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SOLVENT PURIFICATION PROCEDURES USED IN ORGANIC GEOCHEMISTRY LABORATORIES

by Keith A. Kvenvolden and J. M. Hayes

Ames Research Center
Moffett Field, Calif.

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SUMMARY

Analyses of organic compounds in geochemical samples usually require that a number of reagents come in contact with the sample. Where trace concentrations of organic compounds are to be analyzed in these samples, particular attention must be given to the purity of reagents. Contaminants of the type that would interfere with the investigation must be minimal. Among the various sources of contamination in organic geochemistry are organic and inorganic solvents. This report concerns solvents and solvent purification procedures used by a number of organic geochemical laboratories.

INTRODUCTION

In October 1967, a meeting was held at Ames Research Center of the Group for the Analyses of Carbon Compounds in Carbonaceous Chondrites. At this meeting, interest was expressed in the problem of contamination in various solvents used in organic geochemical work. As a result of this meeting, we solicited information from the organic geochemical community concerning the use and purification of solvents. This report results from answers to a questionnaire (appendix A) that was sent to approximately 50 laboratories. We are grateful to those who were willing to take part in this survey.

Our approach was to find out (1) which manufacturers provide solvents for the organic geochemical community, (2) how the solvents are prepared for use, and (3) how the quality of the solvent is evaluated. The quality of the solvents used for a given investigation is usually defined by the type of investigation being conducted. A "practical grade" solvent distilled in a simple system may be adequate in certain applications, whereas "reagent grade" solvent purified by distillation and additional super-purification techniques may be necessary in other cases. We recognize that commercial solvent quality may vary, and evaluation of one batch may or may not reflect the condition of the solvent in general.

We have collected and organized the information sent to us into a brief but, we trust, informative report. We have made no judgments concerning the quality of any solvent preparation procedure. Because of the variety of reports received, we have condensed much of the information. This report (1) lists the respondents and the solvents considered, (2) discusses the quality of commercially available solvents, (3) points out steps taken, if any, prior to or in place of distillations, (4) describes various distillation setups and techniques, (5) tells of a method for purification of HF not involving distillation, (6) considers super-purification techniques, and (7) comments on evaluation of solvent quality.

RESPONDENTS, SOLVENTS, AND REAGENTS COVERED

Our survey elicited a wide response, both in terms of number of laboratories replying and in terms of variety of solvents and reagents. We will concentrate on the most common solvents, but in table I all the compounds mentioned in the replies are listed. This listing is intended as a guide to laboratories that have dealt with problems of purity for the less common reagents. Direct correspondence with the individual laboratories concerning these problems is certainly advisable. Appendix B lists all laboratory addresses. For the more common reagents, the various purification procedures reported are outlined in the remainder of this report.

QUALITY OF COMMERCIALLY AVAILABLE SOLVENTS

There was widespread agreement among both American and European laboratories that analytical reagent grade solvents (marketed under a variety of specific purity designations by nearly all chemical manufacturers) were not of sufficient purity for organic geochemical use. Benzene seemed by far the worst offender in this regard, nearly all respondents finding it unacceptable. Specific examples included 0.1 percent heavy alkanes and methyl cyclohexane in "benzene crystallizable extra pure," traces of incompletely chlorinated alkanes in analytical grade carbon tetrachloride, and acetaldehyde in "extra pure" dioxane.

In contrast, there were a number of reports of satisfactory use of spectroscopic grade and super-pure ("pesticide quality," "nanograde," etc.) grade solvents without further purification of any kind. It should be borne in mind, of course, that the main consideration in organic geochemistry is very low residue on evaporation, while the only consideration for spectroquality solvents is the absence of interfering chromophores in a given spectral range. Nevertheless, offending chromophores are presumably removed by distillation, a process that can also greatly reduce residue on evaporation. The solvents intended for pesticide isolation are definitely purified with the goal of low residue on evaporation. They are generally better packaged, for example, caps lined with teflon instead of paper, than spectroscopic grade solvents, and are thus preferred when available. Careful evaluation of any solvent used directly from the bottle is obviously in order.

