HANDBOOK OF LABORATORY WASTE DISPOSAL

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CHAPTER 14

Materials Recovery

14.1 GENERAL COMMENTS

The salvaging of worthwhile material from waste has much to recommend it, providing it does not interfere with the safe and efficient operation of the laboratory. Management should realistically cost the time and effort involved, compared with the costs of disposal and purchase. For example, a complex distillation process may not be justified to recover a cheap solvent in modest quantities. On the other hand, a chemically and physically identical process may be well worth while to recover a deuterated or ^{14}C labelled version of the same solvent.

The hoarding of items which are unlikely to be used is not uncommon, generally on the grounds that 'it is a pity to throw it away'. Such practices are not economically justified, and can detract from the safety and efficiency of the laboratory by cluttering the place with broken apparatus, unwanted chemicals and often a large amount of combustible plastic and cardboard.

It is suggested that the following items are *not* kept, unless an actual financial saving can be demonstrated, and there is no hazard in retention.

(1) Non-functioning electronic apparatus where replacement parts are no longer available.
(2) Electric devices which cannot easily be made to conform to current legal safety requirements.
(3) Gas cylinders near to (or past) their regular pressure testing date. (See section 9.4.)
(4) Part-filled gas cylinders which are unlikely to be used for any specific

(5) Boxes, bottles and used containers beyond the obvious uses in the next two weeks.
(6) Used disposable plastic items such as syringes and single-use pipettes. It is impractical and unsafe to try to clean them and defeats the advantage of disposables.
(7) Rubber and plastic items (tubing, gloves, etc.) which are visibly perishing with age or usage.
(8) Chemicals and assay kits or other limited life items which are well past their stated expiry date.
(9) Obviously degraded chemicals.
(10) Bottles or jars of chemicals which have been more than three-quarters emptied and where the residue is worth less than £1 sterling or $1 US.
(11) Damaged glassware which cannot be repaired within the institution (or where experience has shown that it will not be) in a reasonable time to a safe standard.
(12) Exceptionally hazardous substances beyond the immediate need for them.

14.2 GLASSWARE

Many technicians and scientists have the skill to make small repairs to glassware using a simple gas torch. However, it is important that individuals do not attempt repairs beyond their skill or facilities. Work with ground glass joints or with more complex items normally requires inspection by a professional glassblower, who is able to judge whether the item can be safely repaired.

CAUTION: items for use under vacuum must be properly annealed before use. It is preferable if they are also inspected with a polarized light viewer for strains. Annealing is also recommended for repaired apparatus where a breakage would be costly or dangerous.

It is usually easy and worth while repairing small chips in the top of measuring receivers such as beakers and measuring cylinders. With a diamond saw it is possible to cut down a damaged (say) 100 cm^3 measuring cylinder to give a squat 50 cm^3 one. However, it is generally impractical to repair calibrated items such as volumetric flasks, pipettes or flow measuring tubes.

Items with ground glass joints are usually worth repairing owing to the value of the joints themselves. Even if the apparatus is too badly broken, a glassblower may be able to cut off joints for use in making other items.

CAUTION: it is the responsibility of the laboratory to ensure that items

14.3 SCRAP METAL

Many laboratories find themselves with substantial quantities of metal goods which may have a scrap value. Even where the value is low (as is the case with most steel) there is some satisfaction in receiving a small payment instead of giving it. When many kilograms of copper, brass, tin or some alloys are involved, then there may be a useful sum involved. This most commonly applies to electric motors, resistance boxes and the like. Some electronic apparatus has significant quantities of precious metals, which specialist scap dealers are prepared to extract. An unwanted stock of photographic film, prints or X-ray plates has some scrap value for its silver content. Lead from acid batteries can be sold, and the same dealers are usually interested in relatively small amounts of the elements antimony, arsenic and bismuth in various forms.

It is rarely worth while a laboratory trying to separate out the metal from items such as those mentioned above. The process can be hazardous and are better left to the scrap dealer. As a rule of thumb, no laboratory manager can expect to get the better of a scrap dealer in a commercial transaction.

14.4 PRECIOUS METALS AND MERCURY

14.4.1 General Comments

Mercury, silver, platinum and palladium are frequently used in laboratories. Gold, osmium, iridium, rhodium and ruthenium have specialized usage. These metals are all regularly traded by precious-metal dealers. The lanthanides (also called 'rare earths') are expensive but mainly of interest to specialist chemical suppliers.

Recovery procedures are of two kinds: (1) where the laboratory is saving a metal for further use itself; and (2) where the material is to be sold. In the latter case, some suppliers will accept waste of certain specifications and make an allowance against future orders. This is usually easier than trying to sell material on the open market.

In the first case, where a laboratory intends to re-use the element, it is essential that the laboratory has sufficient knowledge of the chemistry to be able to prepare the desired compounds in the necessary quality. An example is the preparation of certain kinds of metal catalyst.

In the second case it is mainly required to concentrate the metal and present it in a form acceptable to the purchaser. Note that for metals of very high value, some companies will buy solutions, and most will buy precipitates containing a few per cent of precious metal. It is by no means necessary to prepare the metal, though it does of course command a higher price.

14.4.2 Recovery from Solutions

A simple method which is often overlooked is to evaporate down solutions of valuable metals and ignite the residue. If

up in further chemical solution. This is not always practical, and should not be carried out where the likely solids are either explosive (as is the case with some nitrogen compounds including cyanides) or volatile (as is often the case with mercury, osmium and some ruthenium compounds, and many metal-organic compounds). However, concentration by evaporation is frequently a useful preliminary to chemical treatment.

Sodium borohydride is a particularly useful reagent since it will reduce aqueous solutions of most valuable metals direct to the metals. This can be applied to a wide range of solutions, often by simply stirring in an appropriate quantity of borohydride solution (sometimes heating helps, and for strongly basic solutions some acidification is required). Metals recoverable in this way are platinum, palladium, rhodium, gold, silver, mercury. Less valuable metals which may be simultaneously produced are lead, copper and cadmium. Note that other species present may also be reduced — for example nitrate NO_3^- is reduced to ammonium NH_4^+ — which will require some equivalents of the borohydride. Some transition metals may precipitate out as their borides.

Instead of production as a powder, the metal can be deposited onto a solid (so-called electroless plating) such as a piece of the metal itself or copper sheet or mesh. The solid should be clean, best of all etched with acid, and usually gives best results if it is treated with (i.e. immersed in, or brushed with) an aqueous solution of tin(II) chloride or palladium(II) chloride immediately prior to the borohydride process.

CAUTION: there may be a fire hazard from hydrogen production and some metal powders may be pyrophoric (spontaneously combustible in air). The presence of arsenic, antimony, bismuth, germanium, selenium, tellurium, tin or very strong acid may in some cases result in toxic gases (the hydrides) being given off.

Some solutions are only stable under acid conditions so the metal or its oxide can be produced by careful treatment with alkali. Alternatively, an insoluble compound can be precipitated out by the addition of the appropriate ion — for example, sulphide will precipitate mercury sulphide; chloride will precipitate silver chloride. Such processes are most effective within a limited pH range and may be hindered by the presence of complexes of the metal, such as cyanide complexes. Thioacetamide is more convenient to use than hydrogen sulphide, though it is slower and is a weak carcinogen. Zinc dithiol usually gives a better quality precipitate than sulphide, with only marginal contamination by the zinc.

For a relatively noble metal under neutral-to-acid conditions, it is often possible to displace it from solution with a cheaper and less noble metal. For example, iron is used to displace silver from solution in commercial recovery from photographic and other waste.

