Determination of air quality in a petroleum extraction area

V M Dragan\textsuperscript{1}, B D Tudor\textsuperscript{1} and L G Pintilie\textsuperscript{1}
\textsuperscript{1}`Dunarea de Jos’ University of Galati, str. Domnească nr. 111, 800201, Galați, Romania

E-mail: geanina.tiron@ugal.ro

Abstract. Direct measurements on atmospheric pollutants have the advantage of measuring emissions in real time rather than by theoretical calculations. In order to determine the air quality in the analyzed area, the measurements of the emissions, at several points of work in order to identify as many sources of noxious emissions were made. A series of noxious emissions measurements were performed from several points of the analyzed perimeter to detect the level of pollutants in the atmosphere. To estimate the amount of pollutants, emitted into the atmosphere, four pollutant sources were taken into account: combustion plants, reservoir parks, traffic inside the enclosure, wells. The results of the four monitored areas of activity were compared with the current legislation \cite{1} on the safety and health of workers against the risks related to the presence of chemical agents.

1. Introduction

Petroleum is a finite resource. Because it formed over millions of years and is being used faster than it is being formed, petroleum is non-renewable on any human time scale; at some point supply will fall short of demand. The point at which petroleum production reaches its maximum is known as peak petroleum. Thereafter, perhaps following a plateau of a year or more, production inevitably declines \cite{2}.

Different processes such as extraction, distillation, hydrogenation, reforming, cracking and blending are used in a modern refinery which is a highly integrated industrial plant to produce high yields of valuable products such as petroleum gas, gasoline, diesel fuels, bitumen, petrochemicals, wax and lubricants from a crude oil feed of variable composition \cite{3}.

By its nature, the Oil Industry is a threat to nature. Generally, the operation of large oil refinery industrial plants such as fiesta associated with the emission of different substances into the atmosphere stems from production processes, storage tanks, transport pipelines and the waste area \cite{4}.

Among the most important emission sources from the oil industry are flares, crude oil spills, cuttings from drilling activities and discharges to water. Flares release approximately 82\% of all pollutants discharged into ambient air by the oil industry in this region. Chemical analysis of the flue gas emitted into the air by flares indicates volatile organic compounds (VOCs), unburned hydrocarbons (HC), carbon monoxide (CO), sulphur dioxide (SO\textsubscript{2}), hydrogen sulphide (H\textsubscript{2}S), nitrogen oxides (NO\textsubscript{x}), and particulate matter (PM), methane, are the major constituents \cite{5}.

The composition of emissions from each of different sources varies widely depending on factors such as feed composition \cite{6}.

Determining the concentration of atmospheric pollutants, based on direct measurements, it has the great advantage of measuring real-time emissions during process operation.
2. Methods and analysis

In order to determine the air quality, a range of portable detectors, (Microclip XT, Altair 4X, Altair 5X), were used to indicate the air quality, indicating the gas concentration directly. These offering the possibility to know the level of the pollutants from the atmosphere, in real time, and at the same time, the chance to leave the location in the shortest time, when the situation demands it.

To estimate the amount of pollutants, emitted into the atmosphere, three pollutant emission sources were considered, as follows:
- the combustion plants - these, emitting the gas, from methane gas combustion: sulphur oxides, nitrogen oxides, CO, powders, hydrocarbons;
- the parks of the reservoirs - these emitting the sulphur compounds, hydrocarbons, volatile organic compounds, during filling and emptying operations;
- the probe - these, which emits gas, both from its own source and from the operation of the on-site machinery: H₂S, CO₂, CO, CH₄ [7].

3. Results and discussion

3.1 Sampling of the combustion gases

Combustion plants (boilers) are one of the sources of atmospheric pollutants. They provide the heat demand in the process, by heating water under pressure, and burning fuel - the natural gas. Through the combustion process, the flue gases, which contain sulphur oxides, nitrogen oxides, carbon dioxide, are released into the air [8]. These, being the most important sources of pollution from combustion plants. For the fluidization of crude oil, boilers consume 383 Nm³/h of natural gas.

