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## HEADSPACE DETERMINATION OF SOLUBILITY LIMITS OF THE BASE NEUTRAL AND VOLATILE COMPONENTS FROM THE ENVIRONMENTAL PROTECTION AGENCY'S LIST OF PRIORITY POLLUTANTS

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### SUMMARY

Static headspace or vapor equilibration analysis where the aqueous solution is allowed to equilibrate with the gaseous phase above it, was recently reported as a simple method for determining the solubility limits of some volatile aromatic priority pollutants and a few purgeable halocarbons<sup>1</sup>. The technique used for those analyses can be used to determine the solubility limit of other compounds on the Environmental Protection Agency's list of priority pollutants. We report solubility limits of halogenated alkanes and alkenes of the volatile fraction of the priority pollutant list and additional compounds of the base neutral fraction as determined by the gas chromatographic headspace analysis technique.

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### INTRODUCTION

As analysis of priority pollutants in water is more widely conducted, the static headspace (vapor equilibration) technique followed by gas chromatography is used to a greater extent. Initially, our investigations were undertaken because the solubility limit of a particular compound was needed to calculate the exact concentration of an organic priority pollutant in water. The theoretical basis as well as the equations necessary to calculate concentration have been outlined completely by Cowen and Baynes and show the need for an accurate solubility limit<sup>3</sup>.

During our investigations, solubility limits of several compounds of interest were unavailable in the literature. Values for other compounds from different references were variable, or cited as "about" a particular numerical value. In some cases, a compound was classified as insoluble or slightly soluble if its solubility was less than 1000 ppm (1 g/l or 1 mg/ml). Table I shows a review of reported solubility values from different sources. The values in this table are not given as a comprehensive list but rather as a representation of available known solubility values from the literature. The use of headspace analysis to calculate water contamination levels requires more accurate solubility data than is available in the literature.

Prerequisites for successful headspace analysis of a compound are high volatility (vapor pressure), low boiling point, and relatively low molecular weight. Gen-

TABLE I

## LITERATURE VALUES FOR SOLUBILITY LIMIT (IN mg/l) OF HALOGENATED ALKANES AND ALKENES

(n.b.) Ref. 7 Solubility not usually reported. Can be calculated from values given for  $H_{vap}$  and Hildebrand's constant for some of the compounds. Ref. 5 values usually reported as *ca.* 1 part per number of parts of water. Temperature not always reported. Ref. 6 values usually reported as grams per 100 ml of water. Temperature conditions given. Ref. 8 values usually reported as parts per 100 parts of water. Temperature conditions given. Ref. 2 values reported as mg/l at 25°C.

Compound (n.b.)	Ref. 5	Ref. 6	Ref. 8	Ref. 2
Bromoform	1250	3190 (30°C)	1000 (cold)	3190
Bromodichloromethane	*	*	*	*
Chloroform	7420 (25°C)	10,000 (15°C)	8200 (20°C)	9300
Chlorodibromomethane	*	*	*	*
1,1-Dichloroethane	5000	5500 (20°C)	7000 (0°C)	5500
			5000 (30°C)	
1,2-Dichloroethane	8330	8690 (20°C)	9000 (30°C)	8690
		9200 (0°C)	9000 (0°C)	
1,2-Dichloropropane	sl. sol.**	2790 (20°C)	2700 (20°C)	2700
<i>cis</i> -1,3-Dichloropropylene	*	*	*	*
<i>trans</i> -1,3-Dichloropropylene	*	*	*	*
1,1,2,2-Tetrachloroethane	2860 (25°C)	ins.***	2900 (20°C)	2900
1,1,1-Trichloroethane	ins.	ins.	ins.	4400
1,1,2-Trichloroethane	ins.	ins.	4400	4500
Trichloroethylene	ins.	1000	1000 (25°C)	1100

\* Not available.

\*\* sal. sol. = Slightly soluble.

\*\*\* ins. = Insoluble.

erally, the higher volatility a compound exhibits the easier it is for that compound to be detected by headspace analysis and the lower the limit of detection. Previously, the compounds whose solubility limits were investigated and reported were those of halogenated aromatic fraction of the Environmental Protection Agency's (EPA) list of priority pollutants<sup>1,3,4</sup>. These compounds, although amenable to headspace analysis, have relatively high molecular weights and boiling points therefore lower volatility (vapor pressure) which can result in experimental limitations.

