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Technologies for standoff detection of liquid chemical warfare agents

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English summary

The topic of this report is a review of technologies that can be used for standoff detection of chemical warfare agents in the liquid phase, with the aim to point out technologies that could be topic of a further study. Required sensitivity for the technology to be operationally interesting is estimated both in view of exposure limits and existing capacities.

An attempt is made to evaluate the potential sensitivity, standoff distance and special features of the different technologies. It is found that several technologies that use active illumination of the target are likely required to obtain sufficient sensitivity to be of interest in a further study. For long range standoff detection (>10 m) technologies involving short-pulse (femtosecond) lasers are most interesting, but infrared spectroscopy with either wavelength scanning lasers or Fourier-transform spectroscopic systems should also be considered. For short range (~1 meter) detection, several other potential technologies are also identified that could be a topic for a further study. A few short range technologies also have the capacity to detect subsurface contamination.

Two of the promising techniques that could easily be started at FFI are pointed out. These are particularly interesting because the Institute both have high level competence in the field as well as most of the expensive instruments required to initiate an investigation, and include wavelength scanning with an infrared laser and Fourier-transform spectroscopy with active illumination. The final choice of technologies for a further study would, however, depend on the intended mode of operation as defined by the user. This has not been a topic of this work.

Sammendrag

Denne rapporten gir en oversikt over teknikker og teknologier som kan benyttes til avstandsdeteksjon av kjemiske stridsmidler i væskeform, og noen teknikker for videre studier blir anbefalt. Det gis først et estimat på hvor god sensitivitet som er nødvendig for at en teknikk skal kunne være operasjonelt interessant, både i lys av faregrenser og av eksisterende kapasiteter.

Videre forsøkes det å estimere potensiell sensitivitet, mulig deteksjonsavstand og andre spesielle egenskaper for hver teknikk. Det konkluderes med at aktive teknikker (teknikker som belyser det som skal måles på) mest sannsynlig er nødvendig for å oppnå tilstrekkelig sensitivitet. For avstandsdeteksjon over relativt store avstander (>10 m) vil antagelig teknikker som bruker kortpuls (femtosekund) lasers være det beste valget, men teknikker som benytter infrarød spektroskopi enten ved hjelp av avstembare lasere eller instrumenter for Fouriertransformspektroskopi bør også vurderes. For kortere deteksjonsavstand (~1 meter) er flere teknikker interessante. Det finnes også noen få kortholdsteknikker som muliggjør deteksjon av forurensning under overflaten.

To av de lovende teknikkene er plukket ut som forslag til for en oppstartsaktivitet på FFI. Disse teknikkene er spesielt interessante fordi instituttet allerede har kompetanse på høyt nivå innen dem samt at det er relativt godt utrustet med utstyr som vil være kostbart å anskaffe for en oppstartsaktivitet. De foreslåtte teknikkene er bølgelengdeskanning med infrarød laser og Fouriertransformspektroskopi med aktiv belysning av målet. De endelige valg av teknologier i en videre studie vil imidlertid avhenge av hvilken operasjonsform Forsvaret ser for seg for denne type utstyr. Dette har ikke vært tema for denne studien.

Contents

1 Introduction

Detection of chemical warfare agents (CWA) at standoff distance has great operational interest, both because of the possibility to avoid contamination and the ability to perform quick searches. Equipment for standoff detection of CWA in vapor phase use infrared spectroscopic techniques, and several instruments are currently commercially available (for a recent overview, see [1]). However, as all CWAs are in the liquid phase at normal operating conditions, only agents with relatively high volatility (or high vapor pressure) obtain high enough vapor concentrations that can be detected by such instruments. As many CWAs have low volatility (see Table 2.1), ability to detect liquid CWA is often required.

State-of-the-art detection of liquid CWA includes collecting samples with subsequent analysis in an instrument. The samples can be collected by scrubbing with a cloth, or, as is the case for some reconnaissance vehicles, by dragging a silicone wheel along the surface with subsequent investigation in a mass spectrometer. An alternative method is to use a gas point sensor to look for traces of gas from vaporization of the liquid CWA, but this method has considerable limitations in detection of CWAs with low vapor pressure. Therefore, there is considerable interest and significant effort put into developing standoff detection techniques for liquid CWA. Applications may range from detection at high speed in a reconnaissance vehicle, to examination of potentially contaminated surfaces before or after decontamination. Several of the techniques that can be used for liquid CWA detection can also be used to detect traces of explosives. As this is an area with very high research effort, it seems clear that detection of liquid CWA may benefit from this. This report provides an overview of the technologies that can be used for standoff detection of liquid CWA, as well as of research activities and products within this field.

The report is organized as follows: In Chapter 2, some physical properties of CWA are listed and requirements for a detector are outlined. Chapter 3 reviews the potential technologies that can be used, and Chapter 4 lists known research and development efforts in the field. The report is rounded up with conclusions and recommendations for further work.

2 Charateristics of common CWA threats

2.1 Properties of chemical warfare agents

Table 2.1 lists different properties of the most common CWA, as well as similar properties for water. All agents are liquids in the temperature range -30ºC to +50ºC, except for HD (see Table 2.1 or Appendix A for an overview of names and abbreviation of the chemical warfare agents) which freezes at 14.4ºC. It should be noted that the volatility (and hence the vapor pressure) varies substantially between the agents.

There exist several sets of exposure limits to the various agents, both for civilian [2] and military [3, 4] personnel[1], for a summary, see [5]. Table 2.1 also lists lethal doses for military personnel (LD_{50}) of liquid on human skin (percutaneous liquid) for a 70 kg human, and lethal concentration (LC_{50}) of inhalation of vapor during 5 minute exposure.

	Unit	GA Tabun	GB Sarin	GD Soman	GF Cyclosarin	VX	HD Sulfur Mustard	Water
Chem. formula		$C_5H_{11}N_2O_2P$	$C_4H_{10}FO_2P$	$C_7H_{16}FO_2P$	$C_7H_{14}FO_2P$	$C_{11}H_{26}NO_2PS$	$C_4H_8Cl_2S$	H_2O
Mol. weight	g/mol	162.1	140.1	182.2	180.2	267.4	159.1	18
Density	g/cm^3	1.09	1.09	1.022	1.120	1.008	1.27	1
Specific heat	J/kg·K		2253		2610	1928	1381	4186
Boiling point	C	247	158	198	239	298	217	100
Melting point	C	-50	-56	-42	-30	-50	14.4	0
Vapor pressure @ 25^{o}C	mbar	0.09	3.9	0.5	0.08	0.0008	0.09	31.67
Volatility	mg/m^3	610	22 000	3 900	600	8.9	920	23 010
Solubility in water	%	10	Miscible	2	~2	Slightly	None	NA
Viscosity @ 25^{o}C	mPa·s	2.27	1.40	3.17	5.40	10.0	3.95	0.89
Viscosity @ 0^{o}C	mPa·s	4.32	2.58	6.79	14.8	37.5	7.70	NA
Surface tension @ 25^{o}C	mN/m	32.5	25.9	24.5	37.3	31.3	42.5	72.0
Diffusion coeff. in air @ 20^{o}C	mm^2/s	5.1	5.9	4.5	4.9	3.3	5.7	20
Toxicity levels [4].								
Inhalation vapor: LC_{50} @ 5 min	mg/m^3	14	7	7	7	3	180	NA
Percutaneous liquid LD_{50} @ 70 kg	mg	1500	1700	350	350	5	1400	NA

Table 2.1 Overview of various properties of CWA [4, 6-9]. The LC_{50}/LD_{50} is the exposure limit where 50% lethality among unprotected military personnel can be expected

The toxicity values for the inhalation vapors translate to ~1 ppm for the G-agents, 0.2 ppm for VX and 25 ppm for HD. If the surface is covered with a 1 µm thick layer of CWA, this corresponds to an area density of ~1 g/m^2, hence a 100 cm^2 exposure to this film contains 10 mg. The thickness of liquid films is affected by many factors, including the viscosity and surface tension of the liquid, the amount of liquid as well as the properties of the contaminated surface, and may therefore vary substantially. It is therefore difficult to translate the LD_{50}-dose in Table 2.1 to a limit for exposed body area.

