

ANILINE

AMINO BENZENE, AMINOPHEN, ARYLAMINE, BENZENAMINE, ANILINE
OIL, AND PHENYLAMINE

C6860 Modern Methods of Pollutant Analysis

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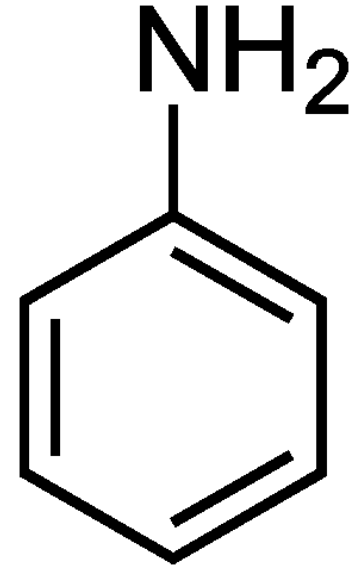
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INTRODUCTION: BASIC CHARACTERISTICS

- CAS No: 62-53-3
- Molecular weight: 93.12 g/mol
- Molecular formula: C₆H₅NH₂

- Vapor density: 3.22 (185 °C vs. Air)
- The vapor pressure: 0.7 mmHg (25 °C)
- log Kow: 0.90
- Solubility: 36 mg/mL at 25°C

- Oily liquid: Colorless to yellowish to brownish with a musty fishy odor



INTRODUCTION: BRIEF HISTORY

- In 1826 Otto Unverdorben, isolated Aniline from the destructive distillation of indigo: crystallin
- In 1834, Friedrich Runge isolated from coal tar, a substance that produced a beautiful blue colour on treatment with chloride of lime- kyanol or cyanol
- In 1841, C. J. Fritzsche obtained an oil, by treating indigo with caustic potash- aniline
- N. N. Zinin found that, on reducing nitrobenzene, a base was formed- benzidam
- In 1855, August Wilhelm von Hofmann established these variously-prepared substances were identical - Aniline or phenylamine.



MANUFACTURING PROCESS

- Catalytic vapor phase reduction of nitrobenzene with hydrogen
- reduction of nitrobenzene with iron filings using hydrochloric acid as catalyst
- catalytic reaction of chlorobenzene and aqueous ammonia;
- ammonolysis of phenol (Japan)



USES

- Methylene diphenyl diisocyanate (MDI)- used to produce polyurethane foam
- Rubber accelerators and antioxidants to vulcanise rubber
- Intermediates for herbicides and pesticides, and dyes and pigments.
- Minor uses: textile and photographic chemicals, pharmaceuticals, amino resins and explosives.

Use	Percent
MDI(p,p1-methylene diphenyl diisocyanate and polymeric MDI)	73-85
Rubber processing Chemicals	18
Pesticides and fibers	9
Pharmaceuticals	2
Dyes and pigments	3
Miscellaneous(agricultural chemicals, specialty resins and photographic chemicals)	3



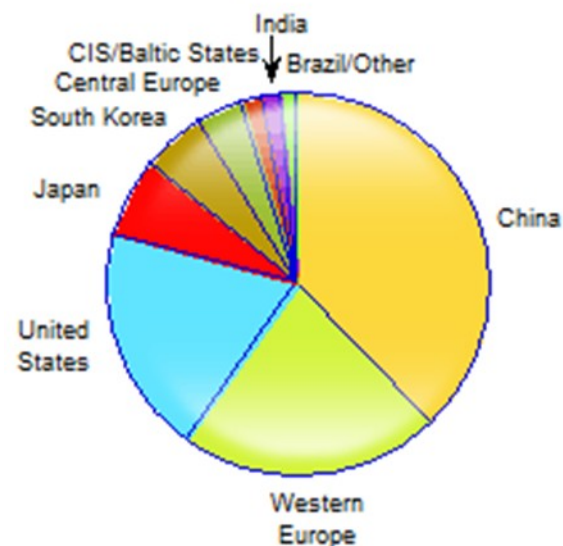
ANILINE PRODUCTION & CONSUMPTION

Supply and demand for Aniline in 2006

Region	Consumption Million tonnes/year	Production Million tonnes/year
Western Europe	1.32	1.62
USA	1.19	1.38
Eastern Europe	-	0.316
Asia Pacific	0.717	1.15
Japan	0.32	0.474
Latin America	0.073	0.07
Asia/Middle East	0.098	0.064

