Reducing Waste Generation and Radiation Exposure by Analytical Method Modification (U)

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REDUCING WASTE GENERATION AND RADIATION EXPOSURE BY ANALYTICAL METHOD MODIFICATION

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SUMMARY

The primary goal of an analytical support laboratory has traditionally been to provide accurate data in a timely and cost-effective fashion. Added to this goal is now the need to provide the same high quality data while generating as little waste as possible. At the Savannah River Technology Center (SRTC), we have modified and reengineered several methods to decrease generated waste and hence reduce radiation exposure. These method changes involved improving detection limits (which decreased the amount of sample required for analysis), decreasing reaction and analysis time, decreasing the size of experimental set-ups, recycling spent solvent and reagents, and replacing some methods. These changes had the additional benefits of reducing employee radiation exposure and exposure to hazardous chemicals. In all cases, the precision, accuracy, and detection limits were equal to or better than the replaced method. Most of the changes required little or no expenditure of funds. This paper describes these changes and discusses some of their applications.

INTRODUCTION

Our laboratory provides analytical support for many different types of research programs within SRTC and throughout the Savannah River Site. A wide variety of sample types including ground water, organics, laboratory waste, process control, sludge, soils, and others are received for many different analyses. These samples are both radioactive and non-radioactive and may contain hazardous materials such as RCRA metals, organics, and flammable solvents. The sample size is often limited by these chemical hazards or by the level of radioactivity. Hazardous substituents present in the sample may prohibit its disposal to the laboratory drain system and therefore may limit the size of the sample or, in some cases, may prevent its analysis entirely.

The nature of an R&D support organization is to perform accurate analyses on unknown and uncharacterized samples and to be able to adapt analysis methods to compensate for difficult or hazardous sample matrices. To enable analysis of all samples received while minimizing hazardous waste generation and radiation exposure, we performed a systematic evaluation of all methods performed in our Wet Chemistry and Ion Chromatography Laboratories. Evaluation of the more than thirty methods performed in these labs took approximately two years and is still continuing. Each method was evaluated for reagent content, detection limits, sample size, and its necessity in being offered. Improvements were tested and evaluated on both standards and actual samples. Method changes were implemented once the validity of the method was proven and documented. The changes that were made fell into three categories: method modification, reagent recycle or replacement, and method replacement.
DISCUSSION

Modification of Existing Methods

- Ion Chromatography
  Ion chromatographic analysis is one of the most frequently requested analyses in our laboratory, with over 7000 samples being submitted in 1995. This method is used to determine common anions and cations in aqueous sample matrixes. In this analysis, a sample is introduced into a flowing stream (mobile phase) which carries the sample through an ion exchange resin. Ions in the sample are separated by differential interaction with the resin and quantified through conductivity detection. Originally, the analysis took approximately 20 minutes per sample run and generated approximately 100 mL of aqueous waste per run. On average, complete determination of the commonly requested anions (fluoride, formate, chloride, nitrite, nitrate, phosphate, sulfate, and oxalate) required three different dilutions (three runs) so a typical sample analysis generated 300 mL of aqueous waste. Cation analysis followed a similar pattern. Several method changes were tested and implemented which lowered the waste generated to 20 mL per sample.

The existing suppression system, which was used to decrease or "suppress" the conductivity of the eluent mobile phase, was a counter-current ion exchange system. Once the sample had passed through the anion exchange resin (for anion analysis) and the anions in solution were separate, the eluent stream was passed through a cation exchange resin. The separated anions passed through unaffected, but the cations in the eluent (predominantly sodium) were exchanged for hydrogen ions contained in a counter-current (regenerant) stream. This converted the eluent to a weak acid with very low conductivity. The regenerant stream flowed at 4 to 5 mL per minute and represented 80% of the liquid waste generated.

This suppression system was replaced with an electrochemical suppression system which produces a regenerant stream by electrochemically reducing the waste from the eluent stream. The self regenerating suppressor (SRS) employs a self-contained electrochemical membrane and thus requires no preparation of reagents. It is therefore less time consuming and less costly that the previous system. The cost of the SRS membranes is the same as that of the counter current suppressor membranes. Minimal instrument and procedural modification was required. The suppressor system is more effective at decreasing the background conductivity and so enhances detection limits. The lower background conductivity enabled modification of the detector to increase the sensitivity of the analysis by an order of magnitude. This lower detection limit decreased the required sample volume by 90% with a corresponding decrease in radiation exposure.

