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Determination of Octanol/Water Distribution Coefficients, Water Solubilities, and Sediment/Water Partition Coefficients for Hydrophobic Organic Pollutants

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DETERMINATION OF OCTANOL/WATER DISTRIBUTION COEFFICIENTS, WATER SOLUBILITIES, AND SEDIMENT/WATER PARTITION COEFFICIENTS FOR HYDROPHOBIC ORGANIC POLLUTANTS

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FOREWORD

Environmental protection efforts are increasingly directed towards prevention of adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Environmental Processes Branch studies the microbiological, chemical, and physico-chemical processes that control the transport, transformation, and impact of pollutants in soil and water.

Difficulties in determining octanol/water distribution coefficients, water solubilities, and sediment/water partition coefficients for certain organic pollutants produce discrepancies in studies by different investigators. This report discusses specific problems associated with each determination and suggests techniques that can eliminate potential sources of error.

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ABSTRACT

Octanol/water distribution coefficients, water solubilities, and sediment/water partition coefficients are basic to any assessment of transport or dispersion of organic pollutants. In addition, these determinations are prerequisites for many chemical or biological process studies. In response to the accepted need for this type of data and in light of the widespread discrepancies in reported data, this report sets forth conventional methods of measurement and identifies potential sources of measurement error for these three physical properties.

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SECTION 1

INTRODUCTION

Octanol/water distribution coefficients, water solubilities, and sediment/water partition coefficients involve the distribution of an organic solute between an aqueous phase and a second phase that might be loosely characterized as hydrophobic (that is, octanol, organic crystals or liquid, or organic components in the sediments). It is not surprising, then, that these three physical properties are highly correlated and have been interrelated quantitatively (Chiou, 1977; Leo, 1971; Briggs, 1973; Karickhoff, 1979). For hydrophobic solutes, these determinations are beset with difficulties that produce widespread discrepancies in studies by different investigators. Contributing sources of error include:

(1) low aqueous phase concentrations that may result in large analytical errors.

(2) inadequate separation of crystalline, octanol, or sediment phases from the aqueous phase.

(3) losses of solute from aqueous phase subsequent to phase separation -- volatilization, photolysis, or handling losses including sorption to filters or containers.

(4) incomplete equilibration -- organic crystal/water and sorption equilibria commonly require hours or in some cases days to achieve.

(5) the presence of solute impurities that are not analytically distinguished from the "parent" compound.

No general procedure for measuring these three physical properties is universally adaptable for all organic solutes. Numerous methods are available from the literature, but in most cases, they are tailored to meet time constraints or specific conditions of measurement or to suit specific compounds or sorbents. This document discusses specific problems associated with each determination for hydrophobic solutes (that is, water solubility of a few parts per million or less) and suggests techniques that can eliminate or circumvent each of the difficulties or potential sources of error.

SECTION 2

OCTANOL/WATER DISTRIBUTION COEFFICIENTS

The tendency of a neutral organic chemical to partition out of water into other environmental compartments containing hydrophobic constituents (that is, aquatic biota, sediments, or microorganisms) can be inferred from the octanol/water distribution coefficient (K_{OW}) of the chemical. Although K_{OW} provides an excellent base from which to estimate environmental partitioning behavior for most organic chemicals, the range in K_{OW} (10^2 to 10^6) has perhaps the most utility for this purpose. Chemicals with K_{OW}'s less than 10^2 will not partition into, or tend to accumulate in, any hydrophobic compartment. Chemicals with K_{OW}'s in excess of 10^6 will tend to accumulate into any (or all) hydrophobic compartments. For chemicals outside this range, K_{OW} can be categorized as $< 10^2$ or $> 10^6$ with no further quantification. The procedure described here focuses on the range of K_{OW} measurement, 10^2 to 10^6.

Measurement of the K_{OW} is an excellent first step in any sequence of physical measurements involving partitioning of hydrophobic compounds between water and a second phase. This physical measurement is useful because:

(1) The measurement is fast; 15 minutes or less is required for system equilibration as opposed to a minimum of several hours for solubility or sorption measurements.