This report examines lower-molecular-weight halogenated alkanes and alkenes, which tend to have lower boiling points and higher volatilities, and are thus suitable for headspace analysis. Table II shows some of the physical constants of the compounds investigated in this report.

## EXPERIMENTAL

*Apparatus*

A F&M Scientific Model 402 gas chromatograph equipped with dual columns and dual flame ionization detectors was used with on-column injection. The carrier gas was helium which was dried and purified over molecular sieves and calcium sulfate.

A constant-temperature bath equipped with a Thomas (Philadelphia, PA,

TABLE II

PHYSICAL CONSTANTS OF HALOGENATED ALKANES AND ALKENES WHOSE SOLUBILITY LIMIT WAS EXAMINED BY HEADSPACE ANALYSIS

<i>Compound</i>	<i>M.W. (g/mole)</i>	<i>Boiling point* (°C)</i>	<i>Specific gravity**</i>	<i>Vapor pressure***</i>
Bromoform	252.77	149.5	2.890	5.6
Bromodichloromethane	163.83	90.0	1.980	§
Chloroform	119.39	61.7	1.4832	160.0 (20°C)
Chlorodibromomethane	208.29	119-20 (748 torr)	2.451	§
1,1-Dichloroethane	98.96	57.3	1.175	230.0
1,2-Dichloroethane	98.96	83.5	1.258	85.0
1,2-Dichloropropane	112.99	96.4	1.1560	40.0 (19.4°C)
<i>cis</i> -1,3-Dichloropropylene	110.97	104.3	1.217	§
<i>trans</i> -1,3-Dichloropropylene	110.97	112.0	1.224	§
1,1,2,2-Tetrachloroethane	167.86	146.5	1.600	16.0
1,1,2-Trichloroethane	131.41	113.8	1.4397	32.0 (30°C)
1,1,1-Trichloroethane	133.41	74.1	1.3390	96.0 (20°C)
Trichloroethylene	131.29	87.0	1.4642	77.0

\* 760 torr Hg unless otherwise indicated.

\*\* At 20°C with water at 4°C.

\*\*\* Torr Hg at 25°C unless otherwise indicated.

§ Not available in references checked (refs. 5-9).

U.S.A.) thermoregulator relay control box (Model 9368-D80) and a Precision Scientific (Chicago, IL, U.S.A.) Micro-Set direct-reading Thermoregulator (Model 9366-H10) with a temperature range of 10 to 104°C ( $\pm 0.01^\circ\text{C}$ ) were used as controls.

A Precision Sampling Pressure-Lok Series A2 gas-tight syringe was used for sample introduction into the gas chromatograph (Supelco, Bellefonte, PA, U.S.A.). Serum-type reaction vials (Catalogue No. 3-3109) with crimp-on seals and Hycar septa (Catalogue No. 3-3198) were used during the equilibration and sampling stages of the analysis (Supelco, Bellefonte, PA, U.S.A.).

### Reagents

All chemical priority pollutant standards were purchased from Chem Service (West Chester, PA, U.S.A.) and were the purest grade available.

Water used in preparing the standard solutions of each compound was the house-distilled, which was then run through two Barnstead purification cartridges (Catalogue Nos. D8904 and D8902) (Sybron/Barnstead, Boston, MA, U.S.A.). The first cartridge was for reduction of organic impurities, exact packing not listed. The second, a mixed-bed ion-exchange cartridge for high purity applications, was used for anion and cation removal.

### Solubility determinations

Standard solutions of increasing concentration of the compound being investigated were prepared in volumetric flasks, as described previously<sup>1</sup>. In headspace analysis<sup>10,11</sup>, an aqueous organic system under investigation is allowed to reach equilibrium with the vapor phase above it. In this study the aqueous organic phase was 25.00 ml and the gas phase was 35.00 ml. In such a case, the partial pressures

of the components in the aqueous solution and organic phase are equal, yielding the following equation:

$$(\gamma p^0 x)_{\text{org}} = (\gamma p^0 x)_{\text{aq}} \quad (1)$$

where  $p^0$  = vapor pressure of the pure component;  $x$  = mole fraction of the component in solution;  $\gamma$  = activity coefficient of compound in solution.

