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SOLVENT USAGE, RECYCLING POTENTIAL, and TREATABILITY STUDIES in a RESEARCH and DEVELOPMENT SETTING

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ABSTRACT

The use of solvents in a research and development setting is a difficult waste stream to apply typical waste minimization techniques to. There is typically a large variety of solvents used in small quantities by a large number of people. Argonne conducted a study of research and development uses of solvents to identify quantities, contaminants, and recycling criteria. The second phase of the project identified a typical solvent user and demonstrated technology that could be applied to the waste stream.

INTRODUCTION

Argonne National Laboratory (ANL) is a multi program research and development center. This facility, with more than 1,100 scientists, uses thousands of gallons of chemicals each year.

The focus of this study is on a group of about 20 organic solvents which constitute a large volume of the total chemicals used at Argonne. There is concern regarding the main usage of these solvents as well as their end contamination.

The scope of this effort is to describe methods of collecting data on solvent waste and to determine the feasibility of implementing reuse or recycling programs at a large research and development laboratory.

OBJECTIVES

The main objectives of this study were to:

1. Verify quantities of solvents being used at the laboratory and identify specific users.
2. Determine what the main uses of the solvents were and main contaminants at the end of usage.
3. Determine the purity level needed for recycle by each individual user.
4. Determine if the solvents had any recycling potential either in the laboratory or off-site.

METHODOLOGY

The following is description of the data collection process used in this study. This was a two-phase process.

Phase 1: Review and organize existing data:

The waste requisition forms for 1994 were used to identify specific chemicals, quantities, and users. The forms were reorganized identifying the generating individual, division, and quantity. As seen in Fig 1.0, the total number of users for each solvent was found and totaled. Further information was created using existing data to define trends.

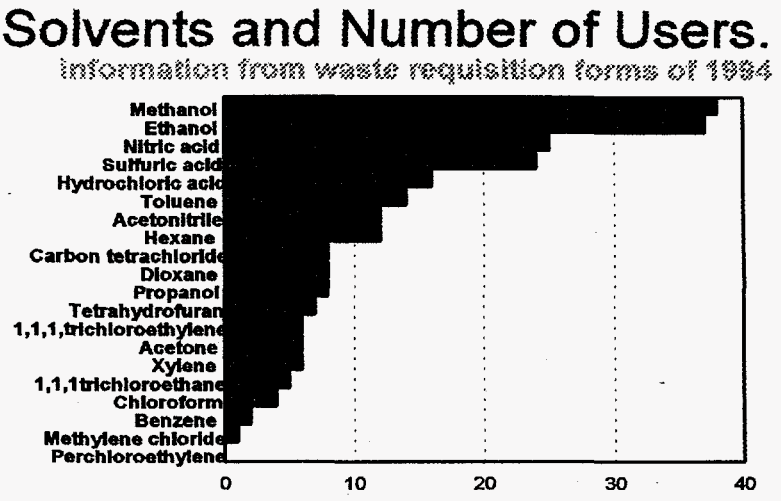

Fig 1.0

The list of users was sorted by quantity of chemical used. The result was to identify and target only people who contributed a quantity large enough to warrant a reduction or recycling step. This quantity can be any amount determined by the laboratory to be worth while to explore the possibility of recycling. For ANL, the volume was arbitrarily set at 5L/year for individual users.

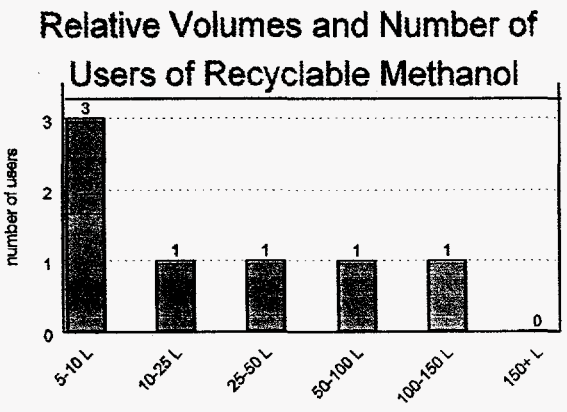

Fig 2.0

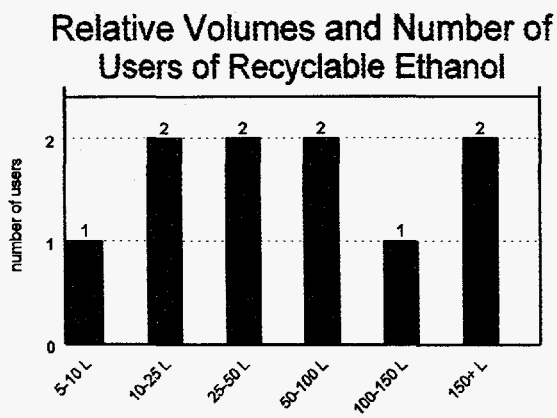

Fig 3.0

As indicated above, the number of users for the top two used solvents and the relative volumes are presented. This provides an estimate as to how many large solvent users there are and their contributions to the waste stream.