(2) In most cases, a good estimate of the value of K_{OW} can be easily computed from the works of Leo (1971 and 1975). This facilitates the measurement by establishing the relative solvent volumes required for quantification of the solute in each phase.

(3) For crystalline solutes, a three-phase measurement (octanol, water, solute crystals) provides a rapid measurement of water solubility.

(4) K_{OW} measurements also can be used to estimate solubility (Chiou, 1977; Hansch, 1968), sorption to sediments (Briggs, 1973; Karickhoff, 1979), and biological accumulation (Southworth, 1978; Branson, 1975; Neely, 1974).

(5) K_{OW} measurements can be used to identify elusive solute impurity problems that can affect other physical measurements.

The octanol/water distribution coefficient is the ratio of the equilibrium concentrations of the chemical in the two phases. By convention, the ratio of concentrations is expressed as octanol over water. The concentrations are volume referenced (that is, mass or moles of chemical per unit volume of liquid) with the same units chosen for both phases. The standard temperature for measurement is usually 25°C.

The basic technique for determination of K_{OW}'s was developed by Hansch (1967) and Leo (1971). The following are extensions or refinements of this method for hydrophobic solutes.

Reagent grade octanol is extracted once with 0.1 N NaOH, twice with distilled water, and distilled twice. This process removes the surfactant-type contaminants (primarily organic acids) that tend to create stable emulsions in water/octanol systems. The solutes are prepared in octanol at or near saturation concentrations for the solids or approximately 0.1M for liquids. (The 0.1M concentration is an arbitrary upper limit established to insure that the physical properties of the octanol phase not be altered significantly by the presence of the solute.) A small volume of this octanol solution (1 to 5 milliliters) is equilibrated with variable volumes of water (determined by the amount of compound required for analysis and thus the analytical sensitivity and water solubility of the compound). Equilibration is achieved by gentle shaking of the sample for approximately 15 minutes.

For most solutes, the mixing is done in stainless steel centrifuge tubes with sealable caps. This minimizes solute losses by volatilization and handling (that is, sorption to vessels, etc.). Subsequent to equilibration, the samples are centrifuged at 10K for 10 minutes* (30 minutes if organic crystals are present), and the phases are sampled out of the centrifuge tubes. This phase sampling process is critical. A subsample of the octanol phase (usually one half or less of the total phase) is withdrawn by pipet and added directly into an analysis cell or diluting solvent suitable for analysis. The remainder of the octanol phase (and interfacial solute crystals if present) is removed prior to aqueous phase sampling. A aqueous phase sample is then withdrawn by pipet and the pipet stem is wiped to remove any droplets of water containing traces of excess octanol (picked up from the water surface) prior to discharging the water into an extraction solvent or analysis

*Centrifugation conditions are given in units of K (10^3) rpm in a Sorvall ss-34 rotor.

cell. The extraction solvent should not be allowed to contact the exterior of the pipet stem.

Some solutes (generally with K_{OW}'s in excess of 10^6 and solubilities less than 1 part per billion) require an aqueous phase volume greater than 40 ml for solute analysis. These solutes are phase-equilibrated in separatory funnels, and transferred to centrifuge tubes, which have been prerinsed with a portion of the aqueous phase, for the final phase separation. After centrifugation, aliquots are withdrawn from each tube (as in the procedure described previously) and recombined for extraction and analysis.

Additional distribution ratios should be determined at reduced concentrations (that is, water concentrations $\leq$ half the water solubility). This is accomplished by dilution of the stock octanol solutions prior to mixing with water.

Generally, the distribution coefficient is relatively independent of the solute concentration. If the K_{OW} differs significantly (more than one standard deviation for replicate determinations) at the two solute levels, an intraphase interfering equilibrium (solute association or dissociation) is suggested. Changes in speciation must be accounted for and experimental conditions controlled accordingly, such that the partition coefficient of individual chemical species can be determined (Leo, 1971). Acid-base "protolyses" equilibria are indicated by pH changes in the aqueous phase as a function of solute concentration. Buffered solutions should be used covering a pH range sufficient to resolve the octanol/water partitioning of individual species.

If association (aggregation) effects are suggested, the monomer K_{OW} can be determined by reducing the solute concentration below the aggregation threshold concentration, which is experimentally determined by consecutive dilution.