The range of the concentrations chosen was determined by the expected solubility limit. At times, this was simply a range of concentration values on either side of the known solubility limit, in other instances it was a range of concentration values around two solubility values reported for the same compound so that the correct solubility limit could be determined and the incorrect one eliminated. When a solubility limit was previously not reported as a numerical value, a preliminary screening of a large range of concentrations was first conducted so that a narrower range of stock solutions could be prepared, and the actual unknown solubility limit could then be determined with greater accuracy.

After the stock solutions had been prepared, they were mechanically shaken for 15 min to accelerate equilibrium. Then the solutions were allowed to equilibrate in a constant temperature bath at 30°C for a minimum of 24 h. Longer periods proved to be advantageous for some compounds; less experimental deviation from sample to sample was seen. In all cases, the chief concern in handling stock solutions was consistency, *e.g.* if one solution was allowed to equilibrate longer, then all the solutions in the series were subjected to the extra-equilibration time.

When the compound under investigation was fully dissolved in the aqueous phase, the standard solutions were allowed to come to room temperature. Aliquots were pipetted into headspace vials, which were then sealed, shaken for 1 min and equilibrated in a constant temperature bath at 30°C for 1 h. After that, a sample was removed from the vapor phase using a gas-tight syringe and injected into the gas chromatograph. The gas chromatographic conditions which were used are listed in Table III. Experimental headspace conditions were held constant during our experiments and are shown in Table IV.

When the solubility limit is being determined by headspace analysis, the expected experimental results can be seen in the theoretical curve of Fig. 1. In the graph, the detected signal rises linearly with concentration until the solubility limit is reached. Before the solubility limit, the concentration in the gas (headspace) phase increases with the concentration in the aqueous phase. When the solubility limit is reached the concentration in the gas phase no longer rises linearly but has attained

TABLE III  
GAS CHROMATOGRAPHIC CONDITIONS

Column	6 ft. $\times$ $\frac{1}{4}$ in. glass
Support	Supelcoport 100-120 mesh
Liquid phase	10% Carbowax 20M
Column oven temperature	120°C
Injection port temperature	128°C
Detector	Flame ionization
Detector temperature	180°C

TABLE IV  
CONSTANT HEADSPACE CONDITIONS

Amount of headspace injected	2.0 ml
Headspace gas	Laboratory air
Headspace temperature	30°C
Headspace vial equilibration time	1 h
Size of headspace vial	60.08 ± 0.55 ml*

\* Calculated by weight of water necessary to fill the headspace vial completely.

a constant value as does the corresponding signal height. Extrapolation of the slope and the plateau lines drawn tangent to the resultant curve to their point of intersection yields the solubility limit (a perpendicular line is dropped from the intersection point to the  $x$  (or concentration) axis).

To establish accurately the tangent lines drawn to the curve, linear regression analysis was performed on the experimental data points. The slope of the graph was treated as a separate line from the horizontal portion. The demarcation point was chosen by the decrease in the correlation coefficient of the slope when successive linear regression calculations were performed. This was done starting with the first three lowest concentration data points, then adding another data point pair with the next successive calculation. The data points were plotted by a Calcomp plotter, which positions points more accurately over a wide range of concentration values than can be achieved manually. In our previous report, the tangent lines of best fit for the graph were first calculated by linear regression then drawn by hand over the plotted graph. To achieve greater accuracy in this report, the generated linear regression lines were plotted by the Calcomp plotter separately from the original experimental graph. With this technique the intersection of the two tangent lines is more accurately located and the perpendicular line dropped to the concentration axis can be drawn more accurately. Thus, two graphs were plotted for each of the compounds whose solubility limit was being determined. (Graph 1 is the actual experimental data points and graph 2 is the two linear regression lines generated.)

