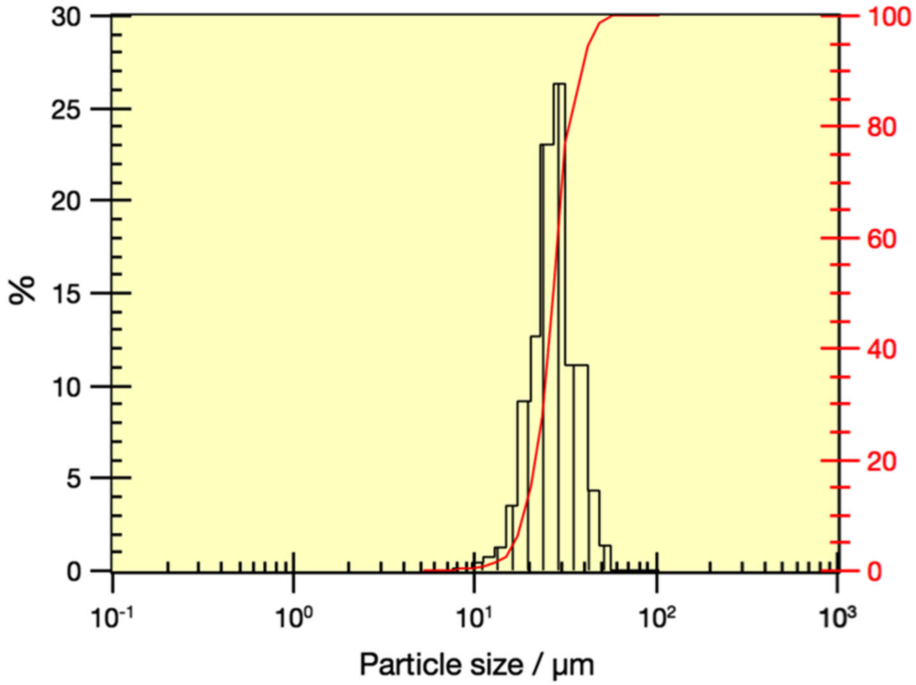

**Fig. 4** Particle size distribution $TiO_2$–$Al_2O_3$

**Table 2** Specific surface and porosity measurements

| Material | $S_{BET}$ ($m^2$ $g^{-1}$) | $P$ (g $cm^{-3}$) | $D_{[v,0.5]}$ (µm) | $S_{geo}$ ($m^2$ $g^{-1}$) |
|---|---|---|---|---|
| $TiO_2$ | 296.34 ± 2.30 | 4.23 | 5.84 | 0.12 |
| $TiO_2$–$Al_2O_3$ | 361.79 ± 0.91 | 4.09 | 14.17 | 0.05 |

- Laboratory Scale
- Pilot Plant Scale (COUNTERFOG-Lab)
- Real Scale

For each type of surrogate and combination of countermeasures, different tests were carried out, first the persistence of the agent in the environment was measured, then the interaction of the agent with the fog generated and finally with the combination and application of different additives. Samples were taken at different times to trace the evolution of the radiochemical in the air.

## 3 Results

The most important results obtained from each of the scales of the related tests are shown below.

