DETERMINATION OF THE SOLUBILITY LIMITS OF ORGANIC PRIORITY POLLUTANTS BY GAS CHROMATOGRAPHIC HEADSPACE ANALYSIS

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SUMMARY

Up to now, most data tables and literature references listing solubility limits have used g per 100 ml or mg/ml as the units. Compounds which have solubility limits that fall within the parts per million (ppm) range have generally been listed as insoluble, with no numerical value given. Previously, such low solubility limits were not needed, nor was it possible to detect accurately these quantities. Headspace or vapor equilibration analysis, where the aqueous solution is allowed to equilibrate with the gaseous phase above it, can be used to determine the solubilities of compounds with even moderate volatility. Organic priority pollutants are a class of compounds where this information is not only useful but is needed. The use of the headspace or vapor equilibration method to determine these solubilities is discussed.

INTRODUCTION

In different literature sources a wide range of solubilities for the same substances are often listed or, in the case of the EPA priority pollutant list[1], it is not unusual to find the solubility listed simply as "insoluble"[2]. Originally this problem arose as the methods used were not sensitive enough to detect the lower limits at which these compounds are soluble. More recently, methods have been developed that can determine the solubility of organic species in aqueous systems at parts per million (ppm) levels. The difficulty with these methods are the many experimental steps involved. One such solubility determination involved the direct injection of hydrocarbon-saturated water into a gas chromatograph[3]. A special fractionator tube packed with firebrick and Ascarite placed before the gas chromatographic (GC) column was used to provide partial separation of the dissolved hydrocarbon from water as well as to prevent water from entering the chromatographic column. Unfortunately, the packing of the fractionator tube had to be replaced after three successive 50-μl injections, making the procedure time consuming.

In another report[4] GC is preceded by filtration through Millipore filters followed by triple extraction with hexane and finally evaporation from a 30-ml volume to a 0.1 ml. Although these methods, with lower detection limits, are available, many handbooks and even older reference books that have recently been revised list com-

TABLE I

SOLUBILITY CLASSES

Rating	Maximum solubility
Practically insoluble	20 mg/l (ppm) or less
Slightly soluble	20 200 mg/l (ppm)
Moderately soluble	200–1000 mg/l (ppm)
Highly soluble	1000–10,000 mg/l (ppm)
Extremely soluble	10,000 mg/l (ppm) or more

pounds as insoluble if the solubility is lower than 1 g/l (1000 ppm)[5].

For organic priority pollutants found in the environment, 1000 ppm is a relatively high concentration. Hazardous substances need to be detected in aqueous environmental systems at much lower levels. Solubility limits for these substances become a factor to be considered in water analysis.

In the *Handbook of Environmental Data on Organic Chemicals*[6] there is suggested a listing of solubility classes for compounds with solubility limits from 20 to 10,000 ppm. These classes are listed in Table I.

The use of these solubility classes would be satisfactory to classify the solubilities of priority pollutants in aqueous systems if the exact solubility value were not needed. In the work that prompted these studies in our laboratory, where headspace analysis is used to calculate the exact concentration of an organic priority pollutant in water, the actual solubility limit must be used to determine concentration.

Cowen and Baynes[7] have outlined the equations necessary to carry out these calculations starting with Raoult's law:

$$p = \chi p^0 \, \gamma \tag{1}$$

where p = partial vapor pressure of component of interest; p^0 = vapor pressure of the pure component; χ = molar fraction of component in solution; and γ = activity coefficient of compound in solution.

Generally, for dilute solutions (ppm range) the activity coefficient can be assumed to be a constant. This was reported by Kolb[8] for concentrations less than or equal to 1% or 10,000 ppm. With constant activity coefficient Raoult's law can be simplified to Henry's law, which states that vapor pressure of the pure component is given by

$$p = K \, \chi \tag{2}$$

where K = Henry's constant and is the product of γ and p^0.

