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Reclamation and Reuse of Freon in Total Petroleum Hydrocarbon Analyses

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RECLAMATION AND REUSE OF FREON IN TOTAL PETROLEUM HYDROCARBON ANALYSES

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SUMMARY

At the Savannah River Technology Center (SRTC), we have successfully demonstrated the use of a solvent recycling system to reclaim spent Freon solvent in total petroleum hydrocarbon (TPH) analyses of radioactive samples. A wide variety of sample types including ground water, organics, laboratory waste, process control, sludge, soils, and others are received by our lab for total petroleum hydrocarbon analysis. This paper demonstrates the successful use of a commercially available carbon bed recycle system which we modified to enable the recovery of 95-98% of the radioactive contaminated Freon. This system has been used successfully in our lab for the past three years.

INTRODUCTION

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 has been the method of choice because it is simple, rugged, inexpensive, and applicable to both solid and liquid samples and to 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.

Several methods have been proposed to replace the Freon extraction method. These 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, and a larger amount of sample is therefore required due to the decreased sensitivity. The solid phase extraction method cannot accomodate solid samples. Supercritical fluid extraction requires expensive instrumentation ($100,000) and facility services (high pressure ultrapure carbon dioxide) and the instrumentation requires a significant amount of bench top and hood space, which makes the method not feasible for radioactive sample analysis. All replacement methods would require procurement of new equipment and retraining of analysts.

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.

EXPERIMENTAL

Principle of the Method and Experimental Details

The spent Freon is collected and then passed in 500 mL batches through an Horiba Solvent Reclaimer. This unit consists of an activated carbon bed through which the spent solvent is passed. Hydrocarbons are trapped by the carbon bed. The bed has a capacity of 5 grams of hydrocarbon. This bed is replaced routinely every 6 months or if the measured hydrocarbon content of the reclaimed Freon is above 0.2 ppm (twice the minimum detection limit of the analyzer). The fresh carbon bed must be conditioned with approximately 500 mL of Freon before the system can be used to reclaim spent solvent. The Freon used in this priming is also recycled.

Method Validation

The infrared absorbance of this reclaimed solvent is measured in the oil content analyzer. The content must be less than 0.2 ppm hydrocarbon. If the measured oil content exceeds this value, this is an indication that the hydrocarbon content of the carbon bed is near capacity and the bed is changed out. The accuracy and precision of measurements using fresh and reclaimed solvent are the same since the Freon is tested for purity before use.

DISCUSSION

Separation Efficiency

The carbon bed traps organic material which is soluble in Freon. Freon containing up to 0.1 % by volume of hydrocarbons (1000 ppm) has been introduced into the unit and essentially all the hydrocarbons have been removed. The separation is effectively 100% provided that the capacity of the bed has not been exceeded. The batches of Freon introduced into the unit for recycle are generally less than 25 ppm hydrocarbon. This is because the linear calibration limit of the unit is 50 ppm. Sample which contain greater than this amount are diluted. There is usually three times the amount of Freon used to rinse and zero the instrument between samples.

Recovery Yield

Freon evaporates very quickly. The waste from the oil content analyzer is kept in a closed container until enough is accumulated for recycle. When the Freon contacts the carbon bed, some heat is given off due to interaction with the carbon. This heat causes a small volume of the Freon to evaporate. In addition, some evaporative loss is experienced on collection. Approximately 95 to 97% of the volume of Freon introduced into the carbon bed unit is recovered.

Effect of Radionuclides

The effect of radionuclides was of concern when recycling Freon which had been contacted with radioactive samples. When a radioactive sample was extracted with Freon, the radionuclides present in that sample could follow one of three paths: the radionuclides could remain in the aqueous portion of the sample; the radionuclides could be extracted with the hydrocarbons into the Freon and remain in the Freon when passed through the carbon bed; the radionuclides could be extracted into the Freon and be trapped by the carbon bed. Determining the fate of the radionuclides was essential to ensure that radioactive material was not being concentrated in either the Freon or the carbon bed.

Since the radioisotopes present in the waste are inorganic it was believed that they would not be extracted into the Freon. This proved to be true for strontium, cesium, and plutonium isotopes, however a measurable amount of tritium was extracted from aqueous samples into the Freon. This transfer was probably effected via hydrogen ion exchange with organic species present in the sample. This tritium activity remained in the Freon after passage through the carbon bed. Washing the contaminated Freon with an equal volume of deionized water effectively removed all the tritium activity so that the Freon could be passed through the carbon bed for recycle. Reclaimed Freon is analyzed for radioactive material to ensure that no build-up of radioactive material is occurring.

CONCLUSION AND PATH FORWARD

Using the carbon bed unit, 95-97% of Freon can be reclaimed and reused. We have modified the reclamation method to enable the recycle of Freon used in radioactive sample analysis. Our laboratory is currently developing a sealed reclamation unit which will decrease the loss of Freon due to evaporation and allow continuous rather than batch solvent recycle.