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Substance flow analysis of 4-nitrotoluen

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Preface

The current document presents the result of a substance flow analysis of 4-nitrotoluene in Denmark. The objective of this investigation has been to find possible sources and flows of 4-nitrotoluene in Denmark.

The work has been carried out during autumn 2003, using information mainly from the period.

The project was initiated and financed by the Danish Environmental Protection Agency.

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Sammenfatning og konklusioner

Rapporten præsenterer resultaterne af en undersøgelse af massestrømme for 4-nitrotoluen i Danmark.

Formålet med undersøgelsen var at kortlægge kilder og brug af 4-nitrotoluen i Danmark. Kortlægningen er gennemført ved at undersøge alle relevante statistiske kilder i Danmark, suppleret med en stikprøveundersøgelse af relevante virksomheder indenfor kemisk industri og farve/lak-branchen.

I undersøgelsen blev der kun fundet en enkelt anvendelse af 4-nitrotoluen i Danmark i 2002, nemlig 250 gram anvendt til forskning i en farmaceutisk virksomhed.

Det konkluderes, at det er usandsynligt at 4-nitrotoluen findes eller anvendes i signifikante mængder i Danmark, hverken som råmateriale eller som element i importerede produkter.

Summary and conclusions

The current report presents an investigation of the flow of 4-nitrotoluene in Denmark.

The objective of this investigation was to find possible sources and flows of 4-nitrotoluene in Denmark. The knowledge presented is based on all available statistical sources in Denmark and a spot check among chemical and paint/pigment manufacturing companies in Denmark.

The project only found an insignificant consumption of 4-nitrotoluene in Denmark. The only consumption identified is 250 grams used for research by a pharmaceutical company.

It can be concluded that 4-nitrotoluene is unlikely to be present in significant amounts in Denmark, neither as raw material nor as part of imported products.

1 Introduction

1.1 Purpose of the analysis

The purpose of this substance flow analysis has been to investigate the use, consumption and dissemination of 4-nitrotoluene in Denmark.

The report presents the existing (and limited) knowledge about the use of 4-nitrotoluene in Denmark. It includes import/export, use, consumption, content in products and waste flows as well as the exposure of humans and the environment.

A human and ecotoxicological assessment has been carried out as part of the project and included in the report.

1.2 Methodology and limitations

The investigation is made as an ***overview*** analysis of the flows of 4-nitrotoluene in Denmark. The investigation was supposed to be carried out according to the guidelines for substance flow analysis presented by the Danish EPA (Lassen & Hansen, 2000), identifying the main fields of application and the sources of environmental exposure related to 4-nitrotoluene. However, lack of data has made it unsuitable for a full substance flow analysis. Therefore, only this short report has been prepared.

The investigation was carried out during autumn 2003. The information and figures reported are in general from 2000 to 2002, but there are few exceptions, which have been specified in the text.

1.3 What is 4-nitrotoluene?

4-nitrotoluene [Cas. No. 99-99-0] is one of the three structural isomers of nitrotoluene. The isomers are produced commercially, as a mixture, by nitration of toluene. Figure 1-1 illustrates the molecular structure of 4-nitrotoluene.

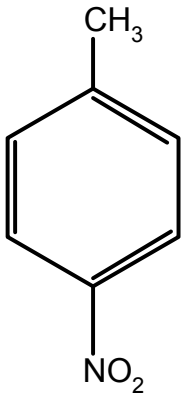

Figure 1-1. The molecular structure of 4-nitrotoluene.

All three isomeric mononitrotoluenes are industrially important products obtained from the sequential nitration of toluene. After distillation of the meta fraction from the isomer mixture, the still residues are cooled in a crystallizer to separate technical quality 4-nitrotoluene. Further distillation of nitrotoluene residues and fractions should be implemented with great care because this has been reported to cause explosions. Holding residues at 150-200 °C results in an undefined "aging" process that can lead to unpredictable evolution of heat, especially if air is introduced (Iuclid, 2000).

