



Project Summary

Pollution Prevention Opportunity Assessment USDA Beltsville Agricultural Research Center Beltsville, Maryland

A pollution prevention opportunity assessment (PPOA), performed during the spring of 1991, identified opportunities for waste reduction at the U.S. Department of Agriculture's Beltsville Agricultural Research Center (BARC), Beltsville, MD. These opportunities involved general hazardous materials handling and use, total Kjeldahl nitrogen (TKN) analyses, and high performance liquid chromatography (HPLC) analyses.

One pollution prevention option applicable to total Kjeldahl analyses involved use of an automated nitrogen analyzer. Acid and base wastes are virtually eliminated, and chemical and labor costs are reduced significantly. Other pollution prevention options for total Kjeldahl analysis included use of phenate autoanalyzer, micro analysis, and alternate catalyst. Pollution prevention options for HPLC included solid phase extraction, supercritical fluid extraction, solvent recovery, and column/particle size reduction.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

EPA has developed a systematic approach to identify, evaluate, and implement options to reduce or eliminate hazardous waste. The approach is presented in a guidance document entitled

"Waste Minimization Opportunity Assessment Manual" (EPA/625/7-88/003). The procedure described in the EPA manual provides detailed worksheets and a process/option evaluation method for use in industrial settings. For BARC, appropriate worksheets were used to quantify waste generation, evaluate options, and calculate payback. To encourage use of this manual, EPA is conducting a series of pollution prevention assessment projects.

BARC employs approximately 1000 scientists and technicians who perform research work in all areas related to the Agricultural Research Service activities. State-of-the-art research is conducted on livestock diseases, animal and human nutrition, animal genetics and physiology, plant productivity and diseases, and a host of other topics. The pollution prevention assessment was conducted for the U.S. Environmental Protection Agency's (EPA) Risk Reduction Engineering Laboratory (RREL) under the purview of the Waste Reduction Evaluations at Federal Sites (WREAFS) Program of EPA's Pollution Prevention Research Branch. This report summarizes the application of the EPA procedure to selected processes at BARC.

Procedure

EPA's systematic assessment procedure can be used by a facility's own employees to identify pollution prevention opportunities. As a structured program, it provides intermediate milestones and a step-by-step procedure to (1) understand the facility's processes and wastes, (2) identify options for reducing waste, and (3) determine whether the options are technically and economically feasible enough to



justify implementation. The Waste Minimization Opportunity Assessment Manual contains a set of 19 worksheets designed to facilitate the pollution prevention assessment procedure. This procedure consists of four major steps:

- Planning and organization—organizing and goal setting.
- Assessment—carefully reviewing a facility's operations and wastestreams and identifying and screening potential options to minimize and prevent wastes.
- Feasibility analysis—evaluating the technical and economic feasibility of the options selected and subsequently ranking the options.
- Implementation—procuring, installing, implementing, and evaluating (at the discretion of the facility).

As the result of discussion with the BARC environmental staff, researchers, and EPA personnel, the investigation focused on:

- general hazardous materials handling and usage,
- TKN analyses, and
- HPLC analyses.

General Hazardous Materials Handling and Usage

The BARC facility generates approximately 5,300 gal of hazardous waste annually at a disposal cost of approximately \$423,000. A strong site-wide hazardous waste management program is led by the Safety, Occupational Health, and Environmental Section Office. This program includes state-of-the-art marshalling facilities for solvent bulking, site-wide hazardous waste training, the presence of collateral hazardous waste duty officers in each research institute, an electronic mail system for trading chemicals onsite, recycling programs, and others. An existing strong incentive for pollution prevention on the site is the charge-back policy, by which management units are assessed for disposal costs. This incentive, coupled with the environmental ethic of many researchers and their desire to minimize raw material costs, has already led to significant pollution prevention onsite. Additional approaches to pollution prevention were identified in this study.

Total Kjeldahl Nitrogen

The Kjeldahl method is a widely used standard method of chemical analysis, first described in 1883, for determining protein nitrogen in grains, meats, and other biological materials. Samples requiring analysis are oxidized in hot, concentrated

sulfuric acid, with bound nitrogen converted to ammonium ions. Subsequent steps include treatment with an excess of strong base, distillation, and titration of the liberated ammonia.

