

# Air Quality Issues

## Air Monitoring Needed for Cleanup Workers in Vessels

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### 1. Executive Summary

After the mixture of BP crude oil and dispersants were spilled into the Gulf of Mexico in April, the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) recognized that it was important to protect the health and safety of Deepwater Horizon Response (DHR) workers and volunteers.

Both NIOSH and OSHA recognized that exposures to toxic chemicals should be comprehensively and routinely assessed during work activities under varying conditions, and that validated methods for area and personal breathing zone sampling should follow an approved, standardized and comprehensive DHR air sampling plan coordinated among all relevant government agencies and non-governmental organizations (and their contractors) to conduct sampling activities.

According to the Louisiana Department of Health and Hospitals (DHH), from April 25, 2010, five days after the explosion aboard the Deepwater Horizon Rig, until September 18, 2010, there were four hundred and forty one (411) reports of health complaints believed to be related to exposure to pollutants from the oil spill.<sup>1</sup> Three hundred and twenty-five (325) reports came from workers and eighty-six (86) from the general population. Most frequently reported symptoms include headache, dizziness, nausea, vomiting, weakness/fatigue and upper respiratory irritation. But because of a lack of chemical-specific air monitoring for cleanup workers in vessels, direct specific causes and determination of health effects to workers from chemical exposures are not possible.

### 2. Looking Back

#### OSHA BP Oil Spill monitoring

OSHA monitored worker exposures and looking for levels of airborne exposure shown likely to cause health effects from chemical exposure to fresh crude oil, weathered oil, dispersants, cleaning agents and other materials. OSHA states air sampling did not detect any hazardous chemical levels of concern. However, in reviewing the OSHA Website above, air monitoring samples and methodologies are revealed that were last updated August 4, 2010, entitled “Direct Reading Results by Site,” beginning May 24, 2010, and ending June 19, 2010, using varying instrumentation for selected chemicals<sup>ii</sup>; however, the instrumentation used at fixed sites were not capable of chemical-specific detection and measurement.

#### USEPA BP Oil Spill monitoring

In response to the BP oil spill, USEPA monitored air quality along the Gulf. The air monitoring conducted found levels of ozone and particulates ranging from “good” to “unhealthy for sensitive groups”

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<sup>ii</sup> [www.osha.gov/oilspills/oil\\_directreading\\_bysite.html](http://www.osha.gov/oilspills/oil_directreading_bysite.html)

on USEPA's Air Quality Index found that *“these are at levels well below those that would cause short-term health problems... The air monitoring conducted to date has not found any pollutants at levels expected to cause long-term harm. With the well capped and no new oil coming into the Gulf, we expect air monitors to continue to show pollution levels that are well below levels of concern.”*<sup>2</sup>

However, a review of air monitoring locations and technologies by USEPA reveals a troubling pattern of inadequate monitoring.<sup>iii</sup> All USEPA air monitoring locations were on fixed sites on land, and none were in vessels where cleanup workers are most likely to be exposed to chemicals from crude and/or chemical dispersants. USEPA states that it performed air monitoring offshore on four days in May, but only for the chemicals in the dispersant, 2-Butoxyethanol and Propylene glycol, and no chemical-specific detection of compounds found in crude oil, such as BTEX, which includes Benzene, Toluene, Ethylbenzene, and isomers of Xylene.

The air monitoring technologies used by USEPA at their fixed sites used a technology known as PID, or “photoionization detection”, and could only measure mixtures of volatile organic compounds, referred to as “VOCs”, not specific compounds, such as Benzene, Toluene, Ethylbenzene, and isomers of Xylene. Therefore, there was no chemical-specific air monitoring for BP Oil Spill cleanup workers working in vessels, and at most risk to chemical exposure.

EPA monitored the air at multiple sites on shore along the Gulf Coast to see if spill-related pollutants were present in the air at levels that might cause health problems for people onshore in the Gulf region. EPA monitored for pollutants that: a) can evaporate from fresh crude oil, b) can evaporate from weathered oil, and c) came ashore from burning oil out at sea.