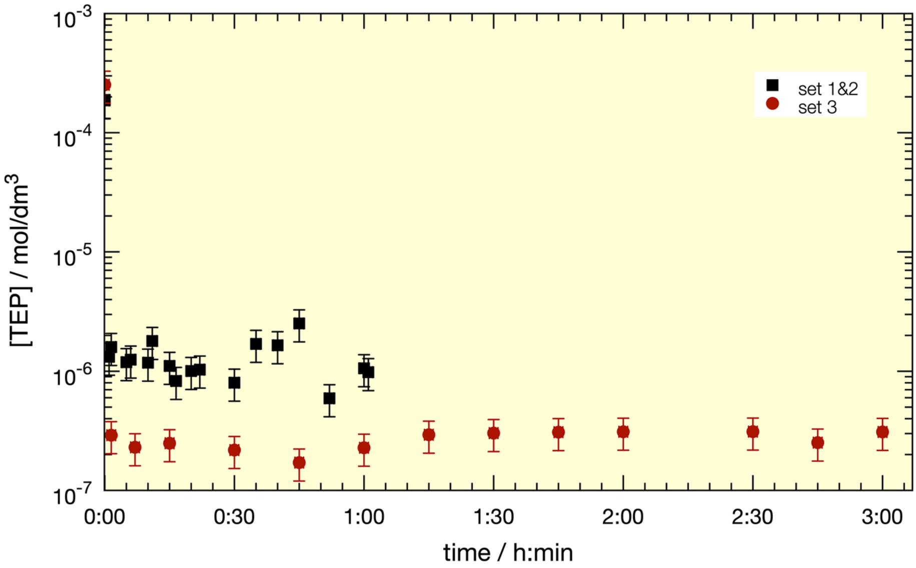

**Fig. 5** Evolution of the TEP concentration in a reactor with 3 mg of ceramic particles

### 3.1 Laboratory scale

These first results were promising as they seem to confirm the specific sorption capacity of ceramic particles by TEP already published in the literature [25], but although this information is of great relevance, it is necessary to check whether or not other parameters such as chemical potential or amount of solute in contact with metal oxides have a relevant effect on the sorption of TEP by the ceramic particles.

### 3.2 Pilot plant

Once the efficiency of these particles in the laboratory scale was proven, the Time Of Flight (TOF) of these particles in the pilot plant was analysed and their interaction with the fog generated with the COUNTERFOG nozzles was studied, observing how it influences their collapse (Figs. 5, 6). The data plotted in the figures were quantified using a laser particle counter. This system allows to measure the number of particles of a determined diameter size in each channel. This device allows to follow the evolution of a particle size suspension in air (atmosphere of the COUNTERFOG Lab—pilot plant) during each one of the experiments done (Figs. 7, 8).

The results of the different tests carried out on this scale are shown below. As can be seen, each graph shows the evolution of the different selected CWAs (Figs. 9, 10, 11), their interaction with the fog, with the ceramic particles and with both (ceramic particles and fog with isopropanol).

In the case of iodine, according to the results obtained (Fig. 12), with a small addition of AgCl in the repository of the fog-generating solution ($\simeq 7$ mg for each dm$^3$ of solution), a significative reduction of the concentration of $I_2$ in the air is achieved. This effect can be justified by the chemical reaction with silver ions to give AgI(s), which favours the precipitation of the fog drops.