All determinations should be done in triplicate. The analysis method should be tailored to the compound in question; chromatographic methods are preferred because of their compound specificity in isolating the parent compound, free from interfering impurities.

Large errors in the octanol/water distribution coefficient can be incurred as a result of traces of more-water-soluble contaminants that are not analytically distinguished from the parent compound. This problem is especially apparent when the analysis involves radiolabels or UV absorption spectroscopy (which can be very nonspecific for many solutes), but becomes far less important when chromatographic analysis is used. Regardless, the presence of contaminants can be easily checked by subjecting the solute-containing octanol phase to consecu-

tive extractions with water. The K_{OW} should remain constant under consecutive extraction. The presence of a more-water-soluble impurity is indicated by a significant increase in K_{OW}. The impurity can be removed by exhaustive extraction with water (that is, until the K_{OW} is unchanged by further extractions). Also, chromatographic analysis can potentially isolate the parent compound and thus determine the K_{OW} of the parent species. Only in rare cases would one expect the presence of an impurity to affect significantly the true K_{OW} of a chemical species.

THREE-PHASE MEASUREMENT

For solutes that are crystalline in the pure state, a crystalline third phase often appears when a near saturated solute-octanol solution is mixed with water. The solubility of hydrophobic solutes is decreased substantially by the equilibrium water content (2.3M at 25°C) in the octanol phase. The quantity of crystallized solute produced in this way is more than the amount required to saturate the aqueous phase even at water-to-octanol volume ratios as large as 100. This three-phase system equilibrates rapidly (10 to 20 minutes). After centrifugation (10K, 30 minutes) the crystalline phase is largely at the interface of the two liquid phases. The two liquid phases can be sampled (free of crystalline contamination) as described previously. If the saturation concentrations of the chemical do not exceed 0.1M in either phase, the three-phase K_{OW} will not differ appreciably from that measured at lower solute levels, unless solute association occurs. Also, aqueous phase solute concentrations are within a few percentage points of measured aqueous phase solubilities. Apparently the octanol dissolved in the aqueous phase (0.0045M at 25°C) does not significantly affect the water solubility of these hydrophobic solutes. For hydrophobic solutes that are unstable in water and therefore cannot be equilibrated with water for long periods, the method provides a good means of getting a water solubility. For water-stable solutes, it provides a quick estimate of the solubility. We have used these three-phase measurements only for polycyclic aromatic hydrocarbons. This technique has not been tested for other families of compounds and has not been published.

ALTERNATIVE METHODS

The basic technique, as described earlier, is that of Leo (1971) and Hansch (1967). More recently, however, a new method of determining octanol/water partitioning utilizing high pressure liquid chromatography (HPLC) has been demonstrated by McCall (1975), Carlson (1975), and later by Mirrlees (1976), Veith (1978) and Unger (1978). This method combines solute phase partitioning and analysis into a single step that permits a faster and, for many solutes, more precise determination of

hydrophobic/hydrophillic phase partitioning that can be directly related to K_{OW}. Briefly, the technique utilizes a chromatographic column, the stationary phase of which contains functional groups (either as a coating substance or chemically bound on the surface) that simulate the octanol phase. In reverse phase liquid chromatography, the elution volume can be related to the partitioning of solute between the stationary and mobile phases. For solutes whose water solubilities are 1 ppm or greater, water (saturated with octanol) can be used as the mobile phase and octanol as the stationary phase coating, thereby providing a "direct" measurement of K_{OW}. For compounds of lesser solubility, organo-water solutions (methanol/-water, acetonitrile/water) are used for elution and a stationary phase matrix containing silanol groups is commonly used to simulate octanol. Solute partitioning in this system can be related to K_{OW} through the use of calibration standards (compounds whose structure is similar to the compound to be measured and whose K_{OW} is known). With the continuous evolution of more sensitive liquid chromatographs, this technique promises to become the most precise and reliable method of making partitioning measurements of this type. The technique potentially can circumvent the sources of error in K_{OW} determinations described previously. To date, however, this technique is not available to all who need partitioning information and will not likely be so in the near future.