EPA also monitored onshore air to determine whether chemicals in the dispersants used offshore are reaching onshore air, primarily 2-Butoxyethanol and Dipropylene glycol monobutyl ether, and said:

“On four days in May 2010, EPA deployed staff in boats to sample the air following the application of dispersant. The samples were collected to see if dispersant-related compounds could be detected in air following application. Sample locations ranged from about 30 to 60 miles offshore. Samples were analyzed for two chemicals 2-Butoxyethanol and Propylene glycol that are ingredients in the dispersant named COREXIT.

In addition to being found in dispersants, these compounds are common in a variety of household, cleaning, and other products. The Coast Guard and OSHA are currently addressing occupational safety concerns at off-shore locations, including conducting occupational exposure monitoring as part of their efforts. *“As such, EPA does not anticipate conducting additional off-shore sampling but will continue its sampling and monitoring efforts on land.”*

EPA has used a number of different types of monitors to measure *“what is in the air and in what quantities.”* Specifically:

- Existing fixed-site monitors that are in place as part of the nationwide monitoring network. These monitors record fine particulate (PM2.5) and ozone levels that are used to calculate the Air Quality Index (AQI) values.

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<sup>iii</sup> [www.epa.gov/bpspill/air.html](http://www.epa.gov/bpspill/air.html)

- Temporary monitors were set up in specific areas in response to the spill. These additional PM2.5 monitors were deployed to supplement the fixed-site continuous monitors.
- Monitors that can be moved to different locations to respond to odor complaints
- Mobile monitoring using EPA’s Trace Atmospheric Gas Analyzer (TAGA) buses that provided initial assessment of air quality and EPA’s remote-sensing aircraft known as ASPECT (Airborne Spectral Photometric Environmental Collection Technology) that collected air monitoring data and provided aerial photographs of the oil slick.

### **TAGA Monitoring for VOCs**

Equipment in the TAGA buses monitors air toxics known as volatile organic compounds (VOCs) using a combination of gas chromatography and mass spectrometry (GC/MS). The specific VOCs being monitored are Benzene, Toluene, and Xylenes. These substances are also associated with facilities such as gas stations, oil refineries, paper mills, and auto body shops. The TAGA monitoring found that these substances are not present or are being detected at low levels in the areas monitored along the Gulf Coast and in New Orleans, Louisiana. The levels found have been well below levels that would cause temporary discomfort, irritation, or other minor effects.

### **TAGA Monitoring for Dispersants**

From May 18, 2010 to June 6, 2010, EPA’s TAGA buses monitored for the two chemicals found in the COREXIT dispersants that have the highest potential to get into the air in any significant amounts, 2-Butoxyethanol and Dipropylene glycol monobutyl ether. In addition to being found in the COREXIT dispersants, these compounds are found in cleaning products and coatings. As a result, USEPA was unable to identify the source of the measured compounds. The TAGA buses detected very low levels of these chemicals in the air, at a limited number of the locations sampled along the Gulf Coast. The levels USEPA found at these locations on land were well below those that are likely to cause health effects, and suggested that the use of dispersants on the oil spill would not have a significant impact on air quality on land.

### **ASPECT (Airborne Spectral Photometric Environmental Collection Technology)**

The ASPECT plane, a twin-engine Aero Commander 680 aircraft based in the Dallas, Texas, vicinity, is equipped by Los Alamos National Laboratory with a multi-spectral infrared mapping system and a Fourier Transform Infrared (FTIR) spectrometer package. The spectrometer detects and locates chemical vapors, and can see through smoke and dust to get a measurement of the location and concentration of the vapor plume. A second sensor, a high-resolution Infrared Line Scanner, records an image of the ground below, as well as plume information. This sensor package is the only “stand-off infrared” detection tool in the nation devoted to emergency domestic response applications.

The technology provides first responders with critical information regarding the size, shape, composition, and concentration of gas clouds. The system uses Global Positioning System mapping data and digital images of the site to create exact maps and digital data overlays of chemical plumes, as well as low-area locations where toxin-laden air may accumulate.

