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# Decontamination of the chemical warfare agent simulant dimethyl methylphosphonate by means of large-area low-temperature atmospheric pressure plasma

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ABSTRACT

Dimethyl methylphosphonate (DMMP), a chemical simulant of the nerve gas GB, was decontaminated with a nonthermal atmospheric pressure plasma. The decontamination efficiency was measured qualitatively by means of Fourier transform spectroscopy and quantitatively by means of gas chromatography. With helium gas only, 10 $g/m^2$ of DMMP on an aluminum surface was 99.9% decontaminated in 2 min, furthermore, with the addition of 5% of oxygen gas, it was 99.99% decontaminated in 10 min. Given the low input power (<100 W) and temperature (<75 °C), this plasma is eligible for nondestructive decontamination of almost all material surfaces.



## 1. Introduction

During the Second World War, Germany produced 61 tons of GB (sarin), a chemical nerve gas agent. Following the war, the Soviet Union, United States, and other members of the North Atlantic Treaty Organization began mass producing GB. The development and production of chemical weapons was not limited to a few powerful countries, because these types of weapons are simple and inexpensive to make. During the war between Iraq and Iran, Iraq initiated the use of chemical weapons, including GB. GB has also been used in terrorist attacks. In 1995, the Aum Shinrikyo cult released GB in a Tokyo subway, killing seven people and injuring about 500 [1]. Because the potential of chemical weapon usage remains high, there is a need for the development of effective methods of destroying chemical weapons.

Chemical warfare agents often need to be decontaminated not only in battlefields but also in production and storage sites. Furthermore, the surfaces of equipment, personnel, and so on may also need to be decontaminated. Hence, interactions between the surface and the agent are a major concern, together with the contamination density, decontamination time, and destructivity [2]. Conventional methods of destroying GB are mostly wet-type chemical reactions with solutions such as decontamination solution #2, hypochlorite bleach slurries, and dilute alkalis. In the case of human skin, absorbent materials such as towels, tissues, and powders are generally used, because of the detrimental nature of chemical solutions [1]. These conventional methods have severe problems in terms of destructivity and environmental safety as well as efficiency, portability, and cost. Hence, there is a need to develop alternative methods that are portable, selective, dry, noncorrosive, safe, and efficient. The thermal, photo, and chemical catalytic decomposition methods, which are less destructive and more 'green', tend to take a minimum of a few hours and sometimes scores of hours [3–6]. On the other hand, plasma is known to be one of the best candidates as a decontamination tool, because it meets all the above-mentioned requirements [7]. Still, in contrast to the abundant studies on the decontamination of biological warfare agents, only a few studies have experimented on the use of plasma in the decontamination of chemical warfare agents, and those studies focused mainly on high-powered thermal plasmas.

Plasma, which is an ionized gas containing chemically active radicals, has reportedly been used in the successful decontamination of the chemical warfare agent GB. Those experiments generally used dimethyl methylphosphonate (DMMP), which is a chemical simulant of GB. Moeller et al. used a low-frequency capacitively

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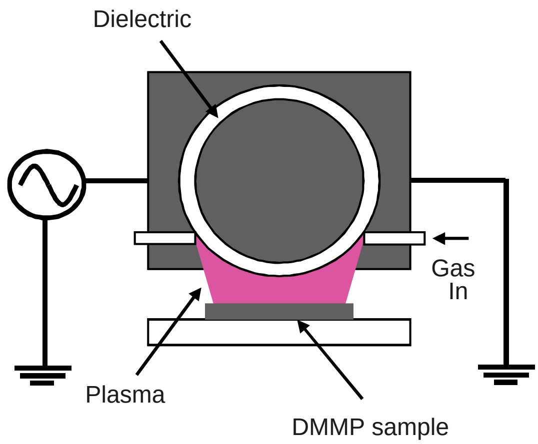


**Fig. 1.** Atmospheric pressure rf plasma source used for the DMMP decontamination.

coupled air-plasma flare to decontaminate liquid DMMP on an aluminum surface at atmospheric pressure [8]. In addition, Uhm et al. used an atmospheric pressure microwave-induced air-plasma torch to destroy a sprayed liquid sample of DMMP [9]. The low-frequency plasma decomposed a minimum 0.5 g/m$^2$ sample of DMMP to a level of 99.99% in 10 min, and the microwave-induced plasma destroyed a sample of DMMP at a rate of 1.14 l/h, which is about 20 g/min. Although the low-frequency plasma temperature was not given, it is assumed to be quite high, because of the high input voltage of 30 kV and the high power of 200 W. The microwave power had an input power higher than 1 kW and a temperature of 6000 K. The high power means more cost. Furthermore, the temperature is higher than the DMMP boiling temperature of 181 °C and high enough to be thermally destructive.

