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Industrial Safety Analysis of Accidents Involving Ammonia, with Special Regard to Cold-Storage Facilities

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Anhydrous ammonia is widely used in industry and it is one of the most dangerous materials produced, transported and used in largest quantities. From the viewpoint of industrial safety, this material is essential, as it is present at almost every branch office of disaster management, and the number of major industrial accidents involving ammonia has recently increased. In fact, few articles and literature deal with this issue.

The main purpose of the article is to remedy this deficiency as well as to provide professional help for first responders, members of the professional authority and the higher education students in the field of industrial safety.

Keywords: *ammonia, ammonium hydroxide, chemical reconnaissance, respiratory protection, protection of body*

Introduction

Before we dive into chemistry, practical industrial safety and chemical protection, the definition of first responder is in order. A first responder may be a firefighter (professional, volunteer or industrial), but according to the Government Decree 219/2011 (X. 20.) Hungarian on the protection against major accidents involving dangerous substances, the first responder may also be a "civilian" member of the so-called industrial intervention team at establishments obliged to develop an internal safety plan and an Operations Security Plan. [1] This article attempts to make this work easier and to offer a practical assessment of a dangerous material from the viewpoint of industrial safety and the related emergency planning procedure.

Anhydrous ammonia is one of the inorganic substances produced in the largest quantities. As a direct result of its wide use, industrial safety professionals and counsellors definitely encounter it at some point in their work. Establishments producing ammonia start with the production of the liquid anhydrous ammonia and then they manufacture the aqueous solution of ammonia, which is a raw material in chemistry acting as an intermediate and a processing aid in industry (mainly chemical industry). The wide range of uses of ammonia and the fact that it is often stored, transported and used in great amounts in residential areas make this topic an imperative issue.

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The paper attempts to present the use of anhydrous ammonia in cold storage facilities from the viewpoint of industrial safety, from planning for emergencies to emergency responses. Due to the complexity of the topic, the article will be published in two parts. The first one describes the physical and chemical hazards of ammonia together with the evaluation and impact analysis of safety risks, whereas the second one deals with emergency response. (Table 1)

Table 1. The summary of data needed to label anhydrous ammonia.
([2] [3], compiled by the authors)

UN number	1005
CAS number	7664–41–7
R-phrases	R10 Flammable R23 Toxic by inhalation R34 Causes burns R50 Very toxic to aquatic organisms
S-phrases	S1 Keep locked up S2 Keep out of the reach of children S9 Keep container in a well-ventilated place S16 Keep away from sources of ignition – No smoking S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice S36/37/39 Wear suitable protective clothing, gloves and eye/face protection S45 In case of accident or if you feel unwell seek medical advice immediately (show the label where possible) S61 Avoid release into the environment. Refer to special instructions/safety data sheet
H-phrases	H221 Flammable gas H280 Contains gas under pressure; may explode if heated H314 Causes severe skin burns and eye damage H331 Toxic if inhaled H400 Very toxic to aquatic life
P-phrases	P210 Keep away from heat/sparks/open flames/hot surfaces – No smoking P260 Do not breathe dust/fume/gas/mist/vapours/spray P273 Avoid release into the environment P280 Wear protective gloves/protective clothing/eye protection/face protection P303+P361+P353 IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower P403+P233 Store in a well ventilated place. Keep container tightly closed P501 Dispose of contents/container to hazardous or special waste disposal collection site
GHS/CLP pictograms	

Industrial Uses

Main uses of ammonia:

- as an intermediate: production of nitric acid, fertiliser, bases, dyes, pharmaceuticals, vitamins, cosmetics, synthetic textile fibres, plastic;
- as a processing aid: photographic processes, cooling systems, insulation, ink cartridges, toners, diluents and paint removers, detergents, textile dyeing and treating;
- as a treating substance: treating paper, leather, rubber/latex, wooden and metal surfaces, electronics and semiconductor industry.

Further uses:

- a laboratory chemical, refrigerant (in cooling systems), heat treatments, ph-regulation and neutralisation, processing aid in food production;
- in the following products: water treatment materials, fertilisers, diluents and paint removers, photographic chemicals, detergents, leather and other surface treatment materials;
- in the following products: diluents and paint removers, insulation materials, detergents, cosmetics, hygiene products;
- excavation of metallic ores, removal of nitrogen oxide and sulphur dioxide (as a reducing agent).

