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The use of the charcoal tube-gas chromatographic method to evaluate workplace air contamination has proliferated greatly in the last 10 years. This report documents early efforts by NIOSH researchers to evaluate several sampling and analytical parameters and their effect on the reliability of the technique. The effects of humidity, sample stability, sample migration and variations in the desorption efficiency are presented. A protocol is suggested for basic testing of the method for new substances.

Performance testing of the NIOSH charcoal tube technique for the determination of air concentrations of organic vapors

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introduction

In 1970 workers at the Bureau of Occupational Safety and Health (BOSH), now the National Institute for Occupational Safety and Health (NIOSH), published a method for the determination of mixtures of organic vapors in industrial atmospheres.[1] Activated charcoal tubes were used for collection of the samples and gas chromatography for analysis. The authors were extending work done by three other groups of researchers.[2–4] Shortly thereafter, the design of the charcoal tube was modified to contain a primary adsorbing section with 100 mg of charcoal and a back-up section with 50 mg.[5] Tubes of this design are still recommended by NIOSH and are available from commercial sources.

Since the work was completed, NIOSH has analyzed in excess of 100,000 samples collected on charcoal tubes. Experience with actual field samples raised questions about certain aspects of the technique. As these questions arose, experiments were devised to answer them. The results provided us a clearer understanding of the strengths and weaknesses of the technique. These experiments led NIOSH to develop continuing, formal research projects on several aspects of sampling and analysis with activated charcoal tubes.[6–8] This paper documents these early experiments which were devised to show the effectiveness of field sampling procedures. Occurrence of breakthrough was studied for six compounds. Variables studied included relative humidity, sampling rate, sampling time and concentration. In addition, the effects on sample stability of time, temperature, light and partial vacuum were investigated. The effects of different charcoals and different sample loadings upon the desorption of the collected substance are discussed.

experimental

A dynamic vapor pressure system was used to generate known concentrations of organic vapors in air for these tests. The apparatus was essentially the same as that described elsewhere.[9] The system consisted of a nitrogen stream saturated, at a precisely controlled temperature, with the vapor under study which was mixed with a metered stream of purified air to dilute the vapor to the test concentration.

Some of the tests were performed at elevated humidity. In order to produce this condition, the dilution air stream was split, and control valves

TABLE I
Charcoals Used in Experiments

Designation	Type	Vendor*
BC-580-26	Petroleum	Barnebey Cheney, Columbus, OH
MSA-0**	Coconut	Mine Safety Appliance Co., Pittsburgh, PA
MSA-1	Coconut	Mine Safety Appliance Co., Pittsburgh, PA
MSA-4	Coconut	Mine Safety Appliance Co., Pittsburgh, PA
MSA-6	Coconut	Mine Safety Appliance Co., Pittsburgh, PA
SKC-104	Petroleum	SKC, Inc., Pittsburgh, PA
SKC-105	Coconut	SKC, Inc., Pittsburgh, PA

*Mention of names of commercial materials does not constitute endorsement by NIOSH

**In this case, "O" is not the manufacturer's lot number but is used by NIOSH to distinguish it from later lots.

added to each side so that a portion of the air could pass over water in a container equipped with a controlled heating mantle. By varying the amount of air passing across the water, the relative humidity was regulated at the desired level. The relative humidity levels were monitored by an electric hygrometer.

Charcoal tube samples were drawn at a nominal flow of one liter per minute from the contaminant concentrations established by this method using vacuum pumps with calibrated critical orifices. The charcoal tubes were the standard 150 mg tubes.[5-8,10] The charcoal for these tubes was obtained from the sources identified in Table I.