This work attempts to decontaminate DMMP with a low-temperature radio-frequency (rf) capacitively coupled helium plasma instead of a plasma with a high gas temperature. If similar decomposition efficiency is achieved, the lower gas temperature is better, because it enlarges the application range by including thermally weak materials. Furthermore, with the relatively large area of the rf plasma, the actual decontamination efficiency is increased by the simultaneous treatment of larger surfaces.

## 2. Experimental setup

Fig. 1 illustrates the plasma source, which consists of a dielectric covered cylindrical powered electrode in a rectangular grounded case. A 13.56 MHz rf power (Young-Sin RF YSE06F) was applied through an impedance matcher, and helium gas was supplied as a feeding gas at a fixed rate of 6 slpm. The dimensions of the plasma generated in the ambient air cover an area of about 15 mm × 110 mm, and the height, which is usually in the order of several mm's, depends on the discharge condition of the input power, the gas flow, and the additional ungrounded or grounded object at the bottom. In this work, the DMMP sample was placed 2 mm from the source. The plasma dimensions can be expanded if the device is larger.

Fourier transform infrared (FTIR) spectroscopy was used for qualitative measurements of the DMMP decomposition. A FTIR spectrometer (Bruker Equinox55) was used at a resolution of 1/4 cm$^{-1}$ and an aperture of 10 mm. For the measurements, DMMP was applied to an NaCl crystal (Sigma–Aldrich z123595) with a diameter of 2.5 cm and a thickness of 4 mm. A gas chromatograph and a mass analyzer (HP5972-Mass) were utilized for quantitative measurements of the plasma DMMP decomposition efficiency and for analysis of the byproducts. For this experiment, DMMP was applied to an aluminum plate of 18 mm × 18 mm × 1 mm dimensions. After the plasma treatment, the DMMP sample was placed in a solvent of methane dichloride and shaken in a vortex manner for residue collection. The gas chromatograph (HP5890 with HP-5 column) was used to obtain the DMMP concentration through a calibration process.

## 3. Results and discussion

The plasma used for the experiment has features of a relatively large-area at atmospheric pressure, a low discharge current, and a low gas temperature, all of which make it electrically and thermally efficient and safe. Most importantly, as measured with a fiber thermometer, the input power ranged from 50 W to 100 W, and the gas temperature varied from 20 °C to 75 °C [10]. This temperature range is lower than the DMMP boiling temperature of 181 °C and low enough to be thermally nondestructive. Hence, this plasma can be touched with a bare hand, which means it can be used in the decontamination of human skin.

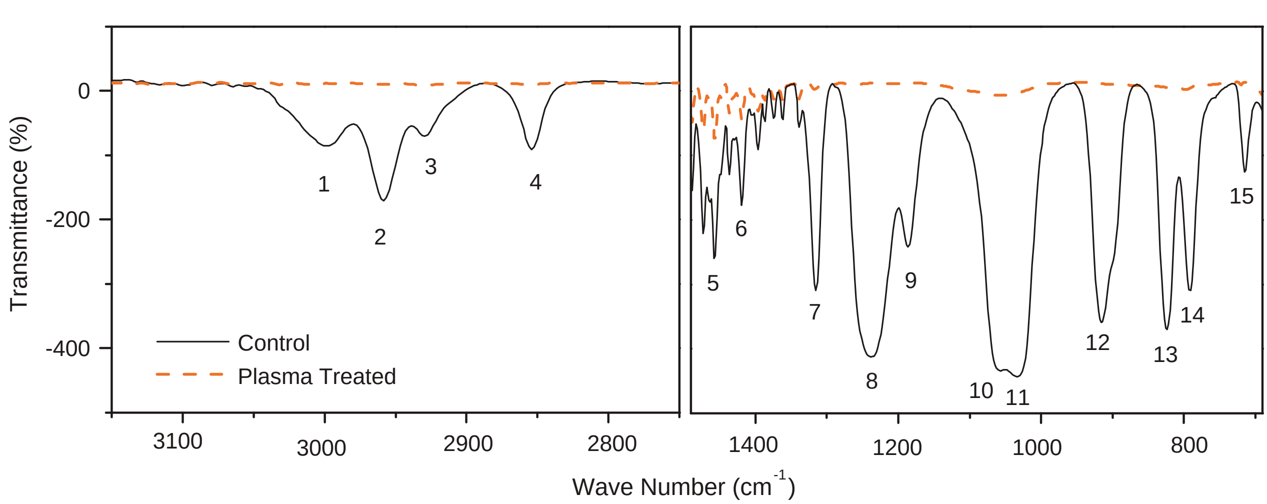


**Fig. 2.** FTIR spectrum of a DMMP control sample (solid) and a plasma-treated sample (dotted).