Phase 2: Survey use of chemicals.

A survey and interview schedule were prepared and meetings were held with primary users. Rather than sending out a questionnaire to the users, meeting with each user in person assured cooperation and a first hand inspection of the laboratory and waste generating facility.

A meeting was held with the Environmental Compliance Representatives (ECRs) of each building informing them that there is an interest in reduction of chemical use or recycling in their division. This step was advantageous because it helped to obtain division and line management support for the project. The Environmental Compliance Representatives also have an excellent working knowledge of their own division regarding environmental aspects and could have possible suggestions for the recycling or reuse of the targeted solvents.

In meeting with the primary users, the questionnaire was a key tool pertaining to usage of solvent and recycling potential of the used solvent in addition to volumes used allows for in-depth analysis of each individual. At ANL, forty-six users were targeted for an interview. After each meeting, a summary sheet was completed which included whether they could recycle or use a recycled solvent and the relative volumes involved.

In addition, vendors outside of the laboratory were contacted to determine if they would be able to take a contaminated solvent and recycle it and return it either to the laboratory or to other consumers. Determining which company the laboratory deals with and determining if they would be able to take recyclable solvents was a necessary step in the process.

RESULTS

The raw data consisted of the actual completed questionnaires and notes taken during interviews. Once this was collected and the summaries written for each user, it could be determined which users targeted have some recycling potential no matter how trivial it may be.

Once the individuals were categorized as either someone who can use a recycled solvent or someone who gives a recyclable solvent as waste or both, relative volumes for each individual were calculated. Each solvent volume was calculated as well. Upon

analysis of the relevant calculations, a chart was prepared which matched up large users of solvents that are only slightly contaminated with smaller users of that solvent who could use non high-purity solvent. Lists of users who could recycle within their own labs were also prepared.

At ANL, it was determined that the largest recoverable solvent was ethanol, contaminated with only oils and dust from cleaning. There was a total of six solvents out of the twenty that were both used in a substantial quantity and displayed recycling potential (contaminated only lightly--no radioactive elements, no contamination with other organic materials, only lightly contaminated with dust, grease, oils, and trace parts of metals). A chart was prepared displaying the volume of each recyclable solvent and the number of users.

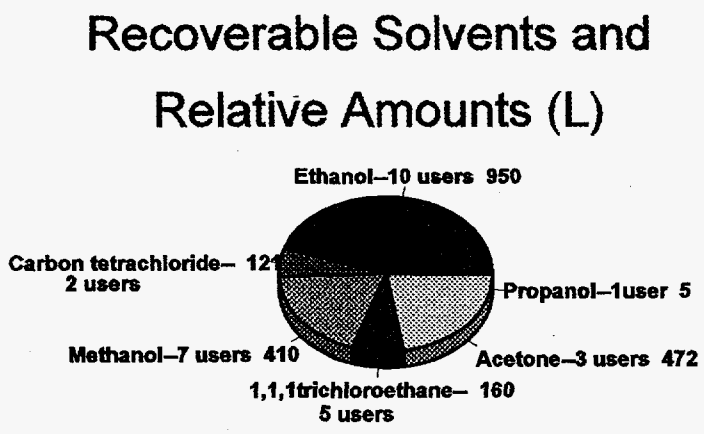

Fig 4.

Figure 4. provides a clear view of the amount of recoverable solvent that is disposed, the volume and users. These users are targeted for reuse and recycling options.

FEASIBILITY OF REUSE/RECYCLE PROGRAMS

There are three options of action regarding the reduction, reuse, or recycling of the given solvents.

1. **An individual recycling program.** The individual reuse process would be accomplished by the scientist. This process is done by individuals requiring both a high and low purity of the same solvent. Individuals could either purify the material and use it to high quality standards or to a lower quality standard.

Another aspect to this would be raising the question if the addition of one step (filtration, small distillation, etc.) would allow the user to recycle the solvent themselves.

