# Treatment and disposal of chemical wastes in daily laboratory work

## Introduction

### What is waste?

Waste is defined in the *Recycling and Waste Management Act (KrW-/AbfG)* as movable goods which are intended by the owners to be disposed of or their disposal in an appropriate way is imperative to safeguarding public welfare and to protect the environment.

### How are wastes formed in a laboratory?

Life cycle of a chemical at an university begins with providing the substances needed from the chemical store to a coworker or student in laboratory courses. They are used for syntheses or analyses. Due to the application purposes contaminated starting materials, by-products, spent solvents, and spent chemicals are formed, which have to be decomposed or disposed of, if their recycling is not possible. In contrast to industrial wastes the chemical wastes from university laboratories occur usually as small amounts of highly complex mixtures. Overall these represent a significant waste amount which has to be disposed of from the university at its own expenses.

To dispose of laboratory wastes, which may be different at different places, in an appropriate way depends on the type of the experiments conducted and chemicals used. But some type of hazardous wastes produced cannot be disposed of in the original form and have to be conditioned first. With the help of suitable processes these wastes can be detoxified on site. An advantage of detoxification is also to reduce the risk of contamination of inexperienced staff while handling, of accidents with these wastes and, hereby, to avoid the risk of environmental contamination.

## Waste management concept:

## Avoidance, reducing, and disposal of laboratory wastes

Of course, it would be best to avoid the formation of waste from the very beginning. This is also the primary aim of *German Recycling and Waste Management Law* (KrW-/AbfG) that came into force in 1996. (Full name: *Law to promote the recycling management and to secure the environmentally compatible disposal of wastes.*) According to these regulations, everybody who develops, produces, treats and processes, or distributes goods is committed **to avoid wastes**. If it is impossible to avoid then the **waste amount has to be reduced** by separate collection and recycling measures. Finally, after all these efforts are made the still remaining waste amounts must be **disposed of "without risks"** to health and environment.

The reutilization of laboratory wastes can be done, e.g., for spent chemicals after an appropriate recycling procedure. For instance, this is most applicable for spent solvents. Organic solvents like ethanol, acetone, chloroform, and diethyl ether are collected in laboratories separately and worked up through distillation.

During all operations (here: chemical experiments) where **large amounts of wastes** are formed it should be checked carefully whether it is possible to reduce the waste amounts by application of suitable measures (e.g., alternative reaction conditions, down scaling of the batch volume). Only in case that it is not possible to further **reduce the waste amounts** by prophylaxis and recycling measures, an orderly **waste disposal** should be performed.

## Hazardous wastes in the laboratory

An important group of wastes are remainders of chemicals which are usually categorized as hazardous wastes. These substances are forbidden to be disposed of via municipal waste collections or via wastewater.

Waste types which are categorized as hazardous wastes have to be collected separately and handed over by the producer to approved disposal companies. The waste producer has also to deliver suitable data on the type of the hazardous waste. According to the waste type certain

  

limit values for chemical constituents and properties have to be met. Substances which can only be disposed of to high costs should be avoided resp. replaced by appropriate substitutes, if possible, which could be disposed of more cost-effective and in an environmentally friendly way.

**Collecting of hazardous wastes**

Hazardous wastes are collected in special containers observing the statutory regulations (e.g., "Ordinance on the Hazardous Substances"; refer also to: "Legal Conditions for the Handling of Hazardous Substances" and "Technical Guidelines on Safety in Chemical Laboratory Courses"). Different types of wastes should not be mixed together. For each type of waste special containers should be used for collection which are provided by the university. These containers will be given back to the waste repository, whereby the containers should not be filled above 90% (to avoid spillage during transportation). The containers must be sealed and labeled correctly. Otherwise disposal companies are not allowed to accept them. Containers being damaged, leaking, or contaminated with hazardous substances on the outside will also not be accepted.

The general rule for the handling of hazardous waste is to avoid any risk of endangering men and the environment during storage, transportation, and disposal of these materials.

## Wastewater formed in laboratories

Laboratory wastewater are any liquids which are coming into washbasin. In the ideal case they contain only water. In daily practice they usually consist of aqueous solutions which are previously neutralized to pH 6 to 8 and does not contain heavy metals.

**During the disposal of wastewater the limits have to be met which are usually given in municipal wastewater statutes.** It should be obeyed that it is **forbidden to dilute wastewater** in order to meet the limits. Tables 1-3 contain the threshold values for different pollutants at the Technical University of Braunschweig as an example, of their exceeding results in increased wastewater treatment fees. If the threshold values are doubly exceeded this can lead to prosecution. Only those substances are allowed to be discharged into the wastewater which are not listed in the following tables and are not categorized as hazardous

substances, and if they are harmless to the environment and for the operation of wastewater treatment plants.

