

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Application of Gas Chromatography in Monitoring of Organic and Decontamination Reactions

Pranav Kumar Gutch

*Defence Research & Development, Establishment Jhansi Road, Gwalior,  
India*

## 1. Introduction

Gas chromatography (GC) is a separation technique commonly used for organic compounds which can be converted into gaseous phase without decomposition. The components to be separated are carried through the column by an inert gas (Carrier gas). The separation of the analyte usually takes place in a long capillary tube (the column). The wall of the column is coated with a thin film of a very high boiling liquid (stationary phase), through which an inert gas (mobile phase) flows. The component of a mixture are portioning between the two phases. The stronger the interaction of a component with the stationary phase, the longer will be the retention. The rate of movement of the various components along the column depends upon their tendency to absorb in the stationary phase. Component of mixture are separated at different time interval and it give only a single peak for each separated component of mixture. A plot of the time necessary for a compound to move through the column (retention time) versus its amount (intensity) is called a chromatogram. The time for injection point to peak maxima is called retention time. Retention time depends on various factor viz Flow rate of carrier gas, Temp of column, and nature of stationary phase.

## 2. Monitoring of organic reactions by GC

GC (Pattison 1973) is generally used for determination of purity, identification of samples and monitoring of organic reactions. Decontamination reaction of chemical warfare agents can also be monitored by GC. N-Chloro compounds (Kovari, E. 2007) have been extensively exploited, both for fundamental research and a wide range of industrial applications, (Koval, I. 2002, 2001) owing to their easy handling, commercial availability and high storage stability. As a result, intensive research and studies have been carried out over long period of time on their chlorination, (Ghorbani, Vaghei. 2009) oxidation, water disinfection (Bogoczek, R. 1989)& some other applications (Kowalski, P. 2005) in synthetic organic chemistry. N-chloro compounds (Singh, R. 2011) have also been reported for decontamination of chemical warfare agents.

The polymeric N-Chloro resin proved to be very strong chloridine agent and found to be easily reusable. The additional advantage of polymeric chloramines (Gutch, P. 2011) in

higher stability as compared to low chloramines such as chloramines-T and dichloramine – T. Active chlorine content does not decrease with prolonged storage time. Hetrogenised reagent has evinced the attention of researchers because of their handling ease, lower toxicity, nonexplosive, and malodorous nature. Another impotent motive of supported reagent is facile isolation of pure product than their solutions phase equivalents.

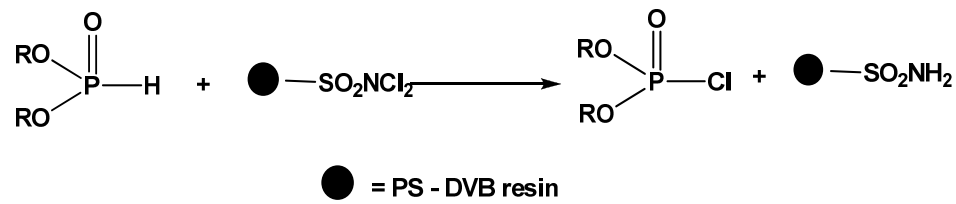
N-chloramines (Gutch, P. 2011) in which chlorine is directly attached to nitrogen can generate positively charge chlorine ( $\text{Cl}^+$ ) which is an oxidising species. N-Chloro compound macroporous poly(styrene-co-divinylbenzene) resin having *N,N*-dichlorosulfonamide groups have been used as a polymer supported reagent for chlorination, oxidation for residual sulfides, cyanides, thiocyanates, water disinfection and some application in synthetic organic chemistry. In recent year the use of recyclable reagents has received considerable interest in organic synthesis. This prompted us to explore the possibility of using the stable, non toxic, recyclable, and efficient positive chlorine releasing reagent, N, N-dichloro poly (styrene-co-divinylbenzene) sulfonamide polymeric beads for oxidation, chlorination and decontamination reactions.

## 2.1 Synthesis of dialkylchlorophosphate from dialkylphosphites at room temperature

Organophosphorus compounds (OPs) (Eto, M. 1974) have attracted the attention of researchers because of their wide applications in industrial, agricultural, biochemical, and medicinal areas. Naturally occurring OPs play an important role in the maintenance of life processes. It is interesting to note that chemical, physical, and biological properties of OPs are governed by the stereochemical disposition of substituents around the phosphorous atom. One such class of compounds is the dialkylchlorophosphates. These chlorophosphates are used for the transformation of various functional groups. Recently, diethylchlorophosphate has been used as an efficient reagent in cyclization reactions and in regioselective ring opening of epoxides.

Methods described in the literature for the preparation of dialkylchlorophosphates, involve chlorination of the corresponding phosphites (dialkylphosphites/trialkylphosphites) with reagents such as elemental chlorine, phosgene,  $\text{SO}_2\text{Cl}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{SCl}_2$ ,  $\text{CCl}_4$ ,  $\text{CCl}_3\text{NO}_2$ ,  $\text{PhSO}_2\text{NCl}_2$ ,  $\text{C}_2\text{Cl}_6$ ,  $\text{ClSCCl}_3$ ,  $\text{CuCl}_2$ , perchlorofulvalene, and *N*-chlorosuccinimide. Among these procedures, only a few can be considered as convenient laboratory methods for the synthesis of dialkylchlorophosphates. Most of these reported methods either use reagents or produce undesired by-products, which are difficult to remove from the sensitive chlorophosphates, while others are time consuming, involve expensive and unstable reagents, and require harsh conditions.

Having established a commercially synthetic procedure for N, N dichloro poly (styrene-co-divinylbenzene)(Gutch, P. 2007) sulfonamide polymeric beads( we investigated its use as an alternative reagent for the conversion of di alkylphosphite to dialkylchlorophosphate (Gupta, Hemendra. 2008).This development enable us to obtained almost all quantitative yields of products in short reaction times. The room temperature (20-25°C) reaction of various dialkylphosphite with N, N dichloro poly (styrene-co-divinylbenzene) sulfonamide polymeric beads afforded the corresponding dialkylchlorophosphates in 3-4 h in excellent yields (Scheme 1).The reaction was monitored by removing an aliquot and analyzing by GC-MS. The progress of a typical reaction as monitored by GC-MS is depicted in fig. 1.



Scheme 1. Dialkylchlorophosphate prepared from dialkylphosphites using polystyrene divinylbenzene (PS-DVB) bound reagent.