Electroplating can be carried out with commercial apparatus where there

simple, and many laboratories can use existing d.c. apparatus to recover small quantities, where electric efficiency and speed are not important. For example, a piece of silver or platinum foil may be built up (perhaps over a period of years) to a saleable weight by the regular recovery of quite tiny amounts. A range of 2 to 4 volts is usually sufficient. A milliammeter is useful to indicate the rate of deposition: when this begins to fall off the solution is depleted, and the plating should be stopped. Best results are obtained from slow deposition. Graphite is suitable as the other electrode because it does not add metal to the system, though it can degrade in strong sulphuric acid. Lead is suitable in sulphuric acid and in some other solutions. The receiving electrode does not have to be identical to the metal to be plated: both copper and stainless steel have been used successfully. The process is usually most efficient within a particular pH range.

It is possible that liquid–liquid extraction might be appropriate for some solutions. It should be considered if there is sufficient value in the metal to warrant the extra trouble, and where other methods are not suitable. Usually an organic complexing agent is used to form a compound with the element, the compound being soluble in an organic solvent into which it passes. (See section 9.3.6.4.) The appropriate reagents are generally expensive, and the chemistry involved is somewhat specialized, but it has some possibility of giving a very clean separation from a complex or difficult solution.

A promising alternative is certain plastic resins with a selective affinity for some metals. The solution can be passed through a bed of resin, or beads can simply be stirred into a container and filtered off. The metal is recovered by ashing the resin. At the time of writing, the authors know of no resins readily available in laboratory quantities. However, there is very active commercial development for industrial recovery and pollution control, and products are available in tonnage amounts. The resins are generally referred to as 'macroporous' or 'macroreticular' and should not be confused with ion-exchange resins. Unlike the latter they will absorb valuable metals from solutions of as little as a few parts per million in the presence of large amounts of many other ions. They typically contain active aromatic groups such as vinyl pyridine linkages.

14.4.3 Recovery from Solids

Sludges, precipitates, collections from drains and floor sweepings from spills (or vacuum cleaner contents) may well require some separation before they can be sold or used. The exact process will require some knowledge of the mixture, the chemistry of the metals involved, and a good dose of commonsense.

The following example illustrates some of the techniques which might be used. Suppose that the platinum precipitated in a

The solid is stirred with warm water and a little detergent. This dissolves some dirt and chemicals, and suspends dust and similar material, which can be decanted off after a few minutes settling. This can be repeated several times, allowing the heavy metal particles time to settle to the bottom. The process is then repeated with warm dilute nitric acid to dissolve out any other metals such as iron. The remaining solid is filtered with ashless paper and washed with water. It is then dried and heated in a furnace to 450 °C to burn off any organic residues. The solid is allowed to cool and dissolved in aqua regia. The resulting solution is filtered through glass-fibre paper to remove any sand. The relatively pure solution can now be recovered by electroplating, precipitation or ashing.

14.4.4 Silver

Because of its extensive use and considerable value, silver is the element most commonly worth recovery. There are many commercial and personal methods, of which the following is only a selection of the more common.

For recovery from Chemical Oxygen Demand (COD) test solutions, the following method has been recommended. The amount for one test is small, but as it is routine in many laboratories it can accumulate useful quantities. It can be applied to many other solutions of silver salts.

The solution is brought to about pH 2 (use test paper) by the addition of 6 mol dm^{-3} HNO_3 or dilution as appropriate. (Neutralization with base may cause some silver to come out as colloidal oxide.) A near saturated solution of sodium chloride is stirred in, to precipitate out silver chloride. A 10% excess is adequate. The precipitate is filtered off and washed with dilute H_2SO_4, then twice with de-ionized water, and dried. The resulting solid is saved until there is sufficient for recovery, when it is ground into a powder. The powder may be sold as such, or it may be dissolved in photographic fixer and added to photographic solutions for recovery. Otherwise the following method can be used.

100 g of the powdered silver chloride is mixed with 50 g of granulated zinc (not zinc dust — the reaction may be too violent). This is then stirred into 500 cm^3 of warm dilute (2 mol dm^{-3}) H_2SO_4 in a fume cupboard. The zinc dissolves with vigorous evolution of hydrogen. The liquid is decanted, and the solid treated with a further 50 g of zinc and 500 cm^3 of H_2SO_4 as before. When the second batch of zinc has dissolved, then about 5 cm^3 of concentrated H_2SO_4 is added and the mixture heated with stirring to 90 °C. The mixture is allowed to cool and the silver metal filtered off, and well washed with de-ionized water until no sulphate is detected by the $BaCl_2$ test.

Any residual silver chloride can be tested by dissolving a sample in concentrated nitric acid, which should give a clear solution. Turbidity indicates silver chloride, which can be removed by a further treatment of the

large-scale use of photographic solutions should really have a commercial electroplating unit. This can be rented and a service arranged whereby payment is made each time electrodes are replaced (on a time or weight schedule). For smaller or intermittent users there are several systems possible.

The simplest system is a replaceable cartridge which fits into the drain line. It contains steel wool which exchanges with the silver, iron going into solution and a sludge of silver falling to the bottom of the unit where it is collected. This is inexpensive and little trouble. It requires an effluent between pH 4 and pH 6.5, which is usually the case. (Below pH 4 the steel dissolves away; above pH 6.5 the process is not very efficient.) The initial efficiency is high, but becomes lower as the cartridge nears exhaustion.

CAUTION: if a steel wool cartridge is removed before it is exhausted it should not be allowed to dry out. The rusting reaction on its extended surface can generate sufficient heat to become a fire hazard.

Another commercial device uses a different electrochemical principle. Zinc and stainless steel are placed in electrical contact in the solution. The zinc dissolves and silver is plated onto the stainless steel. The device is usually placed in a fixing bath. As well as recovering silver it has the benefit of extending the useful life of the thiosulphate fixing solution.

Silver can be recovered on a batch basis from photographic solutions by precipitation. Sodium chloride will produce a mixed chloride and dichromate precipitate from used 'bleach-fix' solutions. This can be sold to a refiner direct, or dissolved in fixer for recovery by one of the above devices. Sodium sulphide will precipitate-out silver sulphide from alkaline fixers.

CAUTION: on no account should sulphide and acid come into contact, as they liberate the extremely toxic gas, hydrogen sulphide.

It is better not to add an excess of sodium sulphide as this could give rise to smell and other problems with the effluent. It may take some days for the silver sulphide to settle properly. This can be improved by stirring in some silver sulphide (which was made previously) before adding the sodium sulphide.

It is possible to convert the silver sulphide to metal, but it is more usual to sell it to a refiner.

The silver in fixing baths may also be reduced directly to the metal by the use of either sodium dithionite or sodium borohydride. Note that the former gives off toxic sulphur dioxide gas. Both in practice can give problems, with the silver coming out as too fine particles which tend to stick to the walls of the vessels.

CAUTION: solutions of silver containing ammonia (e.g. mirror silvering solutions, Tollen's Reagent) should not be stored for recovery. They should be decomposed on the same day on which they are made, or explosive compounds may form.

14.4.5 Mercury

Mercury can be a very troublesome material. Its compounds are highly toxic and thus unwelcome in the environment. The elemental form is extremely difficult to clean up if spilled (see also section 15.2). Note that tiny drops of mercury metal, or even the vapour from mercury spillages can have a devastating effect on delicate electric and electronic apparatus. It is therefore wise to take particular care to avoid (or at least to contain) spillages and to ensure that as much as is practicable is collected for recycling.

Many university chemistry departments (and some physics departments) operate mercury recovery procedures. They may be willing to accept small quantities (say 10 g or more) from local schools or other laboratories. A quantity of a kilogram or more may even have some value for a local scrap merchant (see section 14.3).

CAUTION: the preparation of pure mercury metal from dirty mercury or its compounds can be extremely hazardous. It should only be carried out by a knowledgeable person with special facilities in a controlled environment, such as a commercial refiner or the laboratory of a professional chemist.