In headspace analysis[9,10], an aqueous organic system under investigation is allowed to reach equilibrium with the vapor phase above it. Typically when using headspace analysis, equal volumes of the aqueous organic phase and the gas phase are placed in a sealed vial. In such a case, the partial pressure of the components in each phase must be equal, yielding the following equation:

$$(\gamma p^0 \chi)_{\text{org}} = (\gamma p^0 \chi)_{\text{aq}} \tag{3}$$

The pure component vapor pressure terms (p^0) cancel on both sides of this equation. This leaves the activity coefficient (γ), which is approaching unity for an organic component in water with a low solubility. The molar fraction of the organic component (χ) in the organic phase remains a constant that is also very close to unity. Thus, the equation is reduced to

$$\gamma\,(\chi)_{aq} = 1 \tag{4}$$

and further rearranged to

$$(\gamma)_{aq} = 1/(\chi)_{aq(s)} \tag{5}$$

where $(\chi)_{aq(s)}$ = molar fraction of the compound in water at saturation.
    If the solubility limit is known, $(\chi)_{aq(s)}$ is calculated from

$$(\chi)_{aq(s)} = (S/1000MW)/(55.5 + S/1000MW) \tag{6}$$

where S = solubility limit (mg/l) of organic compound and MW = molecular weight of organic compound (g/mole). If the solubility limit is 2% (20,000 mg/l or 20,000 ppm) then

$$(\chi)_{aq(s)} = S/(1000MW/55.5) \tag{7}$$

The activity coefficient can then be calculated from aqueous solubility data by using the equation

$$\gamma = 55,500MW/S \tag{8}$$

and Henry's constant can be calculated as

$$K = 55,500MW\,p^0/S \tag{9}$$

Of course, without knowing the exact solubility limit or by just knowing the solubility class, these calculations could either not be done or done only to an approximation. The concentration of a component in the headspace or in the aqueous solution below it would not be able to be determined.

EXPERIMENTAL

Apparatus
    An F&M 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, U.S.A.) thermoregulator relay control box and a Precision Scientific (Chicago, IL, U.S.A.) Micro-Set thermoregulator with a temperature range of 10–104°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 with crimp-on seals and Hycar septa were the vials used during the equilibration and sampling stages of the analysis (Supelco).

Reagents

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

Water used in prepararing the standard solutions was distilled and then run through two Barnstead purification cartridges (Sybron/Barnstead, Boston, MA, U.S.A.). The first cartridge was for organic compound removal and the second, a mixed bed cartridge, was for anion and cation removal.

Solubility determinations

Standard solutions of increasing concentrations of the compounds being investigated were prepared in 100-ml volumetric flask. They were shaken for 5 min, then allowed to equilibrate in a constant-temperature bath held at 30°C for a minimum of 24 h. This step was conducted to assure that the compound under investigation was fully dissolved in the aqueous phase. The samples were then allowed to come to room temperature, pipeted in headspace vials, sealed, equilibrated in a constant-temperature bath held at 30°C for 1 h and then examined by GC. Compounds with known solubility limits were investigated first to determine the relative amount of error that can be expected with the method. Second, compounds found on the EPA priority pollutant list for which no solubility limits have been reported were investigated. The GC conditions used are given in Table II.

When using headspace analysis, optimum results are obtained if as many parameters as possible are held constant. Experimental headspace conditions that were held constant during our experiments are given in Table III.

Fig. 1 represents the theoretical graph expected when the solubility limit is being determined by headspace analysis. Basically, as the concentration in the aqueous phase increases, so does the concentration in the gas phase. At the point where the solubility limit is reached the maximum value of the signal becomes independent of the amount of organic solute present in the liquid or solid state and the graph of the detector signal *versus* concentration no longer rises linearly but levels

TABLE II

GAS CHROMATOGRAPHIC CONDITIONS

Parameter	Conditions
Column	6 ft. × ¼ 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 III

CONSTANT HEADSPACE CONDITIONS

Parameter	Conditions
Amount of headspace injected	2.0 ml
Headspace gas	Laboratory air
Headspace temperature	30°C
Headspace vial equilibration time	1 h
Ratio of headspace to aqueous	
organic phase	1
Size of headspace vial	60.08 + 0.55 ml

off. This leveling off allows the solubility limit to be determined from the intersection of the two lines, as shown on the graph.

