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Manipulating Chemicals at Small- and Semimicro-Scale in Inert Atmosphere

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The present note is dedicated to the late Professor Romolo Francesconi.

The rational use of chemicals requires that their properties be compatible with the planned application. These properties are modified by the interactions to which the chemical substance is subjected, among which particularly relevant are those with the components of the lab atmosphere, collectively labelled air sensitivity. The air sensitivity of chemicals is remarkably amplified in the presently common small- and semimicro-scale samples and operations, due to the increased surface-to-mass ratio with respect to the time-honoured multigram scale. In this note we present ergonomy-aware procedures implemented in small- and semimicro-scale laboratory operations, which enable to work easily in an inert atmosphere without the need for awkward or expensive apparatuses such as glove box or vacuum line.

1. Introduction

When a chemist plans to use a substance taken from its container, only rarely she/he carries out a test of its composition. Proceeding in this way, she/he implicitly assumes that the composition of the material is that indicated on the label, unchanged since its packing or last update. Neglecting the possibility of modification of composition during shelf time and previous withdrawals, bringing about reduced reproducibility of all procedures. Frequent and harmful causes of change of composition are the contact with the laboratory atmosphere, exposition to light and improper storage temperatures. While the latter causes can be eliminated by choosing a suitable place of storage, contact with laboratory atmosphere will take place on any withdrawal. Hence we present below some expedients to minimize this source of contamination. Air contains the species O_2, H_2O and CO_2, easily incorporated and quite reactive with many substances, then called air sensitive. Oxygen produces aldehydes or ketones from alcohols, explosive peroxides[1] from ketones, ethers, olefines; phosgene from chloroform, oxides on the surface of metals. Water reacts with many compounds, inorganic (such as hydrides: LiH, NaH; oxides: Na_2O, K_2O, P_4O_{10}; all drying agents; carbides CaC_2, Al_4C_3; sulfides: Al_2S_3, P_2S_3; halides: $AlCl_3$, $SnCl_4$, $TiCl_4$) organometallics such as carbonyls, and organic such as anhydrides, acyl halides, orthoesters, esters – with pressure build-up in the case of di-*tert*-butyldicarbonate, "BOC anhydride"- and must be substantially absent in many chemical procedures. Carbon dioxide, especially in presence of water vapor, reacts with most basic substances giving various carbonates. Even very stable compounds like squaric acid show surface discoloration unless the atmosphere of the container is made inert; "activated" zinc becomes inactive in contact with air.[2]

Contact of chemicals with lab air occurs at shelf time through their interface with the container headspace, enhanced by leaking or permeable closures, and when part of the substance is removed by pouring, as a result of exposition of the transferred portion and the residual contents to open air.

Presently, in research and upper level preparative or manipulative chemical laboratories the normal or common scale of manipulations is the small (2–0.2 g) or semimicro (200–20 mg) scale. This is due to the increased sensitivity and frequently non-destructive nature of the procedures utilized to establish the identity and properties of the sample and the thrust to decrease the danger, cost of manipulations and of disposal of the samples[3] and their containers, all of which are mostly proportional to the masses handled.

Consequences of the current "normal", with respect to the past "normal", multigram (100–10 g) scale of handling,[4] is the non-negligibility of the role of the interphase surfaces in the degradation of the samples by atmospheric components. The sensitivity of the small scales is due to the fact that adsorption and absorption, preludes to contaminating dissolutions and chemical reactions, take place through the interfaces, whose relevance, quantified by the area-to-volume ratio, increases with the reciprocal of the characteristic dimension of the sample.

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This means that both reactants and solvents are *always air-sensitive*, even if, depending on the planned use, not so sensitive to require a glove box, a Schlenk line (1–10^{-2} Torr), or a high vacuum (10^{-3}–10^{-7} Torr) line for their manipulations. Degradation by contact with lab air is particularly relevant for solvents, which commonly represent around 90% of the mass of a reacting mixture or solution. Without minimizing the effects of the contact of all chemicals with the lab atmosphere, the progressive withdrawals introduce increasing amounts of contaminants, making unreliable the indication of the composition shown on the label.