This handbook does not set out to instruct such experts, and therefore details of final refining are not given here.

Where an organization has many separate laboratories using mercury metal (e.g. an academic institution, a group of schools, a research institute, or group of industrial laboratories) it is strongly recommended that a centralized mercury service be set up. If the organization has the necessary facilities and expertise the mercury may be recovered in-house, otherwise there should be an arrangement with a local refiner.

The mercury service has obvious economic and safety benefits, but can also improve the scientific effectiveness of some work. In particular, it can ensure that the liquid mercury in certain apparatus is in good condition and therefore the apparatus works correctly. Old mercury usually has oxide film (and often other contamination) which alters its electrical conductivity, its flow properties, meniscus shape, etc.

The mercury service should have the following features.

(1) A central record of mercury purchase, waste removal and distribution. This should be examined to see if there are any losses which may be due to faulty equipment or practice. (The authors know of one institution which discovered more than 100 kg in floor drains due to cracked dashpots which were periodically topped up.)

(2) In issuing mercury, steps can be taken to ensure that users are properly

equipped (with trays, spill control aids, etc.,) and aware of the proper procedures for safety and for returning used material.

(3) In addition, the amounts issued can be just as much as are required. It will not then be necessary to have part used commercial containers kept in the general laboratories.

(4) There should be a probable date when the mercury is to be returned for each issue. If this is more than a year, the mercury should (if possible) be inspected annually.

(5) Apparatus containing mercury metal should, where practical, be inspected annually by a competent person. If the mercury is dirty it should be replaced. If the apparatus is unlikely to be used in the foreseeable future, consideration should be given to return of the mercury to the secure central service store. (Possibly with the apparatus.)

(6) The majority of users should not attempt to clean mercury themselves. The best technique is for the dirty mercury to be exchanged for a similar quantity of clean material. There is great merit in deciding that only certain persons should actually handle mercury. In particular, it may be possible to avoid spillages by people who are not experienced in its unusual liquid properties. For example, it may be the procedure that a student reports that mercury appears dirty, and for a technician to actually drain and refill the apparatus.

Mercury metal waste is best collected in strong polyethylene or polypropylene bottles or jars, which have been made without a seam (because the seam may burst). Glass jars should only be used for items such as broken thermometers, where the pieces and droplets are collected under water for proper treatment later.

The isolated user can sometimes clean up mercury sufficient for his needs without fully refining it, by the following techniques. Particles of glass from broken apparatus can be strained out with a plastic mesh (e.g. a tea strainer). As mercury is heavier than virtually all the common items of dust, debris and its own oxide, much contamination can be removed by simple gravity sedimentation. The mercury is placed in a suitable device, such as a glass separating funnel, and the tap opened to allow the mercury to drain away slowly, leaving oxide and dirt in the top layer.

CAUTION: the funnel must be strong, well supported and have a secure tap which cannot come loose.

A modification of this technique is to place a filter paper in a funnel, load with mercury then carefully pierce the point of the cone with a stainless steel pin. The mercury drains through the pin-hole, and oxide and dust are retained on the rough surface of the paper.

Where contamination by other metals such as zinc or copper is known to have occurred, some users like to convert these to oxide by gently bubbling

air through the mercury for a day or two. The resulting oxide crust is then removed as above.

To remove any remaining traces of oxide, it is possible to treat the mercury with dilute nitric acid. Some device is required to expose the maximum surface area. This is usually a fine dropper leading into a tall column (0.5 to 1.0 m) of the nitric acid solution.

Note that the solutions and oxides collected in the above procedures must be disposed of as toxic mercury waste by a technique appropriate to the amount and local situation.

Regular amounts of solution, or a single large batch, can have mercury removed by the methods given in section 14.4.2. Electroplating and reduction by borohydride are quite practical, but the most common technique is to treat the solution with hydrogen sulphide, sodium sulphide or thioacetamide under acid conditions, so that the sulphide is precipitated. A solution of 13% thioacetamide is commercially available especially for this purpose.

CAUTION: hydrogen sulphide is highly poisonous. Sulphide and thioacetamide may release hydrogen sulphide if the acid is very strong. Thioacetamide is a cancer suspect agent. Proper protection must be used against these dangers.

The sulphide precipitate should be sold or given to a competent refiner. Note that it will contain some pure mercury metal if the solution contained the mercury(I) ion. Excess sulphide reagent (particularly sodium sulphide) may cause some of the precipitate to redissolve.

As an alternative, solutions of mercury(II) and chloride can be reduced with sodium bisulphite to give insoluble mercury(I) chloride precipitate. Solutions of mercury(I) compounds give the same precipitate if treated with dilute hydrochloric acid, providing they are not strongly complexed. The chloride precipitates are less acceptable to refiners.

Where mercury metal is used in any great quantity, it is likely there will be special local exhaust ventilation. If the exhaust air is passed through a suitable absorber then mercury will accumulate to a level which can be worth salvaging. Ordinary activated charcoal is surprisingly effective. Iodized charcoal may give more efficient capture, but it is less easy to salvage. Sulphurized charcoal gives at least as good efficiency of capture, and it is easy for the refiner to recover the mercury from it. Sulphurized charcoal cartridges are commercially available for this purpose. They can be fitted to extract ducts or the outlets of vacuum pumps or other mercury apparatus.

14.4.6 Gold and Platinum Group Metals

The very high scrap value of these metals means that even tiny scraps are usually worth keeping. It should not be forgotten that they are used in

various instruments, and it may be worth salvaging broken electrodes, heating coils, ionization heads, etc. There is little the amateur can do with scrap items other than collecting them in separate metal categories, and offering gram or larger amounts to a precious-metal dealer. Unused chemicals are normally most saleable if presented in their original containers. This applies to alloys, compounds and preparations such as precious-metal coated catalysts.

Regrettably, many textbooks on practical chemistry with precious-metal catalysts do not give any advice at all about recovery of the used catalyst, and it is likely that a significant amount is discarded. The properties of catalysts vary, and the chemistry of the elements more so, so a single recipe cannot be given. However, as a rule of thumb, solid catalysts should be kept wet after use, should be well rinsed to remove any of the reagents or by-products and should be kept under water until a recovery procedure has been found.

Vogel's is probably the most widely available textbook which gives detailed advice on the preparation and recovery of different platinum catalysts, though there are others. For recovery of metals from compounds it is necessary to consult with books or people having specialist knowledge of the chemistry of these elements.

14.4.7 Lanthanides

This group of elements provides a number of specialist reagents, notably due to their electronic and spectroscopic properties. A laboratory handling significant quantities of a particular element for some particular work is advised to look into the necessary chemistry for recovery.

Generally they can be precipitated from aqueous ammonia, although the presence of complexing agents such as citrate may prevent this. It is convenient to prepare the carbonates by precipitation with sodium hydrogen carbonate, as the product can be readily dissolved in acid and is more easily filtered than the hydroxide. Note that sodium carbonate should not be used, as the precipitate tends to redissolve in the reagent.

The cost of individual elements varies considerably, but there is not a ready market for waste. The facilities of the individual laboratory and the use of the element will determine if it is practical to re-use it.

14.5 GENERAL CHEMICALS

It often happens that stocks of chemicals become slightly dirty, or suffer surface degradation. It is sometimes worth while purifying the chemical. This will of course cost money, effort and the time of skilled staff. On the other hand it will save the cost of repurchase and the cost of disposal. More importantly, it will reduce the quantity of harmful waste and the attendant difficulties of legal disposal. There may be some incidental benefit in (say) training of junior staff, or in finding interesting projects for certain categories of student.

As an example, take sodium metal. It is quite cheap to buy, but rather difficult to dispose of (see section 9.3.8.1). Stock bottles can often become unusable owing to the formation of oxide, hydroxide and carbonate crusts on the sticks or pellets of metal. Clean sodium can be got out of the crust in the form of 'shot' or 'eggs', which is in fact preferred by many chemists.