Natural gases are mixtures of light paraffins, in which methane (CH₄), with varying but small percentages of ethane, propane, butane [7]. Fuel, poor natural gas, is a low-grade fuel. However, if the combustion is not complete, or the heaters are fed with rich gas, the emissions may be significantly higher. Incomplete combustion can also lead to the emission of carbon monoxide.

The Microclip XT gas detector, located in the workstation, was used to collect atmospheric emissions from inside the boiler battery. It is a portable, multi-gas detector with a continuous gas concentration display. The detector has four sensors, detecting methane, hydrogen sulphide, carbon monoxide and oxygen.

| Place where measurements were made | Carbon monoxide (CO) [ppm] | Hydrogen sulphide (H₂S) [ppm] | Methane (CH₄) [ppm] | Carbon dioxide (CO₂) [ppm] |
|----------------------------------|--------------------------|-------------------------------|---------------------|-------------------------|
| Boiler No. 2                     | SLD                      | SLD                           | SLD                 | x                       |
| Boiler No. 3                     | SLD                      | SLD                           | 15                  | x                       |
| Mandatory exposure limit values, according to GD 1218/2006, modified by HG 359/2015 (ppm) (8 hours / 15 min) | 17.5 / 26 | 5 / 10 | 1834 / 2292 | 5000 / - |

Note: SLD - below the detection limit of the device; X - The machine does not display CO₂.

At the monitoring of the perimeter, it has been found that at one of the combustion boilers, namely the boiler number three, methane emissions (in a very low concentration) were identified, which varied, around the 15 ppm. The other gases are below the detection limit of the appliance (see Table 1).
Figure 1. Concentration of the emissions, in the boilers of the battery.

As can be seen, the values recorded in the boilers of the battery, are not exceeded, taking into account the mandatory exposure limit values, in accordance with the GD in force, specified in Table 1, on the establishment of minimum safety and health requirements in work, for the protection of workers, against risks, related to the presence of chemical agents.

3.2. Determination of the amounts of pollutants, in the parks of the reservoirs

In the area under study, 13 parks are in operation, collecting the fluids extracted from the oil wells. Besides, there is also the central warehouse, from where the oil, after being treated, is sent to refineries. The parks of the reservoirs require permanent gas monitoring, because they contain a range of possible sources of pollution, such as, pumps, oil tanks, etc. Emissions of gases, (H$_2$S, methane, etc.), or volatile organic compounds from storage, and oil handling in tanks, or leakage to the valves, or corrosion of tanks may take place.

In order to identify these emissions, the workers are obliged to permanently monitor the existing gas concentration by wearing the gas recording devices. At the sampling of atmospheric emissions, was used, the Microclip XT gas detector, used by the employees of the two parks from where the measurements were made. For a better analysis of pollutant factors, have been made the measurements, for the emissions, in several areas at the parks, and in work barracks, where the working staff carry out much of their work. Among the points chosen, we mention: the gas manifold, the gas separator, the decanter, the injection pump, the fluid reservoirs (SOTs), and even the access road, where all the staff of the park passes from an area to another.

Since there were several sources, the potential for gas emissions, monitoring, was done over a period of about 45 minutes, for each park, with the aim of tracking the evolution of long-term emissions.

After the sampling, it was found that the only existing gas, but not everywhere in the park, is methane, but in concentrations that are quite low, taking into account the exposure limit concentration, according to the law in force (see Table 2). The petroleum parks have been modified in terms of pipes, valves, manometers, etc. These have been changed, together with the modernization of the petroleum parks, which provides greater safety for both, the working place and the environment.

