



Project Summary

Evaluation of Methods Used to Desorb the Constituents Adsorbed on the Charcoal Contained in Automotive Evaporative Canisters

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This summary represents a two-part study which evaluated current extraction methods for analyzing charcoal canisters used to control evaporative emissions in automobiles. The second part of this study investigated the use of solvent-free extraction methods such as high pressure CO₂ soxhlet extraction and vacuum transfer extraction. The results of the solvent-free methods were then compared to the CS₂ soxhlet extraction method.

The results of this study showed that the CS₂ method extracted up to 8% more material (by weight) from the charcoal than did the vacuum transfer method and up to 15% more material (by weight) than did the high pressure CO₂ soxhlet extraction method. In addition, more total hydrocarbons were measured with the CS₂ method than were measured in either the vacuum transfer or the high pressure CO₂ methods.

The vacuum transfer apparatus used for this study was a modification of the apparatus that had been used for a previous study. More of the higher molecular weight hydrocarbons, mainly alkylated aromatics greater than carbon number 9, were measured in the extracts obtained from the modified vacuum transfer apparatus than were measured in the extracts from the previous method. Lower quantities, however, of the lower molecular weight hydrocarbons were measured than before.

The high pressure CO₂ soxhlet extraction method gave the lowest hydrocarbon measurements of the three methods.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, N.C. 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

This laboratory conducted a two-part study in order to determine the most accurate, practicable and cost effective method of evaluating charcoal canisters. Charcoal canisters are used to collect evaporative hydrocarbon emissions from gasoline powered vehicles. When the Manufacturers Operations Division (MOD) at EPA began testing vehicles to determine their compliance with the federal emission standard, a significant number of the vehicles failed to meet the evaporative hydrocarbon emission standard. The MOD suspected that these failures were caused by a decrease in the ability of the charcoal canister to capture hydrocarbon vapors. As an aid in their assessment of canister performance, MOD requested our laboratory to determine the nature and quantity of the material adsorbed and retained on the charcoal contained on these canisters. There was concern, however, that using the present (CS₂ soxhlet extraction) method in the

analysis of the canisters might alter the quantity and quality of hydrocarbons or other materials desorbed from the canister's carbon. In addition, it was also unknown which of the current methods of desorbing the hydrocarbon constituents from the carbon would be the most accurate, practicable and cost effective.

The first phase of this study involved the use of various solvents or a combination of solvents to extract the charcoal in a soxhlet extraction apparatus. We also ultrasonicated the charcoal using CS₂ as the solvent. Solvent extractions are most often the standard method to be compared with and usually provide an indication of the maximum amount of adsorbed material that can be extracted from the charcoal. On the other hand, solvent extraction introduces impurities, such as benzene in CS₂, and the potential for errors with many sample handling steps. The results of the first phase of this study show that CS₂ was the most practicable solvent for the extraction and analysis of the charcoal. The total quantity of material soxhlet extracted from the seven charcoal samples analyzed was the same for the various solvents tested, except for methanol. CS₂ was the preferred extracting solvent because, in the GC/FID analysis of the CS₂ extracts, the CS₂ solvent peak only interfered with the measurement of the C₅ hydrocarbons. When using solvents such as CH₂Cl₂ or hexane, the solvent peak interfered with the measurement of the C₆ and C₇ hydrocarbons.

The second phase of this study investigated solvent-free extractions of the charcoal and included a modified vacuum transfer method and a high pressure CO₂ soxhlet extraction method. We did not investigate the use of microwave desorption, thermal desorption or super-critical fluid (using CO₂ under high pressure) extraction, to extract these charcoal samples because of equipment unavailability and budget constraints.

Solvent-free extraction of the charcoal would have been the preferred method because this method minimizes sample handling and reduces the potential for heat induced artifacts to be formed during the extraction process. In addition, solvent free extractions eliminate the solvent peak interference in the GC/FID measurement of the hydrocarbons in the extracts.