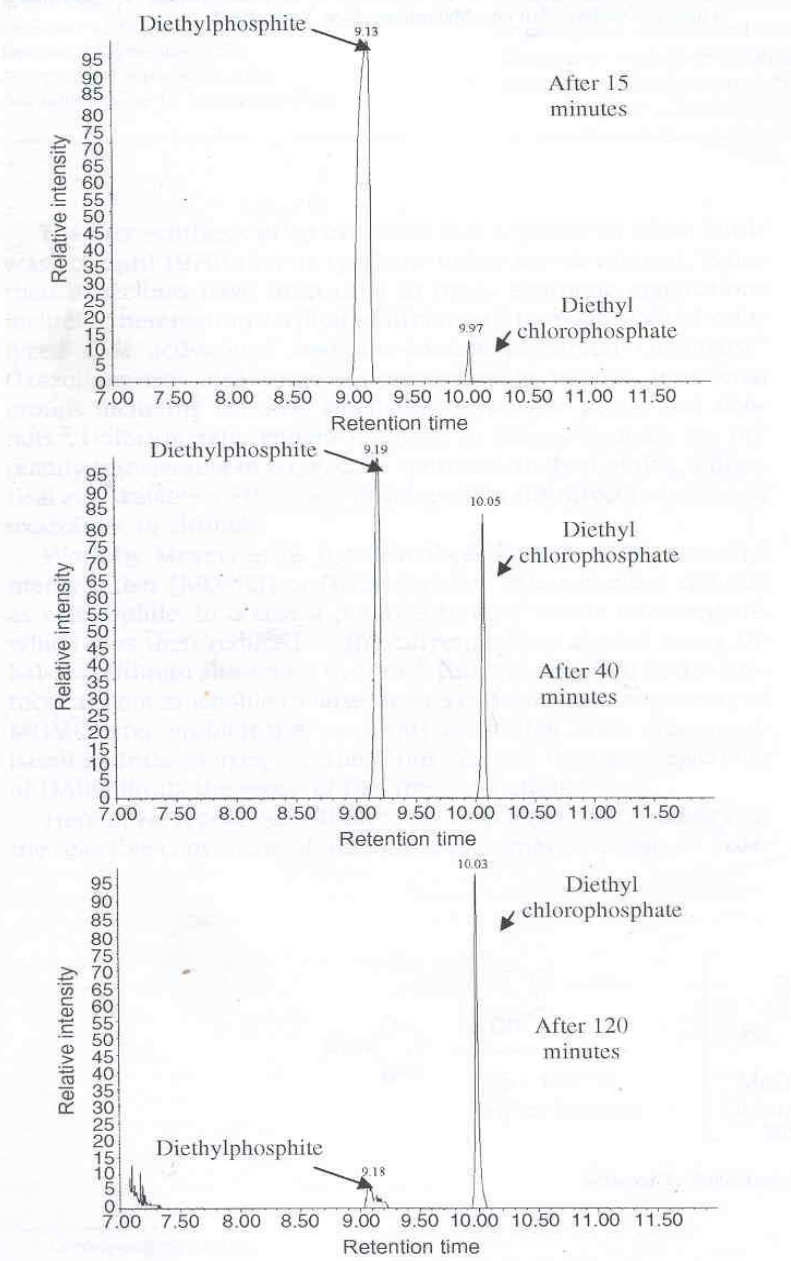


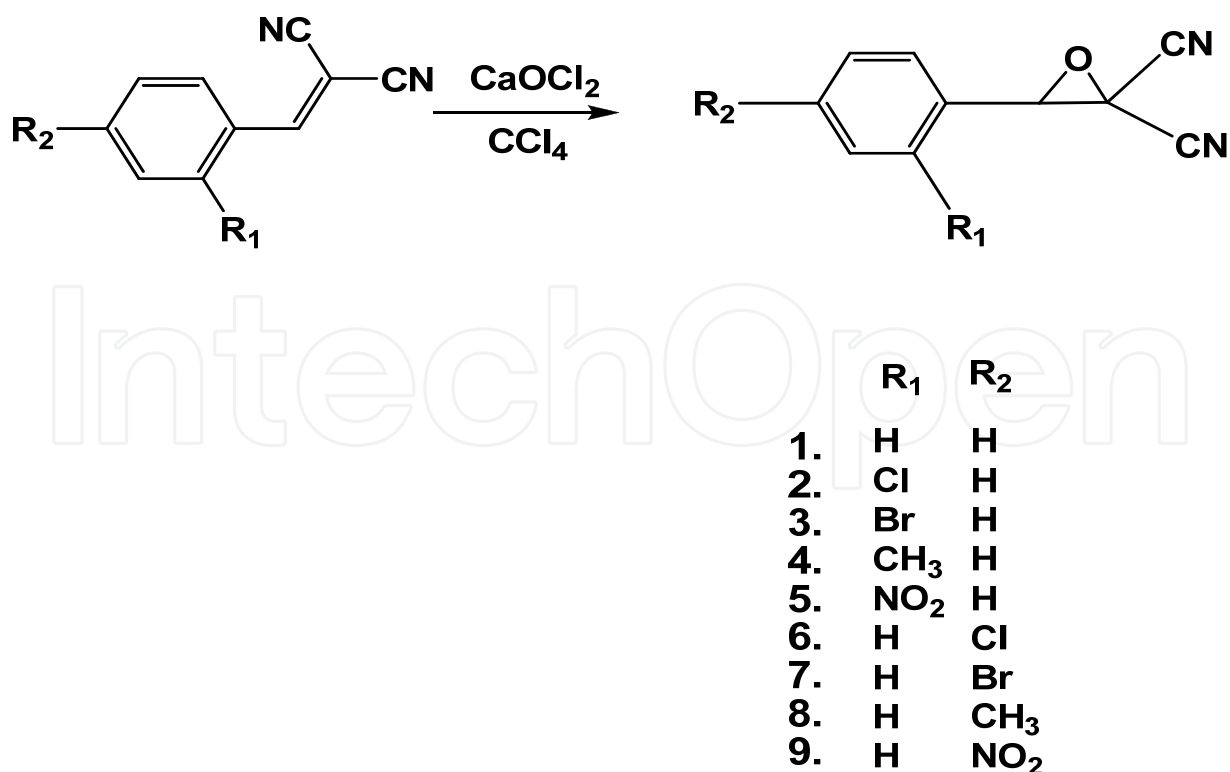
Figure 1. Progress of a typical reaction as monitored by GC-MS analysis at different time intervals.

Fig. 1. Progress of a typical reaction as monitored by GC-MS analysis at different time intervals.

In conclusion, we have described an efficient reagent for the rapid and convenient conversion of dialkylphosphites to dialkylchlorophosphates under mild conditions using *N,N*-dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads, as a stable and non-toxic reagent at room temperature. Here in this work it is proved to be an important and valuable reagent.

## 2.2 Synthesis of dicyanooxiranes derived from benzylidenemalononitriles

Benzylidenemalononitriles (Rose, S. 1969) have received much attention as cytotoxic agents against tumors and some derivatives have also been used as rodent repellents. 2-Chlorobenzylidene Malononitrile (CS) (Jones, G. 1972) is one of the most potent lachrymator and skin irritants used as riot control agent. Benzylidenemalononitriles (Gutch, PK, Thesis 1997) are highly sensitive to oxygen and form Gem-dicyano epoxides which constitute an important class of synthetic intermediates. These epoxides react with a variety of reagents such as alcohol, water, hydrazine, and hydroxylamine in presence of halogen acid to give useful products including hydroxamic acid which is an interesting material for the synthesis of intermediates aziridinones used in situ as precursor to  $\alpha$ -hydroxy and  $\alpha$ -amino acids. We have developed an improved method for the synthesis of substituted phenyl-1,1-dicyanooxiranes (Scheme 2) from benzylidenemalononitrile using calcium hypochlorite (Gutch, P. March 2001) in carbon tetrachloride at 25°C. The reaction completion within 90 min and results in 98-99% yields of dicyanooxiranes. The reaction does not require any maintenance of the pH and no side products are formed. The reaction was monitored by GC (fig. 2) using FID as a detector at 140 °C



Scheme 2. Synthesis of substituted phenyl-1, 1'-dicyanooxiranes

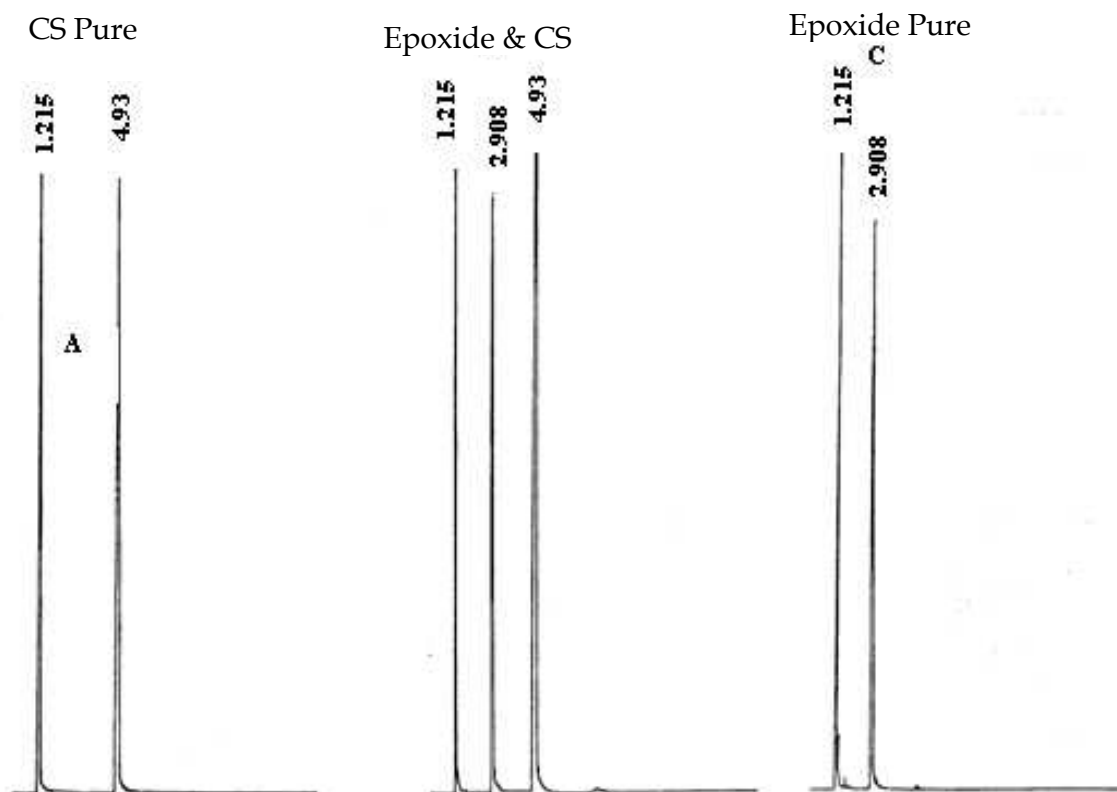


Fig. 2. Reaction of CS with calcium hypochlorite on DB-1701 column at 140 °C: Chromatogram: A= Reaction mixture at zero time showing only CS: B=Reaction Mixture after 20 minutes showing the formation Epoxide: C=Reaction mixture after 45 minutes showing disappearance of CS.