These considerations demonstrate that to make reliable the information supplied by the label on the container of the substance, it must reflect faithfully the composition of the contents. Since a frequent updating of such composition is impractical, the composition has to be kept fixed as much as possible, implementing suitable practices and apparatus to bring the substances from the site of storage to that of use, *when it is planned to take out repeatedly part of the contents* from the container where it is stored.[5] There are hints about the necessity to adjust the capacity, material and design of containers considering the expected use.[6] But we were unable to find systematic studies aimed at optimizing the devices and procedures for the storage and transfer of laboratory chemicals in order to minimize their degradation and their impact on the environment along their complete lifecycle.[7]

Below, we discuss and report the solutions elicited during many years of ergonomically concerned laboratory activity on the small- and semi-micro scale, point out the details still waiting a satisfactory settling and propose some ways out.

2. Results and Discussion

2.1. Contacts Air-Chemical

During the shelf time, between successive withdrawing, the relevant processes tending to equilibrium are adsorption (involving mainly surfaces), absorption (involving the bulk of the material), mixing and, when possible, reactions of the substance with the components of the atmosphere internal to the container. Most of these processes lead to significant contaminations in times short with respect to storage time,[8] allowing to approximate the inside of a container to a closed thermodynamic system in equilibrium. Consequently, *any* chemical in a condensed phase there contains as solutes the components of the internal atmosphere, because their initially zero concentration in the hypothetically pure substance implies, in the usual absence of impermeable or semipermeable boundaries, a very large propensity (initial $\Delta_{mix}G \rightarrow -\infty$) to reach a finite concentration.

To use a solid or liquid chemical, we must temporarily open the normally closed and (assumed) *gas-tight* closure (cap or valve) of the container to take out a portion of the chemical. During such operation the system becomes open, and if the chemical is taken out in free atmosphere (not in a glove box or glove bag) by pouring, it will remove intentionally part of the chemical and exchange unintentionally the internal atmosphere with the external atmosphere containing the necessarily soluble and reactive oxygen, water, carbon dioxide. This is the main cause of alteration of solid or liquid chemicals. In thermodynamic terms, such mode of withdrawing introduces uncontrolled composition variables, sometimes labelled "chemical noise".

2.2. Pouring? No, Thanks!

We *banned pouring*[9] because it *replaces by gravity and diffusion* the headspace atmosphere of the container, whose volume increases with each withdrawal (see Table 1), with lab atmosphere which contains the reactive gases oxygen (≈20% of volume), water (≈2% of volume), carbon dioxide (≈0.04% of volume). Gravity rapidly exchanges the headspace atmosphere with lab air because the atmosphere in the closed bottle contains the vapours of the substance at their equilibrium partial pressure, which (with the exception of water and deuterium oxide) cannot have a molecular weight, hence gas

Table 1. Laboratory air entered in a 60 mL bottle containing initially 50 mL of liquid, taken out 5 mL at a time by aspiration and pouring.[a]

n	V_G [mL] [b]		V_L [mL]	V_G/V_L		O_2 entered [mg] [c]		H_2O entered [mg] [c]	
	aspiration	pouring		aspiration	pouring	aspiration	pouring	aspiration	pouring
0	10	10	50	0.2	0.2	2.5	2.5	0.30	0.30
1	15	10 + 15 = 25	45	0.33	0.55	3.75	12.5	0.45	0.75
2	20	25 + 20 = 45	40	0.5	1.12	5.0	22.5	0.60	1.35
3	25	45 + 25 = 70	35	0.71	2.0	6.25	35.0	0.75	2.10
4	30	70 + 30 = 100	30	1.0	3.33	7.5	50.0	0.90	3.00
5	35	100 + 35 = 135	25	1.4	5.4	8.75	67.5	1.05	4.05
6	40	135 + 40 = 175	20	2.0	8.75	10.0	87.5	1.20	5.25
7	45	175 + 45 = 220	15	3.0	14.6	11.25	110.0	1.35	6.60
8	50	220 + 50 = 270	10	5.0	20.0	12.5	135.0	1.50	8.10
9	55	270 + 55 = 325	5	11.0	65	13.75	162.5	1.65	9.75
10	60	325 + 60 = 385	0	–	–	15.0	192.5	1.80	11.55