Procedure

Handling and Storage of Charcoal Canisters

The seven canister samples analyzed for this second part of the study were the same as those analyzed in Part 1. Five of the canister samples had been prepared and

analyzed for previous canister studies. The other two canisters were taken from an in-house evaporative emission project where the loading and purging of the canisters had been done under controlled conditions. One canister was loaded with gasoline vapors from a base stock gasoline and was labeled gasoline-base. The other canister was loaded with gasoline vapor containing 10% oxinol (5% methanol + 5% t-butyl alcohol). The preparation and handling of the samples has already been described in Part 1. The two unused (blank) charcoal samples that were analyzed in Part 1 were analyzed in the initial set up of the high pressure CO₂ soxhlet and vacuum transfer methods. No material was extracted from the blanks (except water) and, therefore, no hydrocarbons were measured.

High Pressure CO₂ Soxhlet Extraction

A high pressure soxhlet extractor (J&W Scientific, Folsom, Calif.) was used to extract the charcoal (Fig. 1). CO₂ was used as the

extracting solvent. The high pressure CO₂ extraction procedure used was the same procedure as described in the operating and supplementary instructions provided by J&W Scientific.

The charcoal sample (approximately 1.00g) was weighed into a preconditioned cellulose thimble and the thimble was then placed into the soxhlet extractor. The soxhlet extractor was placed in a pressure chamber and the chamber was then sealed. The chamber and filling lines were then evacuated under moderate vacuum. After the inlet and outlet valves to the chamber were closed, the inlet lines were filled with liquid CO₂ and the lower part of the chamber was placed into a preheated (60°C) water bath. The chamber was immersed in the water bath for 15 min. and then it was moved, in a vertical position, to a ring stand. The pressure chamber was then filled slowly with liquid CO₂ to its operating pressure of 820 PSI (ambient temperature of 21°C). The lower part of the loaded pressure chamber was then placed back into the water bath and