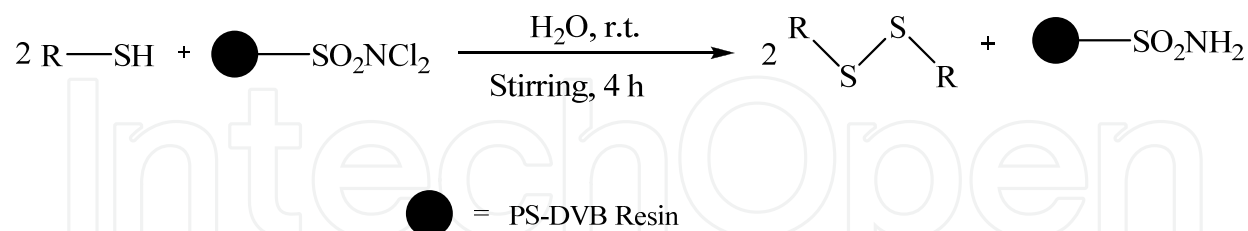
### 2.3 Synthesis of disulfide from thiols

Disulfides (Pathak, U. 2009)) have found industrial applications as vulcanizing agents and are important synthetic intermediates with many applications in organic synthesis. Disulfides are primarily produced from thiols, which are readily available and facile to prepare. Oxidative coupling of thiols to disulfides under neutral and mild conditions is of practical importance in synthetic chemistry and biochemistry. However, synthesis of disulfides from thiols sometimes can be problematic due to the over oxidation of thiols to sulfoxides and sulfones. On the other hand, many successful reagents such as 1,3-dibromo-5,5-dimethylhydantoin, cerium(IV) salts, permanganates, transition metal oxides, sodium chlorite, peroxides, halogens, solid acid reagents, monochloro poly(styrenehydantoin)(Akin, Akdag, 2006) beads, *N*-Phenyltriazolinedione, poly(*N*-bromomaleimide), (Bahman, Tamani, 2009) have been developed for the synthesis of disulfides from thiols, under a range of experimental conditions.

A novel method for oxidative coupling of thiols (Gutch, P. 2011) to their corresponding disulfides (scheme 3) using *N, N*-dichloro poly (styrene-co-divinyl benzene) sulphonamide (PS-DVS) beads was developed. In this study, we have employed *N, N*- dichloro poly (styrene-co-divinylbenzene) sulfonamide beads in water for the conversion of thiols to symmetric disulfides. These polymeric beads did not over oxidize the thiols to sulfoxides or



sulfones and the sole product isolated from these experiments was disulfides. Presumably, the reactions proceed through chlorine transfer from amide *N*-halamine to thiols to yield disulfides and hydrochloric acid.



Scheme 3. Synthesis of disulfides from thiols

Thiol(0.05 mol) was added to a suspension of *N, N*-dichloro poly (styrene-co-divinyl benzene) sulphonamide beads (containing 0.05 mol of active chlorine) in water (30mL). The mixture was stirred at room temperature for 4 hrs and reaction was monitored by GC (Fig. 3). PS-DVS beads act as novel and selective oxidative agents which efficiently reduce the reaction time, increase the product yield without producing over oxidized products and performed under air atmosphere.

In conclusion *N, N*-dichloro poly (styrene-co-divinylbenzene) sulfonamide resin is an efficient reagent for fulfill different required objective in organic synthesis. Here in this work it proved to be an important and valuable reagent for the corresponding disulfide. The conversion was very efficient, with excellent yield and polymeric reagent can be recovered activated and reused. The main advantages of the method is that the reaction was very clean and operationally simple. Therefore the method is very attractive for organic chemist.

### 3. Monitoring of decontamination reaction of chemical reaction for chemical warfare agent

Decontamination (Yu-chu, Yang. 1992) is an important unavoidable part in protection against Chemical warfare agent. The aim of decontamination is to rapidly and effectively render harmless or remove poisonous substances both on personal and equipment. Though a variety of decontaminating agents have been reported over the years, however most of them suffer from drawbacks such as the use of hazardous solvents and prolonged decontamination time. Further, these reagents cannot be used on skin due to the toxicity of solvent and reagents.

Decontamination (Somani, S. (Ed). 1992) may be defined as a method of conversion of toxic chemicals into harmless products which can be handled safely, either by degradation or detoxification using suitable reagents. Decontamination plays a vital role in defence against chemical warfare agents. The toxic materials must be eliminated from the battlefield etc. by application of some efficient decontamination methods as fast as possible for resuming routine activities. Decontamination (Talmage, S. 2007) of CW agents is required on the battlefield, in laboratories, pilot plants and places of chemical agent production, storage, and destruction sites.

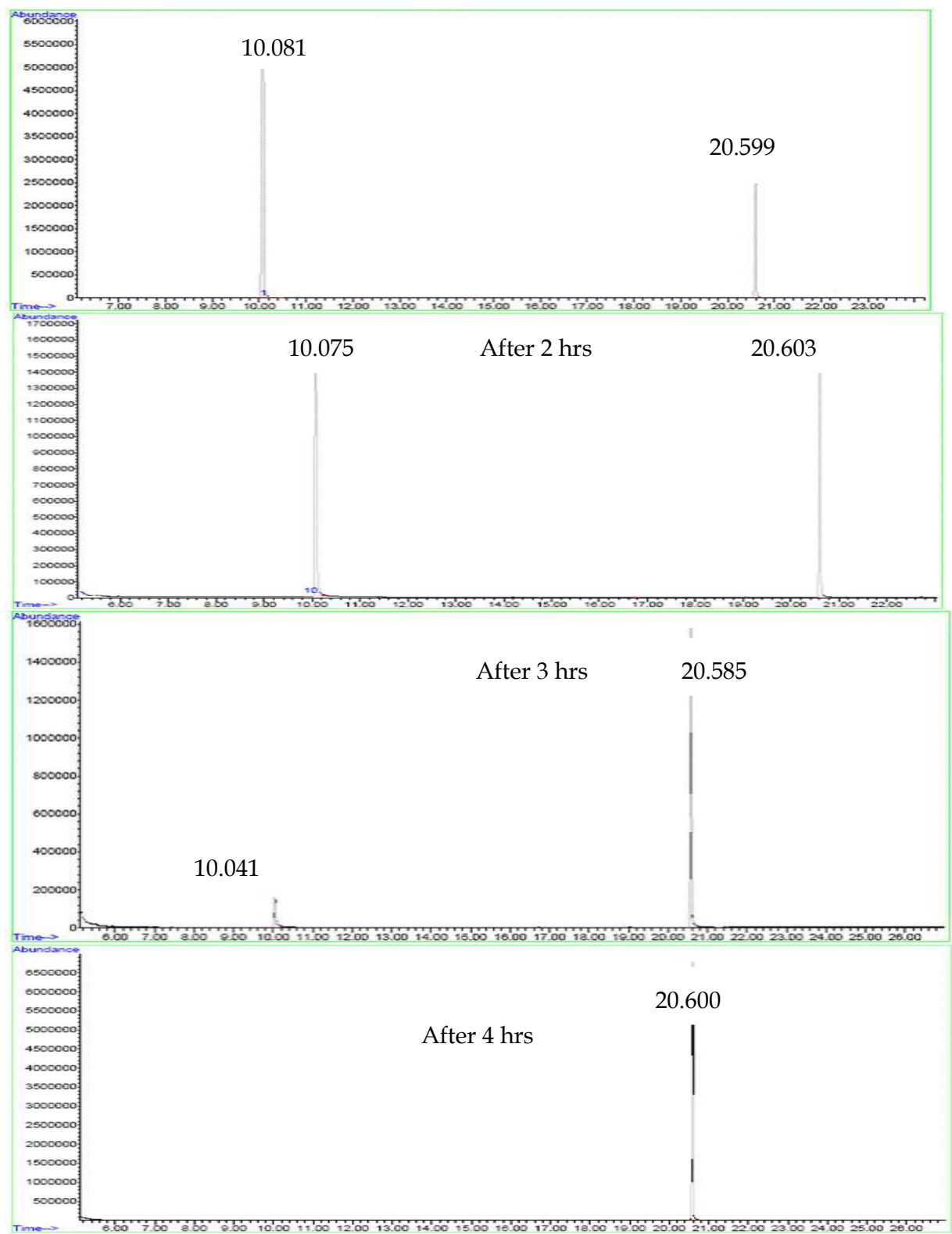


Fig. 3. Progress of disulphide reaction as monitored by GC-MS analysis at different time interval



Toxic substances can also be decontaminated (Yang, Y. 1995) by chemical modification of their toxic structures by using small compounds like hydrogen peroxide. Decontamination (Dubey, D. 1999) through chemical reactions is more reliable and effective as compared to physical methods. Chemical reaction yields less toxic or non-toxic products, while in the physical process they are just removed from the site.

