



Solvent Wastes in the Laboratory – Disposal and/or Recycling

Introduction

Within the framework of the *Sustainable Organic Laboratory Course* (NOP) the avoidance and reduction of wastes stands for an important educational goal. This is, of course, applied also for the use of solvents. Working out solvent-free syntheses can likely be one approach to meet these goals. These must not be automatically more environmentally-friendly, since further factors like working up, yields, and energy supply play also an important role. In many cases one cannot renounce on solvents, but then the number of different solvents should be reduced. Furthermore, solvents used should be environmentally acceptable.

Focusing on few solvents makes it easier to collect them separately for recycling. This is one important measure in order to reduce the volume of spent solvents. For an effective recycling by column distillation the solvents must be collected type-specific and sufficiently pre-cleaned. This is an important prerequisite to ensure high quality of the recycled solvents and, thus, an acceptance by the user. Despite of all efforts, there will always remain a non-recyclable residue like distillation remainders. These types of wastes must be disposed of as halogen containing or halogen-free spent solvents or solvent mixtures via the university's interim store.

In commercial and industrial areas, spent solvents and solvent mixtures have to be recycled for reuse. The users are legally asked for a separate collection of spent solvents according to their main constituents and reutilize them if this is commercially profitable and there is a market for the recycled products. The general conditions of solvent recycling are different between the chemical industry and the research and education laboratories at the universities. In the industry a relatively low number of different solvents occur in high volumes. Their internal working up or external recycling are, therefore, often profitable. A "thermal reutilization" is only permitted if a reuse is not applicable for different reasons.

For the disposal purposes it will be distinguished between halogen containing and halogen-free solvents. Spent organic solvents consist mainly of several constituents. Their classifica-



tion will be done after the main constituents. If it is not possible to assign them to an individual solvent waste the whole amount will be classified as “solvent mixture”.

Compared with commercial application fields the spent solvents arisen at research and education laboratories at universities are much less. Since they usually consist of complex mixtures they were not recycled but disposed of in the past. Nevertheless, by resolutely separate collection of spent solvents it is possible to conduct a profitable recycling by rectification, whereas the quality of the recycled solvents reaches often that of the virgin products. Particularly at education laboratory courses at universities for sustainable chemistry the recycling and reuse of spent solvents should not be only performed for commercial and environmental purposes, but also for the didactic ones. The experiences gained from the very beginning of the chemistry studies in recycling and waste disposal at laboratory scale enable the graduated chemists to apply the principles of “Green Chemistry” later in their professional lives at production level.

In the following paragraphs solvents and solvent mixtures are described in more detail how they often occur in practice in synthetic laboratory courses and while performing analyses.

Description of spent solvents and solvent mixtures

Halogen containing solvents and solvent mixtures

Halogen containing solvents are usually abbreviated as

- **CFC** (chlorinated fluorinated hydrocarbons),
- **CHC** (chlorinated hydrocarbons)
- **HHC** (halogenated hydrocarbons)

These substances are often harmful or toxic and hazardous in surface waters and/or atmosphere. As **water hazardous substances** they should never get into wastewater. Due to their hazard properties there are numerous laws and decrees to control these substances (e.g., HKWAbfV – German Directive on the Disposal of Halogenated Spent Solvents, BGBl. I, p. 1918, October 23, 1989). It should, therefore, be renounced to apply HHC for cleaning and degreasing purposes, if there are less hazardous substitutes available.



Tetrachloromethane (carbon tetrachloride) is banned as solvent since 1992. According to the CFC-Halon-Prohibition-Ordinance the use of fully halogenated CFCs as coolant and refrigerant in large-scale-units and as cleaning agents and solvents is not longer approved.

Halogen-free solvents and solvent mixtures

Common halogen-free organic solvents can be subdivided into following groups:

- aliphatic and alicyclic hydrocarbons
- aromatic hydrocarbons,
- alcohols
- ketones
- esters
- ethers and
- glycol ethers.

Besides these pure solvents and unavoidable mixtures from synthetic chemistry there are also special blends of solvents for technical applications like diluting agents for dyestuff, resins, metals, etc.

Halogen-free solvents can also be dangerous. Usually, they are (highly) flammable. Some of them are harmful or toxic. If they tend to affect the physical, chemical, or biological conditions of water (which is usually the case for aromatic hydrocarbons and different ethers) they are classified as hazardous to water and must not get into wastewater, as it is the valid for halogen containing solvents.