## **RAE PID technology**

EPA is using a private contractor, RAE Systems,<sup>iv</sup> at all Louisiana fixed sites to provide air monitoring. RAE is deploying their MultiRAE and AreaRAE chemical detectors that use a detection technology known as “*photoionization detection*,” or PID, reporting their results as “VOCs”. See previous section on limitations of PID. Because USEPA relied upon PID at all fixed sites, no chemical-specific measurement was possible, only broad ranges of volatile organic compounds, the VOCs.

## **Oil Spill Surveillance by Louisiana Department of Health and Hospitals (DHH)**

The Oil Spill Surveillance Summary reports describe the results of the tracking done by the Louisiana Department of Health and Hospitals Office of Public (OPH) Health Section of Environmental Epidemiology & Toxicology (SEET). These reports relied on data supplied by sentinel surveillance sites, including hospital emergency departments, outpatient clinics, physicians' offices and Louisiana poison control center. SEET tracked and evaluated all acute health effects related to the BP Oil Spill of both cleanup workers and the local general population during the BP Oil Spill.

According to Louisiana DHH, from April 25, 2010, five days after the explosion aboard the Deepwater Horizon Rig, until September 18 2010, there have been 411 reports of health complaints believed to be related to exposure to pollutants from the oil spill.<sup>3</sup> Three hundred and twenty-five (325) reports came from workers and 86 from the general population. Most frequently reported symptoms include headache, dizziness, nausea, vomiting, weakness/fatigue and upper respiratory irritation. But because of a lack of chemical-specific air monitoring, especially for cleanup workers in vessels, direct specific causes and effects from chemical exposure are not possible.

According to USEPA records, 14,959 samples were obtained from fixed monitoring stations on land to measure VOCs. There are no USEPA records of samples obtained from vessels in which cleanup workers were present.

## **3. Review of Air Monitoring Technologies Used by USEPA and OSHA**

### **Dräger X-am 2000 4 gas monitor:**

This model uses electrochemistry to detect chemicals. Electroanalytical methods measure the potential (volts) and/or current (amps) in an electrochemical cell containing the analyte.<sup>4</sup> These methods can be categorized according to which aspects of the cell are controlled and which are measured. The three main categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time), and voltammetry (the cell's current is measured while actively altering the cell's potential).<sup>4</sup>

Limitations: Electrochemical sensors are chemical-specific and can measure only those chemicals at voltages equal to or above those of the specific voltage used in each cell. Electrochemical sensors cannot normally detect and measure individual chemicals in a mixture.

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<sup>iv</sup> [www.raesystems.com](http://www.raesystems.com)

### **Dräger CMS (Chip-Measurement-System):**

The Dräger CMS consists of multiple miniaturized Dräger tubes. Dräger tubes rely upon colorimetric gas detection (also called a “color detector”) for positive measurement of a selected gas at a selected range of concentration. Colorimetric gas detection tubes work on a similar principle: a measured volume of gas (or air) is drawn through a tube which contains chemicals which change in color in response to the presence of a specific target gas (or range of gases) present in the sample. By knowing the volume of gas or air sampled, the amount of color change read on a linear scale on the colorimetric gas detection tube can be translated into a very accurate measurement of level of gas present, described in percentage of the total air or in parts per million (ppm).

### **Dräger XAM 2000**

X-am 2000 by Dräger is designed for personal gas monitoring. Able to detect between one and four gases, the X-am 2000 is able to measure O<sub>2</sub>, CO and H<sub>2</sub>S, plus also combustible gases and vapors.

Limitation: To select the appropriate Dräger gas detection tube, the user needs to know what gas or gases is/are to be detected, and at what probable concentrations the gas may be present, or at what level of exposure the test is to be conducted. It is also important to read the characteristics of the gas detector tube being used, and if there is risk of interference from other gases or chemicals it may be necessary to amend the test procedure, perhaps also including tests for the presence or level of these interferent gases. These instruments must be calibrated for each gas measured.

