Carbon monoxide in the process of uncontrolled combustion - occurrence, hazards and first aid

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Abstract. Carbon monoxide (CO) is a highly toxic gas, odorless and tasteless, belongs to the group of flammable and explosive gases, and is produced by incomplete combustion of fossil fuels in power plants, automobiles, households and various industrial processes. It is very active in chemistry, reacts with many metals, sulfur, chlorine, etc.
As it is flammable and explosive gas, it is a significant risk of its ignition if found near an open flame. Carbon dioxide, dry chemical or water is used for quenching, [1].
The concentration of 1 % carbon monoxide in the air is lethal. Carbon monoxide is toxic and indirectly contributes to global warming as a precursor to ozone. Carbon monoxide emissions from the atmosphere come from a number of sources, most of all traffic. The introduction of catalytic converters, and especially diesel vehicles, has significantly reduced carbon monoxide emissions in the EU and in countries in transition.

1. Introduction
In the process of uncontrolled combustion (fires), substances of organic and inorganic origin, which causes gaseous combustion products, smoke.

Smoke victims are most commonly firefighters and persons present in the facilities affected by the fire. Firefighters and firefighters are often injured by misuse of the equipment or do not use it at all, while others are present because they do not have protective equipment. Toxic effects can occur as acute and chronic. In the fires, both effects are present but are more numerous. Typical chronic poisoning occurs by extinguishing fires in the high temperature. Water during the extinguishing, at these temperatures, decomposes into hydrogen and oxygen, creating a so-called burst gas. The resulting gas will not explode if it is below the lower explosion limit.
The resulting gases (oxygen and hydrogen) get into the smoke, and through it into the body of people exposed to the smoke. In the body, the atoms of hydrogen are bound to the hydroxyl ions in the tissue cells and body fluids, producing acids. This is how acidic diseases such as diabetes, gout and the like occur, [2].

Typically, smaller fires and hearths are viewed with underestimation, though statistics say the opposite. The greatest number of smoke poisoning occurs in such fires, and especially in smoldering fires (fuel matter burns without the presence of sufficient oxygen), [3].
The danger of the effects of smoke on the body is best seen in the example of carbon monoxide. At a concentration of 1 % vol. CO, death occurs after several breaths. Smaller concentrations are also lethal, as shown in Table 1, even concentrated much less than these.
Table 1. Amount of smoke in combustion of one kilogram of fuel [1], [5]

| Fuel                  | Amount of smoke [kg/m³] | Fuel                  | Amount of smoke [kg/m³] |
|-----------------------|-------------------------|-----------------------|-------------------------|
| Acetone               | 8.14                    | Acetylene             | 12.4                    |
| Petrol                | 12.59                   | Butane                | 33.44                   |
| Paper                 | 4.21                    | Hydrogen              | 2.88                    |
| Wood humidity 20 %    | 4.4                     | Methane               | 10.50                   |
| Kerosene              | 12.8                    | Carbon monoxide       | 2.88                    |
| Rubber                | 10.82                   | Propane               | 25.8                    |
| Natural gas           | 10.4                    | Ethane                | 18.16                   |

Carbon monoxide is deadly for health because it damages blood vessels and reduces their elasticity. A large number of firefighters in the world have been dying of "heart" at interventions as a result of the long-term inhalation of this poison in smaller quantities. This, therefore, tells us that carbon monoxide is a very strong blood poison, but its danger is increased because it lacks taste, smell and color, [2].

The rate of carbon monoxide binding to hemoglobin in the blood is influenced by several factors: gender, age, physical fitness, existence of acute and chronic diseases, etc; [3].

2. Carbon monoxide

It occurs in almost all fires, most of which occurs in heterogeneous combustion, in the combustion of solids matters (coal, office furniture, paper, etc.), and especially in indoor fires with poor natural ventilation. Significant amounts are also present in fires with low oxygen diffusion: basement fires, fires in underground garages or underground forest fires.