SECTION 3

WATER SOLUBILITY

At first glance, determination of water solubility appears to be a simple task. In reality, solubility of crystalline hydrophobic compounds proves to be a most difficult physical property to measure. Hydrophobic liquids generally pose no real problem; water-solute equilibration is rapid (less than 8 hours) under gentle shaking. Equilibrium phase separation and solute analysis (and intrinsic problems typically encountered) are quite similar to those incurred in the water phase isolation and analysis of the octanol/water determination (discussed previously). Also, because hydrophobic liquids tend to be highly volatile in water, vapor phase methods of solute introduction and/or determination provide excellent solubility measurements (Farkas, 1965; McAuliffe, 1966 and 1969).

Special measurement problems exist for polychlorinated biphenyls and polybrominated biphenyls because the components of these hydrophobic compounds may be crystalline in their pure form. The definition and measurement of water solubility for these compounds are discussed by Dexter (1978), Paris (1978), Schoor (1975), and Haque (1975).

For hydrophobic crystalline compounds, the literature abounds with methods or recipes for measuring water solubilities, some of which go so far as detailing the effect on the measurement of size or shape of the container in which the compound is equilibrated (Campbell, 1930; Haque, 1975; Wauchope, 1972; Bowman, 1960; Mackay, 1975; Mackay, 1977; Biggar, 1967; Schoor, 1975).

A real problem in solubility measurement centers around getting the crystalline material dissolved and equilibrated with the solution, and subsequently, isolating the solution phase, free of microcrystals or large solute aggregates. Handling problems (degradation, volatilization, sorption) associated with aqueous solutions of these materials are similar to those encountered in K_{OW} determination and will not be readdressed here.

The time required for compound equilibration is primarily a function of the method used to introduce the crystals into the water. Some methods prescribe adding the crystalline compounds

to water as large "chunks" with subsequent stirring extending for days or even weeks; this is done specifically to minimize the formation of microcrystals that are difficult to remove effectively without perturbation of the solute concentration.

Although this time-consuming process may prove necessary for some compounds, it is impractical for many applications and unsuitable for compounds that tend to be unstable in water over the required time frame. A much quicker and more facile procedure for introducing the crystalline material (Haque, 1975) involves "coating" the compound (in excess of the amount required to saturate the water) out of a volatile solvent onto the walls of the container used for equilibration. Potential solvents include hexane, isooctane, methylene chloride, ethyl ether, etc. The vessel containing the compound (dissolved in a minimal amount of solvent) is rotated on its side, allowing the solvent to evaporate and thus plate the solute onto the container walls. The crystalline form varies with the choice of solvent. The best choice (achieved by trial and error) seems to be that which deposits the most translucent crystalline film on the container. Chalky films produce excessive microcrystal loading of the aqueous phase. After the crystalline compound has been "suitably" coated onto the container, membrane-filtered (0.2 micrometer pore size) water is added and the "solution" stirred or swirled gently under controlled temperature conditions. After 24 hours of agitation, aliquots of aqueous phase from which microcrystals have been removed are analyzed periodically until a maximum solute concentration is achieved.

Crystalline material can be removed from the aqueous phase by quiescent settling, centrifuging, or filtering. Quiescent settling requires no additional handling but is time consuming and may not be adequate for many compounds. Centrifugation should be in glass or stainless steel tubes that have been prerinsed with aliquots of the aqueous phase. Centrifugation time and speed are rather arbitrary; generally 30 minutes at 10K will suffice. It should be established that additional centrifugation does not remove appreciable compound from the "solution" phase. If filtration is used, consecutive aliquots of filtrate should be analyzed until a constant solute response is obtained, indicative that the solute is not being further sorbed by the filter material. Suitable filter materials include glass microfiber filters--such as the Whatman, GF/F--or halocarbon membranes such as those manufactured by Chemplast, Inc., Wayne, NJ. (Two or more filters in series may be required in some instances.) If filtration or centrifugation are used, care must be taken to avoid appreciable handling-induced temperature fluctuations in the aqueous samples.

For many crystalline solutes whose solubilities are a few parts per billion or less, these conventional techniques give

at best a coefficient of error of 0.2 to 0.3 in replicate determinations (coefficient of error = standard deviation/ mean). Measurement by two different techniques or in different laboratories commonly agree within a factor of 2.

