

SPILLS IN THE CHEMICAL LABORATORY

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1 Introduction

spills in the chemical laboratory are inevitable. This is true regardless of the level of competence of the people in the laboratory. A spill can be as simple as an overturned beaker of a dilute aqueous solution on a laboratory bench, a broken thermometer or a serious incident such as a collapsed shelf resulting in many breakages and possibly some reactions. These would include an emission of a poisonous gas, a fire or someone being splashed with a corrosive liquid.

Accidents are always going to happen and the best advice we can provide is to take the proactive approach and be prepared for them.

This presentation is an attempt to provide some useful basic information and practical advice that you can apply within your laboratories and thus minimise damage and injuries to both personnel and workplaces. It is a legal requirement for employers to provide a safe working environment for employees, and in the chemical laboratory or indeed any laboratory where chemicals are handled, ensuring a safe working environment can become complicated.

The approach we take is a specific one. That is, look at what specific chemicals are to be used in the lab. and take specific precautions. This is as simple as providing an acid spills kit where acids are being used. For more complex situations say for example where a cyanide assay is being performed, you would need a cyanide antidote kits as well as a spill kit to absorb and oxidise any cyanide spills. The proactive approach to spills is to assume they are going to occur and have on hand the appropriate kits, neutralisers, absorbents or whatever else is required prior to commencing any work. It is certainly feasible to have on hand a plethora of spill kits to cover any type of spill or splash but we consider this approach to be a waste of resources. The exercise of looking closely at the chemicals you are going to use, their reactions and properties and potential dangers, then deciding on the appropriate emergency procedures and equipment is surely of more value.

We have divided chemical spills into two areas, ie spills involving people getting splashed or contacting chemicals, and spills where no one has been splashed or contacted with a chemical. The use of a spill kit is applicable to the second scenario, while the use of personnel protective equipment (ppe) and emergency equipment is applicable to the first scenario. Later we will look at spill kits and chemical neutralisers in some detail with we hope sufficient information to enable you to make up your own spill kits. Part four is some brief information on what we consider to be good chemical practice in the laboratory, particularly the teaching laboratory.

2 Chemical Spills

a) spills to personnel

a chemical splash or contact with any chemical is potentially serious of course and every precaution must be made to reduce this happening. Personnel protective equipment (ppe) must therefore include at the very least safety glasses and gloves. Laboratory coats , safety shoes, long sleeves, hair nets or hats, covered legs and feet are all taken for granted these days in most laboratories. Why take the risk? We are only given one pair of eyes. Glasses are mandatory. Gloves also but things become complicated when we consider what is the appropriate material for the glove. Here the exercise of looking at the chemicals that are involved and their properties will pay off. There is no point in using a glove to protect against an organic solvent if the glove material is not impervious to that solvent. Many halogenated solvents will chew up latex and pvc for example. You may need a nitrile or a butyl rubber glove. This information comes from the chemical compatibility chart. The usability of the thin latex disposable glove these days is usually reduced to medical applications and they are of little use for chemical protection. Strong acids require a careful glove selection particularly when nitric acid is involved.

Any chemical splash to the face or exposed skin can, in the majority of cases, be simply dealt with by water flushing. In fact we can think of no example where a strong spray of water is not appropriate. We use a portable safety shower which is a cylinder of water and lightly compressed air that delivers a soft aerating spray which is even suitable for spraying directly to the eye. We heard of a chemical accident in a laboratory that involved metallic sodium pieces being splashed everywhere including onto a technicians hair. He didn't realise that he had sodium in his hair until he was standing under the safety shower and his hair appeared to catch fire temporarily. The strong spray of the shower however was enough to physically move the sodium from his hair. We all know sodium and water don't mix yet a water spray was still the best (and probably only) way to get the sodium out of his hair.

A safety shower, eye wash station and even eye wash bottles are thus of great help in combatting chemical splashes. If someone is unfortunate enough to have burning solvent on themselves then standing under a safety shower if an extinguisher was not available would still be an appropriate measure. You can also use a simple water fire extinguisher to achieve the same effect. Splashing with a strong acid or alkali is best treated with continuous water flushing. Neutralisers should be only used after careful consideration.