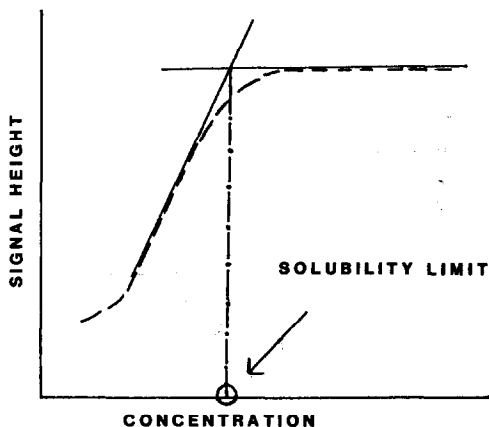


Fig. 1. Theoretical curve for the determination of solubility limit.

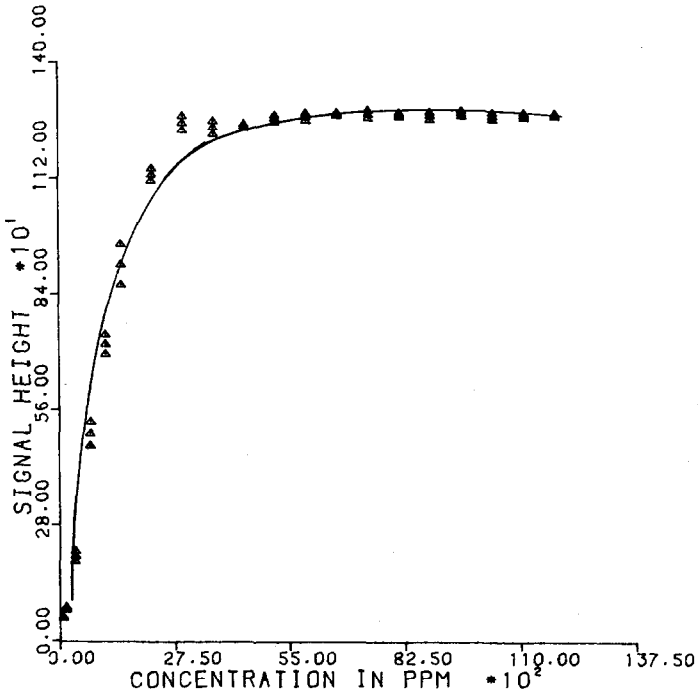


Fig. 2. Experimental graph for chloroform solubility limit determination.

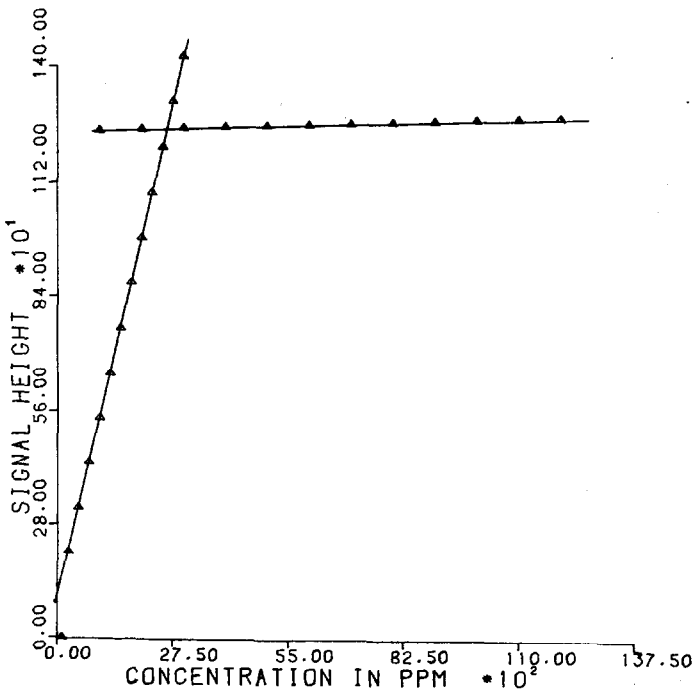


Fig. 3. Linear regression generated graph for chloroform solubility limit determination.

## RESULTS

In our first report, known solubilities were used to determine an average relative error for the method. As was pointed out, known solubility limits seemed to lack accuracy, consistency and at times disregarded the effect of temperature. Previously, to evaluate our method, the experimentally determined values were compared with any available value for the solubility limit of a compound. The reported solubility values of chloroform range from 7420 mg/l to 10,000 mg/l (Table I). Our experimental value for chloroform is 2524.8 mg/l. As seen in Figs. 2 and 3, the results for chloroform follow closely those predicted by the theoretical curve. The experimental average relative standard deviation is low at 1.85% but the relative error from the reported value is extremely high at 65.9%.