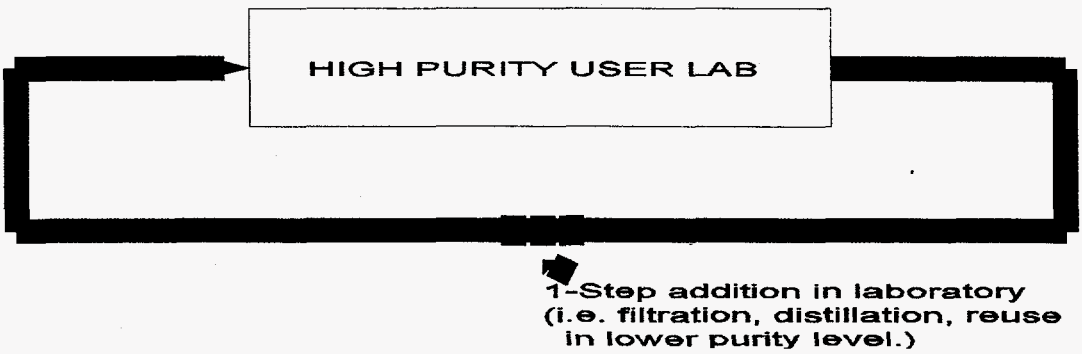

Fig 5

Using the chart from the raw data showing high purity and low purity users, possible connection could be made and then loops could be set up. The following graph displays the process.

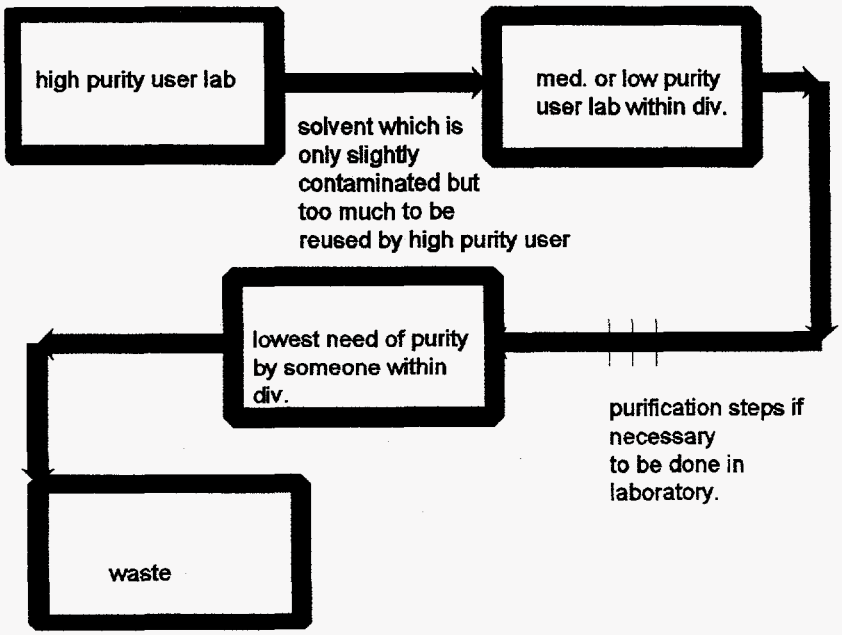

Fig 6

2. **Outside collection programs.** This involves a collection of recyclable solvents and purification of these solvents with written documentation of purity levels. At ANL, the main solvents having recycling potential all have relatively low boiling points (less than 100 degrees C), leaving distillation as a possible option for the recovery of the solvents. The first step in setting up a collection program is to assess total volumes wasted and the cost of purchasing this volume. If the collection process is cost effective, then it might be the best option. The next step is to determine if an off-site vendor would be able to recycle the solvent and the fee involved. Transportation and distance of vendor should be taken into account.

3. **An on-site recovery program.** This is a feasible option if relatively large quantities are involved and the process is uncomplicated.

Persons who are able to contribute a large quantity of solvent who would be wiling to have a separate waste container designated for each recyclable solvent in their labs should be identified. At ANL, the majority of the targeted users have expressed an interest in recovery and seem be willing to contribute. Identifying an area where the recovery program could be set up is dependent on how big the organization is and the amount of solvent targeted. Once an area is found that would be suitable for recovery, solvent handling equipment would be required. Type would be dependent on the type of recovery system best suited to the solvents.

Transportation requirements to the recovery site of the solvents should be determined. The waste removal that is already in use could be utilized to pick up and deliver the recyclable solvents. Once the solvents have been distilled or recovered, written documentation including purity, boiling point specific gravity, acidity and contaminants are needed. A random sampling of recovered solvents can give this information for each batch of solvents distilled.