It is present in homogeneous combustion processes, such as petroleum product fires (petroleum, etc.). Up to 5 % carbon monoxide is present in the smoke of these fuels as well as in the methane smoke. SUS engine exhaust contains 3-7 % carbon monoxide, and cigarette or pipe smoke contains about 4 % carbon monoxide, [1].

The maximum permissible concentration of carbon monoxide in working environments is 50 ppm, or 55 mg/m³, while in fires the concentration of carbon monoxide is always far higher (Table 2).

Thermo-oxidative destructions of solids in a fire result in thermal degradation products of uncontrolled combustion: CO, CO₂, H₂O, lower hydrocarbons, aldehydes, ordinary lower acids, hydrochloride, hydrocarbon, chlorine, acrylonitride, acrolein, ammonia, nitric acid, nitric acid, styrene, amines, methyl alcohol, acetic acid, hydrogen sulfide, etc, [4].

Table 2. Toxicity of some gases and vapors contained in smoke [1], [5]

| Matter                  | Lethal by inhalation at intervals from 5 to 19 min. | Dangerous (poisonous) by inhalation at intervals from 30 to 60 min. |
|-------------------------|-----------------------------------------------------|-----------------------------------------------------------------|
|                         | Concentration                                       |                                                                 |
|                         | vol [%] [mg/l]                                       | vol [%] [mg/l]                                                   |
| Phosgene                | 0.005 [0.2]                                         | 0.0025 [0.1]                                                    |
| Chlorine                | 0.025 [0.7]                                         | 0.0025 [0.07]                                                   |
| Hydrogen cyanide        | 0.02 [0.2]                                          | 0.01 [0.1]                                                      |
| Hydrogen sulfide        | 0.08 [1.1]                                          | 0.04 [0.6]                                                      |
| Carbon disulphide       | 0.2 [6.0]                                           | 0.1 [3.0]                                                       |
| Hydrogen chloride       | 0.3 [4.5]                                           | 0.1 [1.5]                                                       |
| Carbon monoxide         | 0.5 [6.0]                                           | 0.2 [2.4]                                                       |
Petrol & 3,0 & 120,0 & 2,0 & 80,0 \\
Carbon dioxide & 9,0 & 162,0 & 5,0 & 90,0 \\
Acetylene & 50,0 & 550,0 & 25,0 & 275,0 \\
Ethylene & 95,00 & 1100,0 & 80,0 & 920,0 \\

Depending on the type, quantity, composition of the combustible material and the place of burning in the fire, various toxic gases are released. Due to the formation of combustion products, there is a disturbance in the air supply in the combustion zone and consequently carbon monoxide (Table 3).

Table 3. Concentration of individual gases when burning some substances
(approximate values) [1], [5]

| Place of fire | Fuel | Components of combustion products in volume percent |
|--------------|------|--------------------------------------------------|
| Basement of an apartment building | Wood, old things, paper, coal, briquette | 18,0, 1,5, 0,12 |
| Apartment | Furniture, clothes, bedding, bookshelves | 19,0, 1,8, 0,11 |
| Office | Office furniture, shelves, paper | 20,0, 2,8, 0,40 |
| Carpenter's workshop | Material for making furniture, adhesives, upholstery fabrics | 20,0, 0,3, 0,16 |
| Warehouses and sales premises | Paints, varnishes, firmware, crates with goods | 18,0, - , 0,20 |
| Shops and apartments | Books and stationery, food, bread, flour | 20,0, 0,3, 0,3 |

Research conducted in the United States between 2004 and 2006 concluded that the two most common sources of carbon monoxide were stoves and cars in households or garages, while the most common causes and locations were:
- Poorly designed or clogged flue ducts,
- Poor ventilation,
- Gas heating systems,
- Exhaust gases of cars, generators, etc;
- Use of grill (solid or gaseous fuel) in closed spaces,
- Fires caused by a malfunction of household appliances, [3].

2.1 Characteristics of Carbon monoxide
Combustion is accompanied by a bluish smoke-free flame, it is highly toxic because it is easily combined with hemoglobin in the blood and is therefore referred to as blood poison.

