



Project Summary

Interlaboratory Comparison Study: Methods for Volatile and Semivolatile Compounds

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A program is underway within the U.S. Environmental Protection Agency (EPA) to improve the reliability of its analytical methods. As part of this program, test protocols for the determination of volatile and semivolatile organic compounds in hazardous wastes were developed and subjected to a nine-laboratory intercomparison study. Volatiles were determined by the purge-and-trap gas chromatography/mass spectrometry (GC/MS) analysis of a tetraglyme extract. Semivolatiles were determined by fused silica capillary column (FSCC) GC/MS analysis of a methylene chloride extract obtained from a neutralized dried sample. Detailed quality assurance/quality control (QA/QC) guidelines were provided to each laboratory. Seven waste samples and one standard reference material (SRM) were each analyzed in triplicate by GC/MS for a target list of 200 compounds, including 45 sample spikes. The protocols were shown to work best for the less polar aprotic compounds. The between-laboratory analytical precision component for both volatiles and semivolatiles was approximately twice that of the within-laboratory component. The effect of excluding outlier data on precision calculations is dramatically illustrated on analytical data derived from a standard reference material.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, 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

The U.S. Environmental Protection Agency (EPA) is currently involved in a broad program to assess and improve the reliability of the data generated using recommended hazardous waste analytical protocols. This program is essential to maintain the credibility of the EPA as a regulatory agency. Included in this broad program is the submission of those analytical protocols in widest usage to interlaboratory comparison testing. Such interlaboratory comparison testing is one of the most important elements of any methods validation plan. Although substantial expenditure of both time and money is required, multi-laboratory testing of many EPA methods is currently underway. The full report describes the evaluation of analytical protocols for the determination of volatile (boiling up to ca. 200°C) and semivolatile compounds (boiling up to ca. 500°C) in hazardous wastes by an interlaboratory comparison test.

The workplan for this project consisted of three distinct phases:

1. Selection, evaluation and optimization of the best available methods for determining volatile and semivolatile organic compounds in solid wastes.
2. Rigorous single laboratory evaluation of the optimized methods and method revision where necessary. Preparation of all materials for distribution to the participating laboratories. Peer review of the selected methods.
3. Interlaboratory comparison testing.

The guiding workplan philosophy was to severely challenge the selected methods. Thus, the target analytes and sample matrices were selected to represent a broad spectrum of hazardous waste

analytical situations. In addition, each waste sample contained significant quantities of endogenous compounds. This ensured the presence of background interference problems and provided a "real world" matrix background for the spike compounds.

Two analytical test procedures were evaluated in the interlaboratory study. One of the procedures was a GC/MS analysis procedure for the determination of volatile organic compounds. This procedure involved the extraction of a waste sample with tetraethyleneglycol dimethyl ether (tetraglyme), the addition of a portion of the extract to reagent water, and analysis according to the purge-and-trap technique of EPA Test Method 624. The other method, a GC/MS analysis method for the determination of semivolatile organic compounds, involved the methylene chloride extraction of a waste sample by sonification under neutral anhydrous conditions and analysis of the extract using a fused silica capillary column.

Experimental Section

Preparation of Calibration Solutions

All standard solutions required for the interlaboratory comparison study were purchased or prepared in sealed glass ampoules and distributed to the participating laboratories. The standards included calibration solutions, surrogate recovery solutions, and internal standard solutions. The standard solutions distributed for the determination of volatile compounds included six calibration solutions containing a total of 53 representative volatile compounds, a surrogate solution containing four fluorinated compounds as recovery standards, and an internal standard solution containing p-bromofluorobenzene (BFB) as a mass spectrometer tuning standard and three deuterated internal standards. The standard solutions distributed for the determination of semivolatile compounds included four calibration solutions containing a total of 140 representative semivolatile compounds, a surrogate solution containing three fluorinated recovery standards, an internal standard solution containing decafluorotriphenylphosphine (DFTPP) as a mass spectrometer tuning standard, 12 deuterated internal standards and GC/MS performance standards.