Quantities of reagent used for the Kjeldahl procedure vary based on the nitrogen content of the sample being analyzed. Samples with low nitrogen content require increased sample size for analysis. These samples use macro-Kjeldahl techniques that generate approximately 500 to 600 ml of waste per sample. Samples in which the nitrogen content is higher allow for a smaller sample size; therefore, the micro-Kjeldahl analysis is appropriate. Micro-Kjeldahl wastes are estimated at 50 to 100 ml per sample. Wastes requiring disposal after a Kjeldahl analysis consist of the digest, which is alkaline and contains metals used as catalysts, and the distillate, which is either acidic or basic. The total acid and base wastestreams for 1990 for BARC were approximately 850 gal.

High Performance Liquid Chromatography

Laboratories at BARC extensively employ HPLC in their work. Like other forms of chromatography, HPLC is used to separate, isolate, and identify components of mixtures. Compounds of interest are separated on a column containing solid adsorbent based on differing affinities for the packing material. Solvents are used to introduce samples and to elute materials through and off the column. A pump is required for solvent flow. Sensitive detectors identify and quantify compounds eluting from the column. Before using HPLC, a preparative or extractive procedure isolates a specific analyte or characteristic class of compounds. Organic solvents are used for these extractions.

Approximately 2,600 gal of solvent waste was generated by BARC during 1990. A significant amount of this total stems from the use of organic solvents in HPLC and in sample preparation.

The sample preparation step isolates either components of interest or interferents for the sample matrix before analysis and quantitation through HPLC. At BARC, the main procedures used are liquid-liquid or solid-liquid extraction. Aqueous samples may be extracted with an organic liquid, or samples may be extracted directly with solvent. Secondary extractions may also be performed. Extraction solvents used at BARC include chloroform, hexane, methanol, and methylene chloride. Extractions and preparative procedures account for a significant

percentage of solvent wastes generated at BARC.

Hazardous wastes generated directly as a result of HPLC analyses consist of the solvents used as mobile phase to introduce and elute analytes through the chromatography column. Typical solvents used include aqueous mixtures of methanol, acetonitrile, etc. The nature of the HPLC effluent leads to its categorization as a hazardous waste because of its flammability and, possibly, other characteristics of hazardous waste.

Pollution prevention in HPLC begins with an understanding of how the separation process proceeds. The goal of the analyst is to achieve the best separation in the shortest time. To obtain this separation, the analyst can change the following variables:

- mobile phase composition
- stationary phase composition
- temperature
- flowrate
- column configuration
- particle size

Each of these factors plays a significant role in achieving the desired level of separation. The first three variables control the elution time of the component (i.e., the time taken between component injection and detection). The last three variables control the width of the peak. As the peak narrows, sensitivity increases since the signal level rises above the detector's instrumental noise level. Additionally, a faster eluting compound will have a narrower peakwidth since broadening processes have been curtailed.

Results and Discussion

During the course of the project, a number of generic laboratory pollution prevention tools and techniques were identified. These include waste management books and manuals that describe common-sense approaches to reducing wastes generated by laboratories. Specific techniques and references are contained in the project report. One interesting concept is the procedure conducted at the end of laboratory procedures that renders certain wastes nonhazardous.

The project identified a number of impediments to further pollution prevention activities at BARC. Probably the biggest impediment is the nature of waste generation onsite. Because a large number of small quantity wastes streams are generated by the large number of laboratories, standard waste reduction techniques applied at other sites are not directly applicable. Other impediments to pollution prevention include the need for new labo-

ratory methods to be approved by independent boards such as the Association of Official Analytical Chemists (AOAC). Therefore, changes in laboratory procedures are difficult to implement.

General pollution prevention options concerning hazardous materials handling and use are given in Table 1. The major pollution prevention initiative identified in this report is a thorough audit of the types and quantities of hazardous waste generated onsite. Until specific waste streams are identified and quantified, it will be difficult to determine how much further progress is feasible regarding pollution prevention. Additional recommended initiatives include further discussions with regulatory agencies regarding laboratory treatment options; centralizing various operations, where feasible, to reduce the waste, including a central chemical warehouse and a centralized purchasing system; and further education and training of site personnel. Additional pollution prevention concepts for TKN and HPLC are contained in Table 2.

The most interesting finding regarding the TKN assessment was that methods exist to virtually eliminate hazardous waste generated by Kjeldahl analyses. Commercially available automated microcomputer-based systems use combustion techniques to remove nitrogen from the sample and a thermal conductivity detection system to measure the released nitrogen. Nitrogen concentrations are determined in less than 3 min according to one manufacturer's literature. Acceptable sample sizes vary from 1 mg to 1 g, depending on nitrogen concentration and sample density. Some of these units are currently in operation at BARC, and scientists are pleased with their operations. Scientists outside BARC also praise the method, and method approval by the AOAC has been obtained for certain analyses, with additional approvals for other analyses expected shortly.