Chemical Spills

b) spills to surfaces

liquid spills can be wiped up with a rag, absorbent paper towel or soaked up by an absorbent chemical. Usually no further action is required unless the spilled liquid is caustic, corrosive, flammable, an oxidiser or organic peroxide, a cyanide, elemental mercury or a particularly toxic or poisonous liquid. Further treatment with a neutraliser, reducing or oxidising agent or some chemical reactant may be required.

Generally a laboratory would need a spill kit for general use, and probably for acids, and alkalis as they are very common. Specific nasty chemicals such as hydrofluoric acid, cyanides, perchloric acid, iodine, calcium hypochlorite for example will require something further. This is where your proactive research into the specifics of the chemicals to be used will pay off. At the bare minimum a laboratory will get by with a single spill kit consisting of an appropriate all round absorbent. In our opinion the best single use all round all purpose absorbent for all liquids except mercury is vermiculite. It comes in four sizes with grade four being the coarsest (approximately half a cubic centimetre per piece) to grade one being the finest. Section 3 gives some more details on vermiculite and other absorbents. The best features of vermiculite that make it such a good all round absorbent is its lightness, non reactivity, water insolubility and cheapness. It is most importantly an excellent absorbent. We use it extensively. We have other absorbents as well (see section 3) but vermiculite is our first choice.

In common with most mineral absorbents is the fact that they have been "activated", usually by heating to high temperature; this process is also known as calcining, which drives off water and which gives them a high attraction for liquids, particularly water. Cement powder is an example of an heat activated mineral. Other well known absorbents such as kitty litter, attapulgate, charcoal, polypropylene fibres all have their particular weaknesses and strengths and uses. Sand however has little use in the laboratory as an absorbent and really it is only of use as a damming material or physical barrier to prevent liquids running down stairs or into drains for example. It is not absorbent. Some propriety absorbents on the market are useful but we are unable to recommend them either way without knowledge of their chemical make up. Many propriety absorbents are designed to be good absorbers of oil for example and are extensively touted for use in oil spills in the marine environment. This is a somewhat specialised use and no doubt effective but as an all round absorbent, vermiculite is hard to beat.

The use of vermiculite to absorb a liquid spill is as simple as covering the spill with the vermiculite and allowing absorption to occur. After a period of time the vermiculite is simply swept up and disposed of . It cannot be recycled for reuse and must always be disposed of after use. Some chemicals spills may require a further step as mentioned above and some specific examples are provided in part 3 (c) . Elemental mercury is another story and we deal with mercury spills in 3 (d).

3 Absorbents and Neutralisers

a) properties of an absorbent

for an absorbent to be effective it must have as many of the following properties as possible:

- non reactivity with most chemicals
- inorganic and insoluble in organic solvents
- water insolubility
- be an inert material
- be an effective absorbent

It is not necessary for the absorbent to be recyclable.

The difference between an absorbent and an adsorbent is important as an adsorbent can usually be recycled and the liquid adsorbed can be recovered. Activated charcoal is an example of a commonly used adsorbent.

The enclosed sheet summarises some commonly used absorbents.

All we really need an absorbent to do is to soak up a liquid spill without reacting with it and without releasing the liquid and without breaking down. Sounds simple. It must also be inert so that it can be handled without the need for any protective equipment.

b) properties of a neutraliser

a neutraliser in the context of this presentation is simply a mild acid or alkali that is used to neutralise another acid or alkali. Desirable properties for a neutraliser to be used in conjunction with an absorbent or alone include the following:

- preferably not a dangerous good ie not a mineral acid or strong caustic.
- water soluble or semi soluble
- mild enough to be able to handled and stored without ppe or with minimal ppe.