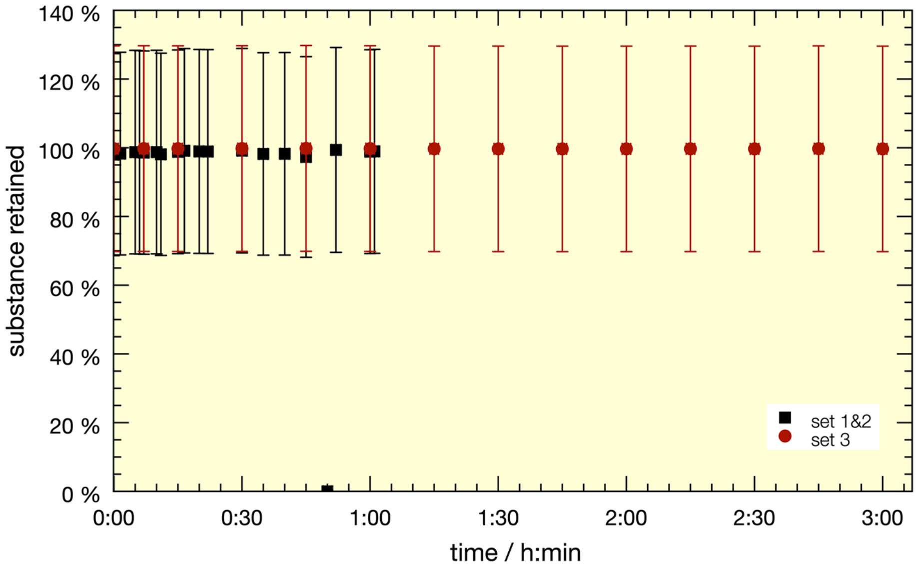

**Fig. 6** Evolution of the amount of TEP retained by ceramic particles

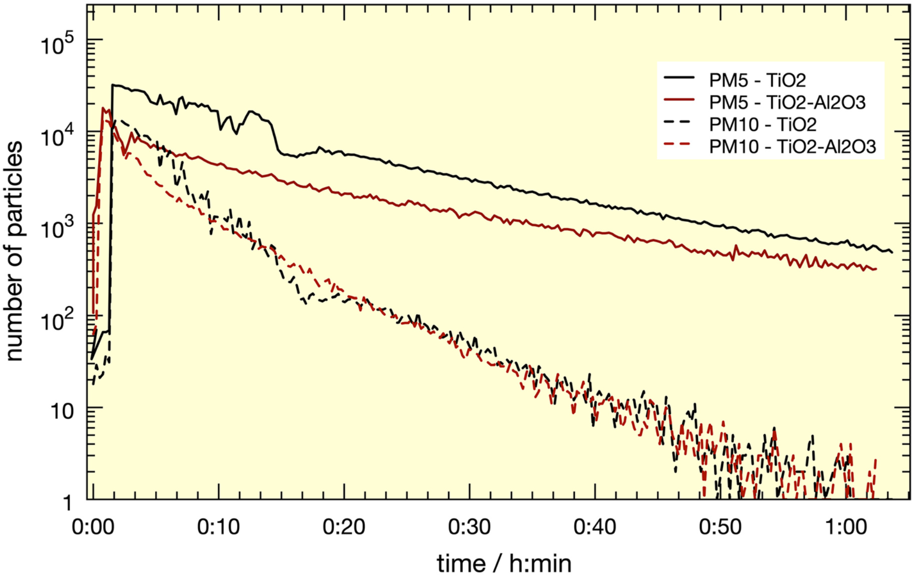

**Fig. 7** Evolution of the time of flight (TOF) of the distribution of $TiO_2$ and $TiO_2$–$Al_2O_3$ particles in the COUNTERFOG laboratory

## 3.3 Real scale test

The last step in this series of tests was to see if these results could be reproduced in a real scale. For this, the MS (Fig. 13) was selected given its easy sampling, detection and quantification. The concentration of CWA surrogate (i.e. MS) in the indoor atmosphere was monitored on-