### **AreaRAE PID**

AreaRAE detectors rely on PID, or photoionization detection. A PID sensor works differently than other sensors. The PID contains a lamp that is rated to a specific ionization potential measured in electron volts (eV). Some common lamps available are 9.8 eV, 10.6 eV, and 11.7 eV. When the lamp ignites and a gas molecule passes through the light emitted from it, the molecule is ionized (if the ionization potential of the molecule is less than the ionization potential of the lamp) or nothing happens (if the molecule’s ionization potential is above that of the lamp). Once ionized, positive and negative ions are collected on electrodes, which produces a signal directly proportional to the amount of ions present at the electrodes. The signal is then displayed in parts per million on the instrument display.

### **UltraRAE PID**

UltraRAE combines both a photo-ionization detector (PID) and a vapor specific separation tube (RAE-SEP™ tube). The benzene-butadiene RAE-Sep tubes are designed for use with RAE Systems 9.8eV equipped PID.

### **Photo VAC 2020 Pro CIUH0030**

The 2020PRO uses photoionization (PID) for detecting VOCs. The 2020PRO is equipped standard with a 10.6 eV UV lamp, and has an optional 11.7 eV UV lamp for ionizing chlorinated compounds.

## **MSA Sirius AO-0220-60**

The MSA Sirius Multi-Gas Detector Kit integrates PID (photoionization detector) sensor into a four-gas detector for volatile organic compounds (VOCs) with low vapor pressures while measuring for combustible, toxic and oxygen-deficient atmospheres.

Limitations: Because a PID ionizes any molecule with an ionization potential less than the ionization potential of its lamp, the detector is not specific to any gas. The detector itself measures the amount of positive and negative ions detected on the electrodes. These ions can come from any compound that was ionized. Unless a specific VOC is known to be the only VOC present in a certain area or to be a byproduct of a specific process, the PID will be able only to accurately inform that a compound has been ionized. It will not be able to distinguish what the compound actually is. Another limitation of a PID is that many of them respond to humidity. If a high-humidity sample is taken, the water vapor could cause false positive readings. This has been a major limitation to PIDs over the years.<sup>5</sup>

## **4. Health Effects from Crude Oil and Oil Dispersant Exposure**

Crude oil is a complex mixture of chemical constituents including various alkanes (butane, pentane, and hexane); aromatic hydrocarbons (benzene, ethyl benzene, toluene, and xylenes); cycloalkanes; other nitrogen, oxygen, and sulfur compounds (hydrogen sulfide); and trace metals such as iron, nickel, copper and vanadium. Some constituents of crude oil can have significant toxicity. For example, several aromatic hydrocarbons are considered to be human carcinogens.<sup>6</sup>

The International Agency for Research on Cancer (IARC) indicates that for crude oil, there is inadequate evidence for the carcinogenicity in humans, although there is limited evidence for carcinogenicity in experimental animals.<sup>7</sup> Hydrocarbon exposures from crude oil constituents will vary based on its exposure to the atmosphere, time in the marine aquatic and coastal environment, treatments with dispersants and interaction of the chemicals, wave action and heat. Generally, the more "aged" or "weathered" crude oil is (by mixing with seawater and traveling long distances from the source), the lower are the concentrations of volatile organic compounds (VOCs). Although it generates less VOCs, weathered crude oil still contains harmful chemicals which can cause skin irritation and other irritant reactions. Thus, use of gloves and protective clothing is recommended to minimize skin contact with weathered oil, including oil deposited on the shore ("tarballs"). Appropriate hand hygiene facilities should be readily available to clean incidental skin exposures.

Weathered crude oil is unlikely to pose an inhalation risk although a potential risk does exist for it to be aerosolized into respirable airborne droplets or volatilized by activities such as pressure washing. Even though detection of hydrocarbon "odors" is common in areas contaminated by crude oil, odor is not a reliable indication of a health hazard. Some individuals, though, are bothered by odors and can develop symptoms (e.g., may report dizziness, nose and throat irritation, headache and/or nausea). These individuals may need medical evaluation when symptoms occur, especially if severe or persistent. Individuals with severe or persistent symptoms should be relocated to perform tasks where symptoms can be alleviated.