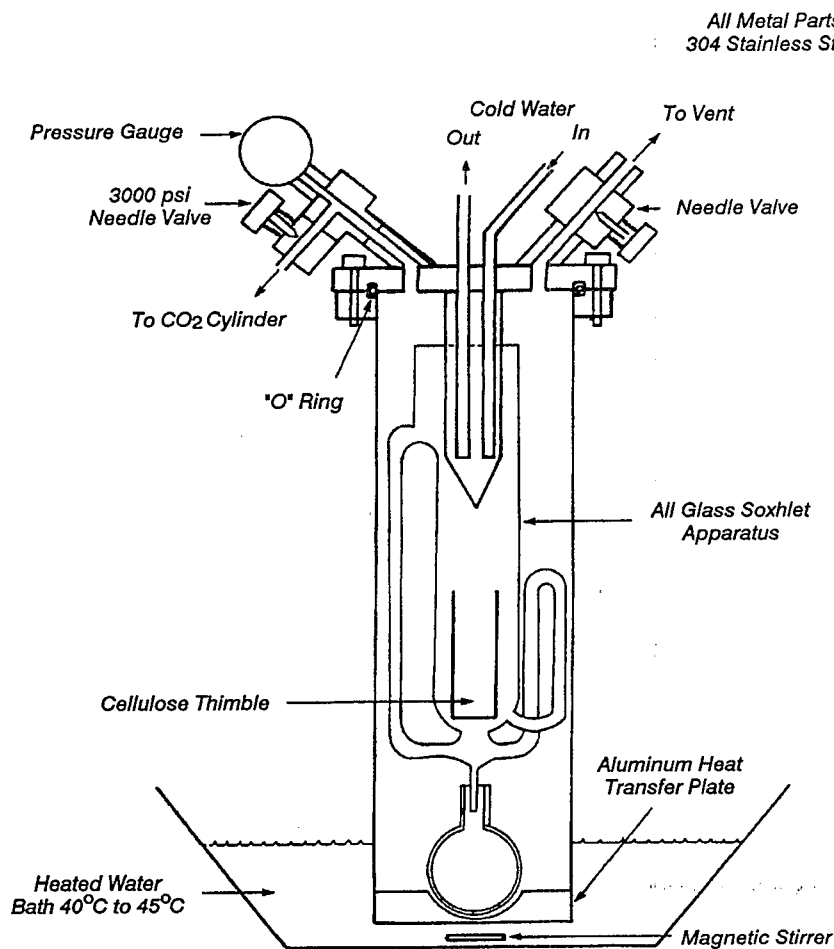


Figure 1. High pressure CO₂ soxhlet extractor.

the flow of the 10°C water to the top of the extractor (cold finger condenser) was turned on. All the extractions were done for 1 hour after initially determining that the amount of material extracted was the same if the extraction time was 1, 2 or 4 hours. The operating pressure in the chamber was maintained at its initial pressure during the entire 1 hour extraction period. After the extraction was completed, the chamber was removed from the water bath, the chilled water for the condenser was turned off and the chamber was then de-pressurized, slowly, to ambient. The time required for de-pressurizing the chamber was usually 20 minutes. The de-pressurized chamber was then opened quickly and the extracted material was transferred from the flask into a pre-weighed vial using a disposable pipet. The vial was stored in a -20°C freezer. The thimble containing the extracted charcoal was placed in a desiccator for 1 hour before determining the weight loss of the charcoal.

Vacuum Transfer

The vacuum transfer apparatus had been modified (Fig. 2) in order to eliminate the apparent limitations of the apparatus previously used (Fig. 3) to do the charcoal extractions. The modifications were made to reduce the potential for vacuum leaks by eliminating as many greased joints as possible and to eliminate cold spots in the manifold so that the less volatile, relatively higher molecular weight hydrocarbons would be transferred into the receiving flask.

This modified vacuum transfer apparatus did not contain any joints that require vacuum grease that would flow as soon as heat was applied to the system and should, therefore, be less likely to leak. All the connections in the extraction region were made using FETFE O-rings. The top of the 250 ml. distilling flask and one end of the manifold were threaded so that a vacuum coupling connector (Ace Glass, Vineland N.J.) could be used instead of a greased joint. The manifold was evacuated from the receiving end of the apparatus instead of the center in order to eliminate a cold spot at the vacuum stopcock manifold connection. The joint at the receiving end of the apparatus was made by using a vacuum adapter with an inner ring design (Ace Glass) to connect to a centrifuge tube. The manifold vacuum gauge was connected directly into the system in order to eliminate another greased connection and to make it possible to monitor the vacuum conditions inside the system during the extraction.

The procedure used to extract the charcoal was the same as had been used for the previous extraction apparatus. Smaller quantities of the charcoal (5.00 to 20.00g.)