These analyzers provide a significant health and safety improvement to laboratory workers because handling of hot acids and bases is eliminated and sulfur

trioxide fumes generated during digestion are eliminated. Of course, suitable health and safety precautions are needed because of the use of flammable gases with the automatic analyzer. Disposal costs for waste from the automated analyzer are estimated at \$0.65 per sample; those for macro-Kjeldahl analysis, \$2.85. Labor per Kjeldahl analysis is estimated to be reduced by approximately 50% with the automated system. Acid and base waste generation is virtually nonexistent; however, copper filings and anhydrous chemicals used for water removal must be disposed of when spent. The \$30,000 cost for this instrument may limit its use in laboratories performing a limited number of analyses yearly. (Treatment steps for TKN wastes are also discussed in the complete Project Report.)

A number of techniques can help prevent the pollution associated with HPLC analyses. Solid phase extraction (SPE) techniques can reduce solvent usage by over 95% when performing certain extrac-

Table 1. General Pollution Prevention Options for BARC

<i>Pollution Prevention Techniques</i>	<i>BARC Options</i>
<i>Training and assessments</i>	<p><i>Expand on the existing pollution prevention ethic with further education and training. Successful efforts are already underway including paper recycling and source reduction in individual operations.</i></p> <p><i>Appoint a pollution prevention "officer" within each research institute to assist researchers with reduction and recycling initiatives. Pollution prevention representatives from all the institutes could meet periodically to discuss and compare efforts among institutes. Such information transfer, crucial for the adoption of pollution prevention throughout the BARC, reduces repetitive pollution prevention development efforts. For example, DOE's Sandia National Laboratories has a pollution prevention network where 60 people throughout the laboratories are points of contact.</i></p> <p><i>Develop and implement a plan to conduct periodic laboratory pollution prevention laboratory assessments using suitable, in-house expertise. Such assessments may uncover additional pollution prevention opportunities over time, and emphasize BARC's commitment to pollution prevention; they can also be used to monitor the success of pollution prevention efforts.</i></p>
<i>Process or equipment modification</i>	<p><i>Keep abreast of commercially available technology changes as they relate to laboratory pollution prevention. When new technology is too expensive for individual laboratories to implement, consider pooling resources and locating instruments at a centralized facility, which may be used by several laboratories.</i></p> <p><i>Reduce atmospheric emissions of chemicals from laboratories as part of a comprehensive pollution prevention program. Glassware and automated extraction systems to reduce these emissions are commercially available. In addition, for some samples, emissions can be reduced through solid phase extraction techniques as opposed to classical liquid evaporation techniques that release the solvent carrier into the fume hood and subsequently to the atmosphere.</i></p>
<i>Waste segregation</i>	<i>Segregate hazardous from nonhazardous wastes. Hazardous waste volumes are often unnecessarily increased due to the addition of wastestreams that are not hazardous. Segregation alone can significantly reduce hazardous waste generation rates and disposal costs.</i>
<i>Pollution prevention policy</i>	<i>Require each laboratory to have a written waste management/reduction policy. Minimum requirements would include annual chemical inventories, the dating of chemicals as received, etc.</i>

Table 2. TKN and HPLC Pollution Prevention Options

<i>Pollution Prevention Options</i>	<i>Waste Stream Affected</i>	<i>Nature of Pollution Prevention Option</i>	<i>Capital Investment (\$)</i>	<i>Net Operating Cost Savings (\$/yr)</i>	<i>Payback Period (yr)</i>
TKN					
<i>Nitrogen autoanalyzer</i>	<i>Acid/base</i>	<i>Equipment</i>	<i>30,000</i>	<i>11,700</i>	<i>2.56</i>
<i>Phenate autoanalyzer</i>	<i>Acid/base</i>	<i>Equipment</i>	<i>30,000</i>	<i>4,050</i>	<i>7.41</i>
<i>Micro analysis</i>	<i>Acid/base</i>	<i>Procedure</i>	<i>Negligible</i>	<i>350</i>	<i>0</i>
<i>Alternate catalyst</i>	<i>Metal catalysts</i>	<i>Equipment/procedure</i>	<i>N/A</i>	<i>N/A</i>	<i>N/A</i>
HPLC					
<i>Solid Phase Extraction</i>	<i>Solvent</i>	<i>Equipment/procedure</i>	<i>N/A</i>	<i>N/A</i>	<i>N/A</i>
<i>Supercritical Fluid Extraction *</i>	<i>Solvent</i>	<i>Equipment/procedure</i>	<i>30,000</i>	<i>20,000</i>	<i>1.5</i>
<i>Solvent Recovery</i>	<i>Solvent</i>	<i>Equipment</i>	<i>12,000</i>	<i>N/A</i>	<i>N/A</i>
<i>Column/Particle Size Reduction *</i>	<i>Solvent</i>	<i>Equipment</i>	<i><800</i>	<i>4,200</i>	<i>0.19</i>