The list above clearly demonstrates the wide range of uses of ammonia, but for the purposes of our paper, the main use is industrial refrigeration, as it affects the relevant division of almost all county directorates for disaster management.

Physical and Chemical Properties of Ammonia and Ammonium Hydroxide

The response team must bear it in mind that when anhydrous ammonia mixes with air, it reacts with moisture in it and ammonium hydroxide is formed usually in the form of a vapour-like cloud. (Table 2)

Table 2. Brief summary of the physical and chemical properties of ammonia and ammonium hydroxide. ([4] [5], compiled by the authors)

Properties	**Chemical compounds**	
Name	ammonia	ammonium hydroxide
Formula	NH_3	NH_4OH
Physical state; appearance	colourless, gas or dense, liquefied gas with distinctive, pungent odour, in the presence of water it can form ammonium hydroxide	colourless liquid with pungent odour, basic, unstable
Physical properties	Boiling point: –33 °C Freezing point: –78 °C Solubility in water at 20 °C: 54g/100ml Vapour pressure at 26 °C: 1013 kPa Relative vapour density (air = 1): 0.60 Autoignition temperature: 651 °C Explosive limits, volume % in air: Lower explosive limit: 16% Upper explosive limit: 25%	Boiling point: 37.7 °C (25%) 24.7 °C (32%) Freezing point: –57.5 °C (25%) –91.5 °C (32%) Solubility in water: in all proportions
Chemical hazards	Ammonia is a strong base. It reacts violently with acids and it is corrosive. It reacts vigorously with oxidants, halogens. It is corrosive to copper, aluminium, zinc and their alloys. While dissolving in water, it produces heat.	It may react violently with acids, strong oxidants, halogens, acrolein, acrylic acid, dimethyl sulphate, silver nitrate, silver oxide, hypochlorite, mercury, etc. Ammonia solutions are corrosive to copper, zinc, aluminium and their alloys.

Operation of Vapour-Compression Refrigeration Systems

Vapour-compression refrigerators remove heat from the enclosed space and transfer it somewhere else (to a clearly separated place) by circulating a refrigerant (characterised by appropriate properties). The refrigerant enters the compressor as a vapour, which raises its pressure and temperature as well. This high-pressure, hot vapour becomes superheated in the compressor. Next, the superheated vapour reaches the condenser, which is a special heat exchanger where vapour is cooled with cooling air or cooling water, and then it is condensed. The refrigerant is routed through the condenser, a coil or several parallel tubes, which rejects the heat extracted from the system to water or air. The condensed, liquid refrigerant then passes through a throttling device (a restriction with a small orifice, a capillary tube or a controllable expansion valve). In the throttle, an adiabatic process occurs: the pressure of the liquid refrigerant suddenly drops and one part of it evaporates, which decreases its temperature to lower than that of the enclosed space. (This phenomenon is similar to the well-known process that occurs when a carbon-dioxide cartridge is pierced: the temperature of the cartridge drops so abruptly that air moisture around the leak freezes.)

The evaporator transfers the heat absorbed from the enclosed space to the circulating refrigerant and finally it is rejected in the condenser. At the end of the refrigeration cycle, the saturated refrigerant vapour leaves the evaporator and enters the compressor once again, and the whole process is repeated. [6]

From the viewpoint of the response team, it is important for them to become acquainted with the whole cycle, including the stages of compressed gas, compressed liquid and vacuumed gas. (Figure 1)

