LIMITATIONS USING SMALL VOLUME CRYOTRAPS

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ABSTRACT

Chemical processes using cryotrapping are found to have fundamental limitations on transfer efficiency due to the presence of small amounts of non-condensable impurities. The impurities may be derived from contaminants in the actual sample, leaks into the transfer apparatus, or residual pressure when pumping out the cryotrap and manifold. When cryotransfer occurs, the non-condensable impurities will collect in the trap and eventually stall out the cryotransfer by effectively filling the cryotrap and not allowing additional analyte mixture into the trap. After this occurs, analyte can still be trapped out but on a diffusion-limited timescale. For practical cryotransfer, it is preferable to design the process so that the necessary amount of analyte is transferred over at the stall pressure and diffusion is not relied upon. For some cases, it will be difficult or impossible to have an efficient transfer based on required sizes of the cryotrap, manifold, or amount of impurities. In those cases, a much higher efficiency may be obtained by breaking the process up into multiple steps—that is, to transfer to intermediate volumes. By stepping the volume down incrementally instead of a single stage, higher levels of impurities can be tolerated while maintaining high transfer efficiency. In fact, the product of individual efficiencies of a multiple stage cryotrap can drastically exceed the efficiency of a single stage.

OBJECTIVES

Multiple projects at PNNL are working on analysis of gas samples for radioactive decay. In most cases, an atmospheric gas sample containing an analyte is collected, processed, purified, and then introduced into a detector cell for radioactive decay counting measurements. A common issue is that the amount of analyte is small and requirements for the decay counting necessitate that analyte concentrations introduced into the nuclear detector are high and that there is little loss of analyte in the overall process (i.e., transfer efficiency). Often a cryotrap is used as an aid for moving the sample to different parts of the system and freeze-pump-thaw techniques are used to maintain and enhance sample purity. Incomplete cryotransfer can lead to significant losses of the gas sample and the gas handling system should be designed to avoid these losses. The presence of small amounts of impurities can cause the cryotransfer to 'stall out' and limit transfer efficiencies. The objective of this research is to gain understanding of this limiting effect and derive appropriate equations to predict the transfer efficiency expected from a system. Results here are not restricted to cryotraps only, but also apply to other cold traps such as ice bath, chiller, or TEC cooled traps.

RESEARCH ACCOMPLISHED

Equation Development

In order to perform a radiological measurement, an analyte sample must be introduced into a nuclear detector cell. A common issue that is encountered is that volumetric expansion efficiency limits how much of the analyte makes it into the actual detector cell. In order to keep this efficiency high, analyte is often condensed using a cryotrap just before volumetric expansion into the detector cell. This helps direct the expansion into the detector cell and isolates the analyte from the rest of the processing manifold volume. The optimum efficiency of moving analyte from a cryotrap to the detector cell requires using a trap that is small compared to the detector cell. The volumetric efficiency is:

$$Efficiency = \frac{V_{detector}}{V_{detector} + V_{transferline} + V_{cryotrap}} \quad (1)$$

where initially the sample is contained in $V_{cryotrap}$ and then allowed to warm and expand into $V_{cryotrap}+V_{detector}$ by means of a transfer line with volume $V_{transferline}$. A typical $V_{detector}$ is on the order of 3-10 cm^3, which immediately limits $V_{transferline}+V_{cryotrap}$ to less than 0.1–0.5 cm^3 for efficiencies of ≥95%. We find that the difficulty is not in making an appropriately small cryotrap that can hold the analyte, but rather the cryotrapping action to condense it. It is often found that transferring from a large manifold volume into a much smaller cryotrap volume gives poor results where the pressure does not reach a small value as compared to the original pressure. The observed pressure is found to decrease initially, but can 'stall out' well before the entire sample is frozen into the cryotrap. The stall-out pressure is in fact a consequence of small amounts of non-condensable impurities and limits the ability to fully trap out the analyte.

Consider an analyte that can be condensed or frozen in the presence of small amounts of non-condensable impurities. For liquid nitrogen temperatures, this is often the case for analytes in the presence of residual nitrogen or dry air. Consider the system shown in Figure 1.

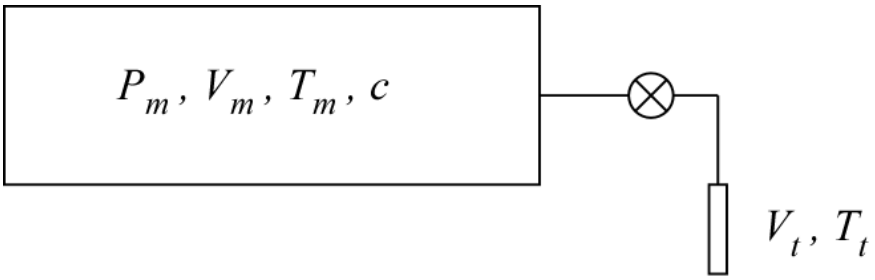

Figure 1. Large volume connected to a small cryotrap

In this case, the initial container (or manifold) is defined by P_m, V_m, T_m, and c where c is the fractional amount of non-condensable impurities. A small cryotrap, with volume V_t, is separated from the initial volume by a shutoff valve. Initially, all of the gas mixture is located in V_m and the trap is evacuated and cooled to T_t. Let us define the following equation using a variable u to be the fractional pressure left in V_m.