**Important basic parameters for wastewater quality**

- *pH values* of wastewater must be in a range between 6.0 to 10.5.
- *Temperature* must not increase 35 °C.
- The toxicity of wastewater must be less than to affect the biological processes in Wastewater Treatment Plants (WWTP), sludge disposal, or sludge utilization.
- Dyestuff concentrations in wastewater must be less than to cause a discoloration in public WWTPs.
- The threshold values for phenols are set low (0.025 mg/L wastewater) since they cause an ill-tasting which is hardly eliminated during water purification.
- The threshold values for oxygen consuming substances like sodium sulfite, iron(II) salts, and thiosulfates are set to 50 mg/L wastewater.

**Table 1**: Inorganic substances – threshold limit values (TLV) for cations

| **Cations** | **TLV (mg/L)** |
|---|---|
| Antimony | 0.25 |
| Arsenic | 0.05 |
| Barium | 1.0 |
| Cadmium | 0.05 |
| Chromium, total | 0.5 |
| Chromium(VI) | 0.1 |
| Cobalt | 1.0 |
| Copper | 0.5 |
| Lead | 0.5 |
| Mercury | 0.025 |
| Nickel | 0.5 |
| Silver | 0.25 |
| Tin | 0.5 |
| Zinc | 2.5 |

  

**Table 2**: Inorganic substances – threshold limit values (TLV) for anions

| **Anions** | **TLV (mg/L)** |
|---|---|
| Cyanide | 10 |
| Cyanide, easily released | 0.5 |
| Fluoride | 25 |
| Sulfate | 300 |
| Sulfide | 1.0 |

**Table 3**: Threshold limit values for group parameters and organic substances

| **Group parameters** | **TLV (mg/L)** |
|---|---|
| Adsorbable organic halogen compounds (AOX) | 0.5 |
| Volatile halogenated hydrocarbons, (VOX) | 0.25 |
| Volatile halogenated hydrocarbons, individual compounds | 0.05 |
| | |
| **Organic compounds** | **TLV (mg/L)** |
| Aliphatic hydrocarbons | 10 |
| Oils and grease, saponifiable | 125 |
| Polycyclic aromatic hydrocarbons (PAH) | 0.025 |
| Aromatics, total | 0.05 |
| Benzene | 0.0025 |
| Ethylbenzene | 0.025 |
| Toluene | 0.025 |
| Xylene | 0.03 |
| Styrene | 0.03 |

*Note*: Aqueous solutions remaining after extraction with dichloromethane or chloroform must be disposed of as hazardous wastes (containing chlorinated hydrocarbons, VOX) or they must be devolatilized from these VOX by suitable methods (e.g., purging).

  

# Selected remarks on the disposal of chemical wastes from laboratory

It is recommended to detoxify small amounts of hazardous chemical wastes in the laboratory by qualified staff. Detailed information on the procedure to be applied is contained in the mode of operation. Following types of hazardous wastes routinely occur in laboratory work. Therefore, here are some information given to treat and to dispose them of.

**Chemical remainders**

As chemical remainders only those materials can be disposed of, which

- constituents are known
- are not classified as explosives, and
- are not radioactive.

They must not contain highly toxic constituents like polychlorinated dibenzodioxins and furans, (PCDD/F), polychlorinated biphenyls (PCB), or warfare agents.

Waste containers must be labeled properly even small vessels. Small vessels and product vials from lab courses can be collected together in containers for solid materials and declared, e.g., as “syntheses products from inorganic chemical lab course in vials.” In case of unknown chemicals (e.g. in unlabelled vessels) it is recommended to elucidate the type of the compound.

Chemicals classified in certain waste groups have to be disposed of according to these groups. Hydrochloric acid should be explained as an example. It is assigned to the waste group “Inorganic Acids, Acid Mixtures, and Mordants”. That means, HCl must not be disposed of as chemical remainder.

Old chemicals in properly closed vessels should be offered to other groups or institutes for further use. They should be only disposed of if nobody is interested in having these substances within a time limit set.

There exists also an external take-back of excess amounts of chemicals and solvents by the producer of these substances. For instance, the Merck Company offers such a service under the name Retrologistics®. The delivered chemicals are checked for their conditions and the

  

types and amounts are documented. The contents of small vessels of defined chemicals are put together to larger amounts. After analysis and quality control these substances are utilized in production and synthesis. If the reutilization is not possible those chemicals are disposed of according to the regulations.