Analysis of the charcoal tube samples was performed according to the NIOSH P&CAM No. 127.[10] In accordance with this method, the charcoal tubes were desorbed with 0.5 ml carbon disulfide. An aliquot of the resulting solution was injected into a calibrated gas chromatograph equipped with a flame ionization detector and a 20 ft x 1/8 in stainless steel column packed with 10% FFAP on acid-washed, silanized Chromosorb W. The results were corrected for desorption efficiency because the desorption procedure does not quantitatively remove the sampled compound from the charcoal. Desorption efficiency is defined as that fraction of the particular compound which can be removed from charcoal under the test conditions. The desorption efficiency was determined by spiking the charcoal with a known weight of solvent by microsyringe injection of the liquid and storing overnight in a sealed container to allow for equilibration.

field sampling variables

breakthrough

The sampling time for charcoal tubes is normally limited to that period during which the tube quantitatively collects vapors. With a steady flow of most organic vapors into the bed, the charcoal tube will normally collect 100% of the vapor for a time. Eventually, a small amount of the contaminant will begin to pass through the bed (breakthrough point). After this point, although the bed still adsorbs some contaminant, the amount of "breaking through" increases until the exit concentration equals the inlet concentration. At this point, the charcoal bed is saturated and will adsorb no more of the contaminant at that specific concentration. Figure 1 illustrates the time rate of change of the exit concentration as a function of the sample volume. Between Points A and B sampling is quantitative. After Point C, the exit concentration equals the inlet concentration.

When using the 150-mg, two-section charcoal tubes, it is desirable to confine sampling to the period before breakthrough of the first section

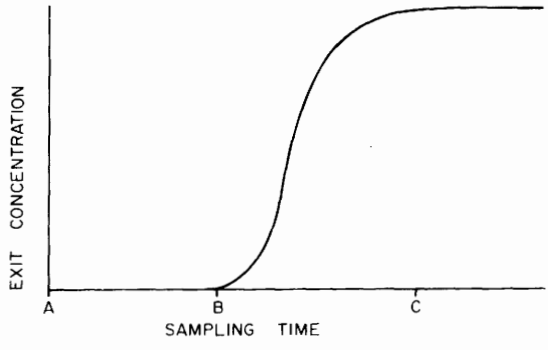

Figure 1 — Breakthrough curve.

TABLE II
One Percent Breakthrough Volumes for Compounds Collected on BC-580-26 Charcoal*

Compound	OSHA Standard (mg/L)	Test Concentration (mg/L)	Total Weight on Tube (mg)	Weight on Backup Section (mg)	Breakthrough Volume (L)
2-butanone	0.59	0.88	7.2	0.07	8.2
Styrene	0.43	0.62	18.0	0.18	29.1
Tetrachloroethylene	0.68	1.04	34.5	0.34	33.2
Toluene	0.75	0.68	15.7	0.16	23.1
1,1,-trichloroethane	1.90	1.96	11.4	0.11	5.8
Trichloroethylene	0.54	1.46	17.4	0.17	11.9

*Flowrate, 1 lpm; relative humidity, 7%.

(point B in Figure I). Besides differing for each compound, the length of this quantitative sampling period is dependent on a number of variables, among which are: contaminant concentration, flow rate through the tube, temperature, pressure, humidity and the type of charcoal adsorbent.

The length of sampling time during which all of the sample is collected on a charcoal tube can be measured in terms of time, volume or weight of contaminant collected. Breakthrough volume is the term denoting the volume of air sampled before breakthrough occurs at a given contaminant concentration. After breakthrough has occured, some of the sample is lost in the exit stream. In order to determine the breakthrough volume for six compounds on charcoal tubes, graduated volumes of a known air concentration of each individual contaminant were drawn through a series of charcoal tubes. The front sampling section of charcoal and the smaller backup section were analyzed separately. A graph of the weight found on the backup section versus the volume sampled produced a curve resembling the portion of Figure I near Point B. In this region there was a linear relationship between the logarithm of the weight found on the backup section and the volume sampled. The equation for the least squares regression line was used to solve for the point at which the weight of the contaminant found on the backup was equal to 1% of the total weight of the contaminant sampled. Up to this in the sampling process, the cumulative collection efficiency of the front section is 99%. Assigning a measurable but negligible amount as the point of breakthrough simplifies the determination and gives a more practical estimate of the capacity of the tube.