ALTERNATIVE METHODS

Three Phase Measurement

For many applications, the solubility determined in the octanol-water-crystalline system (described previously) is adequate. Although this technique remains untested for a wide variety of compounds, its speed and ease-of-use make it most attractive in lieu of the conventional alternatives.

HPLC Method

As in the case of K_{OW} determination, a new HPLC method of measuring water solubilities of hydrophobic organic compounds has recently been reported (May and Wasik, 1978). In this procedure, a saturated aqueous solution is prepared by passing water through a column filled with glass beads onto which the compound has been "plated" out of a volatile solvent (similar to the procedure described in conventional method). A measured aliquot of the saturated solution is passed through a resin column suitable for trapping the compound. The collected compound is then eluted from the resin with an organic solvent (or mixture of solvents) directly into the chromatograph for solute analysis. This method is fast and potentially circumvents all the difficulties commonly encountered with classical methods. The method has been tested on only a few polycyclic aromatic hydrocarbons; solubilities determined by this method tended to be 20 to 40% lower than those measured by conventional methods. The HPLC technique, however, may well prove to be the most accurate and precise method for this difficult determination.

SECTION 4

SEDIMENT/WATER PARTITION COEFFICIENT

The sediment/water partition coefficient (K_p) is the slope of the linear portion of the equilibrium sorption isotherm.* For hydrophobic compounds, sorption isotherms are approximately linear at equilibrium aqueous solute concentrations below one-half of the distilled water solubility of the compound. This linear portion of the isotherm generally passes through the origin with no significant portion of irreversibly bound sorbate. Also, for dilute suspensions (< 1% dry weight solids) the K_p is relatively independent of sediment concentration.

In general, a K_p determination should involve the measurement of at least two points on the linear portion of the isotherm. This is accomplished by equilibrating two aqueous concentrations of solute with a fixed concentration of sediment at a fixed temperature.† For these hydrophobic compounds, the choice of amounts of solute and/or sediment required is greatly facilitated by a computed K_p estimate (Karickhoff, 1979) whereby

$$K_p = 0.6\ K_{ow}\ [O.C.]$$

where K_{ow} is a measured or computed octanol/water distribution coefficient, and [O.C.] is the fractional mass of organic

*By convention, sorption isotherms have sorbed concentrations of compound (computed relative to dry-mass sorbent) given by the ordinate and solution phase compound concentrations given on the abscissa. In expressing the compound concentrations in the two phases, units equivalent in mass are chosen for water and sediment. That is, if the sorbed compound concentration is expressed as microgram of sorbate per kilogram of sorbent, the solution concentration would be given as microgram of solute per liter of solution.

†In soils system (in addition to batch suspension methods) sorption is commonly measured by passing a solute solution through a column packed with soil (Davidson, 1968). Although this technique could be used for sediment sorption, hydrophobic solutes (especially those with solubilities < 10 ppb) would pose a severe problem with conventional column techniques.

carbon in the sediment. The choice of sediment concentrations is rather arbitrary, but one should choose large enough sediment samples to insure adequate analytical precision and if possible allow sediment concentrations to approach naturally occurring levels.

As was the case with solubility determination, many possible recipes for sediment processing and sorption measurement are available. In general, natural sediments should be sieved to remove plant debris or pebbles larger than 2 mm. Samples should be air-dried and ground to uniform texture (free of clumps) and cool-stored (5 to 15°C) until used. Minimal characterization should include particle size distribution (at least sand, silt, and clay) and organic carbon content. If possible, organic carbon should be determined on each particle size isolate. For characterization procedures, one should consult Jackson (1956) and other soils procedures manuals (American Society of Agronomy monograph series, Agronomy #9).

For more hydrophillic chemicals (in particular, organic compounds with potentially ionizable functional groups) sorption may be affected significantly by the hydrogen-ion concentration (pH), the redox potential (Eh), and the cation exchange capacity of the sediment. This introduces sediment collection, handling, and storage problems because these properties vary significantly with aeration and may change irreversibly upon drying.

Sorption measurement can generally proceed by one of two mixing methods.