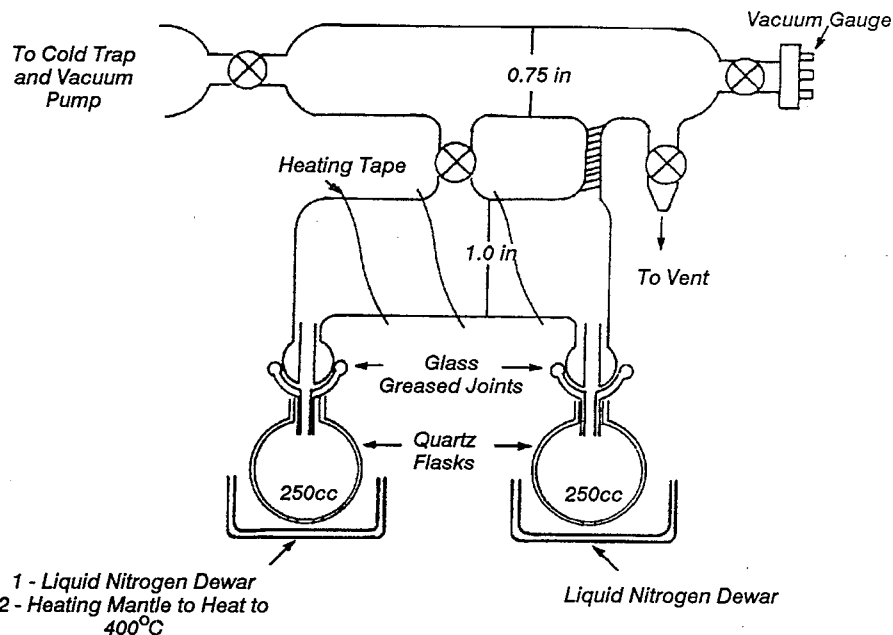


Figure 2. Previous vacuum transfer apparatus.

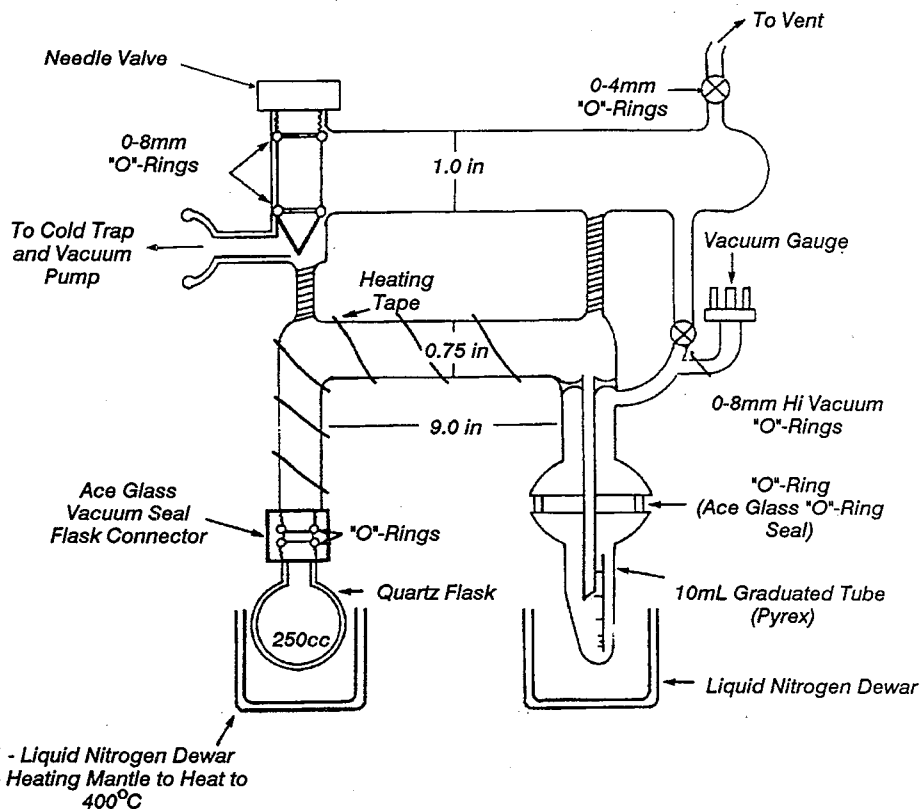


Figure 3. Present vacuum transfer apparatus.

were extracted instead of the 40.00g used previously in order to conserve the samples.