**Inorganic acids, acid mixtures, and mordants**

The pH values of these solutions are below 6. They are aqueous acidic solutions which must be free of

- cyanides (otherwise hydrogen cyanide will be formed!),
- ammonium ions (max. 0.1 mol/L is allowed), and
- any type of organic substances (e.g., solvents, fats and oils).

Spent acids containing nitric acid (e.g., nitrating acid mixtures) have to be neutralized and then disposed of as “Rinsing and Washing Water”.

Acidic solutions which do not contain heavy metals or other hazardous substances can be neutralized with sodium hydroxide or sodium hydrogen carbonate in equimolar amounts and then poured out into laboratory wastewater.

**Bases, alkaline mixtures, and mordants**

This waste category comprises liquid wastes with a pH above 8. They are aqueous alkaline hydroxide solutions which must be free of

- cyanides,
- ammonium ions (max. 0.1 mol/L, otherwise emission of ammonia!) and
- any type of organic substances (e.g., solvents, fats and oils).

Alkaline solutions which do not contain heavy metals or other hazardous substances can be neutralized with equimolar amounts of hydrochloric acid and then poured out into laboratory wastewater.

  

**Rinsing and washing waters, containing metal salts**

This waste category comprises aqueous solutions of metal salts which must be free of

- cyanides,
- ammonium ions (max. 0.1 mol/L is allowed) and
- any type of organic substances (e.g., solvents, fats and oils)..

In case of these aqueous solutions it is possible to reach a significant volume reduction by applying concentration measures.

**Remainders of alkaline metals**

During drying of organic solvents remainders of alkaline metals are obtained. These sodium or potassium remainders are reacted by drop wise addition of ethanol or isopropanol. Finally, these solutions are neutralized and disposed of as halogen-free solvents.

**Heavy metals**

Heavy metals in aqueous solutions can be precipitated as sulphides or carbonates. The precipitates are then filtered, dried, and disposed of as solid wastes.

**Mercury containing wastes (elementary Hg)**

This waste category comprises elementary mercury (e.g., broken thermometers and manometers, mercury containing switch modules, mercury vapor UV lamps, mercury from diffusion pumps) which are collected separately. The collected spent mercury will be worked up and gained back in a special factory. Mercury compounds do not belong to this category of waste, but they will be disposed of as “fine chemicals”.

**Silver containing solutions and wastes**

For these substances it is recommended to collect them separately in order to work them up.

**Hydrocyanic acid and cyanides**

Highly toxic chemicals like hydrocyanic acid and its salts (cyanides) must not be poured out into wastewater. They have to be detoxified by oxidation. At laboratory scale oxidation of these substances with sodium hypochlorite solutions is an appropriate method. Only harmless

  

substances like nitrogen, carbon dioxide, and chloride ions are formed via the intermediate cyanate. An alternative method is the oxidation of cyanide under alkaline conditions (pH 10-11) to nitrogen and carbon dioxide. It can be checked with Merckoquant Cyanide Testkit whether the oxidation was completed.

Note: The disposal of cyanides should not be performed by the students in the basic lab course by themselves. They should be supervised by an expert person (e.g., course assistant). It is possible to form hydrogen cyanide and cyanogen during improper operation.

**Solvents, halogen free**

All organic compounds can be disposed of as halogen free solvents if they meet following conditions:

- The elements C, H, N, Na, O, P, and S may be contained.
- There must not be halogens present, even inorganic halogen compounds like salts.
- These solutions must be liquid at room temperature.
- If they are solids they should be dissolved in a suitable solvent.

The pH value must be adjusted to 6-9 by neutralization if necessary. Halogen free organic solvents should be recycled as much as possible.

**Solvents, containing halogen**

Halogenated solvents must be collected separately and be worked up or be provided to special companies. These solvents are forbidden to be mixed with others.
As halogenated solvents organic compounds can be disposed of which

- may contain the elements C, H, N, O, P, S, F, Cl, Br, and I,
- are liquid at room temperature,
- are dissolved in a suitable solvents if they are solids.

The pH value must be adjusted to 6-9 by neutralization if necessary. Halogen free organic solvents should be recycled as much as possible.