The pieces are cut in half under paraffin, the excess paraffin is removed with filter paper, and the pieces are placed in a flask of dry xylene fitted with a stirrer, nitrogen purge and reflux condenser. The flask is then heated on an electric mantle with stirring. Above 97 ° the sodium melts and forms globules. The speed of the stirrer determines the size: when this has been adjusted, the flask is allowed to cool down.

A similar procedure can be carried out for potassium (melting point 64 °C), but care should be taken not to cut up samples showing an orange or beige coating of peroxide, as they may explode. It is possible, but not usually practical, to carry out an equivalent procedure for lithium, owing to its higher melting point and lower density.

For sodium, it is better to prepare the shot in amounts needed as the experiments demand. For potassium there is an argument for occasional preparation of clean metal so that oxide formation is not allowed to progress to the dangerous superoxide stage.

General methods of purification of laboratory chemicals are given in Fieser and Fieser's classic volumes. A specific book is that of Perrin, Armarego and Perrin. Many practical organic chemistry books give purification methods, but most inorganic texts do not. An excellent example of one that does is Brauer's.

14.6 SOLVENTS

14.6.1 General Comments

Organic solvents are the most obvious chemicals for recovery. The technology is not difficult, and has many advantages in reducing the cost and trouble of waste disposal. Many laboratory workers feel some satisfaction in conserving resources and reducing the volume of chemical waste they contribute to the environment. Educational institutions often feel that student involvement gives both technical and moral teaching which is worth while even though the cost savings may be trivial.

It cannot be stressed too strongly that a successful programme of solvent recovery requires careful organization. Solvents must be kept segregated prior to the recovery process, and care must be taken that unnecessary dirt is not added through poor labelling, poor practice or a careless attitude. For example, a laboratory accumulating a single solvent, very slightly contaminated from a routine test, could have the whole recovery process ruined by a single beaker of mixed solvents being added to the can.

There is a widespread belief among non-scientific workers (and some less experienced scientific ones) that it is possible to separate a mixture of many

solvents ... its pure components by simple distillation. In fact, it is virtually impossible. The ideal candidate is a single solvent containing a non-volatile (and non-degradable) dirt, for example toluene containing a wax. A typical process would produce relatively pure toluene, and a residue which is not pure wax, but a mixture of wax and toluene, probably 10 to 40%, depending on the viscosity.

As a rule of thumb, it is usually possible to separate a mixture of two solvents (or two solvents and a non-volatile dirt) providing their boiling points differ by at least 10 °C. Using the same criterion, it is usually possible to separate out one pure component, often two and sometimes three from a mixture of three solvents. Mixtures of 4 or more solvents are increasingly difficult, and will generally require considerable knowledge in planning the separation, and quite a lot of skilled attention during the recovery process.

Mixtures of solvents with similar boiling points (e.g. n-heptane 98.4 °C and iso-octane 99.2 °C) cannot be separated by ordinary distillation. In addition, some materials form constant boiling mixtures, or azeotropes, of which the best-known example is ethanol and water. Thus pure ethanol cannot be distilled from a mixture with water, even with the most efficient apparatus: the best that can be achieved is 95.6%. Azeotropes are quite common. Another example is cyclohexane (boiling point 81.4 °C) and iso-butanol (boiling point 108.3 °C). These would be easy to separate were it not for the formation of azeotrope containing 86% cyclohexane, which distills off at 78 °C. A random mixture of 4 or more solvents has quite a good chance of an azeotrope combination, which will greatly affect the feasibility of distillation.

Many laboratories, even with experienced chemists, forget that there are many processes other than distillation which may be used. These are sometimes simpler, can often make distillation more effective if used as a pre-treatment, and may even make distillation unnecessary.

In organizing a solvent recovery programme, the person responsible should consider the use of the solvent and the recovery techniques possible. A first consideration should be the changing of use or solvent to aid recovery. For example, if a slightly more expensive solvent would do he job just as well, but be easier to recover, then it may be a better choice. Similarly, when there is a routine procedure for recovery of a particular olvent, then other laboratory work may often be adapted to make use of iat solvent instead of the traditional one.

A primary consideration is safety. Storage of solvents for recovery ould be in suitable containers, correctly labelled, and located so that ey are convenient, safe and legal. See sections 2.4 and 3.5.

In addition the recovery apparatus must be used with regard to the ailable facilities (e.g. fume extract, drains, flame-free areas) and to the chnical skills of the people concerned. It is best if any new solvent covery procedure is checked in advance by a person with sufficient owledge of the chemistry and practical experience to spot any hazards

and deal with them. As an aid, a check list of some common hazards is given in Table 14.1.

14.6.2 Strategies for Recycling

There are many ways in which a solvent can be used several times. Some examples are given below.

(1) Hexane was used to extract a substance from a solid product, which was then measured by UV spectroscopy. The waste solvent from this process contained a small amount of relatively inert solute, but was still of high purity, exceeding the specification for reagent grade chemical. The hexane could be used without treatment in a preparative chemistry laboratory.

(2) A high boiling petroleum fraction became contaminated with several per cent of (low toxicity) plasticizer. It was used to clean paint brushes during laboratory modification.

(3) Spectroscopic quality carbon tetrachloride was used to extract a dye for measurement by visible light absorbance. The dye was removed by treatment with activated charcoal and the solvent could be used again.

(4) At the beginning of a chemistry course, each student was given a limited amount of the necessary solvents. The student had to recover solvent after use for his needs in further experiments, which encouraged careful work and was an exercise in itself.

(5) A regular experiment used 50% aqueous acetone to wash the product. Instead of using pure acetone, it was found that the acetone–water azeotrope (88.5%) could be diluted to the working concentration. This azeotrope was easily recovered from the waste washings, supplemented by acetone waste from another experiment.

(6) Scintillation cocktails were bulked by collection in a suitable can, then treated with activated charcoal to remove volatile radioactives. This gave 3 fractions by batch distillation. The first fraction was toluene (and water which settles out) which was free of radioactivity (i.e. not significantly above background) and pure enough for immediate use. The second fraction was xylene (and water) with a little toluene contamination and radioactivity a little above background. This was added to boiler fuel for disposal. The still residue was water, emulsifiers and the majority of the radioactivity. As this residue was non-flammable, it was acceptable for land disposal. (In some areas it may have been acceptable for sewer disposal.)

(7) A regular student experiment required material to be processed in a large bulk of solvent which was then evaporated down, losing the solvent. The instructions were changed so that the major concentration was carried out on a rotary evaporator. Each student saved the

Table 14.1. Hazards in solvent recovery

The following is a reminder of potentially dangerous characteristics of some solvents and mixtures, as they affect recovery by distillation, adsorption and some other treatments. Examples are given of typical chemical groups, in which it should be assumed that all compounds including that group have the specified hazard. In addition, there is a partial list of common solvents where the usual name does not include the group name (e.g. tetrahydrofuran is actually an ether) or where the hazard is unusual.