Preparation of Spiked Wastes

The wastes used in the study (Table 1) were selected to challenge the sample

Table 1. Interlaboratory Comparison Samples

Sample Number	Waste Name	Physical Description	Analyses Performed ^a
2	Spiked latex paint waste	Semi-solid	S,V
3	Spiked ethanes spent catalyst	Oily powder	S,V
4	Spiked coal gasification tar	Tar	S,V
5	Spiked oxychlorination spent catalyst	Pelletized solid	S,V
6	Spiked POTW sludge	Wet filter cake	S,V
7	Spiked herbicide acetone-water	Liquid	V
8	Spiked chlorinated ethanes waste	Liquid	V
9	Contaminated river sediment [SRM]	Oily powder	S

^aS = determination of semivolatile compounds.

V = determination of volatile compounds.

workup procedure and to represent a broad range of waste types. These wastes were shown to contain a significant number of naturally incorporated compounds, and were available in sufficient quantities for a multi-laboratory study. The wastes were spiked with the representative volatile and semivolatile compounds, these spike concentrations were chosen to be similar to the levels of other volatile and semivolatile components present in the unspiked wastes. Preliminary screening was used to show that most of the spike compounds were different from those naturally incorporated within the unspiked wastes.

To reduce analytical costs, a spiking scheme was devised to minimize the number of GC/MS analyses required for each waste. The scheme involved spiking each waste with pairs of chemically compatible compounds. The two compounds in each pair were selected on the basis of similar properties (volatility, solubility, polarity, or acidity) that would be expected to provide similar recovery efficiencies. A previous intralaboratory study had demonstrated that the two compounds in each pair did yield comparable recoveries. One compound from each pair was spiked at a relatively low level and the other at an approximately five-fold higher level. With this approach, analytical data, for naturally incorporated components and recovery data for different classes of compounds at two spike levels, were obtained simultaneously in a single GC/MS run.

The high and low spike levels used corresponded to those levels that would give approximately 50 ng and 250 ng of volatile compounds or 10 ng and 50 ng of semivolatile compounds on the GC column during analysis if 100% extraction recovery were achieved. Since the degree of dilution or concentration required for each extract varied widely from waste to waste, the actual spike level used also varied widely from waste to waste.

Design of Collaborative Test

Each participating laboratory was sent detailed descriptions of the analysis protocols, ampoules of the standard solutions, samples of the seven spiked wastes and a sample of NBS Standard Reference Material No. 1645. The standard reference material, a contaminated river sediment, was included to obtain reference data for future work. Each laboratory was requested to analyze three replicates of each spiked waste to determine volatile compounds and three replicates of five of the spiked wastes and the standard reference material for semivolatile compounds. The laboratories were requested to search for 53 specific volatile compounds and 140 specific semivolatile compounds, and to quantify the amounts of any of the compounds found. These compounds, which include both spike compounds and naturally incorporated compounds, were selected as representative of various classes of compounds to challenge the method and assess its broad applicability. In addition, the laboratories were requested to report and quantify up to 10 major unlisted compounds found in each sample.

Statistical Design

The data reported by the laboratories participating in this collaborative study include the amount of compound found (AF) in the sample, the response factor (RF) and the retention time (RT) or relative retention time (RRT). These data were reported by nine laboratories for 53 volatile compounds in each of seven sample types, and for 140 semivolatile compounds in each of six sample types.

Since each of the nine laboratories conducted three replicate analyses, there were potentially 27 values to be reported for each compound in each sample type. However, due to various causes, data were not always reported for each replication.

The percent of compound recovered by each laboratory was calculated by

$$\% \text{ Recovery} = \frac{\sum_{i,j} \text{AF}_{ij}}{\text{IAF} + \text{SLQ}} \times 100$$

where IAF is the initial amount-found in the sample by intralaboratory analysis, and SLQ is the spike level quantity. The summation is taken over all AF data reported. The percent of AF data reported was calculated by dividing the number of data reported by 27, the maximum total number of available data points.

For each combination of sample type and compound, the data were analyzed using the random components analysis of variance model

$$\text{Amount-Found}_{ij} (\text{AF}_{ij}) = \mu + L_i + \varepsilon_{ij}$$

$i = 1, 2, \dots, 9 \quad j = 1, 2, 3$

where AF_{ij} is the amount of compound found on the j^{th} replication by the i^{th} laboratory. L_i is the random systematic error due to laboratory i and ε_{ij} is the random within-laboratory error. It is assumed that L_i is distributed normally with mean zero and variance σ_L^2 . The within-laboratory error term, ε_{ij} , is assumed to be normally distributed with mean zero and variance σ_ε^2 .