Studies of tanker oil spill responses have reported adverse health effects in response workers.<sup>8, 9, 10, 11, 12, 13, 14, 15, 16</sup> These studies may underestimate the health effects associated with the Deepwater Horizon Response activities since the magnitude and duration of the Response is unprecedented.

In addition, there is an incomplete understanding about the human health toxicity associated with the use of large amounts of dispersant, about the toxicity of the mixed exposure to large amounts of crude oil, dispersants and combustion products together and the cumulative effect of such exposures occurring over a long duration. Since knowledge about potential inhalational exposures to the mixed exposure of crude oil, dispersant and combustion products associated with the Deepwater Horizon Response work is incomplete and still evolving, NIOSH and OSHA believed it was prudent to reduce the potential for adverse health effects by the responsible use of engineering controls, administrative controls and PPE, including respirators when appropriate.

In the absence of comprehensive and coordinated health surveillance among workers and volunteers, and the absence of interpretable, quantitative exposure data, NIOSH and OSHA recommended that employers take precautions sufficient to ensure workers are protected from the chemical, physical and psychological hazards posed by the Deepwater Horizon Response.

## **5. Looking Forward**

The lack of air monitoring for cleanup workers in vessels responding to the BP Oil Spill provides a microcosm of the vulnerability of cleanup workers, emergency responders, and the public to the health effects of fugitive release of anthropogenic chemicals into the environment.

And while there are unmet needs in air monitoring, and extensive research and development into not only responsive portable air monitoring and a wireless sensor network to continuously collect and distribute chemical measurement data, there are existing emergency response technologies that could be deployed immediately to protect emergency responders and the public in future releases of hazardous chemicals.

### **Micro chemical sensors**

An advanced micro chemical sensor, whose original development was supported by the Central Intelligence Agency (CIA), using Differential Mobility Spectroscopy (DMS) has been developed for the protection of military emergency responders from exposure to chemical warfare agents (CWAs).

Until recently, the only chemical detection and measurement technology for both explosive detection in airport portals and CWAs by both civilian and military emergency responders has been a technology known as Ion Mobility Spectroscopy, referred to as IMS.

### **Ion Mobility Spectroscopy**

IMS is an analytical technique used to separate and identify ionized molecules in the gas phase based on their ion mobility in a carrier buffer gas. Though heavily employed for military or security purposes, such as detecting drugs and explosives, the technique also has many laboratory analytical applications. The molecules of the sample need to be ionized, usually by corona discharge, atmospheric pressure photoionization (APPI), electrospray ionization (ESI), or a radioactive source, e.g., a small piece of <sup>63</sup>Ni or <sup>241</sup>Am, similar to the one used in ionization smoke detectors. In its simplest form an IMS system measures how fast a given ion moves in a uniform electric field through a given atmosphere.

In specified intervals, a sample of the ions is let into the drift chamber; the gating mechanism is based on a charged electrode. For precise control of the ion pulse width admitted to the drift tube, a more complex gating design is employed.

Once in the drift tube, ions are subjected to a homogeneous electric field ranging from a few volts per centimeter up to many hundreds of volts per centimeter. This electric field then drives the ions through the drift tube where they interact with the neutral drift molecules contained within the system.

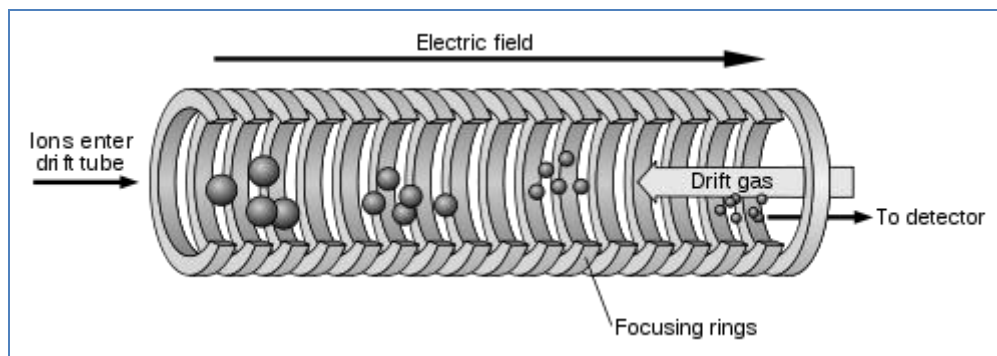


Figure 5.1 – An ion mobility spectrometer separates ions by shape and charge.<sup>v</sup>

In the drift tube, chemical species separate based on the ion mobility, arriving at the detector for measurement. Ions are recorded at the detector in order from the fastest to the slowest, generating a response signal characteristic for the chemical composition of the measured sample.

