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The application of stand-off infrared detection to identify air pollutants

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Abstract. Fourier-transform infrared spectroscopy (FT-IR) enables the passive detection and identification of chemical agent clouds from distances. It can be used for the monitoring of large spaces and protection of industrial installations outside buildings. The aim of the study was show the possibilities and limitations of passive FT-IR. In studies done by the Faculty of Fire Safety Engineering at the Main School of Fire Service were used spectrometer RAPID (Remote Air Pollution Infrared Detector), Bruker Daltonics Company. Hazardous substances such as acetone, methanol, ammonia was identified on-line from several observation points at 25 m, 50 m and 75 m. The tests were carried out at various meteorological conditions. The results indicate that remote infrared detection allows detecting hazardous chemical agents in the atmosphere from a distance. Nevertheless, meteorological and terrain conditions have a big impact on the measurement results. During measurements, the detector indicated the presence of other substances. Moreover, it was found that under cloudy and windy weather, remote detection is not possible.

1 Introduction

The number of substances used in technological processes is constantly rising. Industrial development increases the risk of emergency emission of dangerous substances [1]. The most threatening is emission of potentially toxic gases. Therefore, fast identification of unknown substances is an important element of rescue operations. This process indicates application of different analytical techniques. Standard sampling techniques are performed in hazard zones. When the chemical sample is unknown the risk to the rescuers amplifies. Poland bought the first infrared remote detection devices in 2011. While, at present rescue agents have 19 Bruker Rapids (Fig. 1) [2].

The passive detection of chemical agents is based on a spectral analysis of the ambient infrared (IR) radiation [3, 4]. Chemical agents disseminated in the atmosphere generate unique signatures in the infrared spectrum that can be analyzed by detection systems. It is possible in spectral range from 700 to 1300 cm^{-1} [5–7]. Substances which have IR-lines or significant parts of them within this range could be identified with the highest accuracy because the transmission is high and additionally the signal to noise ratio is maximal [8]. Some few molecules do not show a detectable radiation contrast in the accessible spectral

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range of passive remote detection (e.g. hydrogen chloride, chlorine), so that they cannot be detected.

Due to the FTIR Technique (Fourier Transform Infrared Spectroscopy) obtained optical spectrums on infrared frequency are precise and timely acquired in shorter time than in classical absorption techniques. Measured interferograms were automatically transformed to IR spectra and matched to the spectra of targeted and interfering substances stored in the reference library. Substances which can be detected by passive detection FT IR were presented in Table 1.

Table. 1. Exemplary compounds detected with the use of passive detection FT IR [9].

Group of compounds	Exemplary compounds
Inorganic compounds	Ammonia, Hydrogen Cyanide Nitrogen oxides Sulfurdioxide Phosgene
Alcohols	Methanol, Ethanol
Aldehydes and ketones	Acetone, Butanal
Organic acids	Acetic acid, Formic acid
Ethers	Diethyl ether, Dimethyl ether
Aromatic compounds	Benzene, Xylene
Halogenated hydrocarbons	Chloroform Dichloromethane
Phosphorous organic compounds	Triethyl phosphate, Trimethyl phosphate
Chemical warfare agents	Sarin, Soman

The probability of detection depends on the concentration of an airborne pollutant, the optical path length through the cloud of the substance and the temperature difference between the pollutant and the background (Fig. 1) (as shown in Eq. (1) [5, 6]).

$$P_d \approx c \cdot L \cdot \Delta T \quad (1)$$

where:
P_d – the probability of detection
L – the optical path length through the cloud of the substance
ΔT – the temperature difference between the pollutant and the background
c – the concentration of an airborne pollutant

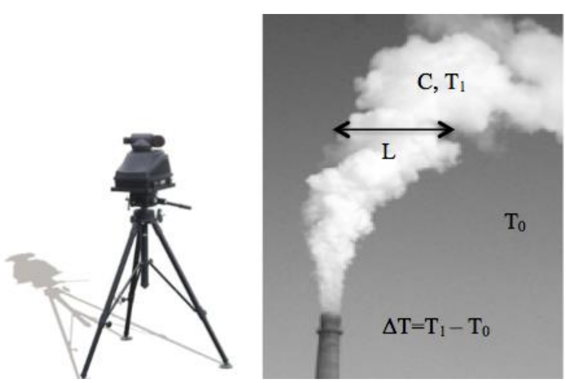

Fig. 1. The factors which determine detection in the passive FT-IR.

Scientific researches proved that increasing temperature difference between background and studied substance causes significant emendation of quality of the spectrum and verification of studied substance. No possibility of verification in the same temperature is a result of radiance of background (Fig.2).