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[1] Doses for civilian and military personnel may differ because of different age and health profiles

2.2 Detection of chemical warfare agents

2.2.1 Existing equipment

As CWAs are in the liquid phase at typical operating conditions and the toxicity is in many cases highest when a gas is inhaled, dissemination in an attack typically includes aerosolisation of the liquid, with subsequent vaporization of the droplets creating a gas cloud. Droplets that are not vaporized can fall out and contaminate the ground. HD and VX can also be sprayed directly on the ground as a barrier (resembling a mine field).

A review of current technologies to detect CWA can be found in [10]. Existing methods to detect liquid CWA include:

- Chemical detector paper
- Collecting a sample and analyzing it with a mass spectrometer
- Using gas sniffers to detect vapor from vaporization of the liquid

Chemical detector paper is the current standard in soldier equipment. It is a fairly quick and sensitive method; about 30 second reaction time is required before the result is presented and droplets of 0.1-0.2 mm diameter or more are required [10, 11]. Collection of samples for subsequent analysis can be a rather sensitive technique, but it involves contamination of both equipment and operator. Since sample collection necessarily only will be done at a limited number of spots, it is clear that the quality of the measurement will depend strongly on how the samples are collected. The last method has limitations in detecting liquids with low volatility or other liquids at low temperatures or in the presence of significant wind. In the following section, an estimate is made as to which concentrations can be expected in the air above a contaminated surface.

2.2.2 Estimation of gas concentrations from liquid vaporization

Calculations of vaporization rate and density of vaporized CWA in an air volume above liquid CWA are complicated and depend on several factors, the most important is perhaps the wind speed across the liquid [12]. In the following, a very simplified approach is used, as indicated in Figure 2.1.

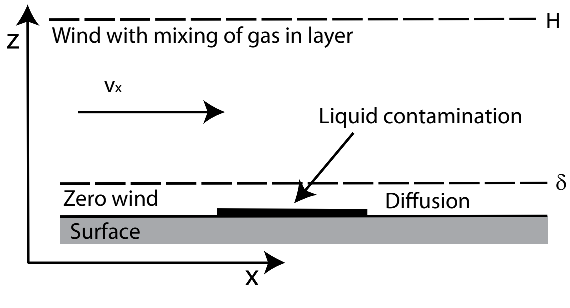

Figure 2.1 Sketch of model for diffusion and mixing of vapor from liquid CWA. The symbols are explained in the text

At the air-liquid interface, the gas density of liquid CWA equals the volatility. This density diffuses outward in a layer of thickness δ with zero air speed according to Fick's law,

$$j = D\left(\frac{dC}{dz}\right)_{0<z<\delta} \tag{1}$$

where j is the transportation of mass per area and time, D is the diffusion coefficient in air, and C is the gas concentration. Empirically, this layer thickness (or diffusion length) has been found to be approximated by [13]

$$\delta = 1.6 \cdot 10^{-3} v_x^{-0.7} \tag{2}$$

where v_x is the shear wind speed (m/s) at the distance δ (m) from the surface[2]. It is common to assume that $C(\delta) \approx 0$, i.e. that $C(z) = C_0(1-z/\delta)$, where C_0 equals the volatility of the liquid. In the zero-wind layer, the vapor concentration will be fairly high, however, this layer is thin. Figure 2.2 shows layer thickness as function of wind speed. While δ is 8 mm at 0.1 m/s, it drops to 1.6 mm at the moderate 1 m/s wind speed. Thus the layer in which vapor from liquid CWA can easily be detected by points sensors (like the LCD3.1 [14]) is very thin.

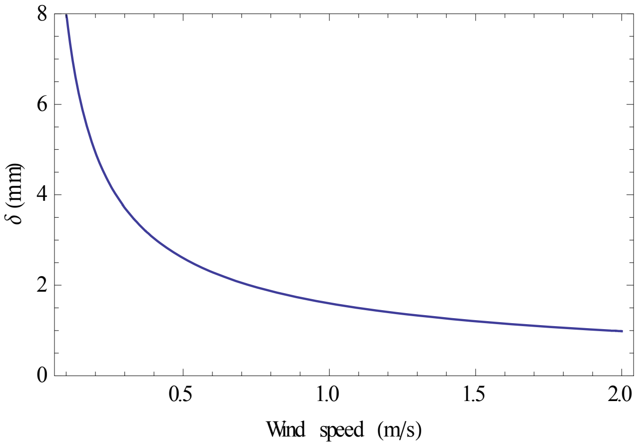

Figure 2.2 Thickness of zero-wind layer as function of wind speed

If the evaporated liquid is assumed to be mixed by turbulent processes in an air sheet outside the zero-wind layer, an average concentration in this sheet can be estimated. The mass diffused into the air volume is given by Fick's equation where the derivative is replaced by its approximate value, C_0/δ. If the width and length (in the wind direction) of the liquid is given by W and L,

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[2] In this simplified model, there is a discontinuity in wind speed at δ. This is, of course, not physically correct, but the model can nevertheless be used for concentration estimates

respectively, and the gas is assumed to be mixed in a volume of thickness $\Delta = H - \delta$, then the average gas concentration in this volume (downwind from the contamination) will be given by

$$\hat{\rho} \approx \frac{D \cdot C_0}{\delta(v_x)} \frac{L}{v_x \Delta} \tag{3}$$

It seems reasonable that the thickness of the air sheet to be mixed depends on the wind speed. In Figure 2.3, the average concentration is plotted as function of wind speed where it has been assumed that Δ takes the same numerical value as v_x (i.e. 0.5 m at 0.5 m/s) and that $L = 0.1$ m. It is seen that while the concentration of GB is well above the 0.1-1 mg/m^3 detection limit (e.g. LCD 3.2E, 10 second exposure [15]) for all wind speeds, GA, GD and HD are only well above for very low wind speeds, while VX is well below for all wind speeds.

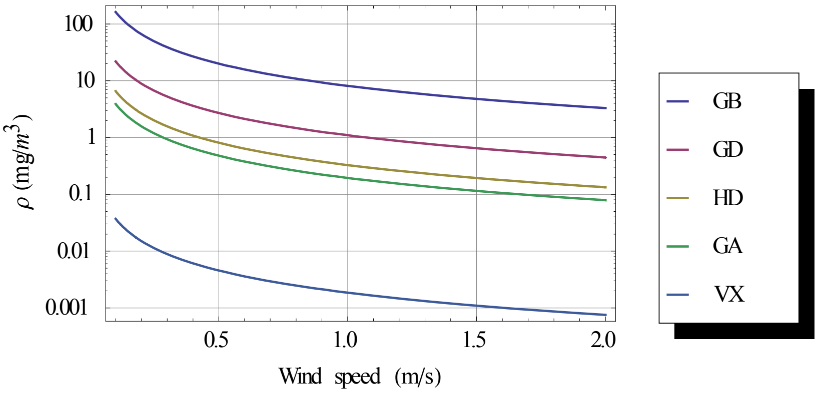

Figure 2.3 Estimated concentrations in air above liquid contaminant

Although this is a crude estimate, it illustrates why agents with a volatility below, say, 1000 mg/m^3 is difficult to detect with conventional point sensors, and why there is a need for detectors that can detect CWA in the liquid phase.