Table II lists the interpolated breakthrough volume found for each of the six compounds at the concentration tested using BC-580-26 petroleum charcoal. Since these breakthrough volumes should vary with concentration, the concentrations at which the tests were performed as well as the OSHA Federal Standard[11] are tabulated. The 1% breakthrough volumes for styrene, tetrachlorethylene and toluene are large indicating that ample size samples (20-30 liters) may be taken. These values indicate that sample volumes greater than the 10-liter sample volume recommended by White et al. are possible under optimum sampling conditions. The conspicuously lower values for 2-butanone, 1,1,1-trichloroethane and trichloroethylene (6-12 liters) are primarily due to their higher vapor pressures. This is expected since the phenomenon of adsorption is said to resemble condensation.[12]

Sampling will be quantitative for any volume of contaminated air less than the breakthrough volume for the contaminant. If sampling is continued beyond this point, some of the sample will be lost to the back section. If this occurs only to a limited extent, then the weight found on the backup section can be added to that found on the front to determine the weight of the total sample. A useful rule of thumb is that for a reliable sample, no more than 20% of the total contaminant weight on the 150 mg tube should be on the backup section. It is desirable, however, to limit sample adsorption to the front section and use the back section as a check on the breakthrough of the front section.

The early breakthrough (low breakthrough volume) of the 2-butanone and 1,1,1-trichloroethane can be avoided even if it is impossible to take short samples. One solution is to sample at

TABLE III
Effect of Humidity on Sampling for Toluene

Relative Humidity (%)	n	Weight on Front Section (mg)	Weight on Back Section (mg)	Total Weight (mg)	Precision (%RSD)
7	10	7.2	—	7.2	1
52	8*	7.1	—	7.1	1
94 dry	5	6.8	0.03	7.1	1
wet	5	4.4	0.6	5.0	36

*-Two others discarded by Q test[14]
n-number of results
RSD-relative standard deviation

lower flow rates. A 5-liter volume can be collected in 10, 50 or 100 minutes by using the appropriate flow rate. Lower flow rates may have the added advantage of increasing the breakthrough volume since the vapors will have a longer time to equilibrate over the whole surface of the charcoal. Moreover, longer period sampling using low flow rates is an economical sampling strategy since fewer samples are needed to determine 8-hour time-weighted average concentrations.

humidity

Some work[2,13] had indicated that the collection efficiency on activated charcoal is not affected by relative humidity because charcoal is a nonpolar material. Experience with field samples, however, suggested that this is not entirely For example, one set of samples submitted to this laboratory had been collected from a distillery stack, and condensate could be seen on the charcoal. Analysis of these samples showed a negligible amount of organic vapors although concentrations would presumably be very high. Further work indicated that the water condensation was the problem. This experience caused concern that even when condensation was not visible, water vapor could cause low results.

In order to determine whether sampling a high-humidity atmosphere would affect adsorption or desorption, charcoal tube samples of a test atmosphere containing 0.75 mg/l toluene and having relative humidities of 7%, 52%, and 94% were analyzed. Ten samples at each relative humidity were collected. Before analysis, it was noted that the charcoal in five tubes was wet. Each of these "wet" samples had drawn from the 94% RH atmosphere through the sampling port at the bottom of the sampling chamber. Condensed water had inadvertantly dropped into these tubes. The other five samples in the high humidity group had been drawn simultaneously through a port in a different part of the sampling chamber. These samples appeared normal. The thirty tubes were analyzed in random order. The back sections were analyzed separately to determine if breakthrough of toluene had occurred. The results are listed in Table III. No breakthrough occurred in the low and intermediate humidity samples. The high humidity group (94% RH) showed breakthrough of the first section in all cases. The "wet" samples in this group (described above) gave very erratic and generally low results. It appears that a substantial amount of the toluene was not collected on the charcoal which contained condensed water vapor. The "dry" samples in this same group showed breakthrough of the first but not the backup section. We can conclude that humidity as high as 94% does affect the *breakthrough volume* of toluene. A comparison of the toluene data from Table II with this data indicates the severity of this effect. The breakthrough volume in Table II determined at 7% RH and at roughly the same concentration (0.68 mg/l vs 0.75 mg/l) was 23 liters. In Table III breakthrough has occurred in the 10-liter sample collected at 94% RH. This is evident from the significant amount of toluene found on the backup section. When the relative humidity was increased from seven to ninety-four percent, a reduction of greater than 50% in the breakthrough capacity was observed. [Note: *The two experiments (Table II, Table III) were performed on different charcoals. This could invalidate comparison of the results. However, more recent experiments performed on a single lot of charcoal have given similar results.*[6]] It had been assumed that charcoal

would have more affinity for toluene than water, causing displacement of absorbed water by toluene. If this is true, this displacement occurs too slowly to be completed before the toluene breaks through the bed. These studies indicate that toluene breakthrough in high humidity situations occurs significantly earlier than in dry air. However, reliable samples can be collected by limiting sampling volumes where high humidity exists.