The measurements carried out in Petroleum Park 3, from Independenta, showed that except for methane, (which indicates 15 to 30 ppm, a very low concentration level), only in some areas of the park, the other monitored items were not identified.

| Place where measurements were made | Carbon monoxide (CO) [ppm] | Hydrogen sulphide (H$_2$S) [ppm] | Carbon dioxide (CO$_2$) [ppm] | Methane (CH$_4$) [ppm] |
|-----------------------------------|--------------------------|---------------------------------|-------------------------------|-----------------------|

Table 2. Determinations of NOx, in Park 3, from Independenta.
| Technological area          | Gas manifold | SLD | SLD | X | 30 |
|----------------------------|--------------|-----|-----|---|----|
| Gas manifold               | SLD          | SLD | X   | 15|
| Gas separator              | SLD          | SLD | X   | 15|
| Petroleum park             | Between SOTs | SLD | SLD | X | SLD|
| Access alley               | SLD          | SLD | X   | 15|
| Thermal plant              | SLD          | SLD | X   | 15|

Mandatory exposure limit values, according to GD 1218/2006, modified by HG 359/2015 (ppm) (8 hours / 15 min)

| Place where measurements are made | Carbon monoxide (CO) [ppm] | Hydrogen sulphide (H₂S) [ppm] | Carbon dioxide (CO₂) [ppm] | Methane (CH₄) [ppm] |
|----------------------------------|---------------------------|-------------------------------|---------------------------|-------------------|
| Technological barrack            | Gas manifold              | SLD                           | SLD                       | X                 |
| Manifold                         | SLD                       | SLD                           | X                          | 22                |
| Decanter                         | SLD                       | SLD                           | X                          | SLD               |
| The park                         | Injection pump            | SLD                           | SLD                       | X                 |
| Access alley                     | SLD                       | SLD                           | X                          | SLD               |
| Thermal plant                    |                           |                               |                            |                   |
| Mandatory exposure limit values  | 17.5 / 26                 | 5 / 10                        | 5000 / -                   | 1834 / 2292       |
| according to GD 1218/2006,       |                           |                               |                            |                   |
| modified by HG 359/2015 (ppm)    |                           |                               |                            |                   |
| (8 hours / 15 min)               |                           |                               |                            |                   |

Note: SLD - below the detection limit of the device. X - The machine does not record CO₂.

Figure 2. Value of NOx concentrations, in Petroleum Park 3, from Independenta.

Analysing the results, we find that the value of methane concentration, is very low, compared to the mandatory limit value of 1834 ppm, imposed by the legislation in force, for 8 hours of work.

Table 3. Determinations of NOx, in Park 11 from Independenta.

Note: SLD - below the detection limit of the device. X - The machine does not record CO₂.

Regarding the measurements made in Petroleum Park 11 Independenta, was observed a decrease in methane concentration, as well as the fact that it was detected only in two of the six analysed points.
Because of the results, it was found that neither of the two petroleum parks would endanger the life of employees in terms of emissions, according to the law, regarding the safety and health of workers, against the related risks the presence of chemical agents.

If in the case of combustion plants, (boilers) and tank parks, we can say that the emissions occur as a result of the principle of operation, the data is different at the oil well. The oil well is emitting gases, both from its own source, by the extraction of fluids (oil and gas), and by the installations / equipment's, related to the work at the probe [9]. When the machinery coming, or leaving, from the probe, produces a lot of dust, because most roads are cobblestone, not asphalted. When, at the probe, a more complex activity takes place, with more than one machine, carbon monoxide, at the machine, is up to 5 ppm. At a distance of more than 1 m, the gas is no longer detected.

The monitoring at the oil well was performed with two detection devices, Altair 4X and Altair 5X. The gas detection device, Altair 5X, is used when starting work and after breaks longer than 30 minutes. It is equipped with a lance, which has the role of keeping the worker away, and it is used especially for low areas, such as the basement at the well. This device identifies hydrogen sulphide, carbon monoxide, carbon dioxide, methane and oxygen. The device, Altair 4X, is worn permanently by one of the workers, in particular, those working at the mouth of the probe, or by the one who monitors the fluid exiting.