PREPURIFICATION STEPS

The questionnaire asked specifically if any prepurification steps were considered worthwhile. Reports were few and all dealt with the percolation of aliphatic hydrocarbon solvents through activated silica gel columns prior to distillation. The Laramie Petroleum Research Center, which generally works only with samples rich in organic matter, reported that this step alone sufficed to purify analytical reagent n-pentane, cyclohexane, and n-heptane for their purposes. Suitable iso-octane was prepared similarly, by percolating it through a molecular sieve column. Sufficient purification of 1,2-dichloroethane was reported accomplished by percolation through an activated alumina column.

DISTILLATION

Without exception, laboratories reporting successful distillation techniques described simple apparatus and few, if any, "special steps." The obvious unspoken emphasis, then, is on careful and consistent practice of basic laboratory technique. Table II summarizes essentially all information provided concerning the various distillation procedures used. All include a good fractionating column operated under high reflux ratio. Table II includes very little information concerning still pots, distillation heads, condensers, or receivers. Nearly all stills described used a 5-liter still pot. A few respondents provided information on heads and condensers, and where it seemed important it has been mentioned in the "remarks" column of the table. By far the most common receiver was the rinsed original container. An interesting comment on column cleaning came from Dr. Hoering at the Geophysical Laboratory, who noted that he had found Blumer's technique of steam distillation effective in removing heavy residues trapped on column packings.

There were no reports on the use of spinning band columns. Usually used in preparative organic chemical techniques, these columns have the disadvantages of low through-put and difficult operation when considered for solvent purification. Additionally, the larger columns generally require some sort of rotary motion feedthrough, which could be a source of contamination problems. Nonetheless, when compared in terms of expense and difficulty of operation with the column crystallization techniques discussed below, spinning band columns seem to merit further consideration.

PURIFICATION OF HF

Because HF is one of the most difficult reagents to handle, we call special attention to an interesting purification procedure suggested by the Berkeley group. They cite the paper by Kwestroo and Visser (ref. 1) in which both a beaker of 75 percent (v/v) HF and a beaker of pure water are placed next to each other in a closed container. The pure water absorbs HF vapor and purified hydrofluoric acid is formed. Hydrofluoric acid of 25 M concentration can be prepared in 4 days.

SUPER-PURIFICATION PROCEDURES

While many uncertainties in sample history tend to reduce somewhat the required solvent purity for investigations of terrestrial samples and even, to some extent, of meteorites, clearly, solvents of the very highest purity attainable will be none too good for investigators of returned lunar samples. Techniques of fractional crystallization and zone melting seem to offer considerable advantages over distillation. In this connection, we mention the column crystallization process developed by Prof. Dr. H. Schildknecht and co-workers at the University, Heidelberg (refs. 2 and 3). This process is analogous to fractional distillation and involves crystallization in a continuous countercurrent system. This method is capable of long-term continuous operation, and an apparatus of modest size produces 30 to 40 ml of super-pure solvent per hour. In his response to our questionnaire, Prof. Schildknecht described applications of the technique to benzene, carbon tetrachloride, chloroform, tetrachloroethylene, dioxane, and dimethyl sulfoxide. Because of the expense of the apparatus and the specialized nature of the procedure, it would seem to be of considerable advantage to find or establish a single supplier for solvents purified by this or some similar method. Professor Oro' has suggested that such a supplier be found to produce standardized solvents for lunar sample analysis, and has noted, in addition, two similar batchwise purification procedures (refs. 4 and 5).

An ultrapurification procedure employing three distillation steps and culminating in a zone melting procedure (ref. 6) is also in use at the Laramie Petroleum Research Center.

SOLVENT EVALUATION

The questions concerning evaluation of solvents elicited a variety of answers listing mainly analytical techniques used, accompanied by little quantitative information on solvent quality. The obvious crucial test of solvent quality is a procedural blank for the analytical use intended. If there are no organic contaminants that could interfere with the analysis, the solvent is judged to be usable. A number of laboratories did provide estimates of the level of involatile aliphatic hydrocarbon contamination introduced by purified solvents in the isolation of a standard alkane fraction. Using pesticide quality reagents, workers at the Geophysical Laboratory estimated the level of contamination amounted to less than 10^{-7} gm/ml of solvent used, while workers at the University of Houston placed the level much lower, at less than 10^{-9} gm/ml of solvent used. Using solvent produced by laboratory distillation, workers at UCLA and Mobil estimated the level of contamination amounted to less than 10^{-7} gm/ml of solvent used, and the Berkeley group estimated a contamination level of less than 10^{-9} gm/ml of solvent used.