Materials recycling of spent solvents

According to the legal specification recyclable solvents are usually not classified as waste and shall be introduced into recycling measures. In general, user of hazardous substances are obliged to collect recyclable materials like solvents separately and regenerate (e.g., by rectification) and reutilize them. Materials recycling has the higher priority vs. disposal, whenever

- it is technically possible



- the costs of recycling are acceptable in comparison with the costs of disposal, and
- there is a market for the recycled materials.

The necessity of recycling is obvious at least for substances like halogenated hydrocarbons which are hazardous to health and the environment.

Organic solvents can usually be recycled easily and reused in syntheses. Separately collected solvents can be recycled by distillation, even if they contain other substances with different boiling points. Even solvent-water mixtures can be regenerated in this way. In practice, numerous solvents, which are used regularly at high volumes and are expensive, can be recycled by distillation (e.g., methanol, ethanol, acetone, acetonitrile, xylene, and all halogenated hydrocarbons.)

Central or decentral solvent recycling?

Spent solvents in laboratories can be recycled in a central unit or decentrally on site.

Decentral recycling is usually more advantageous, since in case of central recycling approaches there are some problems faced with like non-type-specific collection due to mixing up of collection vessels. Contamination of the solvents even with small amounts of foreign substances can sometimes make recycling difficult. Therefore, decentral recycling at the place of origin should be favored. A pre-cleaning can be reached just by the use of a rotary evaporator. The subsequent steps of column distillation can then be conducted easier.

If there is no recycling equipment available at the site of formation, spent solvents will be collected and recycled in a **central unit**. It should be pointed out once again that the type-specific collection of the solvents is of most importance for recycling. In order to support separate collection, volumes of the vessels for different solvent types should be limited to 5-10 liter. By reducing the number of the filling processes the probability of mixing up with foreign solvents is reduced, as well. After purification by column distillation in a central unit the recycled solvents can be given back to the waste producer or be provided to other research facilities. An important condition for solvent recycling is its quality after the purification. It should meet the requirements of the user to be accepted.



How can solvent recycling be put into practice at universities?

Recycling and reuse of spent solvents in research and educational laboratories are usually possible and acceptable. Spent solvents make up the main fraction of wastes in chemical laboratories for research and education. Since the separate collection of hazardous wastes is regulated after the Ordinance on Hazardous Substances (GefStoffV) the so collected solvents can easily be recycled decentrally at institute's levels. By this, chemical lab courses can be designed in a sustainable way.

Integration of solvent recycling into chemical lab courses

The participation of students at different steps of purification is useful in order to sensitize them for a safe and environmentally acceptable recycling. They can learn the approaches of separate collection and reutilization of solvents. At the same time, they will realize which efforts have to be made for labour, technique, and energy for the different steps of recycling. An additional goal could be to solve the problems of acceptance of the recycled materials in practice.

The concept of few solvent types as the basis for solvent recycling in practice

A fundamental approach for the feasibility of recycling is to reduce the diversity of solvents used. Within the framework of a sustainable organic lab course it should be checked first whether the great number of solvents usually applied can be reduced. The use of 5-7 different solvents for all experiments can make separate collection and recycling of solvents much easier.

The selection criteria for the solvents used are i.e. universal applicability, polarity, toxicity, price, and occupational safety aspects like flammability, ignition points, etc. Aromatic solvents like benzene and toluene can be renounced easily. In case of halogenated hydrocarbons the use of tetrachloromethane is banned by law (see above), chloroform and dichloromethane should be substituted by suitable other solvents, if possible. The following properties are of interest for the selection of suitable solvents:

- The whole range of solubility should be met with just a few number of non-aqueous solvents.



- The risk potential of the solvents should be low, i.e. they should be classified as harmful or even less harmful after GefStoffV, and they should not be carcinogenic or mutagenic.
- The handling of the solvents should be easy and safe.
- Their reactivity should be low.
- They should have good recycling properties, i.e., they should be easy to purify and to dry.
- Their costs for purchase and disposal should be low.

The following solvents meet these requirements to a great extent and they can be applied for many reactions. Low risk potential and avoidance of halogenated solvents have, hereby, high priority.