[a] *n* order of removal, V_G volume of lab air entered after removal *n*, V_L volume of liquid remaining after removal *n*, V_G/V_L ratio of air entered to liquid remaining in the bottle. [b] Assuming total replacement of headspace gases by laboratory air. The first column is an arithmetic series, the second a succession somewhat similar to Fibonacci's series, $V_{G,n} = V_{G,n-1} + (V_{bottle}\text{-}V_L)$. [c] As previously mentioned we assume that a millilitre of lab air at about 25 °C contains 0.25 mg of O_2, 0.015 mg of H_2O, and 0.0007 mg of CO_2.

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density, lower than that of air (about 29 g mol^{-1}). Diffusion, driven by the difference of composition between the headspace and laboratory atmosphere, is slower, hence plays a minor role. Hence pouring appears as the main cause of degradation of lab chemicals.

The presence of pouring spouts, Figure S2 (Supporting Information), or plastic pouring rings[10] at the opening of many commercial containers entices to pouring and neglects the fact that the slots between the pouring ring and the glass during liquid pouring are filled by capillarity. Together with the film of liquid left adherent to the inner surface of the bottle, they collect atmospheric water, oxygen and carbon dioxide that will be included in the next pouring.

Moreover, during pouring the vapors contained in the headspace are obviously discharged in the atmosphere releasing possibly dangerous substances.

2.3. Container Design

The benefit of optimized containers is acknowledged by the commercial availability of several specially designed types of "laboratory bottles"[11] which have features generally incompatible with the procedures proposed below, mainly because they are planned for multi-gram operations and to transfer their contents by pouring.

We designed the containers, inclusive of the closure, to minimize the contact of lab atmosphere with the contents during both storage and transfer to the site of utilization, to be indefinitely reusable, easy to clean and self-drying, due to the absence of spaces recessed or limited by surfaces with small radii of curvature. Vacuum-tight connectible to a high vacuum line,[12] for condensing there cryoscopically very high purity substances. And taking into account the physical state of the contents,[13] which can be liquid, powder or lumps.

2.4. Containers for Liquids

As a greener alternative to the small commercial containers suitable for semimicro and small-scale operations, we store liquids, particularly solvents, in *secondary, reusable, self-drying* bottles of borosilicate glass with GL 14[14] screw opening, preferably of about 60 mL volume, with a gastight cap, see scheme in Figure 1-a and picture in Figure S4.

The size of the containers is selected to contain about 50 mL of liquid, allowing a limited number of withdrawals (10 to 20), because the ratio of headspace to remaining liquid volume increases with the order of withdrawal, as shown in Table 1 below. The liquid is taken out with a gas-tight syringe keeping the bottle vertical, then the headspace is purged with argon,[15] details under Experimental. Being heavier than air (average molecular weight of dry air 28.96, decreases if humid), argon (atomic weight 39.792) displaces the atmospheric gases: *no reactant, no reaction*. Furthermore, since adsorption, absorption and solubility are processes reversible in the idle times between successive withdrawals of a chemical, repeated fillings

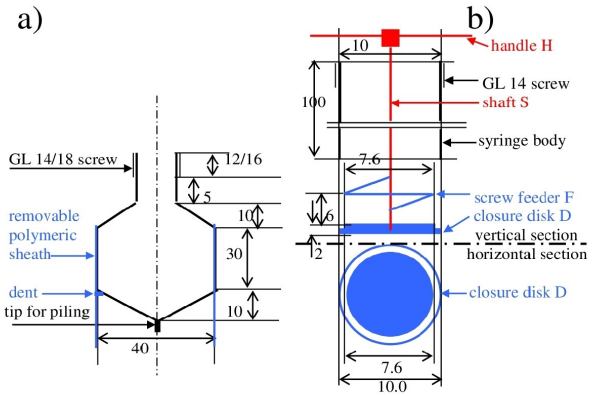

Figure 1. Dimensioned schemes of the containers and of the powder syringe, sizes in millimetres. Black, glass; blue, polymer; red stainless steel. a) vertical section of the container for liquids with opening GL 14 screw, for powders with opening GL 18 screw. b) two sections of the powder syringe separated by point-dash line. Higher part, vertical section, in red the shaft with handle to move the closure disk through a septum inserted under a GL 14 cap with single port.