Vik et al. [16] performed simulations of a release of GB inside a 1x1 m^2 cross section ventilation shaft. The release was in the form of a liquid at one of the shaft surfaces, and vaporization and turbulent flow was modeled using computational fluid dynamics. A major finding was that the vaporization rate was considerably higher (a factor of ~4) when accounting for turbulent flow and mixing compared to the simple model with laminar flow. It was found that the GB concentration in the middle of the shaft cross section downstream from the release was in the range 5-10 mg/m^3 for the ~0.2 m/s wind speed. This is far below the estimates presented in Figure 2.3 although the vaporization rate is much higher. The reason for the deviation is that turbulence gives mixing over a much larger volume than was assumed in the calculations. Hence, the concentration estimates presented in Figure 2.3 are likely to be too high. This does not alter the main conclusion that detection of chemical vapors is difficult with gas sniffers.

3 Technologies for standoff detection

This chapter reviews technologies that have potential to be used in standoff detection of liquid CWA on a solid surface. The operating principles are briefly described and the potential sensitivity is in some cases estimated. Most of the techniques involve illumination of the surface to be examined by a laser and measuring the return radiation. The approaches vary greatly, however, and there are quite different physical or chemical properties that are measured.

Internationally, there has been a strong focus on standoff detection on traces of explosives on surfaces.[3] Many of the techniques studied in this context also have potential for use in standoff detection of CWA.

A few general remarks can be made:

- In most cases, the detection distance of a short-range technique can be increased by increasing the light collection aperture (e.g. a telescope) and a more powerful laser (if applicable). Typically, the signal at the observer is reduced by the square of the distance, so the sensitivity of standoff detection will be reduced with increasing distance to target.
- The wavelength region below ~300 nm is called the *solar blind* region because there is no (or very little) solar radiation at the earth surface at these wavelengths owing to absorption by the ozone layer. This is a great advantage as detection in this wavelength region then requires much smaller signals to be above the background signal. It should, however, also be noted that absorption by e.g. pollution generated ozone in the air may reduce the range of such techniques to a few hundred meters. Figure 3.1 shows the calculated transmission through 100 m and 500 m of a standard atmosphere (Modtran USTD [21]) and through the same atmosphere, but with 100 ppb ozone added. This corresponds to an ozone concentration that may appear midsummer in moderately polluted areas [22].

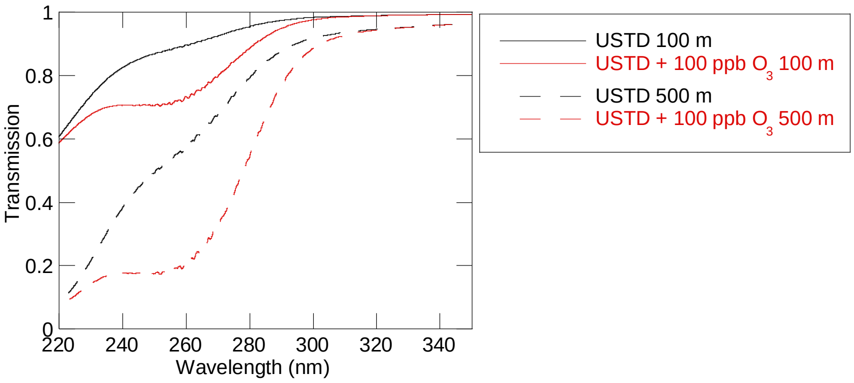

Figure 3.1 Calculated transmission through 100 m and 500 m US Standard atmosphere (black curves) and for the same conditions with 100 ppb ozone added (red curves) [21]

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[3] See, e.g., the annual SPIE Defense, Security and Sensing conference [17-20]

3.1 Techniques using an active laser

3.1.1 Laser Induced Breakdown Spectroscopy

Laser Induced Breakdown Spectroscopy (LIBS) uses a high intensity laser pulse that is focused onto the surface to be investigated. The high intensity in the focal point generates plasma by ablating a very small amount of the surface material (and potential contaminant) and breaking the atomic bonds of this material.[4] When this material cools down (after ~10 µs), characteristic emission spectra are emitted from the excited atoms or ions, and e.g. CWA can be identified by the presence and relative strength of carbon, phosphorus, chlorine and sulfur. As LIBS ablates surface material, it is a (partly) destructive technique. It is a fairly sensitive technique and can detect the individual substances on the order of 1-100 ppm with respect to mass in the material ablated [24]. As it is the ratio of the content of the different elements that leads to identification of a specific substance, estimation of detection threshold for different agents is difficult. LIBS is normally considered a short-range technique (sub-meter detection range), but >50 m detection distances have been demonstrated [25, 26]. Like other standoff techniques, however, increased detection distance inevitably also leads to a lower sensitivity.

There are several methods that can increase the sensitivity of LIBS. One is by using lasers with femtosecond pulse duration (compared to the usual nanosecond pulse duration) to reduce the so-called *brehmsstrahlung* emitted by the plasma and thus increasing the signal to background radiation [27]. This benefit comes at the cost of a significantly more complex laser source. Another method is to use two similar laser pulses separated by a few µs [28]. The operating principle of this method depends on the delay between the laser pulses and the experimental arrangement (the laser beams can be sent parallel with each other or orthogonal with each other at the material). For the arrangement suited for standoff detection (parallel laser beams), the energy of the second laser pulse is partly absorbed by the plasma from the first pulse and partly generating new plasma, leading to up to a factor 100 stronger signal than with single-pulse LIBS [29]. This technique is used in standoff detection of explosives. A third and experimentally fairly similar technique is to use two laser pulses separated by a few µs where the second pulse is weaker and at a longer wavelength. The second pulse is too weak to generate plasma by itself, but instead heats the plasma generated by the first pulse utilizing the Ramsauer-Townsend effect [30], and can lead to more than two orders of magnitude increase in the emission from the plasma [31].

Figure 3.1 gives a schematic overview of the LIBS technique. The two latter approaches discussed above use two laser sources, but experimental arrangements are otherwise similar.

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[4] Required electric field strength for optical fields to produce plasma varies significantly with pulse length, and is on the order of 10 GW/cm^2 for a 5 ns pulse [23]. This intensity can be obtained with ~250 mJ pulse energy when focused to a 1 mm^2 area. For 100 fs pulses, the required intensity is ~5 TW/cm^2 [23], thus the required energy is ~2 mJ when focused to a 1 mm^2 area (or 20 µJ for a 100 µm diameter spot).