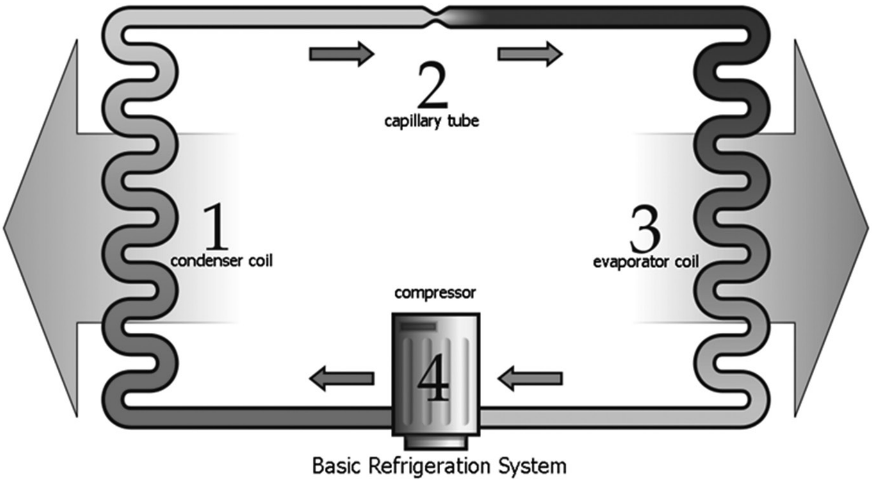

Figure 1. Simplified representation of a typical single-stage refrigeration system. Condenser coil (1), capillary tube (2), evaporator coil (3) and compressor (4). [7]

Potential Accidents and Related Hazards of Refrigeration Systems

The risks are basically associated with the physical and chemical characteristics of refrigerants in addition to the pressure and temperature in the refrigeration cycle. Inadequate preventive measures and responses might lead to the following events:

- damage or even explosion of fittings, including the risk presented by flying particles;
- release of refrigerant as a result of fracture or refrigerant leak due to poor design and maintenance, improper operation, repair or recharge;
- fire risk resulting from leaking refrigerant, which is flammable and explosive.

Anhydrous ammonia and its chemical compounds with oils, water and other substances in the refrigeration equipment chemically and physically affect materials in the equipment, for example as a result of pressure and temperature. If the chemical compounds have dangerous properties, they may directly or indirectly endanger the staff, other equipment, the environment or even the population. The dangers coming from the pressure and temperature conditions are basically rooted in the combined presence of gas- and liquid-phase. Furthermore, the condition of the refrigerant and the various fittings depends on external effects as well, in addition to internal processes.

The Following Dangers Are Worth Mentioning

Due to direct effects of low temperature:

- materials become rigid;
- freezing of liquids in the closed system (water, saltwater, etc.);
- thermal stress;
- change in volume as a result of change in temperature;
- personal injuries as a result of low temperature.

Due to high pressure:

- increased condenser pressure caused by inappropriate cooling, the partial pressure of uncondensed gas or the presence of refrigerant oils or liquids;
- increased saturated vapour pressure caused by significant excess heat getting in the refrigeration system, for example when defrosting air-cooled water chillers;
- volume change (expansion) of the liquid refrigerant in closed space without the presence of gas, caused by the increase in external temperature;
- fire.

Due to immediate effects of the liquid phase:

- overcharged refrigeration system;
- presence of water in the compressor as a result of siphon effect or condensation in the compressor;
- liquid slugging in the pipeline;
- poor lubrication as a result of oil emulsion formation.

Due to release of refrigerants: [8]

- fire;
- explosion;
- toxic effect;
- irritation;
- frostbite;
- suffocation;
- panic.

Industrial Safety Assessment [9] [10]

In this part of the paper, the industrial safety assessment of below-tier establishments is introduced. In Hungary, the use of ammonia in cold storage facilities does not exceed the threshold level.

Threat presented by below-tier establishments is assessed on the basis of 5.3 and 5.4, Appendix 7, of the Government Decree 219/2011 (X. 20.).

To assess the threat of fire and explosion to assembly buildings, the extent of the consequences of major accidents need to be taken as the basis first. The threat is acceptable without further examination if thermal radiation caused by the fire does not exceed 8 kW/m^2, and the shock wave caused by the explosion does not reach 10 kPa in the given dwelling area or assembly building.

Threat of exposure to toxic materials without further examination is acceptable provided that expected death rate in case of a major accident is not higher than 1%.

The possibility of an accident has to be examined if its frequency reaches 10^{-8}/year. To determine this value, frequency analysis is used, which is mostly performed by HAZOP method in Hungary.

If the death rate of an incident with frequency over 10^{-8}/year is higher than 1% in a dwelling area or in an assembly building and exposure to thermal radiation is over 8 kW/m^2 or 10 kPa, the threat is considered non-neglectable.

In the case of a non-neglectable threat, responsibility is determined with the help of quantitative risk assessment as part of the standard assessment procedure in dangerous establishments. Individual and societal risks that come from the activities in the plant are expressed and evaluated according to Appendix 7, of the Government Decree 219/2011 (X. 20.).