with Ar progressively displace dissolved or adsorbed oxygen, water, and carbon dioxide, thus *improving or maintaining the quality* of the compound or sample if it was previously stored, respectively, under lab atmosphere or inert gas. If the substance has appreciable vapor pressure, within a few minutes from the closure of the cap its partial pressure attains its equilibrium value, which sums up to that of the injected inert gas at atmospheric pressure. Thus, the equilibrium pressure in the interior of the container becomes higher than that of the external atmosphere, hindering leaks from there.

Beware! The rise of the concentration of a solution of a non-volatile substance in a volatile solvent, such as EtONa in EtOH by repeated withdrawing is increased by purging with a gas. This occurs because the volume of the purge is larger than the decrease of headspace volume due to just the removal of the solution, as shown in Table 1.

Table 1 shows that the volume of atmospheric gases entered in a 60 mL bottle after ten successive equal withdrawals is drastically reduced by employing a syringe with the bottle vertical rather than by tilting it for pouring. Even if the headspace were flushed with Ar after each withdrawal by pouring, it is convenient to minimize the volume of air entering into the container: again, *no reactant, no reaction.*

The "aspiration" columns also apply to the common solvent dispensers (both complete and bottle top),[16] that avoid replacing the full headspace with air, but intake an amount of air[17] equal to the volume of the liquid dispensed.

The crucial part of the container, the cap, should be easy to open and close, be resistant to the contents, gas tight and impermeable to preclude both entering of laboratory atmosphere and any escape of vapours, both enhanced by the periodic changes of room temperature and pressure over the 24 hours.

We found that a lip seal screw cap of HDPE (high density polyethylene) or PP made of one piece, hence having a uniform

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composition and small overall surface area, is the best closure commercially available, when resistant to the contents. Being gas tight, it allows the storage of "incompatible reagents" in small spaces. However, even chemically suitable polymers have some permeability to gases or vapours, 18 while nonporous metal films are impermeable. Thus, the overall best closure for design and materials should be of the lip seal type, made of the highly inert thermoplastic *polyvinylidenedifluoride* (PVDF) and *metal plated externally* (with gold, aluminum, chromium, nickel) to approach zero permeability.

For handling strongly air-sensitive liquids (for instance CD_3OD) we used special containers,[19] Figure S5, exploiting the slow diffusion of gases and vapours in capillary conduits.[20] Alternative but expensive containers are commercially available.[21]

2.5. Containers for Powders

Powders[22] are kept in the original containers if expected to be consumed in ten or less withdrawals, taken out and followed by Ar purging as detailed under Experimental. The heavy Ar *accumulates from the bottom* of the container, hence displaces atmospheric gases present between the grains of the powder. The presence of argon as an interstitial fluid is expected to keep or improve the purity of the sample even more so than in the case of liquids, owing to the much larger surface-to-volume ratio.

We designed a special gas-tight container for substances in powder or granules which are strongly air-sensitive (for instance $AlCl_3$). It is equipped with the rather small GL 18 screw opening, which is just a bit larger than that employed for the liquids. Its scheme is shown in Figure 1a and a picture of its realization in Figure S6. It is used with the help of a syringe for powders,[23] to take out powders from their container without contact with air, particularly risky in this case, because the large surface area per mass unit of the compound could result in a rapid deterioration of the reagent.

The powder syringe scheme is shown in Figure 1b and its picture in Figure S7. The present prototype of this syringe for powders does not allow to charge a precisely programmed quantity of powder, so that we are trying to implement this feature.

2.6. Containers for Lumps

Materials in lumps like Na metal, $CaCl_2$, supported P_4O_{10}, $MgSO_4$, often purchased in rather large quantities are transferred into secondary gas tight containers, and used as those for powders.