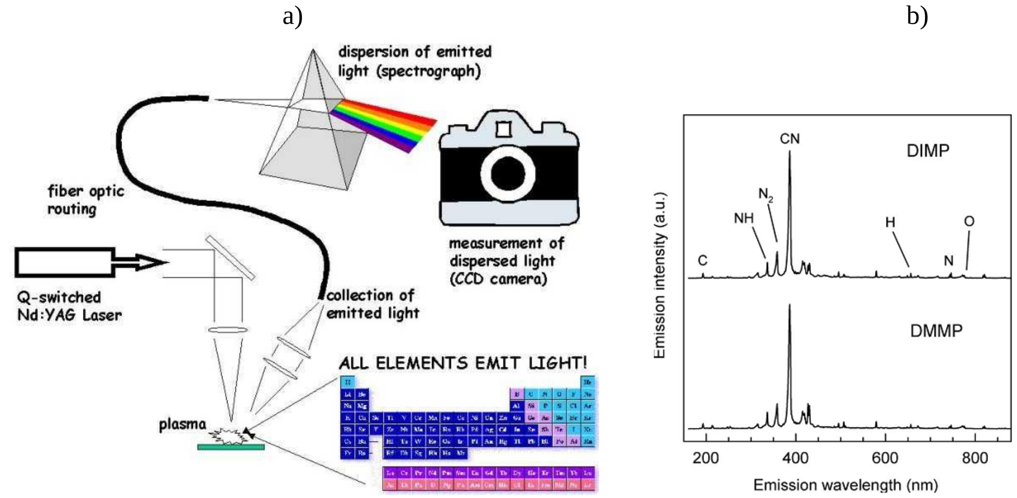

Figure 3.1 a) Sketch of LIBS operating principle (source: Wikipedia). b) LIBS spectra of CWA simulants DIMP and DMMP in a N_2 atmosphere [32]

3.1.2 Raman spectroscopy

Raman scattering is a well-known effect that occurs when photons are scattered on an atom or a molecule. The energy of a small fraction (~10^{-7} [33]) of the scattered photons is shifted with an energy that is characteristic of the scattering molecule.[5] In the processes interesting for this work, this energy corresponds to the energy spacing between the vibrational energy levels of the molecule, and is typically in the range 500-3000 cm^{-1}. The scattered photons can both gain or, much more commonly, lose this energy. These effects are known as Anti-Stokes and Stokes Raman Scattering, respectively.

In Raman spectroscopy the spectral content of the backscattered radiation is measured after illumination with a monochromatic laser pulse. The backscattered light can thus give a fingerprint of the molecular vibrations in the material tested. For the G-agents, the frequency shift is on the order of 500-2000 cm^{-1} [34], see Figure 3.2.

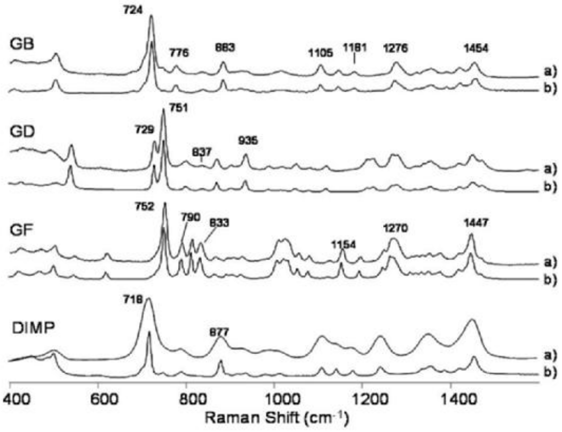

Figure 3.2 Comparison of measured Raman spectra at 248 nm (a) and 785 nm (b) laser wavelength for different G agents and DIMP [34]

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[5] The remaining photons are scattered elastically (Rayleigh scattering)

The sensitivity of Raman spectroscopy is relatively low, but can be enhanced by using a shorter laser wavelength, and it has been found that the Raman cross-section is a factor 200-700 higher[6] for 248 nm laser radiation than for 785 nm [34]. Interference with fluorescence from the background can also be a major problem in Raman spectroscopy. This is reported to be a smaller problem at 248 nm than at wavelengths >260 nm [34-36]. Fluorescence interference can also be reduced by a factor of ~2 by using a polarized laser and applying a polarizer in front of the detector because Raman scattering maintains the polarization, while fluorescence is unpolarized.

There exist other techniques that are based on Raman scattering that with special experimental arrangements can improve the sensitivity of Raman spectroscopy by several orders of magnitude. The most important techniques are listed below. A brief review of the use of different technologies based on Raman technologies in homeland security can be found in [37].

3.1.2.1 Surface Enhanced Raman Scattering

Surface Enhanced Raman Scattering, or SERS, involves the use of specially prepared surfaces, where the Raman signal is greatly improved by interaction with surface plasmons[7]. It is a widely used laboratory technique, but is not considered suited for standoff detection [38, 39].

3.1.2.2 Resonance Raman Spectroscopy

In Resonance Raman Spectroscopy, or RRS, the fraction of scattered photons is increased by several orders of magnitude by using a laser frequency that is in resonance with an electronic transition in the atom or molecule. This resonance wavelength will vary from substance to substance, and will thus require several laser sources or a rapidly tunable laser source to be used in standoff detection of several different agents. It may therefore be less suited for this application. However, there are reports on the use of this technique with very short wavelength lasers at 248 nm [36].

3.1.2.3 Coherent Anti-Stokes Raman Scattering

Coherent Anti-Stokes Raman Scattering, or CARS, uses the Raman frequency shift in a nonlinear optical process involving four waves (so-called four wave mixing). Here, the excitational wave in the material with the Raman frequency ω_r is coherently excited by beating two incoming waves at ω_1 and ω_2 so that $\omega_1 - \omega_2 \cong \omega_r$ and then mixed with the wave ω_1 to yield a combined output at the anti-Stokes frequency, $\omega_a = \omega_r + \omega_1 = 2\omega_1 - \omega_2$ [40, p 267]. This process is therefore a coherent version of the spontaneous Raman scattering process. Since CARS is a four-wave nonlinear process, its efficiency depends strongly on the incident fields. Therefore, pico- or femtosecond laser pulses are used as the exciting waves. The setup can be rather complicated involving two pulsed lasers that must be synchronized and separated in wavelength by the Raman shift, but the inherently wide bandwidth of femtosecond laser pulses allows CARS to be accomplished with a single laser beam provided that the spectrum of the laser pulse is properly adapted so that there is

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[6] In Figure 3.2 the spectra are 'normalized' before comparison

[7] A surface plasmon is coherent electron oscillations that may occur at the surface of e.g. a metal when excited by an optical or electron beam

no laser radiation at the anti-Stokes frequency [41]. Standoff detection of explosives at >10 m distance has been demonstrated with this technique [42, 43].

3.1.2.4 Spatially Offset Raman Scattering

Spatially Offset Raman Scattering, or SORS, is a method that can be used to study contents inside the material or behind a thin cover. The detector field of regard is located some distance (typically 1-5 mm) apart from the position of the laser spot on the surface. The laser radiation penetrates into the material through diffuse scattering, and Raman scattering from this scattered laser light is observed [44]. The return signal is much weaker than for traditional Raman scattering, so this is therefore a short range technique. Detection of concealed material covered by paint, plastic or cloth has been demonstrated [45].

3.1.3 Laser Induced Fluorescence

3.1.3.1 Laser Induced (Native) Fluorescence

Excited molecules or atoms emit radiation at frequencies that are characteristic of the energy levels in the molecule or atom. This can happen on a slow (~minutes) or fast (subsecond) time scale after excitation. The fast process is known as fluorescence, and can be used to gain knowledge about the fluorescing material. For a specific substance, the emission lines are in many cases narrow and can provide a fingerprint of the substance if measured with proper spectral resolution. The excitation is usually generated with a laser pulse, in which case the technique is called laser-induced fluorescence (LIF). In some applications, fluorescent markers are used. Therefore, the term Laser-induced *Native* Fluorescence is frequently used to emphasize that the fluorescence stems from the molecule or substance studied. While LIF is a well-known technique for detection biological material [46] and in laboratory environment studying specific molecules [47], we are not aware of work using this as the sole technique for standoff detection of CWA. It has, however, been used in combination with Raman scattering with an excitation wavelength at 248 nm for detection of traces of explosives [36]. This approach takes advantage of the fact that there is little or no fluorescence from organic material below 270 nm regardless of excitation wavelength [35, 36], so that interference between the Raman scattering and the fluorescence is avoided.