RESULTS

The compounds used in this study were all members of the EPA priority pollutant list. Table IV lists the chlorinated aromatic compounds and some chlorinated alkanes whose solubility limits are already known but which were also subjected to our method of determining solubility. The average relative error was then calculated and used as a guideline for the results obtained for the compounds with unknown solubility.

Table V lists the compounds that were investigated whose solubility limits were unknown or not reported. Hexachlorobenzene is a member of the priority pollutant list in the chlorinated aromatic groups. This compound has a boiling point of 322°C and therefore has a relatively low volatility. A compound with a high boiling point and a low volatility does not lend itself readily to headspace determination. The solubility limit of hexachlorobenzene was below the detection limit by headspace analysis in our laboratory and therefore was not able to be determined by this
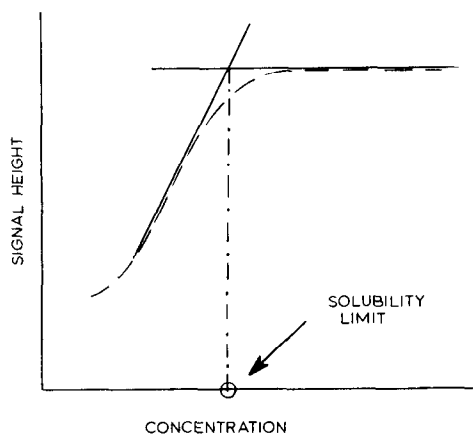

Fig. 1. Theoretical graph expected when the solubility limit is being determined by GC headspace analysis.

TABLE IV

COMPOUNDS INVESTIGATED WITH KNOWN SOLUBILITY LIMITS

Compound	Known solubility (ppm)*	Determined solubility (ppm)	Relative error (%)
o-Dichlorobenzene	145	149.4	3.03
m-Dichlorobenzene	123	125.5	2.03
Chlorobenzene	488	474.0	2.87
p-Dichlorobenzene	80	92.13	15.17
1,2-Dichloropropane	2700	2420.4	10.36
1,1-Dichloroethane	5000	4834.4	3.13

* Ref. 11–14.

method. Categorizing hexachlorobenzene into one of the solubility classes from the *Handbook of Environmental Data on Organic Chemicals*[6] places the compound into the lowest or practically insoluble class with a maximum solubility of 20 ppm or less. This classification is based on visual inspection of the standard solutions prepared for the investigation; part of the solid compound remained visible at this and lower levels of concentration.

For the calculation of solubility limit, the graphs of the data were plotted by a Calcomp plotter, allowing for more accurate positioning of the data points over such a wide range of concentration values. The lines of best fit for the graph were calculated by linear regression and were drawn by hand for the plotted data points. Figs. 2 and 3 show the plots for o-dichlorobenzene and 1,1-dichloroethane obtained for the solubility determinations. These compounds have known solubility values and were run to determine the·relative error. The corresponding linear regression data for Figs. 2 and 3 are given in Table VI.

The vertical rising portion of the graph is treated as a separate line from the horizontal flat portion of the curve. The points chosen for the two separate lines were determined by a drastic decrease in the correlation coefficient of the vertical line when the linear regression calculations were conducted. This was done by starting with the first three lowest concentration data points, calculating the linear regression values, then adding the next lowest concentration data point to the set of data points and performing the linear regression calculations again.