### 3.1 Simulants

As with all chemical warfare agents, testing with the actual agents which are often very toxic is difficult to synthesize, their handling is also difficult, and they are expensive and are not commercially available. The developmental work on their process is often done on surrogate chemical that possesses many of the important features of the agent. Surrogate, also called a simulant or analog, must be carefully chosen to reasonably substitute for the target agent in the specific reaction pathway or reaction conditions under investigation. In the case of the partial oxidation of sulfur mustard, for example, an appropriate surrogate should clearly have a sulfide bond. Ideally, the surrogate would have similar structural features allowing for the same reaction mechanisms that would detoxify the agent, and would also have similar physical properties like solubility and vapor pressure. Also, one should consider secondary reactivity when possible, allowing for any foreseeable side reaction.

Simulants are those compounds which are less toxic but they have same chemical reactivity like toxicants. For the standardization of the chemical reactions, simulants can be used in place of actual agents. In order to gain a more complete understanding of CW agent chemistry, it is often necessary to study the reactions of a series of agent-analogs under the same conditions. For example, the monofunctional derivatives of mustard,  $\text{RSCH}_2\text{CH}_2\text{Cl}$  ( $\text{R} = \text{Me, Et, Ph}$ ),  $\text{RSCH}_2\text{CH}_2\text{X}$  ( $\text{X} = \text{tosylate, brosylate, Br, I, or other leaving groups}$ ), react via the same mechanism as those of HD, but their reaction products and kinetics rate expressions are much simpler. 2-chloroethylphenylsulfide, 2-chloroethyl ethylsulfide (half mustard) and dibutyl sulfide (DBS) are all simulants of HD. The use of simulants makes it easier to isolate the variable that affects the agent chemistry. VX analogs,  $(\text{C}_2\text{H}_5\text{S})(\text{CH}_3)\text{P}(\text{O})-(\text{C}_2\text{H}_5\text{O})$ ,  $(\text{C}_2\text{H}_5\text{S})(\text{C}_6\text{H}_5)\text{P}(\text{O})-(\text{C}_2\text{H}_5\text{O})$  have also been studied to isolate the effect of the diisopropylamino group on the reaction chemistry of VX. Simulants are those compounds which are less toxic but they have same chemical reactivity like HD & VX. For the standardization of the chemical reactions, simulants can be used in place of actual agents. 2-chloroethyl phenyl sulphide & methyl phosphothioic acid O, S- diethyl ester are simulants of HD & VX respectively.

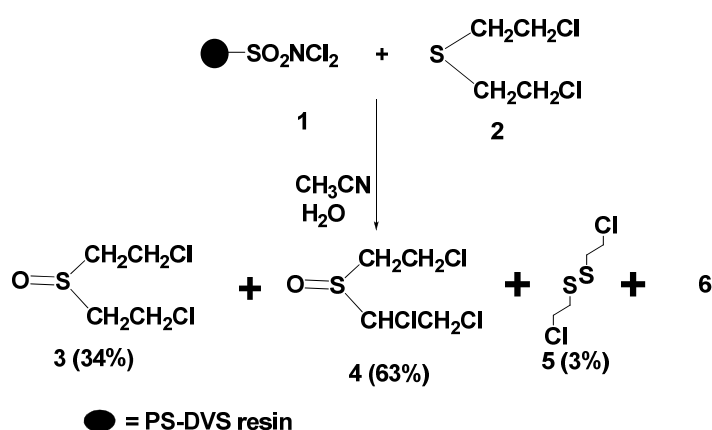
Our aim in this work is to overcome the limitation and drawbacks of the reported decontaminants (Prasad, G. (2009)). It has been incorporated as a reactive ingredient in a formulation developed in our laboratory to decontaminate bis (2-chloroethyl) sulfide (SM), a chemical warfare agent. N,N-Dichloro poly(styrene-co-divinyl benzene) sulfonamide, a new class of readily available, economical, commercially viable, and recyclable chlorinating reagent was chosen for use as a decontaminating agent in this study.

### 3.2 Decontamination of Sulfur Mustard (SM)

We have already reported N, N-dichloro poly (styrene-co-divinyl benzene) sulphonamide polymeric beads for decontamination of simulant of SM. N,N-dichloro poly(styrene-co-

divinylbenzene) sulphonamide reacts with 2-chloro ethyl phenyl sulphide, a simulant of sulfur mustard (SM), at room temperature, yielding corresponding nontoxic sulfone and sulfoxide in aqueous as well as aprotic medium.

Sulfur mustard (SM) is a cytotoxic and persistent blistering agent that was used as a weapon of mass destruction in the World War I and recently in the Iraq-Iran war (1980-1988). Detoxification (Gutch, P. 2008) of the chemical warfare agent (CWA), sulfur mustard is one of the primary goals to get rid of its toxic effects. An efficient and operationally simple method is developed for chemical decontamination of sulfur mustard. A new chlorine bearing reagent *N,N*-dichloro poly (styrene-co-divinyl benzene) sulphonamide was developed to deactivate the sulfur mustard (**Scheme 4**) in aqueous (acetonitrile: water) medium. This decontamination reaction was monitored by GC-FID (Fig.4) and the products were analyzed by GC-MS (Fig.5).