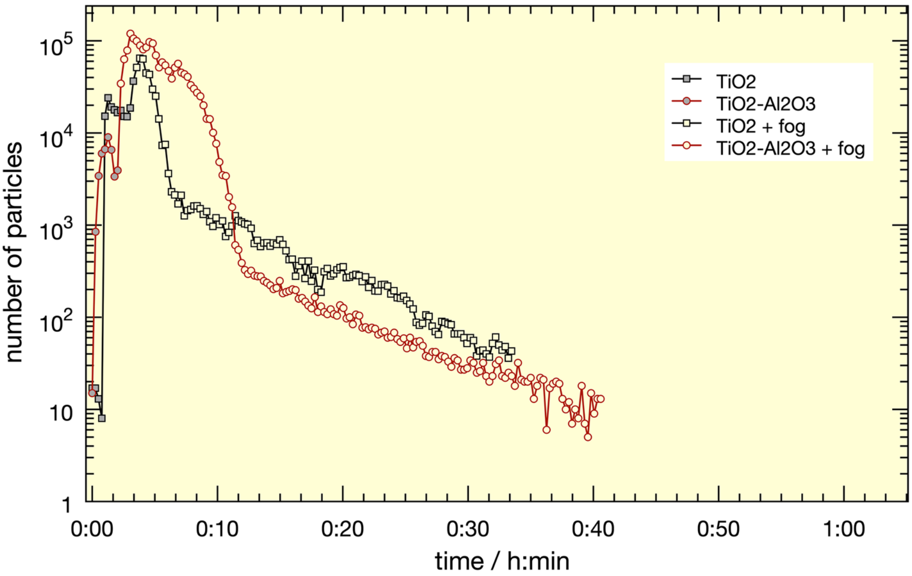

**Fig. 8** Evolution of PM5 measurements in tests with powdery material ($TiO_2$ and $TiO_2$–$Al_2O_3$) and fog

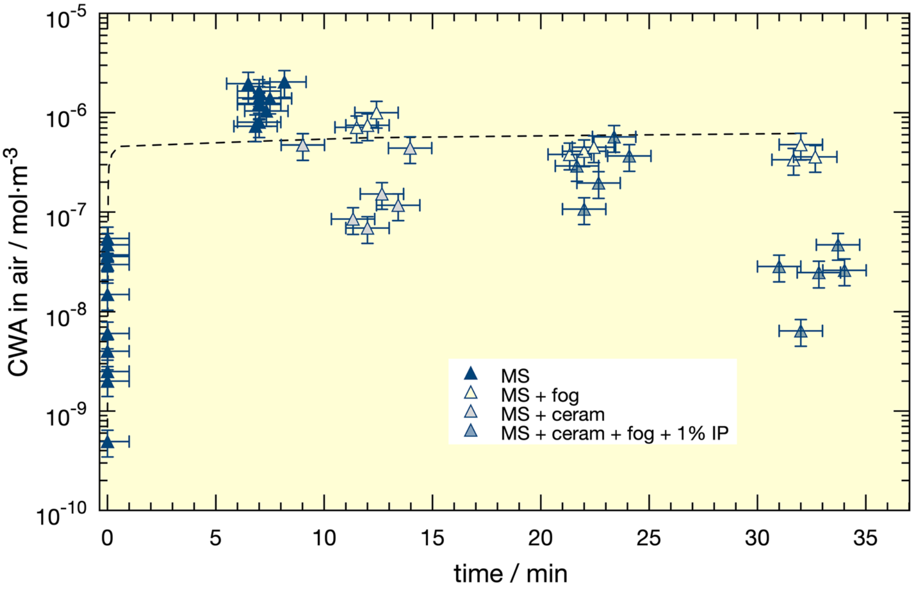

**Fig. 9** Interaction of the MS with the different countermeasures applied

line by passing the air through filters using a high-volume sampling system. For following the precise evolution of the MS concentration in the atmosphere, these filters were quantified by UV–Vis (as was described in point 2.2). The graphical representation of the results obtained for the different combinations of countermeasures is shown below.

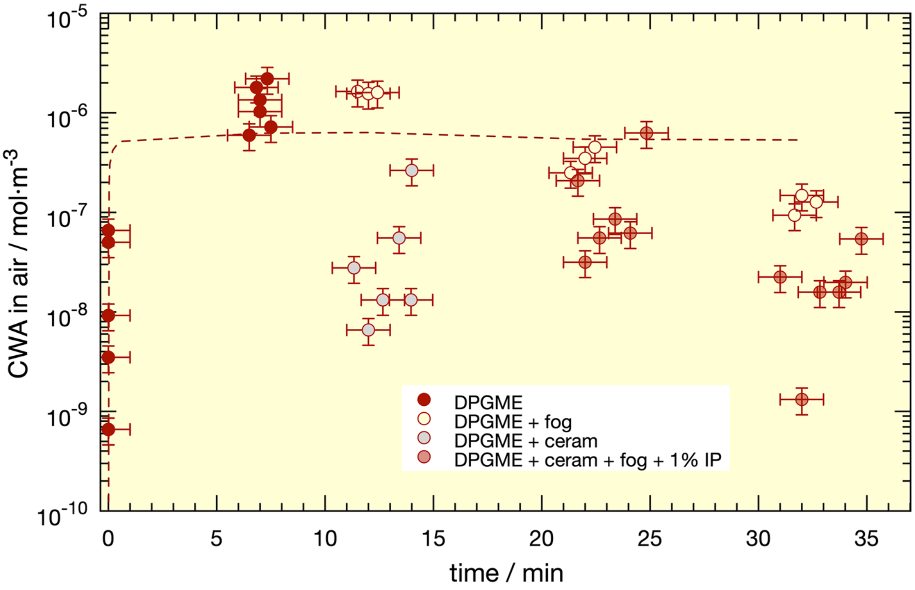

**Fig. 10** Interaction of the DPGME with the different countermeasures applied

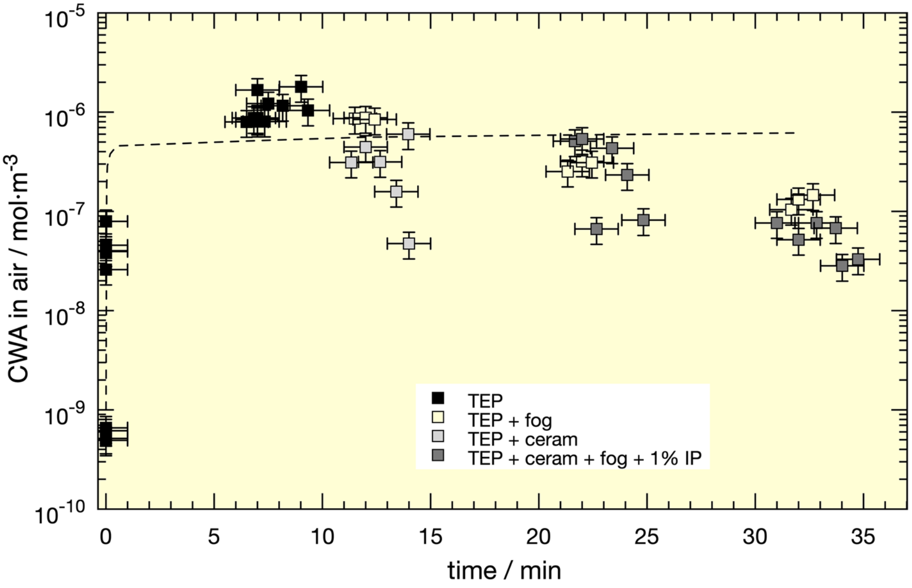

**Fig. 11** Interaction of the TEP with the different countermeasures applied

## 4 Discussion

The interaction mechanism proposed from these results (Fig. 14) is the following: (i) at the instant following the dispersion of the particles, the sorption of these chemical agents occurs on the surface of the solid (S, ceramic particles) and given that, as has been shown, only