Figs. 4 and 5 show the solubility-determining graphs for 1,3-dichloropropylene

TABLE V

COMPOUNDS WITH UNKNOWN SOLUBILITY LIMITS

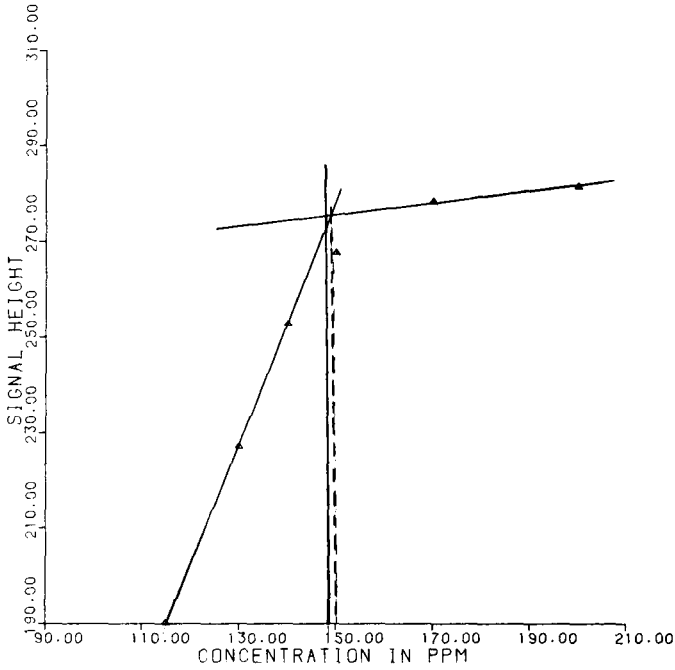| Compound	Determined solubility (ppm)	Experimental standard deviation (ppm)
Chlorodibromomethane	1049.9	36.4
Dichlorobromomethane	3031.9	150.0
1,3-Dichloropropylene (cis)	1071.0	93.4
1,3-Dichloropropylene (trans)	1188.1	126.8
1,2,4-Trichlorobenzene	64.51	7.77

Fig. 2. Graph of signal height *versus* concentration for *o*-dichlorobenzene obtained during solubility determination.
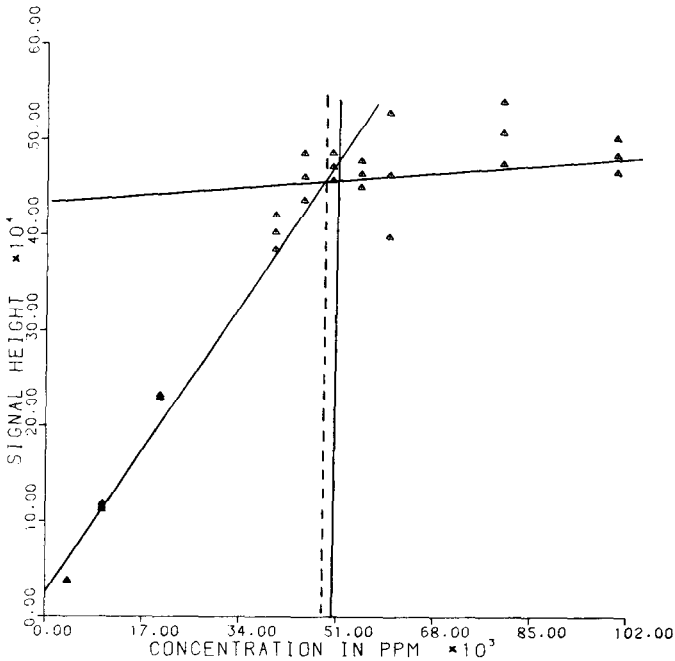

Fig. 3. Graph of signal height *versus* concentration for 1,1-dichloroethane obtained during solubility determination.

TABLE VI

LINEAR REGRESSION DATA FOR COMPOUNDS WITH KNOWN SOLUBILITY LIMITS

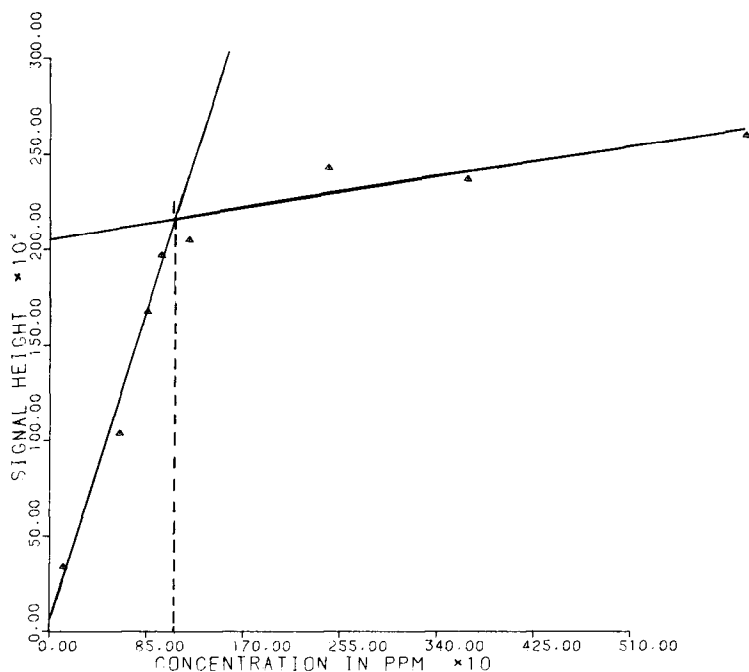| Compound	Parameter	Vertical portion of curve	Horizontal portion of curve
o-Dichlorobenzene	Correlation coefficient	0.982	0.999
	Slope	3.84	0.16
	Intercept	−267.2	260.2
1,1-Dichloroethane	Correlation coefficient	0.986	0.978
	Slope	88.28	18.81
	Intercept	29,372	356,494