Scheme. 4. Reaction of SM with polymeric Beads in aqueous medium

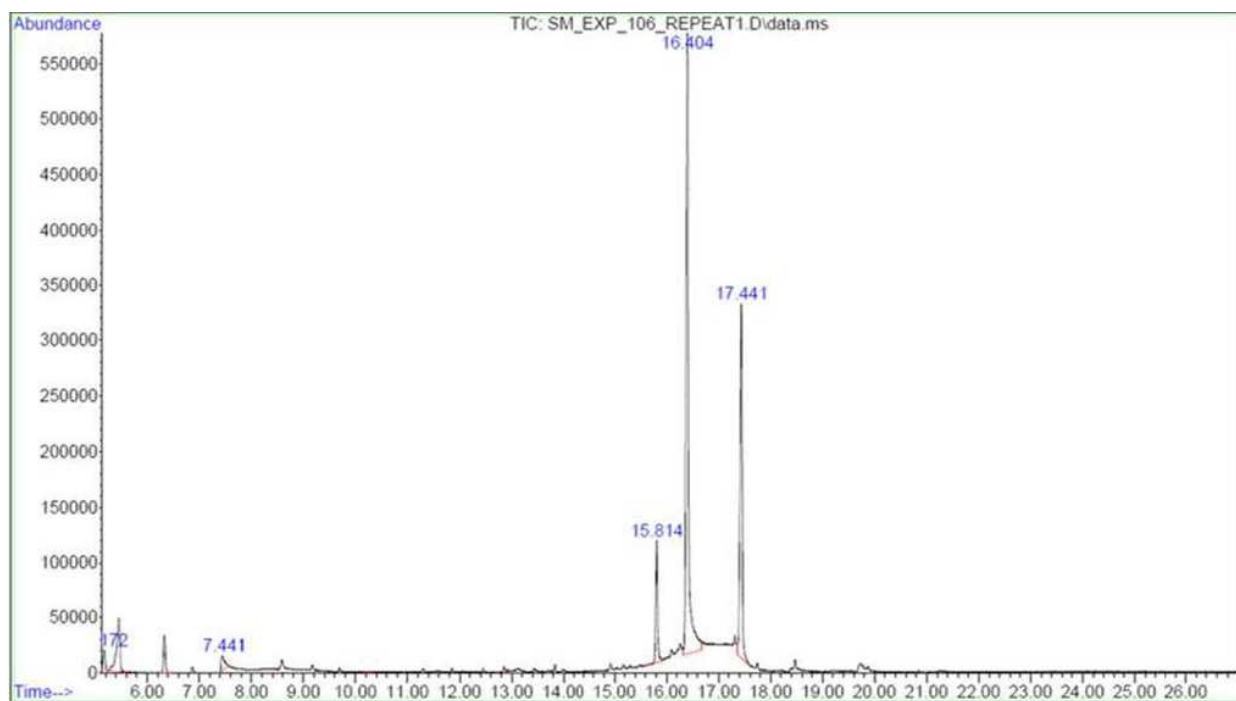


Fig. 4. Gas Chromatogram of SM after decontamination

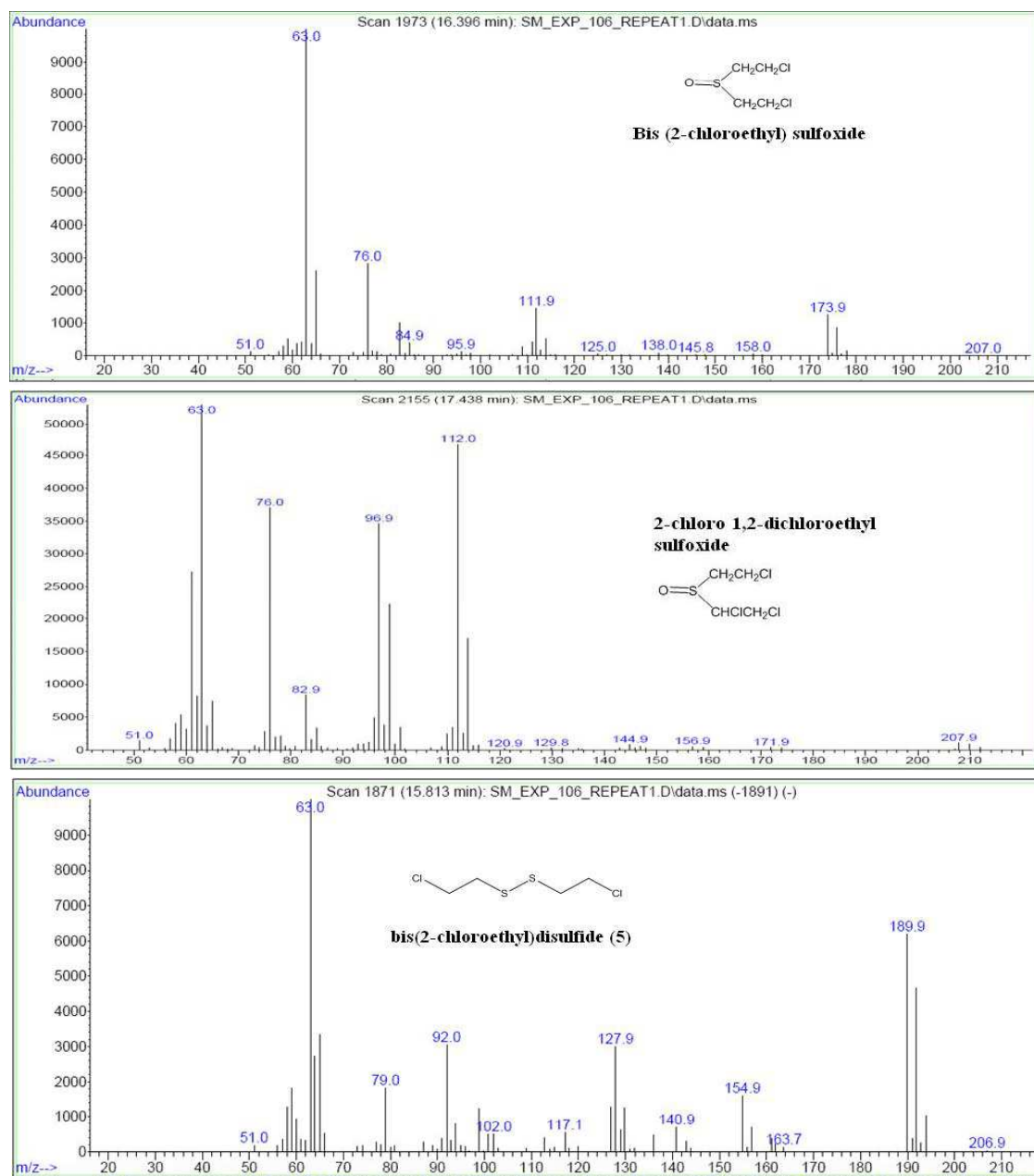


Fig. 5. Mass spectrum of decontaminated products (3-5) of SM in aqueous medium

*N, N*-dichloro poly (styrene-co-divinyl benzene) sulphonamide (Gutch, P. 2011) polymeric beads (3.0 mmol) was added slowly to a stirred solution of SM (1.0 equiv.) in acetonitrile water mixture (5 ml) at room temperature. It was found that 100 % SM was decontaminated instantaneously in aqueous medium and decontaminated products were identified by Gas Chromatography-Mass Spectrometry. The GC conditions used were as follows; column HP-

5 (30m× 0.250mm i.d., 0.25 µm film thickness) with a temperature programme of 50°C for 2 min followed by a linear gradient to 250°C at 10°Cmin<sup>-1</sup>, and hold at 250°C for 5 min. The injector temperature was maintained at 250°C.

The decontamination reaction of SM is studied with varying molar concentration of active chlorine available in PS-DVB. At equimolar ratio of SM and active chlorine on PS-DVB, the major product is bis (2-chloroethyl) sulfoxide(3). At 1:2 molar ratio, in addition to (3), 2-chloro 1,2-dichloroethyl sulfoxide(4) is also formed; whereas, at 1:4 molar ratio the major product is 2-chloro 1, 2-dichloroethyl sulfoxide (4) with a trace amount of bis(2-chloroethyl)disulfide (5). In all the reactions N, N-dichloro poly (styrene-co-divinyl benzene) sulfonamide (PS-DVB) polymeric beads (1) were converted into poly (styrene-co-divinyl benzene) sulfonamide (PS-DVB) polymeric beads (6).

This reagent has advantage over earlier reported reagents in terms of effectiveness, stability, non toxicity, and cost, ease of synthesis, recyclability (collected after filtration, rechlorinated and used for further reaction) and instantaneous decontamination of sulfur mustard at room temperature.

### 3.3 Decontamination of S-2-(diisopropylamino) ethyl O-ethyl methylphosphonothioate(VX)

Organophosphorus compounds (OPs) have been widely used in the industry, veterinary and human medicine, in the agriculture as pesticides or can be misused for military purpose i.e. as Chemical Warfare Agents (CWA). The chemical warfare nerve agents, commonly known as nerve gases, are in fact not gases but polar organic liquids at ambient conditions. Most of these nerve agents are P (V) organophosphorus esters that are similar in structure to an insecticide.

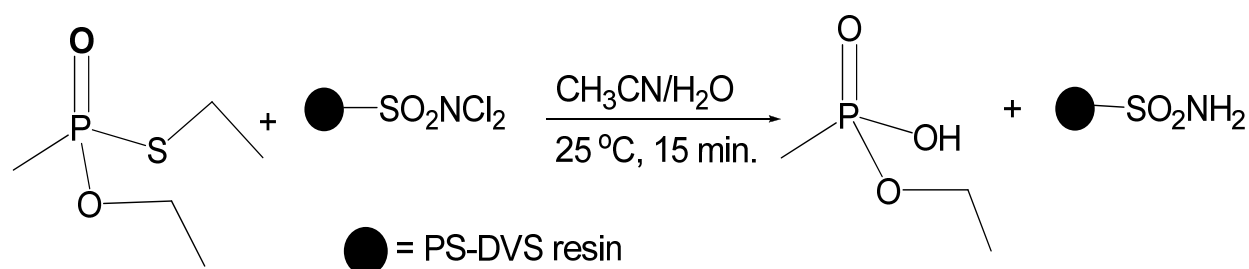
Highly toxic organophosphorus compounds (OPCs) that are nerve agents such as sarin, soman, tabun and cyclosarin are lethal chemical warfare agents, also known as G-agents and were developed by G. Shrader in Germany during World War-II. It was then followed by the discovery of VX (S-2-(diisopropylamino) ethyl O-ethyl methylphosphonothioate), a nerve agent that was much more potent than all the known G-agents. Currently there are two known V-agent stockpiles; VX (S-2-(diisopropylamino) ethyl O-ethyl methylphosphonothioate), with thousands of tons in the USA, and an analogue and isomer, RVX (Russian-VX, S-2-(diethylamino) ethyl-O-isobutyl methylphosphonothioate) in Russia.