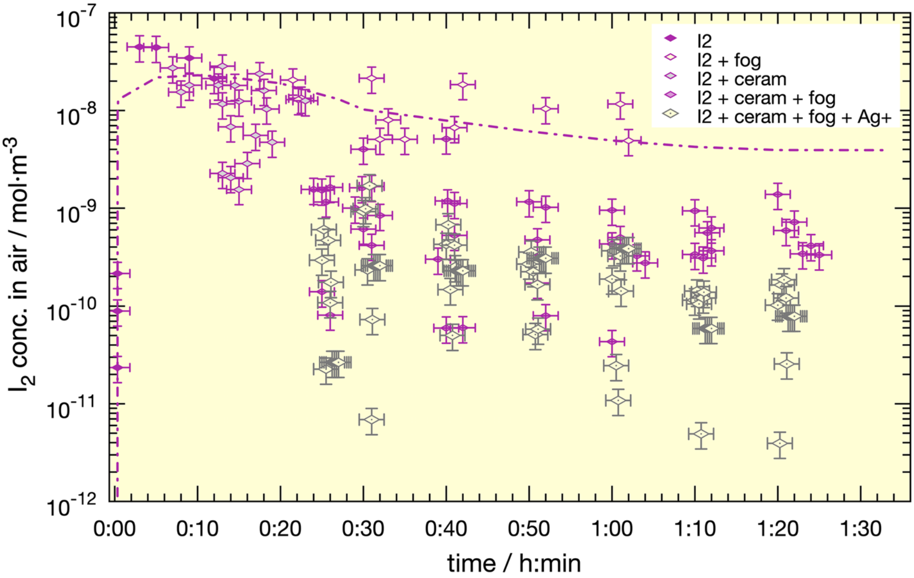

**Fig. 12** Interaction of the iodine with the different countermeasures applied

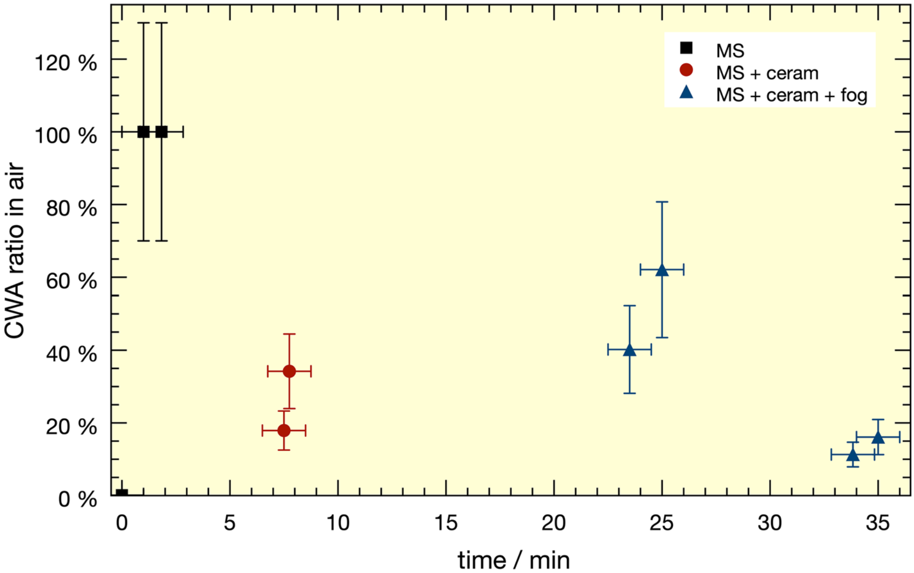

**Fig. 13** Percentage of pollutant agent remaining in the atmosphere of the CIEMAT warehouse during the application of the COUNTERFOG countermeasure designed in this research work

some of the PM10 particles will precipitate before firing the surfactant fog, a reduction in the concentration of CWA in the air is observed; (ii) since the fog is triggered and up to $\simeq 10$ min, the fog (water droplets) interact with the gas (G), dissolve the CWA and S suspended. The solid particles in the atmosphere could be embedded or not in the water-droplets showing different behaviour as a function of its final size. Whereas if the final particle generated is