The separation of ions is affected by passage through a low capacity ion exchange column. The existing columns required 20 minutes for complete separation of anions and 15 minutes for complete separation of cations. These columns were replaced by lower capacity ion exchange columns (called "fast-sep" columns) which effect the same separation in 5 minutes. Since the instrument generates waste based on the length of an analysis run, this change decreased the waste generated per sample by 75%. The precision of the data, +/- 3 to 5% depending on the sample matrix, is equal to that of the original columns. Since the column is of lower capacity than the previous column, column damage was of concern when running concentrated samples. However, the column has proven to be fairly resilient and can be easily cleaned and regenerated after poisoning by concentrated samples. The column lifetime, 12 to 18 months on average, is comparable to the previous column. Currently, our lab is testing a smaller diameter column which effects the same separation using one fourth the eluent flow rate and one fourth the sample volume.
The combined effect of these changes was to decrease the liquid waste generated by 95%, decrease the required sample volume by 90% with a corresponding decrease in radiation exposure, lower the detection limits by an order of magnitude, and cut the analysis time by 75%. The precision and accuracy were virtually unchanged.

- **Titrations - Microelectrodes and Buffer Volume Reduction**
  Many of the analyses performed in the wet chemistry laboratory are titrations which use either potentiometric, pH, or ion selective electrodes to determine the titration endpoint. Waste reduction can be accomplished by decreasing the size of the analysis system and by using smaller, more sensitive electrodes (microelectrodes).

  The most common titrations performed in the lab are pH titrations to determine acid and base concentrations and halide determinations using ion selective electrodes. The standard sample cup used required a minimum sample volume of 25 mL to adequately cover the surface of the electrode. This cup was replaced with a narrower cup which required only 10 mL to cover the electrode surface. Data validation tests on standards and samples showed the precision and detection limits to be comparable to that of the 25 mL volume method. This change, which decreased the liquid waste generated by 60%, was simple to make and required minimal procedure modification and virtually no analyst training.

  Microelectrodes are small working surface electrodes, anywhere from 5 mm to less than 1 mm in diameter. A standard size electrode, which is usually 12 mm in diameter, typically requires clearance in solution of twice the electrode diameter in order to obtain accurate data. If a smaller solution volume is used, the electrode experiences electrochemical feedback from the sides of the reaction vessel. This feedback distorts the electrochemical response and corrupts the acquired data. Smaller electrodes require proportionally less clearance in solution and thus smaller volumes of solution. In addition, reducing the size of the electrode surface decreases the electrochemical noise caused by the unequal distance of all points on the surface of the electrode to the reference or counter electrode. For these reasons, smaller electrodes offer lower detection limits and require correspondingly lower sample volumes. Micro pH electrodes have been implemented in pH measurements, as described in the next section. They are still being evaluated for routine use in the titrations performed in the laboratory.

- **pH Determinations**
  The measurement of pH, hydrogen ion concentration, is one of the simplest laboratory measurements to make. It is also one of the easiest to do incorrectly, particularly with unbuffered samples. The most frequently made error is not allowing the electrode to equilibrate sufficiently in the sample. Therefore it is important to measure an adequate sample volume (20 to 25 mL with a standard size 12 mm electrode) and to repeat the measurement with fresh volumes of sample until successive measurements agree within 0.1 pH unit. In general, 50 to 100 mL of sample are required to accurately determine pH.

  We replaced the standard size pH electrode which had been in use in the lab with a smaller 5 mm diameter electrode. This electrode requires only 5 mm clearance to obtain accurate data. Using a 10 mL vial, accurate pH measurements can be made using 1.5 mL of sample. The waste generated by this analysis was reduced by 95%. A wide variety of samples between pH 2 and pH 14 was measured using both the standard size electrode and the microelectrode. The pH results agreed within 0.1 pH unit and so were essentially equivalent.
Reagent Substitution and Recycle

• Karl Fisher Titrant
  Determination of volume percent water in liquid samples is accomplished by a potentiometric titration commonly known as the Karl Fisher method. An aliquot of sample is introduced into anhydrous methanol and titrated with a pyridine containing titrant. The titrant complexes with water, thus changing the solvent potential which is measured electrochemically. Pyridine is a RCRA listed waste and cannot be introduced into the 773-A high or low activity drain systems. To reduce the hazard of the waste generated, we replaced the pyridine containing Karl Fisher Titrant with a pyridine-free titrant, hydranal. Hydranal contains a non-hazardous amine which complexes with water in the same manner as pyridine does in the Karl Fisher titrant. No method modification or instrument reprogramming was required and so the transition to this new solvent was essentially effortless. The precision and accuracy of the titration using hydranal is the same as that obtained using the pyridine-containing solvent. The relative standard deviation of the method is 3% in both cases.