CONCLUDING REMARKS

This report has been concerned with solvent purification procedures used by 16 organic geochemical laboratories in North America and Europe. From an analysis of the information we received as a result of our questionnaire, we can make the following general statements:

(1) Analytical reagent grade solvents generally are unacceptable for organic geochemical use unless they are purified by some kind of column chromatography or distillation.

(2) In some applications, spectroscopic grade and pesticide or nanograde quality solvents have been used successfully as received from the manufacturers.

(3) Pretreatment of solvents before distillation is not a common practice.

(4) Laboratories reporting successful distillation techniques use simple distillation setups with good fractionating columns operated under high reflux ratios.

(5) In a few instances, the level of residue contamination in solvents used for analyses was reported and varied from 10^{-7} to 10^{-9} gm/ml.

(6) Techniques of fractional crystallization and zone melting seem to provide higher purity solvents than can be prepared by distillation.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif. 94035, Oct. 14, 1968
189-55-01-30-00-21

APPENDIX A

QUESTIONNAIRE

(1) Solvent name or formula.

(2) Manufacturer of solvent and solvent grade. Also please list manufacturers who have provided unsatisfactory solvents and describe the reasons these solvents are no longer used.

(3) Please summarize if possible the character and quantity of impurities in the starting solvent.

(4) What purification steps are used before distillation (i.e., molecular sieves, alumina, ion exchange, etc.)?

(5) Details of distillation (include the following information if applicable).

a. What substances, if any, are added to the starting solvent (i.e., drying agent, etc.)?
b. Describe fractionation columns (dimensions, packing). Manufacturers name and catalog number may be given as alternate.
c. Describe still head, condenser, receiver, and storage.
d. What take-off rate and reflux ratio do you use?
e. List important steps of distillation procedures which are not evident from above list, and describe details of distillation which you consider critical.

(6) How is quality of product evaluated?

a. Gravimetry - evaporation procedures, starting volume, and weight of residue.
b. Gas chromatography - experimental conditions, estimation of impurities, and chromatogram if available.
c. Spectroscopy - IR, UV, MS - experimental conditions, estimation of impurities, and spectra if available.

APPENDIX B

ADDRESSES OF ORGANIC GEOCHEMICAL LABORATORIES

	Table Entries
Dr. Ian Kaplan (respondent, Dr. Ted Belsky) Department of Geology University of California Los Angeles, California 90024	UC/LA
Dr. Bartholomew Nagy (respondent, Sister Mary Carol Bitz) New Address: Department of Geochronology University of Arizona Tucson, Arizona 85721	UC/San Diego
Dr. Ellis E. Bray Mobil Oil Corporation Research Department P. O. Box 900 Dallas, Texas 75221	Mobil
Dr. Brian S. Cooper Department of Geology The University of Newcastle Upon Tyne St. Thomas Street Newcastle Upon Tyne, England	Newcastle
Dr. Thomas C. Hoering Geophysical Laboratory Carnegie Institution of Washington 2801 Upton Street N.W. Washington, D. C. 20008	Geophysical Lab.
Dr. Gordon W. Hodgson Research Council of Alberta 87th Avenue and 114th Street Edmonton, Alberta, Canada	R. C. Alberta
Dr. I. Havenaar Koninklijke/Shell Exploratie en Produktie Laboratorium Psotbus 4560 Rijswijk (Z.H.) The Netherlands	Shell