It should be noted also that the literature values used for comparison with the experimentally determined solubility limits were not always listed for the same temperature as that used in our analysis (30°C).

Table V lists the experimentally determined solubility limits of the halogenated alkanes and alkenes investigated, the standard deviation, the standard relative percent deviation, and the reported solubility limit. Figs. 4 and 5 show the experimental graphs for the compounds bromoform and 1,1,2-trichloroethane, respectively. The experimental standard deviation for each point is illustrated by the presence of three signal height points for each concentration value. Figs. 6 and 7 show the linear

TABLE V  
EXPERIMENTAL RESULTS

<i>Compound</i>	<i>Experimental solubility limit (mg/l)*</i>	<i>Experimental standard deviation (mg/l)</i>	<i>Relative standard deviation (%)</i>	<i>Best reported solubility limit (mg/l)</i>
Bromoform	3931.2	228.8	5.82	3190
Bromodichloromethane	2967.9	211.3	7.12	**
Chloroform	2524.8	46.7	1.85	7420**
Dibromochloromethane	2509.6	87.1	3.47	**
1,1-Dichloroethane	4588.5	207.8	4.53	5000
1,2-Dichloroethane	3505.9	172.1	4.91	9000**
1,1-Dichloroethylene	2232.3	81.9	3.67	2500
1,2-Dichloropropane	2069.5	121.9	5.89	2700**
<i>cis</i> -1,3-Dichloropropylene	911.2	79.5	8.72	**
<i>trans</i> -1,3-Dichloropropylene	1019.9	109.1	10.7	**
1,1,2,2-Tetrachloroethane	2914.9	158.3	5.43	2900**
1,1,1-Trichloroethane	479.8	24.8	5.17	480**
1,1,2-Trichloroethane	4365.3	340.1	7.79	4500**
Trichloroethylene	743.1	24.1	3.24	1000**
Composite average relative standard deviation 5.60%				

\* Values reported are an average of at least five linear regression results as obtained from the Calcomp plotter.

\*\* Indicates solubility limit unavailable or, if given, reported for a different temperature from that at which our studies were conducted.

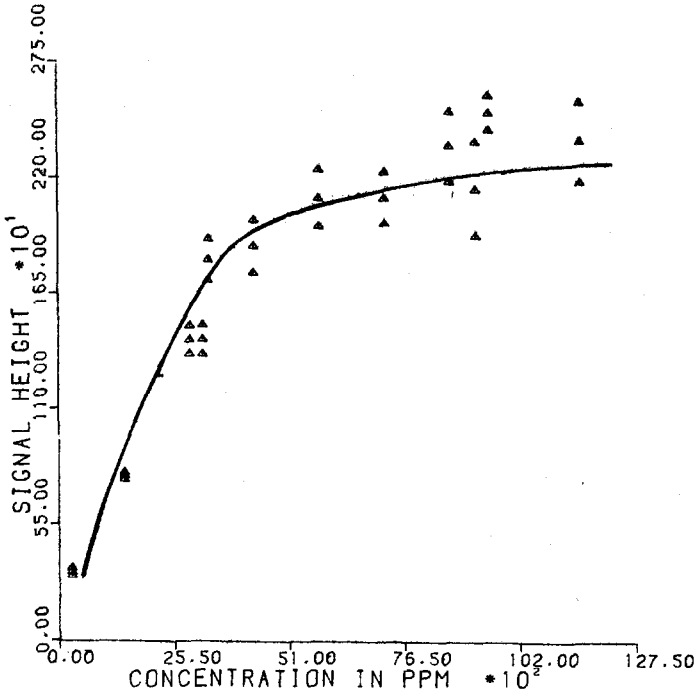


Fig. 4. Experimental graph for bromoform solubility limit detection.