(1) Direct mixing -- Aliquots of aqueous stock solution of the hydrophobic compounds are mixed with sediment suspensions and shaken until equilibrium is achieved. Equilibration, as judged by sequential sampling is generally complete (to within experimental error) in 8 hours, but the sample should be allowed to mix for at least 24 hours, unless the compound shows significant attenuation losses over this period.

(2) Compound plating -- Many hydrophobic compounds (those having solubility less than 0.1 ppm) are difficult to prepare, handle, and store in aqueous solutions. Also these compounds tend to be highly sorbed, and thus when an aqueous solution of the compound is mixed with sediment, the aqueous phase solute concentration may drop to a small fraction of the initial concentration, and in the presence of the natural organic background, solute analysis in the aqueous phase may pose a severe analytical difficulty. These problems can often be circumvented by plating the compounds out of volatile solvents (as described in solubility determination)

onto the containers in which sediment is to be equilibrated. Sediment suspensions can then be added and gently swirled until equilibration is achieved. This step requires at least 24 hours under these conditions; 48 hours should be allowed if possible.

Subsequent to compound-sediment equilibration (regardless of mixing procedure), the suspensions are phase separated, by filtering or centrifuging, and the compound concentration in each phase is determined. The degree of phase separation required may or may not be critical depending upon the magnitude of the K_p. At equilibrium, the fraction of compound sorbed (F) is given by

$$F = \frac{\rho K_p}{1 + \rho K_p} \qquad (2)$$

where ρ is the sediment concentration (expressed in equivalent mass units as described earlier). After centrifugation or filtration, a sediment concentration (remaining in the "water" phase) equal in magnitude to $1/K_p$ will produce a factor of 2 error in the <u>measured</u> water phase concentration.

For most compound/sediment systems, centrifugation at 20K for 60 minutes or filtration through filters (0.2 μm or less in pore size) should suffice.

In sampling and processing the aqueous phase component, many of the same experimental difficulties (attenuation and handling losses) discussed in the sections on K_{ow} and solubility measurements, are encountered, and require similar techniques and precautionary measures. In general, handling should be minimized, vessels prerinsed, filters preequilibrated, etc.

The sediment phase compound analysis can be a direct determination (labeled compounds) or the compound can be isolated from the sediment for analysis. Many compounds are difficult to extract from natural sediments. Adequate recovery often requires prolonged use of continuous extraction or sonication of the sediment in the presence of the extraction solvent.

ALTERNATIVE METHODS

For the measurement of solubility and K_{ow}, the most attractive recent methodology involved the use of "flow-through" HPLC integrated methods in lieu of the conventional techniques involving batch-equilibration followed by phase isolation and analysis. In the case of K_p measurement, however, no such technological breakthrough has occured.

Alternative techniques that show promise include:

(1) The previously described soil-column technique that uses high pressure (such as is availble to HPLC) and membranes or microporous glass fibers to adequatly remove the sediment fines from the flow-through water.

(2) A flow-through suspension system (Grice, 1972) that involves the flowing (or circulating) of solute-containing solution through a suspended sediment retained in a column by membranes or filters. As with the previous technique, the proper choice of membranes and the use of high pressures could adapt this technique to hydrophobic compounds.

(3) A three-phase method (Hance, 1977) that involves the equilibration of compound in a three-phase system (water, sediment, and a water-immiscible organic solvent). The sediment/water partition coefficient of the compound is derived from its measured concentration in the organic phase, coupled with a knowledge of the distribution coefficient of the compound between water and the organic phase. Hance (1976) used this technique in low-moisture soil systems from which a water-phase sample could not easily be isolated for analysis. Potentially this method could be used to estimate sediment-water partitioning for hydrophobic compounds for which a direct water phase measurement of solute is not easily accessible analytically.

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16. ABSTRACT

Octanol/water distribution coefficients, water solubilities, and sediment/water partition coefficients are basic to any assessment of transport or dispersion of organic pollutants. In addition, these determinations are prerequisites for many chemical or biological process studies. In response to the accepted need for this type of data and in light of the widespread discrepancies in reported data, this report sets forth conventional methods of measurement and identifies potential sources of measurement error for these three physical properties.

17. KEY WORDS AND DOCUMENT ANALYSIS

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