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Original Research

Using a Mobile Multigas FTIR Analyzer in Four Different Environmental Accidents

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Abstract

Our study presents results of air-pollutant measurements in four types of environmental accidents using a mobile multi-gas FTIR apparatus. Fuel leakage at a gas-station caused extremely high concentrations of pollutants. During a fire at a landfill the release of CO, SO_2, NO_2, heptane, ethane, propane, benzene, toluene, xylene, and styrene was also high. An accident in defense industry facilities did not lead to endangerment of the environment. An emitter-air condenser in an industrial facility released dangerous concentrations of hydrogen sulfide, mercaptans, benzene, toluene, xylene, and styrene. A mobile FTIR gas analyzer is useful in diverse ecological accidents.

Keywords: spectroscopy, Fourier transformed infrared; accidents; air pollutants

Introduction

Fourier transformed infrared spectroscopy (FTIR) has recently been used with considerable success in the biological sciences, where it is often referred to as biospectroscopy. It is a non-destructive technique that allows analysis of a large number of samples and rapid identification of very small amounts of the analyte, even to billionths of a part [1]. Potential fields of application of this method include cytological, histological and microbiological diagnostic studies [2]. Its use is not limited to the analysis of biological fluids, but also applies to macromolecules, isolated cells, tissues, or whole pieces of tissue [3-5].

Original or modified FTIR spectroscopy techniques are also successfully and widely used in ecotoxicology for identification of different substances with different phases of matter and in different conditions. Studies that have analyzed the presence of cadmium, chromium, lead, and zinc in contaminated water and fish [6], harmful chemicals accumulated in bird feathers [7], hazardous organic chemicals in plastic waste in ecological zones [8], and air pollutants [9] are some recent examples of the successful use of this method. The close relationship of the living environment and health of the population requires a multidisciplinary approach in using FTIR methods and the interpretation of their results in terms of public health and ecotoxicology. Examples of the successful use of FTIR spectroscopy in the quality control of medical products such as drugs [10], then in the regulatory affairs related to food control [11] and in the analysis of the existence of environmental pollutants (organophosphate pesticides) in organisms in vulnerable populations such as in breast milk of nursing mothers [12], points to the necessity of joint work of various profile experts in order to protect and improve health.

The dynamism of modern society also requires rapid action and direct participation of relevant organizations and experts in a considerable number of ecotoxicological situations. In addition, mobility, accuracy, and reliability of

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the analytical method itself and control of the whole process of surveillance are of particular importance. Modern equipment commonly based on FTIR spectroscopy has all the features that correspond to such requirements. They control the air quality in both urban and working environments, as shown in the study of the analysis of gases, acetylene, carbon monoxide, hydrogen cyanide, and ethane [13], and the analysis of multiple volatile organic compounds (VOC; toluene, xylene, styrene, methanol, acetone, 2-butanone) around a color factory [14]. Mobile FTIR systems have been successfully tested since the 1990s [15] and the recent results of the study where the content of oxygen and carbon dioxide in the cargoes of the goods on the transport ships in the sea ports was monitored [16], thus confirm their utility.

Despite the fact that the systems based on FTIR spectrometry, used separately or combined with other analytical techniques, are a potentially useful tool in the management of accidental ecotoxicological situations, in real time, available bibliography gives a few studies on the experiences of real examples. Most of the published studies with similar topics discussed simulated or potential accidental situations [17, 18], or the after-effects of already existing ecotoxicological incidents in terms of biological damage or forensic requests [19, 20]. Environmental emergencies are the source of inorganic and organic chemicals of paramount toxicological significance for nearby organisms. The combustion of natural (wood, fossil fuels) and synthetic materials (plastic, hazardous chemicals) during the fires, for example, releases dangerous asphyxiants (carbon monoxide, carbon dioxide, hydrogen cyanide), compounds with strong irritant effects on mucosal surfaces (halogen acids, oxides of nitrogen, ammonia, acrolein), and molecules with complex toxicological effects (polycyclic aromatic hydrocarbons, dioxins). Therefore, the aim of this paper is to discuss the potential benefits and difficulties in using the mobile multi-gas FTIR analyzer in four emergencies (environmental accidents) in different circumstances that have occurred in the Republic of Serbia in the recent past.