sample stability variables

Charcoal tube samples are generally collected at various workplaces and returned to a central laboratory for analysis. The interval between sampling and analysis introduces several variables which may affect the stability of that sample. Some compounds may be affected by one or more of these variables. The variables reported below included time, temperature, light and atmospheric pressure.

stability with time

To evaluate the stability of charcoal tube samples held for long periods of time prior to analysis, replicate samples of a synthetic atmosphere containing the contaminant of interest collected, divided into groups, and stored at room temperature. These groups were analyzed at selected time intervals after collection. Five compounds were studied in this manner: dichloromethane, 2-butanone, trichloroethylene, toluene and styrene. The 2-butanone and trichlorethylene experiments were performed with tubes containing BC-580-26 petroleum charcoal; the others contained MSA-1 activated coconut charcoal.

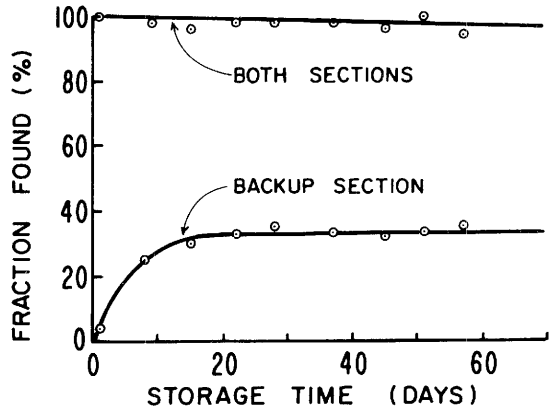

Figure 2 — Stability of dichloromethane-on-charcoal samples. Sample size 5.2 mg. Activated coconut charcoal MSA-1.

In one storage study, 31 dichloromethane samples were generated by sampling 5 liters at an approximate concentration of 1 mg/1. The results shown in Table IV indicate that no significant loss from the charcoal tube occurred over the entire 57 day period. As storage time continued, less dichloromethane was found on the front section and more was found on the backup. On the twenty-second day 33% of the dichloromethane present on the tube was found in the backup section. This distribution remained constant throughout the rest of the study The data is graphically represented in Figure 2. It appears that the volatile dichloromethane migrated during storage until an even distribution over the charcoal was

TABLE IV
Stability of Dichloromethane on Charcoal Tubes

Storage Time (Days)	Total Weight Found (mg)	Weight Found on Backup* (mg)	Percent on Backup (% of 5.2 mg)
		Room Temperature Samples (25°C)	
1	5.2	0.2	4
8	5.1	1.3	25
15	5.0	1.5	29
22	5.1	1.7	33
28	5.1	1.8	35
37	5.1	1.7	33
45	5.0	1.6	31
51	5.2	1.7	33
57	4.9	1.7	33
		Refrigerated Samples (4°C)	
28	5.1	1.4	27
57	5.0	1.5	29

*Average of Three Samples Each

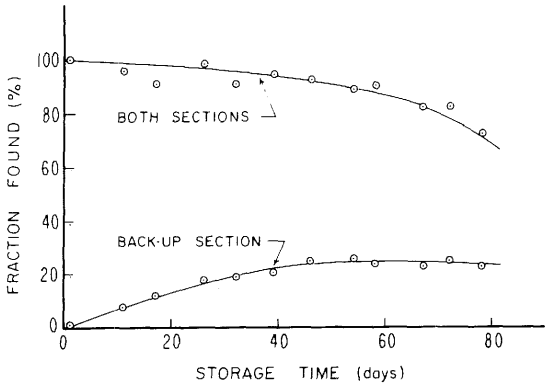

Figure 3 — Stability of 2-butanone-on-charcoal samples. Sample size 7.8 mg. Activated petroleum charcoal 580-26.