1.3.1 Synonyms

Various synonyms and abbreviations of 4-nitrotoluene are used in the literature. In this report the chemical name 4-nitrotoluene is used. Some of the synonyms used include methyl nitrobenzene; 1-methyl-4-nitrobenzene; 4-methylnitrobenzene; p-methylnitrobenzene; p-nitrophenylmethane; 4-nitrotoluol; PNT (IUCLID, 2000).

1.3.2 Physical and Chemical Properties

4-nitrotoluene is a mass of colourless or yellowish crystals/rhombic needles with the following properties (NTP, 2003):

Molecular weight:	137.15
Melting point:	54,5ºC
Boiling point:	238.3ºC
Density/specific gravity:	1.1038 (at 75/4ºC)
Vapour pressure:	1 mm Hg at 53.7 ºC
Solubility in water:	< 1 mg/ml at 20.5ºC
Solubility in 95% ethanol:	50-100 mg/ml at 20.5ºC
Solubility in acetone:	>= 100 mg/ml at 20.5ºC
Very soluble in benzene, ether, chloroform, carbon tetrachloride	
log Kow:	2.37

1.4 International market and Trends in consumption

Approximately 20,000 tons of 4-nitrotoluene is produced annually in the EU (European Commission, 2001). The global production is expected to be between 50,000 – 100,000 tons/year (Iuclid, 2000). Worldwide 4-nitrotoluene is produced in Germany, Belgium, Italy, United Kingdom and the United States (Iuclid, 2000).

4-nitrotoluene is an important commercial chemical used to synthesize agricultural and rubber chemicals, azo and sulfur dyes, and dyes for cotton, wool, silk, leather, paper and explosives. 4-nitrotoluene is used as an intermediate for plastic foams, dyestuffs, paints and pharmaceuticals (Dunnick, 1992).

4-nitrotoluene derivatives are used primarily as intermediates for colorants and related products; for example, p-toluidine, 4-nitrobenzoic acid (by oxidation of 4-nitrotoluene with 15 % HNO_3 at 175 °C), 4-amino-2-chlorotoluene (by reduction of 2-chloro-4-nitrotoluene), and 4-nitrotoluene-2-sulfonic acid, which is of great importance in forming stilbene intermediates for fluorescent whitening agents (Ullmann's, 2002).

2 Applications in Denmark

The Danish product register has not recorded any applications of 4-nitrotoluene in Denmark. Based on the known global applications of 4-nitrotoluene a spot check among relevant Danish companies only identified a small consumption of 4-nitrotoluene used for research purposes.

3 Turnover of 4-Nitrotoluene in Denmark

The turnover of 4-nitrotoluene in Denmark has been investigated by using available statistical information and by survey of the industries where consumption is assumed to take place.

3.1 Statistical information

3.1.1 Statistics Denmark

There is no record of production of 4-nitrotoluene in Denmark and there has not been registered any sale of goods containing 4-nitrotoluene in Denmark between 1998 and 2003 (Statistics Denmark, 2003).

The data in Table 3-1 presents the available import and export of nitro and nitroso derivatives of carbohydrates (KN 2904 2000) (Statistics Denmark, 2003).

Year	Import (kg)	Imported from	Export (kg)	Exported to
2002	20,942	Germany, France	0	
2001	35	France, Germany	2,211	Italy, USA
2000	32	France, Germany, UK	0	
1999	85	Germany, France, Sweden, UK	0	
1998	0		0	

Table 3-1. Import and export of nitro and nitroso derivatives of carbohydrates to/from Denmark (Statistics Denmark, 2003).

It should be emphasised that the figures include nitro and nitroso derivates in general and not only 4-nitrotoluene. In theory, this means there may not be any import of pure 4-nitrotoluene, thus the figures presents a worst-case scenario. 4-nitrotoluene does have an individual KN number (KN 2904 2000 90), which can be found in the European Custom Register on chemical substances, but no Danish statistics are made at this level of detail (Statistics Denmark, 2003).

The figures in Table 3-1 do not show a trend in neither import nor export of 4-nitrotoluene to/from Denmark and there is no correlation between the import and the export figures.

3.1.2 The Danish Product Register

To obtain a cross reference on the import and export figures from Statistics Denmark, the amount of products containing 4-nitrotoluene has been investigated based on data from the Danish Product Register (PR). It is the notifying companies alone that are responsible for updating in PR. The companies are obliged to send in any relevant information about changes regarding their notified products. There is no record of any products

containing 4-nitrotoluene in Denmark in PR (Danish Product Register, 2003).