Experimental Procedures

The study covers analyzed data from the archives of the Ćuprija Pomoravlje Institute of Public Health obtained from the testing and the measurements of immission and emission of pollutants. The four environmental accidents, which occurred in 2010 and 2011 in a variety of circumstances, are analyzed in this study Three of them involved measurement of immission of pollutants (malfunction in an industrial facility for public use, fire and explosion) and another one concerning harmful emissions due to a malfunction in the production line of an industrial plant. The overall study structure, data collection of data, and result presentation were based on similar previously published research relating to the detection of the analytes, FTIR-based equipment, and chemical accidental situations [13, 14, 16, 19].

The Ćuprija Pomoravlje Institute of Public Health is the national institution that is authorized to conduct the necessary tests in environmental accidents that can occur in all media (air, water, soil). For the purposes of engaging in accident situations the institution has equipped a mobile ecotoxicological laboratory, hired specially trained personnel, and provided a special vehicle (equipped with an independent electrical supply) in order to transport the necessary equipment and to apply all necessary measurement procedures.

Tests for the presence of chemical pollutants in the air are carried out outside, using a Protea ProtIR 204M apparatus. This device is a multi gas analyzer used for the analysis of gases in immissions, emissions, and working environments. The device works using infrared (IR) technology, and Fourier transformation (FT) is required to turn the raw data into the current spectrum. General features of the ProtIR 204M analyzer are described in detail in the product manual. The analyzer has MCERTS accreditation certificate, used by laboratories accredited according to ISO17025 standard and is recognized by the Accreditation Board of Great Britain UKAS. It is designed for both mobile and continuous measurements and its unit incorporates a zirconia oxygen sensor, providing a parallel determination of oxygen with other gases. Both characteristics of the apparatus are very important in accident situations, especially fires.

The Protea 204M ProtIR-type unit has extremely high sensitivity due to very low detection limits. An example of its detection limits for most commonly used substances – gases – is as follows: H_2O (<0.4%), CO_2 (<0.2%), NO (4.20 ppm), NO_2 (0.82 ppm), SO_2 (0.99 ppm), CO (1.70 ppm), HCl (0.43 ppm), NH_3 (0.56 ppm), HF (0.40 ppm), N_2O (<0.5 ppm), CH_4 (<0.5 ppm), C_3H_8 (<0.5 ppm), formaldehyde (<0.5 ppm), HCN (<0.5 ppm), and O_2 (<0.2 ppm). For measurement of the analytes EPA Method 320 was used and their concentrations are expressed in mg/m^3. The following substances were measured: acetone (C_3H_6O), acrolein (C_3H_4O), ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), nitrogen oxides (NO_x), benzene (C_6H_6), n-butanol ($C_4H_{10}O$), cyclohexane (C_6H_{12}), dichloromethane (CH_2Cl_2), diisopropyl ether (C_6H_{14}), ethane (C_2H_6), ethanol (C_2H_6O), phenol (C_6H_6), inorganic fluorine compounds (such as HF), hexane (C_6H_{14}), heptane (C_7H_{16}), inorganic compounds chlorine (such as HCl), chloroform ($CHCl_3$), xylene (C_8H_{10}; including a separate one for the analysis of m-xylene, o-xylene and p-xylene), methane (CH_4), methanethiol (methyl mercaptan) (CH_4S), methanol (CH_4O), 1-propanol (C_3H_8O), propane (C_3H_8), styrene (C_8H_8), sulfur dioxide (SO_2), toluene (C_7H_8), 2,4-toluene diisocyanate ($C_9H_6N_2O_2$), carbon monoxide (CO), and hydrogen sulfide (H_2S). The results of measurements are analyzed descriptively, presented in the tables in detail [21], and discussed taking into account official emission limit values (ELVs) for a detected chemical [22, 23].