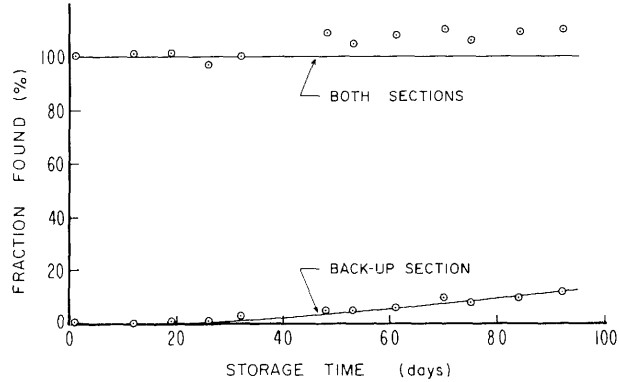

Figure 4 — Stability of trichloroethylene-on-charcoal samples. Sample size 9.5 mg. Activated petroleum charcoal 580.26.

achieved (the backup holds 33% of the total weight of charcoal). Equilibrium is reached at that point. To test the hypothesis that the rate of migration is due to vapor pressure, samples were refrigerated at 4° C and analyzed after 28 and 57 days of storage. The backup sections held an average of 27% and 29% respectively. Refrigeration slowed the migration by lowering the vapor pressure. One should be aware that a large amount of compound (~33%) found on the backup section can indicate either the occurrence of breakthrough during sampling or sample equilibration in the charcoal tube after sampling and prior to analysis.

In another storage study, 46 samples were generated by sampling 10 liters of a 0.8 mg/l concentration of 2-butanone in air. In contrast to the dichloromethane case, there was an apparent loss from the tube almost immediately as indicated by the decrease in the total weight found on both sections (Figure 3). By the 78th day, 24% loss had occurred. The loss could be due to migration out of the tube, or to decomposition of 2-butanone. Comparing the amount found on the backup section of the tubes in Figure 2 and 3, the process of migration appears slower with 2-butanone than with dichloromethane. The butanone does not reach a steady state until after 40 days; whereas dichloromethane, a more volatile compound, took about 20 days to equilibrate throughout the tube. Since 2-butanone appears to migrate less readily than dichloromethane, it does not seem likely that migration out of tube could be responsible for the loss seen here. In the analyses of the 2-butanone samples stored for longer times, the presence of several extraneous GC peaks was noted. The compounds responsible for these peaks were not identified, but presence of these peaks points to decomposition of 2-butanone on charcoal.

In a stability study for trichloroethylene, 48 samples (10 liters) were collected from a concentration of about 9 mg/l. No loss of trichloroethylene occurred during the 92-day period (Figure 4). In the latter half of this study greater than 100% recoveries were observed. This high recovery was considered to be an unexplained experimental anomaly. Migration occurred, but was low; only 12.7% of the trichloroethylene was found on the backup after 92 days of storage. An earlier 3-month experiment also had indicated that migration was slow. In that experiment an average of 15% of the trichloroethylene had migrated to the backup section at the end of the time period. Two other stability tests of toluene and styrene for more than five weeks showed no significant loss of the analyte from the charcoal.

With the exception of 2-butanone, all the compounds studied were stable on charcoal tubes for periods of time greater than two weeks. The experience with 2-butanone, however, demonstrates the importance of performing such a test if samples are to be stored for a time before analysis. Correction of results from the stability curve is not recommended unless the deterioration is reproducible. If this is not the case, sam-

TABLE V
Exposure to Heat Cycles
Toluene and Styrene

Storage Conditions	Amount Found on Tube (mg)* Toluene	Styrene
Control - 25°C	6.82	7.56
8 hr @ 48°C and then storage @ 25°C	6.87	7.15
Three 8 hr periods @ 48°C alternated with 16-hr periods @ 25°C	6.89	7.60
Seven 8 hr periods @ 48°C alternated with 16 hr periods @ 25°C	6.88	7.46
Three 8 hr periods @ 48°C alternated with 16 hr periods @ -13°C	6.94	—
Two 8 hr periods @ -13°C alternated with 16 hr periods @ 25°C	—	7.50

*Average of Four Samples per Group

ples which could deteriorate significantly should be analyzed soon after collection. Refrigeration should slow sample decomposition. It is now routine NIOSH procedure to store charcoal tube samples under refrigeration (4°C) if the analyses cannot be performed immediately.