3.1.3 The SPIN Database

SPIN – Substances in Preparations In the Nordic countries – is a database that contains "non-confidential" information on substances from each of the Nordic product registers.

The intention behind the database SPIN is to make available to the public as much data as possible from the registers. Secrecy rules as in the Product Register can then be overcome by aggregation of the data from each register. Thereby, the number of products within a certain use or industry category is increased. The information included is for example the number of products containing the substance, the annual tonnage, industrial categories and use categories, the annual tonnage within these categories and the presence or absence of the substance in consumer products.

There is no information about the consumption and use of 4-nitrotoluene in the SPIN database (SPIN, 2003).

3.2 Information from spot check

The Confederation of Danish Industries has made a spot test among selected chemical and paint/pigment manufacturers. The objective of the spot check was to cross check the statistical information and verify that no consumption of 4-nitrotoluene is taking place in Denmark.

The spot test found that one pharmaceutical company used 250 grams of 4-nitrotoluene for research in year 2002.

3.3 Summery and conclusion

Based on the statistical information and the spot test it can be concluded that very little 4-nitrotoluene is being used in Denmark, and only for research.

4 Exposure of humans and the environment

Since there do not seem to exist any significant applications of 4-nitrotoluene in Denmark there will not be any exposure of the environment from manufacturing processes or use of the substance.

4.1 Consumption as trace element and unintended uses as contaminant

Despite that no applications of 4-nitrotoluene seems to take place in Denmark that may still be an exposure of the substance as unintended contaminant.

One analysis for 4-nitrotoluene has been found in the literature. 17 textiles and laundry sewage samples were analyzed for a content of 4-nitrotoluene because it is used in the manufacture of raw material for production of dyestuff. Two textiles and one laundry sewage sample contained 4-nitrotoluene. The amount of 4-nitrotoluene in the textiles corresponded to less than 6 mg/kg textile and the content in the sewage corresponded to 0.016 mg/kg (Larsen et al., 2000).

The content of 4-nitrotoluene may result in dermal exposure. Larsen et al. (2000) makes the following estimate of the potential exposure based on measurements of 4-nitrotoluene in textiles: If 0.5 kilo of clothes contains maximum 3 mg of 4-nitrotoluen and it is assumed that a child of 10 kilo absorbs all the 4-nitrotoluene, the exposure is equivalent to approximately 0.3 mg/kg body weight, i.e. about 6,500 times below the LD_{50} for rats. The authors states that it is difficult to estimate the exposure concern based on the figures, but it is concluded that acute clinical effects cannot be expected (Larsen et al., 2000).

4-nitrotoluen can also be emitted to air, which may affect human health, if the textile is stored in a small room with poor ventilation. If 20 sheets of 0.5 kilo are stored in a room of 3 x 4 x 2.5 meters and the entire content of 4-nitrotoluene is released to the air, the maximum concentration can reach 2 mg/m^3. This is 6 times below the occupational exposure limit, thus the exposure is not considered a significant health concern (Larsen et al., 2000). This is supported by other literature sources. IUCLID also mentions that exposure to the substance in the workplace can occur by inhalation of vapour and absorption through intact skin. Basic atmospheric monitoring indicates that exposure by inhalation is generally well below the occupational exposure standard (UK) (IUCLID, 2000).

5 Environmental and health hazards of 4-nitrotoluene

5.1 Toxicity and ecotoxicity of 4-nitrotoluene

5.1.1 Classification and labelling

4-nitrotoluene shall in Denmark and the EU be classified as Toxic (T) and dangerous to the environment (N) and shall be labelled as such with the following risk and safety phrases

- R23/24/25 (Toxic by inhalation, in contact with skin and if swallowed)
- R33 (Danger of cumulative effects)
- R51/53 (Toxic to aquatic organisms, may cause long-term adverse effect in the aquatic environment).
- S(1/2) Keep locked up and out of the reach of children
- S28 After contact with skin, wash immediately with plenty of water
- S37 (Wear suitable gloves)
- S45 (In case of accident or if you feel unwell seek medical advice immediately)
- S61 (Avoid release to the environment. Refer to special instructions/safety data sheets)

The following details provide some of the background data for the classification of the compound.