3.1.3.2 Photo-dissociated LIF

An alternative use of LIF is to excite the material with an ultraviolet laser beam intense enough that the material is photolyzed (or photo-dissociated), and observe fluorescence from the resulting molecules after photolysis [48, 49]. In this case, the emission from the molecules may be at shorter wavelengths than that of the excitation laser.

3.2 Infrared absorption techniques

All molecules have characteristic absorption lines in the infrared spectral region, and there are both spectroscopic and other techniques that can utilize these spectral fingerprints in detection.

3.2.1 Hyperspectral imaging/FTIR

Fourier-Transform Infrared (FTIR) Spectroscopy is a well-known technique which can rapidly measure the infrared spectrum with high spectral resolution with a single detector [50]. Recently, commercial instruments that use this technology in combination with a detector array to obtain an imaging FTIR spectrometer have become available [51, 52]. Hyperspectral images can also be generated with other equipment utilizing gratings [53] or spectral filters [54]. It is also possible to use a single-pixel FTIR instrument in a scanning fashion [55].

Common for these techniques in measuring liquid on a surface is that the surface must reflect radiation from a source with a different temperature than the surface (and potential liquid). The reflected radiation will be masked with the absorption spectrum of the surface contaminant, but this masking will depend linearly with the temperature difference between source and contaminant, and will vanish at zero temperature difference. On a clear day (or night), the radiation from the sky would normally have a significant temperature difference from the ground. Alternatively, a significant temperature difference can also be accomplished by active illumination. Harig et *al.* used both these techniques to detect droplets of methyl salicylate in a ~20 µm thick film on different surface materials (wood, clay tile, steel) at ~1 m distance [56], see Figure 3.3.

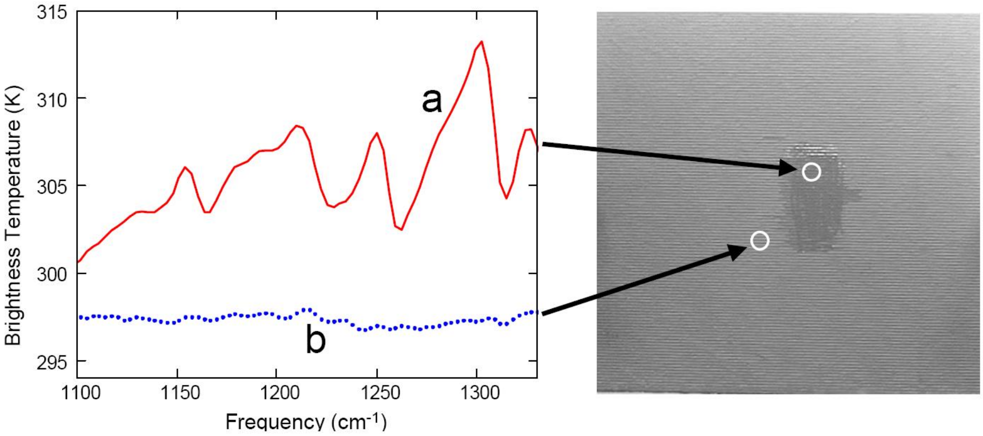

Figure 3.3 Measured brightness temperature at 1 m distance on (a) a clay tile covered with methyl salicate and (b) a naked clay tile [56]

3.2.2 Thermal contrast

If the surface contaminant is illuminated at a frequency where it absorbs, the contaminant will be heated and the temperature rise can be observed with a thermal camera. Many commercial cameras can detect temperature differences well below 0.1K [57], making this a potentially sensitive method.

A tunable laser or several fixed-wavelength lasers are required to identify a specific compound. The requirements for this laser source can be estimated as follows: If energy per area, F, is absorbed in a liquid film of thickness d of a material with specific heat capacity c_v and density ρ, the instantaneous temperature rise (ignoring heat conduction) is given by

$$\Delta T = \frac{F}{c_v \rho d} \tag{4}$$

Using the values for GB and HD in Table 1, we find that for a 0.1 K temperature increase in a 20 µm liquid film, the required absorbed energy per area (assuming that this is converted to heat) is 0.4-0.5 mJ/cm^2. The spatial resolution of the camera also needs to be sufficient to distinguish contamination from other spots. Typically, thermal cameras have 3-500 pixels in each direction. If the imaging system of the camera leads to a pixel size of 1x1 mm on the surface to be studied, the image is 30-50 cm across and the required energy for 0.1 K temperature increase would be ~1 J. If the laser needs to scan 10 different wavelengths to classify agents and we assume that the laser can be scanned without a delay for the material to cool down, a 3W laser would need ~3 seconds to perform the wavelength scan for this image. Therefore, it seems clear that this technique is best suited for examination of rather small areas and not for wide area searches. Small-area standoff detection of traces of explosives has been demonstrated at distances up to 150 m using this technique [58].

3.2.3 Negative contrast imaging

In this approach, a tunable laser source illuminates the area to be investigated and a camera monitors the light reflected from the area. The camera should therefore be sensitive at the laser wavelength. If the laser is at a wavelength that is absorbed by the liquid, the reflection will be lower than if it is not absorbed. Tuning the laser wavelength across molecular absorption lines then gives a hyperspectral image of the area investigated. Standoff detection at a few meter distance of droplets of different simulants has been demonstrated [59]. Examples of these results are shown in Figure 3.4.

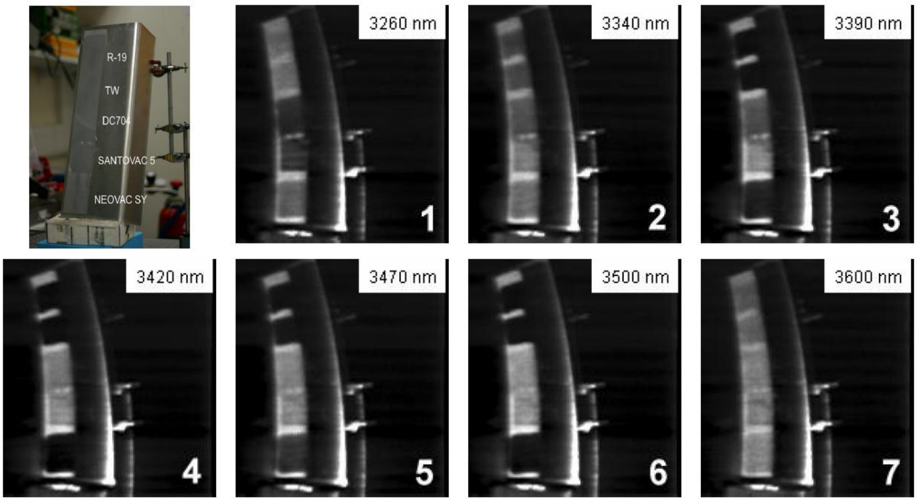

Figure 3.4 Example of images obtained with different illumination wavelengths. The test substances are five different vacuum pump oils [59]

3.2.4 QCL scanning

Recent laser development has resulted in the so-called Quantum Cascade Laser (QCL). This is a semiconductor laser that can be designed to emit at long wavelengths [60]. While traditional semiconductor lasers are limited by the band gap in the material to ~2 µm emission wavelength, QCLs can be designed to operate at wavelengths above ~3 µm. It is also possible to obtain tuning of the output wavelength, giving possibility to scan the wavelength over absorption lines [61]. Therefore, QCLs are finding large applications in e.g. gas spectroscopy [62, 63], and a few instruments have been demonstrated using a scanning QCL for liquid detection [64, 65]. One of the instruments states 5-60 cm standoff detection distance and < 0.1 g/m^2 detection limit [65].