(a) Solvent groups

Chemical group	Examples	Hazards
Acrylic	Acrylic acid, acrylonitrile, methyl acrylate	1, 3
Aldehyde	Acetaldehyde, crotonaldehyde	3
Allyl	Allyl chloride, diallyl ether	3
Bromo- Chloro- Fluoro-	Bromoform, carbon tetrachloride, trichloroethane, fluorotrichloroethane	1, 4
Diene	Cyclohexadiene	2, 3
Ether	Diethyl ether	1, 2, 5
Ethoxy- Methoxy-	Dimethoxyethane, ethoxyethyl acetate	2, 5
Glyme	Diglyme, monoglyme	2, 5
Isopropyl	Di-isopropyl ether, isopropyl alcohol	2, 5
Nitro-	Nitromethane, nitrotoluene	6
Vinyl	Vinyl acetate, divinyl benzene	1, 3

(b) Some individual solvents

Common name	Other names	Hazards
Acetonitrile	Methyl cyanide	3
Acrolein	Acrylaldehyde, propenal	1, 3
Cellosolve	2-ethoxyethanol, ethylene glycol monoethyl ether	2, 3
Cumene	Isopropyl benzene	2, 5
Dekalin	Decahydronaphthalene	2, 5
Propan-2-ol	Isopropyl alcohol	2
Pyridine		5
Styrene	Vinyl benzene	1, 2, 3
Tetrahydrofuran		1, 3, 5
Xylene		5

(c) Hazardous mixtures

Substance 1	Substance 2	Hazard
Any solvent liable to peroxides, i.e. those with note 2. above	Any ketone, e.g. acetone and methyl ethyl ketone	The ketone aids the formation of peroxides. Substances such as cumene or propan-2-ol which are usually only slowly oxidized can become explosive in a short time
Bromo-, chloro-, or fluoro- solvents, especially chloroform	Ketones, especially acetone	Violent reaction in the presence of base (e.g. KOH) or some other catalysts
	Alcohols + NaOH or KOH	Violent reaction with base, aided by the alcohol as co-solvent
Nitro-solvent, especially nitromethane	Amines, e.g. methylamine, aniline and diaminoethane	Mixtures may detonate on impact or friction
	Bases, e.g. KOH and NH_4OH	
	Acids, e.g. H_2SO_4 and HCOOH	
	Chloroform or bromoform	

Hazards

1. Normally supplied with an inhibitor. Recycled material may have lost the inhibitor, and therefore be especially likely to undergo the following hazardous reactions.
2. Forms peroxides on storage. Distillation may lead to an explosion. Air contact during processing, e.g. an air bleed to a distillation flask, may lead to high peroxide concentration in the product. Materials stored without an inhibitor may become shock-sensitive explosives.
3. Liable to polymerize. This can cause degradation of product, or may even be explosive, particularly on heating or in the presence of certain chemicals.
4. Violent reaction with aluminium (and its alloys), titanium or zinc when subject to heat, friction or impact.
5. Laboratory residues often contain sodium wire, or solid KOH as drying agents.
6. These compounds should not be distilled, as they are liable to explode. Can form shock-sensitive explosives with amines or alkalis.

(8) A quality assurance laboratory used chloroform to extract wax from a commercial product for infra-red analysis. The solutions were accumulated until 2 litres were available, then batch distilled (with no column). A little ethanol was added to the wax-rich residue before placing in the discard can. An occasional check was made that the recycled chloroform contained sufficient ethanol (1 to 2%) as stabilizer. This normally distills over in the first part of the recovery process.

(9) A group of Research and Development laboratories agreed to standardize as far as possible on a few solvents. Each scientist used his knowledge to judge if a particular waste was recoverable. If so, he carried out any preliminary removal of solids, neutralized any acids or bases, etc. It was common to carry out a rough separation into 'clean' and 'dirty' solvent by partial distillation or rotary evaporation. These solvents were then collected in separate 'recoverable solvents' cans, distinct from the discard cans. When near full, a particular solvent was distilled in a standard preparative still by an experienced technician. The product was checked (by gas chromatography) and labelled as to its purity. A stabilizer was added to one solvent. Some batches were of excellent quality; others were suitable for less critical work.

(10) A major hospital histology laboratory collected its xylene waste, and distilled it on a commercial automatic still. Care was taken that the waste did not become contaminated with other solvents or materials from other laboratories or procedures. This produced a 60% saving in solvent purchase, and a similar reduction in disposal costs. The payback time for the capital cost of the still was less than 6 months.

(11) Experiments on droplet coalescence were found to have considerable variation, even if a fresh bottle of solvent was used each time. This was probably due to very tiny quantities of surface active and unstable compounds. However, it was found that it the experiments were repeated with the same solvents recycled by distillation, the results became consistent.

(12) A routine procedure involved 3 washes of a material with solvent. The third wash liquid was saved and used for the first wash on the next procedure.

14.6.3 Preliminary Treatments

t is generally a good idea to consider other physical and chemical methods rior to distillation. Section 9.3.6 gives some suggestions. In particular, here contamination is very small, say less than 1%, then other procedures may be more economic, safer and less trouble. A chemical reaction ay sometimes be found which converts contamination to an insoluble rm, or conversely to a water-soluble form which can be extracted.

but only really economic for low concentrations. Adsorption is, however, a very valuable technique for removal of peroxides or other dangerous substances.

Many uses of solvent produce waste containing acidic components (e.g. acetic acid, acyl halides), where it is generally a good idea for these to be neutralized before recycling. In fact, most chlorinated solvents tend to become acid with time, owing to breakdown of the solvent, and this acidity should be neutralized with solid sodium carbonate or an aqueous solution of alkali. Note that some solvents are hydrolysed on heating with alkali, so it is equally important to ensure that solid or liquid or dissolved base (NaOH, KOH, Na_2CO_3) is removed before distillation.

14.6.4 Distillation

The following are notes on practical aspects of distillation for waste recovery processes only, including some very rough and ready short-cut methods of calculation. It is assumed the reader is familiar with basic laboratory practice, but may not be used to the design and operational characteristics of distillation apparatus. Some gross oversimplifications will be obvious to anyone with a chemical engineering background, but the simple approach is generally adequate for this purpose.

A typical still consists of a heated flask in which the mixture is boiled, a vertical column in which the actual separation occurs, an adaptor or 'head' of various designs on the top of the column which takes some vapour to a side arm, and a water-cooled condenser to convert that vapour to liquid. In batch distillation, the flask is filled to its working level with liquid, and vapour boiled off through the column until (a) sufficient top product has been collected or (b) the quality of the top product is no longer good enough, or (c) the level in the flask has fallen to its minimum safe working level.

Continuous distillation is more efficient in several ways but is more complicated to set up. As its name implies, liquid is continually added to the system, while an equal total quantity is removed from the top of the column and from the flask liquid. To achieve this, the column may be made in two parts, with a central section for addition of feed liquid. It is best if this liquid is pre-heated to near the column temperature. The main practical problem is to control the rates of liquids going in and out, but this is quite possible on an automatic unit, which may be set up to process a large volume through quite a small apparatus.

An approximation to continuous distillation can be made where a low-boiling solvent is to be removed from a small amount of higher-boiling material, e.g. if 99.5% hexane is to be removed from its oil contamination. For this purpose, there is a continuous or frequent addition to the flask to keep it at its working level. The low-boiling material comes off the top of the column, while the high-boiling material accumulates in the flask. This can be achieved by the use of a small dosing pump, preferably passing the liquid

through some kind of heating coil (e.g. a coil tube in a water bath) so that it is fairly close to the still temperature.

An important practical point is that all columns work better if heat loss is reduced. Commercial stills may be fitted with a vacuum jacket or an electrically-heated shield. For a unit made from standard laboratory items, then a wrapping of aluminium foil is better than nothing. A convenient method of insulation is the pre-formed sections of lagging used for industrial and domestic pipes. The plastic foam ones are suitable for lower temperature distillation, but the fibre-glass ones are suitable for all temperatures. They are much more convenient than wrapping loose fibre-glass around the column.

The effectiveness of a distillation column is measured in terms of units called 'theoretical plates' which is based on the idea of liquid and vapour coming to perfect equilibrium on an imaginary industrial-type plate column. Real plates may be equivalent to 0.4-0.8 theoretical plates. A flask with no column, just a still head and condenser, will have an efficiency of just under one theoretical plate. The number of theoretical plates in the column will vary with design, flow rate, and the properties of the mixture to be separated. It can even vary significantly during a batch distillation.