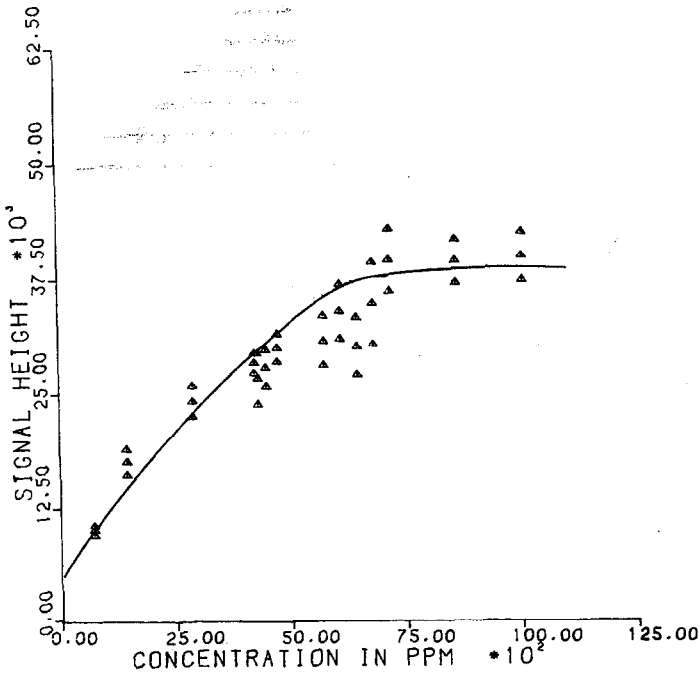


Fig. 5. Experimental graph for 1,1,2-trichloroethane solubility limit determination.



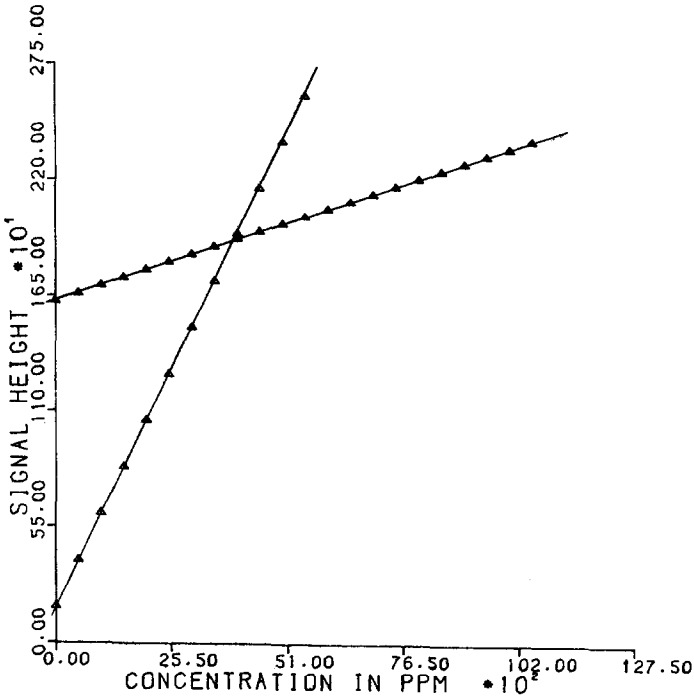


Fig. 6. Linear regression generated graph for bromoform solubility limit determination.