3.2.5 Multiheterodyne detection

While measurement of the exact optical frequency is challenging, radio frequencies are easily measured. This is utilized in heterodyne detection where two beams with closely spaced optical frequencies are combined at an optical detector. The resulting optical field will oscillate with the frequency difference between the two beams (the *beatnote*). With a proper choice of frequencies, this beatnote will be at a radio frequency that can much easier be detected and analyzed.

This principle is utilized in a recently developed technique for rapid recording of high resolution spectra that involves the use of two femtosecond lasers. The spectrum of such lasers contains a large number of equidistant frequencies, a *frequency comb*, where the spacing between the frequencies is given by the length of the laser resonator. If these laser beams are combined on a detector, the resulting signal will contain a frequency comb in the radio frequency range [66].

In multiheterodyne spectroscopy, the beam from one femtosecond laser is passed through the medium to be analysed and is beated with the reference laser at a detector. The resulting radio spectrum is colored by absorption lines of the medium and can easily be extracted from the signal.

3.3 Other techniques

3.3.1 Gas detection after heating

It is well known that the volatility of the chemical warfare agents increases significantly with temperature [6], thus heating the liquid (or the contaminated surface) will lead to more agent vapor which may be detected by other means – either by using existing points sensors or by other gas sensors, e.g. standoff sensors. An increase in temperature from 20ºC to 40ºC results in a factor of ~4 increase in vapor pressure for GB and HD and a factor of ~10 for VX [6]. However, the gas concentrations for HD and VX would still be low, and it therefore seems not likely that this approach will enhance existing detection capabilities.

3.3.2 Microwave spectroscopy

While visible and infrared light can probe transitions between energy levels in atoms or molecules, microwave radiation can be used to probe rotational levels inside the molecules. It has reportedly great potential for a sensitive point sensor [67], and is used for gas detection at standoff distances [68]. We are, however, not aware of any use in standoff detection of liquids.

3.3.3 Thermal luminescence

This technique utilizes that emission emitted from a material when heated will be colored by its emission lines, e.g. from electron transitions or from rotational and vibrational transitions. It has been demonstrated in detection of chemical agent simulants in soil by excitation with microwave radiation at a water absorption line and spectroscopic detection in the 7-14 µm range [69]. The standoff distance in these experiments was ~1 m.

3.3.4 Polarization modulation infrared reflection absorption spectroscopy

Infrared reflection absorption spectroscopy (IRRAS) is a well known technique for studying thin films and monolayers deposited on metallic surfaces. Here, the surface is illuminated with *p*-polarized light[8] at grazing incidence[9] and the absorption lines in the reflected light are measured, usually with an FTIR spectrometer. At grazing incidence, the absorption spectrum in a thin film depends strongly on whether the incident light is *s*- or *p*-polarized. Thus, using a combination of *s*- and *p*-polarized light can help to discriminate near-surface absorption from strong isotropic ambient absorptions and almost completely compensate for instrumental instabilities and the background, allowing for selective analysis of chemical contaminants at the surface [5, 70, 71]. Researchers at Canada’s DRDC have shown that polarization modulation IRRAS (PM-IRRAS) can be used to detect VX and simulants for G-agents on diffuse surfaces painted with US Chemical Agent Resistant Coating [72, 73]. At about 10 cm detection distance, the detection limit for the G-agent simulants was about 1 g/m^2. It should be noted that PM-IRRAS is a short range technique because of the requirements of grazing incidence both for the incident and the reflected beam; in the DRDC experiments, the angle of incidence was 84º, limiting the practical working distance from the surface to a few tens of cm.

3.3.5 Photoacoustic detection

If a material is abruptly heated, the thermal shock wave can generate a sound wave which can be detected by acoustic detectors (microphones). If the light source (laser) is chopped and tuned across an absorption line in the material, the absorption and thus the resulting sound wave will vary, and the variation in sound can be used to detect the absorption line. The photoacoustic effect has been know since the late 1800s, but has gained renewed interest and increased sensitivity with the development of tunable quantum cascade lasers (QCLs). Instruments that require the chemical samples to be contained in a photoacoustic cell can detect trace amounts at ppb or ppt levels [74]. For standoff detection, a main challenge is sensitivity, both in terms of sufficient tunable laser power, sensitivity of the microphones and ambient noise. Recently, standoff detection of a gas sample of isopropanol at 13 m distance was demonstrated with a system that uses a QCL at 7.9 µm, a sensitive microphone and a 50 cm diameter parabolic sound

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[8] *p*-polarized light is polarized in the plane of incidence, while *s*-polarized light is polarized normal to this plane

[9] Incident light nearly parallel with the surface

concentrator [75]. The technique has also been used for standoff detection of liquid contaminations at 8 m distance in a laboratory environment [76, 77].

3.4 Summary

Below, a summary of the techniques described in this chapter with cons and pros is listed. See Appendix A for a list of acronyms

3.4.1 Laser Induced Breakdown Spectroscopy (LIBS)

Maturity of technology/Active research

Well-known short range technique. Research underway to increase distance

Used in standoff detection? Standoff distance

Yes, sub meter distance. Several efforts to increase distance to > 10 m

Cons and Pros

\+ mature technology
\+ sensitive technique

\- Requires powerful laser (eye safety, cost, complexity)
\- Destructive technique

3.4.2 Laser Induced Fluorescence (LIF)

Maturity of technology/Active research

Well-known technique used for other purposes. Research under way for use in standoff detection of liquids in combination with other techniques

Used in standoff detection? Standoff distance

No. Research effort to be used at 2-5 m range

Cons and Pros

\+ mature technology
\+ can be combined with Raman scatter at UV-wavelengths

\- Requires powerful laser (eyesafety, cost, complexity)
\- Insensitive, not standalone technique

3.4.3 Raman spectroscopy

Maturity of technology/Active research

Mature technology, primary candidate in several standoff research activities

Used in standoff detection? Standoff distance

Yes, a few meters standoff distance

Cons and Pros

- \+ Mature technology, standoff detection demonstrated
- \+ Sensitivity and specificity

- \- Interference with fluorescence leads to lasers < 250 nm wavelength
- \- Requires powerful laser (eyesafety, cost, complexity)

3.4.4 Spatially offset Raman spectroscopy

Maturity of technology/Active research

New application of Raman spectroscopy. Commercial provider. ‘Hot topic’ in short-range standoff detection research

Used in standoff detection? Standoff distance

Lab demonstrations. 10 cm distance to locate absorbed/concealed material

Cons and Pros

- \+ Potential to locate hidden material
- \+ Commercial provider of technology

- \- Short range technique

3.4.5 Quantum Cascade Laser (QCL) scanning

Maturity of technology/Active research

Mature basic technology (IR spectroscopy). Laser source technology rapidly maturing. Commercial provider of instrument.

Used in standoff detection? Standoff distance

Yes, commercial instrument states up to 60 cm detection distance.

Cons and Pros

- \+ Rapidly maturing laser technology (fairly low cost)

- \- Limited standoff range

3.4.6 Fourier Transform Infrared (FTIR) Spectroscopy

Maturity of technology/Active research

Mature technology for many applications, but there may be a problem with sensitivity. Use in standoff detection pursued by several teams.

Used in standoff detection? Standoff distance

Yes. Standoff detection distance can be large (100 m) when operated passively. With active illumination the standoff distance is significantly shorter.