Dr. Keith A. Kvenvolden NASA-Ames Research Center Moffett Field, California 94035	Ames
Dr. Klaus Biemann (respondent, Dr. Sanford Markey) Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	M.I.T.
Dr. Melvin Calvin (respondent, Dr. J. R. Maxwell) Department of Chemistry University of California Berkeley, California 94720	UC/Berkeley
Dr. Warren G. Meinschein Department of Geology Indiana University Bloomington, Indiana 47401	Indiana
Dr. Patrick H. Monaghan Esso Production Research Company P. O. Box 2189 Houston, Texas 77001	Esso
Dr. John Oro Department of Biophysical Sciences University of Houston Cullen Boulevard Houston, Texas 77004	Houston
Dr. W. E. Robinson Laramie Petroleum Research Center P. O. Box 3395, University Station Laramie, Wyoming 82070	Laramie
Prof. Dr. H. Schildknecht Organisch-Chemisches Institut Der Universitat 69 Heidelberg, Den Tiergartenstrasse Germany	Heidelberg
Dr. Fred M. Swain Geology Department University of Minnesota Minneapolis, Minnesota 55414	Minnesota

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1. Kwestroo, W.; and Visser, J.: The Ultrapurification of Hydrofluoric Acid. Analyst, vol. 90, 1965, p. 297.

2. Schildknecht, H.; and Powers, J. E.: Laboratoriumsmassige Trennung und Reinigung von Aromaten durch kontinuierliches Kolonnenkristallisieren. Chemiker-Zeitung, Chemische Apparatur, vol. 90, 1966, p. 135.

3. Schildknecht, H.: Zone Meeting and Columnar Crystallization as Analytical Tools. Anal. Chim. Acta, vol. 38, 1967, pp. 261-273.

4. Huckle, M. T.: A Low Temperature Zone Melting Technique For the Concentration of Flavours. Chemistry and Industry, 1966, p. 1490.

5. Beynon, J. H.: Examination and Separation of Samples by Auxiliary Techniques. *Mass Spectrometry,* Elsevier, 1960, p. 191.

6. Ball, J. S.; Helm, R. V.; and Ferrin, C. P.: Zone Meeting - New Purification Tool. Petrol. Engineer, vol. 30, no. 13, 1958, pp. 36-39.

TABLE I.- REAGENTS USED AT ORGANIC GEOCHEMICAL LABORATORIES

[For complete identification of responding laboratories and their addresses, see appendix B.]

Reagent	Responding laboratories and type of use*
Water	UC/Berkeley (3), UC/San Diego (3), Geophysical Lab. (3), M.I.T. (3), Minnesota (3), Shell (deionized), Ames (3)
Hydrogen perioxide	Shell (1a)
Ammonium hydroxide	M.I.T. (1a), Ames (5)
Hydrofluoric acid	UC/Berkeley (Diffusion + 2), M.I.T. (1a), Ames (1a)
Hydrochloric acid	UC/Berkeley (2), UC/San Diego (3), M.I.T. (1a), Shell (1a), Ames (5)
Sulfuric acid	Minnesota (1a), Shell (1a)
Sodium sulfate	M.I.T. (1a)
Potassium hydroxide	M.I.T. (1a), Shell (1a)
Calcium chloride	M.I.T. (1a)
Formaldehyde	Shell (1a)
Methanol	R.C. Alberta (3), Ames (3), UC/Berkeley (3), UC/LA (3), UC/San Diego (3), Esso (3), Geophysics Lab. (1c,3), Houston (1b,1c), M.I.T. (1b), Mobil (3), Newcastle (3), Shell (3), Ames (3)
Carbon disulfide	Mobil (3), Shell (1a,1b)
Methylene chloride	M.I.T. (1a)
Chloroform	R.C. Alberta (3), UC/San Diego (3), M.I.T. (1a), Heidelberg (4), Shell (3)
Carbon tetrachloride	Ames (3), UC/San Diego (3), Heidelberg (4), Mobil (3), Shell (3), Ames (3)
Ethanol	Minnesota (1a), Shell (3)