Data collection and organisation, preliminary analysis

Before carrying out the analysis, it is necessary to obtain the instructions for use and maintenance of the technologies of the establishment. Based on the available documents, missing information can be requested from the establishment under investigation.

Compiling a list of hazardous materials present

In accordance with Appendix 1 of the Decree, the first step of the analysis is to identify which hazardous materials are present and then to carry out calculations to identify the establishment.

The general guidelines of the list are the following:

- In the case of a refrigeration system, the nominal (maximum) net weight has to be taken into account.
- The operator makes conservative estimates on the amount of the hazardous materials present.

According to the calculations, it can be determined whether the given materials listed in Chart 1, Appendix 1 of the Government Decree 219/2011 (X. 20.) reach the threshold level or not in the establishment under investigation. The identification numbers regarding the threshold levels are determined based on the summation rule laid down in Appendix 1 of the Decree.

If the result of the calculation does not reach 0.25, the establishment do not belong to any of the categories. However, due to the 1000kg of ammonia present, it has to be regarded as an establishment of high priority (and below-tier establishment) in line with Act CXXVIII of 2011 (Disaster Management Act).

Identifications of Dangerous Facilities

1. Analysis based on selection and indication numbers

Examining the characteristics of materials present in the establishment and potential inherent risks presented by them.

2. Excluding certain materials

In accordance with Paragraph 6, Article 9 of the SEVESO Directive and Appendix 6 of the Government Decree 219/2011 (X. 20.), safety reports and the quantitative risk assessment included do not need to contain certain substances which are present (in the plant or in any division of the plant) only in a state that cannot generate a major accident hazard. In the analysis, none of the dangerous materials present can be omitted or neglected as they might affect the requirements for exemption.

3. The selection process

If the safety plan is included in the Operations Security Plan, it is not necessary to consider the threat posed by each division of the establishment. However, it is essential to take into account the divisions that significantly contribute to the overall threat presented by the establishment. A selection process, the so-called *Dutch* method[5] was developed, which is based on the quantity of the materials present in the establishment and the technological conditions. Its purpose is to select establishments that need to undergo a detailed quantitative assessment. The selection process consists of the following steps:

- The plant has to be divided into separate establishments. In each establishment, the quantity of the material, its dangerous characteristics and the nature of the technology define the establishment's own risk. Indication number "A" signals the extent of the establishment's own risk. This number is calculated according to the procedure described below.
- The danger presented by an establishment is calculated for several points in the vicinity of the plant. The indication number and the distance between that point and the establishment determine the hazard itself. The level of the risk in the given point is expressed in the selection number S.
- An establishment needs further analysis if its selection number exceeds one at any point on the boundary of the establishment (or on the bank opposite the establishment) and this number is over 50% of the highest calculated selection number for all establishments at the point nearest to the residential area (that is already existing or just planned to be built in the future).

Effects of toxic substances can reach considerably farther than the effects of flammable substances. If we only select establishments with flammable substances, and the selection number of establishments with toxic substances is similar to the highest selection number, the establishment with toxic substances must not be neglected in the quantitative risk assessment.

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5 Reference Manual published by the National Institute of Public Health and the Environment (RIVM) in the Netherlands is recognised as benchmark in our analysis. The purpose of this publication is to offer a uniform approach to the emerging practical issues in SEVESO analyses. Paragraph 3.4.6.10 of the literature cited deals with toxic gases with low reactivity despite being flammable and explosive (allyl chloride, epichlorohydrin, carbon monoxide, ammonia, etc.)

In the selection process, the database on the quantity of hazardous materials is consulted and those materials that are taken into account which are considered dangerous by Government Decree 219/2011 (X. 20.) on the detailed rules for certain procedures and activities related to dangerous substances and dangerous preparations. The results of the assessment are presented in a table.