$$P = uP_m \tag{2}$$

In the initial state, the shutoff valve is closed and u=1. After opening the shutoff valve, gas starts to expand into the cryotrap with analyte freezing out and non-condensable impurities collecting in the trap.

$$\frac{P_m V_m c(1-u)}{T_m} = \frac{P_{imp} V_t}{T_t} \tag{3}$$

$$P_{imp} = \frac{T_t}{T_m}\frac{V_m}{V_t} P_m c(1-u) \tag{4}$$

P_{imp} is the partial pressure of the impurities that have collected in the trap. Initially, P_{imp} will be much smaller than uP_m, which is the remaining pressure in the manifold, and mass flow will continue toward the trap due to the pressure drop. At some point in the transfer, $P_{imp} = uP_m$ which corresponds to the situation where the impurities collected in the trap will equal the remaining pressure in the manifold.

$$\frac{T_t}{T_m}\frac{V_m}{V_t} P_m c(1-u) = uP_m \tag{5}$$

Solving for u gives:

$$u = \frac{1}{\left(\frac{T_m}{T_t}\frac{V_t}{V_m}\frac{1}{c}\right)+1}. \tag{6}$$

Defining the pressure that this happens as P_{stall}=uP_m and substituting gives:

$$P_{stall} = \frac{P_m}{\left(\frac{T_m}{T_t}\frac{V_t}{V_m}\frac{1}{c}\right)+1} \tag{7}$$

The equation for P_{stall} gives a good indication of how much analyte can be transferred into the cryotrap. We have compared the results from Equation (7) to experimental observations and found excellent agreement; however, a detailed experimental study was not conducted. A trapping efficiency can also be considered.

$$\frac{P_m - P_{stall}}{P_m} = 1 - \frac{1}{\left(\frac{T_m}{T_t}\frac{V_t}{V_m}\frac{1}{c}\right) + 1} \tag{8}$$

The equations for P_{stall} and the trapping efficiency will be favorable when the term in brackets is significantly larger than 1. For pure analyte with no additional impurities (c approaches zero), the equations predict P_{stall} approaches zero and complete transfer is accomplished. In order to obtain good cryotransfer in the presence of finite amounts of impurities, the term in brackets must be significantly larger than 1. Alternatively, one can write a criterion for a limit on the impurities for a good transfer.

$$c << \frac{T_m}{T_t}\frac{V_t}{V_m} \tag{9}$$

For a 90% transfer, c must be 1/9 the term on the right, for 95% c must be 1/19 the term on the right, and for 99% c must be 1/99 times the term on the right. As an example for: V_t=0.1 cm^3, V_m=10 cm^3, V_t=77 K, and V_m=300 K, then for a 99% transfer there must be no more than 0.21% non-condensable impurity in the analyte.

After the stall pressure is reached, mass flow into the trap is drastically reduced as the trap is filled with non-condensable impurities. Diffusion then becomes dominant where additional analyte can slowly migrate into the cryotrap and be frozen out. Diffusion rates will be dependent on the total pressure, gas species, temperature, and strongly dependent on geometry of the system. In many cases with gas handling systems that are optimized for small volumes, diffusion rates can be quite slow even at relatively low pressures of several Torr. Figure 2 gives an approximation of time evolution occurring during cryotrapping.

The stall-out pressure can often be reached quickly even if there is poor conductance from the manifold to the cryotrap. This rapid process is due to the mass transfer that occurs before the pressure is equilibrated and gas mixture is effectively pushed into the cryotrap. The diffusion-limited trapping action occurs on a much slower time scale. In fact, leak rates for the overall manifold and cryotrap can limit the amount of time that one can try to trap out the analyte. When the integrated leak rate becomes comparable to the impurity level, the cryotransfer can stall out sooner than predicted.