Specialist manufacturers will usually be able to quote the theoretical plate capacity of a column for certain standard mixtures such as benzene and toluene. As a rough guide, a typical interchangeable column (24 mm joint) of 200 mm working length has just over half a theoretical plate when empty, 3 plates with a coarse packing, up to 5 with a fine or efficient packing. A 300 mm Vigreux column of the same diameter gives about 3 to 4 theoretical plates. Table 14.2 gives some values for common laboratory columns.

Other things being equal, the number of theoretical plates is proportional to the height of the column. Narrow columns have more theoretical plates but lower capacity. One of the most efficient designs is the spinning band column, which is often used in commercial units. A 500 mm height of 6 mm diameter column of this type is likely to be the equivalent of 20 theoretical plates.

A commercial unit or one built by a person with specialist knowledge will have some means of controlling the reflux ratio. Simply defined, this is the ratio of liquid which is passing down the column at any time, to the amount of liquid which is being taken off as top product. A larger unit will typically control this by condensing the vapour at the top of the column, and then splitting it using a so-called 'dividing head'. As a rule of thumb, the reflux ratio should be similar to the number of theoretical plates. For very critical separations it will be necessary to control the reflux ratio precisely, as it is a major factor in column operation. For less critical work it is suggested that the above guide be used initially, then experiments are carried out to see how much more material can be taken off without lowering the product quality too much.

Table 14.3 shows how the column efficiency can vary with reflux ratio. Note that efficiency is maximum at total reflux (i.e. no product) and that efficiency falls off drastically for reflux ratios much below the maximum number of theoretical plates.

Table 14.2. Characteristics of distillation columns

The following are typical of values that might be found for commercial glass columns used for laboratory distillation. Actual values can vary considerably, particularly with reflux ratio. All are of 25 mm diameter or thereabouts.

Column	Throughput cm^3/min	Plate efficiency: theoretical plates per actual plate
Plate columns		
Bubble	10	0.8
Oldershaw	15	0.8
Other columns		Column height (mm) to give one theoretical plate
Vigreux	5	100
Packed: 6 mm Raschig rings	20	100
Packed: 3 mm Fenske helices	30	40

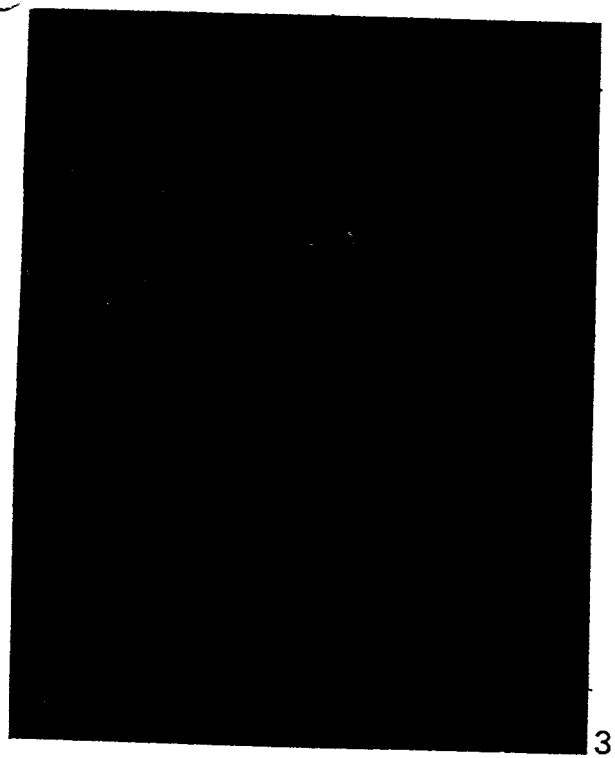
Table 14.3. Effect of reflux ratio on column efficiency

Data from a 1 inch × 48 inch Oldershaw column, separating n-heptane and methylcyclohexane.*

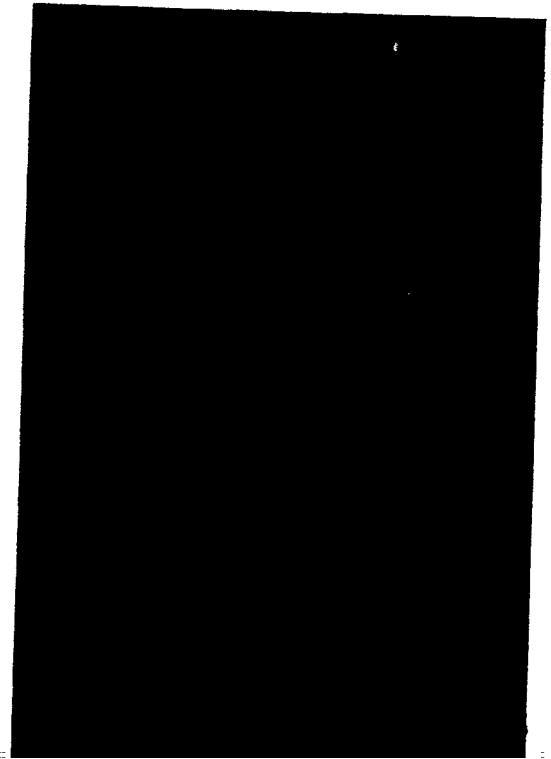
Reflux ratio	Theoretical plates
(Total)	28
120	25
80	24
40	21
20	16
10	10
4	5

*Goldsbarry, A.W. and Askevold, R.J. (1947) Evaluation of Laboratory Batch Fractionating Columns, *Proc. Am. Petroleum Inst.*, **26** (III), 18–22.

To decide on the column needed, or how an existing still can be operated, it is necessary to know something about the mixture to be distilled, and also the realistic requirements of the product. For example, there is no need to use a very high efficiency still with low capacity to produce extremely pure product, when a 90% purity would be adequate.



31



equilibrium behaviour of the components, and also to have someone such as a chemical engineer or a specialist chemist who is capable of interpreting the data and carrying out some sophisticated calculations. However, the following short-cut method is often adequate and illustrates some important features of batch distillation.

Take the example of a mixture of 2 solvents. A full calculation would require step-by-step analysis of data on the vapour pressure of mixtures. Instead, it is assumed that the materials have a constant relationship called the relative volatility α. For example, at its boiling point, a solvent A has a vapour pressure of 760 mm Hg. At the same temperature, solvent B has a vapour pressure of 380 mm Hg. Thus the relative volatility α_{AB} is $760 \div 380 = 2.0$.

Obviously, in this case solvent A would be removed at the top of the column. Roughly speaking, every theoretical plate will enrich the product by the ratio α_{AB}. For example, if the flask has a mixture of 50% A, then the liquid has a ratio of 1:1. After one theoretical plate it will be 2:1 or 67%. After 5 theoretical plates it will be 32:1 or 97% pure. Note that these are actually mole ratios and percentages.

This can be expressed in the following formula:

$$N = \frac{\log((x_a/1 - x_a)(y_a/1 - y_a))}{\log \alpha_{AB}} \qquad (14.1)$$

where

N = number of theoretical plates
a_{AB} = relative volatility of A to B
x_a = mole fraction of A in the flask
y_a = mole fraction of A in the top product

In the example, the expression is:

$$5 = \frac{\log((0.5/0.5)(0.97/0.03))}{\log 2.0}$$

As a flask with no column gives nearly one theoretical plate, 5 theoretical plates would be given by a still with a Vigreux column or well-packed column of 4 theoretical plates. However, if the reflux ratio is not well adjusted there can be a loss of up to one theoretical plate, so for a conservative calculation it is wise to consider only the column, and we could therefore only rely on a top ratio of 16:1 or 94% pure.