Consequence analysis

To simulate the release of the toxic gas, the dispersion modelling common in disaster management is applied and the results of the calculations are illustrated on a map. (Figure 2)

Specifying the Zone of Ammonia

Probit regression

The expression "probit" itself was created by the blending of probability unit. It is a commonly used unit in statistics to study the relationship between dose and effect, that is, to what extent (in percentages) certain doses trigger a reaction in the experiment. We start from the hypothesis that sensitivity of the individuals is log-normally distributed, so the logarithm of the doses follows a normal distribution. The distribution shows the relative frequency of a reaction at a certain log-dose value. To start with, the percentage is transformed into a probit by dividing the standard normal distribution into parts with a lot of similar cases. To avoid negative numbers we add 5 to the normal deviate and the result is called the probit. Tables are available to generate probits. [11]

$$P_{let} = 0,5 \cdot \left[1 + erf\left(\frac{Pr - 5}{\sqrt{2}}\right)\right]$$

$$Pr = A + Bln\left(\int_0^t C^N dt\right)$$

P_{let} = probability of lethality;
Pr = probit value;
C = concentration [ppm];
n = substance-specific exponent;
t = the exposure period;
A and B are constants.

The relationship between the probability of lethality and the concentration of NH3 can be determined with the help of the probit values proposed by the *Rijksinstituut voor Volksgezondheid en Milieu* (RIVM):

A = –15.6; B = 1; N = 2 (Determining the toxicity of ammonia.)

The proposed probit values can be used if the concentration is expressed in units of mg/m^3.

- Red zone represented on the map: after 30 minutes the expected probability of lethality = 1 (it corresponds to NH3 concentration of 4348 mg/m^3)
- Ochre yellow zone: after 30 minutes the expected probability of lethality = 0.1 (it corresponds to NH3 concentration of 2509 mg/m^3)
- Lemon yellow zone: after 30 minutes the expected probability of lethality = 0.01(it corresponds to NH3 concentration of 1678 mg/m^3)

The consequence analysis of a hypothetical scenario by applying the methods above

The 8.4 m^3 separator tank in the refrigeration system contains ammonia to 80% of the total volume, when the tank splits open and scenario G.1 follows (found in Table 3.3, CPR 18). As a result of a LOC event, 5168 kg of ammonia at –8 ^{o}C is released. The pressure in the tank is 3.15 bar. Ammonia is a gas lighter than air, so its spread is defined by meteorological conditions, especially the external temperature. Typically, in winter ammonia leaks form "thick clouds". (Table 3)

Analysis conditions:

- To illustrate the most serious consequences, D5 atmospheric conditions are hypothesised, following internationally accepted practices.
- The value of the articulateness of surface corresponds to industrial or suburban areas.

Table 3. The brief summary of a hypothetical incident involving ammonia.
(Generisk Kft, compiled by Kocsis Zoltán)

Characteristics of the scenario	**Value**
Total amount released	5168 kg
Amount immediately released in the atmosphere	448 kg
Release time	immediate
NH3 flux	–
Air temperature	20 °C
Humidity	50%
Wind speed	5 m/s
Pasquill class	D
Altitude of release	3 m
Articulateness of surface	0.03 m

Toxic effects of ammonia

The program is called *Breeze Incident Analyst* used for modelling.

The probit relations between concentration and lethality are calculated on the basis of the above mentioned description.

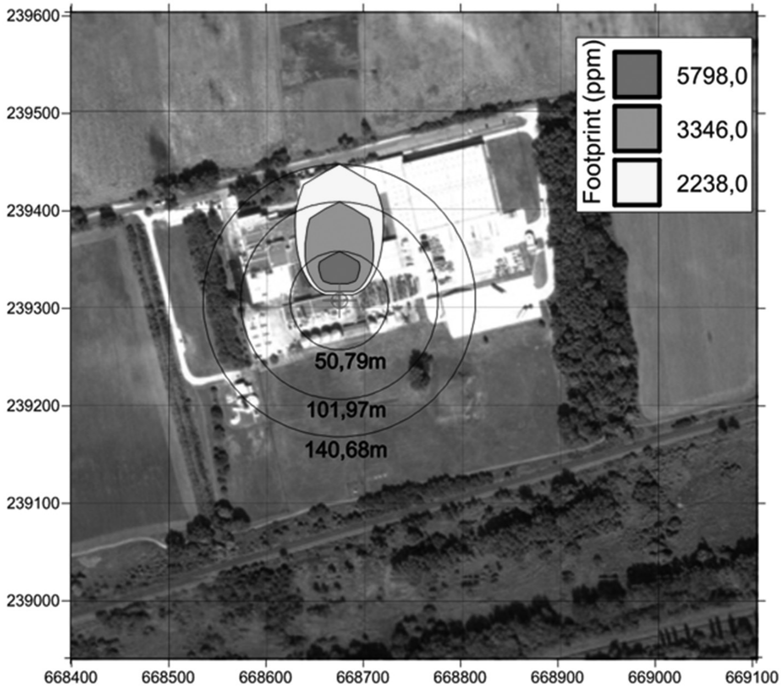

Figure 2. The map represents the various danger zones of a hypothetical incident involving ammonia. (Generisk Kft, compiled by Kocsis Zoltán)