- Ethyl acetate (polar, non-protic).
- Acetone (polar, non-protic).
- Ethanol (polar, protic; ethanol is a suitable substitute for the toxic methanol).
- Cyclohexane (non-polar, non-protic; cyclohexane substitutes benzene and can be used as azeotrope former instead of toluene to remove water by distillation. It can also be applied in free-radical reactions instead of tetrachloromethane).
- *tert*-Butyl methyl ether (non-polar, non-protic. It can substitute diethyl ether in almost all cases, except in Grignard reactions).

The use of only few solvents is possible in almost all fields of research and education (syntheses, chromatography, extractions). The use of other solvents (at low volumes) should be restricted to those cases where it is essential. An example for that is the Grignard reaction, which necessitates the use of water-free polar solvents, e.g., diethyl ether or tetrahydrofuran (THF).



Aspects of separate collection of spent solvents for recycling purposes

For an effective recycling of spent solvents it is necessary to collect them type-specific in order to reduce the purification efforts. Although it is principally possible to separate mixtures with several constituents (³ 3) into the individual components by chemical and/or physical measures, this is highly complicated and, therefore, uneconomical. Type-specific collection calls for high attention and care of the staff than the disposal as it was customary in the past. Separate collection should produce batches which should consist of at least 80% of one solvent type at the introduction phase. Later the batches should be better than 90-95% formed of one solvent.

In order to meet these goals it is recommended to provide the laboratories taking part with separate collection canisters for each solvent or solvent mixture used (e.g., cyclohexane / ethyl acetate). These canisters should have a volume of 3-10 liters and be clearly labeled with durable and solvent-resistant tags. Following figure shows an example for such a label on the collection canister.

Large size collection canisters are unsuitable. The volume should be limited to 5 liters. With this, space requirement for each canister is reduced and different canisters can be provided for different solvent types. Furthermore, the total amount of flammable solvents stored in the laboratory is limited, as well. In case of large size canisters many filling procedures are necessary until the canister is getting full. With this, the risk of mixing up with foreign solvents is also increased. However, this affects the quality of the recycled solvents. Too small canisters are unsuitable as well, since they have to be drained too often.



Cyclohexane

Distilled solvent from liquid-liquid extraction

R-Phrases: 11-38-50/53-65-67

S-Phrases: 2-9-16-33-60-61-62

Location: Room A, Fume Hood 2



harmful



highly flammable

!

- Tightly close the collection canister!
- Cap must have an intact seal!
- If anything is spilled while filling and running down the outer wall, exhaust the flask in the fume hood.
- Do not exceed the maximum filling level (see mark)!



How is solvent recycling organized in daily practice?

Conducting solvent recycling should consist of the following steps:

Spent solvents are collected in the different laboratories type-specifically in canisters of 5 L volumes. The user already should have distilled the solvents once in a rotary evaporator before filling into the collection canisters. Water pumps should not be used for vacuum formation. Distillation remainders will be disposed of as hazardous organic wastes.

After filling up canisters will be provided to the unit responsible for solvent recycling. This unit might be a recycling laboratory or a medium-size distillation unit. The canisters will be marked with an inter-office slip which contains informations about the origin of the solvent (name of the deliverer, laboratory) in order to complain in case of unsuitable batches.

The provided canisters will be checked in the central unit by gas chromatography for correct declaration. If the purity is above 90% this batch will be further treated. Batches having more than 10% impurities will be given back. In these cases it is recommended to advice the person involved how to proceed in future in order to increase the separation quality.

Checked batches will be combined in interim store to larger volumes. Two groups will be formed. Recyclable solvents will be assorted after their individual types and than worked up. The others being too highly polluted will also be combined but for disposal purposes.

Recyclable spent solvents will be pre-cleaned in large-size rotary evaporators first. Coarse impurities will remain in distillation residues. The pre-cleaned solvents will then be distilled in computer-assisted rectification units to the final quality of at least 98 %, which is similar to fresh commercial products. In some cases distillation produces azeotropic mixtures which are also suitable for laboratory purposes (e.g., the two components mixtures of cyclohexane/ethyl acetate for gel permeation chromatography). All distillation residues will be disposed of as halogen containing or halogen-free solvent waste according to their halogen content (5 %).