Cons and Pros

- \+ Mature technology
- \+ Potentially long standoff range

- \- Low sensitivity
- \- Strongly dependent on temperature/weather conditions

3.4.7 Thermal contrast

Maturity of technology/Active research

Using mature technology developed for other applications (thermal camera), and rapidly maturing technology (tunable laser). Used in detection of trace of explosives.

Used in standoff detection? Standoff distance

Explosives detection at 150 m distance.

Cons and Pros

- \+ Potentially long standoff range
- \+ Imaging technology

- \- Measurement can be slow
- \- Requires potentially complex laser

3.4.8 Negative contrast

Maturity of technology/Active research

Using mature technology developed for other applications (thermal camera), and rapidly maturing technology (tunable laser). Demonstrated standoff detection of droplets.

Used in standoff detection? Standoff distance

Yes, laboratory measurements at a few meters distance

Cons and Pros

- \+ Potentially long standoff range
- \+ Imaging technology

- \- Sensitivity may be low (large variations in background signal)

3.4.9 Multiheterodyne detection

Maturity of technology/Active research

Technology relativity new, but rapidly maturing.

Used in standoff detection? Standoff distance

Not yet. Potentially large detection distance.

Cons and Pros

- \+ fast measurements
- \+ sensitive, potential for long detection distance

- \- Requires sophisticated laser source (cost, complexity)

3.4.10 Gas detection after heating

Maturity of technology/Active research

Can use existing technology for detection of vapor phase.

Used in standoff detection? Standoff distance

No. Potential standoff distance and sensitivity unclear.

Cons and Pros

- \+ Can use existing FTIR technology

- \- Probably low detection sensitivity

3.4.11 Microwave spectroscopy

Maturity of technology/Active research

Strong interest for explosives detection.

Used in standoff detection? Standoff distance

No. Probably fairly short distance.

Cons and Pros

- \+ See-through capacity

- \- THz-source technology immature
- \- Probably short detection distance

3.4.12 Thermal luminescence

Maturity of technology/Active research

Mature components. Some recent research.

Used in standoff detection? Standoff distance

Yes, at 1 m distance

Cons and Pros

- \+ Mature components
- \+ Potential for high speed detection

- \- Limited standoff distance
- \- Unclear sensitivity

3.4.13 Polarization Modulation Infrared Reflectance Absorption Spectroscopy (PMIRRAS)

Maturity of technology/Active research

Mature technology, commercial instruments available. Some research for standoff applications

Used in standoff detection? Standoff distance

Yes, at ~10 cm distance

Cons and Pros

+ Commercial instrument

- Short standoff distance
- Possibly too low sensitivity

3.4.14 Photoacoustic spectroscopy

Maturity of technology/Active research

Mature technology, but further development of key components necessary. Some research for standoff applications

Used in standoff detection? Standoff distance

Yes, at ~10 m distance of liquids and gases

Cons and Pros

+ Well known technology

- Unclear sensitivity in standoff applications
- Sensitive to ambient noise level

3.4.15 Need for illumination source

In Table 3.1 the need for illumination source in the techniques described in this work is listed. Table 3.2 summarizes what kind of laser source that is required for those techniques that require a laser source.

Light source → ↓ Technique	None (passive)	Light (no laser)	Laser	Other (µwave, THz)
LIBS			X	
Raman			X	
LIF			X	
Line scanning (QCL)			X	
FTIR	X	X		
Thermal contrast			X	
Negative contrast			X	
Heterodyne detection			X	
Gas det. after heating	(X)*	X		
Microwave				X
Thermal luminescence				X
PMIRRAS		X		
Photoacoustic spec.			X	

*Table 3.1 Required illumination source in the techniques described in this chapter. *) Current detection method include using gas sniffers close to the surface to be investigated*

	UV	Vis	IR	CW	ns	fs	Tuneable
LIBS			X		X	X	
Raman	X	X	X	X	X	X	
LIF	X				X		
Line scanning			X	X			X
Thermal constrast				X			X
Negative contrast				X			X
Heterodyne detection			X			X	
Photoacoustic sp.			X	X			X

Table 3.2 Specification of laser needed for techniques that require laser. UV/Vis/IR: Wavelength of laser, CW, ns,fs: Pulse length of laser (continuous wave, nano- or femtosecond). Tuneable: Tuneable laser required

4 Current research activities

Chapter 3 summarizes techniques that have been used or can be used to detect liquid chemical agents at standoff distance. Through conferences [17, 18, 78-80] and NATO meetings, we have become aware of research activities that are directed towards this kind of detection. These are briefly described in this chapter. The few commercially available systems for this application are briefly described at the end of the chapter.

4.1 USA

There have been several efforts in this field in USA that include many of the technologies listed in the previous chapter. In a new activity the use of spatially offset Raman scattering to locate chemicals inside a material is to be studied [81]. This would be for standoff detection at short range (tens of cm).

The US Army wants an instrument that can be mounted on reconnaissance vehicles looking down or slightly forward, capable of real time detection at operationally interesting speeds to replace the current silicone wheels that are dragged along the surface. In their test methodology, desired detection levels for surface contaminants are 0.1-0.5 g/m^2 and the vehicle speed is 11-56 km/h [82]. ITT Industries has been awarded contracts to develop a vehicle-mounted instrument based on UV laser Raman scattering [83, 84]. This project, named LISA, is still running.

4.2 Canada

DRDC has several research activities in this field. An FTIR system has previously been used to detect chemical contamination at 60 m distance [85]. The sensitivity of this instrument seemed, however, to be too small to be of practical interest (around 10 g/m^2). Recently, a project to use the newly developed Catsi [86] in detection of explosives and liquid chemicals has started. The Catsi is significantly more sensitive than traditional FTIR spectrometers, and may lower the detection threshold to operationally interesting levels [87]. DRDC is also studying the PM-IRRAS technique for short-range (10 cm) standoff detection [73].

4.3 UK

DSTL in United Kingdom has completed a project on negative contrast imaging and have demonstrated standoff detection of droplets on various surfaces at a few meters distance [59]. DSTL also has collaborated with University of Hamburg on the use of an imaging FTIR in standoff detection. Standoff detection with high spatial resolution at 1 m distance of simulants on various backgrounds was demonstrated with an estimated simulant layer thickness of ~10 g/m^2 [56]. DSTL has also recently started an activity using spatially offset Raman scattering to look for chemicals below the surface [88]. Previously, DERA (and later Qinetic) studied photoacoustic spectroscopy [76, 77].

4.4 France

DGA CEB in France has an ongoing activity to develop standoff detection of liquid and biological surface contaminants at 2-5 m distances. They have found that a combination of LIBS at 266 nm and LIF at 266 nm and 355 nm has the best potential to fulfill their requirements.

4.5 Sweden

FOI in Sweden has studied detection of trace explosives with Raman scattering [89, 90]. Recently, they have started a study to investigate detection of liquid contaminants on a surface with Raman scattering after excitation with a tunable ultraviolet laser.

4.6 Commercial instruments

4.6.1 Block Engineering

LaserScan developed by the USA-based company Block Engineering is based on QCL-scanning in the 6-10 µm or 7-12 µm wavelength range. Stated detection distance is 5-60 cm and the instrument analysis time is a few seconds for a single point of ~5 mm diameter. The stated sensitivity is 0.02 g/m^2 [65].

4.6.2 Daylight solutions

Daylight Solutions in the USA offers their product Swept Sensor, which is based on QCL-scanning. Originally developed for detection of gases, it can also be designed to detect liquids [64].