2.7. Results

The use of the above containers and procedures allowed to obtain reproducible results in the study of adducts in solution,[24] to avoid degradation of reagents and solvents stocked for more than five years as evidenced by FT-IR or FT-Raman spectroscopy; to take out without contamination 10 times CD_3OD from a 50 mL- and D_2O from a 100 mL bottle; to preserve the brightness of recovered sodium spheres (under kerosene) for over five years. Thus, we could minimize degradation and the consequent expensive and environmentally harmful disposal of degraded chemicals and of their containers.

3. Conclusion

The suppression of pouring, purging with argon, and the use of special, reusable containers allows to exceed the expiry terms of most chemicals without measurable degradation. This produces a considerable economy of time and money and avoids the environmental pollution consequent to the purchase of untarnished substances, disposal of expired chemicals and empty containers. A gold plated lip seal cap made of HDPE or PVDF, at present not available, would provide the best reversible closure of the containers.

Experimental Section

Containers

Containers and syringe for powders as shown in Figure 1 and Figures S4 and S6 were built by a glassblower as last exemplars of several lab made prototypes.

Closures

We checked several types of closures, both made in-house and commercial, for tightness and permeability to gases. Gas tightness, difficult to measure, was evaluated indirectly by means of the more demanding but easily evidenced vacuum tightness, carried out by using a corona discharge tool (Tesla vacuum leak tester) on the cap closing a glass container connected to a vacuum line. Permeability to gases was evaluated on the basis of the minimum thickness of the cap and the coefficients reported in Ref. [18].

Procedures for Liquids

In the case of the most common solvents, the Ar filled containers are loaded from a larger one using a borosilicate glass syringe with a stainless steel or PTFE low gauge (say, 12) needle, or, alternatively, with a PP syringe, but paying attention to avoid contact between the liquid and the plunger's elastomers.[25]

The liquid is taken out with a gas-tight syringe or an all-glass, argon filled pipette while keeping the bottle vertical. Then the headspace is purged with about two times its volume of argon.[26] The gas is injected slowly through the needle of a previously filled, sufficiently large, PP syringe (permeation of H_2O and O_2 in Table 1, Supporting Information) while holding the cap of the bottle in a position that allows its rapid closure.

The label on each container included the name of the person who filled the container or withdrew the contents to her/his particular goal and the dates of all the withdrawals and purity checks since the first opening.[27] We found that this personalization[28] *greatly*

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reduced human errors, a very significant cause of deterioration of chemicals.[29]

Procedures for Powders

Powders are generally taken out with an L-shaped spatula to transfer it directly to the place of utilization. The container is always kept vertical, flushed with argon after each withdrawal and labelled as specified for the case of liquid compounds.

After the withdrawal, the headspace is flushed with argon as detailed for liquids. But *purging must be avoided* when the headspace contains gases present at *non-negligible equilibrium partial pressure* due to decomposition of the contents, such as happens for example with hydrates, solvates, hydrogen carbonates, ammonium carbamate,[30] because it favors the decomposition of the contents.

To withdraw a strongly air sensitive sample, the syringe for powders is firstly filled with argon with the disk D closing the lower end of the tube, weighted and then introduced into the container. The closure is opened by moving away from the tube end the disk D by using the externally controlled handle H, then the tube is charged with the powder by rotating the screw feeder F by means of the handle H and closed by pulling back the disk D. Finally, the syringe is extracted from the container, re-weighted and the contents discharged at the place of utilization.

Spectra

To analyze our samples, we used infrared spectra (IR) to monitor the presence of the strongly absorbing water. Measured by means of a Bruker IFS 66v/S spectrometer from 4000 to 500 cm^{-1} at a resolution of 2 cm^{-1}. Using demountable, vacuum tight cells with ZnSe windows and special syringes,[31] allowing transfer of liquids in Ar atmosphere, without contact with lab air. Figure S7 shows the OH stretching region of the IR of tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and dimethylsulfoxide-d6 (d6-DMSO) previously handled in free and Ar atmosphere. The fraction in weight of water in THF, evaluated by a rough comparison with a 0.5% w/w solution prepared and measured in Ar, is of the order of 0.2% w/w.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: absorption · adsorption · interfaces · sustainable chemistry · waste prevention

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