Migration, which was observed with dichloromethane, 2-butanone and trichloroethylene, but not toluene or styrene, appears to be related to contaminant volatility. The compounds in these experiments were discussed in order of increasing boiling point; in each successive case the migration was slower. Migration does not affect accuracy; however, it is undesirable because it mimics breakthrough. If analysis of a sample shows the presence of the contaminant on the back section (> 25%) the results do not distinguish between breakthrough of the front section, and migration. This leaves the analyst undecided as to whether some sample was lost during sample collection or whether there was merely redistribution of the analyte between the two sorbent solutions. Migration can be slowed by sample refrigeration as shown by the dichloromethane data. Lower temperatures would be even more effective for highly volatile compounds. Based upon this assumption, vinyl chloride samples are stored at -20° C by NIOSH. A more detailed description of the vinyl chloride work is provided elsewhere.[7] Another solution to severe migration is sample collection using two charcoal tubes in a series. In this case the second tube acts as a backup section which is capped and stored separately from the first. In analysis each tube is treated as an individual section by pooling the two parts of each tube for analysis. With this dual tube technique the contaminant could only appear on the second tube by breakthrough, thus indicating an unreliable sample. Dual tubes are now used routinely for vinyl chloride sampling.[10]

stability with heat

It had been suggested that exposure to heat cyles could cause apparent contaminant loss due to vaporization and redeposition of the contaminant into deeper pores. This kind of exposure could occur to samples left on the dashboard of a closed car for several days.To determine the effect of this type of exposure for toluene and styrene, twenty replicate charcoal tube samples for each compound were stored at 48° C for varying periods of time. The exposure conditions and results are described in Table V. The differences between the control and the exposed groups were not significant. There are no discernible trends with increasing numbers of heat cycles. From this data we can conclude that heat cycles do not affect the amount of these contaminants which can be removed from charcoal. However, it is probable that long periods at high temperatures could enhance migration or decomposition of some compounds.

TABLE VI
Effect of Partial Vacuum on Toluene
Charcoal Tube Samples (MSA-1)

Conditions	Weight Toluene Found* (mg)
Air shipped, round trip Cincinnati to Salt Lake City, Utah	7.1 ± 0.2
Stored, 4 hours at 450 mm Hg pressure	7.1 ± 0.1
Control, atmospheric pressure	7.2 ± 0.2

*10 Samples per Group with 95% Confidence Interval

stability with light

Concern has been expressed about the possibility of styrene polymerization on charcoal tubes. The analytical technique can detect only the monomer; so polymerization after sampling would give low results. Styrene is known to polymerize on exposure to heat or light.,[15-16] However, heat was shown to have little effect in the previous experiment (Table V). To study the effect of light, sixteen replicate styrene-on-charcoal samples were exposed in groups of four to light. One group was exposed to sunlight on the dashboard of an automobile during a 19-day trip to Florida. Another set was stored for the same period in the glove compartment of this auto. A third group was exposed, with periodic turning, to a sunlamp for 24 hours. The final group was protected from light and was used as a control group. The results in milligrams were 3.56, 3.54, 3.52 and 3.56 respectively, showing that no styrene was lost under these conditions. In practice, styrene samples are nearly always collected where polymerization catalysts are used. Whether a charcoal tube containing styrene and a catalyst (if trapped) would be as unaffected by heat, light and time as these pure samples have been is not known.

stability under partial vacuum

It is often necessary to ship charcoal tube samples by air from the sampling site to the analytical laboratory. Because some airplane baggage compartments are unpressurized, the question of whether possible sample loss occurs at low pressures becomes pertinent. Analysis of thirty replicate toluene samples exposed to simulated and actual air transport showed no significant difference from the control group. See Table VI.

desorption of the analyte

Prior to receiving a sample in the laboratory, the major variables involve reliable sampling and the stability of the sample. The prime analytical variable in the use of solid sorbents such as activated carbon is the ability to remove a known portion of the analyte from the solid sorbent.