If the concentration of carbon monoxide in the air is only 0.3 %, death in humans occurs after 5 minutes, and at a concentration of 1 %, death occurs instantaneously. At higher temperatures, it reduces metal oxides to pure metal, while combusting it can deprive oxygen of other chemical compounds.

This gas combined with hemoglobin in the blood, squeezing out oxygen, creating a compound carboxyhemoglobin, which is more stable than oxyhemoglobin. The affinity of hemoglobin for carbon monoxide is greater than its affinity for oxygen, [4].

This gas is poisonous, lighter than air and first fills the upper parts of the premises, which should be kept in mind during a fire, and is a fire gas that causes flashover or backdraft.

We use spray water, carbon dioxide and dry chemicals to extinguish.
Table 4. Carbon monoxide property [5]

| Property                                      | Value       |
|-----------------------------------------------|-------------|
| Molecular weight                             | 28.01       |
| Molecular volume                             | 22,400 ml   |
| Weight 1 l at 0 °C and 760 mm of mercury column | 1,250 gr    |
| Boiling point                                | -191.5 °C   |
| Density (air = 1)                             | 0.9669      |
| Density (water = 1)                           | 0.00125     |
| Melting point                                | -207.0 °C   |
| Critical temperature                         | -140.2 °C   |
| Critical pressure                            | 34.5 bar    |
| Flash point                                  | -140.2 °C   |
| Lower explosive limit                        | 12.5 %      |
| Upper explosion limit                        | 74.2 %      |
| Specific gravity of liquid carbon monoxide at -140 °C | 0.4258     |
| Specific gravity of liquid carbon monoxide at -205 °C | 0.8558     |

2.2 Presence of Carbon monoxide in the Atmosphere

The amount of carbon monoxide in the unpolluted atmosphere is small and ranges from 0.008 to 0.174 ppm, with average concentrations being about 0.0877 ppm. The main emitters of carbon monoxide in the atmosphere in addition to traffic and energy are industrial processes, solid waste landfills (due to fire), forest fires, waste combustion in agriculture, fires in homes, coal mines, etc.

If there were no processes that eliminate carbon monoxide from the atmosphere, concentrations would emerge that would have incomprehensibly dire consequences. The fact is that the lifetime of carbon monoxide in the atmosphere is 0.2 - 3.0 years and that there is no global increase in the content of this pollutant in the atmosphere. From this it can be seen that in the atmosphere processes are taking place which eliminate it.

From many of these processes, some of the most significant will be pointed out. The carbon monoxide found in the lower atmosphere, atmospheric currents, can reach the upper layers, where it converts to carbon dioxide with the help of ultraviolet radiation and the present nitrogen dioxide.

Carbon monoxide in contact with soil can oxidize to carbon dioxide and can also be converted to methane by anaerobic microorganisms that produce methane (Methanosarcina bakterii and Methanobacterium formicum), [6].

The elimination of carbon monoxide from the atmosphere by water absorption in the oceans and seas can logically be assumed. This is supported by the fact that the composition of seawater is suitable for the absorption and dissolution of carbon monoxide, [6].

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For the colorimetric determination of carbon monoxide, palladium-impregnated silica gel is also used in the carbon monoxide rapid measuring apparatus, such as in the Dräger accessories.

In a glass tube about 10 cm long, narrowed and warmed on one side, there is first a layer of sulfur trioxide impregnated silica gel to purify the suction air and then silica gel with palladium. When used, the top of the pipe breaks off and the air is sucked in by a hand pump of a certain volume. With 20 pumping, 0.05 % of the carbon monoxide volume can be demonstrated, based on the change in color from gray to completely black, i.e. from green-yellow to yellow-brown, [7].

Depending on the technology used to make the sensor, as well as the type of detection, we distinguish the following types of CO detectors:

1. An optical-chemical detector sensor with a substance insert that in contact with CO changes the color, thereby identifying its presence. The advantage of this type of detector is the low cost, while the disadvantage is reflected in the low degree of protection, because the color change information of the sensor is more difficult to transmit remotely (to the control panel).