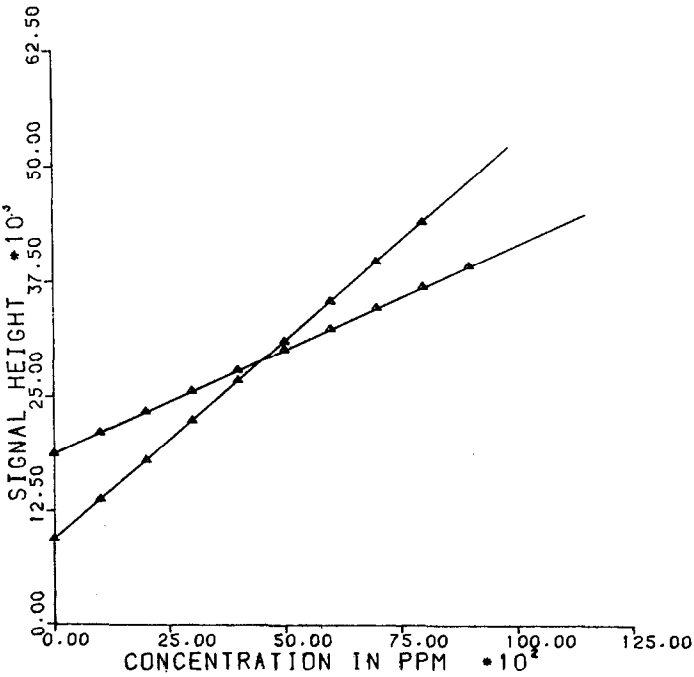


Fig. 7. Linear regression generated graph for 1,1,2-trichloroethane solubility limit determination.

TABLE VI  
LINEAR REGRESSION DATA FOR THE INITIAL GRADIENT TANGENT LINES

<i>Compound</i>	<i>Corr. coeff.</i>	<i>Slope</i>	<i>Intercept</i>
Bromoform	0.981	0.440	171
Bromodichloromethane	0.997	12.6	947
Chloroform	0.971	0.442	103
Chlorodibromomethane	0.999	9.78	-117
1,1-Dichloroethane	0.998	100.1	$1.116 \cdot 10^4$
1,2-Dichloroethane	0.999	44.8	845
1,1-Dichloroethylene	0.992	416.7	$-3.883 \cdot 10^4$
1,2-Dichloropropane	0.927	47.6	$6.635 \cdot 10^4$
<i>cis</i> -1,3-Dichloropropylene	0.989	23.1	427
<i>trans</i> -1,3-Dichloropropylene	0.998	49.3	1750
1,1,2,2-Tetrachloroethane	0.969	0.043	19.2
1,1,1-Trichloroethane	0.985	227.7	107
1,1,2-Trichloroethane	0.945	5.09	$1.1472 \cdot 10^4$
Trichloroethylene	0.992	16.6	79.8

regression lines for these compounds. It is from these graphs that the actual solubility values were determined.

Tables VI and VII show the linear regression data for the compounds investigated since our last report. Table VI gives the correlation coefficient, the slope, and the intercept (cm) for the initial gradient of the curve, Table VII shows the same parameters for the plateau. It should be noted here that the values for the intercept are large in many cases because of the high detector response for the compound.

Of the base-neutral and purgeable aromatic compounds investigated since our last report, two compounds, 2-chloronaphthalene and 3,3'-dichlorobenzidine seem to exhibit solubility values below the limit of detection that we can attain in our laboratory. Fig. 8 shows the graph of 2-chloronaphthalene. The first two points on

TABLE VII  
LINEAR REGRESSION DATA FOR PLATEAU TANGENT LINES

<i>Compound</i>	<i>Corr. coeff.</i>	<i>Slope</i>	<i>Intercept</i>
Bromoform	0.830	0.073	1626
Bromodichloromethane	0.607	-0.371	$4.080 \cdot 10^4$
Chloroform	0.750	0.003	1240
Chlorodibromomethane	0.985	1.09	9250
1,1-Dichloroethane	0.688	5.01	$4.370 \cdot 10^5$
1,2-Dichloroethane	0.636	2.50	$1.490 \cdot 10^5$
1,1-Dichloroethylene	0.903	92.9	$6.840 \cdot 10^5$
1,2-Dichloropropane	0.571	-2.49	$1.700 \cdot 10^5$
<i>cis</i> -1,3-Dichloropropylene	0.876	1.18	$2.040 \cdot 10^4$
<i>trans</i> -1,3-Dichloropropylene	0.889	2.78	$4.920 \cdot 10^4$
1,1,2,2-Tetrachloroethane	0.458	0.00	123
1,1,1-Trichloroethane	0.737	118.0	$1.870 \cdot 10^4$
1,1,2-Trichloroethane	0.721	2.93	$2.090 \cdot 10^4$
Trichloroethylene	0.779	3.11	$1.007 \cdot 10^4$