We investigated its use as an alternative reagent for decontamination of simulant of chemical warfare agent VX at room temperature. In order to gain more complete understanding of agent chemistry, a simulant of VX; O, S-diethyl methylphosphonothiolate (OSDEMP) was synthesized initially for decontamination study.

An efficient and operationally simple method is developed for chemical decontamination of simulant of VX. N, N-dichloro poly (styrene-co-divinyl benzene) sulfonamide was developed to deactivate the simulant of VX (Scheme 5) in aqueous medium. This decontamination reaction was monitored by gas chromatography.

The decontamination of CWAs from structure, environment, media, and even personal has become an area of particular interest in recent years because of increased homeland security

concern. In addition to terrorist attacks scenario such as accidental releases of CWA or from historic, buried, munitions are also subjects from response planning. VX is one of the most difficult CWA to destroy. In general, the decontamination of VX can be achieved either by hydrolysis or by oxidation. However, hydrolysis of VX leads to toxic hydrolyzed products. Therefore, decontamination of VX by oxidation is the preferred method. VX contain bivalent sulfur atoms that can be readily oxidized.



Scheme. 5. Decontamination of OSDEMP with polymeric Beads in aqueous medium

We investigated its use as an alternative reagent for decontamination of simulant of VX at room temperature. To gain more complete understanding of agent chemistry, a simulant of VX, O,S-diethyl methyl phosphonothiolate (OSDEMP) was synthesized initially for decontamination study. The most common and widely used process is the oxidation of VX using N-chloro compounds, which decontaminates it with the formation of nontoxic product.

Decontamination studies of OSDEMP (Gutch, P.2011) were carried out at room temperature in aqueous medium using a mixture of acetonitrile and water (5 : 1). Decontaminated product was separated by GC (Fig 6). OSDEMP was decontaminated 100% with N,N-dichloro poly(styrene-co-divinyl benzene) sulfonamide. The decontaminated product was analyzed as their methyl ester derivatives by reacting with freshly prepared diazomethane in ether. The organic layer did not show any peak corresponding to OSDEMP indicating the reaction of N, N-dichloropoly (styrene-co-divinyl benzene) sulfonamide with OSDEMP. The degradation of OSDEMP with N,N-dichloro poly(styrene-co-divinyl benzene) sulfonamide followed by P-S bond cleavage via oxidation and hydrolysis leading to the formation of nontoxic product ethyl methylphosphonate (EMPA).

In conclusion, the study reveals that N, N-dichloro poly (styrene-co-divinyl benzene) sulfonamide works as an excellent decontaminating agent against OSDEMP, which bears oxidizable bivalent sulfur by its oxidation followed by hydrolysis to nontoxic product EMMP in aqueous medium at room temperature. This reagent has advantage over earlier reported reagent in terms of effectiveness, stable, nontoxic, cheap, easy to synthesize, recyclability (collected after filtration, rechlorinated, and used for further reaction), and decontamination of simulant of VX to give nontoxic product EMPA at room temperature.

N, N-dichloro poly (styrene-co-divinyl benzene) sulphonamide is a efficient reagent to fulfil different required objective to organic synthesis. The main advantage of this reagent is that reactions were clean and operationally simple.

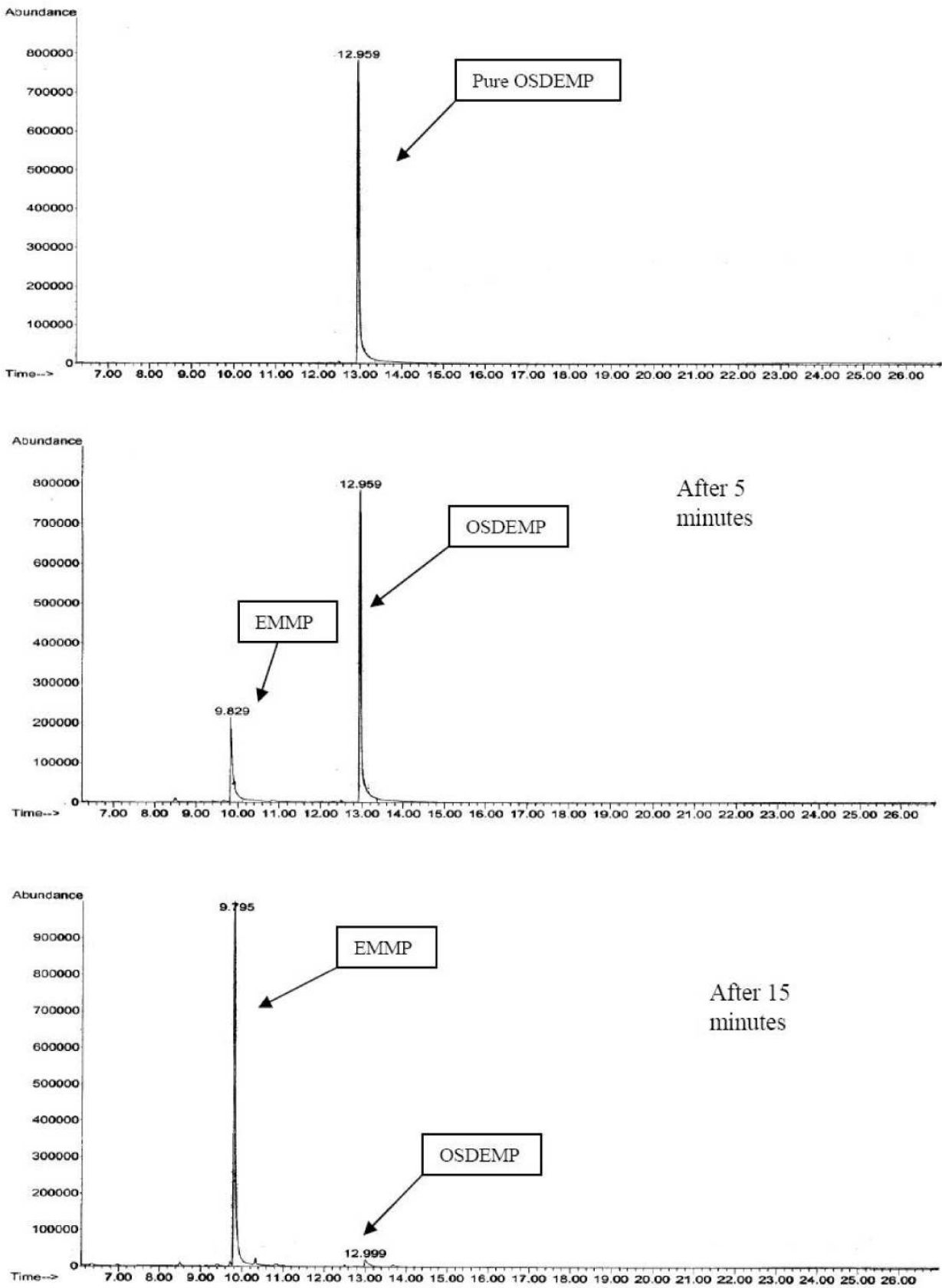


Fig. 6. Progress of a decontamination reaction of OSDEMP as monitored by GC-MS analysis at different time intervals



#### 4. Identification of tear gas compounds in air

Chemical warfare agents can be classified into two general categories, those that exert a lethal effect and those that act in an incapacitating manner. Lethal chemical warfare agents include nerve agents such as Sarin, Soman and Tabun, while incapacitating agents include irritants (tear gases or riot control agents). Acute exposure to irritants causes a number of incapacitating effects including burning or irritation of the skin and eyes, coughing, nausea and vomiting. The incapacitating nature of these chemicals has led to the development of dispersal devices for their use in riot control situations, during military training exercises and to a lesser extent as chemical weapons on the battlefield. The most commonly employed irritants (Malhotra, R. 1987) are o-Chlorobenzylidenemalononitrile, (Gutch, P 2005) often referred to as tear gas, and 2-chloroacetophenone. Dibenz [b,f]-1,4-oxazepin has been used less frequently and 1-methoxycycloheptatriene was evaluated as a possible military training agent.

The text of the 1997 "Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and their Destruction" states in Article 1 that: "Each state party undertakes not to use riot control agents as a method of warfare". United Nations peacekeeping forces could encounter use of irritants during active duty in regions of the world where there is a threat of chemical warfare agent use. Intelligence gathering, through the collection of contaminated samples, and subsequent analysis of the samples would enable identification of the suspect chemical and confirm use of a controlled chemical for warfare purposes. The results of such analyses would likely contribute to the development of appropriate strategic and political positions. Gas chromatographic (GC) methods, including methods based on GC retention indices, have been used for the detection of irritants in suspect samples.