The total variance for the AF data is given by:

$$\sigma_T^2 = \sigma_L^2 + \sigma_\varepsilon^2$$

Applying this model and analysis of variance techniques, the total, between-laboratory and within-laboratory relative standard deviations defined by $\sigma_T/\mu \times 100$, $\sigma_L/\mu \times 100$, and $\sigma_\varepsilon/\mu \times 100$, respectively, where μ is the average amount found across all laboratories, was estimated using the AF data obtained from the laboratories. Since there were instances of missing data, appropriate formulas for the construction of one-way analysis of variance tables with unequal sample sizes were employed.

In addition to the above analyses, the percent recovery of each compound and sample type was calculated for each laboratory as:

$$\% \text{ Recovery} = \frac{\sum_{i,j} \text{AF}_{ij}}{\text{IAF} + \text{SLQ}} \times 100$$

Items Supplied to Participating Laboratories

The following items were supplied to each participating laboratory:

- Instruction manual (step-by-step analytical protocols and quality control directions)
- Data report forms
- Two performance evaluation samples
- Seven waste samples

- One NBS standard reference material sample (SRM 1645)
- Fourteen standard solutions
 - 10 calibration standards
 - 2 internal standards
 - 2 surrogate standards
- One DB-5 fused silica capillary column
- GC/MS data for 200 organic compounds
- GC/MS library for laboratories with Finnigan INCOS software

Items to be Delivered by Participating Laboratories

The following data were to be submitted by each participating laboratory on appropriate supplied forms.

1. A run log of the GC/MS analyses performed for the study including run number, identity of run, date of extraction, date of analysis, and the area counts and retention time of the primary internal standard.
2. Amount, retention time or relative retention time, and response factors used for each of the 200 listed compounds detected in each sample analyzed, including process blanks.
3. Amount, tentative identification, most intense ions, and retention time or relative retention time for as many as 10 major unlisted volatile or semivolatile compounds found in each sample.
4. Relative ion abundances of the mass spectrometer tuning compound for each GC/MS run.
5. Retention time and response factor, relative to benzene- d_6 for volatile compounds and relative to phenanthrene- d_{10} for semivolatile compounds, for each internal standard in each GC/MS run.
6. Recovery, amount added, internal standard level, retention time or relative retention time and response factor used for each surrogate standard in each sample.
7. Response factor, and retention time or relative retention time, found for each of the listed compounds in each calibration run.
8. Total solvent extractable content and major volatile compounds content determined during the GC screening of each sample extract.
9. A copy of the total ion chromatogram from each GC/MS run.
10. The background corrected mass spectrum and library search results, both identified by scan

number, for each unlisted compound reported.

11. A brief narrative description of the GC/MS system used to acquire data and the computer software and/or manual processes used to obtain the qualitative and quantitative results reported.
12. Comments and recommendations regarding the use of the methods.

Quality Assurance/Quality Control (QA/QC)

To ensure the reliability of the data generated by the participating laboratories, a rigorous QA/QC program was designed as an integral part of this interlaboratory comparison test. This QA/QC plan contained many of the elements currently employed in the uncontrolled chemical dump sites program. These QA/QC elements included (in part):

- An on-site audit to determine if the requisite personnel, equipment and facilities were present.
- Analysis of performance evaluation (PE) samples to allow the participating laboratory to gain experience with the analytical protocols.
- Standard traceability ensured by distributing internal standards, surrogate standards and calibration standards to each laboratory.
- A requirement that the participating laboratory obtain GC/MS response factors for 20 specified compounds to within ± 40 percent for all GC/MS calibration runs at the 50- $\mu\text{g}/\text{mL}$ level.
- A requirement that each mass spectrometer be tuned daily using BFB for volatile analysis and DFTPP for semivolatile analysis, to meet EPA-provided specifications.
- The use of a standard reference material, NBS river sediment, to monitor each laboratory's ability to use the subject protocol on a solid material containing naturally incorporated semivolatile compounds.

Results and Discussion

Intralaboratory Results

Prior to the interlaboratory comparison study, the test samples were analyzed, both before and after spiking, to determine the levels of naturally incorporated compounds and to evaluate the test protocols. Each sample was found to contain significant levels of background contaminants.