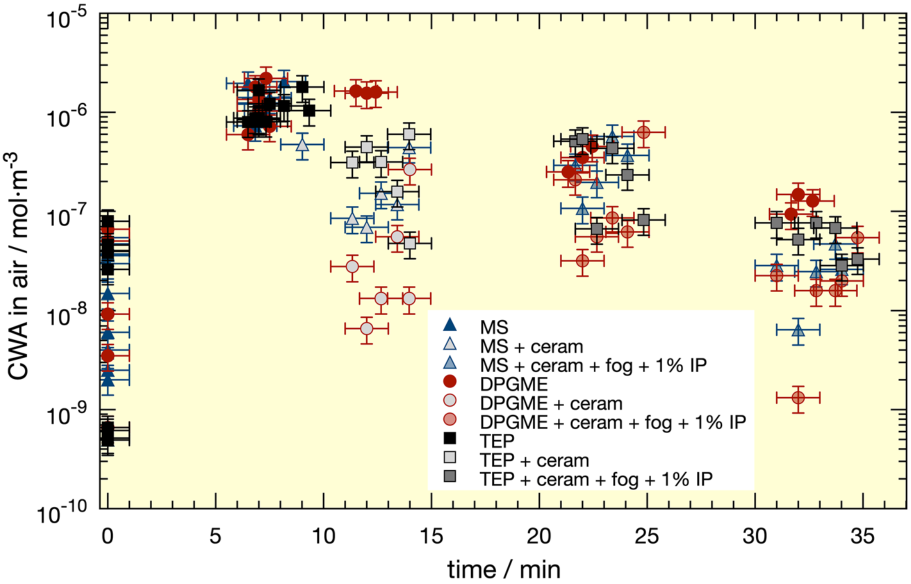

**Fig. 14** Comparative cleaning study with the new COUNTERFOG countermeasure against CWA surrogates *vs.* time

higher than PM10 will quick precipitate. Although those with a particle size in the range of PM5 remain suspended in the atmosphere (i.e. contamination remains); (iii) after 10 min from the fog release, and due to coalescence and weight increase in remaining PM5 particles (particle or water drop—particle) precipitate, which justifies the decrease in concentration of CWA in the atmosphere.

As can be seen from the results shown, the dispersion of ceramic particles and subsequent dispersion of fog with surfactant (L) (1% solution in isopropyl alcohol) have the following features and it is the best combination:

- The general response of the countermeasure is very similar regardless of the chemical agent evaluated.
- The presence of dispersed particles of $TiO_2$ and/or $TiO_2$–$Al_2O_3$ increases the G-S and G-L-S interaction, which produces a better uptake of the CWA dispersed by the atmosphere.
- The fog with isopropanol favours the precipitation of these particles that otherwise would remain in the environment for a longer time, as could be seen in Fig. 8, with the agent or possible sub-products.

In the case of iodine, the use of a combined countermeasure (by the dispersion of metal oxide particles and subsequent generation of fog) for the removal of $I_2$(g) radionuclides dispersed in the atmosphere, achieves reductions in environmental concentration of more than 2 orders of magnitude.

In general, it can be seen that the effect of the combined countermeasure is much higher than that of each of the measures separately, since, as has been shown, the joint interaction favours the reduction of the concentration of the dispersed radiochemical in the atmosphere.

Also, the tests carried out in COUNTERFOG laboratory, being a pilot plant scale, allow the validation of the results obtained at the scale of reactors in a laboratory and is closer to reality, as has been demonstrated when comparing the data obtained in both cases. For all these reasons, the COUNTERFOG countermeasure proposed in this research report is highly efficient in reducing the concentration of CBRN pollutants.

## 5 Conclusions

Operational procedure to test and evaluate the effectiveness of the COUNTERFOG system for countering, with CWA surrogates had been accomplished (20–30 min for being deposited).

The use of metal oxides in the process has pursued a dual objective:

- Remove the dispersed compounds from the laboratory atmosphere, taking advantage of its high adsorption capacity.

The proposed cleaning procedure involves three agents (CWA, metal oxides and fog):

- The fog can effectively clean the CWA surrogates and metal oxides particles if both are individually dispersed in the laboratory.

The countermeasure system propounds against dispersion in the atmosphere of RN and/or CWA has probed its usefulness.

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