Perhaps ion mobility spectrometry's greatest strength is the speed at which separations occur—typically on the order of tens of milliseconds. This feature combined with its ease of use, relatively high sensitivity, and highly compact design have allowed IMS as a commercial product to be used as a routine tool for the field detection of explosives, drugs, and chemical weapons. A major manufacturer of IMS screening devices used in airports is Smiths Detection, a firm based in England.

### IMS weaknesses

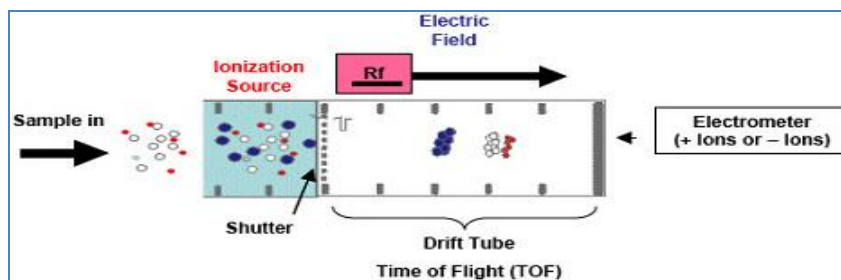


Figure 5.2 – Schematic of IMS process flow.

Ions are lined up using a shutter mechanism and then directed into a drift tube. Because traditional IMS lines up the ions, IMS typically uses only from 1% to 3% of the sample, reducing accuracy. IMS relies upon a single charge, either positive or negative, in an electrical field to control path of ions.

<sup>v</sup> See enlarged graphic at [http://en.wikipedia.org/wiki/File:Ion\\_mobility\\_spectrometry\\_diagram.svg](http://en.wikipedia.org/wiki/File:Ion_mobility_spectrometry_diagram.svg)



Sample vapor is introduced into the reaction region where ion–molecule reactions convert sample neutrals to product ions. A shutter is used to periodically (at 30 Hz) introduce the ions into a drift region where ion separation and characterization occur on the basis of the speed of the ion swarms in an electric field and in a supporting atmosphere, usually air at ambient pressure.

The resolution of the IMS or the ability to distinguish ions of different mobilities is given by:

$$R = \mu/\Delta\mu = t/\Delta t$$

where R is drift tube’s resolving power,  $\Delta t$  is the width of the ion pulse and  $t = (L/\sim E)$  is the time it takes the ions to transit a drift tube of length L. Thus for a given electric field shorter drift tubes result in a loss in resolution. Increasing the field gradient can restore the resolution.

Without pre-separation of samples, it is difficult for IMS to provide clear cut data interpretations in case of interference from a complicated matrix. Another weakness of IMS, and many other chemical detectors, is the requirement of each chemical measured to be calibrated in the field before detection and measurement. This requires users to have significant expertise in analytical chemistry.

A chemical detection technology utilizing both positive and negative charges used simultaneously in an oscillating asymmetrical Rf field has been developed. It is referred to as Differential Mobility Spectroscopy, or DMS.