Gas Chromatographic Equipment and Procedures

All the extracts were analyzed using a Perkin Elmer Model 3920 gas chromatograph equipped with a flame ionization detector. An aliquot of the sample was vaporized into a tedar bag and then introduced into the GC system using a 10 mL sample loop. This method of sample introduction had been used in the previous canister study and the procedure already described in Part I. A 60m x 0.32 mm i.d. DB-1 (J & W Scientific) capillary column with

a 1.0 μ film thickness was used to separate the C4 to C13 hydrocarbons. Upon injection of the sample to the capillary column, the sample is cryogenically trapped in the column which was initially cooled to -95°C. After the one-minute injection period, the temperature to the capillary column is ramped to -45°C and then slowly increased at the rate of 8°C/min up to a final temperature of 235°C. The Helium carrier gas flow was maintained at 1.5 mL/min using a Matheson Model 8240 mass flow controller (Matheson Corp., East Rutherford N.J.). The peak area and peak retention time data was recorded and plotted on a Perkin Elmer Sigma 15 chromatographic data station. In

addition, the peak area and peak retention time data was stored on cassette tape for later transfer to a computer using a standard RS 232 serial port.

Results And Discussion

The CS₂ extraction method extracted up to 8% more material (by weight) from the charcoal than was extracted by using the modified vacuum transfer procedure, for six of the seven samples tested. In addition, the CS₂ extraction method extracted up to 15% more material (by weight) from the charcoal samples than was extracted by using the high pressure CO₂ soxhlet extraction procedure (Table 1 and Fig. 4).

Table 1. Comparison of Charcoal Extraction Methods - Percent (by Weight) Material Extracted from Charcoal

Sample Number	Methods		
	CS ₂ Soxhlet Extraction	Modified Vacuum Transfer	High Pressure CO ₂ Soxhlet Extraction
A152/0237	31.10	23.30	16.60
A151/0420	44.59	47.36	36.80
A151/0320X	36.60	33.98	24.00
A151/0282	35.20	30.40	28.20
A152/0599	25.60	19.40	17.80
Gasoline-base	22.40	21.40	14.30
Gasoline-blend	20.85	18.20	19.70

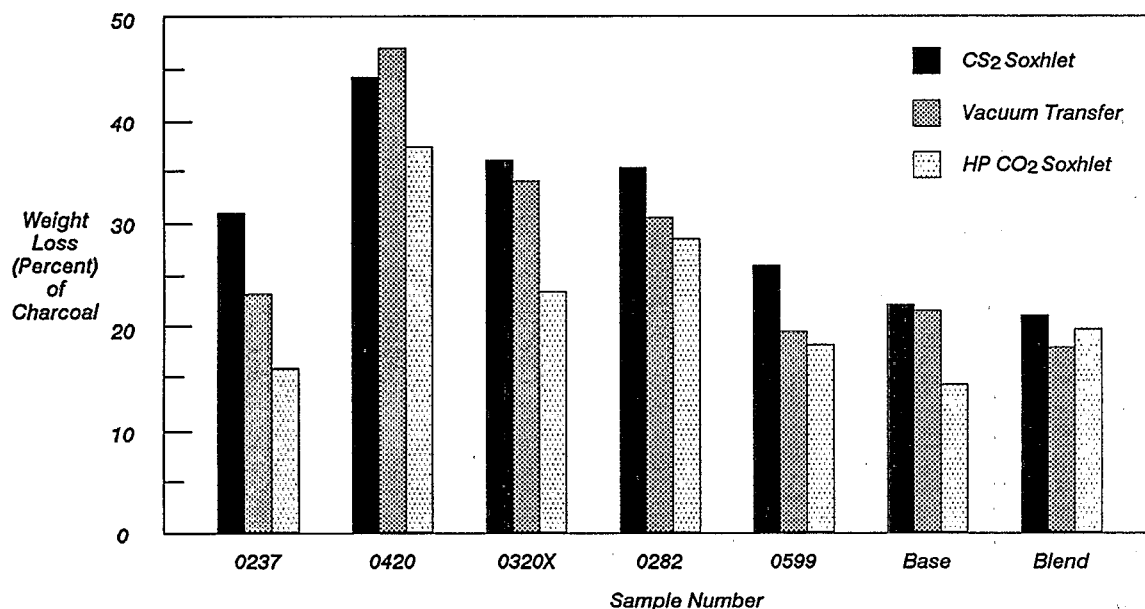


Figure 4. Comparison of charcoal extraction methods - weight loss (percent) of charcoal.