This doesn't leave much but the neutralisers shown on the accompanying summary are usually sufficient for the job. They are all fairly mild and therefore easy to handle. The reactions between strong acids and strong alkalis are far too vigorous to be of use in a laboratory for neutralisations. Neutralisers are only of use in acid or alkali spills and a spill kit consisting of a neutraliser and absorbent can easily be made up in the laboratory. The double action of neutralising and soaking up the neutralised liquid is easier than neutralising then soaking up. One step instead of two.

c) other chemical reactants

other chemical reactants are required when a spill needs to be treated to remove harmful toxic or reactive chemical residues. This can occur before or after the use of an absorbent. The usual practice is for a large spill to be soaked up and the area swabbed with the reactant. A small spill can sometimes be successfully treated in situ followed by absorbent to soak up the hopefully inert mixture. Specific examples are :

-reducing agents for treating oxidiser spills include sodium or potassium metabisulphite, ferrous sulphate, sodium sulphite and reducing sugars such as dextrose or glucose (not sucrose) . Metabisulphite solutions are excellent for the reduction of chromic acid where the chrome is still in the VI oxidation state, ie orange or yellow. Green signifies the III state which is not an oxidiser and is an indication when the reaction is completed. Chrome VI is a powerful oxidiser and can cause a fire if in contact with organic solids such as paper or wood. Metabisulphite can also be used for potassium permanganate spills. The purple colour will disappear as the redox reaction proceeds and again is a self indicating reaction. Reducing sugars have the same reaction. A hydrogen peroxide spill is best dealt with by dilution with water rather than a

reducing agent as the reaction can be vigorous accompanied by heat.

-oxidisers used for reacting chemical spills are usually confined to the use of calcium hypochlorite to oxidise cyanide spills. A safer reactant is sodium hypochlorite which is not an oxidiser but an alkali corrosive. This tends to lose its chlorine fairly quickly over time so is best used fresh. You should be able to smell chlorine, if not it is of no use. Sodium azide is a reducing agent that is best treated with the oxidiser cerium ammonium nitrate, but there is a lot to be said for the heavy water flushing instead. Sodium hypochlorite is an excellent source of dissolved chlorine without the dangers associated with gaseous chlorine or calcium hypochlorite. It has many uses in the chemical waste industry.

-cyanide spills must at the least be treated with an alkali prior to oxidation or treatment with chlorine. The risk of cyanide poisoning is considerably reduced if the cyanide is strongly alkaline and this is one of the few example where the use of sodium or potassium hydroxide solutions are called for. It is not necessary to use a strong solution, a 5% solution is usually good enough. The cyanide is best treated prior to absorption. A solid cyanide spill is no different however any broom, shovel or other equipment used should be treated with alkaline chlorine. If cyanides are to be used it is necessary to fully understand the process of oxidation that may be required in the event of a spill.

-hydrofluoric acid and bromine spills are best treated with lime or gypsum as the neutraliser. This will precipitate any soluble fluorides as insoluble calcium fluoride. Soluble fluorides are extremely poisonous.

-spills of infectious materials or materials containing microbiological or viral materials in sufficient number to constitute a danger are best treated with one of the common bacteriacides . These include chlorine (sodium hypochlorite eg Domestos, White King,etc) , phenolics such as Pinocleen or quaternary ammonium compounds . Alcohol is only of use if there is at least 20-30% water present. Autoclaving this type of material is the best way of treating if possible.

-radioactive material spills are treated according to the matrix, ie a radioactive solvent is treated as for a solvent. The radioactivity is a physical property and the removal of the material through absorption will also remove the radioactivity. There is no special decontaminant for radioactive materials.