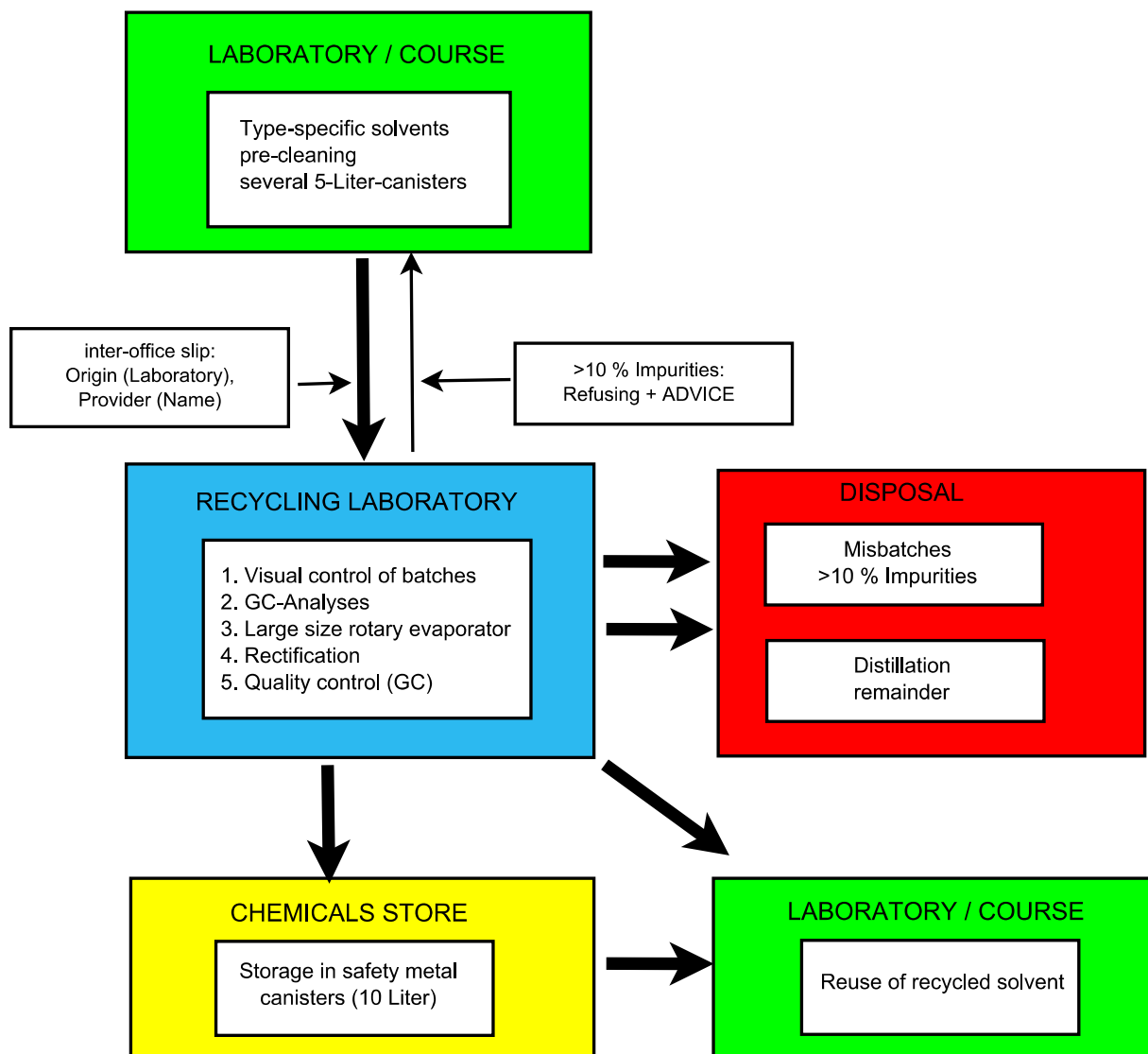
For quality control the distilled solvents will be analyzed by gas chromatography (GC-FID). Their water contents can be determined by Karl-Fischer titration. The analytical results will be documented and provided with the recycled solvents as written certificates. With this



documents the users will be in a position to assess the purity of the recycled solvents by themselves. The quality assurance measures and the transparency of the whole procedure is very important for the acceptance of solvent recycling. In case of careful planning and organization a recovery rate of more than 70 % is achievable.

The distilled solvents will be filled in safety metal canisters of 10 L volumes after being passed the quality control and labeled. Since these safety canisters are explosion- and break-proof even flammable solvents can be stored in laboratories.