**Table 4.** Analysis of the amounts of pollutants recorded at the two probes.

| Place where measurements are made | Carbon monoxide (CO) [ppm] | Hydrogen sulphide (H₂S) [ppm] | Carbon dioxide (CO₂) [ppm] | Methane (CH₄) [ppm] |
|----------------------------------|---------------------------|-------------------------------|---------------------------|-------------------|
| The probe for overhaul Oil well mouth | SLD                        | SLD                           | SLD                       | SLD               |
| AM installation Pumps            | 5 (< 1 m)                 | SLD                           | SLD                       | SLD               |
| The probe for intervention Oil well mouth | SLD                        | SLD                           | SLD                       | SLD               |
| IC₅ installation                | 5 (< 1 m)                 | SLD                           | SLD                       | SLD               |

Mandatory exposure limit values according to GD 1218/2006 modified by HG 359/2015 (ppm) (8 hours / 15 min)

| Carbon monoxide (CO) | Hydrogen sulphide (H₂S) | Carbon dioxide (CO₂) | Methane (CH₄) |
|----------------------|-------------------------|----------------------|---------------|
| 17.5/26              | 5/10                    | 5000/-               | 1834/2292     |

Note: SLD - below the detection limit of the device.

Following monitoring, gases with carbon monoxide content were found near the machines at less than 1 m (see Table 4). At a distance of more than 1 m the gas is no longer detected. This gas is not
always detecting even if we are very close to the machine. At the distance less than 0.5 m, carbon monoxide exceeds 30 ppm.

![Figure 4](image)

**Figure 4.** Emissions concentration to the capital repair well.

For a more complex assessment, two probes, one for intervention, and one for overhaul, where there are several machines were chosen. At each of the two probes measurements were made at different points. Gas monitoring is done permanent basis, but for the sampling, was considered, the normal 8-hour working day schedule.

The methane concentration level recorded at the probe for overhaul is very low compared to the exposure limit value, even if one of the workers would have to work near the machinery at less than 1 meter.

![Figure 5](image)

**Figure 5.** Concentration of emissions, at the intervention oil well.

As can be seen, from the two charts, methane has been identified in both situations, in the work, and drive systems of mechanized pliers. The results obtained, as a result of gas monitoring, emanating from the on-site, or work-related equipment, (mouth of the probe), do not indicate, that the worker’s staff, would be at risk, in either of the two probes.

4. **Conclusions**
The results recorded in the four monitored areas of activity, were compared with the Legislation in force, namely, GD no. 1218/2006 modified, by GD 359/2015, laying down minimum safety and health requirements at work, to ensure the protection of workers from the risks related to the presence of chemical agents.

According to art.7 of GD 1218/2006, the mandatory national limit values for professional exposure to chemical agents reflect the utility factors to ensure the health of workers at the workplace. The set limit values, are maximum admissible values [10].

In order to reduce or eliminate emissions from the atmosphere, it is necessary to observe some measures, such as:

- using machines equipped with efficient engines, with low emissions;
- reducing the idling time of the machinery and the means of transport;
- rapid detection of possible leaks, or malfunctions, and immediate intervention to eliminate the causes;
- increasing attention when manipulating fine powders;
- no other sources of polluting gases in the atmosphere, such as open fire, fuelled by solid / liquid fuels;
- in order to limit the emissions of volatile organic compounds into the atmosphere, it will be monitored, the rhythmic evacuation, of the contents of the probe cell, by vacuuming, and the discharge of the contents to the deposit.

Based on the determinations made, we consider that the objective analysed does not affect the environmental factor, (air), under the conditions in which the above mentioned measures are observed, and in the absence of accidents.

By comparing the data with the regulations on the establishment of the minimum safety and health requirements for workers' protection against the risks related to the presence of chemical agents, it was found that the level of the concentration of pollutants discharged into the atmosphere is below the limit values emissions, and below the alert thresholds, and intervention, set for each particular NOx.

5. References

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