  The solvent used in the Karl Fisher Method, methanol, is also hazardous from a flammability standpoint. However, less than 20% of the waste from the method is methanol, so the total waste stream from the method contains less than 10% total organic carbon. The total waste stream therefore is non-hazardous. Development work in progress on this method involves reducing the volume of methanol required by employing a microvoltammetric system.

• Strontium Chloride
  Determination of carbonate and free-hydroxide is accomplished by first precipitating the carbonate out of solution and then determining the carbonate and free hydroxide concentrations separately with pH titrations. The standard method in use involved precipitation of the carbonate with excess barium chloride. Barium is a RCRA listed waste due to its toxicity and can no longer be introduced into the laboratory’s high or low activity drain system. We replaced the barium chloride with strontium chloride which is non-hazardous. Method validation experiments showed the strontium to be equivalent in a variety of sample matrices. Samples commonly run for carbonate and free-hydroxide were analyzed in duplicate using both methods and the results were found to be equivalent in all cases. As with the Karl Fisher titrant replacement, no method changes or instrument modifications were required.

• Freon Recycle
  The standard analysis method for determining total petroleum hydrocarbons (commonly known as oil and grease determination) involves solvent extraction of the hydrocarbons using Freon followed by quantitation using infrared detection. This had been the method of choice because it was simple, rugged, inexpensive, and applicable to solid and liquid samples and radioactive samples. Due to its deleterious effect on the ozone layer, the use of Freon and other chloro-fluorocarbons (CFCs) has been greatly restricted. Freon has become very expensive ($800/liter) and will soon be unavailable entirely. Proposed replacement methods include solid-phase extraction, solvent extraction, and supercritical fluid extraction all of which use gravimetric determination or infrared analysis of the extracted hydrocarbons. These methods are not as precise or as sensitive as the Freon extraction method, they require a larger amount of sample due to the decreased sensitivity, and the solid phase extraction method cannot be used with solid samples. Supercritical fluid extraction requires expensive instrumentation ($100,000), facility services (high pressure ultrapure carbon dioxide), and a lot of bench top and hood space. This method is therefore not feasible for radioactive sample analysis. All replacement methods would require procurement of new equipment and analyst training.
We opted to keep the existing Freon method and recycle the solvent. An inexpensive solvent reclamation system was procured to reclaim the spent Freon. This reclaimer removes hydrocarbons from the Freon solvent by passage through an activated carbon bed. The operation is simple: spent Freon is poured into the top of the instrument and clean Freon is obtained from a tap at the bottom. The hydrocarbon content of the reclaimed Freon is measured to ensure its purity. The capacity of the carbon bed is 5 g of hydrocarbon. This bed is changed out routinely every 3 months or if the hydrocarbon content of the reclaimed Freon is above 0.2 ppm (twice the minimum detection limit of the analyzer).

Using the carbon bed unit, 95-97% of Freon can be reclaimed and reused. The reclaimer has been used successfully for non-radioactive sample analyses for over two years. A contained unit is currently being tested for radioactive samples.

**Instrument Replacements**

- **High Temperature TOC**
  
The existing instrument for determining total organic carbon (TOC) and total inorganic carbon (TIC) used a persulfate oxidation method. A sample was oxidized with sodium persulfate and the carbon in the sample was evolved as carbon dioxide gas. The evolved gas was quantified using infrared detection. This method had several undesirable characteristics. First, it used a flow cell reaction chamber which required a large sample volume (50 to 100 mL) per analysis. The instrument could only accommodate liquid samples, so the frequently requested analyses on sludges and soil samples could only be accommodated by making a slurry of the sample and then aspirating this slurry, while stirring, into the instrument. Sampling variability and absorption of carbon dioxide while the sample was stirring had a deleterious effect on both the precision and the accuracy of the data. In addition, the aspirated particulates frequently clogged the flow cell which contributed to a high percentage of down time while the instrument was being cleaned and repaired. The analysis method required hazardous chemicals (sodium persulfate) and generated a high volume of hazardous and radioactive waste. The instrument was also ten years old and was at the end of its useful life.