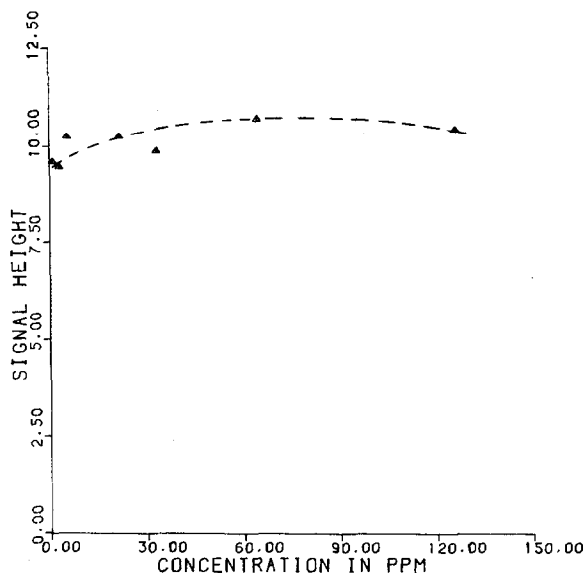


Fig. 8. Resultant data point graph for 2-chloronaphthalene solubility limit determination. The solubility limit of this compound is below the minimum detectable limit in our laboratory.

the left-hand side of the graph show a slight decrease in signal height indicating that perhaps we are approaching the solubility limit. Below these concentration levels no 2-chloronaphthalene detector signal can be seen on the chromatogram. This compound, classified as having a solubility of less than 1 ppm, cannot be assigned a specific numerical value for its solubility limit unless more points on the slope of the curve could be seen. The same was seen with 3,3'-dichlorobenzidine; the actual solubility limit is below the detectable limit for the compound in our laboratory. Both of these compounds have high boiling points (256°C and 400°C, respectively) therefore their volatility is also low and they cannot be easily detected by static headspace analysis. Table VIII lists the cumulative results of the solubility limits that have been determined by headspace analysis thus far.

#### CONCLUSION

The number of compounds that have been examined by static headspace gas chromatography to determine solubility limits has been increased. Values for the base-neutral, purgeable aromatic and purgeable halocarbon fractions of the EPA's list of priority pollutants have now been tabulated. The method can be used for preliminary screening to classify the solubility of a compound or to determine accurately the solubility limit.

As long as compounds exhibit some degree of volatility, static headspace analysis can be used to determine the solubility limit.

#### ACKNOWLEDGEMENT

The authors acknowledge the assistance of Dr. Jose de la Vega of the Chem-

TABLE VIII  
CUMULATIVE RESULTS

<i>Compound</i>	<i>Experimentally determined solubility (mg/l)</i>	<i>Experimental standard deviation (mg/l)</i>	<i>Relative standard deviation (%)</i>
Bromobenzene	330.0	27.5	8.33
Bromodichloromethane	2968	211.3	7.12
Bromoform	3931	232.7	5.92
Chlorobenzene	474	31.1	6.57
Chloroform	2524	46.7	1.85
2-Chloronaphthalene	Less than 1	*	*
Dibromochloromethane	2509	87.1	3.47
3,3'-Dichlorobenzidine	Less than 1	*	*
1,2-Dichlorobenzene	142.3	13.4	9.42
1,3-Dichlorobenzene	125.5	2.55	2.03
1,4-Dichlorobenzene	94.4	9.11	9.65
1,1-Dichloroethane	4589	207.8	4.53
1,2-Dichloroethane	3506	172.1	4.91
1,1-Dichloroethylene	2232	81.9	3.67
1,2-Dichloropropane	2069	121.9	5.89
<i>cis</i> -1,3-Dichloropropylene	911.2	79.5	8.72
<i>trans</i> -1,3-Dichloropropylene	1019.9	109.1	10.7
Ethyl benzene	147.7	9.70	6.57
Hexachlorobenzene	Less than 1	*	*
1,1,2,2-Tetrachloroethane	2915	158.3	5.43
Toluene	466.9	23.2	4.97
1,2,4-Trichlorobenzene	64.5	4.46	6.92
1,1,1-Trichloroethane	479.8	24.8	5.17
1,1,2-Trichloroethane	4365.3	340.1	7.79
Trichloroethylene	743.1	24.1	3.24

\* Indicates method used to classify solubility does not lead to a relative or experimental deviation.

istry Department of Villanova University, for thoroughly checking all the theory and equations upon which these studies were based.

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