This fraction has been called the desorption efficiency.[1] The average desorption efficiency is applied to the results of sample analyses to correct for the amount of the contaminant which was not removed from the charcoal. The desorption efficiency is not a constant for all types of solid sorbents, or for that matter for all activated carbons. The variation of this important analytical parameter as a function of different charcoals and the loading of the analyte on the charcoal directly affects the accuracy of the method.

variation among lots of charcoal

In order to determine the effect on the magnitude of the desorption efficiency for different lots of charcoal, desorption experiments were performed. Desorption samples were prepared in the manner of the NIOSH charcoal tube method.[10] Results of the analysis of these samples were compared with analytical standards and the percentage of the contaminant removed in the desorption process was calculated.

Desorption efficiency was determined for a number of compounds on different batches of activated charcoal. These efficiencies are expressed in percent in Table III.[6] The data for trichloroethylene,styrene and tolune show no significant variation from one batch of charcoal to another. Some variation is apparent with n-butanol, 2-ethoxyethyl acetate and 2-butanone. The difference between the efficiency of removal from MSA-6 and SKC-105 is the most pronounced; the efficiencies differ by as much as 20 percentage points. These large variations in desorption efficiency between batches of charcoal show the importance of determining desorption ef-

TABLE VII
Desorption from Various Lots of Charcoal

Compound loading (μl pure compound)		Charcoal BC 580-26*	MSA 0	1	4	6	SKC 104*	105
Trichloroethylene	4.0	100	101	100	101	98	101	
Styrene	5.0	85			87	88	89	87
Toluene	0.44					100		
	2.2					100	98	98
	4.5					100		
	9.0			99				
	10.0				99			
	13.05	97						
	22.0					100		
n-Butanol	0.9			91				
	3.8				63	59	47	
2-Ethoxyethylacetate	1.4					90	88	72
2-Butanone	1.8					90	89	70
	7.0	97	89	93	93	90		84

*Petroleum Based Carbon; All Others Coconut Shell Based.

ficiencies for each compound on the specific batch of charcoal used in sampling. Since these values may vary with slight changes in desorption technique, each lab should use values determined in-house.

variation with contaminant loadings

The efficiency of desorption of 2-butanone from SKC-105 charcoal shows an apparent dependence on the loading (Table VII). Loading is the amount of contaminant collected on the charcoal during sampling or that amount applied to determine the desorption efficiency. At a loading of 1.8μl a desorption efficiency of 70% is obtained, while at 7 μl the efficiency is 84%.

Another experiment was performed to test the effect of different methods of desorption tube preparation. The results, for these experiments using cyclohexanone, are listed in Table VIII. The first technique (I) is the usual NIOSH method as described above. The second technique (II) involved injection of the liquid cyclohexanone into a glass wool plug situated below a 100 mg charcoal bed in a vertical tube. The liquid vaporized and was adsorbed onto the charcoal. This technique was suggested by Lowell White as one way to insure that the contaminant would be adsorbed by the charcoal from the vapor state as occurs in sampling.[17] The samples thus prepared were analyzed in the same manner as described for the first method. In the third technique (III), 0.5 ml of CS_2 was spiked directly with the appropriate amount of cyclohexanone. To this solution, 100 mg of activated charcoal was added, and the analyses performed after at least thirty minutes. The data presented in Table VIII show that there was no significant difference in the results from the first two techniques. The third technique is not equivalent to the other two. The point of equilibrium (i.e., the fraction of cyclohexanone left on the charcoal after the desorption period) is not the same as when the compound is first air adsorbed and then removed by carbon disulfide. The fact that charcoal does absorb some cyclohexanone from the carbon disulfide solution is significant. Compounds of this type should not be used as internal standards in the analysis of charcoal tube samples. When an internal standard is used with this technique, the CS_2 is spiked with a known weight of a compound (internal standard) similar to the analyte. The charcoal is desorbed in the normal way. All results are corrected to a constant weight of internal standard. This corrects for any losses, evaporation or injection error, and it increases precision. However, if charcoal absorbes some internal standard from the CS_2,

TABLE VIII
Percent Desorption Efficiency of Cyclohexanone Using Three Techniques*

Technique	Desorption Efficiency (%) 0.2 mg	1 mg	10 mg
I Direct injection of liquid onto charcoal	42	64	91
II Injection of liquid on glass wool below charcoal	42	64	92
III Addition of charcoal to solution	70	76	96

*100 mg MSA-6 charcoal, 0.5 ml carbon disulfide

then the weight of the internal standard in solution is no longer known, and normalizing the results to the internal standard would give erroneous results. The gas chromatographic method gives good precision with the use of external standards. However, if internal standards are desired, care should be taken to select a compound which charcoal will not remove from solution.