A three-laboratory intercomparison test was employed to determine the

GC/MS response factor performance criteria to be recommended for the interlaboratory comparison study. A list of 20 response factors was prepared, and a response factor precision of ± 40 percent was recommended to ensure data quality. The recommended ± 40 percent range was based on twice the percent relative standard deviation (% RSD) for compounds with % RSD up to 20 percent in order to provide at least a 95 percent confidence level.

Homogeneity Study

A study was undertaken to determine if the spiked and naturally occurring compounds were uniformly distributed among the sample aliquots to be distributed to the interlaboratory test participants. Aliquots taken from replicate vials of the homogenized spiked waste samples were extracted following the test protocol procedures. The extracts were analyzed in duplicate by GC to quantify the GC-resolvable components, and in triplicate by a microcoulometric method to determine total purgeable organic halogen. Analysis of variance treatment indicated that the samples in the individual vials were homogeneous within the precision of the methods used, with the single exception of the semivolatile compounds determined in sample number 6. The net vial-to-vial variability of the compounds in that sample was about 15 percent. The study indicated that the spike compounds were as homogeneously distributed within each sample as the naturally incorporated compounds.

Recovery, Precision, and Detectability of Volatile Organics

The average percent recoveries and the total between-laboratory and within-laboratory relative standard deviations for the spiked and naturally incorporated volatile compounds in the seven wastes were determined. If data were reported for fewer than 20 percent of the required analytical runs the percent RSDs were not determined. The variability of volatile organics results exhibited a dependence on sample matrix.

The within-laboratory variability for analysis of volatiles was generally less than 30 percent but ranged from 5 to 300 percent depending on the compound. The total variability generally ranged from 20 to 80 percent for most of the waste samples. The between-laboratory variability was usually less than 70 percent but ranged from 5 to 300 percent. The highest variabilities, both total and

component, were reported for non-spike compounds that are common background contaminants such as methylene chloride, dichloroethane, chloromethane, and chloroform. Only in the case of sample 4 were high percent RSD's reported for spiked compounds.

The effect of laboratory on detectability of specific volatile compounds was ascertained from the reported data. Variability dependent on the laboratories was evident and was not reproducible on a per-sample basis, i.e., a certain laboratory could report a larger number of data for one sample than the other laboratories and report the fewest number for another sample.

Recovery, Precision and Detectability of Semivolatile Organics

The sample-to-sample variability noted for the volatile compounds was also evident for the semivolatile compound analyses. The differences in amount of data reported were greater for the determination of semivolatiles than for the determination of volatiles. For example, for sample 3, the number of compounds reported varied from 1 to 27, with 20 being the average number of compounds reported. The total RSD generally ranged from 30 to 80 percent. The RSD for the within-laboratory component was less than 30 percent and the between-laboratory variability was about twice that value. The ranges of both components were the same as those reported for volatile organics, 5 to 300 percent. No difference in ranges of values is apparent for the spiked versus non-spiked compounds; however, some of the poorer precision may be attributable to polarity and to background contaminants, such as phthalates.

Effect of Compound, Sample and Spike Level on the Detectability of Volatile and Semivolatile Organics

A presentation of percent detection data for each waste sample, arranged according to specific compounds, is provided in Table 2 for volatile compounds and in Table 3 for semivolatile compounds. These two tables provide information regarding the effect of compound and sample type on the method detection capability. In addition, the data are identified by either low spike level (underlined values) or high spike level. The average percentage of reported compounds was higher for both volatile

and semivolatile compounds spiked at the high level (73 and 70 percent, respectively). The low level spikes were reported 57 percent of the time for the determination of volatiles and 47 percent for the determination of semivolatiles. The more difficult waste samples are also apparent from these data, namely samples 5 and 6 for volatiles and samples 3, 5 and 6 for semivolatiles analysis.