Source: ICIS Chemical Business

World Consumption of Aniline—2014



Source: www.ihs.com/products/aniline-chemical-economics-handbook.html



ENVIRONMENTAL RELEASES

- Production and processing
 1. Processing to MDI
 - <0.013 to 78 ppm to wastewater
 - 0.014 to 105 ppm to atmosphere
 2. Processing to rubber chemicals
 - 0.44 to 75 ppm to wastewater
 - 24 to 380 ppm to atmosphere
- as a degradation product of plant protection agents (biotransformation from phenylurea and carbamate derivatives)
- microbial reduction of nitrobenzene



ENVIRONMENTAL RELEASES

- rubber chemicals (degradation product)-tyres abrasion
 - In new and used tyres, aniline was detected in concentrations near the detection limit of 100 mg/kg rubber- abrasion
 - In distilled water, 3.99-86.4 µg aniline/l were detected, while in artificial rain water (pH = 4), concentrations of 5.91-828 µg/l were found (Baumann and Ismeier, 1997)
- thermal degradation of polyurethanes – in foundries manufacturing aluminum, Iron, Steel -occupational risks
 - The highest 8-hour TWA of 6.4 mg/m³ exposure level- Swedish study
- coal and oil industry
 - At three shale oil manufacturing sites, aniline concentrations of 0.48 to 5.4 mg/l (Hawthorne and Sievers, 1984).
- Landfills
 - level of 9.9 µg/l was detected in Canadian landfills



EXPOSURE ROUTES AND HEALTH CONCERNS

- Inhalation and/or oral uptake- odour can be detected at 1 ppm

Aniline vapor is heavier than air and may cause asphyxiation in enclosed, poorly ventilated, or low-lying areas

Aniline is rapidly absorbed from the gastrointestinal tract. Ingestion can lead rapidly to severe systemic toxicity, nausea and vomiting usually occur

- Readily absorbed through the skin both from the liquid and gaseous phases



EXPOSURE AND HEALTH EFFECTS

- Aniline is well absorbed after oral, dermal and inhalation exposure.
- The extent of absorption after oral intake amounts 89-96% for rats. The corresponding figures for mice, sheep and pigs are lower (72%, 80% and 56%, respectively).
- Dermal absorption in humans was estimated to amount up to 38%
- Aniline is metabolised to different metabolites by N-acetylation (acetanilide), aromatic hydroxylation (2- and 4-aminophenol) and N-hydroxylation to N-phenylhydroxylamine which is responsible for the formation of methaemoglobin
- The metabolites are predominantly excreted in the urine.



EXPOSURE AND HEALTH EFFECTS

Acute Exposure

- Many health effects of aniline are due to formation of methemoglobinemia
- Affects the heart, CNS, kidney, liver, skin, eyes
- In humans 60 ml of orally administered aniline causes death.
- 0.4-0.6 mg/l air may be borne without much harm for 0.5-1 hour, but 0.1-0.25 mg/l for several hours produces slight symptoms.
- Average lethal inhalation dose for humans 0.35-1.43 g/kg body weight.
- With respect to methaemoglobin formation the no-effect dose of aniline in adult man is about 0.21 mg/kg body weight

Chronic exposure

Anemia, headaches, tremor, parathesia, pain, narcosis or coma, and cardiac arrhythmia. Heart, kidney, and liver damage may also occur, possibly as secondary effects of hemolysis

- Considered a Non Threshold carcinogen :



ECOTOXICOLOGICAL IMPACTS

- Aniline is deposited in the soil from the atmosphere and via degradation of plant protection agents.
- In soil, aniline will biodegrade and/or bound covalently onto the organic matter. The latter pathway leads to aniline-humic acid adducts which are immobile and only slowly degraded
- Aniline found in food such as Rhubarb, black tea

- Active trees were exposed for 3 hours at a temperature of 25-30°C to aniline
- At 0.4 ppm, produced as much damage as higher concentrations (up to 10 ppm) - Cheeseman et al. (1980)

- In vivo studies shows that aniline causes methemoglobinemia in animals
- LC50 for dermal absorption in rats: 478 ppm
- Oral LD50 in rats: 250 mg/kg
- The LC50/96-hour values for fish -10 and 100 mg/L
- EC50/ 48-hour values for daphnia - less than 1 mg/L



ENVIRONMENTAL FATE

Degradation rates

	k	t _{1/2}
k _{deg_{water}}	$4.6 \cdot 10^{-2} \cdot \text{d}^{-1}$	15 d
k _{bio_{sed}}	$1.98 \cdot 10^{-4} \cdot \text{d}^{-1}$	3,500 d
k _{bio_{soil}}	$1.98 \cdot 10^{-3} \cdot \text{d}^{-1}$	350 d
k _{deg_{air}}	5.1 d^{-1}	3.2 h

BIOACCUMULATION

A BCF of 2.6 ± 0.06 . Bioaccumulation potential due to the exposure of the organisms via water is very low. (Zok et al., 1991).