Methods for detection, identification and quantitative determination of various tear gas compounds such as Dibenz [b,f]-1,4-oxazepin (CR) (Gutch, P (2007),  $\omega$ -Chloroacetophenone (CN) (Nigam, A. 2010), 2-Chlorobenzylidene malononitrile (CS) and their analogues are required during their production and also for verification of their use for prohibited activities under Organisation of prohibition of chemical weapons ([www.opcw.nl](http://www.opcw.nl))(OPCW). The availability of identification data on CS, CR, CN and related compounds would facilitate the verification of in case of alleged use of these chemicals. United Nations peacekeeping forces could encounter use of irritants during active duty in regions of the world where there is a threat of chemical warfare agent use. Intelligence gathering, through the collection of contaminated samples, and subsequent analysis of the samples would enable identification of the suspect chemical and confirm use of a controlled chemical for warfare purposes. The results of such analyses would likely contribute to the development of appropriate strategic and political positions. Gas chromatographic (GC) methods, including methods based on GC retention indices, have been used for the detection of irritants in suspect samples. The correlation of retention indices between an unknown and reference compound on two or more columns of different polarities is generally sufficient for identification purposes. For the evolution of retention indices, a homologues series of n-alkanes is commonly used as a reference compound.

##### 4.1 Measurement of retention indices

In order to measure the retention indices generally solutions containing several tear gases in acetone together with n-alkanes standards were injected onto the GLC column, the sample

size in each instance was about 0.1 ml. The amounts of individual compounds and n-alkanes present in the range 10-15 mg. The retention times (Fig.7) were recorded with the accuracy of up to 0.01 min with the help of Shimadzu CR3A data processor. In order to identify individual components in the mixture, an authentic sample of each tear gas was injected separately and its retention time was compared with that of the component in mixture. Temperature-programmed retention indices for individual compounds was calculated by using equation 1. The measurement of retention indices in two columns with different polarities is shown to be applicable for identification of tear gases compound in air.

#### 4.2 Determination of retention indices under programmed temperature conditions

Programmed temperature GC allowed the analysis of a number of compounds over a wide range of volatilities in a single run. Under programmed temperature conditions, a linear relationship exists between the retention time of n-alkanes and their carbon number. Hence, under these conditions, it is possible to calculate retention index value using retention time only. The retention indices under programmed temperature chromatographic condition ( $RI_p$ ) were calculated using the van den Dool and Kratz formula. (Equation 1).

$$RI_p = 100 \left( \frac{t_c - t_z}{t_{z+1} - t_z} \right) + 100z \quad (1)$$

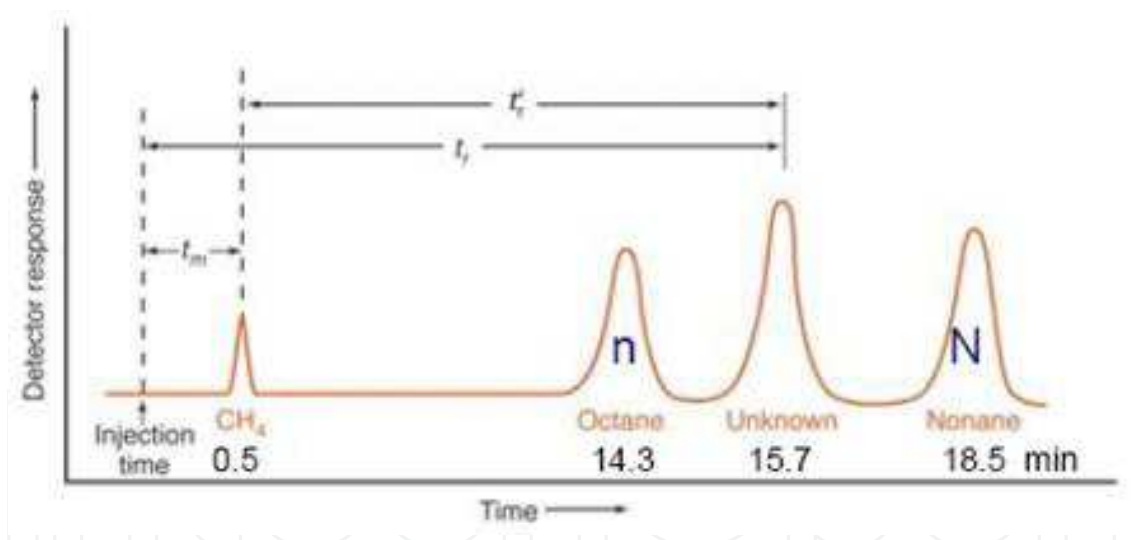


Fig. 7. GC chromatogram of mixture of n-alkane with tear gas.

Here  $t_c$ ,  $t_z$  and  $t_{z+1}$  were retention times of the solute, alkane eluted immediately prior to the compound with  $z$  number of carbon atoms (lower alkane), and alkane eluted immediately after the compound with  $z+1$  number of carbon atoms (higher alkane), respectively.

#### 4.3 Determination of retention indices under isothermal chromatographic conditions

Under isothermal conditions unlike programmed temperature conditions, there exists a non-linear relationship between retention time and number of carbon atoms of n-alkanes. Therefore, for the calculation of retention indices under these conditions, logarithm of the

corrected retention time was taken into account. Retention indices under isothermal experimental conditions ( $RI_1$ ) were calculated using the Kovats formula (Equation.2)

$$RI_I = 100 \left( \frac{\log t'_c - \log t'_z}{\log t'_{z+1} - \log t'_i} \right) + 100z \quad (2)$$

Here  $t'_c$ ,  $t'_z$  and  $t'_{z+1}$  were corrected retention times of the solute, alkane eluted immediately prior to the compound with  $z$  number of carbon atoms (lower alkane), and alkane eluted immediately after the compound with  $z+1$  number of carbon atoms (higher alkanes), respectively.

We have reported temperature programmed retention indices for several tear gas compound using Van den Dool's equation. GC of these compounds as a class on a fused silica capillary column and temperature -programmed retention indices for most of them were not previously reported. Further the measurement of retention indices on two columns with different polarities is shown to be applicable for the identification of tear gases in air. We have reported temperature programmed retention indices (Gandhe, B. 1989). on various tear gas compounds such as Methyl ethyl ketone, Chloro acetone, Bromo acetone, Ethyl bromo acetate, Benzoyl chloride,  $\omega$ -Chloroacetophenone (CN), and 2-Chloro benzylinemalononitrile (CS) on polar DB-1 and non polar DB-1701 fused silica capillary column.

Riot control agent 2-Chlorobenzylidenemalononitrile (CS) and its analogues have both skin irritating and lacrymating properties. We have also reported retention indices (RI) of CS and its thirteen analogues (Gutch, P 2004) relative to the homologues  $n$ -alkanes series. These values are determined on nonpolar BP-1 and polar BP-10 capillary column under programmed temperature and isothermal chromatographic condition. The analogues differ in substitution at ortho or para position of phenyl ring and retention indices are found to vary according to the nature of the substituent.

## 5. Conclusion

Gas chromatography has been successfully applied to the separation of mixtures of numerous organic and inorganic compounds that have appreciable vapour pressure. Gas chromatography is also used for analysis of pollutants, analysis of alcoholic beverages, analysis of pharmaceutical and drugs, analysis of clinical applications, analysis of essential oils, analysis of Fatty acids, analysis of explosives, and analysis of pesticides. Gas chromatography is very useful analytical technique for identification of known and unknown volatile and thermo labile compounds and monitoring of various organic reactions. Gas chromatography with a fused silica capillary column is the method of choice due to its high resolution and sensitivity.

## 6. Acknowledgment

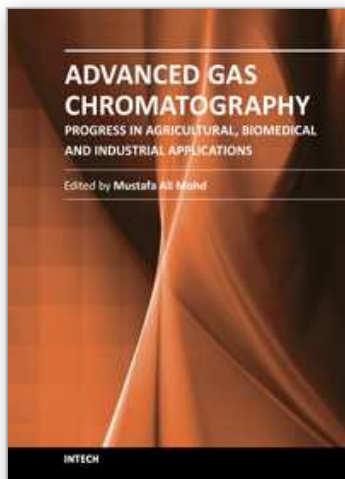
We thank Dr. R. Vijayaraghavan, Director, DRDE, Gwalior, for providing necessary facilities and for useful discussion.