Total Volatile and Semivolatile Organic Compounds Reported

It was instructive to examine the total number of volatile and semivolatile compounds reported by each laboratory for each sample. Such an examination could identify difficult samples and differences in laboratory performance. The two samples for which the poorest VOA results were obtained were sample 3 (oxychlorination spent catalyst) and 6 (POTW sludge). These two solid sample matrices might be the least retentive for volatile compounds, and appreciable amounts of the spike or naturally incorporated volatile components may have been lost during sample storage. The best results were obtained with samples 2, 3, and 8 while 4 and 7 provided intermediate results. The differences in laboratory performance are more difficult to assess. However, the VOA performance of laboratory no. 8 was definitely poorer than that of the other laboratories. The poorest semivolatile results were reported by laboratory no. 7 while the best performance was noted for laboratory no. 2. The problem samples for semivolatile determinations were samples 5 and 6, closely followed by sample 3. The best semivolatiles results were obtained for samples 4 (except by laboratory no. 7) and 2. Laboratory no. 4 experienced considerable difficulty with sample 3 while laboratory nos. 1 and 5 experienced unusual detection problems with semivolatiles in sample 5.

Outlier Effect on Standard Reference Material Results

The results of all reported data for the National Bureau of Standards SRM were surprisingly variable. The total variabilities ranged from 28 to 338 percent and averaged 160 percent. The quantities of compounds reported were lower than those of most of the other test samples, however, the quantities of compounds found in samples 5 and 6 were comparable. The homogeneity of this sample should be better than the other test samples since NBS prepared this material.

Table 2. Effect of Compound, Sample and Spike Level on Volatile Compound Detectability

Compound Number	Compound	Percent of Data Reported for Given Sample ^{a,b}							Average Percent		
		2	3	4	5	6	7	8	Low ^c	High ^d	Total ^e
12.	Propionitrile	<u>11</u>	<u>0</u>	22	11	<u>0</u>	11	26	4	18	12
24.	2-Chloroacrylonitrile	100	<u>96</u>	<u>4</u>	<u>11</u>	<u>4</u>	<u>4</u>	<u>78</u>	24	67	42
25.	1,1,1-Trichloroethane	100	<u>93</u>	<u>78</u>	<u>11</u>	7	<u>78</u>	<u>89</u>	65	65	65
33.	1,2-Dichloropropane	<u>100</u>	<u>96</u>	<u>100</u>	<u>56</u>	<u>48</u>	<u>100</u>	<u>78</u>	75	88	83
44.	Bromoform	<u>100</u>	<u>85</u>	<u>56</u>	<u>67</u>	<u>4</u>	<u>56</u>	<u>89</u>	67	63	65
46.	2-Hexanone	89	<u>52</u>	<u>37</u>	<u>11</u>	26	<u>52</u>	<u>89</u>	38	68	51
47.	1,1,2,2-Tetrachloroethane	<u>89</u>	<u>93</u>	67	100	<u>4</u>	100	100	62	92	79
50.	Chlorobenzene	<u>96</u>	<u>96</u>	100	89	100	<u>100</u>	100	97	97	97
51.	Ethylbenzene	<u>100</u>	<u>96</u>	<u>89</u>	<u>41</u>	<u>89</u>	<u>89</u>	<u>89</u>	77	95	87
	Average	87	79	61	44	31	66	82	57	73	64

^aThe maximum number of analytical runs for which data could be reported for each sample was 27 (3 replicates x 9 laboratories).

The percent of data reported = $\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$

^bPercent of data reported for compounds spiked at the low level are underlined.

^cAverage of the percents of data reported for samples in which the compound was spiked at the low level.

^dAverage of the percents of data reported for samples in which the compound was spiked at the high level.

^eAverage of the percents of data reported for all samples.

A closer inspection of the data reported revealed that most of the variability could be attributed to outlier values reported by one laboratory. In some cases a significant portion of the variability was caused by outlier values reported by a second laboratory. The improvement in the total variabilities obtained by omitting the data from one laboratory or two laboratories in the calculations are shown in Table 4. By omitting the data from two laboratories the total variabilities ranged from only 13 to 90 percent and averaged 31 percent. An average total variability of 31 percent for the analysis of complex sample is unexpectedly good. The within-laboratory component of the variability would be much less. Amount-found values for 8 of 12 compounds reported in Set C of Table 4 are within a factor of 2.2 of the values reported for this SRM in a previous study. This is surprisingly good agreement for the determination of naturally incorporated compounds by two different analytical methods. One of the four compounds with values outside the factor of 2.2 was obtained for di-n-butyl phthalate, a common laboratory background contaminant.