  We replaced this system with a Rosemount DC-190 High Temperature Total Organic Carbon Analyzer. This instrument oxidizes samples by combustion in a 900°C furnace, so there are no reagents to prepare or dispose. The analyzer is automated and requires only 50 microliters per analysis. In addition, ADS reconfigured the instrument by placing a small sampling system and analysis chamber in a radiologically contained hood. This enabled the analysis of radioactive samples, using as little as 25 microliters of sample. The contained module can accommodate solid samples so the need to dilute the samples into a slurry, and the accompanying detection limit and instrument damage problems, is eliminated. The detection limits of this instrument are 0.1 parts-per-million, which represents an order of magnitude improvement over the previous system. The instrument is also capable of determining purgeable organic carbon and non-purgeable organic carbon, methods which were unavailable with the previous instrument.

  The overall benefit from this instrument change was a 98% reduction in the total liquid waste generated, a thousand fold decrease in the required sample size, and an order of magnitude decrease in the detection limits. The precision was slightly improved, from +/- 5% to +/- 3% RSD. The contained module is approximately one third the size of the previous system's contained module. This compactness is a huge benefit considering the scarceness of radioactive hood space. Unlike the previous instrument, in which 100 mL of
radioactive sample was placed in an open flask while being aspirated into the instrument, the new contained analysis requires that 25 microliters of sample be introduced into a sealed furnace. This smaller sample volume combined with the shielding provided by the furnace significantly decreases radiation exposure to the analyst.

**Flashpoint Tester**

Flashpoint is a frequently requested waste characterization analysis. Liquids which have a flashpoint below 140°F are considered hazardous due to flammability and must be treated as hazardous waste. We had a Pensky-Martens closed cup flashpoint tester which is the standard method for flashpoint determination. The temperature of the sample was raised at a specified rate and a flame was periodically introduced into the space just above the sample. The flash was detected by a heat sensor and recorded. This open cup system required 60 mL of sample. Since many of the samples received for flashpoint are organic, such as diesel fuel and solvents, this method presented a particular waste disposal problem, especially with radioactive samples. As with the TOC analyzer, the flashpoint tester had been put into service in 1980 and was at the end of its useful life. When the unit was taken out of service in 1993, it had failed and could not be repaired.

This instrument was replaced by a Petrolab multi-position mini-flashpoint tester. This unit is an open cup flashpoint tester requiring only 1 mL of sample per analysis. The flash is sensed by a pressure transducer which monitors the pressure change when the sample flashes. The system is much smaller (approximately one fourth the bench top footprint of the previous instrument) and requires no facility services other than 110 V electrical power. The unit has an autosampler which can accommodate eight different samples and can be programmed to perform different analysis protocols on each sample. The single sample unit is even smaller than the multiposition unit and one of these smaller units has recently been procured to be placed in a radiologically contained hood.

Open cup flashpoint values are slightly higher than closed cup values. For example, the closed cup flashpoint of dodecane, which is the check standard used with the analysis method to ensure that the instrument is functioning properly, flashes at 165°F in a closed cup tester and 174°F in an open cup tester. The standard laboratory method, upon which all hazard data is based, requires a closed cup value. The programming in the open-cup tester was therefore modified to give closed cup values. The accuracy of this modified temperature program is verified before each set of samples is analyzed. The precision of the method is +/- 1 to 3% when analyzing standards and samples. Reducing the sample size had no effect on the precision or accuracy of the data as long as the sample cups in the tester are well cleaned between samples.

The overall benefit was a 98% reduction in the amount of waste generated. The automated system greatly reduced the hands-on analysis time which decreased the analyst's exposure to chemicals and increased productivity.

**CONCLUSION AND PATH FORWARD**

We have successfully decreased the waste generated by these methods and decreased the total waste generated by the Ion Chromatography and Wet Chemistry laboratories by 60%. In all cases, the analytical precision and accuracy remained the same or improved and in most cases the detection limits were improved. The cost per sample decreased not only by streamlining methods but also by decreasing the costs associated with chemical procurement and waste disposal. The benefits of waste reduction and minimizing radiation exposure were achieved. Current efforts to further decrease waste generated include
additional implementation of microelectrodes and buffer volume reductions in titrations and solvent recycling.