Results

The study covers four environmental accidents that occurred in 2010 and 2011 in several circumstances, of which three involved measurement of immission of pollutants (the malfunction in an industrial facility for public use, a fire, and an explosion) and one concerning harmful emissions due to a malfunction in the production line of an industrial plant.

Leakage of Gases and Vapors in and around a Gas Station

Analysis of this environmental accident is described as an example of the malfunction of the facility that is intended for general, public use. Therefore, the damage that occurred can have immediate effects on the health of employees and the general population that resides or lives nearby. Measurement of emissions of pollutants that come from pouring fuel lines on an OMV gas station, Gornji Milanovac, "Obilazni put bb" Street, was performed in the period from 11:00 to 14:30 hours on 17 May, 2011, in continuous mode. The measuring points are placed next to a nearby manhole (drainage, sewage, ventilation). This gas station has all kinds of motor fuel and liquefied petroleum gas that is believed to have been the main cause of the odor that was spreading in the area around the station. Measurement and leak detection of organic vapors at selected measuring points included continuous sampling during the three-hour period, noting that the outdoor temperature and the weather conditions were poor, with low outside temperatures (6-9ºC) and rain. The measurement results of immission of pollutants are calculated on the dry gas, and calibration temperature of the device is set to 120/180ºC. Content of the immission substances is shown in Table 1.

Table 1. Measurement results of air quality during gas and vapor leaks in and around the OMV gas station, Gornji Milanovac.

Analyte	Value[1]	(Minimum-Maximum)[2]
2,4-toluene diisocyanate	9	(0-15)
Acetone	530*	(5-1330)
Acrolein	160*	(10-370)
Benzene	4240*	(10-9,600)
Chloroform	450*	(20-800)
Cyclohexane	275	(15-740)
Diisopropyl ether	24	(10-89)
Ethanol	6,800*	(70-13,500)
Heptane	540*	(60-12,000)
Hydrogen sulfide	690*	(25-1,200)
l-Propanol	580*	(30-1,800)
Methanethiol	8,670*	(150-25,000)
Methane	480*	(90-1,590)
m-Xylene	3,500*	(100-6,300)
n-Butanol	720*	(25-1,580)
o-Xylene	1,400*	(10-2,700)
Phenol	240*	(10-560)
Propane	400*	(50-2,350)
p-Xylene	2.3	(1.9-2.6)
Styrene	280*	(40-1,090)
Toluene	3,680*	(20-7,350)

[1]the most frequent measured concentration (mg/m^3)
[2]the minimal and the maximal concentration (mg/m^3)
*exceed emission limit values (ELV)

Fire at a Landfill

In the fire, the recycling copper from waste cables that was manufactured in the local Cable Industry was burning. Prevailing waste material included plastic liners, which are insulated copper conductors. The landfill was open, with plenty of waste, about 15 tons, with a multi-layer structure, occasional thickness up to 3 m. Measurement of air quality during and after the fire was conducted at several locations from 16:30 on 11 April to 06:00 on 12 April, 2011. Although the landfill site itself is outside populated areas, because of the scale of immission of harmful chemicals it also included the urban part of the city. Thus, the measurements were made on three occasions per 15 minutes, at the following locations:

a) Pomoravka, Jagodina – 10 to 150 m from the place of fire on 11 April, 2011 (from 16:30 to 18:30) (location 1)
b) Kneza Miloša St. – 600 to 800 m from the place of fire on 11 April, 2011 (from 18:30 to midnight) (location 2)
c) Kralja Petra St. – 600 to 800 m from the fire on 11 April, 2011 (from 18:30 to midnight) (location 3),
d) Žarka Smiljkovića St. – control point on 12 April, 2011 (midnight to 06:00) (location 4).

During a fire at landfill "Pomoravka" in Jagodina when the equipment was switched on to products of combustion, "Combustion mode" such as CO (carbon monoxide), SO_2, NO_2, beside the high values of these gases measured in addition the high quantity of easy-volatile organic compounds (VOC), heptane, ethane, propane, and other such groups and especially toxic chemicals: benzene, toluene, xylene, and styrene also were measured (Table 2).