* Based on literature specifying at least 150 extractions per week

* Based on one BARC laboratory that conducts 1000 HPLC analyses per month

tions. SPE employs small disposable columns containing sorbent of which analytes of interest can be bonded and then eluted off the sorbent. One to two milliliters of solvent and an SPE filter or cartridge can accomplish the same function as 200 to 300 ml of solvent in a standard HPLC system.

Supercritical fluid extraction (SFE) is an innovative technique that offers great promise for replacing chlorinated solvent extractions in the relatively near future. SFE requires a gas compressed above its critical temperature and pressure points. The gas is thus transformed into a supercritical fluid exhibiting high diffusion coefficients and low viscosities. These properties allow for very efficient transfer of solutes from the sample matrix into the supercritical fluid. Carbon dioxide is typically used, and modifiers may be added to selectively extract fractions or compound classes from a sample. Varying the temperature and pressure (density) of the supercritical fluid also can allow for very selective extractions. For example, low density carbon dioxide extraction is similar to that for hexane, whereas higher density carbon dioxide extracts similarly to benzene. SFE also offers shorter extraction times compared with organic solvents. After the extraction, supercritical carbon dioxide returns to a gaseous state at room temperature and pressure. Given a capital cost of \$30,000 for instrumentation, the payback period (based on an average workload of 150 extractions/wk) would be less than 1½ yr. This relatively short payback is because both the pur-

chase of organic solvents and disposal costs are eliminated.

Additional source reduction methods are available for HPLC analyses. The majority of analyses involve the use of HPLC columns, with a typical column packing of 5 μ C₁₈ on silica. The column configuration is also standard at 4.6 mm i.d. x 25 cm length with typical flowrates of approximately 1 mL/min. Switching to a smaller column internal diameter while holding the column length and particle size constant will reduce solvent consumption as shown below:

Flowrate Comparisons

<i>Column Dimensions [i.d., (mm) x length (cm)]</i>	<i>Flowrate [mL/min]</i>
4.6 x 25	1.0
2.0 x 25	0.2
1.0 x 25	0.05

The narrower column reduces the amount of sample needed and, hence, reduces the waste from the sample preparation step. The narrower column can affect sensitivity, however. To prevent column overloading, the sample size and analyte level are smaller.

The analyst may also choose to reduce the packing particle size from 5 μ to 3 μ . This change enhances sensitivity by narrowing the analyte peakwidths. Furthermore, solvent consumption can be reduced if the column length is lessened. A shorter column length should produce shorter elution times while preserving the separation resolution.

By converting to a different column inner diameter or length, waste reduction of approximately 80% per HPLC analysis (at negligible additional column costs) are feasible. These techniques may not be feasible for all HPLC analyses performed at BARC, however.

Additional source reduction methods and recycling techniques for extraction and HPLC waste are contained in the Project Report.

Conclusions and Recommendations

Pollution prevention at laboratory facilities similar to BARC is a difficult process because of the distribution of small-quantity waste generators. Nevertheless, significant pollution prevention progress can be made. Source reduction and treatment techniques are available that will reduce waste overall, and specifically waste for TKN and HPLC analyses. The total quantity of wastes generated at BARC by TKN and HPLC analyses has not been quantified. In addition, some identified source reduction techniques may not be economically feasible unless implemented at a centralized facility. Therefore, specific estimates of waste reduction at this site have not been projected for many of the options in Table 2. The Project Report contains sufficient information so that the reader can determine economic payback periods based on savings per individual (unit) analysis.

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This Project Summary was prepared by the staff of Science Applications International Corporation, Cincinnati, OH 45203

James S. Bridges is the EPA Project Officer (see below).

The complete report, entitled "Pollution Prevention Opportunity Assessment: USDA Beltsville Agricultural Research Center, Beltsville, Maryland," (Order No. PB92-146843; Cost: \$19.50, subject to change) will be available only from:

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