Conclusions and Recommendations

The non-aqueous neutral extraction followed by fused silica capillary column GC/MS analysis eliminates separate acid/base extractions and reduces the required number of GC/MS runs. The analytical data reported for all samples will be investigated in greater detail to determine the causes of statistical outliers. If these outliers result from laboratory deviations from the test methods and quality control protocols

they can be excluded from the pooled precision results. However, the validity of discarding outlier results is still a subject of disagreement among statisticians and chemists. If outliers are shown to be a result of protocol ambiguities, the appropriate protocol sections should be clarified. These steps may reduce the number of outliers generated in future applications of these methods. The between-laboratory to within-laboratory ratio of about two for the precision of these test methods compares favorably with the recently compiled results of over fifty AOAC interlaboratory comparison tests.

The wide variation in individual laboratory performance demonstrates the need for strong QA/QC monitoring of laboratories performing routine environmental analyses. Although each participating laboratory had some prior experience with the test protocols, it is anticipated that further experience will lead to improved analytical performance.

Further examination of the analytical results and observations of the interlaboratory comparison study for evaluation of hazardous waste methodology will significantly enhance the value of this complex study. The volume of data generated far exceeds data obtained for any previous interlaboratory method evaluation. The scope of the study thus far included statistical evaluation of only a small portion of this data base. In addition, no provision was included for statistical reanalysis excluding outlier results. Based on the interpretation of the analytical data the following specific recommendations are presented:

- Expand the statistical treatment of the interlaboratory comparison data to

include analysis of data to identify sources of observed variabilities.

- Repeat statistical analysis of percent recovery data excluding obvious outliers.
- Investigate sources of significant data variability in the following method steps:
 - 1) Prescreening
 - 2) Extraction (Investigate reasons for the wide variation in extract aliquot size chosen for GC/MS analysis.)
 - 3) Instrumental Analysis
 - 4) Response factor determination (Are anomalous GC/MS response factors correlated?)
 - 5) Confirmation of compound identification and quantification procedures
 - 6) Calculation
- Conduct interviews of participating laboratories to evaluate interpretation of instructions (both excellent and poor performances would provide valuable insight).
- Modify method instructions and quality control protocols to eliminate potential sources of analytical variability.

The completion of these recommended tasks will result in a more thorough evaluation of the data generated by this collaborative study. It is anticipated that the revised statistics will be significantly improved, over those reported in this study, in terms of precision and accuracy. Further, the resulting revisions in description of the methods for volatile and semivolatile organic analysis will result in more uniform application of these methods in the future.

Table 3. Effect of Compound, Sample and Spike Level on Semivolatile Compound Detectability

Compound Number	Compound	Percent of Data Reported by Given Laboratory ^{a,b}					Average Percent		
		2	3	4	5	6	Low ^c	High ^d	Total ^e
5.	4-Chlorotoluene	96	89	89	11	33	44	93	64
12.	Bis(2-chloroethyl)ether	100	67	96	78	22	45	91	73
13.	2-Chlorophenol	100	67	89	0	44	44	84	60
15.	2,4,6-Trimethylpyridine	59	78	37	22	11	23	69	41
16.	1,4-Dichlorobenzene	70	89	100	78	93	80	90	86
22.	Acetophenone	89	89	89	67	44	72	89	76
25.	Hexachloroethane	89	85	100	78	0	43	89	70
28.	4-t-Butylpyridine	44	56	89	67	85	50	80	68
33.	2,4-Dimethylphenol	56	4	89	0	89	30	59	48
36.	Propiophenone	89	78	89	89	89	78	89	87
43.	4-Chloroaniline	74	11	56	0	11	22	43	30
50.	Quinoline	100	78	89	89	44	61	93	80
51.	Bis(2-chloroethoxy)ethane	56	100	89	56	78	67	89	76
56.	4-Chloro-3-methylaniline	41	22	78	0	44	32	41	37
57.	4-Chlorobenzoic acid	33	0	78	44	22	11	52	35
64.	1-Chloronaphthalene	33	0	44	44	59	40	30	36
65.	4-Methylquinoline	63	67	89	67	78	73	73	73
66.	2-Ethyl-naphthalene	100	11	89	89	78	45	93	73
69.	4-Bromobenzoic acid	22	11	22	0	96	15	54	30
74.	1,3-Dinitrobenzene	63	19	78	78	0	10	23	48
76.	2,6-Dinitrotoluene	44	56	78	52	0	58	28	46
77.	3-Nitroaniline	44	7	78	0	0	4	41	26
80.	2,4-Dinitrophenol	0	0	56	44	0	0	33	20
84.	4-Nitrophenol	11	11	11	11	0	8	11	9
85.	Pentachlorobenzene	74	78	100	78	100	76	93	86
98.	2-Chloro-4-nitroaniline	22	15	59	11	0	31	8	21
100.	Hexachlorobenzene	100	89	89	78	44	70	95	80
117.	Anthraquinone	100	78	89	81	33	68	89	76
118.	Fluoranthene	100	89	100	93	100	98	89	96
120.	2-Methylanthraquinone	78	67	89	78	89	73	85	80
121.	Pyrene	100	22	100	100	100	22	100	84
123.	4,4'-DDD	78	89	89	81	89	84	89	85
125.	4,4'-DDT	85	74	89	89	0	74	66	67
126.	Triphenyl phosphate	89	89	78	59	33	57	89	70
132.	Tri-(p-tolyl)phosphate	63	41	89	70	85	52	81	70
137.	Dibenzocarbazole	56	11	11	0	52	22	32	26
	Average	67	51	77	52	48	47	70	59