2. The bioimitation detector sensor is a disc made of synthetic hemoglobin and in contact with CO, reacts like hemoglobin in the blood, and an infrared beam of light passing through the disc is monitored in the detector.

3. The semiconductor detector is based on the SnO2 tin oxide semiconductor, which is heated by electric current to a temperature of about 400° C at certain intervals, at which contact with CO changes the resistance (O2 increases and CO decreases the resistance). The advantage of this type of detector is its durability and responsiveness, but they also have disadvantages over other detectors, which are reflected in: more expensive maintenance, a preference for false alarms caused by CO-free gases and vapors.

4. Sensors of electrochemical detectors are semiconductor elements of tin oxide (SnO2) or zinc oxide (ZnO), and in contact with CO change the electrical resistance. They can also be used to detect hydrocarbons. This type of detector uses two platinum electrodes and an electrolyte (most commonly sulfuric acid); CO is oxidized at one electrode, converted to CO2, while oxygen is released at the other electrode, so that the concentration of CO in the immediate atmosphere can be accurately determined based on current measurements. Compared to the types of sensors listed above, the electrochemical cell has a high precision and almost linear response to the rise of CO.

According to the latest standards in developed countries, carbon monoxide detectors are required to be placed in schools, hospitals, hotel rooms or other rooms for children, the elderly or handicapped, and the alarm signal generated after the detection of carbon monoxide must be different from other alarms, [3].

3. Carbon monoxide poisoning

The toxic properties of carbon monoxide are based on its reaction with hemoproteins. Such is the irreversible reaction of carbon monoxide with hemoglobin to produce carboxyhemoglobin. Oxygen and carbon monoxide react with chemo-globin in a similar way and their further blood transfer depends on the reaction with iron in the chemo-prosthetic group. The affinity of hemoglobin for carbon monoxide is about 210 times greater than the affinity for oxygen, [8].

The presence of carboxyhemoglobin in the blood blocks the process of oxygen exchange in the cells and thus the introduced carbon monoxide into the body directly affects the central nervous system and the cardiovascular system.

In order to understand the importance of the effect of carbon monoxide on the central nervous system, it should be recalled that the human brain makes up 2 % of the total body, and consumes 20 % of the total oxygen input. It can be seen that the higher presence of carbon monoxide in the air can have serious consequences on the central nervous system, but to a certain extent it also depends on the individual characteristics of the person, [6].

Important facts about the manifestations of the effect of low concentrations of carbon monoxide on humans, [6]:

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- Constant or intermittent exposure to CO leads to headache,
- The toxic impact of CO on the cardiovascular system is especially pronounced in people who already have a problem with this system,
- The effect of CO is more pronounced at higher altitudes due to the lower partial pressure of oxygen in the air,
- Exposure to CO at concentrations that typically occur in urban air may lead to increased carboxyhemoglobin content in the blood. On prolonged exposure, it can lead to disruption of the oxidation process in tissue cells, that is, disruption of the metabolism and energy in tissue cells,
- Continuous exposure to low concentrations of CO can lead to a constant toxic reaction, e.g. chronic carbon monoxide poisoning syndrome,
- Drivers who are often on the road are constantly reduced in oxygen content, which is one of the causes of traffic accidents. This is especially pronounced with older drivers,
- CO has the effect of reducing visual sensation, psychological stability, and sense of time intervals. This can lead to road accidents for drivers who are long on the road, that is, constantly exposed to carbon monoxide.

A fatal outcome occurs when exposed to a large amount of carbon monoxide over a short time interval, or from exposure to a lower dose of carbon monoxide over a longer time interval (Table 5).

| Concentration [ppm] | Symptoms |
|---------------------|----------|
| 50                  | No effect when exposed to up to 8 hours. |
| 200                 | A slight headache after 2-3 hours. |
| 400                 | Headache and nausea after 1-2 hours. |
| 800                 | Headache, nausea and dizziness after 45 min; loss of consciousness after 2 hours. |
| 1000                | Loss of consciousness after 1 hour. |
| 1600                | Nausea, dizziness, after 20 min. |
| 3200                | Nausea, dizziness, after 5-10 min; loss of consciousness after 30 min. |
| 6400                | Nausea, dizziness, after 1-2 min. loss of consciousness after 10-15 min. |
| 12800 (1.28 %)      | Instant psychological effects, loss of consciousness, death after 1-3 min. |

During short-term inhalation of air containing a high percentage of carbon monoxide leads to rapid loss of consciousness, cessation of breathing, and then death.