Up to 4% more total hydrocarbons on carbon was measured by the GC/FID analysis of the extracts from the CS₂ soxhlet extraction method in comparison to the hydrocarbons measured in the extracts from the vacuum transfer method. Moreover, up to 8% more total hydrocarbons on carbon was measured in the CS₂ extracts than were measured in the extracts from the high pressure CO₂ soxhlet extraction procedure (Table 2 and Fig. 5).

The results of the comparison between the CS₂ extraction method and the vacuum transfer method were the same as had been reported in a previous canister study. More material (by weight) had been extracted from the charcoal with the CS₂ soxhlet extraction method than had been extracted by the vacuum transfer method. In addition, the total hydrocarbons on carbon that were measured in the extracts with the CS₂ soxhlet extraction method were greater than

the total hydrocarbons measured in the extracts from the vacuum transfer method. The total hydrocarbons on carbon measured in the CS₂ extracts were greater than the total hydrocarbons measured in the vacuum transfer extracts because CS₂ extracts more of the high molecular weight, alkyl aromatics than the other method. In our previous canister studies we had determined that used "aged" canisters contained significant quantities of alkyl aromatics.

Table 2. Comparison of Charcoal Extraction Methods - Percent (by Weight) Hydrocarbon on Carbon from GC/FID

Sample Number	Methods		
	CS ₂ Soxhlet Extraction	Modified Vacuum Transfer	High Pressure CO ₂ Soxhlet Extraction
A152/0237	21.54	17.34	14.54
A151/0420	33.13	32.13	25.53
A151/0320X	14.96	13.43	10.97
A151/0282	22.87	21.15	18.19
A152/0599	15.39	15.63	10.31
Gasoline-base	15.01	13.82	Not Measured
Gasoline-blend	11.90	10.90	6.69