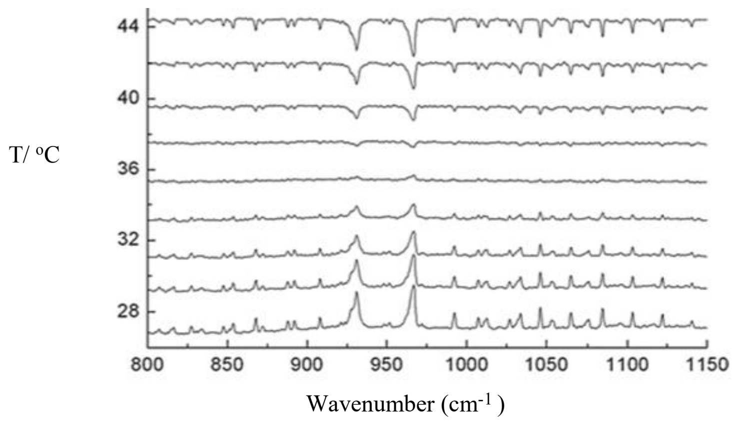

Fig. 2. Brightness temperature diagram of ammonia, measured with different background temperatures. Ammonia always has the same concentration and temperature (36.4°C) and the background temperature varies between 27°C and 44°C [5, 9].

2 Measurement device

The Remote Air Pollution Infrared Detector (RAPID) enables the passive detection and identification of chemical agent clouds from distances (Fig. 3). It can be used for the monitoring of large spaces and protection of industrial installations outside buildings. The RAPID is a stand-off detector, which consists of a scanner for spatial resolution with the IR scanner window and a video camera, internal optics and Michelson interferometer. The technical specification RAPID is summarized in Table 2.

Table 2. RAPID - technical specification [9].

Method detection	**Fourier-transform infrared spectroscopy**
Spectral range	700–1300 cm^{-1}
Spectral resolution	4 cm^{-1}
Sensitivity	< 0.05 K for a single spectrum with a resolution of 4 cm^{-1}
Detection limit (for ammonia)	1 ppm for a cloud length of 100 m and a temperature difference between cloud and background of 3°C
Measurement Speed	20 spectra/s at 4 cm^{-1} spectral resolution
Azimuth circle Azimuth Rotation	360° max. 120°/s
Field of Regard (FOR)	-10° to 50° elevation
Operating mode	Point scan (Fig. 3a) Full scan (Fig. 3b) Sector scan
Weight	~30 kg
Dimensions	500 x 331 x 386 mm

a)
b)

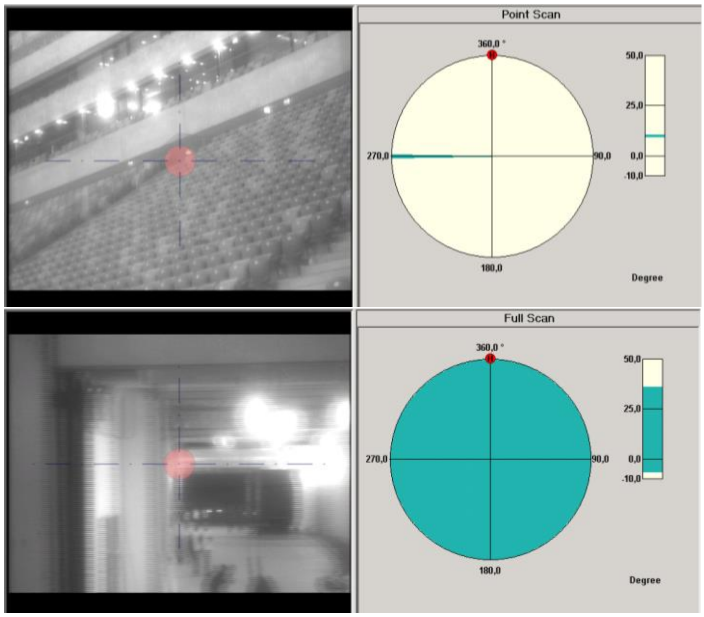

Fig. 3. Standard mode: a) point scan; b) full scan.

3 Materials and methods

The research was aimed at determining the possibility of remote detection of selected chemical compounds by RAPID, Bruker Daltonics. In real conditions, a series of tests was carried out to determine the detection capabilities of ammonia water 25%, methyl alcohol and acetone, depending on:
- the pool surface (emission intensity),
- the emitter distance from the detector,
- the weather conditions.

The detection of analyzed substances was performed from the following distances: 25 m, 50 m, 75 m (Fig. 4) and 3 pool surfaces: $35 \cdot 10^{-3}$ m^2, $65 \cdot 10^{-3}$ m^2, $100 \cdot 10^{-3}$ m^2 (source of emission).