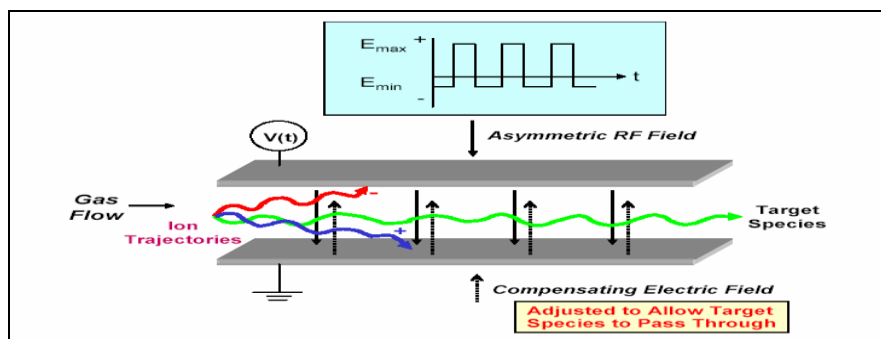


Figure 5.3 – Schematic of DMS process flow.

DMS can simultaneously detect both positive and negative ions. As illustrated above, the compensation voltage ( $C_v$ ) is a perpendicular DC tuning field that is applied on an asymmetrical oscillating radio frequency (Rf) field. The asymmetric Rf field and the compensating voltage ( $C_v$ ) can be switched rapidly. A carrier gas carries a sample past an ionization source, creating charged chemical ions. An electric field, Rf, causes ions to “vibrate” up and down, and some contact either of the capacitive plates, where ions lose their charge, and are *not* detected. A second electric field, compensating voltage ( $C_v$ ), causes selected chemical ions to remain in the center of the two plates, thus *not* losing their charge, and *are* detected.

The DMS sensor acts as a tunable ion filter. DMS filters out *all* of the chemicals *except* the ions of interest, which *are* detected in a mixture of chemicals, significantly reducing false positive or negative detection by keeping target ions centered between the parallel plates.

The DMS sensor has successfully resolved a mixture of a chemical warfare agent, Tabun, diesel, and AFFF (Aqueous Fire Fighting Foam).

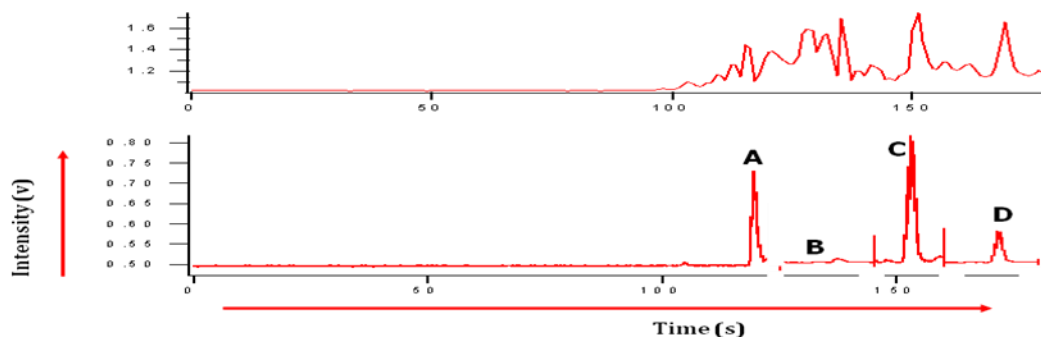


Figure 5.4 – Resolution of mixture of diesel, AFFF and Tabun precursors by DMS plotted by voltage intensity versus time.

The schematic above illustrates how DMS sensor technology was able to resolve a mixture of diesel and AFFF, common interferents, and a CWA, Tabun, and its precursors, or chemicals used in the formulation of Tabun. Typical IMS sensors cannot distinguish individual components in chemical mixtures with such precision.

### Wireless chemical sensor network

Numerous wireless sensor networks are commercially available, including the DHS ICBRNE (Integrated chemical biological radiological nuclear and explosive)<sup>vi</sup> sensor test bed managed by program manager Safe Environmental<sup>vii</sup> in Los Angeles.

Chemical sensors that operate in wireless sensor networks create a virtual mutual aid network that would provide 24/7 real-time technical and chemical analysis expertise to cleanup workers and both emergency responders and managers.

By deploying commercially available software in chemical sensor, the sensors could be operated by cleanup workers and emergency responders without requiring expertise in chemical or software.

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<sup>vi</sup> [www.icbrne.org](http://www.icbrne.org)

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