Procurement and the costs of waste disposal and recovery programs should be determined. The feasibility of the collection program is dependent on cost effectiveness. If the process is cost effective, then a solvent recovery program could be initiated. This process is currently being undertaken by conducting pollution prevention opportunity assessments in individual streams.

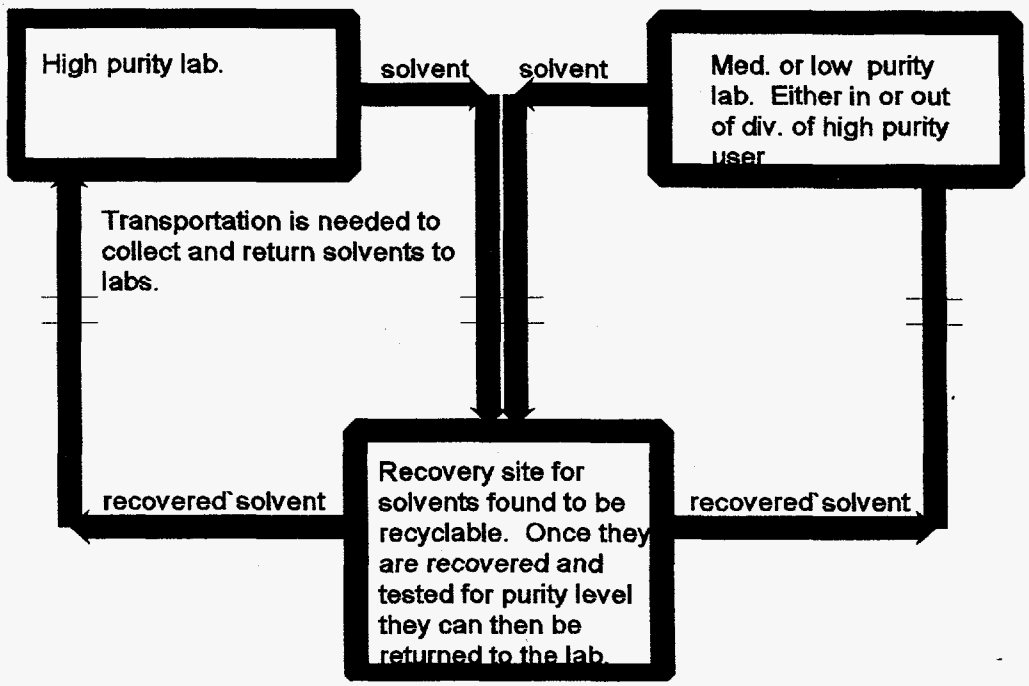

Fig 7.0

CONCLUSION AND RECOMMENDED COURSE OF ACTION

The three options outlined above each have certain advantages that make them unique. Of course, there are the disadvantages that one must look upon before selecting a course of action. The following is the amount that ANL could save each year for each chemical recycling or recovering instead of purchasing new chemicals.

Possible Costs of Purchasing New Solvents from Volumes Wasted with Recycling Potential.

Prices are from 1994-1995 Aldrich Catalog:

Ethanol	$9,000.00
Carbon tetrachloride	$7,800.00
Methanol	$5,800.00
Acetone	$3,800.00
1,1,1 trichloroethane	$1,800.00
Propanol	$200.00

Option 1, the individual recovery program, appears to be the most practical and cost effective. It would be relatively easy to implement through communicating to the scientists and providing the means necessary to accomplish recovery. The downside is that it is targeted toward individuals and this changes from year to year, with different people and different amounts of solvents being used.

Target primary users should be identified annually. As indicated in Fig 5.0, an exchange of solvents, with people's needs changing would require further gathering of information as well. Given the simplicity of instituting this program it appears to be feasible at ANL.

Option 3, an on-site recovery program, has several advantages over the individual recycling. Once it has been implemented, regardless of changes in solvent use by individuals, it could still operate effectively. There is a larger amount of solvent that could be recycled than could be recovered in the lab. However, the issues of transportation and safety must be taken into account as well as an area for recycling to occur. In addition, someone would be required to operate the entire process and this would require extra funds. The cost effectiveness of the on-site recovery program is critical.

Overall, an on-site recovery program could most productively provide for a comprehensive recycling program. Given the parameters of costs and safety requirements, however, the most feasible option in the recovery and recycling of solvents at Argonne is to implement an individual recycling program as described in option 1, above.