d) elemental mercury

a specific spill kit for mercury is a good idea for a laboratory. The propriety kits usually contain a miniature shovel and broom for scooping up any free mercury, and some type of secret absorbent. If you do not have one of these kits a simple Pasteur pipette with a rubber teat is usually good enough to suck up the small pieces after all the free running mercury has been swept up. For mercury you can't get at or suspect is hidden in cracks and grooves, a good reactant to use is fine granulated zinc, (not zinc dust). The zinc will form a zinc amalgam with any free mercury; this is a crystalline solid easily vacuumed or swept up. Sulphur is of no use and only makes a bigger mess. Mercury residues including all the bits of the thermometer should be placed inside a plastic vessel such as a large jar with a screw cap. Water can be added to reduce the vapour pressure of the mercury although the amount of water that needs to be actually added to completely reduce any mercury vapour is usually very great. All you can do is to slow down the escape of the mercury vapour. Glass jars are rarely suitable to store elemental mercury. There is no reason to evacuate the area for a thermometer breakage as the mercury takes some time (weeks) to completely vaporise. Simply collect up as much as can be seen then treat the area with an absorber or the zinc and leave for a few hours before sweeping up. There is no need to panic.

e) useful tools and equipment

- portable eye wash/safety shower
- water extinguisher
- plastic pails for storing used absorbent prior to disposal
- a mercury spoon
- small scoop and brush (eg a paint brush)
- spot test kits for acids/alkalis, cyanides, peroxides etc
- mercury disclosing powder (available from Merck)
- compatibility charts for gloves and safety glasses

4 Good Chemical Practices in the Laboratory

a) chemical manifest

every laboratory should keep a manifest of chemicals with details of date purchased, dangerous goods class if any, amount, number and storage location. Chemicals that deteriorate with age can be checked, the dangerous goods factor can be calculated easily if required, correct storage, ie according to dangerous goods class (not alphabetically or liquids and solids) can be applied. It is essential to know what you've got if you are to control it

b) correct storage of chemicals is achieved by following the segregation rules as stipulated in the Australian Code for Transport of Dangerous Goods by Road and Rail, 6th edition. The Code is for transport and warehousing but the principles apply for laboratories in the absence of an alternative Code or standard (yet). The correct storage rules will for example tell you that you do not store acids and alkalis together although they are both class 8s. You must keep some of the three class 4 materials separate ie classes 4.1, 4.2, 4.3. Class 5 chemicals must never be stored with class 3 materials. All nitrates are class 5 materials. etc etc. The days of storing liquids with liquids and by alphabetical order are long gone. Storage is by class.

c) information sources today abound and many are free. The internet of course is an excellent one, but the printed word is still supreme. All the major chemical suppliers will give you their catalogues on floppy or CD-ROM. The catalogues have plenty of information on dangerous goods, hazardous substances with the risk and safety phrases, disposal information and the omnipresent MSDS. If all else fails call us at Envirochem. There really is no excuse these days for not knowing about a particular chemical you are using or proposing to use.

d) spill kits

buy them and pay a fortune or make up your own. An examination of some of the commercially available spill kits reveals that they contain disposable gloves, glasses, plastic bags, shovel and brooms and some absorbent. All of this material you can provide yourself at a fraction of the cost. Refer to the absorbent and neutraliser chart supplied for the right combination for you and remember to make your spill kit appropriate for the chemicals you are using.

e) personal protection equipment

everyone in a lab must have their own ppe, and this should include

safety glasses of appropriate type (check the chemical compatability charts) , a selection of gloves, dust masks if appropriate, face mask if appropriate. Base your ppe on what you are intending to do. Never skimp on ppe, use the best .

f) disposal procedures

waste chemicals have the same properties of “good” chemicals and therefore must be treated, handled and stored exactly the same way as the good chemicals, ie according to dangerous goods class. Always label your chemical wastes especially for the consolidation wastes such as “solvent wastes”. Don’t put codes or chemical formulae without the translation on the label. Use appropriate containers to hold the waste. If you are going to use an empty container make sure it is suitable for that type of waste. You wouldn’t use a metal drum to put strong acids into yet people put chlorinated solvent wastes into metal drums. Chlorinated solvent wastes are inevitably corrosive and will rapidly attack a metal drum if it is not a lined drum (as was used for the pristine chlorinated solvent) . We recommend the use, for all liquid wastes, of plastic carboys , UN approved, ie approved for the containment and transport of dangerous goods. The carboy will have a small UN symbol and some code stamped into the container.