## 7. References

- Akin, Akdag. (2006). Oxidation of thiols to disulfides with monochloro poly (styrenehydantoin) beads. *Tetrahedron letter*, Vol. 47, pp. 3509-3510.
- Bahman, Tamani. (2009). Synthesis and application of cross-linked Poly (N-bromomaleimide) in oxidation of various organic compounds. *Iranian. Polymer. Journal*, Vol. 18, 12, pp. 957-967.
- Bogoczek, R. (1989). Studies on a macromolecular dichloramine: The N, N-dichloro poly (styrene-co-divinyl benzene) sulfonamide. *Angew Makrohmolec Chem*, Vol. 169, pp. 119- .
- Dubey, D. (1999). Reaction of bis (2- chloroethyl) sulphide with N,N'-dichlorobis (2,4,6-trichlorophenyl) urea. *J Org Chem*, Vol. 64, pp. 8031-8034.
- Eto, M. (1974) *Organoo phosphorous pesticides organic and biological chemistry*. CRC press, USA.
- Gandhe, B. (1989). Gas chromatographic retention indices of tear gases on capillary columns. *Journal of Chromatography*, Vol. 479, pp. 165-169.
- Ghorbani, Vaghei. (2009). Poly (N, N'-dichloro-N-ethylbenzene-1, 3-disulfonamide) and N, N, N', N'-tetra-chlorobenzene. *Synthesis*, Vol. 6, pp. 945-950.
- Gupta, Hemendra. (2008). N,N-Dichloro poly (styrene-co-divinyl benzene) sulfonamide polymeric beads: an efficient and recyclable reagent for the synthesis of dialkyl Chlorophosphates from dialkylphosphites at room temperature. *Tetrahedron Letters*, Vol. 49, pp. 6704-6706.
- Gutch, P (2004). Chromatographic analysis of BMN analogues of 2-chloro bezylidenemalononitriles. *J Indian Chem.Soc*, Vol. 81, pp. 874-878.
- Gutch, P (2005). Structure and biological activity relationship of 2-chloro bezylidenemalononitriles, A Riot Control agent. *Defence Science Journal*, Vol. 55, pp. 447-457.
- Gutch, P (2007). A Simple, Convenient And Effective Method For the Synthesis of Dibenz (b,f) 1,4-Oxazepines (CR); A New Generation Riot Control Agent And Its Analogues. *Heterocyclic Communication*, Vol. 13, pp. 339- 396,
- Gutch, P. (1997). Studies on the synthesis, structure-activity relationship and degradation of substituted malononitriles. Ph.D Thesis , Jiwaji University Gwalior.
- Gutch, P. (2007). N,N-Dichloro Poly(styrene-co-divinyl benzene) Sulfonamide—Synthesis, Characterization and Efficacy against Simulant of Sulfur Mustard. *J. Applied Polymer Science*, Vol. 105, pp. 2203-2207.
- Gutch, P. (2008). Polymeric decontaminant 2 (N,N-dichloropolystyrene sulfonamide): Synthesis, characterization, and efficacy against simulant of sulfur mustard. *J. Applied Polymer Science*, Vol. 107, pp. 4109-4115.
- Gutch, P. (2011). New Effective Synthetic Method for Preparation of N,N-Dichlorocarbamates. *Synthetic Communications*, Vol. 41, pp. 1554-1557,
- Gutch, P. (March 2001). Synthesis, Characterization and Mass Spectrometric fragmentation of gem. Dicyano oxidants derived from Benzilidene malononitriles. *Indian Journal of Chemistry, Part B*, Vol. 40, B, pp. 243-247.
- Gutch, P. (2010). N, N-Dichloro poly (styrene-co-divinyl benzene) sulphonamide polymeric beads: An efficient and recyclable decontaminating reagent for Sulfur Mustard. *Proceeding in Macro 2010 at IIT Delhi*. pp. 15-17.
- Gutch, P. (2011). N, N di chloro poly (styrene-co-divinyl benzene) sulphonamide polymeric beads An Efficient recyclable decontaminating reagent for O,S diethyl methyl

- phosphonothiolate a simulant of VX. *J. Applied Polymer Science*, Vol. 121, pp. 2250-2256.
- Gutch, P. (2011). N, N-dichloro poly (styrene-co-divinylbenzene) sulfonamide beads as an efficient, selective and reusable reagent for oxidation of thiols to disulfides. *International J. Polymeric Materials*, Communicated.
- Gutch, P. (2011). Polymeric Decontaminant: N, N - Dichloro 2, 6 - Dimethyl 1, 4 - Phenylene Oxide Sulphonamide: Synthesis, Characterization & Efficacy against Simulants of Sulfur Mustard. *J. Polymer Materials*, Vol. 28, 1, pp. 5-13.
- Jones, G. (1972). CS and its chemical relatives. *Nature*, Vol. 235, pp. 257-259.
- Kolvari, E. (2007). Application of N-halo reagents in organic synthesis. *J. Iran. Chem. Soc*, Vol. 4, 2, pp. 126-174.
- Koval, I. (2002). N-halo reagent: N-halosuccinimide in organic synthesis and in chemistry, a natural compound. *J Iran Chem Soc*, Vol. 38, pp. 301-337.
- Koval, I. (2001). N-Halo Reagents. Synthesis and Reactions of N-Halocarboxamides. *Russ J Org Chem*, Vol. 37, 3, pp. 297-317.
- Kowalski, P. (2005). Oxidation of sulphides to sulfoxide, Part 1: Oxidation using halogen derivatives. *Tetrahedron*, Vol. 61, pp. 1933-1953.
- Malhotra, R (1987). Chemistry and toxicity of tear gases. *Def. Sci. J*, Vol. 37, pp. 281-296,
- Nigam, A. (2010). Thermal decomposition studies of riot control agent Chloro acetophenon (CN) by Pyrolysis-gas chromatography-mass spectrometry. *J. of Hazardous Materials*. Vol. 184, pp. 506-514.
- (1977). *Convention on the Prohibition of the development production stockpiling and use of Chemical weapons and on their destruction, technical secretariat of the organization for prohibition of chemical weapons to The Hague*, Available from: < [www.opcw.nl](http://www.opcw.nl) > Accessed 28 May 2008.
- Pathak, U. (2009). Efficient and convenient oxidation of thiols to symmetrical disulfide with silica-PCl<sub>5</sub> / NaNO<sub>2</sub> in water. *Syn. Comm*, Vol. 39, pp. 2923-2927.
- Pattison, J. (1973). *A Programmed Introduction to gas Chromatography*. Spectrum House Alderton Crescent, London, Great Britain,
- Prasad, G. (2009). Modified titania nanotubes for decontamination of sulphur mustard. *J. Hazard. Mater*, Vol. 167, pp. 1192- 1197.
- Rose, S. (1969). CS – a case for concern.. *New Sci*, Vol. 43, pp. 468-469.
- Singh, R. (2011). Decontamination of Toxic chemicals by N-chloro compound. Ph.D Thesis , Jiwaji University Gwalior.
- Somani, S. (Ed). (1992). *Chemical Warfare Agents*, Academic Press, New York,
- Talmage, S. (2007). Chemical warfare agent degradation and decontamination. *Curr. Org. Chem*, Vol. 38, pp. 953-959.
- Yang, Y. (1995). Chemical reaction for neutralizing chemical warfare agents. *Chem Ind*, Vol. , pp. 334-336.
- Yu-chu, Yang. (1992). Decontamination of chemical warfare agents. *Chem. Rev*, Vol. 92, pp. 1729-1743.





## **Advanced Gas Chromatography - Progress in Agricultural, Biomedical and Industrial Applications**

Edited by Dr. Mustafa Ali Mohd

ISBN 978-953-51-0298-4

Hard cover, 460 pages

**Publisher** InTech

**Published online** 21, March, 2012

**Published in print edition** March, 2012

Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Pranav Kumar Gutch (2012). Application of Gas Chromatography in Monitoring of Organic and Decontamination Reactions, Advanced Gas Chromatography - Progress in Agricultural, Biomedical and Industrial Applications, Dr. Mustafa Ali Mohd (Ed.), ISBN: 978-953-51-0298-4, InTech, Available from: <http://www.intechopen.com/books/advanced-gas-chromatography-progress-in-agricultural-biomedical-and-industrial-applications/application-of-gas-chromatography-in-monitoring-of-organic-decontamination-reaction-identification-o>

**INTECH**  
open science | open minds

### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821



© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen