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The National Institute for Occupational Safety and Health has undertaken a program to provide reliable sampling and analytical methods for a number of industrial hygiene uses. Recommendation of methods to the Department of Labor for compliance testing and inclusion of methods in criteria for Recommended Standards for Occupational Exposures are two prime areas of utilization. This paper presents the results of our initial efforts in collaborative testing. The method is a charcoal tube sampling procedure and a gas chromatographic analytical technique. Samples of seven single component solvents which included benzene, carbon tetrachloride, chloroform, dioxane, ethylene dichloride, trichloroethylene, and xylene along with two solvent mixtures which consisted of a benzene-xylene combination and an ethylene dichloride-trichloroethylene combination were tested in two phases by 15 participating laboratories. The data analysis indicates the overall error associated with the method and identifies sources of error within each segment of the method.

Collaborative testing of a gas chromatographic charcoal tube method for seven organic solvents

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introduction

Under the Occupational Safety and Health Act of 1970, the National Institute for Occupational Safety and Health is HEW's primary program directly dealing with safety and health in the workplace. NIOSH's responsibilities include the development of criteria for standards to protect the working population from the multitude of health and safety hazards to which it is exposed. The Occupational Safety and Health Administration of the Department of Labor is the enforcement agency while NIOSH provides the technical support. The presence and the extent of hazardous conditions are determined by various measurements which eventually yield numerical values. The sampling and analytical methods being used to obtain these values become very significant both to the enforcement agency and perhaps even more so to the industry upon which the standards are imposed. This compliance activity must be capable of withstanding legal challenge and the industry must be assured that true existing conditions are being represented. The sampling and analytical methods used must therefore be backed by an adequate program to document proper control and application of all factors which affect final results. The significance of technical data and possible resulting actions which it may produce strongly justify a comprehensive program which has as its objectives development of reliable new methodologies, and widespread use of these methodologies. Many similar programs are

being conducted by industrial groups, research laboratories and professional societies. Few of these efforts have related specifically to industrial hygiene. Only recently has the Intersociety Committee and the American Society for Tesing and Materials become involved in industrial hygiene measurements. The American Conference of Governmental Industrial Hygienists developed a referee type collaborative testing program which dates back to about 1949.[1] The importance of securing uniform and reliable analytical methods for industrial hygiene use was recognized by that organization at a very early date. Unfortunately, this effort has not been continuous nor has it developed into a contemporary program.

This collaborative test program was conducted by Scott Research Laboratories, Incorporated of Plumsteadville, Pennsylvania, under Contract No. HSM 99-72-98 (June 1972 - September 1973). To eliminate as much bias as possible, laboratories selected for this test represented a cross section of organizations such as government laboratories, commercial service laboratories and university laboratories. In obtaining this cross section, it was desirable to have analysts who were routinely using the procedure and therefore required no training prior to the collaborative test.

The primary objective of this program was to determine whether the use of activated charcoal tubes should be presented by NIOSH as a recommended method for sampling and analysis of organic vapors. This method of sampling and analysis was suggested by other researchers.[2] A more exhaustive study of the method for sampling and analysis of organic vapors using the charcoal tube technique was undertaken in what is now the NIOSH Cincinnati Laboratory[3] Following the development of the method and because of its convenience and general application to organic solvents, it has been widely and routinely used by NIOSH personnel and by many other industrial hygienists in the field.

design of the test program

Fifteen laboratories were selected to participate in the test. All of the laboratories involved were compensated for their efforts, with the exception of NIOSH laboratories. Some nine thousand tubes prepared from a single batch of charcoal were acquired from a commercial source. Random samples of the tubes were tested by Scott and by the NIOSH engineering laboratory. Specifications tested were: Pressure drop at a flow rate of one liter per minute and the weight (150 mg) of charcoal in the tubes.

One out of 36 tubes failed the pressure drop specification ($\leqslant$1.0 mm Hg at 1.0 lpm) and about 4 out of 38 tested deviated from the 150 mg in front and back sections by more than 10%. The number and degree of variations were acceptable and it was determined that this lot would not have adverse effect upon the test results.

A one-day seminar was held for the analysts from each of the collaborating laboratories. The seminar was conducted in the NIOSH facilities by Scott with NIOSH experts present to answer questions and demonstrate techniques. The purpose of the seminar was to assure that all participating analysts fully understood the method and would carry it out in a uniiform manner. It was stressed very strongly that the object was to test the specific method presented and not to evaluate improvements or modifications.

The overall test program was made up of two phases. Phase 1 involved the analyses of standard samples on charcoal prepared by the contractor. Phase II involved the collection of samples by each collaborator from a common source and analyses of these samples in their own laboratories. Seven solvents were selected as the test substances. These seven were selected based upon data generated in NIOSH's laboratories regarding their behavior on charcoal. Table I shows the solvents and levels. Each of the mixtures were used at one level in both phases.

phase I experimental design

Each of the 15 collaborators analyzed 144 samples each containing one or two of seven organics over a 10-day period. The samples were composed of four repeated samples of each of 36 compound/concentration combination. The plan was to obtain data for the intralaboratory error, precision, day-to-day error and accuracy at each level. The design was set to limit the analysis to two substances on a given day. In the interest of efficiency and time it was decided to

TABLE I
Test Substances and Concentration Levels

Solvent(s)	1 5% OSHA[8] Standard	2 60% OSHA Standard	3 100% OSHA Standard	4 160% OSHA Standard	5 Excursion Limit
Benzene	0.54	6.25	10.3	19.3	48.7
Carbon Tetrachloride	0.44	6.78	11.0	23.0	245.
Chloroform	2.44	31.9	50.6	98.6	--
Dioxane	6.25	59.6	106.	162.	192.
Ethylene Dichloride	2.41	34.2	53.1	94.4	209.
Trichloro-ethylene	3.37	65.0	106.	185.	273.
m-Xylene	4.75	57.9	111.	153.	193.
Mixtures					
Benzene/m-Xylene	--	--	10.9/103	--	--
Ethylene Dichloride/Tri-chloroethylene	--	--	51.1/104	--	--

analyse the back-up section from only one of each set of four repeated samples. The four repeated samples of each substance/concentration were divided into two pairs. Both members of a pair were to be done on the same day. Each of the 15 laboratories were assigned a randomized schedule of analysis days and presented with a list of samples to be analyzed on a given day.

The apparatus used for generation of Phase I samples is shown in Figure 1. The mixtures were prepared with purified air in high pressure cylinders. The accuracy of the mixture's concentrations was determined to be ±2%. The analyses were done by gas chromatography against primary standards prepared by Scott following proprietary procedures which are utilized in producing close-tolerance gas mixtures for sale to government and industry. The cylinders were attached to the generation system and the mixtures passed through a pressure regulator, the charcoal tube, flowmeter and wet test meter. Four samples were collected simultaneously in the four separate sampling legs. The wet test meters were calibrated both before and after samples were collected. The corrected wet test meter data were used to calculate the volume of mixture passed through the charcoal tubes. A flow rate of approximately one liter per minute was used.

The concentration of gas flowing through the system was monitored continuously with a total hydrocarbon analyzer and periodically with a gas chromatograph. Analyses were made alternately directly from the cylinder and from the flow system until the two yielded identical readings. This indicated that the system was equilibrated and collection on the tubes could commence. During the collection period, the instrument readings were used to verify that the concentration did not change. Figure 2 shows a typical set of data recorded during the collection

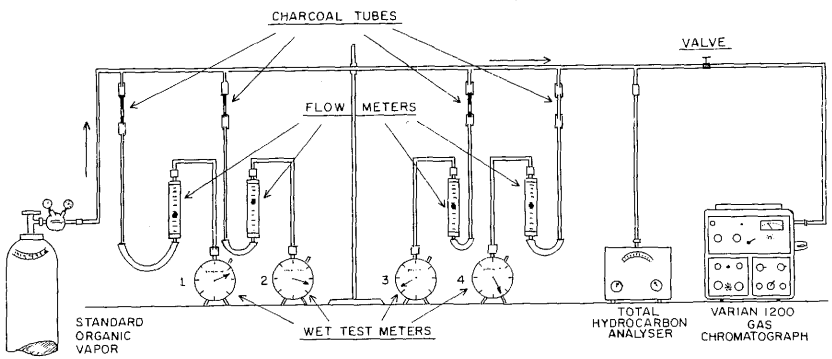

Figure 1 — Vapor collection manifold.

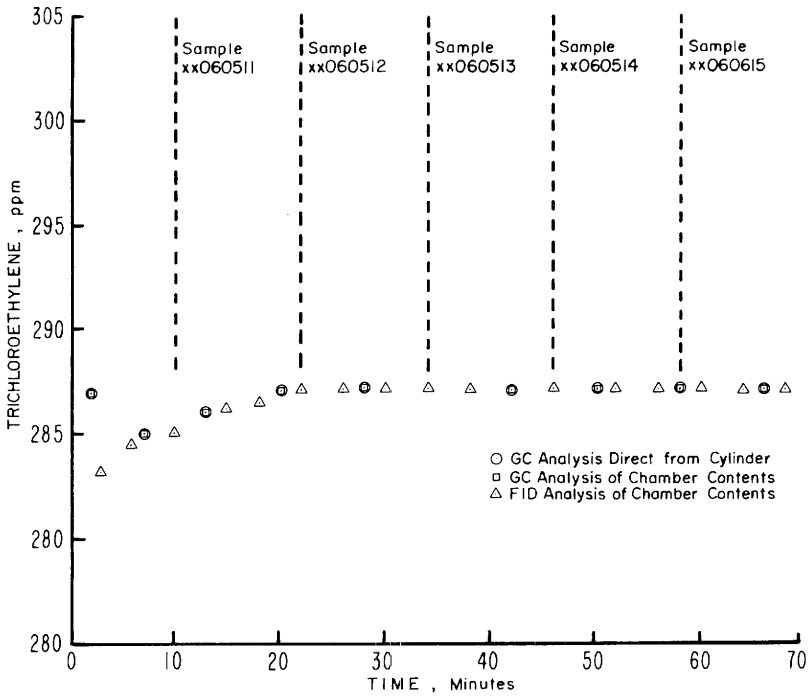

Figure 2 — Tricholroethylene monitoring during phase II sample collection.

of trichloroethylene samples. Eighteen samples of each test mixture were then collected on each wet test meter. This provided a set of samples for each of the 15 laboratories and 3 spare sets. The volume sampled in the four legs ranged from 9 to 11 liters but were constant for each leg. This manner of collection ensured that identical sets of samples would be submitted to each laboratory. The introduction of deliberate variations within each set of four repeated samples was made to eliminate the temptation on the part of the collaborators of revising analytical data to reduce variations between similar samples.

Each tube was capped and labeled with an identification number. A set of 180 charcoal tube samples, 70 blank tubes for desorption determinations and pure samples of each solvent (under separate cover) were shipped to each collaborating laboratory. The analyses were performed and the results reported to Scott on prepared data sheets.

data analysis of analytical results from phase I

The collaborative study was designed around well established statistical techniques for collaborative tests.[4] Prior to the actual data analysis, the data was subjected to tests for outliers. This topic is dealt with in greater depth in another section of this paper. Estimates of the precision were obtained by analyzing the differences between repeat determinations made on the same day. The interlaboratory error which is the same for all analyses made the same day drops out upon taking this difference and thus these different quantities can be used to analyze the precision. Hence,

$$S_r^2 = \frac{\Sigma (Di-\overline{D})^2}{2 (n-1)}$$

where S_r^2 = variance component of the precision

D = difference quantity of repeat determinations in the i^{th} laboratory

$\overline{D}$ = average difference

n = number of laboratories

The standard deviations of the data were calculated by using the sum of the determinations rather than the individual data in order that S_d^2 could be conveniently used in the F ratio for determining the presence of interlaboratory error. Thus,

$$S_d^2 = \frac{\Sigma (Ti - \overline{T})^2}{2(n-1)}$$

TABLE II
Expected Mean Squares for Pooled Estimate

Analysis	Precision	Systematic Error
unaveraged data (repeated)	S_r^2	$S^2day + S_b^2$
averaged data (repeated)	$S_r^2/2 + S^2day$	S_b^2

where S_r^2 - precision
S_b^2 - between lab error
S_{day}^2 - day-to-day error

where

S_d^2 = variance component of the total error in the data
Ti = sum of the repeat determinations in the laboratory on a given day
$\overline{T}$ = average of the sums
n = number of laboratories

The relationship between the variance components for the total error (S_d^2), interlaboratory errors (S_s^2) and precision errors (S_r^2) is $S_d^2 = 2S_s^2 + S_r^2$.

Table II, summarizes the relationship between the different estimates of variance components for results obtained from the unaveraged data (values were not averaged over the two days) as well as results obtained by averaging the data (four values were averaged together). The chief difference between these two methods is that the day-to-day effects have been eliminated by averaging the data.

It was desirable to be able to pool the variances from all the different levels: however, this ability is dependent upon homogeniety of the variances at the different levels. Pooling of the variances would allow more general statements to be made about the data, otherwise we would be limited to speaking of different variance components of each level for each substance.

In order to test for homogeniety of variance, independence must be established between the precision estimate, S_r^2, and the averge amount found. It was determined that a logarithmic transformation would do this. This means that the analysis was performed on the logarithms of the data rather than the actual data itself. This transformation is used quite commonly with analytical data of this type.

The test for homogeneity was then performed. None of the compounds exhibited homogeniety in the precision variance. However, upon excluding level 1 from this test we find homogeniety exists for the higher levels of all compounds, except for carbon tetrachloride and

TABLE III
Summary of Phase I Analysis
(Percent Relative Error Contribution of Variance Component)

SINGLE COMPONENTS

	Excluding Level 1				Level 1			
	Precision	Between Labs	Day-to -Day	Total	Precision	Between Labs.	Day-to -Day	Total
Benzene	6.29	5.81	6.08	10.50	36.38	17.48	26.43	49.84
Carbon Tetrachloride	9.71	8.36	5.77	14.05	32.70	833.42	51.47	1047.26
Chloroform	5.77	2.44	8.66	10.69	13.06	7.01	22.26	26.96
Dioxane	3.89	5.82	3.86	8.00	14.28	987.39	12.29	1005.09
Ethylene Dichloride	5.67	4.48	3.46	8.01	5.38	4.93	6.39	9.71
Trichloroethylene	6.16	1.46	4.93	8.02	261.65	*	340.46	739.98
Xylene	4.77	3.71	3.83	7.15	8.64	24.26	8.68	27.36

MIXTURES

	Precision	Between Labs	Day-to -Day	Total
Benzene	3.25	2.18	4.01	5.60
Xylene	2.96	5.95	0.77	6.69
Ethylene Dichloride	5.97	5.06	6.53	10.21
Trichloroethylene	4.27	4.33	9.88	11.62

*Negative pooled estimate

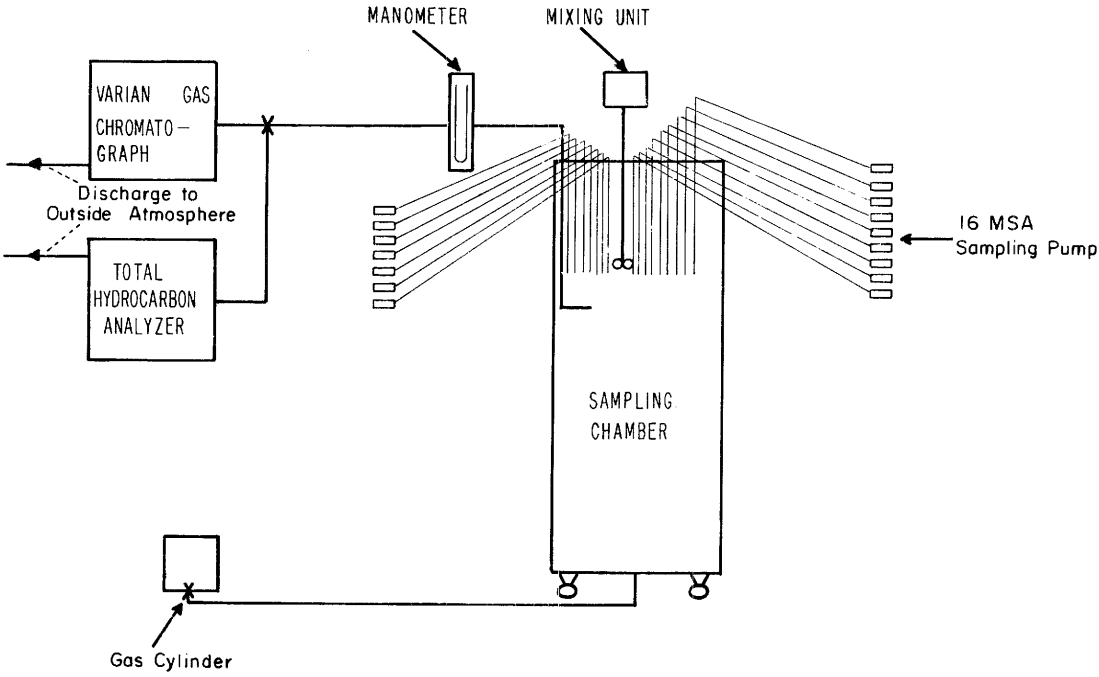

Figure 3 — Replicate gas sampling unit.

ethylene dichloride. However, the data for these two compounds were close enough to satisfy the homogeniety requirements in order to allow their inclusion for obtaining pooled estimates on all levels of concentrations except for the lowest level.

It was then possible to compute the variance component estimates from the relationships described in Table II.

Table III summarizes the results of the Phase I analysis. The results are reported as per cent relative error where

$$\% \text{ relative error} = \frac{S}{\bar{x}} \times 100$$

and S = estimate of an error component standard deviation

$\bar{x}$ = average level of concentration.

In Table III the total percent relative error is shown. This is computed as the root mean square of all the other error components. For example, the total per cent relative error for benzene is shown to be 10.50%. This is calculated as follows $\sqrt{(6.29)^2 + (5.81)^2 + (6.08)^2} = 10.50$.

phase II experimental design

The experimental design and analysis schedule for Phase II was quite similar to that used in Phase I. Phase II was performed for the purpose of determining the magnitude of error due to sampling. In order to accomplish this some assumptions had to be made. The Phase I sample generation error was assumed to be negligible and Phase I/Phase II were assumed to have identical analytical error. There were reasons to believe that the analytical error of Phase II might be less than Phase I. Familiarity through use of the method was expected to improve data. It was learned that some collaborators who had noticed deficiencies in their chromatographs in Phase I were taking steps to improve them.

In order to provide a better estimate of the relationship between analytical error in Phase I and Phase II, it was decided to analyze some of the spare samples prepared for Phase I. Thus, 22 Phase I samples were scheduled for analysis in Phase II.

generation of phase II samples

Collection of Phase II samples were performed by representatives from each of the 15

TABLE IV
Chromatographs and Columns Used by Collaborators

ıromatograph Make/Model(s)	Column Stationary Phase(s)
ırian 2700	DC-200
ırian Aerograph 1520	Di isodechlphthalate, Carbowax 1540, FFAP
ɜwlett Packard 700	FFAP, Porapak Q
ɜwlett Packard 7620A	Durapak (Carbowax 4000)
ɜckman GC-55, Barber-Colman 20	Apiezon L., Porapak Q
ɜwlett Packard 5750	UC-W98
ɜwlett Packard 7820 & 562	DC-200, PEG 600-Terephthallic Acid
ırian Aerograph 204B	FFAP
ɜM Scientific 400	FFAP
ırian 1800	FFAP, Carbowax 20M
ırber-Colman 5000	FFAP
ɜrkin-Elmer 881	FFAP
---a	---a
ɜrkin-Elmer 900, Hewlett Packard 7600A	FFAP
ɜrkin-Elmer 900 & 990	FFAP

[a] Collaborator did not supply information

TABLE V
Number of Outlier Data Pairs

Lab. No.	Phase I	Phase II
1	15	19
2	0	0
3	3	1
4	9	10
5	4	2
6	1	0
7	1	15
8	1	0
9	3	1
10	6	13
11	0	0
12	0	0
13	40	35
14	0	1
15	5	5

collaborating laboratories. In some cases the samples were collected by industrial hygienists and in others by chemists. Whatever the case, the collaborators were asked to provide a person who would normally collect samples for analyses by the laboratory. The collection was performed in Scott's Plumsteadville laboratory. The apparatus used is illustrated in Figure 3. Two sampling chambers were used, 180 and 60 liters in capacity. The internal surfaces consisted of glass, Teflon, and stainless steel. Each chamber was fitted with separate sampling lines for each sampler plus lines for monitoring the chamber concentrations. The chambers were purged, a gas chromatographic analysis was made and compared to a similar analysis of the cylinder mixture. The recording of concentration data was similar to that used in Phase I. When the chamber reached equilibrium, the samplers were given the signal to proceed. During sampling the chambers were maintained at a positive pressure of 1″ of water to prevent dilution by room air.

The pumps used were battery operated personal sampling pumps (MSA Model G or equivalent) operated at approximately 1 liter per minute. At the time of the test the low volume pumps (Sipin type or equivalent) were not available. The pumps were all calibrated at the beginning of the day and no further calibration was permitted during the day. The only adjustments allowed were to bring the flow meter float back to its calibrated level.

Once the signal to sample was given, each sampler collected five consecutive ten-liter samples. Approximately one hour was required for each set. The samples collected in Phase II were analyzed according to a randomized schedule. The chromatographs and columns used by the various collaborators are listed in Table IV. The data acquired by the collaborators were entered on prepared sheets and mailed to Scott upon completion of each phase.

outliers

Prior to analyzing the Phase I and Phase II data, the results reported by each laboratory were carefully screened for obvious reporting and computational errors. Questionable values were reconfirmed with the laboratory making the report. These values were "corrected" using the desorption efficiency factors previously determined for each laboratory and compound.

These corrected values were then checked for outliers according to two criteria. The first was an outlier test which eliminated observations too "far" from the average of the other participating laboratories results.[5] The second criterion was the two sample charts which eliminated duplicates having too large a difference in results, i.e., poor precision. A summary of the outliers found is presented in Table V.

As a result of the outlier tests, the decision was made to omit all of Laboratory No. 13's data from the Phase I data analysis, however, in Phase II only the actual outliers were omitted. In addition, it was noticed that Laboratory No. 1 had a disproportionately large number of outliers for dioxane and hence, the data from

TABLE VI
Comparison of Phase I Sample Variation with Phase II Sample Variation

Compound		Phase I Scott Value	Phase I Lab Mean	Phase I Lab Std. Dev.	Phase II Scott Value	Phase II Lab Mean	Phase II Lab Std. Dev.	F Ratio
Benzene	1	0.0170	0.0158	0.0068	0.169	0.0148	0.0024	8.03*
	3	0.3255	0.3220	0.0312	0.3224	0.3360	0.0146	4.57*
	5	1.5422	1.6102	0.1759	1.5156	1.4756	0.2232	0.62
Carbon Tetrachloride	1	0.0269	0.0408	0.0280	0.0266	0.0297	0.0152	3.39*
	3	0.6750	0.7337	0.1276	0.6741	0.6994	0.1801	0.50
	5	15.2222	15.2188	1.9452	15.0937	15.2904	1.8929	1.06
Chloroform	2	1.5142	1.5040	0.1102	1.5073	1.5356	0.1248	0.78
	4	4.7028	4.6682	0.2804	4.6566	4.4725	0.4946	0.32
Dioxane	1	0.2217	0.2247	0.1090	0.2209	0.2089	0.0124	77.5
	3	3.7733	3.9861	0.4696	3.7466	3.7277	0.3693	1.62
	5	6.8023	6.8571	0.4278	6.7233	6.6520	0.6466	0.44
Ethylene Dichloride	1	0.0940	0.1019	0.0073	0.0938	0.1098	0.0275	0.07
	3	2.0908	2.0185	0.1034	2.0788	2.1244	0.1046	0.99
	5	8.2563	7.4422	0.3038	8.3542	6.9260	0.9489	0.11
Trichloro-ethylene	1	0.1765	0.2061	0.0878	0.1749	0.1834	0.0206	18.17*
	3	5.6863	5.8552	0.2298	5.6718	5.5015	0.5138	0.20
	5	15.5072	15.1193	1.6227	14.3925	15.0966	2.0343	0.64
Xylene	1	0.2016	0.1918	0.0419	0.2001	0.1962	0.0190	4.86*
	3	4.6392	4.4470	0.3151	4.6063	4.7234	0.3669	0.72
	5	8.0552	8.3722	0.4335	7.9981	8.0320	0.6292	0.48
Mixtures								
Benzene	3	0.3347	0.3274	0.0185	0.3319	0.3358	0.0458	0.16
Xylene	3	4.2988	4.0809	0.3453	4.2624	4.0507	0.4911	0.49
Ethylene Dichloride	3	2.1258	2.0488	0.2595	2.1092	1.9583	0.2228	0.72
Trichloro-ethylene	3	5.4257	5.0453	0.4584	5.3834	5.3198	0.5493	0.70

*Indicates statistical significance at the 0.05 probability level.

Laboratory No. 1 was omitted from the dioxane data analysis.

data analysis of analytical results from phase II

Since all the Phase I samples were prepared in an identical manner, it was felt that we could assume a negligible generation error, i.e. the error in Phase I (E_I) represents only analytical error. Since the collaborating laboratories did their own sampling in Phase II, it was assumed that the error (E_{II}) in Phase II consisted of both sampling error (E_S) and analytical error. Hence, the sampling error could be determined by simple difference. Thus, $E_S^2 = E_{II}^2 - E_I^2$. By analyzing extra Phase I samples in Phase II it was possible to determine if there were any significant improvements in the laboratory sample variance estimate which would have to be accounted for. This was accomplished by using an F-ratio test. The F-ratio for each level is the ratio of Phase I analysis to the Phase II analysis. An F ratio greater than 2.55 indicates a significant difference at the 5% significance level. Table VI shows the results of this comparison.

A careful study of this table indicates that the only significant improvement in the Phase II sample analysis is at the lowest level, i.e., the 5% OSHA standard level. The most noticeable changes were for dioxane and trichloroethylene. Since no significant improvement is detected for other levels and compounds, it seemed safe to assume that the analytical error in the two Phases was not drastically different. Hence, the above relationship can be used to estimate the sampling error.

The data for the Phase II analysis was statistically analyzed in an identical manner to the Phase I data, i.e., the same tests for outliers, logarithmic transformations, tests for homogeniety of variance and pooling of error estimate were performed. Of the seven compounds only the results for benzene and carbon tetrachloride did not exhibit homogeniety of variance at all levels including level 1. However, in order to be able to compare

TABLE VII
Summary of Phase II Analysis
(Percent Relative Error Contribution of Variance Components)

	SINGLE COMPONENTS							
	Excluding Level I				Level 1			
	Precision	Between Labs.	Day-to -Day	Total	Precision	Between Labs.	Day-to -Day	Total
Benzene	9.47	0.00	9.50	13.35	78.9	0.00	126.3	148.9
Carbon Tetrachloride	9.03	8.40	8.19	14.86	104.5	482.6	0.00	493.7
Chloroform	9.40	8.23	2.47	12.76	23.2	0.00	13.74	26.96
Dioxane	7.20	9.72	9.94	15.72	9.44	12.82	6.88	17.42
Ethylene Dichloride	6.80	7.83	5.39	11.71	5.36	12.90	9.07	16.72
Trichloroethylene	7.26	5.54	6.21	11.07	15.71	14.71	4.33	22.09
Xylene	5.83	5.86	4.75	9.54	5.75	7.43	8.55	12.74
	Precision	Between Labs.	Day-to -Day	Total				
Benzene	5.06	7.82	6.65	11.46				
Xylene	5.71	6.83	7.01	11.35				
Ethylene Dichloride	8.56	11.79	8.92	17.16				
Trichloroethylene	10.99	9.58	3.44	15.03				

(1) Negative estimate assumed zero.

TABLE VIII
Summary of Sampling and Analytical Errors
(Percent Relative Error)

Single Components	Analytical + Sampling Error (Phase II)	Analytical Error (Phase I)	Sampling Error
Benzene	13.35	10.50	8.24
Carbon Tetrachloride	14.86	14.05	4.84
Chloroform	12.76	10.69	6.97
Dioxane	15.72	8.00	13.53
Ethylene Dichloride	11.71	8.01	8.54
Trichloroethylene	11.07	8.02	7.63
Xylene	9.54	7.15	6.32
Average	12.72	9.49	8.01
Mixtures			
Benzene	11.46	5.60	10.00
Xylene	11.35	6.69	9.17
Ethylene Dichloride	17.16	10.21	13.79
Trichloroethylene	15.03	11.62	9.53
Average	13.75	8.53	10.62

Phase II and Phase I results, the data from level 1 was not pooled with the other levels.

Table VII provides a summary of the Phase II analysis. Comparing this with the Phase I summary we see that the individual error components and total percent relative error are generally 50% greater than in Phase I. However, it appears that the analysis at level 1 have noticeably improved in Phase II over the analyses at level 1 in Phase I. Interestingly, the errors at 5% OSHA standard concentration level were up to twice as large as for the other levels for the five compounds present at weights above 0.1 mg and significantly greater for two compounds (benzene and carbon tetrachloride) at less than 0.1 mg.

results and conclusions

A summary of the sampling and analytical errors for the two phases is provided in Table VIII. The estimated errors for the seven compounds in the range, 60% OSHA standard through the excursion limit are estimated as follows: Relative total error 12.72; analytical error 9.49, and sampling error 8.01. A selected group of back-up sections of charcoal tubes were analyzed in Phases I and II. The amounts found on these sections were very small in most cases. However, the individual back-up data showed wide variation from lab to lab at high levels. The possible causes are variations in the tubes themselves, analytical error and migration from front to back sections. It appears that analysis of

back-up sections is necessary especially at high levels. The desorption factors determined by each laboratory for each compound are shown in Table IX. Again the data obtained by individual laboratories showed wide variation. For example, the 15 desorption factors reported for benzene ranged from 0.87 to 1.00. Since desorption factors are applied to each analytical result to arrive at a corrected value, a significant portion of the lab to lab error is in determining desorption factors. The substantially high error observed at the 5% OSHA standard level can most likely be traced to instrument and operator performance. If limitations in the method were

TABLE IX
Desorption Factors Obtained by Collaborators

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Avg.
Benzene	0.958	0.931	0.989	0.927	0.950	0.988	0.984	0.988	0.921	1.000	1.007	0.973	0.871	0.977	0.915	0.959
m-Xylene	0.926	0.974	0.974	0.978	0.970	0.953	0.981	0.958	0.961	0.912	0.992	0.985	0.852	1.000	0.901	0.954
Trichloroethylene	0.982	0.993	0.953	0.947	0.895	0.979	0.985	0.940	0.964	1.000	0.999	0.985	0.966	0.990	0.912	0.966
Carbon Tetrachloride	0.863	0.989	1.004	0.890	0.921	1.074	0.970	0.984	0.977	0.893	1.007	0.984	0.999	0.970	1.010	0.970
Chloroform	0.976	0.979	0.964	0.918	0.964	0.978	0.902	0.955	0.962	1.000	1.016	0.976	0.889	0.983	0.936	0.960
Dioxane	0.876	0.959	0.896	0.968	0.815	0.885	0.974	0.949	0.842	0.883	0.951	0.927	0.911	0.981	0.880	0.913
Ethylene Dichloride	0.991	0.959	0.994	0.950	0.924	0.946	0.990	0.976	0.944	0.968	0.992	0.924	0.915	0.985	0.881	0.956
Average	0.939	0.969	0.968	0.941	0.920	0.972	0.969	0.964	0.939	0.951	0.995	0.965	0.915	0.984	0.919	

TABLE X
Pump Calibration Data

4/3/73				4/4/73						4/5/75			
Calib.* Flow Rate at Start 1/min.	Calib.* Flow Rate at End 1/min.	No. of Samples Collected	Meas.** Flow Rate at End 1/min.	Calib.* Flow Rate at Start 1/min.	Calib.* Flow Rate at End 1/min.	Rate at Samples Collected	Meas.** Flow No. of End 1/min.	Calib.* Flow Rate at Start 1/min.	Calib.* Flow Rate at End 1/min.	No. of Samples Collected	Meas.** Flow Rate at End 1/min.
1.00	-	40	1.166	1.00	-	50	1.15	1.0	-	50	1.026
1.0	-	35	.992	1.0	-	50	.842	1.0	-	50	.847
1.00	1.0	40	1.006	1.00	-	50	1.02	1.0	-	50	1.07
1.00	-	24	1.012	1.0	-	50	1.036	1.0	-	50	.993
1.00	1.00	40	.988	1.0	1.0	50	.914	1.0	1.0	50	.917
1.0	-	40	1.006	1.0	1.0	50	1.0	1.0	-	50	1.11
1.01	-	40	.946	1.01	1.01	50	1.11	1.01	1.01	50	.817
1.00	1.00	40	1.014	1.00	1.00	50	.834	1.0	1.0	50	1.005
.974	1.027	40	1.152	.993	-	50	1.05	1.0	-	25	1.024
1.01	1.00	40	1.14	.975	.960	50	1.29	.993	.914	50	.958
1.01	.996	40	.972	1.00	1.00	40	1.036	1.0	1.0	50	1.128
1.00	.841	40	.960	1.00	-	–	1.026	1.0	-	50	1.135
1.00	1.00	40	.998	1.0	-	50	.992	1.0	-	50	.997
1.00	1.00	40	.946	1.00	1.00	50	.936	1.0	1.0	50	.923
1.01	1.01	40	1.020	1.01	1.01	50	1.016	1.01	-	50	1.036
1.00	1.00	40	.982	1.00	1.00	50	1.006	1.0	1.0	50	.979

*Reported by Collaborator
**Measured by Scott

the cause of outliers, we would expect a normal distribution of outliers from each laboratory about the mean of all laboratories. In Phase II, five of the 15 laboratories accounted for more than 90% of outliers. This strongly indicates that the method is satisfactory and that the analytical techniques used by five of the laboratories were inadequate. The estimates of sampling error for the single components and the mixtures are 8.01 and 10.62 respectively. These values compare very closely to a percent relative error of 9.70 for the pump calibration. The pump calibration error was calculated using the 27 observations in Table X where flow rate data were available at the start and end of sample collection periods for three consecutive days. At the end of each day Scott measured the flow rate for each pump using a bubble meter. This data should depict the true variation from one sampler to another. The average measured flow rate was close to 1.0 liter per minute. On the other hand a significant number of pumps gave flow rates that were less than 0.9 and greater than 1.1 liters per minute. These facts indicate that the calibration method is adequate and that some collaborators did not perform the calibration correctly. The data further indicates that the pump error is the major source of error in sampling.

Generally, the results of this collaborative study agree with validation studies[6] which have been performed on the charcoal method since the collaborative study was performed. A complete report[7] is available which gives details of all aspects of the study. The results have been summarized here to present pertinent statistical evaluations and major conclusions.

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