4.6.3 Cobalt

Cobalt inc in the UK has developed the spatially offset Raman spectroscopy technique [91] which is a hot topic in several countries. The perhaps most important application for their technology is pharmaceutical inspection, and they offer several products based on the technique [92].

5 Important considerations for a new research activity

If one is about to enter this field of research, several important considerations should be made in order to maximize the potential benefit of such a research activity. The potential sensitivity of the technology will affect the obtainable standoff detection distance and how useful an instrument may be, the measurement speed will also affect the potential scanning speed, the sensitivity to different background signals can both affect the false alarm rate and operational restrictions (e.g. to low ambient light conditions). Other issues not related to sensitivity, but that should still be considered are technological maturity of the basic technology, expected cost and size of detection system (advanced lasers are often expensive), as well as operational considerations like eye safety and whether testing will be destructive (like for LIBS) or nondestructive. These topics were to some extent listed in Chapter 3.

5.1 Sensitivity and standoff distance

In general, active techniques (involving a laser or other means for active illumination) tend to have potential for a higher sensitivity than passive techniques. On the other hand, while the sensitivity (or detected signal) of active techniques depends strongly on the distance to the target ($1/R^x$ where $x \geq 2$), passive techniques may be less sensitive to this distance. However, since sensitivity is important for this application, active techniques are still likely to be the best choice.

Some of the active techniques will require a slant angle of incidence to the sample to be tested or that the return light is detected at a different angle than the incident light. Such techniques are likely to be short-range (cm to tens of cm) techniques. For an active system to have potential for longer standoff range (several meters) illumination and detection should be collinear (or close to) and relatively independent of angle of incidence on the surface to be tested.

5.2 Measurement speed/scan rate

The scan rate of most active techniques tend to be relatively slow as only a single point or a few points are examined at a time. Techniques involving array detectors (e.g. thermal cameras or imaging FTIR spectrometers) may have higher scan rates provided that the illumination source can cover the sensor field of view. The instrument that was tested by the US Army based on Raman scattering (see Section 4.1) was a vehicle mounted single-pixel instrument with a fixed field of view [83]. Scanning in this case was thus obtained by moving the vehicle.

5.3 Environmental conditions

Some of the active techniques, like Raman scattering, works best when using ultraviolet light in the solar blind region (wavelength below ~300 nm). The sensitivity of such techniques is therefore not affected by ambient light conditions. Passive techniques, like FTIR, depend on the background radiation. Since FTIR uses infrared light, the sensitivity depends more on the temperature of the surroundings than the ambient light level (except that this influences the ambient light level). Long range techniques are likely to be less sensitive in the presence of smoke, fog or other atmospheric obscurants.

5.4 Other considerations

Instruments that include lasers often require laser safety measures. Besides the obvious eye protection, also skin protection may be necessary. This is the case for LIBS where the laser intensity is very high. Additionally, skin should not be exposed to UV-lasers with wavelengths shorter than 310 nm. Such lasers are typically used for Raman scattering. Generally, IR lasers needs less protective measures for the same intensity levels than visible and UV lasers. The wavelength range above 1.5 μm is often referred to as the “eyesafe” wavelength range. This does not mean that eye protection by default is not necessary, but refers to the fact that the safe intensities are >100 times higher than for visible and near-infrared light.

Adding lasers may also make the instrument more expensive and with a larger physical footprint. Therefore, instruments that use this technology would not be able to replace e.g. the LCD or similar handheld detectors. One exception here may be instruments that use QCLs, which can be made very small.

Some of the active techniques use lasers with high intensities. To some extent, this may damage or affect the surface tested. This is particularly true for LIBS which is based on ablation, but also other techniques may (unintentionally) leave a permanent mark on the surface tested. This may or may not be a problem, pending on operational requirements and procedures.

6 Conclusions and recommendations

Standoff detection of liquid chemicals is more challenging than standoff detection of vapors. While there exist several commercial instruments for the latter application, liquid detection is with only a few exceptions at a research level. There is a long range of technologies that may be used for such an application, and this report has listed most, if not all, of them. The detection problem has much in common with the current ‘hot’ topic of standoff detection of explosives, and one can benefit of results obtained here.

Sensitivity is a very important parameter for such a technique. Its seems therefore clear that some form of active technique should be approached in a future study. Techniques that can use quantum cascade lasers (QCLs) have potential to be lightweight and arguably less expensive than techniques using other lasers. It is at present not clear if QCLs can provide sufficient laser intensities that standoff detection at several meters distance can be obtained with the required sensitivity. This should be investigated in a future study. If long range standoff detection is a target techniques like coherent anti-Stokes Raman spectroscopy (CARS), thermal contrast imaging, and multiheterodyne detection seem to have the greatest potential, but Fourier transform infrared spectroscopy with or without artificial illumination should also be investigated. For short range (~meter) standoff distance, also techniques like Raman scattering, laser induced breakdown spectroscopy (LIBS), laser induced fluorescence (LIF), or a combination of these have interesting potential. A few technologies also have the potential to detect subsurface contamination. These include spatially offset Raman spectroscopy (SORS), microwave spectroscopy and thermal luminescence, of which SORS seems to attract most interest currently.

FFI has currently a high level of expertise and is also well equipped with instruments in areas related to FTIR and lasers. A possible startup activity that would benefit from this base knowledge could include active and passive FTIR as well as wavelength scanning with infrared lasers. The final choice of technologies for a further study would, however, depend on the intended mode of operation as defined by the user. This has not been a topic of this work.

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List of acronyms

Acronym	Acronym for	Explanation
CARS	Coherent Anti-Stokes Raman Scattering	Detection technique
CW	Continuous Wave	Continuous laser light (no pulses)
CWA	Chemical warfare agent	
DERA		DSTL’s predecessor
DGA CEB		France’s “FFI”
DIMP	Diisopropyl methylphosphonate	Simulant for chemical warfare agent
DMMP	Dimethyl metylphosphonate	Simulant for chemical warfare agent
DRDC		Canada’s “FFI”
DSTL		UK’s “FFI”
FOI		Sweden’s “FFI”
fs	Femtosecond (10^{-15} s)	Ultrashort pulselength in some lasers
FTIR	Fourier Transform Infrared	Detection technique
GA	Tabun	Chemical warfare agent
GB	Sarin	Chemical warfare agent
GD	Soman	Chemical warfare agent
GF	Cyclosarin	Chemical warfare agent
HD	Sulphur mustard (Mustard gas)	Chemical warfare agent
IR	Infrared light	
IRRAS	Infrared Reflection Absorption Spectroscopy	Detection technique
LC_{50}	Lethal concentration	50% of exposed unprotected military personnel die
LCD	Leightweight Chemical Detector	Instrument for CWA gas detection
LD_{50}	Lethal dose	50% of exposed unprotected military personnel die
LIBS	Laser Induced Breakdown Spectroscopy	Detection technique
LIF	Laser Induced Fluorescence	Detection technique
ns	Nanosecond (10^{-9} s)	Typical pulse length of pulsed laser
PMIRRAS	Polarization modulated IRRAS	Detection technique
ppb	Parts per billion, 10^{-9}	

Acronym	Acronym for	Explanation
ppm	Parts per million, 10^{-6}	
ppt	Parts per trillion, 10^{-12}	
QCL	Quantum Cascade Laser	
RRS	Resonance Raman Spectroscopy	Detection technique
SERS	Surface Enhanced Raman Scattering	Detection technique
SORS	Spatially Offset Raman Scattering	Detection technique
UV	Ultraviolet light	
Vis	Visible light	
VX		Chemical warfare agent