The Defense Industry Explosion

The accident in this factory of the defense industry took place within an enclosed industrial plant and, due to the nature of its activity, the mobile toxicological team was not allowed access inside the facility. The explosion could have a direct effect on the employees, and the vulnerability of the general population depended on the type of affected products (chemicals), extent of damage, and the meteorological conditions influencing the spread of harmful gases. Given

Table 2. The measurement results of imissions of pollutants in the Pomoravka Jagodina landfill fire.

Analyte	Location 1			Location 2			Location 3			Location 4		
	1	2	3	1	2	3	1	2	3	1	2	3
Carbon monoxide	59	564*	1,665*	4	6	8	4	4	6	1	2	1
Sulfur dioxide	54	468	1,288*	6	9	12	6	7	8	0	0	0
Nitrogen dioxide	52	264	896*	4	4	5	3	3	4	1	0	0
Heptane	12	56	90	14	18	20	10	14	17	2	0	0
Ethane	2	48	82	8	19	12	8	12	12	2	2	2
Propane	9	34	55	6	12	15	6	11	12	1	3	3
Xylene	12	28	32	2	4	6	3	4	4	0	0	0
Toluene	16	24	34	9	10	12	5	8	6	0	0	0
Benzene	12*	26*	30*	6*	6*	9*	3	5	4	0	0	0
Acetone	3	4	6	0	0	0	0	0	0	0	0	0
Methanethiol	2	4	6	0	0	0	0	0	0	0	0	0
Styrene	12	15	17	3	6	8	2	5	10	0	0	0

Concentrations are in mg/m^3; *exceed emission limit values

the circumstances, the measurements of immissions of pollutants during and after the explosions at the plant were conducted on 27 December, 2010 about 50 m from the entrance (main gate) in from 08:30 to 10:30. Measurement results were converted to dry gas – calibration temperature of the device was set to 120/180ºC. Content of moisture (H_2O) and oxygen (O_2) is expressed as a percentage (%), and the concentration of other substances in mg/m^3. Similarly to the previous, a significant number of polluting chemicals was found in the air, but their concentrations were mostly within acceptable values (Table 3).

Emission of Pollutants at a Plant

This case is an example of an ecological accident in the working environment that may have a direct effect on the health of employees and, indirectly, delayed impact on the health of the general population because of the spread of mass emissions from factory chimneys. Due to a failure in the plant, the object of measurement was emission of pollutants from the factory itself and are eliminated through the condenser. From the destructor during the technological process the secondary vapors are separated, containing malodorous gases. Secondary vapors leak through the system of canals, pipes, and cyclones, using a fan drain to the air condenser where smelly gases are being condensed, i.e. translated into waste water. No condensing gases are then dissolved in cold water and drain by sewage. Gases that are not condensed in the air condenser and that are not dissolved in cold water are emitted into the air. The air condenser that is used in the factory is a HAARSLAV A/S No. 195-500, which is designed for vapor condensation, i.e. its purpose is to remove unpleasant odors arising from the operation of the plant, which for the process of production uses animal confiscates as a resource. Measurement results were converted to dry gas and the calibration temperature of the device was set at 120ºC. Measuring point was at the condenser emitter and the date of measurement was 12th of November, 2010. Gas temperature (ºC) and the oxygen ratio (O_2) are presented as a percentage (%), whereas the concentrations of other substances are expressed in mg/m^3. In the products of emission a large number of chemicals-contaminants were found (Table 4), some of them, for example methane, could cause a fire or explosion.

Discussion of Results

Chemical accidents constitute important threats for today's communities around the globe. They emerge from a variety of circumstances including industrial and professional exposure. Among the many environmental and societal issues of such disasters, the health-related consequences make a great challenge for medical professionals [24]. Consequently, the stakeholders on both the national and the regional levels raise current awareness in order to increase societal capacity for successful responses to chemical emergencies [25]. On the other hand, there are a few studies in the literature that suggest the use of FTIR technology in emergency-accident ecological situations. This is opposite to many studies reporting the use of this technology in the field for measuring the concentration of trace gases, and intervals covering the scales and the distances from those commonly used by biologists (microenvironment) to those operated by climatologists (continental) [26, 27].