The data in Table VIII (I and II) show the dependence of desorption efficiency on loading of cyclohexanone on the charcoal tube. The desorption efficiency decreases as the loading decreases. This is not due solely to irreversible assorption of a fixed weight on the charcoal, because the weight held also decreases with loading. It seems that a portion was irreversibly held on the charcoal and at the same time the reversibly held cyclohexanone was equilibrated between the solution and the charcoal surface. Regardless of the cause, this data demonstrates the necessity of determining desorption efficiencies at the loading levels of the samples, or determining the desorption efficiencies over a range of levels and plotting a curve to be used for correcting the analytical results.

approaching new compounds

A large number of volatile organic compounds may be sampled in workplace air using the charcoal tube. Many organics have never been tested using the charcoal tube method. However, it is possible to establish the validity of the method for a new compound with a minimum of effort. When charcoal tube samples contain a new compound, separate analysis of front and back sections is usually an effective test for breakthrough. If little or none of the contaminant is found on the backup section, then the breakthrough volume has not been exceeded. After the amounts have been determined, desorption efficiency experiments can be performed at the same loading as found on the samples. By holding some desorption efficiency tubes for an extended period, a storage study can be performed. Highly volatile compounds should be tried using the dual tube sampling technique as is used for vinyl chloride.[7,10] This short procedure can give the essential information to insure that the results are accurate.

other research undertaken by NIOSH

Some of the work presented above paved the way for more intensive research. The advantages of low flow rates led to the development of a personal sampling pump with a flow range of 50-200 ml/min. This device was developed by the Anatole J. Sipin Company, under NIOSH contract HSM-99-71-31. These and similar pumps are now commercially available from several suppliers.

The observed effect of humidity on breakthrough prompted a more complete study of the effects of temperature, humidity and concentration on the breakthrough of toluene.[6] This work may be expanded to include other compounds. NIOSH development work on methods for carbon disulfide includes humidity experiments.[8]

The variations between batches of charcoal indicated the need for a charcoal tube certification program. This proposed program will determine both desorption and breakthrough performance criteria for charcoal tubes and will certify tubes meeting these criteria.

The final evaluation step of any NIOSH method involves collaborative testing. The NIOSH charcoal tube-gas chromatographic method has been collaboratively tested in 15 laboratories.[18] The results of this evaluation indicate that it is versatile and precise. The overall method precision is 10.5% relative standard deviation.

summary and conclusions

The results of the tests presented above indicate that NIOSH charcoal tube methods have a wide applicability for many organic airborne contaminants. It is possible to circumvent most of the factors which have a negative effect on the technique by altering the sampling technique. We will summarize the various facets tested here.

1. Charcoal has a large capacity for many organic vapors. For very volatile compounds, for which breakthrough volume is often low, GC sensitivity is such that small samples are sufficient. Sampling rates can be lowered to

extend sampling times for the calculation of time-weighted average concentrations. Personal sampling pumps are commercially available to sample at flow rates as low as 1.0 ml/min.

2. Humidity has a pronounced effect on the breakthrough capacity of toluene, and possibly other compounds sampled on charcoal. However, smaller sample volumes and lower flow rates can often be used to minimize this difficulty.
3. The stability of five of the six compounds tested was excellent. The variables included time, heat, light and partial vacuum. The only noticeable exception was the decomposition noticeable exception was the decomposition of 2-butanone with time. Early analysis or sample decomposition; however, refrigeration may retard the process.
4. Migration of the sample to the backup section of the charcoal tube that occurred during storage of the more volatile samples can mimic breakthrough. The process can be slowed by refrigeration of the samples. The problem can be eliminated altogether by the use of two tubes in tandem for sampling.
5. Desorption efficiency is dependent on charcoal lot and loading of contaminant. Accurate results can be obtained only by analysis of desorption samples.

of desorption samples under the same conditions as charcoal tube air samples. Desorption efficiencies should always be determined and applied. Neglecting this portion of the technique can be a serious source of error.

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