Based upon the preliminary identification of appropriate solvents and waste generators at the Laboratory, six solvents were identified as preliminary targets: ethanol, methanol, carbon tetrachloride, 1,1,1-trichloroethane, propanol, and acetone. The waste generators were contacted to obtain representative waste samples to perform the preliminary treatability studies. Waste solvent samples were obtained containing ethanol, methanol, 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE). Results of the preliminary treatability studies performed on the waste samples are described below.

Ethanol Waste

For the ethanol waste which was a colorless mixture of ethanol, silver nitrate ($AgNO_3$), water, and some black suspended particulates (Ag_2O), filtration was first applied to remove the suspended particles. The filtrate was transferred to a distillation flask to recover the ethanol by controlling the temperature at the boiling point of ethanol (78.5°C). The system reached equilibrium when the temperature approached 100°C indicating that the residual content was primarily water. The original concentration of ethanol (analyzed by gas chromatography techniques) was 13.8% by volume. After distillation, the distillate concentration was 91.9% ethanol and the residual aqueous concentration was 2.7% ethanol. The mass balance closure for ethanol was 97.1%.

Because $AgNO_3$ is used as a reagent in the silver stain protocol, the presence of $AgNO_3$ was analyzed for in the original waste ethanol solvent, in the distillate, and in the residual. The presence of silver was qualitatively measured, by adding sodium

sulfide (Na_2S) to the solutions; if silver is present, it would precipitate as AgS (a black precipitate). Na_2S was gradually added into these three solutions to visually determine if the sample solutions were silver-ion free or not. After addition of the sodium sulfide into the original waste sample and the residual sample (after distillation), black precipitates were observed immediately. No precipitate formation was observed in the distillate sample, indicating that the recovered ethanol sample was purified and was silver-ion free.

Methanol Waste

Experiments were performed on two different methanol wastes. The first waste sample contained methanol and was contaminated with pump oil, grease, and black nickel laser dusts. It was a gray oily liquid with a strong gasoline-type odor. Filtration was used to remove the suspended laser dust. The distillation temperature was controlled at 65°C (the boiling point of methanol). No residual was left in the distillation flask. The recovered methanol concentration was 88.2% (the original waste solvent methanol concentration was 84.8%). For the second waste methanol sample, pure methanol solvent (100%) was recovered using distillation.

Trichloroethane (TCA)

Experiments were performed on two waste TCA samples. The first sample was a mixture of 58% TCA and 29% TCE and was contaminated by large amounts of pump oil and grease (oil and grease content was 44.86 g/L). This oily liquid had a deep green color. Filtration was used to remove the suspended particles. The distillation temperature was controlled at 70°C (well below the boiling point of TCA (74.1°C) and TCE (87 C)). After the temperature gradually rose to about 80°C, the separation was believed to have reached equilibrium. At this point, the concentration of TCA in the distillate was 90.1% and the concentration of TCE was 10.0%; the concentration of TCA and TCE in the residual was 11.3% and 53.0%, respectively. The mass balance closure for TCA and TCE were 99.4% and 92.0%, respectively.

For the second waste TCA sample, pure TCA solvent (100%) was recovered using distillation.

The preliminary treatability studies (using filtration and distillation) indicated that good quality solvents could be recovered from waste solvents in a research and development setting (such as at Argonne National Laboratory, analytical laboratories, universities, medical hospitals, etc.). Good mass balance closure was observed on all the waste solvents tested. Ethanol can be recovered of approximately 92 vol % concentration from a waste solvent initially containing 13.8% ethanol using distillation. No $AgNO_3$ was carried over into the distillate based upon a lack of silver sulfide (AgS) precipitate formed using a qualitative test.

Using filtration and distillation, good recovery results were obtained for the TCA/TCE waste samples. Because the boiling points

of TCA and TCE are relatively close (74.1°C and 87°C for TCA and TCE, respectively), to completely separate TCA and TCE only by distillation is extremely difficult. However, distillation could be used as a first stage treatment and then another process (such as membrane separation) could be used for further purification.

THE NEXT STEPS

Argonne demonstrated the applicability of solvent recycle using an ethanol waste stream generated by an electrophoresis process. The stream was contaminated with silver nitrate, sodium and ammonium hydroxide, and acetic acid. The solution was distilled and the final product was of a higher quality than the researcher used originally.

This investigation will be carried further to demonstrate the viability of solvent recycle to other streams. Commercial distillation equipment will be investigated in the future.