  

**Pressure cylinders**

Pressure cylinders must be controlled in fixed periods of time according to the gas type they contain. Any cylinder not in use must be given back to an expert company (usually the deliverer) 6 weeks before the control date (imprinted on the cylinder shoulder). If the control date already run out and the cylinder is still under pressure special transportation regulations have to be followed. Such a pressure cylinder is only disposed of or reutilized by a special company at high cost.
Spray cans can be disposed of in special recycling container after being empty completely.

## Cleaning of laboratory equipment

Cleaning of laboratory equipment after their use in chemical experiments can also be a source for hazardous wastes which have to be disposed of according to the regulations.

**It is forbidden to use extremely flammable, very toxic, toxic, carcinogenic, teratogenic, or mutagenic chemicals for cleaning purposes.**

Unsuitable for cleaning purposes are, therefore, diethyl ether (extremely flammable), benzene (toxic, carcinogenic), and tetrachloromethane (toxic, carcinogenic).

Organic residues in lab ware can be dissolved in a suitable solvent (e.g., acetone, 2-propanol, ligroin). The solutions are collected and solvents are recycled by distillation. Distillation residues can be disposed of as “halogen free solvents” (halogen content < 2%) resp. “halogen containing solvents” (> 2%). These substances must not be poured out into wastewater!

Stubborn pollutions can be treated in many cases with saturated sodium permanganate solutions, which will be added in the vessel to be cleaned with the same volume of sodium hydroxide solution (20 wt.-%). The use of chromic acid cleaning mixture for this purpose is forbidden in the meantime since it is carcinogenic! (Prohibition of the use of carcinogenic substances if their substitution is possible.)

There are further (alkaline) cleaning agents like soaps, ethanol or 2-propanol containing KOH solutions (note the fire prevention instructions!), and commercially available cleaning agents like Extrane (Merck), which often degrade easily organic residues in the presence of air.

While using strong alkaline cleaning baths one should carry safety goggles and gloves. Any contact of these agents with the skin or eyes has to be avoided, in order to protect nails, callus, and cornea. Spent solutions of Extant Laboratory Cleaner is usually biodegradable. But if they are contaminated with chemicals hazardous for the environment during the cleaning process they have to be neutralized and disposed of as "salt containing solutions".

Inorganic residues (e.g., salts) are dissolved in diluted acids or bases if needed. Strong oxidizing cleaning agents, like concentrated sulfuric acid, concentrated nitric acid, hydrogen peroxide may only be used when other cleaning measures remained unsuccessful.

## How is the disposal of laboratory waste performed in practice?

Following, an experiment from NOP is given as an example, in order to show which waste fractions are formed in reality and how they are disposed of properly.

**Example:**

**NOP-No. 1001**

**Nitration of toluene to 4-nitrotoluene, 2-nitrotoluene and 2,4-dinitrotoluene**

**Waste treatment**

During working up of the products the following fractions are obtained, which will be treated as laboratory wastes.

A.: Nitrating acid & ice water

After extraction of the product and separation of the organic phase an aqueous solution is obtained which is strongly acidic (pH 1) due to the content on mineral acid (nitric acid, sulfuric acid). These nitric acid containing wastes will be neutralized and disposed of as hazardous waste under the category "Rinsing and Washing Water". Neutralization can be performed by adding equimolar amounts of sodium hydroxide or sodium hydrogen carbonate (be careful: foam formation due to carbon dioxide).

  

B.: Sodium hydrogen carbonate solution & water from neutral washing

This alkaline phase can be used to neutralize the above mentioned acidic solutions and then be disposed of as hazardous waste under the category "Rinsing and washing water".

C.: Spent drying agent (sodium sulfate)

Sodium sulfate used to dry the organic phase will be collected in a vessel for spent drying agents after filtration and removal of the organic solvent (e.g., by evaporation). Later they can be disposed of as inorganic solids.

D.: Distilled off cyclohexane from rotary evaporator

Separately collected spent solvents will be worked up from time to time by distillation.

E.: Mother liquor from recrystallization

The residues of mother liquors containing methanol resp. ethanol can be disposed of as halogen free organic solvents. If there is a large volume of mother liquor collected that can be distilled in order to recover methanol resp. ethanol.

F.: Distillation residues in the vessels

Distillation residues in the flasks and further organic residues will be dissolved, for instance, in acetone. These solutions can be disposed of as halogen free spent solvents.

## Disposal routes: what happens with the wastes collected?

Following, one possible disposal route for laboratory wastes will be shown as an example.

After collecting the laboratory wastes in various institutes and laboratories of an university the collection containers and original flasks (for fine chemicals) serve as transport vessels till the next interim store. It is recommended to transport the waste containers in regular time periods to this interim store in order to reduce waste amounts in the laboratories.