ASSESSMENT/MEASUREMENT

- NIOSH method 2002 (adsorption to silica gel, elution with ethanol, GC-FID)- measurements at workplace
- Risk Modeling using EASE software for windows
- Inhalation exposure:
 - In vivo tests
 - Measurement of mean Met-Hb in the blood of humans
- Dermal exposure:
 - An investigation of liquid aniline absorption through the skin and urine excretion of the metabolite 4-aminophenol in man was carried out (Piotrowski, 1957)- gauze test
 - Absorption velocity: 0.18 to 0.72 mg/cm² /h at skin temperatures from 29.8 to 35°C
 - Dermal absorption in humans was estimated to amount up to 38%



ASSESSMENT/MEASUREMENT

- Zhu et al., 2004- used GC/MS method to determine aniline and related mono-aromatic amines in indoor air
 - Thermal desorption in place of solvent extraction
 - Smoking-source of aniline
 - Increased concentration of aniline due to shoe polish: initial indoor air concentration of 0.016 Ag/m³ to 0.53 Ag/m
- Delepee et al., used HPLC/MS/MS for real time monitoring of aniline in fresh water
 - Used porous graphitic carbon (PGC) as stationary phase
- Weiss & Angerer: Used GC/MS –urine samples
 - liquid–liquid extraction at pH 6.2–6.4
- Hanley et al., epidemiological study at a rubber manufacturing plant:
 - Company exposure records from 1975–2004 showed a decreasing trend over time, and nearly all breathing zone TWA measurements were well below published occupational exposure limits, yet bladder cancer cases were still reported.



MONITORING DATA

- Aniline is part of a regular monitoring program in the Rhine and its tributaries
- No atmospheric monitoring data available



REGULATORY STATUS

- In accordance to the EU criteria for classification and labelling of carcinogens, aniline is classified as carcinogenic, category 3 and labelled with R 40 “limited evidence of a carcinogenic effect”.
- Reference Concentration (RfC) of 1 ug/m³ for aniline in air for the chronic, noncancer effects (U.S. EPA, 1993)
- Priority Substances List (PSL1) under the *Canadian Environmental Protection Act, 1988* (CEPA 1988).

- The following occupational exposure limits apply in the EU (ILO, 1994):
 - - DK, S: 4 mg/m³ (1 ml/m³)
 - - FIN, B: 7.6 mg/m³ (2 ml/m³)
 - - D: 8 mg/m³ (2 ml/m³)
 - - UK, F: 10 mg/m³ (2 ml/m³)



REGULATORY STATUS

- OSHA PEL (permissible exposure limit) = 5 ppm (skin) (averaged over an 8-hour workshift)
- NIOSH IDLH (immediately dangerous to life or health) = 100 ppm
- SCOEL
 - 8-hour TWA: 0.5 ppm [1.94 mg/m³]
 - STEL (15 mins): 1.0 ppm [3.87 mg/m³]
 - Biological Limit Value (BLV): 30 mg *p*-aminophenol / litre urine (*sampling: 0-2 h after exposure/shift*)
 - SCOEL carcinogen group: C (carcinogen with a practical threshold)
 - For inhalation aniline exposures at the workplace on the background of cancer risks air concentrations of 0.2 mg/m³ should not be exceeded
- High production volume chemical according to European Chemical Substance information system
- Aniline forming plant protection products come under the Council Directive 91/414/EEC



CONCLUSION

- Sources of aniline is diverse and its presence in the environment ubiquitous
- Easily biodegradable in certain conditions, low bio accumulation factor
- The information available for aniline assessment is from early 2000s. Studies with more precise methods to quantify aniline especially in manufacturing and processing industries are crucial
- Cohort studies to ascertain reproductive, carcinogenic, genotoxic effects needs to be under taken focusing on occupational hazards
- long term tests with plants, earthworms and micro-organisms to assess risks on soil to be carried out
- More rigorous monitoring program to evaluate the effects and releases



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