When the injured person begins to feel unwell, he is often no longer able to pull himself out of danger. The poisoning process is accelerated because the effort to breathe is higher, causing oxygen to be consumed more, so those with signs of carbon monoxide poisoning should be referred to an emergency room.

The harmfulness of carbon monoxide to the body is based on the ease with which it is absorbed by the red blood cells (hemoglobin). This substance, which turns blood red, has the task of binding oxygen to the lungs and then transmitting it to the tissues. Hemoglobin has a greater affinity for carbon monoxide than for oxygen from the air, because it binds to it about 210 times easier than with oxygen, [4]. This means that when air contains the least amount of carbon monoxide, they are sufficient to saturate a considerable portion of the red pigment matter of the blood. This is very detrimental because the carbon monoxide absorbed hemoglobin no longer participates in oxygen transfer. Depending on how increasing amounts of carbon monoxide block hemoglobin, the ability of the blood to transport oxygen from the lungs to the tissues is declining and as a result, the body's oxygen supply is diminished, [2].
3.1 Providing help and protective equipment

The most important thing is to remove the poisoned person from the atmosphere containing CO. It is understandably that in such cases lifeguards must take all necessary measures for personal protection (protective masks with filters intended for carbon monoxide; Figures 3 and 4, breathing apparatus of open or closed systems; Figure 5), so as not to endanger their lives and the injured.

Persons who have been diagnosed with carbon monoxide poisoning should be given oxygen and given artificial respiration (if unconscious) and referred to an emergency room. Oxygen in this case acts as an antidote, as it compensates for hypoxia in the blood and soft tissues, displacing CO. Only people who have undergone professional medical training can help to oxygen poisoned persons with CO.

Depending on the atmospheric environment and the need to use respiratory protective equipment, the aforementioned agents can be classified into two groups:

1. Protective means on the basis of filtration – dependent surrounding:
   - Protection made of aerosol (mechanical protective filters with halfmasks for protection of respiratory organs pic. 1a)
   - Combined protection from gases and aerosol (halfmask or mask for the whole face and filters with the active filling with the specific intention for protection of respiratory organs, face and eyes; Figure 3 and 4), [4].

![Figure 3. Full face protection mask with a combined filter, [4]](image1)

![Figure 4. Combined section filter, [4]](image2)

The carbon monoxide filter box mask may only be worn when the concentration of carbon monoxide in the atmosphere is not more than 2 % by volume and when there is assurance that the atmosphere contains sufficient oxygen.

Depending on the purpose, the filters can be divided into:

- Mechanical (protection against particles and aerosols),
- Gas (protection against one or more gases),
- Combined (Figure 4) (protection against organic and inorganic gases - for one or more gases, particles and aerosols) and
- Special (e.g; protection against low boiling point materials, including radioactive iodine, mercury vapor, nitrogen gas and carbon monoxide).

Depending on the environment or the contaminated zone, different types of filters are used, (Table 6).
2. Protective means on the basis of isolation – independent surrounding for protection of respiratory organs and face:
   - Tube devices (tube apparatus with air from unpolluted environment, tube apparatus with the bellows, tube apparatus without bellows, tube apparatus with air under the pressure of water).
   - Breathing apparatus with the open system (devices with the container of compressed air, selfrescuer; Figure 5).
   - Regenerative apparatus with the closed system (breathing apparatus with compressed oxygen, and apparatus with chemically bound oxygen), [4].