Based on the results of the consequence analysis, the following statements can be made: (Figure 2)

- The radius of zone P = 1 (4348 mg/m^3) [5798 ppm] at 1 m height is 51 m.
- The radius of zone P = 1 (2509 mg/m^3) [3346 ppm] at 1 m height is 102 m.
- The radius of zone P = 1 (1678 mg/m^3) [2238 ppm] at 1 m height is 141 m.

Summary

All potential threats posed by anhydrous ammonia in cold storage facilities are discussed in the paper. The procedures supporting risk assessment of the establishments are described, namely the threats to personnel or even the population in the surrounding areas. Dispersion modelling can predict the vulnerability zones and the probable consequences of an accident involving anhydrous ammonia, which provide details for a thorough operational safety plan essential for the mitigation and relief following accidents in cold-storage facilities.

These plans are advantageous because no unnecessary safety costs are imposed on the operator. Disaster management and the emergency unit of the establishment can prepare for the risks and their consequences. The personnel and the affected population, being aware of the risks, can be properly prepared to follow necessary instructions smoothly (e.g. evacuation) coming from the authorities.

The paper describes an example of a potential event involving ammonia and depicts it on a map together with the solution.

References

[1] *Government Decree 219/2011 (X. 20.) on the protection against major accidents involving dangerous substances.*

[2] BORSOD CHEM: *Biztonsági adatlap (SDS), Ammónia.* Kazincbarcika: BorsodChem Zrt., 2010. 11. 30. www.ammonia.hu/letoltheto_dokumentumok/sds_ammonia_10_hu.pdf (downloaded: 25 01 2014)

[3] Anhydrous Ammonia – Refrigeration Grade. Safety Data Sheet. *Federal Register,* 77 58 (2012), 1–7. http://msds.simplot.com/datasheets/11004.pdf (downloaded: 25/01/2014)

[4] ORSZÁGOS TISZTIORVOSI HIVATAL. Munkahigiénés és Foglalkozás-egészségügyi Főosztály. www.omfi.hu/index.php (honlap) (downloaded: 25 01 2014)

[5] NITROGÉNMŰVEK Zrt. (honlap) www.nitrogen.hu/(downloaded: 25 01 2014)

[6] JAKAB Z.: *Kompresszoros hűtés, I–II.* Budapest: Magyar Mediprint Szakkiadó, 2000.

[7] FRIDGEMAN: *The Refrigeration Cycle*. June 4, 2008. https://fridgeman.wordpress.com/2008/06/04/the-refrigeration-cycle/ (downloaded: 25 01 2014)

[8] MAGYAR SZABVÁNYÜGYI TESTÜLET: *MSZ EN 378–1 Hűtőrendszerek és hőszivattyúk. Biztonsági és környezetvédelmi követelmények.* Budapest: MSZT, 2002.

[9] CSEH G.: *Kockázatelemzési módszerek a veszélyes anyagokkal kapcsolatos súlyos baleseti veszélyek szabályozása területén.* Budapest, Zrínyi Miklós Nemzetvédelmi Egyetem, Katonai Műszaki Doktori Iskola, 2005. (Ph.D. dissertation)

[10] KORDA E.: *Küszöbérték alatti üzemek azonosítása és elemzése*. Budapest: Generisk Kft., 2012. (Belső szabályzat)

[11] FIDY J, MAKARA G.: *Biostatisztika. Többváltozós regressziószámítás*. Budapest: InforMed 2002 Kft., 2005.

The recommendations and guidelines of Rijksinstituut voor Volksgezondheid en Milieu (Netherlands National Institute for Public Health and the Environment were applied in this paper. (www.rivm.nl/RIVM)