If the interim store is not located nearby (on site) the hazardous wastes have to be transported over traffic roads in special approved vehicles (after the "Dangerous Goods Ordinance for Road and Railroad Transportation" – GGVS/E). If these wastes are removed by a special disposal company then the transfer site for these wastes is the collecting vehicle.

No refilling will be performed in the interim stores in order to enlarge the volume per waste type (except in case of accidents). There is always a risk of exothermic reactions or emission of volatile compounds (e.g., spent solvents) which would necessitate increased safety measures for the interim stores.

Wastes have to be stored separately from the resource materials, e.g., through securing a sufficient distance between both (Fig. 1). In case of a leakage, the content of the containers must not reach other area of the interim store. For this, technical measures have to be taken according to the state and constituents of the wastes stored.


**Fig. 1:** Picture of an interim store. In front, empty solvent drums are located separately from the chemical wastes stored (at the back).

All containers brought to the interim store are checked first and are subject to a visual control. The waste producer has to fill out a disposal document which comprises a legally binding waste declaration. Wastes will be weighed while taking over. Small amounts of wastes will be sorted after danger categories and packed. Following, they will be stored at a certain place with similar waste types.

The content of the packing units will be registered in a covering list along with waste names, UN Codes (four-digit code number for dangerous goods, which are displayed on the orange plates of dangerous goods transport trucks), packing sizes, and origins. The master copy of the covering list will be attached to the work journal of the interim store. One copy will be handed over to the disposal company in order to apply for the acceptance certificate, and another copy will be attached to the packing unit of the waste.

Wastes taking over in the interim store will be registered in a computer based waste management program. These data files serve as work and storage journal and certificates. They balance the storage stock and manage the disposal proofs and accompanying documents.

To operate the interim store an unit laboratory is needed in order to control random samples of the wastes and to verify the declaration of the waste producers.

**Big. 2:** Picture of closed ASP-containers to store and to transport wastes.

The container will be picked up from approved disposal companies in regular time periods. The small packing units will be packed together in larger transport units, if needed, loaded on special trucks and transported to the disposal plants. The special directives of “Dangerous Goods Ordinance for Road and Railroad Transportation” (GGVS/E) have to be met.

Transport can be conducted simpler if the storage space in the interim store is used for the transportation itself. This can be achieved by the utilization of an ASP-container which is approved for the storage and for the transportation of wastes. The wastes delivered to the interim stores will be controlled and immediately stored in these containers (Fig. 2 and 3).

***ASP*** means Collection Container for Pasty Wastes, which may contain pasty and/or solid materials, and is also approved for small collection vessels, which may contain also liquid wastes. These containers are, therefore, transport systems they are intrinsic safe due to there design and technical safety measures built in for storage and transportation of wastes.

**Fig. 3:** Open ASP container with collection canisters

For the separate storage of different waste types according to their danger categories (flammable liquids, organic laboratory chemical remainders, inorganic laboratory chemical remainders, acids, bases) there are four ASP containers. Additionally one ASP container is kept as reserve. After filling the ASP container they will be loaded on a special transport vehicle and transported to a disposal plant.

  

**Treatment of the hazardous wastes through the special disposal company**

Liquid wastes will be incinerated in a high temperature waste incineration plant. The off-gas treatment systems of these plants prevent to emit hazardous pollutants into the environment.

Pumpable inorganic wastes are treated in a stirred-tank reactor in several steps with suitable reactants. Some of the hazardous constituents (e.g., heavy metals) are precipitated as solids and then separated from the liquid phase by a chamber filter press. The sludge obtained will be disposed of in a hazardous waste landfill or in an underground disposal site. The filtrate of chamber filter press will be neutralized and then given into wastewater treatment facility. For quality assurance purposes and to control meeting the limit values an analytical monitoring is needed.

Following, some treatment measures are given for pumpable inorganic wastes as example:

- Cyanide is oxidized in strong alkaline medium (pH > 12) with sodium hypochlorite over cyanate to carbon dioxide and nitrogen. It is also possible to oxidize cyanides at technical scale by ozone.
- Nitrite is oxidized by hydrogen peroxide in weakly acidic medium to nitrate (pH 3.5-4.5).
- Chromium(VI) (chromate) is reduced to chromium(III) by sodium disulfite in strongly acidic medium (pH 2)
- Fluoride is precipitated as poorly soluble calcium fluoride by the addition of lime milk.
- Heavy metals are precipitated as hydroxides in alkaline medium or as sulfides in acidic medium.