In our study we, probably for the first time in the common, peer-reviewed literature, presented successful use of FTIR-based equipment in four environmental accidents of

Table 3. The measurement results of immission of pollutants during explosions in the defence industry, “Sloboda,” Čačak.

Analyte	Measurement		
	1	2	3
Moisture	0.6	0.5	0.7
Oxygen	20.8	20.8	20.8
Carbon monoxide	1.5	1.6	1.5
Sulfur dioxide	0.0	0.0	0.0
Nitrogen dioxide	0.0	0.0	0.0
Nitrogen monoxide	2.4	2.6	2.4
Nitrogen suboxide	0.0	0.0	0.0
Nitrogen oxides (NO_x)	3.2	4.3	3.4
Inorganic fluoride	0.0	0.0	0.0
Inorganic chlorine	4.7	4.2	3.7
Ammonia	0.0	0.0	0.0
Methane	2.6*	2.3*	1.9*
Ethane	4.2	5.4	4.6
Propane	6.2	7.5	9.2
Hexane	8.4	8.2	10.4
Heptane	0.0	0.0	0.0
Methanol	0.0	0.0	0.0
Ethanol	3.6	4.3	3.8
l-Propanol	0.0	0.0	0.0
n-Butanol	3.2	2.8	2.9
Acetone	5.5	5.8	6.2
Chloroform	0.0	0.0	0.0
Dichloromethane	3.4	3.7	3.3
Diisopropyl ether	1.1	0.9	0.8
m-Xylene	0.0	0.0	0.0
o-Xylene	4.2	5.6	5.7
p-Xylene	8.1	11.2	14.9
Toluene	17	13	18.4
Benzene	7.4*	6.5*	9.8*
Cyclohexane	0.0	0.0	0.0
2,4- toluene diisocyanate	0.0	0.0	0.0
Acrolein	0.0	0.0	0.0
Methanethiol	7.8	9.5	10.2
Phenol	0.0	0.0	0.0
Styrene	6.2	5.4	6.8
Hydrogen sulfide	0.0	0.0	0.0

Concentrations are in mg/m^3; *exceed emission limit values

Table 4. The measurement results of emissions of pollutants at the plant Fabim “Napredak,” Ćuprija.

Analyte	Measurement			ELV
	1	2	3	
Gas temperature	18	17	18	-
Oxygen	20.2	20.3	20.3	-
Methane	181*	199*	234*	0
Propane	33	37	42	150
Hexane	56	61	72	150
Heptane	119*	177*	244*	150
Ethanol	81	78	106	150
Acetone	28	36	21	150
Dichloromethane	289*	568*	612*	150
o-Xylene	52	85	77	100
p-Xylene	450*	462*	355*	100
Toluene	402*	522*	526*	100
Benzene	4.3	7.5*	6.8*	5
Acrolein	8.2	7.8	12.4	20
Methanethiol	135*	198*	319*	20
Styrene	154*	177*	196*	100
Hydrogen sulfide	653*	879*	943*	5

Concentrations are in mg/m^3; *exceed emission limit values

different ecotoxicological circumstances, making possible health threats for employees but also the general public. Fast and accurate identification of an array of dangerous chemicals in real-life situations makes the FTIR methods fully complementary with the requirements of modern management of chemical accidents. Immission/emission measurements of harmful and dangerous substances that have arisen as a result of accidental leakage of fuel at the OMV gas station in Gornji Milanovac were carried out in surrounding manholes. The measured concentrations at the time of measurement were extremely high for the specified parameters, and individually and cumulatively pointed to the seriousness of a situation that required urgency in detecting and fixing the cause. There was an urgent need to remove the people from the danger area, which was accomplished furthermore. The repair of industrial assembly was done by a professional team from the company authorized to perform such activities.

An interesting finding was observed in manhole No. 1, located by the Gornji Milanovac-Čačak main road and not belonging to the gas station. The illicit presence of mixture of harmful gases has been found on the entrances of the underground channels than accumulate and transit to the shafts, and beneath the station. This was established by comprehensive measurements, detection of gases, through determining of gas flow direction, and zoning at the gas station.