^aThe maximum number of analytical runs for which data could be reported for each sample was 27 (3 replicates x 9 laboratories).

The percent of data reported = $\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$

^bPercent of data reported for compounds spiked at the low level are underlined.

^cAverage of the percents of data reported for samples in which the compound was spiked at the low level.

^dAverage of the percents of data reported for samples in which the compound was spiked at the high level.

^eAverage of the percents of data reported for all samples.

Table 4. Effect of Removing Outliers on Precision for the Determination of Semivolatile Compounds in NBS Standard Reference Material No. 1645

Compound Number	Compound	Number of Data Using Given Data Set ^a			Amount-Found, µg/g Using Given Data Set ^a			Percent Relative Standard Deviation Using Given Data Set ^a		
		A	B	C	A	B	C	A	B	C
41.	Naphthalene	18	15	12	4	1	1	263	20	18
72.	Acenaphthylene	18	15	12	45	13	17	278	111	90
78.	Acenaphthene	15	12	9	1	1	1	28	27	24
90.	Fluorene	14	11	8	14	2	1	305	42	23
107.	Phenanthrene	18	15	12	28	3	3	338	26	13
109.	Anthracene	18	15	12	10	2	2	287	87	74
114.	Di-n-butyl phthalate	15	12	9	22	4	5	218	48	30
117.	Anthraquinone	17	14	11	15	10	9	102	30	15
118.	Fluoranthene	24	21	18	53	34	32	154	23	18
121.	Pyrene	24	21	18	93	69	61	107	23	15
127.	Benzo(a)anthracene	24	21	18	40	33	30	79	38	32
130.	Chrysene	24	21	18	70	62	60	44	18	17
134.	Benzo(k)fluoranthene	21	18	15	40	27	26	127	28	28
136.	Benzo(a)pyrene	21	18	15	14	9	8	95	33	18
138.	Indeno(1,2,3-cd)pyrene	21	18	15	14	9	8	127	48	36
139.	Dibenzo(a,h)anthracene	21	18	15	10	7	5	87	73	48
140.	Benzo(g,h,i)perylene	20	17	14	18	13	11	93	48	29

^aData set A includes all reported data. The maximum number of data possible is 24 (3 replicates x 8 laboratories). One of the 9 laboratories did not analyze this sample.

Data set B includes all reported data from 7 laboratories. One laboratory has been excluded.

Data set C includes all reported data from 6 laboratories. Two laboratories have been excluded.

The Project Report was prepared by Battelle-Columbus Laboratories, Columbus, OH 43201; the Project Summary was prepared by Donald F. Gurka (also the EPA Project Officer, see below) with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89114.

The complete report, entitled "Interlaboratory Comparison Study: Methods for Volatile and Semivolatile Compounds," (Order No. PB 84-178 482; Cost: \$29.50, subject to change) will be available only from:

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