Note that the composition in the flask has a very important effect. For example, when the majority of component A has been distilled over, its concentration in the flask drops to (say) 10 mole % or $y_a = 0.1$, and a ratio of

(31) An automatic still for the recovery of xylene from a hospital histological laboratory. Photo courtesy of B/R Instrument Corporation, Pasadena, Maryland, USA. (32) Items kept specially for spillages in a convenient corner. Absorbent pillows, neutralizing agents, buckets,

1:9. A column of 4 theoretical plates would enrich this to 16:9 or 64% pure. A column of 5 theoretical plates would enrich it to 32:9 or 78% pure.

Thus during a batch distillation, the purity of the top product tends to fall, even though the column performance may remain the same. It is therefore necessary to stop the process or cease collection when the purity drops to a certain value. A useful alternative is to collect the first portion with an acceptable purity, for example 90%, and collect a second portion of lower purity. The first portion can be redistilled to a higher purity. Its residues and the second portion of distillate are saved and added to the next batch of waste for recycling. In this way, both a good yield and a good purity are achieved.

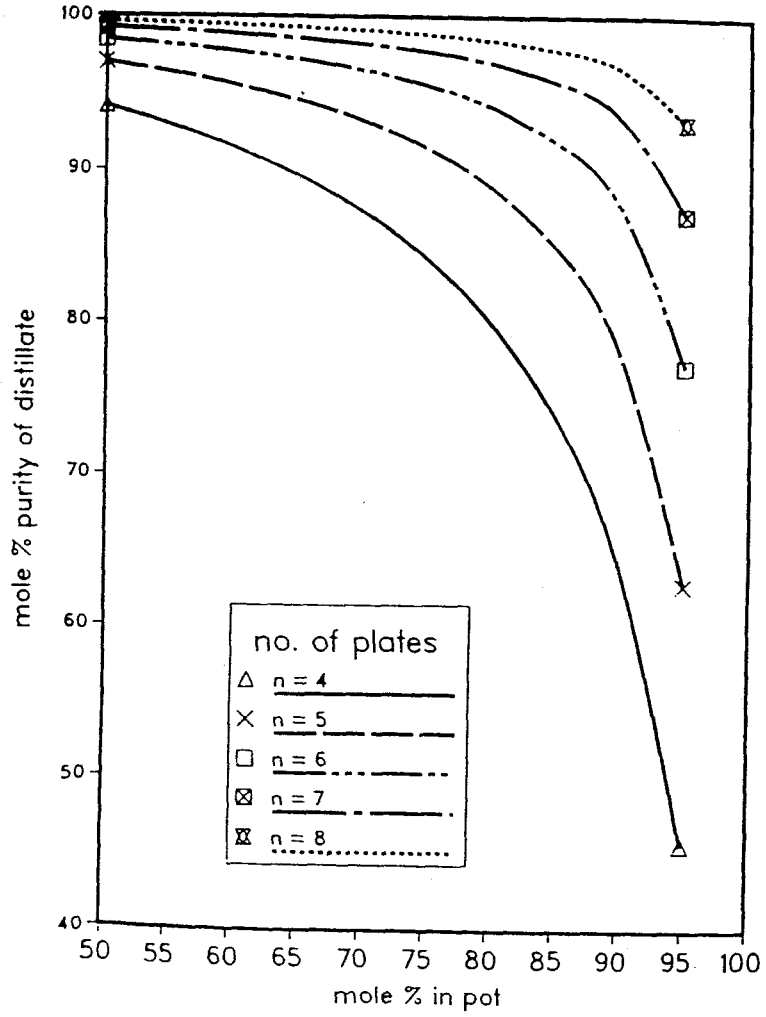


Fig. 14.1 Top product purity from batch distillation.

Fig. 14.1 shows the drop in purity of product as the distillation proceeds, for columns of 4 to 7 theoretical plates, and for a mixture of relative volatility 2. The product composition for any other relative volatility, number of plates, and composition of liquid can be predicted by rearranging equation (14.1) thus:

$$\frac{y_a}{1 - y_a} = \left(\frac{1 - x_a}{x_a}\right) \alpha_{AB}^n \qquad (14.2)$$

This can be solved on most scientific calculators (or microcomputers) in two stages, for example:

```
LET Z = (A ↑ N) * (1 - X)/X
LET Y = Z/(1 + Z)
```

Vapour pressure data is available in a number of compilations, including the Chemical Rubber Co.'s (CRC's) *Handbook of Chemistry and Physics*, and Perry's *Chemical Engineers' Handbook*.

It is possible to carry out these calculations for mixtures of many components, providing the vapour pressure of each substance is known at the same temperature. One of these is arbitrarily set to one, and the ratios of the others taken as before. Then if x_i is the mole fraction of the ith component and α_i is its relative volatility, a still of n theoretical plates will give a top product with components in the ratio

$$A : B : C : D : E \ldots$$

as

$$x_a a_A^n : x_b a_B^n : x_c a_C^n : x_d a_D^n \ldots \text{etc.}$$

It is unlikely that a calculation for many components will be exactly correct (though it may be a useful guide). This is partly due to some approximations in the method, but also on acount of the interactions between the components which may occur. A very important and extreme interaction will be briefly discussed in the next section.

14.6.5 Azeotropes in Distillation

A good description of the theory of azeotropes will be found in many physical chemistry and chemical engineering textbooks. For waste recycling, it is mainly necessary to know if an azeotrope can be formed or not, given the composition of the solvent mixture. The CRC's *Handbook of Chemistry and Physics* gives a very full list of 685 combinations of 2 solvents and 119 combinations of 3 solvents and the properties of the azeotropes which can form. This should be checked before planning a solvent recovery routine, as the presence of an azeotrope has a major effect on the distillation.

As was previously mentioned, an azeotrope is a mixture of two or more

solvents which cannot be separated by distillation (with one proviso — see later) and which comes over as if it was a compound. To predict the course of a distillation where an azeotrope is involved, it is easiest to imagine that the azeotrope is effectively an additional component.

As an example, take one litre of 95% acetone, 5% water to be batch distilled with an efficient column. According to the CRC's Handbook, acetone has a boiling point of 56.2 °C, and water has a boiling point of 100 °C. However, there is an azeotrope which is 88.5% acetone, 11.5% water which has a boiling point of 56.1 °C. what will happen?

If the azeotrope did not exist, then acetone (being the more volatile component) would be expected to distill off as the top product at about 56 °C. In fact, what distills over first is 88.5% acetone, that is, a *lower* purity than that in the flask! Moreover, since its boiling point is virtually identical to that of acetone, the inexperienced laboratory worker might easily assume that the distillate was pure solvent. In this case the azeotrope will distill off until there is no more water left. Thus, contrary to commonsense, the water content in the still flask steadily decreases. A calculation will show that if half the sample were distilled off, the residue would be very pure acetone.

Therefore it is clear that acetone with a small amount of water can be dried by distilling off the azeotrope. This is a well-known method for primary drying of solvents and applies to many common ones, including alcohols, ketones, aromatics and chlorinated solvents. If the waste is near to the azeotrope composition, then distillation will not perform any useful separation (except from involatile compounds and other solvents not involved in the azeotrope). It may sometimes be useful to separate an azeotrope from a mixture of lower concentration. For example, a water waste containing 20% acetone could have the majority of this removed as the azeotrope. The aqueous waste might then be easier to dispose of, or there may be some use for the azeotrope. (See section 14.6.2(5).)

As the CRC's handbook shows, a few azeotropes have the useful property of separating out on cooling. Particularly where the azeotrope is with water, it may often be an advantage to make such an azeotrope. For example, toluene (boiling point 110.6 °C) forms an azeotrope with water which boils at 85 °C and contains 80% toluene, 20% water. When this is distilled off from a mixture allowed to cool, it separates into two layers. The bottom layer is water containing a trace (0.06%) of toluene. The top layer is toluene containing a trace (0.05%) of water. If necessary this trace of water can be removed from the recycled toluene by chemical drying with calcium sulphate.