Measurements showed that the gases do not come as a result of various activities at the gas station, but it still makes the situation very dangerous and urgent in order to point out the origin of gas moving through underground channels. Additional measurements are needed, which would be carried out in the facilities that surround the gas station.

Monitoring air quality during the landfill fire at specified locations in the metropolitan area showed high values of pollutants in short intervals of time (several minutes), all above the MPC. These values occurred as a result of changes in wind speed and direction. The increased values of pollutants due to the short exposure cannot affect the health of the population. FTIR-based measurement allowed zoning of the threat to the populated part of the city as well as to determine the danger zone for employees in the industrial area in relation to the meteorological conditions and, in particular, the wind rose. The most vulnerable were the participants in firefighting and the cable factory workers who were 50 m from the fire, because the wind blew the smoke from the landfill fire toward their facilities. Because of multiply increased values of pollutants, particularly of benzene and its homologues (30 mg/m^3 benzene, and the maximum permissible inhalation of 5 mg/m^3 in 15 minutes in this way was 6 times higher), workers were sent away from their workplaces until the fire was fully extinguished. Participants in firefighting were equipped with masks and oxygen cylinders. A checkpoint with zero pollution was used as a comparison with other potential sources of pollution.

Measurements of harmful and dangerous substances that have arisen as a result of an accident occurred in the Sloboda Čačak defense industry facilities, performed at the time of the accident and in the period of calming down of explosions, showing that pollutants did not lead to damaging the environment, life, and health of the population. Very harmful emissions were limited in duration. Concentrations of xylene, toluene, and benzene were elevated but could not threaten the local population, given the length of exposure. We were unable to assess negative impact on the health of the employees due to the nature of the facility. But we assume that employees are adequately trained and equipped to work in an industry with a high risk of accidents.

Comparing the measured values of pollutants with emission limit values [22, 23], it can be concluded that at the time of measurement at the air condenser emitter – Fabim "Napredak" d.o.o. Ćuprija, ELV for these pollutants greatly exceeded. In particular, very high concentrations of hydrogen sulfide, mercaptans, and then a group of hydrocarbons: benzene, toluene, xylene, and styrene were notified. Environmental impact is the other part to be evaluated on the basis of other parameters specified in the feasibility study of the company and other relevant study documents such as licenses which permit work, etc. Comparing such requirements with the results of measurements performed by FTIR gas analyzer could immediately allow appropriate corrective measures.

A large number of detected hazards in all four accidents reasonably question their cumulative toxicity. However, the assessment of joint effects of harmful substances on biological organisms is not easy and in fact there is not a single method that may be suitable to use in all circumstances [28]. This especially stands for accidental situations where, apart from rapid identification, fast categorization of hazards is required, i.e. aerosols in these examples. With some classification systems that could be applied to a mixture of chemicals by analogy inferred to the situation above, there are some inconsistencies, such as accumulation of toxicity of substances with different states of aggregation and, consequently, different units of measurement that basically categorize such toxicity [29, 30]. Therefore, more accurate evaluation of cumulative toxicity of aerosols raised after accidents described in our study requires further investigation.

Conclusions

Based on the results shown in these examples it can be concluded that using a mobile FTIR gas analyzer is very enforceable in ecological accident situations, especially in fires and chemical accidents, and for explosions with fire, accidental system failure during treatment of emission gases in high-risk industries and in failures of installations gas station. The other devices are also used for continuous monitoring of air pollution. With the results of our measurements we have shown how applicable and useful portable FTIR gas analyzers are in environmental accidents with its ability to quickly identify and quantify a large number of gases, especially those that are highly toxic and can endanger residents and employees. It is important to add that it can be used in many other accident situations, such as breakdowns while transporting toxic and gaseous substances either by road or rail or on other occasions. The most important is that in a short period of time zoning of hazardous concentrations can be made around an accident site, which allows application of appropriate measures. Regarding the fact that an FTIR analyzer can store all IR spectra, and they are preserved forever, the post-analysis can be done on the spectrum in order to determine the known and unknown components that have gone through it.

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