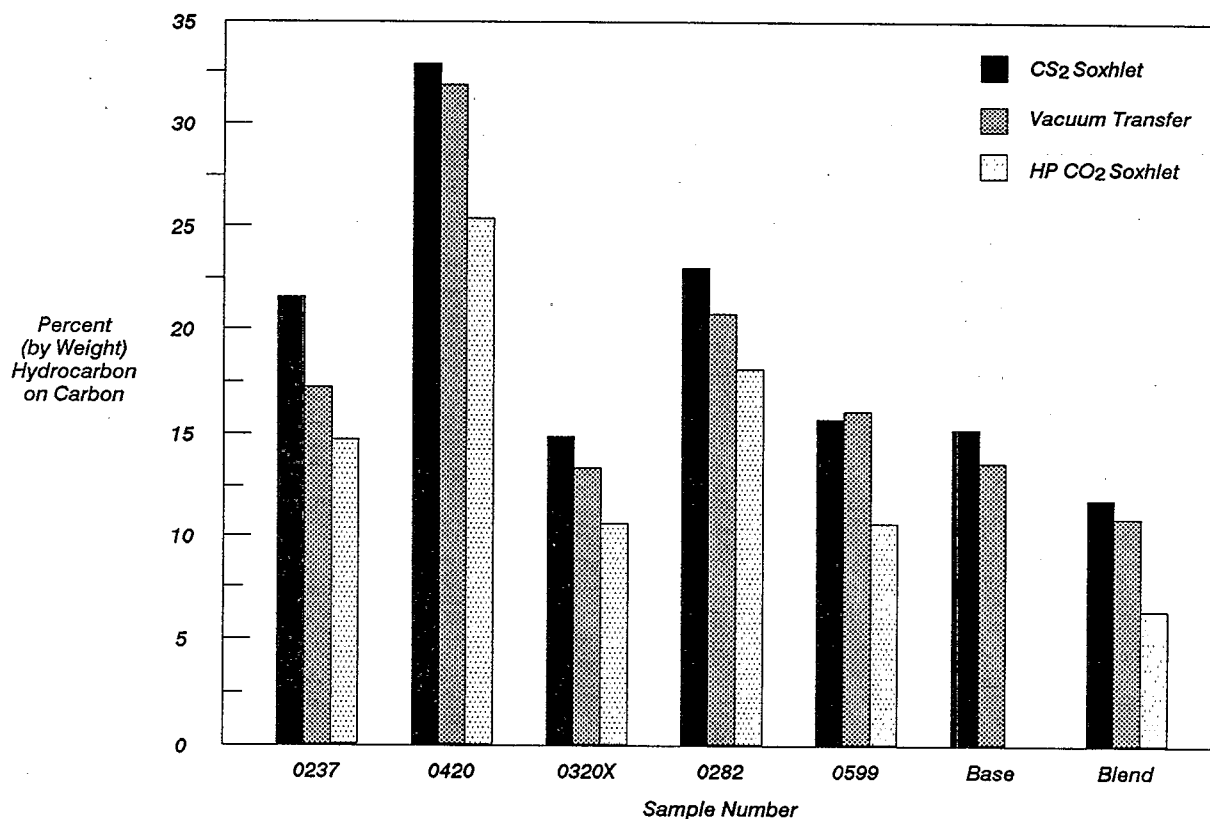


Figure 5. Comparison of charcoal extraction methods - percent (by weight) hydrocarbon on carbon from GC/FID.

Conclusions

The results from the second phase of this study show that, at present, the CS₂ soxhlet extraction method is the most practicable and efficient method for desorbing and analyzing the C₆+ constituents adsorbed on charcoal. This method, however, can only aid in determining the composition of the relatively higher molecular weight compounds on the charcoal, since the more volatile components are lost through the condenser system.

High pressure CO₂ soxhlet extraction is not a practicable method for extracting these charcoal samples because this method does not completely extract the material adsorbed on the charcoal. Moreover, the results showed that the lower molecular weight, more volatile, hydrocarbons were not retained in the extracts.

The modification of the vacuum transfer apparatus did not improve the method sufficiently to be able to recommend this method for extracting charcoal rather than the CS₂ soxhlet extraction method. More of the alkylated aromatic hydrocarbons were measured in the extracts from the modified vacuum method than were measured using the previous apparatus. The quantities of the alkyl aromatics measured using this modified vacuum method were, however, lower than measured by using the CS₂ extraction method. Moreover, lower quantities of the lower molecular weight hydrocarbons were measured in the extracts using this modified apparatus than measured using the previous apparatus.

Recommendations

A mass balance involving the amount of material extracted and the quantity of

hydrocarbons measured in the extracts cannot be attained using the CS₂ soxhlet extraction method. A second extraction of the charcoal, using the vacuum transfer method, must be done in order to determine the quantity of the hydrocarbons less than C₆ adsorbed on the carbon. The vacuum transfer method is time consuming, however, since it requires one day to extract and analyze one sample. Further modification of the apparatus is required to reduce or eliminate vacuum leaks in order to retain the lower molecular weight hydrocarbons. Two other charcoal extraction methods, thermal desorption and High Pressure CO₂ supercritical fluid extraction, should be investigated since these methods are solvent-free, require minimum sample handling, eliminate exposure to toxic CS₂ vapors, and might be more cost effective than soxhlet extraction with CS₂.

David Dropkin is the EPA Project Officer (see below)

The complete report, entitled "Evaluation of Methods Used to Desorb the Constituents Adsorbed on the Charcoal Contained in Automotive Evaporative Canisters - Part I," (Order No. PB 90-188 830/AS; Cost \$17.00, subject to change) and "Evaluation of Methods Used to Desorb the Constituents Adsorbed on the Charcoal Contained in Automotive Evaporative Canisters - Part II," (Order No. PB 90-188 848/AS; Cost \$17.00, subject to change) will be available only from:

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