TABLE I.- REAGENTS USED AT ORGANIC GEOCHEMICAL LABORATORIES - Continued

Reagent	Responding laboratories and type of use*
Acetic acid	R. C. Alberta (3), UC/San Diego (3), Shell (1a)
Dimethylsulfoxide	Heidelberg (4)
1,2-dichloroethane	Laramie (Alumina column)
Tetrachloroethylene	Heidelberg (4)
Acetone	UC/LA (3), UC/San Diego (3), Esso (3), Newcastle (3), Shell (3)
Isopropanol	Shell (1a)
Diethyl ether	R. C. Alberta (3), UC/Berkeley (3), UC/San Diego (3), M.I.T. (1a), Shell (3)
Dioxane	Heidelberg (4)
_n_-Pentane	UC/San Diego (3), Houston (1b), Laramie (SiO_2 column), Shell (3), Ames (3)
Iso-pentane	Shell (3)
Pyridine	Laramie (3), Ames (3)
Ethyl acetate	UC/San Diego (3)
Benzene	R. C. Alberta (3), Ames (3), UC/Berkeley (3), UC/LA (3), UC/San Diego (3), Esso (3), Geophysical Lab. (1c,3), Heidelberg (4), Houston (1b,1c), Laramie (3,4), M.I.T. (1b), Mobil (3), Newcastle (3), Shell (3), Ames (3)
Cyclohexane	Laramie (SiO_2 column), Shell (3)
_n_-Hexane	R. C. Alberta (3), Ames (3), UC/San Diego (3), M.I.T. (1b), Shell (3), Ames (3)
Toluene	Newcastle (3), Shell (3)
_n_-Heptane	UC/Berkeley (3), UC/LA (3), Geophysical Lab. (1c), Houston (1b), Laramie (SiO_2 column), Mobil (3), Ames (3)

TABLE I.- REAGENTS USED AT ORGANIC GEOCHEMICAL LABORATORIES - Concluded

Reagent	Responding laboratories and type of use*
Iso-octane	Laramie (molecular sieve column), Shell (3)
Decalin	Shell (1a)
Petroleum ether	Newcastle (3), Shell (3)

*Key to use of codes
- (1a) Analytical reagent used directly from bottle
- (1b) Spectroquality reagent used directly from bottle
- (1c) Pesticide analysis grade reagent used directly from bottle
- (2) Organic solvent extracted
- (3) Distilled
- (4) Superpurified by column crystallization or elaborate distillation. Solvent percolated through column of activated substance (SiO_2, Al_2O_3, etc.)
- (5) Prepared by bubbling gas through distilled water

TABLE II.- SUMMARY OF DISTILLATION PROCEDURES

Laboratory	Solvents distilled	Column dimensions, cm	Column packing	Reflux ratio	Takeoff rate, ml/min	Notes
R.C. Alberta	Benzene	6×100[a]	Raschig rings	20:1	8	Use 12-liter still pot. Use Corad type still head.[b]
	n-Hexane, chloroform methanol	2×60[c]	Raschig rings		3.3	0.25 percent MeOH added to $CHCl_3$ product to prevent phosgene formation.
Ames	Benzene, methanol, carbon tetrachloride, *n*-hexane, *n*-heptane, *n*-pentane	1.25×60[d]	6 mm glass helices		1.6	Still head is Kontes K-518500. Constant flow of N_2 in apparatus.
UC/Berkeley	Benzene, methanol, *n*-heptane, ether	4 ft Oldershaw 30 plates		6:1	0.5	Still operated under total reflux initially until column is equilibrated.
UC/LA	Benzene, methanol, *n*-hexane, *n*-heptane acetone	2×45	4 mm glass helices		3-6	One still used for benzene only, another used for all other solvents.
Esso	Benzene	4 ft Oldershaw 30 plates		11:1		
Mobil	Carbon disulfide	5×90	Granular SiC.	>10:1	4	Total reflux until column equilibrated.[e]
	n-Heptane, benzene	7.5×127	Granular SiC.	>10:1	4	Fresh solvent feed 56 cm up column, lower 56 cm of column heated.
	Methanol, carbon tetrachloride	7.5×127	Porcelain Berl saddles	>10:1	4	Total reflux until column equilibrated.
Newcastle	Benzene, methanol, toluene, acetone petroleum ether	4 ft Oldershaw 30 plates				

[a] Similar to Scientific Glass No. JD 4440
[b] Similar to Scientific Glass No. D 8975
[c] Similar to Scientific Glass No. JD 4280
[d] Kontes K-502500
[e] Still head similar to Houston Glass Fabricator Co. No. F-2600

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