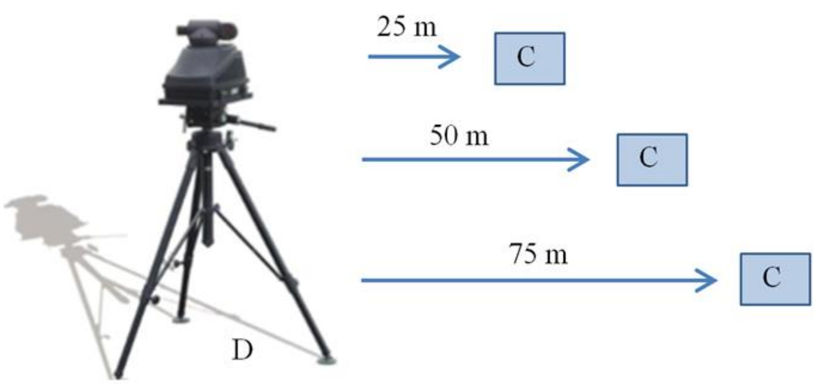

Fig. 4. The distance between the source of emission (C) and the detector (D).

Analysis were performed in 2 measurement series. In the first, analysis was carried out for the following atmospheric conditions: ambient temperature -8°C, relative humidity 70%, sunny and windless day, with no precipitation. For the second analysis tests were carried out on a cloudy and windy day, with a relative humidity of 100% and temperature equal to 5°C.

For both analyses it took about 5 minutes between surface pool preparation and about 30 seconds for the measurement performance. Moreover, the time between consecutive measurements was about 10 minutes.

4 Results

In the first step, all 3 chemical substances were identified during 27 measurements by defining the detection sector, the name of the substance, CAS number and intensity (ppm x m x K).

Table 3. Experimental results.

Substances	**Surface pool [m²]**	**Distance [m]**					
		25		**50**		**75**	
		Intensity [ppm×m×K]					
		I	II	I	II	I	II
Acetone	$35 \cdot 10^{-3}$	1782.1	0	1643.4	0	1515.1	0
	$65 \cdot 10^{-3}$	6639.7	0	5899.5	0	4403.7	0
	$100 \cdot 10^{-3}$	8844.6	0	7852.3	0	7756.2	0
Methyl alcohol	$35 \cdot 10^{-3}$	649.2	0	573.5	0	532.1	0
	$65 \cdot 10^{-3}$	1234.3	0	1056.7	0	965.6	0
	$100 \cdot 10^{-3}$	1285.9	0	1128.2	0	976.5	0
Ammonia water 25%	$35 \cdot 10^{-3}$	2139.8	0	1654.6	0	1367.3	0
	$65 \cdot 10^{-3}$	5154.8	0	4908.7	0	4777.9	0
	$100 \cdot 10^{-3}$	5367.1	0	5034.5	0	4883.6	0

According to the analysis of the first series of results it was found that together with increase of surface pool the value of intensity increased. Moreover, increase of the distance between emitter and detector decreased the value of analyzed parameter (Table 3). Furthermore, during RAPID measurements false substances were also found, e.g. with the use of acetone, detector identified also chloroacetone (CAS 75-00-3) and butane (CAS 78-93-3) (Fig.5).

While, during the second series of tests, the device did not detect any of the analyzed substances or other gas phase compounds.

Analyses indicated that for some conditions remote detection of substances by the RAPID device is possible, as it was performed for the first series of measurements. It was found that the intensiveness parameter *(I)* depended on the following elements: concentration of the analyzed substance, the thickness of the cloud layer and the temperature difference between the cloud and the background. The inability to register one of these parameters prevents effective measurements (the second series of analysis). Moreover, high sensitivity and precision of the device in stable working conditions have been demonstrated.

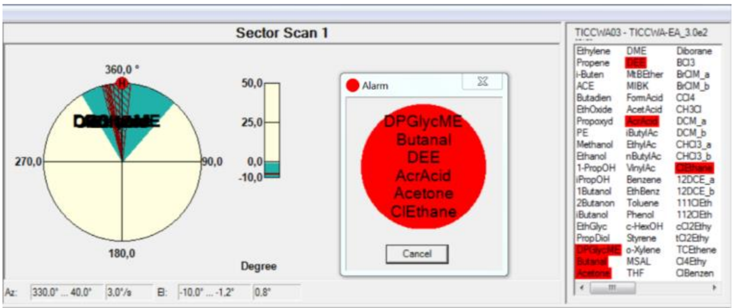

Fig. 5. The View of the detection window for the acetone analysis (The first series of measurement).

5 Conclusions

The aim of the study was to show the possibilities and limitations of passive FT-IR basing on the spectrometer RAPID (Remote Air Pollution Infrared Detector), Bruker Daltonics Company. Hazardous substances such as acetone, methanol, ammonia was identified on-line from several observation points at 25 m, 50 m and 75 m. The tests were carried out at various meteorological conditions. The results indicate that remote infrared detection allows to detect hazardous chemical agents in the atmosphere from a distance. Nevertheless, meteorological and terrain conditions have a big impact on the measurement results. The distance of the emission source from the remote detector has an influence on the intensity value. During measurements for sunny and windless days, the detector quickly indicated the presence of analyzed substance, however together with other substances. Moreover, it was found that passive detection FT IR for cloudy and windy days is impossible.

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