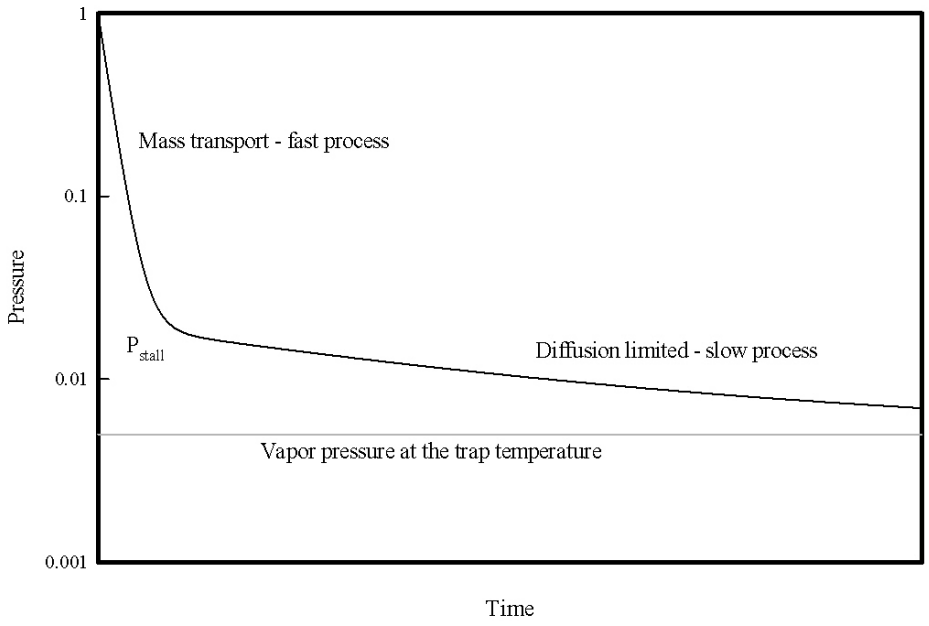

Figure 2. Approximation of result with cryotrapping

Analyte with a Significant Vapor Pressure

This approach may also be extended to analytes that have finite vapor pressure even at the trap temperature. A good example is methane, which has a vapor pressure of about 10 Torr at 77 K, or other analytes that may be liquid at the trap temperature and have significant vapor pressure. The treatment is much the same as before; however, Equation (5) must be modified because $P_{imp} + P_{vp} = uP_m$ must be included. P_{vp} is the vapor pressure of the analyte at the trap temperature. Here the situation is that the impurities collected in the trap in addition to the vapor pressure of the analyte will equal the pressure remaining in the trap at the stall-out pressure. Incorporating this into Equation (5) and using the same algebraic approach, an equation for the stall pressure can be derived.

$$\frac{P_{stall}}{P_m} = \frac{\left(X + \frac{P_{vp}}{P_m}\right)}{(X+1)} \tag{10}$$

In order to simplify to the expression in Equation (10), the following substitution was used:

$$X = \frac{T_t}{T_m}\frac{V_m}{V_t}c \tag{11}$$

Equation (10) has several implications that may be seen by inspection, with the realization that a small X is needed for good transfers. First, the vapor pressure of the analyte will only be significant if the P_{vp}/P_m term is comparable or larger than the X factor. This will cause the transfer to stall out sooner than predicted by Equation (7). Secondly, the X factor should be much less than 1 to have an efficient transfer.

Poor Transfer Conditions and How to Improve the Situation

In some cases, a cryotransfer step is used to pull a gas sample from a manifold or other volume into a small trap so that the volumetric expansion efficiency (Equation 1) into a detector can occur with high efficiency. In order to maximize the efficiency, the $V_{cryotrap}$ is designed to be small, but that can have negative consequences when trying to transfer into the small trap. In many cases, this can be mitigated by performing a multiple-stage cryotransfer.

As an example, consider T_m=300K, T_t=77K, V_m=1000 cm^3, V_t=1 cm^3 and c=0.001. Equation (8) predicts a cryotransfer efficiency of only 79.6%, which in most cases would be considered unacceptable. Breaking this up into a two-step cryotransfer can have a significant improvement on efficiency. Including an intermediate trap with V_{t2}=30 cm^3 would have a beneficial outcome. First, a cryotransfer to the intermediate trap would have an efficiency of 99.2%. Next, the original manifold would be valved off and the intermediate trap is warmed and allowed to expand into the final 1-cm^3 cryotrap where the second cryotrap occurs. That second step would have an efficiency of 99.2%, and would give an overall efficiency of 98.4%, which is a significant improvement over the 79.6% when using a single step. Considering product losses, the single-stage transfer loses more than 12 times the amount of analyte as compared to the two-stage design.

When considering how many stages to utilize, Equation (9) is of importance. For the quoted single-stage example, c is in fact "less" than the term on the right of Equation (9) – but not "much less" as is required. For a two-stage transfer, c is in fact "much less" than the term on the right.

CONCLUSIONS AND RECOMMENDATIONS

Chemical processes using cryotrapping are found to have fundamental limitations on transfer efficiency due to the presence of small amounts of non-condensable impurities. The impurities may be derived from contaminants in the actual sample, leaks into the transfer apparatus, or residual pressure when pumping out the cryotrap and manifold. When cryotransfer occurs, the non-condensable impurities will collect in the trap and will eventually stall out the cryotransfer by effectively filling the cryotrap and not allowing additional analyte mixture into the trap. After this occurs, analyte can still be trapped out but on a diffusion-limited timescale. For practical cryotransfer, it is preferable to design the process so that the necessary amount of analyte is transferred over at the stall pressure and diffusion is not relied upon. For some cases, it will be difficult or impossible to have an efficient transfer based on required sizes of the cryotrap, manifold, or amount of impurities. In those cases, a much higher efficiency may be obtained by breaking the process up into multiple steps—that is, to transfer to an intermediate volume(s). By stepping the volume down incrementally instead of a single stage, higher levels of impurities can be tolerated while maintaining high transfer efficiency. In fact, the product of individual efficiencies of a multiple stage cryotrap can drastically exceed the efficiency of a single stage.