For difficult, expensive or important waste it may be worth while changing the pressure or chemical conditions. For example, distillation of an ethanol-water mixture at ordinary pressure gives an azeotrope which is 95.6% ethanol. However, distillation at a reduced pressure of 95 mm Hg gives an azeotrope which is 99.5% ethanol. If an azeotrope with water is collected and re-distilled in the presence of water-soluble salts, then some enrichment may occur. Potassium citrate seems particularly effective

Alternatively, it is sometimes possible to find a third solvent which can form a ternary azeotrope. This is done commercially where benzene is used to remove water from 95.6% ethanol as the benzene–ethanol–water azeotrope.

14.6.6 Operation of a Batch Distillation

The following is a description of how a batch distillation for waste solvent recovery might be carried out, making some compromises between speed, purity and convenience.

The flask will depend on available apparatus. It should be filled to about 2/3 full and the distillation should be stopped when the flask still has a reasonable amount of liquid in it — say 10% of its volume.

The column will depend on available apparatus, the degree of separation required and the liquid throughput. See Table 14.2. Note that when the distillation is over, the column will still have some liquid in it. A Vigreux column retains very little: a packed column quite a lot. The Oldershaw plate column is self-draining — some plate designs are not.

It is not necessary to have a large enough still to take the whole waste. Sometimes it is more convenient to use a smaller still and process several batches. This should be particularly considered where the solvent is highly expensive or possibly very dangerous, as it limits the consequences of an accident.

It is a very good idea to add some boiling aids (i.e granules or chips of inert solid with a rough surface) to the cold liquid. They should never be added to hot liquid, as sudden explosive boiling may occur. It is very preferable to use fresh boiling aids each time, as the surface tends to become inactivated with use. However, some waste solvents boil very smoothly without any aids — the behaviour varies and is not easy to predict.

It is preferable if the flask is fitted with a thermometer. For all but the easiest separations, there must be a thermometer in the distillation head. It is best if a head is used which allows the take-off rate to be controlled, including zero take-off (i.e. total reflux).

If advisable, the apparatus is purged with nitrogen. The flask heater is switched on at a high setting. If the waste is very viscous, then it should be heated more slowly, or there is a risk of 'bumping' (local explosive boiling) or cracking the flask. The thermometer in the flask will give an indication of the progress of this warm-up. When the liquid is nearing its boiling point, the heat input should be reduced so that it comes to the boil gently.

When the liquid starts to boil, condensing liquid will start to appear in the column. This will gradually rise up the column. At this time, the still head and condenser should be checked to ensure that they will give total reflux. If necessary, the heat is adjusted until vapour reaches the top of the column and refluxes on the condenser.

The heat input can now be adjusted to give the best column conditions. A packed column should be fully wetted but without being flooded, i.e. there should [illegible] of liquid. A plate column should have visible liquid

on all plates but without splashing. For maximum throughput, the column can be brought to the overloaded condition, then the heat reduced to give a satisfactory condition a little below this.

The still head is adjusted to give a very small amount of take-off. Even with a supposed clean solvent it is usual to collect the very first portion separately. This is known as the 'fore-runnings' and usually contains volatile impurities, plus some dirt from the distillation apparatus. After a few minutes the still-head thermometer should have stabilized to a reading similar (not necesarily exactly equal) to the boiling point of the first solvent or azeotrope. This can now be collected.

The rate of take-off can be increased to a suitable value. The column condition should not appear to change, and the still-head thermometer should not alter its reading by more than half a degree. With a regular distillation it will be found by experience what rate can be tolerated with a satisfactory product purity.

It is sensible to collect the product in a series of receivers. Thus if the distillation overshoots then only one receiver is contaminated.

When the take-off temperature changes significantly, then a new receiver is put in place and material collected until the temperature stabilizes on a new value. This is the next product (or azeotrope). A new receiver is fitted and the intermediate liquid discarded.

In principle, though rarely in practice, a whole series of solvents can be distilled off and collected substantially free of contamination. The fore-runnings should always be disposed of, but the intermediates may be saved and added to the next batch. Where the initial waste was relatively pure then the pot residue may be retained for the next batch. Where it is desirable to recover as much as possible from a batch of expensive solvent, then it may be possible to add a cheaper, less volatile solvent (e.g. paraffin) to give the flask a reasonable liquid content when most of the solvent has been removed.

CAUTION: it is very dangerous to allow a still to run nearly dry. The flask may break and some solvents may explode owing to concentration of unstable impurities.

At the end of the distillation, the apparatus is allowed to cool down, then emptied and cleaned as necessary. With tarry residues it may be necessary to remove them while hot, or reflux with a little low-viscosity solvent (which may itself be recovered waste, e.g. intermediates from a distillation).

The column may be left wet if it is to be used for the same job later. However, if the solvent is prone to form peroxides (see Table 14.1) the column should be rinsed with a compatible solvent which does not form peroxides, e.g. methanol, hexane. It is likewise advisable to remove polymerizable liquids such as styrene from a column.

Table 14.4. Solvents which should not be recovered by distillation

Reported accidents suggest that the following solvents and mixtures are especially likely to be unstable owing to peroxide formation or other reactions. It is suggested that they should not normally be recovered from waste, as the economic benefit does not justify the hazard of explosion. Any distillation of these materials in the course of use should be carried out by a skilled person who is knowledgeable about the hazards and the precautions necessary.

Individual substances:

Di-isopropyl ether (isopropyl ether)
Nitromethane
Tetrahydrofuran
Vinylidene chloride (1,1-dichloroethylene)

Mixtures:

Chloroform + acetone
Any ether + any ketone
Isopropyl alcohol + any ketone
Any nitro compound + any amine

14.6.7 Peroxides, Polymers and Other Problems

The principle hazard in distillation of flammable solvents is obviously fire. A vapour leak from an insecure joint or a cracked piece of apparatus is very likely to ignite. It is therefore obvious that solvent recovery stills should have explosion screens and be in a position of forced ventilation, i.e. under a hood or in a fume cupboard. However, even in the absence of a leak, explosions are possible owing to the presence of peroxides. These are unstable compounds which can explode or detonate on heating. It is possible that a peroxide solution (from a chemical experiment or a plastic adhesive) may be included in solvent for recovery, but it is more common that peroxides are formed by the action of air on the solvent.

Table 14.1 gives groups of solvents which are prone to peroxide formation. In addition, Table 14.4 gives a list of some solvents where the hazard is especially great. In fact it is recommended that none of the solvents listed in Table 14.4 should be distilled for waste recovery. It is possible for them to be distilled under certain circumstances by an expert who has good reason, but otherwise the savings do not justify the considerable danger.

CAUTION: if peroxides have been deliberately added to a solvent mixture they should be chemically destroyed before the solvent is discarded. Under no circumstances should such mixtures be distilled until made free of peroxide.

In order to remove peroxides from stock bottles of ether and similar solvents, the best general method is to treatment with activated alumina

by the use of chemical and physical procedures specific to the individual solvent and its intended use. Details are given in many of the better books on preparative organic chemistry or on certain techniques such as liquid chromatography.

A selection of books which give explicit instructions for the purification of a large number of solvents is given in the bibliography.

14.7 OILS

There is a substantial industry involved in the recovery and refining of waste oils, but it is rare for a laboratory by itself to produce sufficient to be of interest, unless it is already associated with the industry. Generally for relatively clean oil, a quantity of 50 litres may be taken away free; a quantity of 500 litres may be bought. It is sometimes possible for a laboratory to lower its disposal costs by carefully segregating oils from solvents for the waste collector.

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[section 14.6.4]

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