With the introduction of breathing apparatus in use, the protection of the respiratory organs, face and eyes was increased, both from aggressive substances, smoke products, and partly from heat. Using them, the user is completely isolated from the atmospheric environment, that is, the action of the contaminated atmosphere, [4].

\[\text{EN 14387}^{1}\]
\[\text{EN 371:1992}^{2}\]
\[\text{EN 371:1992}^{2}\]
\[\text{EN 58620:2007}^{3}\]
\[\text{DIN 3181}^{4}\]

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**Table 6. Respiratory protection filters (color codes) [4]**

| Color | Tip | Protection | Standard |
|-------|-----|------------|----------|
| A     | Organic gases and vapors (boiling point> 650° C) | EN 14387$^1$ |
| B     | Inorganic gases and vapors (not CO); ex: chlorine, H$_2$S, HCN. | EN 14387 |
| E     | Sumpordioxide and acid gases and vapors. | EN 14387 |
| K     | Ammonia and organic ammonia derivatives. | EN 14387 |
| AX    | Organic gases and vapors (boiling point <650° C) or low-boiling substances of Group 1 and 2. | EN 371$^2$ or EN 14387 |
| NO-P3 | Nitrogen oxides; eg NO, NO$_2$, NOx and particles | EN 14387 |
| Hg-P3 | Mercury vapor and particles. | EN 14387 |
| CO$^*$ | Carbon monoxide. | DIN 58620$^3$ or EN 14387 |
| Reactor P$^3$ | Radioactive iodine and particles. | DIN 3181$^4$ |
| P     | Particulate matter. | EN 143 | EN 14387 |

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$^1$ EN 14387 – Requirements, testing and marking of protective respiratory devices, gas and combined filters.
$^2$ EN 371:1992 – Certification of protective respiratory devices, gas and combined filters for organic compounds with low boiling point.
$^3$ DIN 58620:2007-2 – Requirements, testing and marking of protective respiratory devices, gas and combined filters of carbon monoxide.
$^4$ DIN 3181 – gases and vapors of organic and inorganic components, acids and vapors with boiling point >65° C.
4. Conclusion

In order to avoid carbon monoxide poisoning in various processes, it is necessary to strictly consider what protection measures we will apply:

1. Compulsory constant control of carbon monoxide concentration in the working atmosphere, good ventilation of rooms and workplaces, as well as mandatory use of personal protective equipment.

2. In case of fire, exert a natural (free-flowing air) or forced ventilation of the premises (by means of an overpressure or overpressure smoke fan).

3. Regular medical control of workers, once every 6 months, as well as previous medical examinations.

4. Anemic and frail individuals should not be in contact with carbon monoxide during work.

The most reliable method for testing carbon monoxide poisoning is by laboratory testing of blood samples.

As aforementioned, when entering fire-affected rooms, parts of the building or structures, the respiratory, face and eye protection equipment and breathing apparatus must be used to provide adequate protection to users against all hazardous substances and even against biological or radiological agents.

The advantage of insulating appliances over protective masks with strainers is that we need to know in advance what matter is and what strainers provide protection only for the substances for which they are intended, while insulating devices protect against dangerous substances, although we do not know for sure what matter or substances is it.

Ordinary strainers (military destined for war poisons) cannot be protected from some combustion products (especially carbon monoxide and CO2), since the base of the strainer is filled with activated carbon which has the property of absorbing harmful particles from the air but cannot absorb carbon monoxide and CO2 because they have same carbon base.

When entering the above mentioned rooms where there is a large amount of heat and smoky smoke, the spray nozzles must be directed to the upper layers of the rooms, in order to reduce the temperature of the fire gases, including CO, contained in the upper layers by means of the sprayed water. above the upper explosion limit and which are heated to self-ignition temperature. At the same time, there is airflow, and therefore oxygen is introduced from the air, which introduces fire gases into the explosive area, and the current can raise sparks, causing an explosion. In this situation, currents can cause sparks and explosion, which should be taken into account. If the fire gases are heated to the temperature of self-ignition, in the presence of fresh air entering the room, an explosion may occur, although its currents do not raise sparks in the upper layers of the room.
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