5.1.2 Human toxicity

4-nitrotoluene is classified as toxic to humans by all routes (i.e. inhalation, ingestion and dermal absorption). Effects from exposure may include contact burns to the skin and eyes, headache, weakness, dizziness, nausea, shortness of breath, tachycardia and methaemoglobinemia. The onset of symptoms may be delayed by up to 4 hours following exposure (HSDB, 2003).

The classification as toxic is not in accordance with the LD_{50}-values reported in animal tests. An explanation for the classification can be the effects observed in human poisoning (Larsen, 2000).

5.1.3 Animal toxicity

4-nitrotoluene is toxic by ingestion and inhalation in animal tests. NTP (2003) reports the following values in animal tests:

LD_{50} (oral, rat): 1960 mg/kg
LD_{50} (oral, mouse): 1231 mg/kg
LD_{50} (ip, rat): 940 mg/kg
LD_{50} (skin, rat): 16000 mg/kg

RTECS (2003) reports some additional data:

LD_{50} (inh, rat): 975 mg/m^3
LD_{50} (inh, mouse): 419 mg/m^3
LD_{50} (oral, rabbit): 150 mg/kg

5.1.4 Carcinogenicity

IARC (1996) has made the following evaluation of 4-nitrotoluene: There is inadequate evidence in humans for the carcinogenicity of nitrotoluenes. There is inadequate evidence in experimental animals for the carcinogenicity of 4-nitrotoluene. The overall evaluation of IARC is that nitrotoluenes are not classifiable as to the carcinogenicity to humans (Group 3).

5.1.5 Endocrine disruption

4-Nitrotoluene has been assessed at an expert panel meeting as a step in the procedure towards the establishment of a priority list of substances for further evaluation of their role in endocrine disruption (BKH, 2000).

The expert panel concluded that human health relevant endocrine disruption data were of category 1, i.e. that at least one study providing evidence on endocrine disruption in an intact organism was identified. Wildlife endocrine disruption data were evaluated as category 3, i.e. there was no scientific basis for inclusion in the list or no data.

Due to the use pattern of 4-nitrotoluene (in closed systems as an intermediate in the varnish industry, pharmaceuticals and fragrances) and because it does not bioaccumulate, 4-nitrotoluene was prioritised as low concern and is not expected to present a risk to vulnerable groups or create high risk situations.

5.1.6 Environmental fate and exposure

If released to water, 4-nitrotoluene would be susceptible to photolysis, volitilization (estimated half-time in water 1 m deep flowing 1 m/sec is 25 hours), and possibly aerobic degradation provided suitable acclimatization has take place.

If released to soil, 4-nitrotoluene should be resistant to oxidation and chemical hydrolysis. The compound is reported to degrade under anaerobic conditions to form toluidine, but insufficient data are available to indicate the significance of anaerobic degradation as a possible removal mechanism. One study under aerobic conditions resulted in persistence > 64 days. It is expected to be moderately to highly mobile in soil and volatilize slowly from dry soil surfaces.

If released to the atmosphere, 4-nitrotoluene is expected to exist almost entirely in the vapour phase. The dominant removal mechanism would be reaction with photochemically generated hydroxyl radicals (estimated half-life 19.9 days) and direct photolysis.

The bioconcentration factor (BCF) for 4-nitrotoluene has been measured to be less than 100 in carp. BCF values of 37 and 20 have been calculated based on a log octanol/water coefficient of 2.37 and a measured water solubility of 442 mg/l at 30ºC. These values suggest that 4-nitrotoluene will not bioaccumulate significantly in aquatic organisms.

5.1.7 Ecotoxicity

4-nitrotoluene is toxic to aquatic organisms. The following excerpt from the data in the AQUIRE database demonstrate this (AQUIRE, 2003):

EC_{50} (daphnia): 9 mg/l
LC_{50} (daphnia): 6.6-7.5 mg/l
LOEC (algae): 3.3 mg/l
LC_{50} (fish): 19-50 mg/l

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