Fig. 4. Graph of signal height *versus* concentration for *cis*-1,3-dichloropropylene obtained during solubility determination. The solubility limit for this compound was previously reported as insoluble.

TABLE VII

LINEAR REGRESSION DATA FOR COMPOUNDS WITH UNKNOWN SOLUBILITY LIMITS

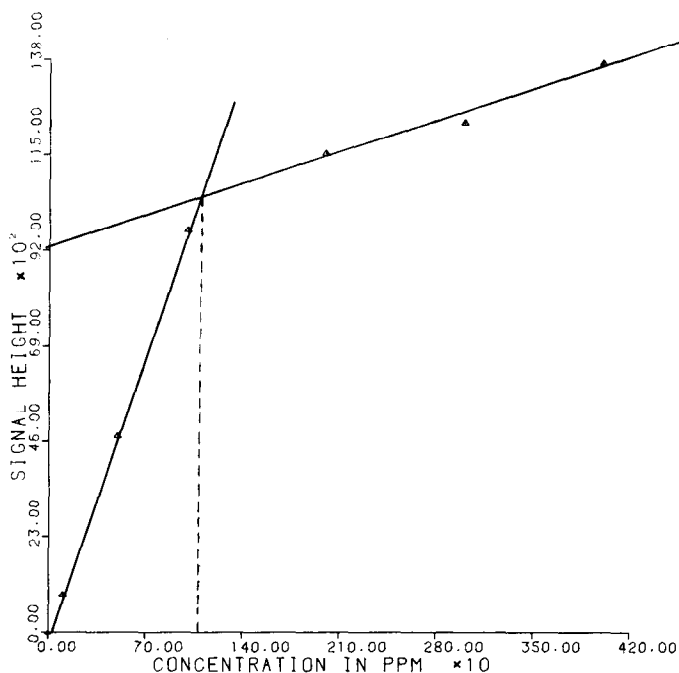| Compound	Parameter	Vertical portion of curve	Horizontal portion of curve
Chlorodibromomethane	Correlation coefficient	0.999	0.985
	Slope	9.777	1.087
	Intercept	−116.9	9251
1,3-Dichloropropylene	Correlation coefficient	0.989	0.876
	Slope	23.140	1.180
	Intercept	426.9	20,380

Fig. 5. Graph of signal height *versus* concentration for chlorodibromomethane obtained during solubility determination. The solubility limit for this compound was previously reported as insoluble.

and chlorodibromomethane, respectively. Both of these compounds have unreported solubility limits in the literature. The corresponding linear regression data for these compounds are given in Table VII.

CONCLUSION

The solubility limits of priority pollutants are needed in headspace analysis. The method described in this paper accurately determines the solubility limits of these compounds. The method is simple and fairly rapid to use. It should not be overlooked for use with other compounds whose solubility limits are not known and are not members of the EPA priority pollutant list. As long as the compounds exhibit some degree of volatility (vapor pressure), this method can be used to determine their solubilities. So far the method has been used to determine accurately the solubility limit values of members of the chlorinated aromatics on the EPA priority pollutants lists. Chlorinated alkanes and alkenes as members of the purgeable and basic–neutral fractions of the EPA priority pollutant list and other classes of priority pollutants are currently being studied.

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