The following block diagram schematically shows the most important steps of solvent recycling procedure:





Thermal reutilization and energy recovery from spent solvents

Another approach for the reutilization of spent solvents is the thermal treatment and energy recovery. For thermal reutilization purposes relatively less polluted and halogen-free spent solvents can be applied for as cost-effective input materials. Suitable solvents for this purpose will be collected separately which consist especially of flammable substances like alcohols (methanol, ethanol, isopropanol), ketones (acetone), different esters, xylene, benzene, toluene, etc. These solvents should not contain solid materials nor reaction products which could affect the incineration process. The spent solvents should contain only small amounts of water. It is strictly emphasized that these solvents only consist of **hydrocarbons and oxygen containing solvents** (as individual substances or mixtures of them), **but they should not contain compounds having halogen, sulfur, and nitrogen in the molecule**. While providing to the disposal company it should be declared whether an energy recovery is possible from these solvents.

Disposal of spent solvents

In the past, spent solvents were not recycled but disposed of in daily laboratory practice. This is still routinely practiced in many institutions. Despite of all reutilization efforts applied there will remain some fractions which have to be disposed of as hazardous wastes and be incinerated in approved plants.

When will spent solvents be disposed of? Aspects of categorization

It is already pointed out that complex solvent mixtures cannot be recycled profitably. If they additionally contain halogenated compounds even thermal reutilization (energy recovery) is not possible. Mixtures of halogenated hydrocarbons will be disposed of as

- **solvent mixtures, containing halogens**

If these mixtures contain also water, then they will be declared as

- **solvent-water mixtures, containing halogens**



Halogen-free solvent mixtures consisting of several constituents will be best declared as

- **solvent mixtures, halogen-free**

Many halogen-free solvents, particularly the strongly polar ones, are partly or completely miscible with water. If those mixtures contain high amounts of water then it is not profitable to distil them due to high energy demand. They will be disposed of as

- **solvent-water mixtures, halogen-free**

Mixtures of solvents with water are not further defined regarding their constituents. But for the disposal company it is of importance to roughly know how much water these mixtures contain, since this might influence their combustibility. In these cases it is useful to roughly describe these mixtures as “consists mainly of solvents” or “consists mainly of water”. Herewith, the following disposal schemes are determined.

For an organic solvent content up to 20 % (“consists mainly of water”) the disposal routes are following (while considering the further impurities):

- **Aqueous laboratory wastes** (only in case of ordinary water miscible solvents like methanol, ethanol, isopropanol, acetone, etc.),
- **Solvent-water mixtures, halogen-free** (if the content of aromatic solvents like benzene, toluene, xylene, pyridine, etc. are above 1 %, and/or of halogenated hydrocarbons are below 5 %),
- **Solvent-water mixtures, containing halogens** (if the content of halogenated compounds are above 5 %).

If the solvent contents are about 20 – 80 % these mixtures will be disposed of as

- **Solvent-water mixtures, halogen-free, or**
- **Solvent-water mixtures, containing halogens,**

depending on further impurities.

For spent solvents consisting of more than 80 % (“consist mainly of solvents”) the following disposal routes are recommended:



- **Spent solvents, halogen-free** (type-specific solvents will be declared. In these case, recycling is a desirable alternative)
- **Solvent mixtures, halogen-free,**
- **Other non-halogenated solvents.**

Collection of spent solvents for disposal purposes. What should be considered?

Spent solvents for disposal should be classified after different categories and collected separately. It is prohibited by law to intentionally mix up with foreign substances or solvents.

Obeying this rule is also important in order to ensure the occupational safety in the laboratory, since in opposite case the substances may undergo dangerous reactions with each other. **Chlorinated hydrocarbons** can react with some other compounds under explosion, particularly with **alkaline and alkaline-earth metals** as well as with their oxides and hydroxides. Another serious problem may arise if chloroform is mixed up with acetone, which often led to accidents in the past.

For safety reasons halogen-free spent solvents should be checked whether they contain peroxides. The batches should be neutralized and the peroxides should be reduced, if necessary.

Plastic canisters of 5 liter volumes are best suited for the disposal of spent solvents. They should be of durable quality and clearly labeled. By separate collection of halogen-free and halogen containing spent solvents institute's money will be saved since the disposal of halogen containing spent solvents are much more expensive than of the halogen-free ones. After being filled up the collection vessels (canisters) will be temporarily stored at the interim store of the university in large-size leak-safe metal containers. After reaching certain amounts there these laboratory wastes will be handed over to special disposal companies for hazardous waste incineration purposes.